THE UNIVERSITY OF HULL

SOME REACTIONS OF METHYLSILANE CATALYSED BY METALS

being a Thesis submitted for the
Degree of Doctor of Philosophy
in the University of Hull

by

David Ian Bradshaw, B.Sc. (Liverpool)

September, 1975

ACKNOWLEDGEMENTS

I am grateful to Professor N.B. Chapman for providing facilities for this work and the Science Research Council for the award of a maintenance grant.

I wish to express my gratitude to Dr. R.B. Moyes and Dr. P.B. Wells for their enthusiastic interest and guidance throughout the course of this work.

I would also like to thank Mr. A. Roberts for his assistance with the mass spectrometry.

The mass spectrometers were purchased with the aid of grants from the Science Research Council and Imperial Chemical Industries Ltd.

Finally, I would like to thank Mrs. Smith for the great care she has taken in typing this thesis.

CONTENTS

SUMMARY

The chemisorption of methylsilane at 273 K, and the catalysed hydrogen isotope exchange in methylsilane in the range 195 - 300 K have been studied using evaporated metal films of molybdenum, tungsten, rhodium, nickel, and gold.

Chemisorption is strong, and is accompanied by dissociation of hydrogen bonded to silicon, dissociation of carbon-silicon bonds, and dissociation of hydrogen bonded to carbon, the processes occurring in that order. The empirical composition of the adsorbed layer at complete coverage by methylsilane is reported for each metal.

Isotope exchange in the silyl group is rapid, whereas exchange in the methyl group does not occur. Three exchange reactions have been investigated: self exchange in which CH_3SiD_3 was sole reactant, mutual exchange in which the reactants were CH_3SiH_3 and CH_3SiD_3, and exchange with molecular deuterium which involved CH_3SiH_3 and D_2. None of the metals used catalyse self exchange. Mo, W, Rh, and Ni catalyse each of the other two exchange reactions, but Au only catalyses mutual exchange because of its inability to chemisorb molecular deuterium. Specific rates for the two latter exchange reactions respond differently to the presence of surface poisons, which indicates that these reactions occur at different regions of the surface and involve different intermediates. Mechanisms of exchange are proposed.

Means of providing quantitative mass spectrometric analyses of deuteriated methylsilanes were required, and various methods have been developed to achieve this.

Exchange in methylsilane is compared with that in methane and in ethane.

The origin of the activity of gold lies in the ability of this element to chemisorb methylsilane, apparently by electron donation from gold to silicon. A novel associatively adsorbed state may be involved. Gold has a higher specific activity for mutual exchange than the earlier transition metals studied. This reaction has importance for the general theory of catalysis since gold has negligible catalytic activity for reactions of carbon compounds, which has been ascribed to the presence of the nominally filled d-band in gold.

SECTION 1

INTRODUCTION

1.1 General Introduction

Catalysts are substances that increase the rate at which chemical systems approach equilibrium without themselves being permanently involved in the processes that occur. Consequently, catalysts are of great commercial importance.

Catalysis may be homogeneous or heterogeneous; in the former the catalyst and reactants are in the same phase, whereas in the latter, the catalyst is normally a solid and the reactants are in the liquid phase or the gas phase. The most common heterogeneous catalysts are metals, oxides, and sulphides. Transition elements are very effective catalysts for a wide range of reactions such as hydrogenation, dehydrogenation, hydrogenolysis and isomerisation, and this thesis extends their use into the field of heterogeneously catalysed reactions of silicon-containing compounds. Subsequently in this thesis, the term 'catalyst' normally refers only to 'heterogeneous catalyst'.

Choice of catalyst is of great importance, because catalysts are frequently selective, that is, they yield a specific product. For example, ethanol is dehydrogenated over copper but dehydrated over alumina:

$$C_2H_5OH \xrightarrow[470\ K]{copper} CH_3CHO + H_2 \qquad (1.1)$$

$$C_2H_5OH \xrightarrow[470\ K]{alumina} C_2H_4 + H_2O \qquad (1.2)$$

Indeed, generally, metals catalyse hydrogenation and dehydrogenation, whereas neutral insulator oxides readily catalyse dehydration. Furthermore, activity for a specific reaction varies from one catalyst to another; e.g. at 373 K platinum-silica has a higher activity for benzene hydrogenation than cobalt-silica (1). Consequently, the choice of an industrial catalyst involves consideration of the need to optimise the rate of formation of the desired product whilst minimising capital outlay on plant and catalyst. For example, nickel catalysts are widely used because of their activity for hydrogenation and because they are inexpensive.

Any catalysed reaction occurs by a series of five processes:

- (i) transport of reactants to the catalyst surface;
- (ii) chemisorption of one or more of the reactants;
- (iii) reaction of adsorbed species;
- (iv) desorption of products;
- (v) transport of products away from the surface.

Transport to and from the surface is seldom rate-limiting in academic studies, although it is of importance in industrial reactors. In general, catalyst behaviour is characterized by the types of adsorbed species formed and their modes of interaction. Therefore, many studies of chemisorption and catalysis have been made to identify species adsorbed at catalyst surfaces.

Normally, catalyst surfaces are energetically heterogeneous, and hence the heat of adsorption of a reactant decreases with increasing surface coverage (2,3). The types of species present and their strengths of adsorption vary according to the types of catalyst sites available. The range of heats of adsorption may result in some species being reactive and others being unreactive. Thus, many investigations have been directed towards the characterization of surfaces and of the species chemisorbed thereon, and these studies have been at the heart of investigations of catalysis.

Several direct methods of studying species adsorbed on metal catalysts have been developed and have provided much information about chemisorption. Adsorption isotherms and measurements of the magnetic and electrical properties of metal specimens with increasing surface coverage of adsorbate have proved to be useful methods of detecting chemisorption and of determining the mean number of sites occupied by a molecule of adsorbate. Such magnetic and electrical measurements (4) have proved useful because in chemisorption there is an electronic interaction between adsorbate and adsorbent, whereas in physical adsorption no such interaction occurs. Selwood (5) found that the change in the specific magnetization of ferromagnetic metals that occurred during chemisorption could be related to the number of sites occupied by the adsorbate, and hence an understanding of the structure of the most abundant species could be obtained.

Infrared spectroscopy is one of the methods most widely used for the study of adsorbed species (6). Physically adsorbed species and chemisorbed species may each be identified; the presence of the latter is revealed by the appearance of bands which are absent in the spectra of the adsorbent and the gaseous adsorbate. The results obtained by this technique may be difficult to interpret, and studies are frequently confined to the adsorption of fairly simple compounds such as carbon monoxide, carbon dioxide, and simple hydrocarbons (7,8,9). Sometimes reactive intermediates have been detected by this technique; e.g. in the decomposition of formic acid catalysed by nickel-silica (10).

In recent years major advances have been made in various branches of electron spectroscopy, i.e. in Auger electron spectroscopy (11), ultra-violet photoelectron spectroscopy (12), and X-ray photoelectron spectroscopy (12,13). Each technique has proved to be surface sensitive, and has provided information concerning contaminants that aggregate at or near metal surfaces (11) and about the nature of chemisorbed species (12).

The number of methods available for the study of surfaces is continually increasing, one of the most recent innovations being inelastic electron tunnelling spectroscopy (IETS) (14), which may provide information on chemisorption on oxides similar to that obtained by infrared spectroscopy. It is claimed to be a very sensitive technique, less than 1 % of a monolayer being detectable (14). However, sample preparation involves the evaporation of a metal onto the chemisorbed material, and whether this procedure limits the applicability of the information obtained has yet to be assessed.

The aforementioned methods tend to detect the most stable and hence the most abundant adsorbed species which, due to their very stability, may not necessarily be involved in catalytic processes. It is believed that reactive species are sometimes present in low concentrations and often exist at high-index planes, dislocations, and other defects. In practice these species are best identified by indirect methods, particularly by investigations of molecules that undergo desorption and return to the gas phase, and isotopic tracing techniques have proved to be invaluable in this context.

Isotope exchange reactions allow intermediates in catalytic processes to be identified without the compound under investigation being chemically modified. The most commonly used method of identifying intermediates in exchange, isomerisation, and hydrogenation is by use of molecular deuterium or by use of deuterium-labelled compounds.

The heterogeneous nature of catalyst surfaces referred to earlier has been successfully investigated by use of radioisotopes, particularly tritium and ^{14}C-labelled organic compounds. This subject has recently been reviewed by Campbell and Thomson (15) and many applications of it are apparent. For example, ^{14}C-labelled benzene has been chemisorbed on evaporated metal films, and then been retrieved by exchange with unlabelled benzene to provide an estimate of the percentage of each surface active for exchange (16).

Exchange reactions, although of no extensive industrial importance, provide an understanding of the behaviour of catalysts and of the species adsorbed thereon, and this may be of importance in the industrial exploitation of catalysis.

1.2 The System Investigated and Catalysts Used

Exchange of protium for deuterium in many carbon containing compounds has been studied in detail. In the early 1950's the exchange reactions of methane, ethane, and some other simple alkanes were examined (17,18,19,20). Later, similar studies were made using simple amines (21), and thiols (22,23). Protium-deuterium exchange was later extended into the field of hydrogenation and isomerisation of alkenes, alkadienes, and aromatics (24,25).

Isotope exchange in simple silanes, however, provides an almost untouched field for investigation. Silicon possesses low lying vacant <u>d</u>-orbitals which are absent in carbon, and hence the possibility of novel chemistry exists. In the planning of the present work it was realised that an investigation of hydrogen isotope exchange in silane, disilane, and methylsilane would each provide interesting information, and a basis for future investigations of systems involving reactions at centres other than carbon. It was decided that the reactions of methylsilane might be the most illuminating since the relative reactivities of hydrogen bonded to carbon and to silicon would be monitored, and because this system provides one of the simplest analogies with hydrocarbons i.e. by comparison with methane and ethane. Furthermore, the ease with which the carbon-silicon bond breaks could be compared with that of the carbon-carbon bond in ethane.

It was decided that the metals to be used as catalysts should be selected on the basis of their known behaviour for exchange in methane and ethane. Thus tungsten and molybdenum were selected because they are good stepwise exchange catalysts for ethane, and for methane. Nickel and rhodium can each be good catalysts for multiple exchange in ethane and methane (the terms 'stepwise exchange' and 'multiple exchange' are defined in Section 1.3). Catalysis by gold has recently aroused the interest of a few investigations (26,27) and consequently, gold catalysts have been studied for methylsilane exchange.

Metal catalysts can be prepared in the form of foils, evaporated metal films, powders, supported metals, and single crystals. The methods involved in the preparation of powders and supported metals may result in the presence of surface impurities, the effects of which can be dramatic (28); this can be a drawback for fundamental studies. Although the surfaces of single crystals and foils can be cleaned effectively, both types of catalyst have the disadvantage of providing only low surface areas. The decision to use evaporated metal films was made because films can be prepared easily in a clean state and, because they have high surface areas due to their porosity, high activities can be obtained. However these virtues can themselves generate problems. For example, high surface area and cleanliness bestow high activity that can make it difficult to control the rate of a reaction. Films are also more easily poisoned than supported metals and, because they are essentially metastable, they sinter readily and thus the effective surface area is reduced. In addition, because metal films are polycrystalline, the balance of faces exposed may vary from one film to another, with the result that activity is somewhat variable. Thus reactions must be repeated several times in order to obtain reliable mean values for the specific activity of a metal.

Nevertheless, for fundamental studies, the advantages of films over other forms of catalyst more than outweigh their disadvantages, and this form has been used in this investigation.

1.3 A Review of Some Simple Exchange Reactions

Few studies have been made of catalysed protium-deuterium exchange in silicon-containing compounds, and when this investigation commenced such exchange had not been reported in methylsilane. There have been numerous reports of exchange in various organic compounds; however this section will review only the most important literature pertaining to exchange in methane, ethane, and simple silanes.

1.3.1 Exchange in methane

One of the first investigations of exchange of methane with deuterium and also of methane with perdeuteriomethane was made by Morikawa *et al.* in 1936 (29). These authors studied these reactions using a nickel-kieselguhr catalyst at 457 K. Exchange of methane with perdeuteriomethane was faster than exchange with molecular deuterium. The reaction of methane with perdeuteriomethane provided evidence for the dissociative adsorption of methane. However, this investigation is of limited interest because mixtures were analysed by infrared spectroscopy and product distributions were not obtained.

The first detailed reports of exchange of methane with molecular deuterium were published by

Kemball in 1951 and 1953 (17,18). Evaporated metal films were used as catalysts, and exchange was followed by mass spectrometry. Initial product distributions varied from metal to metal, and the form of the distributions suggested the operation of two exchange mechanisms. Monodeuteriomethane was formed by a stepwise exchange mechanism, i.e. only one protium atom was exchanged per residence of an adsorbed methane molecule on the surface, whereas perdeuteriomethane was formed by a multiple exchange mechanism, i.e. more than one protium atom was exchanged per residence of a methane molecule on the surface. Examples of initial distributions using rhodium, nickel, platinum, tungsten, and palladium catalysts are shown in Table 1.1. The

Table 1.1 Initial distributions of products for the exchange of methane over various metals.

Catalyst	Ratio of D_2/CH_4 in reaction mixture	Temp. /K	Percentages of isotopic species[a]			
			d_1	d_2	d_3	d_4
Rh	1.0	435.2	21	5	29	45
Rh	3.4	444.6	21	0	16	63
Ni	0.75	510.2	12	3	24	61
Pt	1.0	532.5	36	12	25	27
W	1.0	423.8	76	1	9	14
Pd	1.0	527.5	95	1	2	2

[a] d_x = CH_x where x = 0,1,2,3 and 4

distributions exhibited maxima for CH_3D and for CD_4, and their relative proportions were dependent on temperature. From this it was concluded that stepwise exchange and multiple exchange occurred independently. Activation energies were determined for each type of exchange and results for nickel, palladium, platinum, rhodium, and tungsten are shown in Table 1.2.

Table 1.2 Activation energies for exchange of methane with deuterium

Catalyst	Temp. range /K	E_a/kJ mole^{-1}		Author
		Disappearance of CH_4	Multiple exchange	
Mo-film	430-470	41.8[a]	71.1	Frennet
W-film	365-447	38.0	48.9	Kemball
Re-film	403-423	35.9[a]	58.5	Frennet
Ru-powder	392-442	113.0	125.0	McKee
Rh-film	411-490	98.6	117.0	Kemball
Rh-film	393-463	52.7[a]	73.2	Frennet
Rh-powder	372-429	46.0	70.6	McKee
Ni-film	479-528	119.0	141.0	Kemball
Pd-film	516-581	98.2	149.0	Kemball
Pd-powder	390-442	119.0	192.0	McKee
Pd-powder	436-462	131.0	179.0	McKee
Pt-film	432-548	95.3	110.0	Kemball
Pt-powder	358-419	85.7	109.0	McKee

[a] Activation energy for stepwise exchange

Between 1964 and 1966 McKee and Norton investigated methane-deuterium exchange using alloy powders as catalysts (30-34). The alloy systems investigated were Pt-Pd, Pd-Rh, Pd-Au, Pt-Ru, Pt-Rh, and Pd-Ru. The metals used were also studied in their pure state. Independent stepwise and multiple exchange mechanisms were found to operate on these metals and their alloys. Gold exhibited no activity for exchange in accordance with its inability to adsorb hydrogen in the usual range of working temperatures. Like rhodium and nickel (17,18), ruthenium was found to be a good catalyst for multiple exchange. Activation energies for the loss of CH_4 and for multiple exchange are shown in Table 1.2. The mode of variation of activity for exchange with changing alloy composition varied from one alloy system to another. However, when an alloy was formed from a metal that readily catalysed multiple exchange with one that did not, activity for multiple exchange was greatly reduced. These authors observed a correlation between the activity of catalysts for multiple exchange and (i) the atomic radii of the metals, and (ii) the number of unpaired d-electrons possessed by a metal (Table 1.3).

Table 1.3 Lattice parameters and the multiplicity of exchange, M[a]

Metal	Atomic radius /Å	No. of unpaired *d*-electrons	M (at 473 K)
Pt	1.38	0.6	1.7
Pd	1.37	0.6	1.1
Ru	1.32	2.2	3.5
Rh	1.34	1.4	3.4
Ir	1.35	1.7	3.0

[a] As defined in Section 4.2

It is probable that in the alloy the number of unpaired *d*-electrons is reduced to less than one for many compositions thus species involved in multiple exchange are not formed as readily.

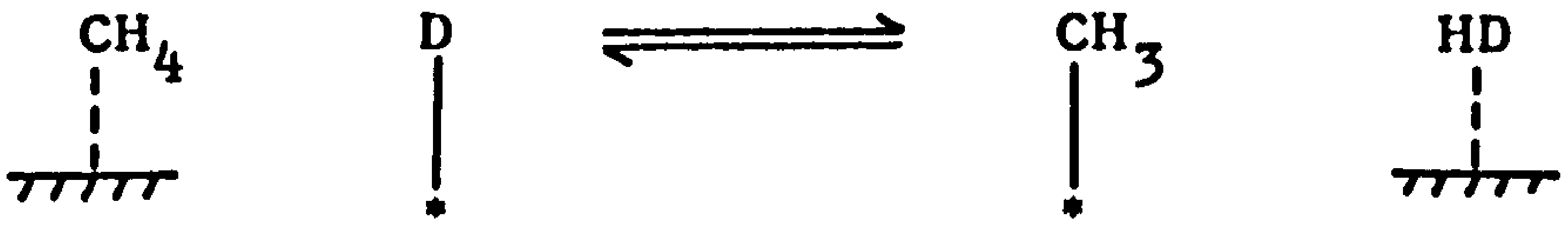
In 1968 Frennet *et al*. reported results for methane-deuterium exchange using evaporated metal films of rhodium, rhenium, tungsten, molybdenum, nickel, and tantalum as catalysts (35). Frennet has reviewed this and other work in 1974 (37). Films were prepared under conditions of ultra-high vacuum, and exchange was studied in a flow reactor. (Most investigators have studied exchange using static reactors). The pressures of reactants used were substantially lower than those used by

Kemball (17,18); however, in agreement with his work (17,18), two mechanisms for exchange were found to operate simultaneously, and the activation energies of each are shown in Table 1.2. Substantial differences exist between the activation energies obtained by Frennet for rhodium and those calculated by Kemball. Both authors observed that perdeuteriomethane could be more readily produced when using rhodium or nickel, than when using either platinum, tungsten or molybdenum, over which monodeuteriomethane predominated.

It is of interest that, for static reactors, catalytic activity for exchange did not apparently vary with reaction time (17,18,30-34), whereas constant catalytic activity using flow reactors was usually obtained after a few hours of operation. For example, in a flow reactor a tenfold increase in catalytic activity was detected over molybdenum during a few hours of continuous use. It was concluded that a slow reaction occurred between the surface of the catalyst and gas phase hydrogen and methane, and consequently that adsorbed species were not present initially in their equilibrium concentrations (37).

In 1973 Cece and Gonzalez reported that reduction of metal crystallite size in nickel-silica reduced the activity of a catalyst for multiple exchange in methane (38). These authors believed that this reduction of activity was due to an alteration in the electronic properties of the crystallites on the basis that a reduction of crystallite size diminishes the ferromagnetism of nickel-silica (39).

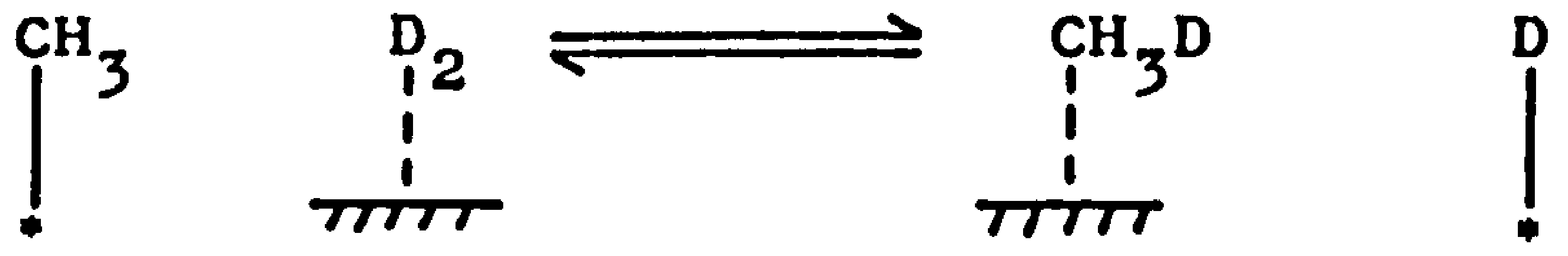
There is general agreement between all of these authors concerning the mechanism of exchange in methane. Stepwise exchange is believed to occur principally by a Rideal-Eley mechanism, thus:



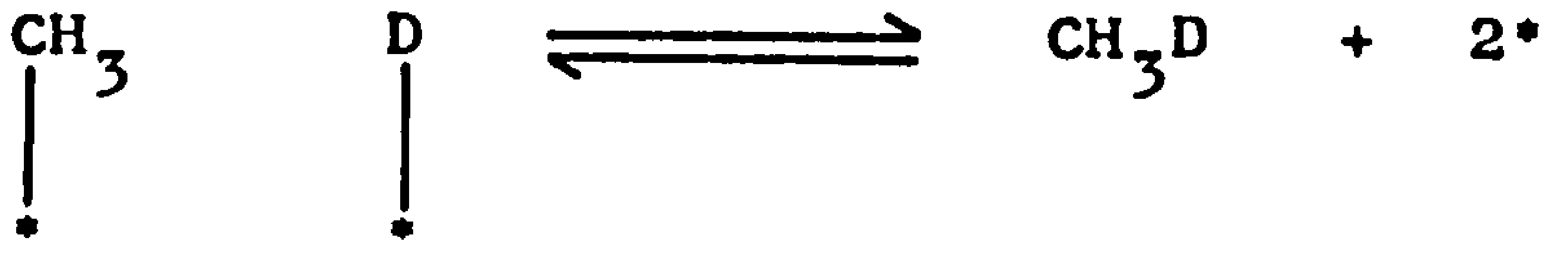
(1.1)

(The asterisk represents a surface site)

Adsorbed-methyl species may then react with physically adsorbed deuterium (equation 1.2) or with chemisorbed deuterium (equation 1.3).

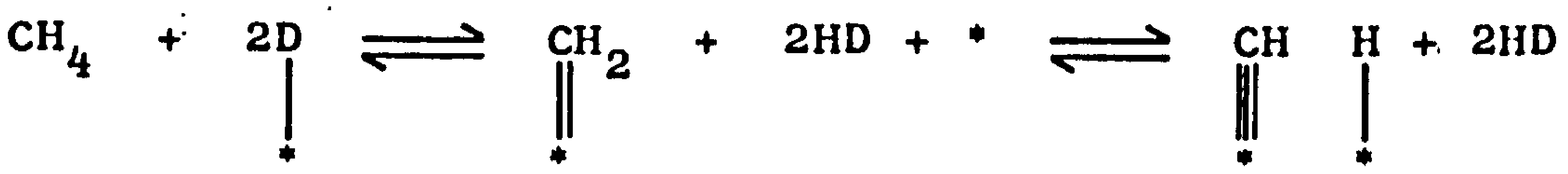


(1.2)



(1.3)

Understanding of the mechanism of multiple exchange in methane is less precise. Exchange is considered to occur by rapid interconversion of adsorbed-methylene and adsorbed-methine. One description of this is:



$$CH_4 + \underset{*}{\underset{|}{2D}} \rightleftharpoons \underset{*}{\underset{\|}{CH_2}} + 2HD + * \rightleftharpoons \underset{*}{\underset{|||}{CH}}\;\;\underset{*}{\underset{|}{H}} + 2HD \qquad (1.4)$$

Product distributions indicate that interconversion of adsorbed-methyl with adsorbed-methylene is not a rapid process, and it has been proposed that this process might be the rate determining step between stepwise and multiple exchange (18,36).

Finally, an order of selectivity for multiple exchange has been determined (37). When the rate of disappearance of light methane 1 % s^{-1} the ratio of CD_4 to CH_3D decreased in the following order for the catalysts used: Rh > Ni > Re > Mo > W > Ta

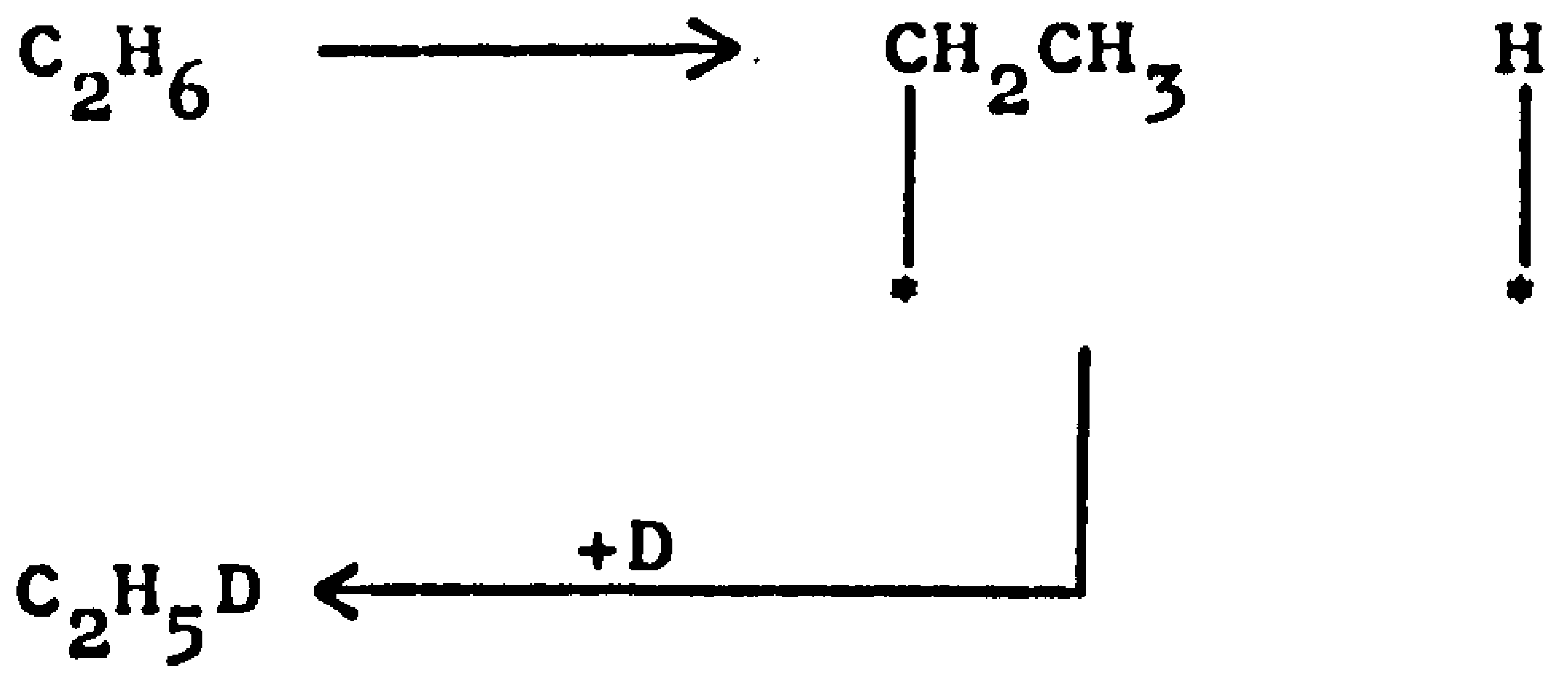
1.3.2 Exchange in ethane

In 1954 Anderson and Kemball reported the occurrence of ethane-deuterium exchange over evaporated metal films of Zr, V, Ta, Cr, Mo, W, Rh, Ni, Pd and Pt (19). Ethane was found to exchange more readily than methane, and widespread multiple exchange occurred at the surface of many metals. Initial product distributions obtained are shown in Table 1.4. These were reasonably temperature independent, with the exception of nickel.

Table 1.4 Initial distributions of products for the exchange of ethane over various metals

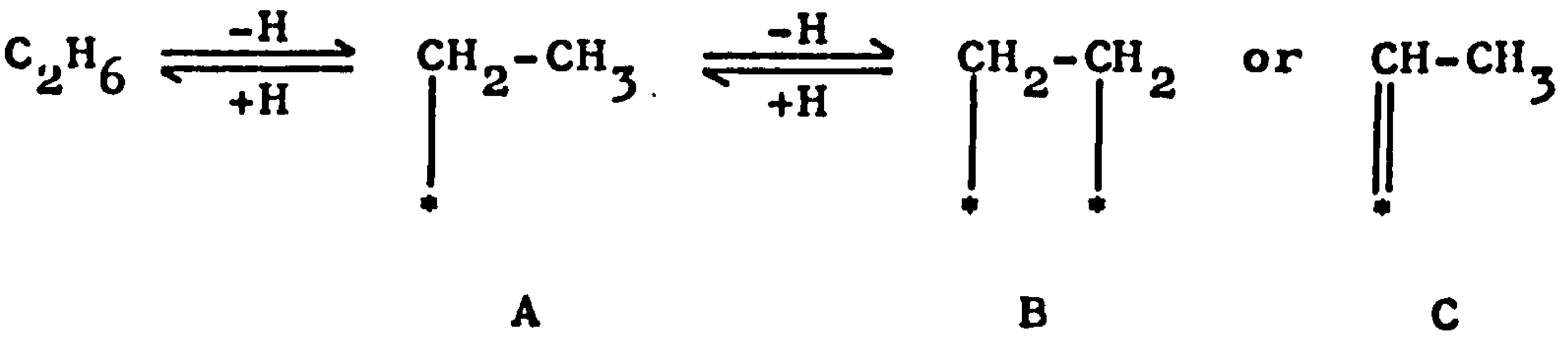
Catalyst	Percentages of isotopic species						M
	d_1	d_2	d_3	d_4	d_5	d_6	
W	79.1	12.2	5.2	2.0	0.9	0.6	1.30
Mo	82.2	14.1	3.0	0.7	0	0	1.16
Ta	81.3	15.0	3.1	0.6	0	0	1.15
Zr	52.4	17.1	5.1	4.3	7.0	14.1	2.3
Cr	47.2	18.0	6.6	6.0	7.2	15.0	2.5
V	46.3	19.2	5.7	5.1	7.5	16.2	2.6
Ni	40.4	10.1	4.0	5.1	10.1	30.3	3.1
Pt	19.4	17.3	12.2	10.2	15.3	25.5	3.5
Pd	5.0	5.9	7.9	10.9	18.8	51.5	4.8
Rh.	4.8	2.9	4.3	7.1	17.1	63.8	5.0

Stepwise exchange occurred by ethane adsorbing to form an adsorbed ethyl species which could react with deuterium to produce ethane with one protium atom exchanged. Thus:



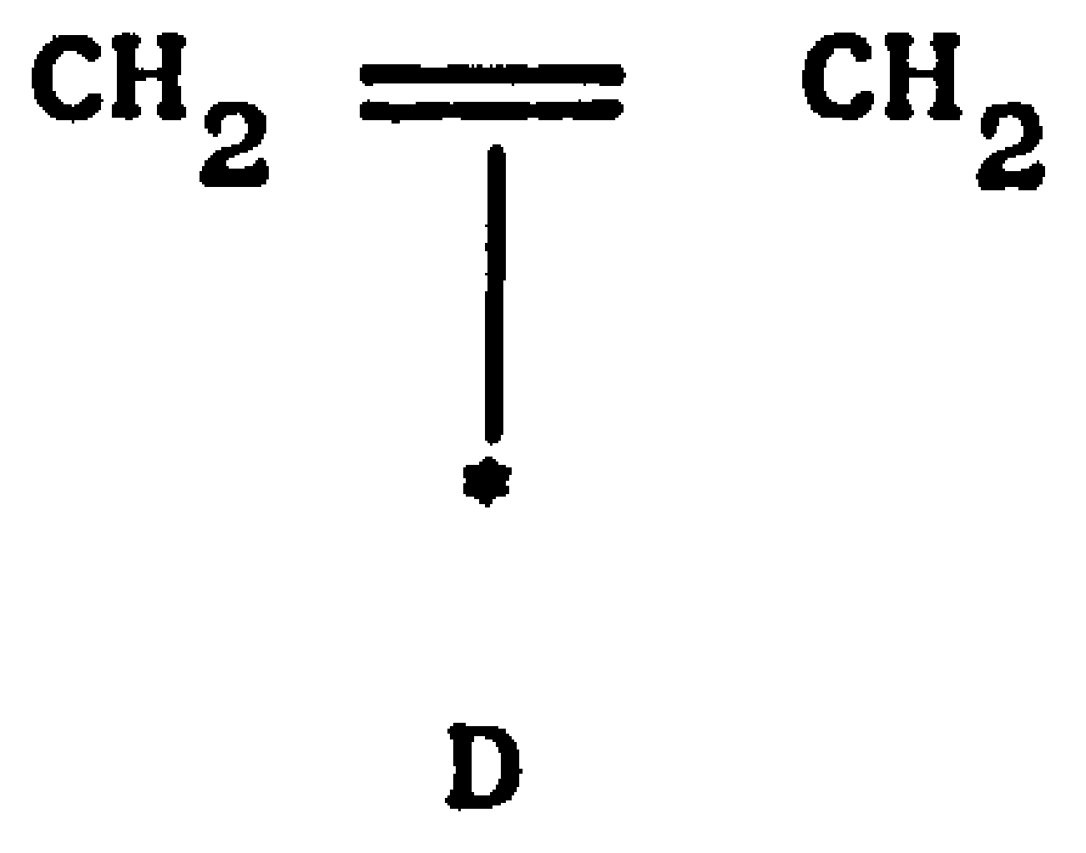
$$C_2H_6 \longrightarrow \underset{*}{\overset{|}{CH_2}}CH_3 \quad \underset{*}{\overset{|}{H}} \xrightarrow{+D} C_2H_5D \qquad (1.5)$$

Interconversion of an adsorbed-ethyl with a di-adsorbed species was postulated to explain multiple exchange (cf. methane). Thus:



(1.6)

Rapid interconversion of species A with species B would provide C_2D_6 as a major product, whereas rapid interconversion of A and C would provide CH_3CD_3 as a major product. Maxima were obtained at C_2D_6 in the initial distributions, but not at CH_3CD_3 (see Table 1.4). Thus it was concluded that species B participated in multiple exchange, but that species C did not. Species B can also be formulated as associatively adsorbed ethylene, D.



(1.7)

Anderson and Macdonald have recently investigated exchange on oriented nickel films (<u>40</u>) and found $C_2H_4D_2$ to be a major initial product with C_2H_5D absent. These authors concluded that in this particular case species C was present.

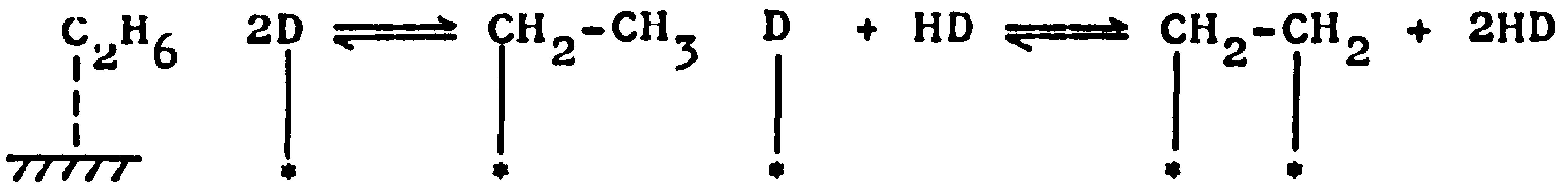
Anderson and Kemball (<u>19</u>) calculated the initial distribution of products by use of a mechanistic parameter P which was defined as:

$$P = \frac{\text{chance of adsorbed 'ethyl'} \longrightarrow \text{'ethylene'} \longrightarrow \text{'ethyl'}}{\text{chance of adsorbed 'ethyl' desorbing as 'ethane'}}$$

Values of P were selected that fitted the theoretical distribution to the experimental distribution. Initial distributions could be calculated by use of one value of P for tantalum, molybdenum, palladium, and rhodium. However, initial distributions over most of the other metals studied possessed maxima at C_2H_5D and C_2D_6 and consequently two values of P were required to obtain good agreement between theoretical and experimental distributions. Hence two different mechanisms occur on these metals, although product distributions are independent of temperature.

In this thesis the scheme described by Anderson and Kemball (<u>19</u>) for the calculation of initial distributions has been extended to embrace distributions obtained at various stages of reaction (see Section 4.3).

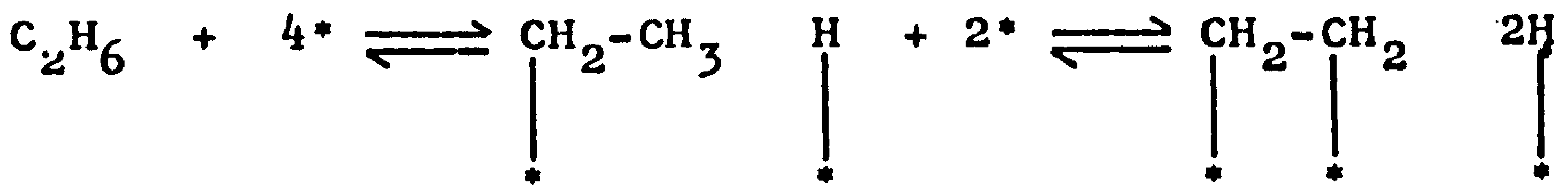
Exchange in ethane has been explained by use of a Rideal-Eley mechanism,



$$\underset{\vdots}{C_2H_6} \quad \underset{|\atop *}{2D} \rightleftharpoons \underset{|\atop *}{CH_2}-CH_3 \quad \underset{|\atop *}{D} + HD \rightleftharpoons \underset{|\atop *}{CH_2}-\underset{|\atop *}{CH_2} + 2HD$$

(1.8a)

and also by a Langmuir mechanism.

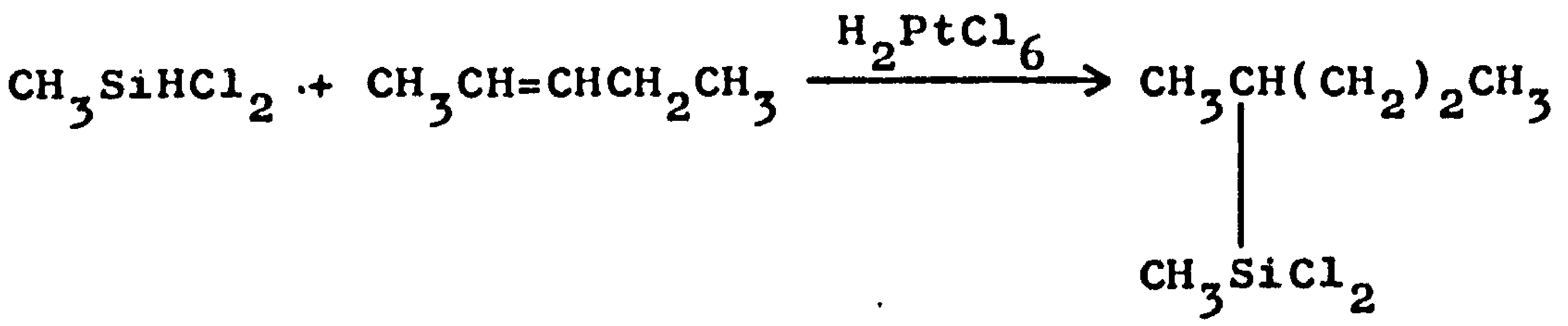


$$C_2H_6 + 4* \rightleftharpoons \underset{\overset{|}{*}}{CH_2}-CH_3 \quad \underset{\overset{|}{*}}{H} + 2* \rightleftharpoons \underset{\overset{|}{*}}{CH_2}-\underset{\overset{|}{*}}{CH_2} \quad \underset{\overset{|}{*}}{2H} \qquad (1.8b)$$

By use of arguments based on the interpretation of orders of reaction, Anderson and Kemball favoured the Rideal-Eley mechanism for the interpretation of tungsten-catalysed exchange, and the Langmuir mechanism for exchange over rhodium and palladium (19).

1.3.3 Exchange in silanes

Studies of isotope exchange in silanes have usually been made to provide information about the mechanism of hydrosilylation, that is, addition of a silane to an alkene or alkyne (41).



$$CH_3SiHCl_2 + CH_3CH{=}CHCH_2CH_3 \xrightarrow{H_2PtCl_6} CH_3\underset{\underset{CH_3SiCl_2}{|}}{CH}(CH_2)_2CH_3 \qquad (1.9)$$

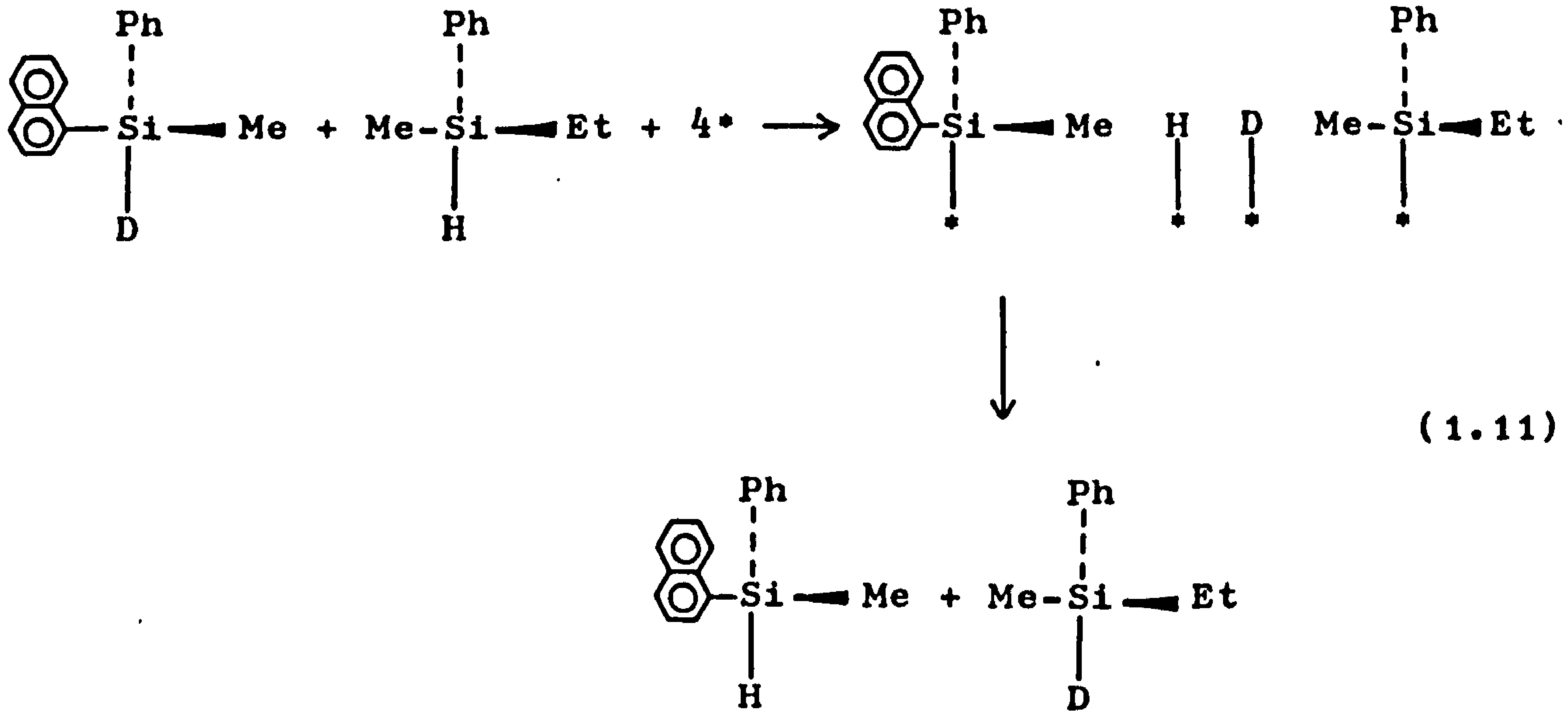
However, no reports of catalysed protium-deuterium exchange in silane, disilane, or methylsilane exist in the literature, and this thesis provides the first investigation of isotope exchange in methylsilane.

One of the first reports of exchange of protium bonded to silicon was made by Ponomarenko in 1960 (42). Hydrogen bonded to silicon was found to be readily exchanged in mixtures of $C_2H_5SiHCl_2$ and $CH_3(C_2H_5)_2SiD$ when chloroplatinic acid or platinized charcoal were present. This author believed that platinized charcoal caused the rupture of the silicon-hydrogen bond, which resulted in the formation of free radicals that initiated the exchange reaction (<u>42</u>).

In 1963 Ryan and Speier (<u>43</u>) reported exchange between $SiDCl_3$ and CH_3SiHCl_2, catalysed by chloroplatinic acid. These authors also reported that exchange occurred during hydrosilylation (<u>43</u>).

$$3.5\ SiDCl_3 + CH_2{=}C(CH_3)_2 \xrightarrow{H_2PtCl_6} (SiCl_3)C_4H_{6.5}D_{2.5} + 1.5\ SiHCl_3 + SiDCl_3 \qquad (1.10)$$

Sommer <u>et</u> <u>al</u>. (<u>44</u>) have investigated protium-deuterium exchange in optically active silanes using palladium-charcoal, platinum-charcoal, Raney nickel, and various transition metal complexes as catalysts. Rapid exchange was observed over each of these catalysts, and the rates of exchange were very much greater than rates of hydrosilylation. Exchange was accompanied by almost complete retention of stereochemistry (<u>44</u>), and this argued against the free radical mechanism proposed by Ponomarenko (<u>42</u>). The following mechanism was proposed to explain exchange over heterogeneous catalysts.



(1.11)

For the reactions discussed so far, analysis was made by Raman (42), infrared (42,44), and n.m.r. (43) spectroscopy. Exchange in silanes was not studied by mass spectrometry.

In 1972 Roberts and Ross published work on the chemisorption, decomposition and exchange of tetramethylsilane (TMS) at tungsten and at iron surfaces that had been prepared in ultra-high vacuum (45). Pronounced yields of hydrogen and of methane were detected after chemisorption of TMS on tungsten films at 293 K, whereas similar decomposition on iron films was detected at 387 K but not at 293 K. By comparison with results obtained for neopentane (46) it was concluded that the carbon-silicon bond was more readily cleaved than the carbon-carbon bond. These authors also determined the number of exchangeable hydrogen atoms present in the chemisorbed layer by monitoring their exchange with deuterium mass spectrometrically; typical values for the number of exchangeable hydrogen atoms per adsorbed molecule of TMS are shown in Table 1.5.

Table 1.5 Exchange of protium for deuterium in tetramethylsilane

Catalyst	θ[a]	No. of exchangeable hydrogen atoms per adsorbed molecule of TMS	
		T = 193 K	T = 293 K
W	0.45	3.9	8.1
W	-	3.5	6.0
Fe	0.34	2.3	8.0
Fe	0.39	3.5	8.0
Fe	0.47	3.9	8.5

[a] θ is the fraction of a monolayer adsorbed.

It has been shown that hydrogen bonded to silicon can be exchanged readily (42-44) and that the carbon-silicon bond is weaker than the carbon-carbon bond. However, no detailed investigation of the type undertaken for exchange in hydrocarbons has been made for silanes. Therefore, one aim of this thesis is to provide a detailed study of catalysed exchange in a simple silane. Methylsilane was chosen for this purpose.

SECTION 2

OBJECT

The object of the present work was to investigate the reactivity of methylsilane when chemisorbed at metal surfaces and to compare the reactivity of methylsilane with that of ethane and of methane. The work falls into two parts, (a) a study of adsorption and decomposition of methylsilane on evaporated metal films of Mo, W, Rh, Ni, and Au; (b) a study of three isotope exchange reactions over the above metals, viz:

self exchange i.e. $CH_3SiD_3 \longrightarrow CH_{3-x}D_xSiH_xD_{3-x}$

(x = 0, 1, 2, 3)

mutual exchange i.e. $CH_3SiH_3 + CH_3SiD_3 \longrightarrow$ products

exchange with molecular deuterium i.e.

$$CH_3SiH_3 + D_2 \longrightarrow \text{products}$$

$$CH_3SiD_3 + D_2 \longrightarrow \text{products}$$

From (a) and (b):

(i) the nature and empirical composition of the chemisorbed layer at complete surface coverage by methylsilane are determined;

(ii) a comparison of the activities for exchange of hydrogen bonded to carbon and hydrogen bonded to silicon is made

(iii) mechanisms of the above exchange reactions are elucidated and hence the types of reactive surface species present are defined.

SECTION 3

MATERIALS, APPARATUS AND EXPERIMENTAL METHODS

3.1 Sources of Materials and their Purification

3.1.1 Methylsilane

CH_3SiH_3 was obtained from Ralph Emanuel Ltd. It was found to be about 99 % pure. The only detected impurity was hydrogen which was removed by freezing the CH_3SiH_3 in liquid air and pumping.

CH_3SiD_3 was prepared by a method similar in principle to that described by Finholt *et al.*(47) for the preparation of silane and organosilanes. CH_3SiCl_3 was reduced by lithium aluminium deuteride (Fluorochem Ltd.; isotopic purity greater than 99 atom % D) in dibutyl ether solution at 273 K in an all-glass apparatus attached to a vacuum line (a full description is given in Appendix A.). The product was purified by trap to trap distillation at 195 K and at 173 K. The only chemical impurity detected was $(CH_3)_2SiD_2$ which was present as less than 1 % of the product. The product was of high isotopic purity (greater than 99 % D bonded to Si) only a trace of protium bonded to silicon being detectable by ^1H n.m.r.

3.1.2 Deuterium

Deuterium as supplied by Air Products Ltd. was diffused through a heated palladium-silver alloy thimble. Mass spectrometric analysis showed it to be about 99.5 atom % D.

3.1.3 Metals

Metals used in this study are shown in Table 3.1

with their source of supply and quality.

Table 3.1 Suppliers and quality of metals

Metal	Supplier	Purity (%)
Nickel	Johnson Matthey and Co. Ltd.	>99.998
Molybdenum	New Metals Ltd.	>99.9
Rhodium	Johnson Matthey and Co. Ltd.	>99.99
Tungsten	Goodfellow Metals Ltd.	>99.95
Gold	Johnson Matthey and Co. Ltd.	>99.99

3.2 Apparatus

3.2.1 General requirements

For the investigation of reactions catalysed by evaporated metal films certain requirements had to be met.

Reaction vessels had to be pumped to pressures of less than 5×10^{-6} torr (7×10^{-4} Nm^{-2}) for the deposition of films of reproducible catalytic activity (25). This condition was fulfilled either by use of a high vacuum apparatus capable of attaining pressures of less than 10^{-6} torr (1.33×10^{-4} Nm^{-2}) or by use of an ultra-high vacuum apparatus capable of attaining pressures of less than 10^{-8} torr (1.33×10^{-6} Nm^{-2}). These are described below.

Grease has a deleterious effect on the catalytic activity of metals and hence in the construction of the high vacuum apparatus, greased joints and taps were not used except on the backing line between the diffusion and rotary pumps and at sample removal points. Reaction vessels on the high vacuum system were baked under vacuum at 670 to 770 K before film deposition in order to remove contaminants (e.g. water) which might otherwise have affected the activity of the film (<u>48</u>). The ultra-high vacuum apparatus was baked at about 490 K before film deposition; the lower temperature was dictated by the fact that the ion pump underwent the baking procedure along with the remainder of the apparatus.

Reaction vessels had to be removed for cleaning, hence the following means of attachment were used. In view of the grease problem, indium seals were used on the high vacuum apparatus. These were made by evenly compressing an indium wire gasket between the Pyrex flanges of the reaction vessel and of the pumping system (Fig. 3.1). The reaction vessel of the ultra-high vacuum apparatus was attached by evenly compressing a gold wire gasket between the stainless steel flanges of the vessel and of the pumping system (Fig. 3.2).

The electrical feedthroughs had to be readily accessible, so that wires to be enclosed in the reaction vessel could be attached to the system easily. The electrical circuitry was required to carry up to 15 amps during the evaporation of some metal wires.

3.2.2 <u>The high vacuum apparatus</u>

The apparatus is shown diagramatically in Figures 3.1 and 3.3. Two Pyrex reaction vessels, A and B (Fig. 3.1) of either 0.30 l or 1.00 l capacity were attached to the pumping system by use of indium gaskets as described in Section 3.2.1. The flanges, which protruded from the furnace, F, were cooled with compressed air to prevent

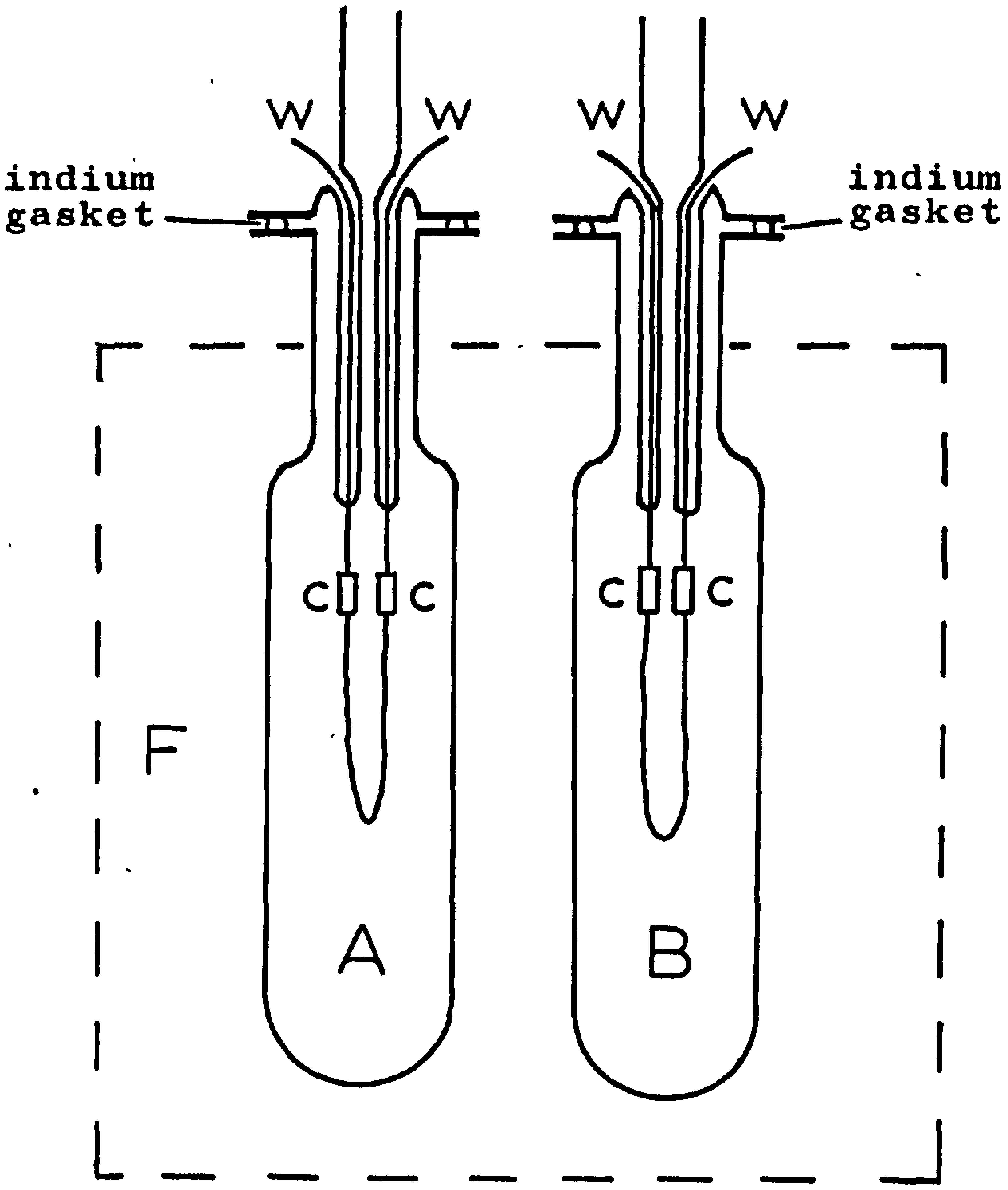


Figure 3.1 Diagram of reaction vessels and furnace (high vacuum)

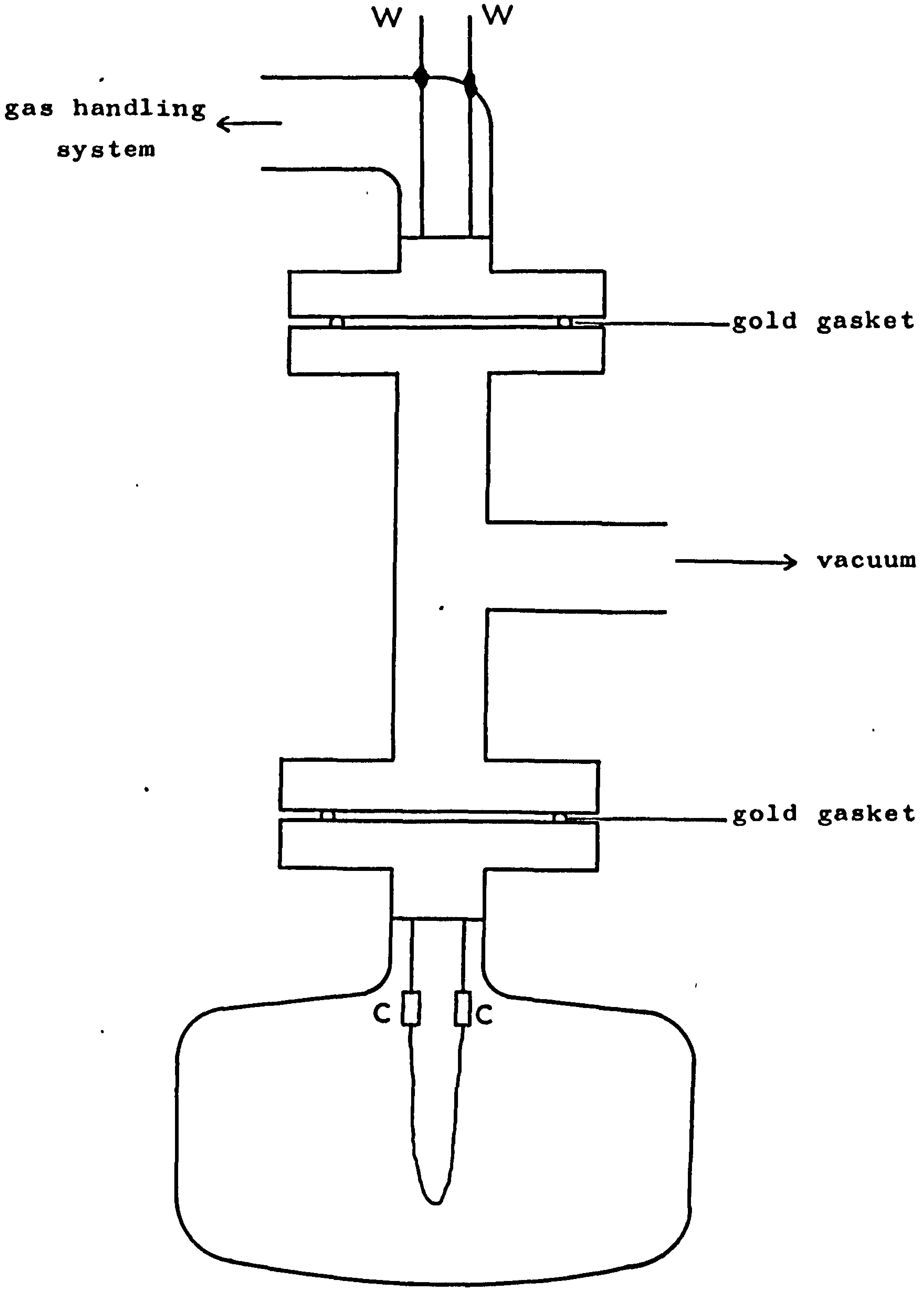


Figure 3.2 Diagram of reaction vessel for u.h.v. apparatus.

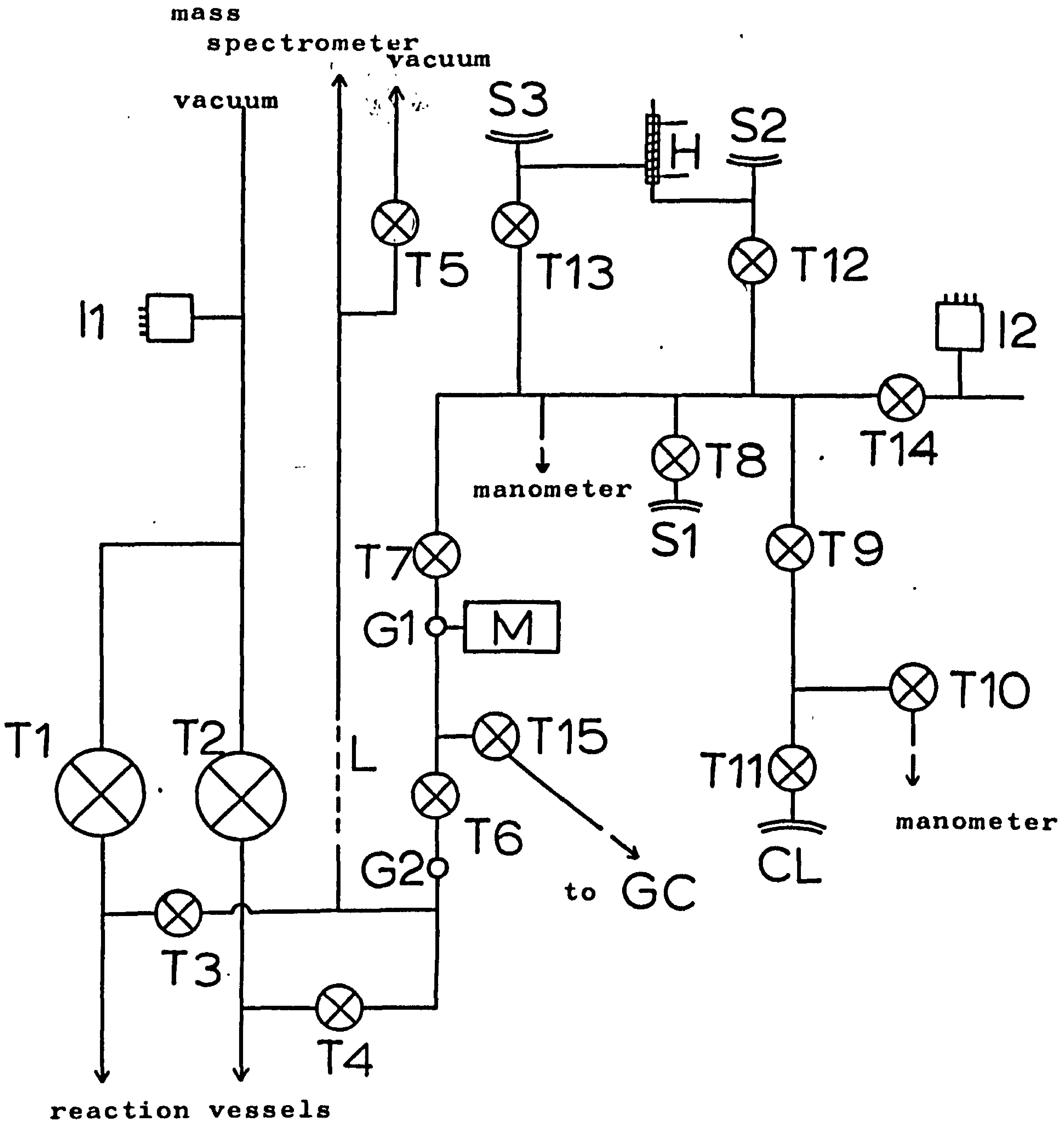


Figure 3.3 Diagram of high vacuum pumping system and ancillary equipment.

the gaskets from melting when the system was baked (In, m.p. = 430 K). Each upper flange incorporated two tungsten leads, W, which ran into the reaction vessel and were terminated in stainless steel barrel connectors, C, to which the metal under investigation was attached, either as a filament or as a pellet supported by a coil of wire of a suitable refractory metal. The reaction vessels were contained in the asbestos furnace, F, the top, front and bottom of which were removable. The furnace was rated at 1,700 watts and could rapidly attain a temperature of about 725 K.

Reaction vessels were separated from the pumping system by taps T1 and T2. They were pumped by means of a 50 mm Edwards mercury diffusion pump which was backed by a two stage rotary pump and was surmounted by a large stainless steel trap filled with liquid nitrogen. The vacuum attained, measured using an Edwards ionization gauge I1, was about 10^{-6} torr (1.33×10^{-4} Nm^{-2}). The pumping manifold, incorporating taps T1-5, was heated to about 373 K. Taps, T3 and T4, gave gases from the reaction vessel access to the mass spectrometer via the leak, L. The line between the leak and the mass spectrometer could be pumped via tap T5. T6 separated the reaction vessels from the sample handling system. The lines from the sample handling system to the reaction vessels and the mass spectrometer were heated to about 380 K in order effectively to reduce the dead space.

The sample handling system included a mixing volume, M, of about 0.075 l, in which samples were made up prior to their admittance into the reaction vessels. Sample pressures were measured using an L.K.B. thermal conductivity gauge, G1.

The storage reservoir, S1, contained CH_3SiD_3 which could be admitted to the mixing volume through taps, T7 and T8; the pressure was measured both on a manometer and on a thermal conductivity gauge. CH_3SiH_3 was introduced from a cylinder, CL, into a calibrated volume between taps T9, T10 and T11. The pressure was measured on a manometer attached to T10 before transfer of the sample to the mixing volume. Impure deuterium was stored in reservoir, S2, and purified by diffusion through a heated palladium-silver alloy thimble, H. The purified deuterium in reservoir, S3, was introduced into the mixing volume via taps, T13 and T7, and the pressure was measured using a manometer. The sample handling system was pumped, via a liquid nitrogen trap, by a 50 mm mercury diffusion pump backed by a single-stage rotary pump. The pumping system attained a pressure of about 10^{-5} torr (10^{-3} Nm^{-2}) as measured on an Edwards ionization gauge, I2.

Tap T15 permitted samples of the mixtures used to be introduced into a gas chromatograph, GC.

Pressures were measured by the following methods:

(a) mercury manometers for pressures greater than 5 torr;

(b) an L.K.B. thermal conductivity gauge (G1 and G2) for pressures between 5×10^{-3} and 5 torr (7×10^{-1} to 7×10^{2} Nm^{-2});

(c) an ionization gauge (I1 and I2) for pressures between about 10^{-7} to 10^{-4} torr (about 10^{-5} - 10^{-2} Nm^{-2}).

3.2.3 The ultra-high vacuum apparatus

The apparatus consisted of (i) stainless steel items supplied by Vacuum Generators Ltd. and items manufactured in the Faculty workshop, (ii) a Pyrex reaction vessel, and (iii) a Pyrex sample handling system. The ultra-high vacuum pumping and sample handling systems utilized metal valves.

The ion pump, IP, was connected to the VG-Q7 quadrupole mass spectrometer, QMS, and valve, V3, via valves, V1 and V2, (Fig. 3.4). The ion pump was capable of attaining a pressure of 10^{-10} torr (10^{-8} Nm^{-2}) as measured on a VG-TCS6 ionization gauge at IG1. The reaction vessel was attached to a T-junction by the method described in Section 3.2.1 (Fig. 3.2). One flange of the T-junction was connected to valve V3, which provided access to the ion pump and the quadrupole mass spectrometer. During the course of reactions in the vessel, RV, the valve V3 was used to leak products into the mass spectrometer.

The upper flange connected to the T-junction (Fig. 3.2) incorporated two tungsten leads, W, which led into the reaction vessel and were terminated in stainless steel barrel connectors, C. The metal under investigation was attached to the connectors either in wire form or as a pellet supported in a coil of wire of a suitable refractory metal.

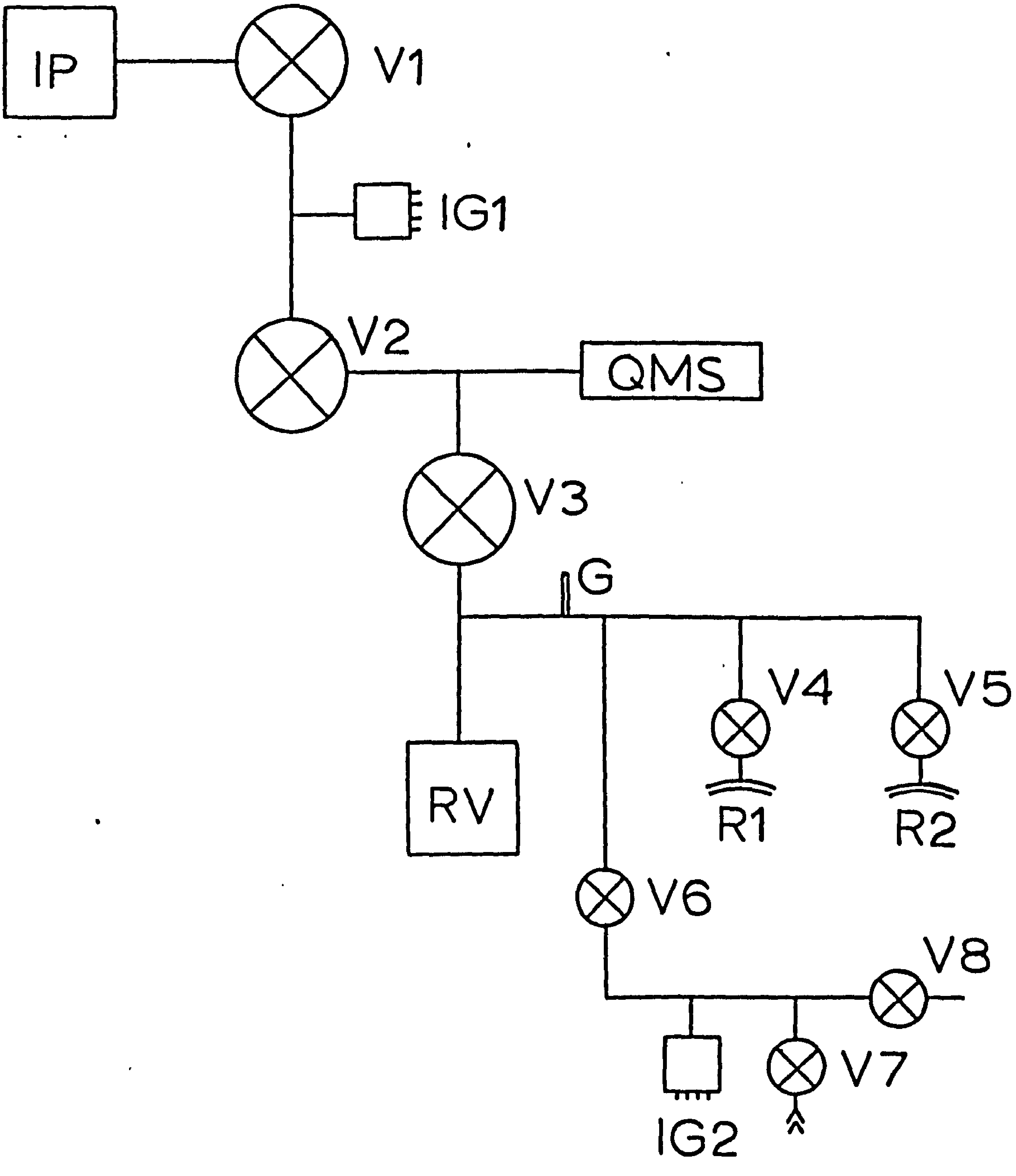


Figure 3.4 Diagram of u.h.v. pumping system and ancillary equipment.

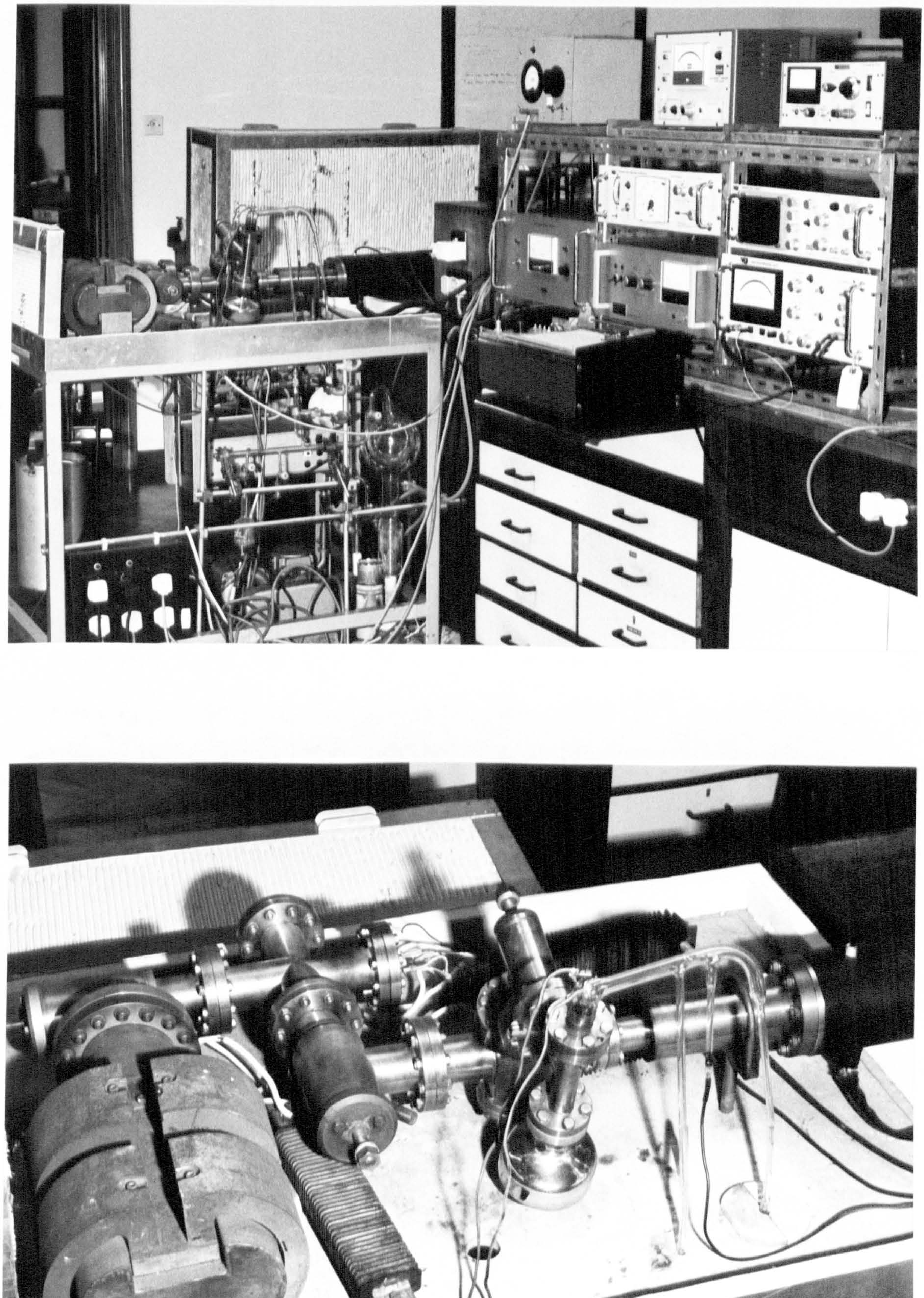


Plate 3.1 General and close-up views of the u.h.v. apparatus

The upper flange of the T-junction also led to the sample handling system. The entire u.h.v. system, up to valves V4, V5, and V6 were, from time to time, baked in an oven that could attain a temperature of 490 K.

A mixture of CH_3SiH_3 and CH_3SiD_3, stored in reservoir R1, was admitted to the system by the valve, V4. The pressure was measured on a calibrated L.K.B. thermal conductivity gauge, G. Similarly, purified deuterium could be admitted from reservoir R2 by valve V5. CH_3SiH_3 or CH_3SiD_3 could be introduced into the vessel via taps V6 and V7.

The products of each reaction were pumped away through taps V6 and V8 by a standard high vacuum pumping system. The system, which consisted of a single-stage rotary pump, mercury diffusion pump, and liquid nitrogen trap, was capable of attaining a pressure of about 10^{-6} torr measured using an ionization gauge located at IG2.

3.2.4 Mass spectrometry

Three mass spectrometers have been used.

The A.E.I. - MS902 was a high resolution, double focussing mass spectrometer, which employed an electron multiplier as detector. Mass spectra were recorded using a high speed recorder utilising an ultra-violet beam and photosensitive chart paper. This mass spectrometer was used for the detection of metastable ions in the spectra of CH_3SiH_3 and of CH_3SiD_3, and to monitor the exchange reactions of methylsilane with molecular deuterium and of CH_3SiH_3 with CH_3SiD_3.

The vacuum Generators Micromass 6 was a low-resolution high-sensitivity single-focussing mass spectrometer, which incorporated a Faraday plate detector. Mass spectra were recorded using a hot-pen chart recorder. The response time of the detector and recorder were such that it was necessary to scan the mass spectra at a rate of less than 20 a.m.u. per minute. This mass spectrometer was used (i) to obtain ionization efficiency curves, (ii) to determine the composition of the gas phase in the reaction vessel during the adsorption of methylsilane on metal films, and (iii) to monitor isotope exchange in methylsilane. This mass spectrometer became available during the course of this study, and due to its higher sensitivity and greater reproducibility of mass spectra, it replaced the A.E.I. - MS902.

The Vacuum Generators Micromass Q7 was a low resolution quadrupole mass spectrometer, which used an electron multiplier as detector. Spectra could be recorded on a chart recorder or photographically from an oscilloscope display unit. This mass spectrometer was used in conjunction with the u.h.v. apparatus. It could be operated at 70 eV or at 18 eV, the latter voltage being obtained using a printed circuit board built in the Department workshop. The higher energy was used solely for degassing the ion source filament.

3.2.5 Gas chromatography

The apparatus consisted of a sample injection unit, a column and a hot-wire katharometer. The katharometer (Gow Mac, Type Pretzel 10-285) contained two matched pairs of rhenium-tungsten filaments; one pair was situated in the sample gas stream, and the other pair in the reference gas stream. The carrier gas (helium) passed through the reference cell, and then through the sample injection unit, which consisted of a U-tube and a bypass. The sample in the carrier gas stream then passed through a 4' column of Poropak P contained in a copper tube of 0.125" i.d., and finally through the detector cell of the katharometer. The operating conditions of the gas chromatograph, and the retention volumes of samples introduced are shown in Table 3.3. A typical chromatogram is shown in Figure 3.5.

Table 3.3 Retention volumes for a 4' Poropak P column.

filament current = 100 mA

flow rate = 0.304 mls^{-1}

column temperature = 293±3 K

Sample	Retention volume (ml)
Hydrogen	4.3
Methane	5.7
Methylsilane	62.8
Propane	113.9

3.3 Preparation of Evaporated Metal Films

The following general procedure has been used for the formation of evaporated metal films under both high vacuum and ultra-high vacuum conditions.

(a) All parts of the system were pumped and on the high vacuum system all the lines were heated.

(b) Weighed filaments were washed with diethyl ether to

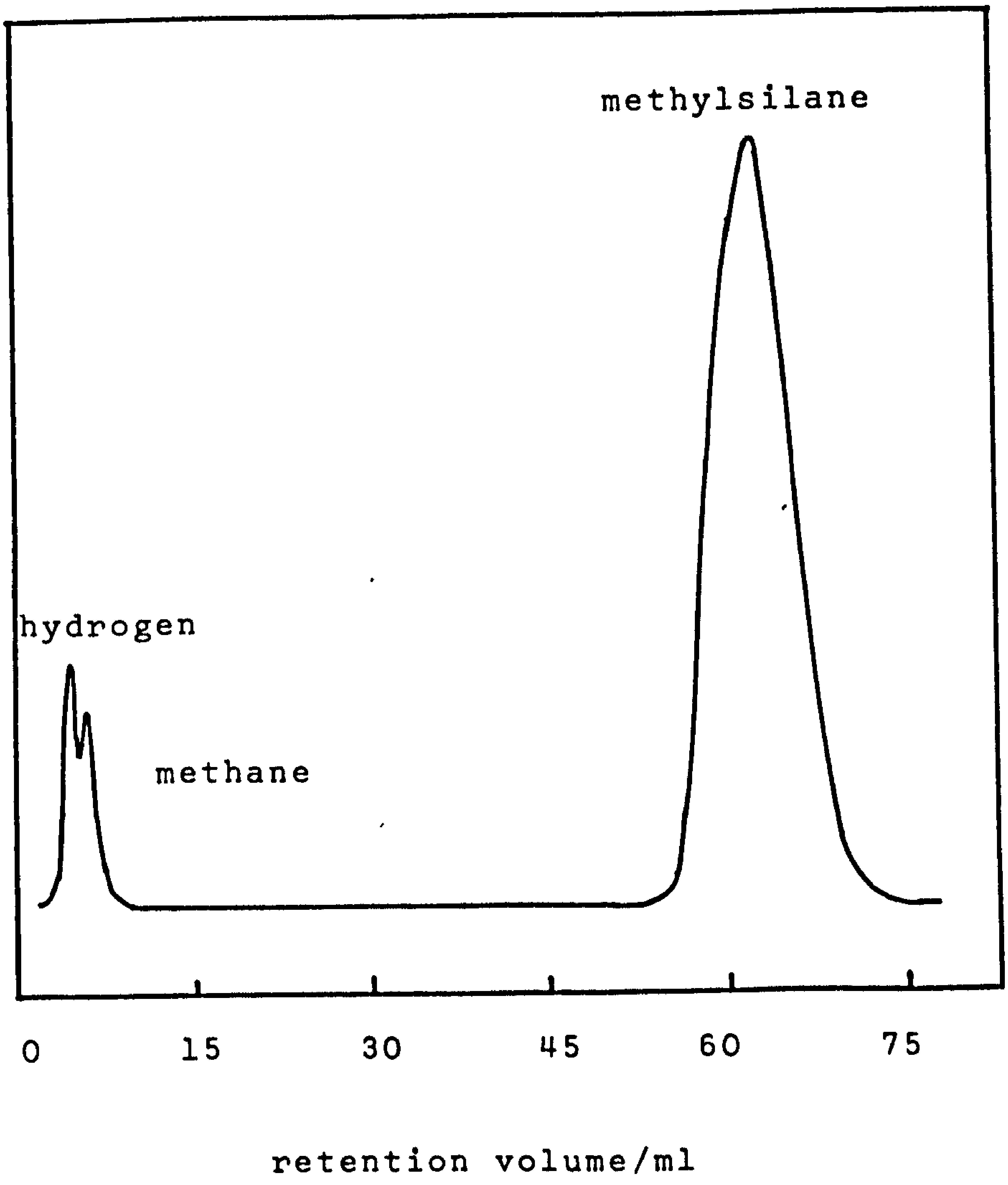


Figure 3.5 A typical gas chromatogram for a mixture of hydrogen, methane and methylsilane (1:0.2:3.5)

remove grease and were attached to the stainless steel barrel connectors. The reaction vessels were sealed to the system as described above. The vessels were then pumped; the vessel on the ultra-high vacuum apparatus was pumped through tap V6 (Fig. 3.4) before being pumped by the ion pump.

(c) The furnace of the high vacuum apparatus was assembled and the reaction vessels were baked at 670-720 K for three hours; during the final hour the filaments were electrically heated to a little below the evaporation temperature to remove dissolved gases. The furnace was removed when no further improvement in vacuum could be obtained. (If the pressure was still greater than 6 x 10^{-6} torr (800 Nm^{-2}) the procedure was abandoned).

The ultra-high vacuum system was enclosed in an oven and baked at 490 K for twelve hours. On several occasions a low current was passed through the filament for the majority of this period, in order to remove weakly adsorbed material. On every occasion, during the final hour, the filament was heated to a little below its evaporation temperature in order to degas the metal thoroughly. A film was prepared if the pressure was less than 10^{-8} torr after this procedure.

(d) The reaction vessel was immersed in a slush bath of suitable temperature (195-273 K). The current in the filament was increased until evaporation occurred. The current was switched off when a film of suitable weight appeared to have been formed. The film produced was used immediately for studies of adsorption or catalysis, before sintering or poisoning by residual gases could occur. Films were normally used at the temperature at which they had been deposited.

(e) Currents for degassing and evaporating the metals used, and the reagents used for cleaning the reaction vessels have been described by Baron (25).

(f) Reaction vessels were removed and cleaned after use. The filaments were re-weighed and film weights were determined by subtraction of the final weight of the filament from the initial weight.

3.4 Experimental Procedure Employed when Investigating the Adsorption of CH_3SiH_3 on Evaporated Metal Films

3.4.1 Calibrations and the analysis of gas mixtures

Pressures of samples in the mixing volume before and after expansion into the reaction vessel were measured using an L.K.B. thermal conductivity gauge, (hereafter referred to as 'an L.K.B. gauge'). It was necessary to calibrate the L.K.B. gauge with respect to each of the gases which might be present during adsorption experiments; that is, CH_3SiH_3, methane, and hydrogen. The gauge was calibrated in the following way. A known pressure of CH_3SiH_3 was introduced into the mixing volume, M, (see Fig. 3.3) and was expanded into a vessel of known volume, A, (the reaction vessel was normally used for this purpose). The new pressure was calculated using Boyle's Law and the reading on the L.K.B. gauge recorded. Vessel A, was pumped and the remainder of the sample in the mixing volume was shared with vessel A. The pressure was re-calculated and the gauge reading recorded. This procedure was repeated until the pressure had been reduced from its initial value of about 20 torr to about 0.001 torr. The L.K.B. gauge was calibrated in a similar fashion for methane and for hydrogen.

During the course of adsorption experiments methane and hydrogen were evolved, thus pressures of mixtures had to be measured. The thermal conductivities of gases are often additive if the overall pressure is sufficiently low (49). The gauge was calibrated with mixtures of hydrogen and methane, and with mixtures of hydrogen and CH_3SiH_3, and for the pressures employed (less than 0.10 torr) the thermal conductivities were found to be approximately additive.

However, to determine the partial pressure of each component in the mixtures formed, it was necessary to know the relative pressures of the gases. This ratio was determined mass spectrometrically. The relative mass spectrometric sensitivities of each gas at 70 eV was determined by the introduction of mixtures of hydrogen and methane, and mixtures of hydrogen and CH_3SiH_3 all of known composition. Thus from the L.K.B. gauge reading and the relative pressures of the components, determined by allowing amounts of the mixture to leak into the mass spectrometer, the partial pressures could be determined in the following way. An approximate value for the pressure of one of the components was selected and the other partial pressures calculated. The corresponding thermal conductivities were added up and compared with the reading recorded on the L.K.B. gauge. If the calculated value were too high, the initial value selected for the pressure of each component to be determined was reduced and the calculation of the thermal conductivity repeated. Likewise, if the calculated value of the thermal conductivity were too low, the value of the pressure of each component was increased, and the calculation repeated. By an iterative procedure good agreement between calculated and observed thermal conductivities was eventually obtained.

3.4.2 Adsorption of methylsilane

After film deposition, a sample of CH_3SiH_3 was expanded into the reaction vessel from the mixing volume. The reading on the L.K.B. gauge was recorded before and after this expansion. A fresh sample was introduced into the mixing volume and this in turn was expanded into the reaction vessel. This procedure was repeated until a standing pressure was detected. The process was then continued with the following modifications. Firstly, the mixing volume was pumped before introducing a fresh sample of CH_3SiH_3 and, secondly, gases from the reaction vessel were now allowed to leak into the mass spectrometer.

After each admission of CH_3SiH_3 to the reaction vessel, the contents of the mixing volume were pumped away. This resulted in a loss of about 20 % of the gases which comprised the standing pressure in the system. Therefore it was necessary to correct the subsequent partial pressures of each component for the loss incurred. The isotherm was plotted as the partial pressure of each component against the quantity of CH_3SiH_3 added. Figure 3.6 shows a typical isotherm obtained before the correction had been made for material pumped away from the mixing volume. Figure 3.7 shows the corresponding isotherm after the correction had been made, and hereafter only corrected isotherms will be shown. The magnitude of the corrections was such that quite marked errors were transmitted in this process.

The results could readily be transformed into a plot of partial pressure of CH_3SiH_3 against the quantity of CH_3SiH_3 adsorbed; this is shown in Figure 3.8. Point A corresponds to the initial appearance of CH_3SiH_3, but not necessarily to complete coverage of the surface. It is more usual to extrapolate the linear section of the graph to the axis (point B) to provide an estimate of surface area. Hence the linear section of the curve representing the variation of methylsilane pressure was extrapolated to point B, as shown in Figure 3.7, when the data were used to estimate the surface area of the film.

The surface composition of the chemisorbed layer was calculated also at point B. This was done by subtracting the material known to be present in the gas phase from that known to have been admitted to the vessel.

3.5 Experimental Procedure Employed for the Investigation of the Exchange Reactions of Methylsilane

3.5.1 Preparation of mixtures

Methylsilane was carefully degassed by being repeatedly frozen, pumped, and thawed before being used for exchange reactions. Mixtures were made up in the mixing volume, M, (Fig. 3.3) before use and the partial

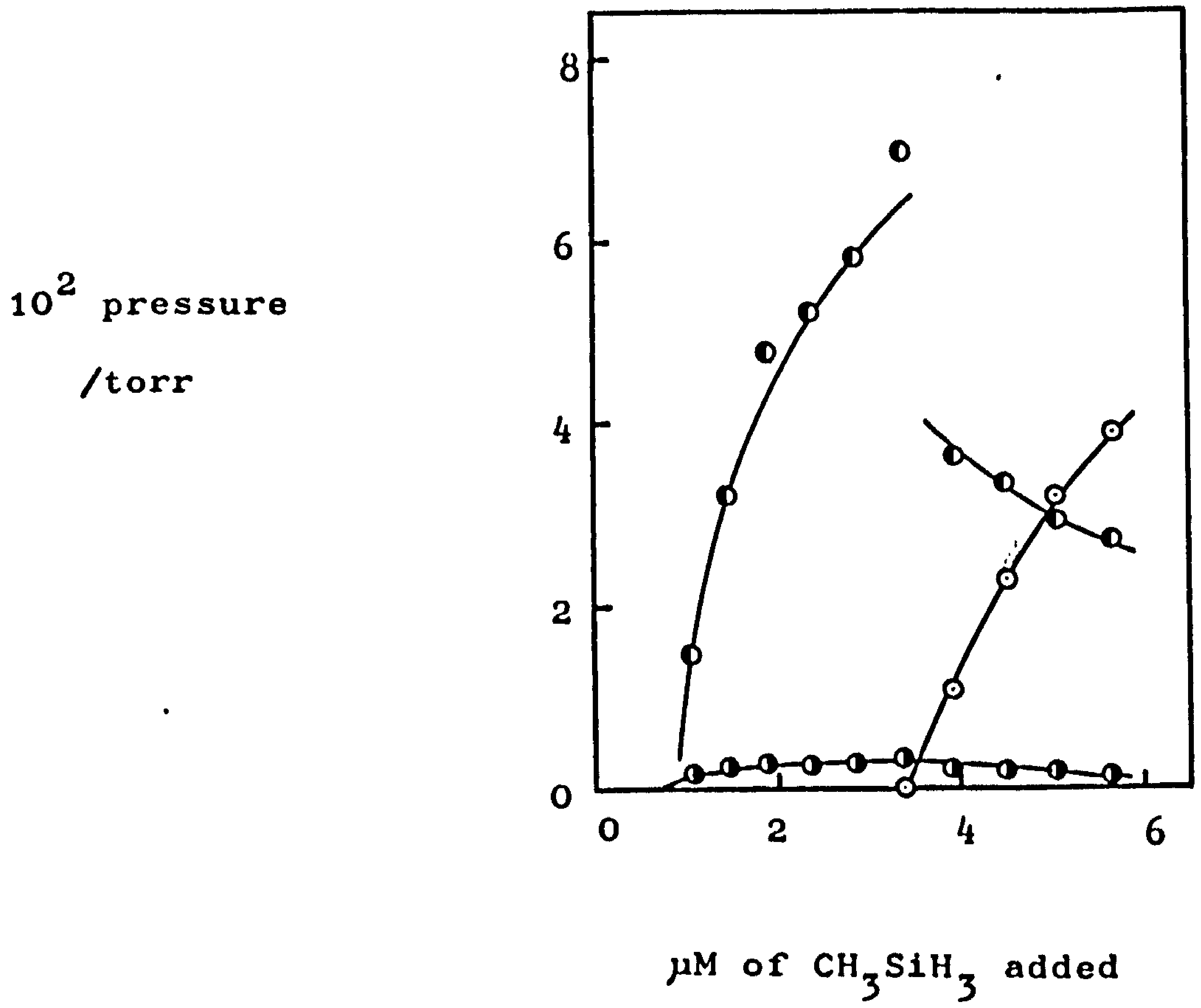


Figure 3.6 Chemisorption of CH_3SiH_3 on tungsten at 273 K (uncorrected): film wt. = 18.3 mg.

Legend:- ⊙ CH_3SiH_3 , ◐ H_2 , ○ CH_4

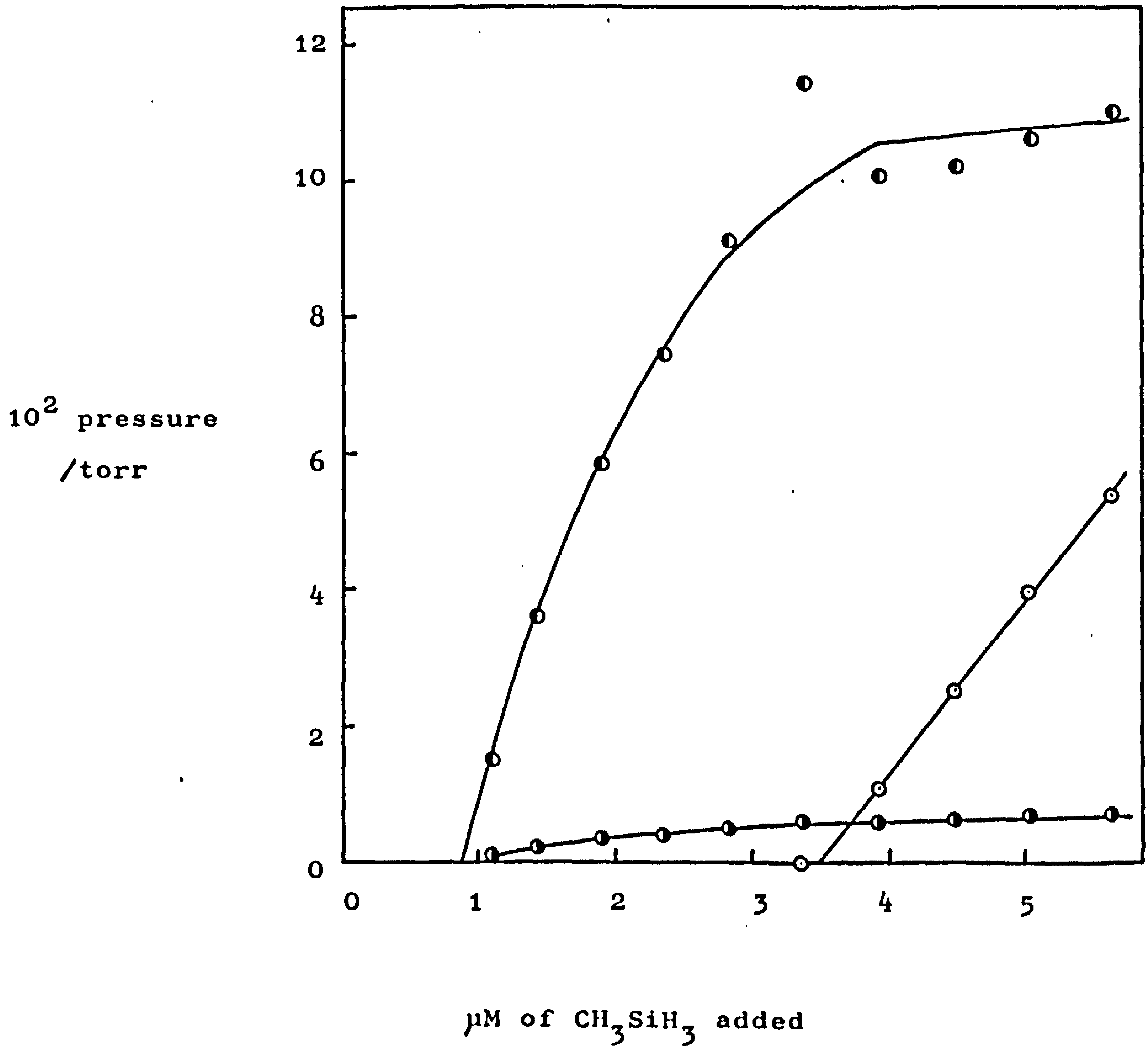


Figure 3.7 Chemisorption of CH_3SiH_3 on tungsten at 273 K (corrected): film wt. = 18.3 mg

Legend:- ⊙ CH_3SiH_3 , ◐ H_2 , ◑ CH_4

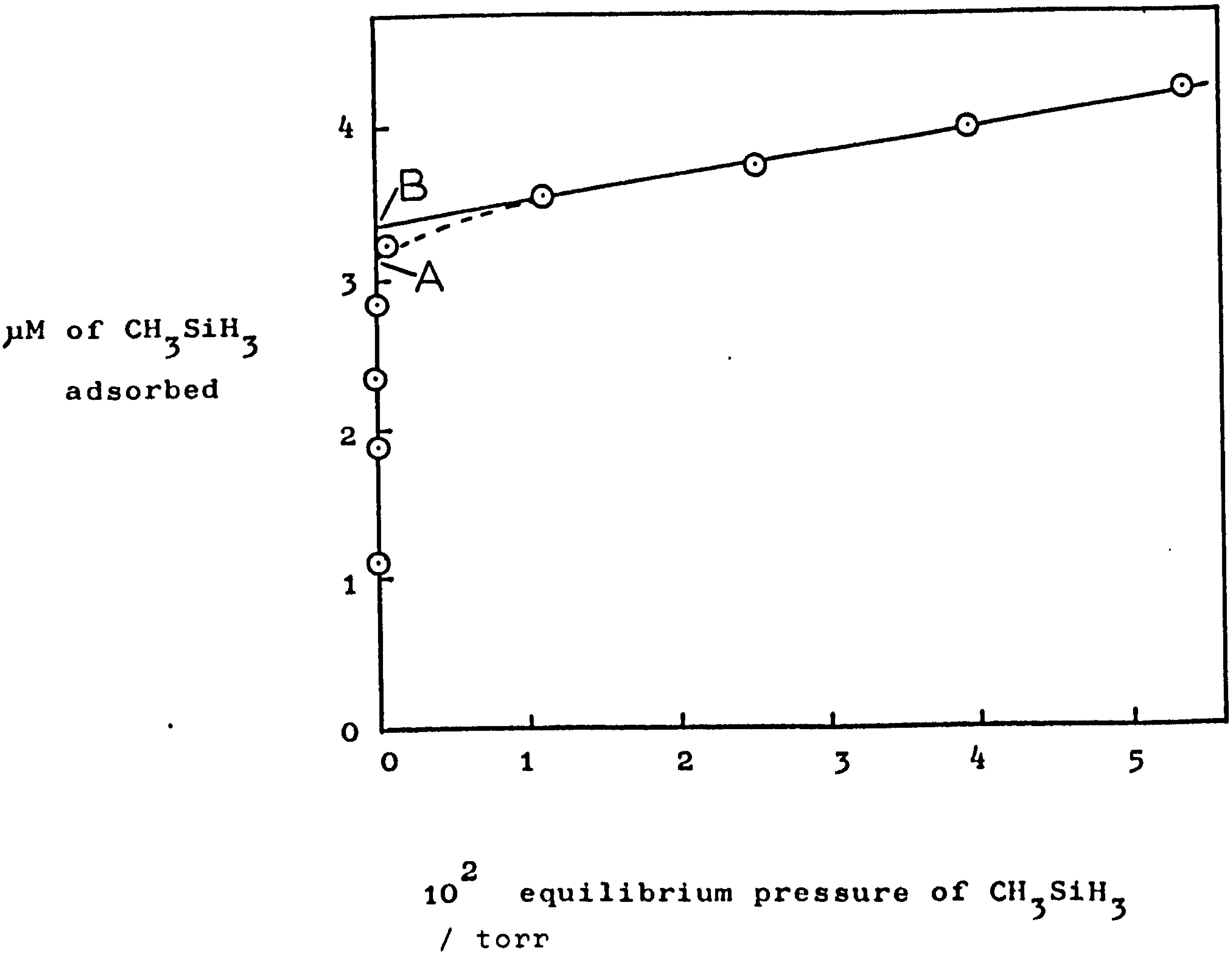


Figure 3.8 Langmuir adsorption isotherm for CH_3SiH_3 on tungsten at 273 K: film wt. = 18.3 mg.

pressure of each component after admission to the reaction vessel is shown in Table 3.2.

Table 3.2 Compositions of reaction mixtures

Reaction	Vacuum conditions	Partial pressures (torr)		
		CH_3SiD_3	CH_3SiH_3	D_2
Self exchange	hv	1.0	-	-
Self exchange	uhv	1.0	-	-
Mutual exchange	hv	0.5-2.0	0.5-2.0	(10.0)[a]
Mutual exchange	uhv	0.5-2.0	0.5-2.0	-
Exchange with D_2	hv	1.0	-	10.0
Exchange with D_2	hv	-	0.5-2.0	5.0-10.0

[a] Deuterium was added to some reactions in which mutual exchange was being studied.

3.5.2 Mass spectra

Mass spectra of deuteriated methylsilane in the range m/e = 43-49 were recorded (using the various spectrometers previously described) using an ionization energy of 18 eV. This value was chosen as a convenient compromise, since it was sufficiently low to reduce the extent of fragmentation to the production of ions by the loss of one, two, or three X-atoms (X = H or D). Fragmentation spectra of CH_3SiH_3 and of CH_3SiD_3 were recorded either immediately before or immediately after that of a sample of deuteriated methylsilane.

The composition of mixtures of isotopically labelled methylsilane was then determined as described in Appendix B.

Mass spectra were also recorded for the m/e ranges 2 to 4, 14 to 20, 28 to 34 and 56 to 64 a.m.u. to detect hydrogen, deuteriated methane, silyl fragments from methylsilane, and dimethylsilane respectively. These spectra were recorded either at 18 eV or 70 eV. Spectra were recorded for mixtures of these substances of known composition so that the total spectrum could be converted into percentages of each product; dimethylsilane, however, was assumed to have the same mass spectrometric sensitivity as methylsilane.

SECTION 4

GENERAL TREATMENT OF RESULTS

4.1 Analysis of Mixtures

A method for the analysis of mixtures containing CH_3SiX_3 (X = H or D) is described fully in Appendix B. This sub-section summarises some of the more important features of the analysis.

The principal problem encountered arose from the absence of a parent ion in the positive ion mass spectrum of methylsilane; thus the common practice of eliminating the contributions of fragment ions from the mass spectrum so as to leave the parent ions could not be used (50). Appendix B describes how analysis can be achieved by use of the fragmentation spectra.

An interpolation procedure was used to obtain the relative intensities of all ions in a mass spectrum at a single time. Mass spectra were corrected for the natural abundances of ^{13}C (1.11 %), ^{29}Si (4.70 %) and ^{30}Si (3.09 %) by use of a computer program described in Appendix C before being used to determine the compositions of mixtures.

As indicated in Appendix B, when exchange occurred in a mixture initially containing equimolar quantities of CH_3SiH_3 and CH_3SiD_3, the products, CH_3SiH_2D and CH_3SiHD_2, were assumed to be formed in equimolar proportions, i.e. possible isotope effects were ignored. The number of equations to be solved then exceeded the number of unknowns, and an analysis could be achieved. For mixtures which were only approximately equimolar (say 55 % of one reactant) the ratio of CH_3SiH_2D to CH_3SiHD_2 was assumed to be the same as that at equilibrium, and so again analysis could be achieved. The mass spectra were converted into percentages of each deuteriated methylsilane by use of the appropriate computer program described in Appendix C.

For mass spectra obtained for the exchange of CH_3SiH_3 with molecular deuterium, it was assumed that CH_3SiD_3 was absent if the ion current for $\underline{m}/\underline{e}$ = 47 was zero or less than about 1.5 % of the total ion current for ions in the range $\underline{m}/\underline{e}$ = 43-47; under these conditions simultaneous solution of the relevant equations was again possible. The mass spectra were converted into the composition of the mixture by use of the appropriate computer program described in Appendix C.

The deuterium content of methylsilane, ϕ, is defined as follows:

$$\phi = \underline{d}_1 + 2\underline{d}_2 + 3\underline{d}_3 \qquad (4.1)$$

where ϕ is the number of deuterium atoms in 100 molecules of the mixture and $\underline{d}_x$ is the percentage of $CH_3SiH_{3-x}D_x$ (x = 0,1,2 or 3) in the mixture. A value of ϕ could be obtained directly from the mass spectrum (equation (9) Appendix B).

4.2 Determination of Rate Coefficients and Specific Rates

Rate coefficients were obtained by use of equations derived by Kemball (51).

For the exchange of CH_3SiH_3 with molecular deuterium the usual equations were used; they are shown in their differential form in (4.2) and (4.3), and in their integrated form in (4.4) and (4.5).

$$d\phi/dt = k_\phi (1 - \phi/\phi_\infty) \tag{4.2}$$

$$d(100-d_0)/dt = k_0 (1 - (100-d_0)/(100-d_{0\infty})) \tag{4.3}$$

$$-\ln(\phi_\infty - \phi) = k_\phi t/\phi_\infty - \ln(\phi_\infty - \phi_0) \tag{4.4}$$

$$-\ln(d_0 - d_{0\infty}) = k_0 t/(100-d_{0\infty}) - \ln(100-d_{0\infty}) \tag{4.5}$$

For the reactant compositions used, $d_{0\infty}$ was close to zero.

The rate coefficient, k_ϕ, for the incorporation of deuterium into 100 molecules of methylsilane was calculated from the plot of $\ln(\phi_\infty - \phi)$ against time. Similarly, the rate coefficient, k_0, for the loss of CH_3SiH_3 was obtained from the plot of $\ln(d_0)$ against time.

The ratio, M, was used to represent the mean number of protium atoms exchanged for deuterium during each residence of a molecule on the catalyst surface in the initial stages of the reaction of CH_3SiH_3 with deuterium. This ratio is defined as

$$M = k_\phi/k_0 \tag{4.6}$$

For the mutual exchange reaction (CH_3SiH_3 + $CH_3SiD_3 \longrightarrow$ products), the rate of consumption of both reactants has been followed, as expressed by equation 4.7

$$-\ln(d_{03}-d_{03\infty}) = k_{03}t/(100-d_{03\infty})-\ln(100-d_{03\infty}) \qquad (4.7)$$

where $d_{03} = d_0 + d_3$. Thus the rate coefficient for mutual exchange is expressed as k_{03}. This procedure is preferred to the alternative of determining rate coefficients for the removal of CH_3SiH_3 and of CH_3SiD_3 individually, since substantial errors sometimes occur in the values of $d_{0\infty}$ and $d_{3\infty}$ due to inaccuracies in making up the initial mixtures. Such errors partially counter each other in the determination of $d_{03\infty}$.

The rate coefficient, k_{03}, was determined from the plot of $\ln(d_{03}-d_{03\infty})$ against time.

The variation of the ratio of CH_3SiH_2D to CH_3SiHD_2 with consumption of the reactants depends upon whether the exchange is of stepwise or of multiple type. For a mixture containing initially equimolar quantities of CH_3SiH_3 to CH_3SiD_3, mechanisms cannot be distinguished. If the initial quantities were not equimolar, mechanisms should become distinguishable. However crude simulation of the possible mechanisms showed that the resultant mass spectra were insufficiently distinguishable for profitable studies to be undertaken using non-equimolar starting mixtures.

Kemball's equations (<u>51</u>) give linear function plots provided the reaction obeys the first order relation described by (4.2) and (4.3), and is unpoisoned. However poisoning was observed for many reactions and in these cases the rate coefficients were determined from the initial slope of the function plots obtained.

The rate coefficients k_{ϕ}, k_0, and k_{03} are each expressed in terms of percentage change in unit time. They are therefore dependent upon the quantities of catalyst and of reactants used; thus the rate coefficients were converted to specific rates, so that reactions carried out in vessels of different volumes and involving different film weights could be compared. These specific rates are expressed as nanomoles of methylsilane converted per second per milligram of catalyst.

4.3 <u>Alternative Methods of Analysing Mixtures Used for Exchange with Molecular Deuterium</u>

A scheme for analysing mixtures of deuteriated methylsilanes formed by protium-deuterium exchange has been described in Section 4.1, and in Appendix B where the terms are defined. The scheme depends upon the assumption that one of the products is not present in the early stages of reaction *viz*. CH_3SiD_3 is not present to any great extent. However, when ϕ is greater than about 0.25 ϕ_{∞}, and if there is extensive multiple exchange, then this assumption is no longer valid. Two alternative methods of determining the value of d_0 for the function plot of $\ln(d_0-d_{0\infty})$ against time are described below. Specific rates determined for the above function plot are henceforth referred to as k_0^I when values of d_0 have been obtained by the method described in Section 4.1, and similarly the multiplicity will be referred to as M^I.

4.3.1 Method 1

This method is relatively trivial as it can only apply to stepwise exchange. However, its value is that it can identify stepwise exchange unambiguously, and thus information about mechanism may be obtained.

The deuterium present in the molecule, and represented in magnitude by ϕ, is assumed to be distributed throughout the silyl groups of the molecules in accordance with a binomial distribution. The distribution of methylsilanes obtained was normalised and introduced into equations 8a to 8e of Appendix B. The mass spectrum thus simulated was compared with the actual spectrum. If the comparison was favourable (i.e. the sum of squares of errors of peak heights was less than 1.5) then a satisfactory value of d_0 was obtained and exchange was apparently stepwise. The processes involved are shown in equations 4.8 to 4.10.

$$100 = IA_{43} + IA_{44} + IA_{45} + IA_{46} + IA_{47} \qquad (4.8)$$

$$100 = IC_{43} + IC_{44} + IC_{45} + IC_{46} + IC_{47} \qquad (4.9)$$

$$SSEP = \sum(IC_N - IA_N)^2 \qquad (4.10)$$

IA is the corrected ion current (peak height) from the recorded mass spectrum, and IC is the corresponding value determined by assuming a binomial distribution of deuterium in the products. Subscripts in (4.8) and (4.9) are the m/e values for each peak. In (4.10) subscript, N, takes the value of each successive m/e value (43 to 47) in the summation and SSEP is the sum of squares of errors of peak heights.

Specific rates for loss of CH_3SiH_3 determined by this method are referred to as k_0^{II}, and the multiplicity as M^{II}. Values of k_0^{II} and of M^{II} are quoted in Section 5 only when favourable values of SSEP had been determined. Deviations of values of M^{II} from unity indicate the extent of graphical errors.

4.3.2 Method 2

This method of determining values of d_0 depends upon simulation of the exchange reaction. This method is simply a dynamic application of the equations described by Kemball (19,51) for calculation of the initial distribution of deuterium in ethane; the principal equation is shown below:

$$Q_m \left(1 + \sum_n \mu_{mn}\right) = a_m (0) + \mu_{lm} \sum Q_l \qquad (4.11)$$

where (i) Q_m is the total probability of a radical leaving the surface to give a molecule of configuration, m; (ii) $a_m(t)$ is the probability at time, t, that a radical is in a configuration that will give a molecule, m, and $a_m(0)$ is the value of $a_m(t)$ at $t = 0$;

(iii) $\mu_{mn} = \lambda_{mn}/\lambda_m$ where λ_{mn} is the probability per unit time of a radical which on desorption would give a molecule m, going to form a radical which on desorption will give a molecule n, and λ_m is the probability per unit time of a radical leaving the surface to give a molecule m;

(iv) Q_1 and μ_{1m} have similar meanings to Q_m and μ_{mn}

It is found that

$$\mu_{1m} = g_{1m}\,P, \quad \mu_{mn} = g_{mn}\,P$$

where $P = \dfrac{\text{chance of adsorbed-'}C_2H_5\text{'} \longrightarrow \text{adsorbed-'}C_2H_4\text{'} \longrightarrow \text{adsorbed '}C_2H_5\text{'}}{\text{chance of adsorbed-'}C_2H_5\text{' desorbing to gas phase}}$

and g_{1m} and g_{mn} are statistical weighting factors that express the probability of loss of a protium atom when the mono-adsorbed species becomes a di-adsorbed species.

This scheme has been modified for methylsilane so that product distributions other than the initial distribution could be calculated. It is, therefore, necessary to introduce two additional parameters, H and D. H is the probability of an adsorbed species interacting with an adsorbed protium atom, and D is the corresponding parameter for deuterium.

The scheme envisaged by Kemball assumed that interaction only occurred with deuterium. However, as exchange proceeds a substantial pool of protium is created and thus:

$$\mu_{1m} = g_{1m}\ DP \text{ or } g_{1m}\ HP$$

$$\mu_{mn} = g_{mn}\ DP \text{ or } g_{mn}\ HP$$

If the new adsorbed species is of higher molecular weight then the factor used is D, and g_{1m} and g_{mn} have the same meaning as before. If the species is of lower molecular weight then the factor used is H, and g_{1m} and g_{mn} are now probabilities of loss of a deuterium atom when the mono-adsorbed species becomes a di-adsorbed species.

For methylsilane

$$P = \frac{\text{chance of adsorbed-}CH_3SiH_2 \rightarrow \text{-}CH_3SiH \rightarrow \text{-}CH_3SiH_2}{\text{chance of adsorbed-}CH_3SiH_2 \rightarrow CH_3SiH_3}$$

and $a_m(0)$ becomes $a_{x,z}(0)$ where x = 1,2, or 3 and z = 0,1,2, or 3.

For CH_3SiH_3 : $a_{1,0}(0) = 1$, $a_{2,0}(0) = 0$, $a_{3,0}(0) = 0$.

For CH_3SiH_2D : $a_{1,1}(0) = 1/3$, $a_{2,1}(0) = 2/3$, $a_{3,1}(0) = 0$.

For CH_3SiHD_2 : $a_{1,2}(0) = 0$, $a_{2,2}(0) = 1/3$, $a_{3,2}(0) = 2/3$.

For CH_3SiD_3 : $a_{1,3}(0) = 0$, $a_{1,3}(0) = 0$, $a_{3,3}(0) = 1$.

The mono-adsorbed species that exist on adsorption of CH_3SiH_3, CH_3SiH_2D, CH_3SiHD_2, or CH_3SiD_3 are described in equation 4.12.

$$Q_{1,z} = (a_{1,z}(0) + HPQ_{2,z}/2)/(1 + DP) \quad (4.12a)$$

$$Q_{2,z} = (a_{2,z}(0) + DPQ_{1,z} + HPQ_{3,z})/(1 + P/2) \quad (4.12b)$$

$$Q_{3,z} = (a_{3,z}(0) + DPQ_{2,z}/2)/(1 + HP) \quad (4.12c)$$

The subscript z takes values of 0,1,2 or 3, and refers to the number of deuterium atoms in the molecule before adsorption. Similarly subscripts 1,2, and 3 appended to Q in equation 4.12 refer to the number of deuterium atoms the molecule will have if that adsorbed species combines with a deuterium atom and desorbs. CH_3SiH_3 and CH_3SiD_3 each have only one value of $a_{x,0}$ and of $a_{x,3}$ (x = 1,2, or 3) that is greater than zero; equations 4.12a, 4.12b, and 4.12c may be solved simultaneously. However, two values of $a_{x,z}$ greater than zero exist for each of CH_3SiH_2D and CH_3SiHD_2; in this case the values are treated as being independent. Thus two sets equations are generated which are additive.

$$Q_{1,z} = Q^{I}_{1,z} + Q^{II}_{1,z} \quad (4.13a)$$

$$Q_{2,z} = Q^{I}_{2,z} + Q^{II}_{2,z} \quad (4.13b)$$

$$Q_{3,z} = Q^{I}_{3,z} + Q^{II}_{3,z} \quad (4.13c)$$

Here z = either 1 or 2. Addition of the two sets of equations provides a new set which is solved simultaneously. By this process the values of $Q_{x,z}$ are obtained, and the overall yield of each radical determined by equation 4.14.

$$Q_x = Q_{x,0} + Q_{x,1} + Q_{x,2} + Q_{x,3} \quad (4.14)$$

The yield of each product is given by equation 4.15

$$d_0 = HQ_1 \qquad (4.15a)$$

$$d_1 = DQ_1 + HQ_2 \qquad (4.15b)$$

$$d_2 = DQ_2 + HQ_3 \qquad (4.15c)$$

$$d_3 = DQ_3 \qquad (4.15d)$$

where d_x is the percentage of $CH_3SiH_{3-x}D_x$ (x = 0,1,2, or 3) in the mixture. The mono-adsorbed species shown above in (4.15) may recombine with either protium or deuterium.

If hydrogen in the gas phase is in equilibrium with adsorbed hydrogen then exchange in methylsilane may be simulated as follows. If a small amount of gaseous methylsilane (say about 1 % of the total) adsorbs on the catalyst, undergoes exchange, and is then entirely desorbed, the composition of the desorbed material can be determined from equations 4.12 to 4.15. A value of the mechanistic parameter, P, is required, usually $P_{INITIAL} = 0$. The desorbed material is assumed to be distributed randomly throughout the mixture. Again, a small quantity of methylsilane is adsorbed; this time a fraction of the adsorbate will contain methylsilane that has undergone exchange. The composition of the material that is desorbed is once more calculated, using the same value of P as before. This process is permitted to continue until the deuterium content of methylsilane is the same or just greater than that determined for the mass spectrum under consideration. As with the method described in 4.3.1, the normalised calculated distribution is introduced into equations 8a to 8e of Appendix B, and the mass spectrum thus simulated is compared with the actual one by use of equations 4.8 to 4.10.

The entire process is repeated with various values of P until the sum of squares of errors of peak heights (SSEP) is minimized to within a pre-set tolerance. The calculated distribution is then believed to be a good approximation to the actual distribution, although this cannot be checked.

The technique described so far has assumed that adsorbed-CH_3SiH_2 and adsorbed-CH_3SiH can interconvert in a fashion analogous to exchange in ethane. However if multiple exchange occurs in the silyl group only, then it might proceed in a fashion more like that in methane than that in ethane. Therefore two exchange mechanisms might operate independently, i.e. one stepwise, and the other multiple. Although this happens for methane, it does not invalidate a single exchange mechanism for methylsilane that can account for stepwise and multiple exchange. The methane type of exchange can be simulated by choosing two values of P ($P \sim 0$ and $P \longrightarrow$), and then varying the extent to which each operates, so as to obtain once more the best fit between calculated and actual mass spectra. The overall product distribution calculated by use of two values of P differ from those obtained by use of one value of P. However, variation between values of d_0 calculated by these two modifications of the general method are about the same, and use of one value of P is preferred to the use of two.

Because of the uncertainty as to which of these processes is the correct or more dominant one, the concept of multiplicity expressed as

$$M^{III} = \frac{k_\phi}{k_0^{III}}$$

has been retained. Specific rates for loss of CH_3SiH_3 determined by this general method are referred to as k_0^{III}, and the multiplicity as M^{III}.

This general method of analysing mixture of deuteriated methylsilanes has certain drawbacks. First, the actual product distribution is not known, and the calculated distribution can only be checked by minimisation of errors between the calculated and actual mass spectrum. Logically, exchange can only occur by a very limited number of processes, and hence it is believed that this method yields good values for the concentration of CH_3SiH_3. A major assumption made in the above treatment is that the pool of adsorbed hydrogen is always in equilibrium with the gas phase. This has been tested by following the exchange $H_2 + D_2 \rightleftharpoons 2HD$ over clean catalysts, and over catalysts used for exchange of CH_3SiH_3 with molecular deuterium. The former exchange was always very much faster than exchange in methylsilane. However, it is still possible that hydrogen available for exchange with methylsilane may not be in equilibrium with hydrogen in the gas phase.

This technique can provide reasonable product distributions and, in particular, reliable values of d_0, despite the various assumptions inherent in the method.

4.4 Treatment of Errors

Errors in specific rates occur due to inaccurate measurement of experimental quantities (Table 4.1) and from graphical errors.

Errors in determining the pressures of reactants have the following consequences. Uncertainties in the partial pressures of reactants result in inaccurate values of ϕ_∞ being determined for the exchange of CH_3SiH_3 with molecular deuterium and hence spurious departures from linearity may occur in plots of $\ln(\phi_\infty - \phi)$ against time as ϕ approaches ϕ_∞. Similarly, uncertainty in the initial composition of a mixture for mutual exchange results in marked errors in the calculated values of $d_{0\infty}$ and $d_{3\infty}$ and hence the appropriate function plots depart from linearity as equilibrium is approached ($d_{03\infty}$ possesses a smaller

Table 4.1 Uncertainties in the measurement of experimental quantities.

Experimental quantity	Method of determination	Magnitude	Uncertainty
P_{SH}	Mercury manometer	Variable	± 5 %
P_{SD}	Mercury manometer or L.K.B. gauge	Variable	± 5 %
P_{D_2}	Mercury manometer	Variable	± 3 %
V_{RV}		0.30 and 1.00 l	± 0.002 l
V_{MV}	Found by a series of expansions of gases into the reaction vessel	0.076 l	± 0.001 l
V_{SH}	Found by a series of expansions of gases into the mixing volume	0.015 l	± 0.001 l
T_{RV}	Measured by mercury-in-glass and by alcohol-in-glass thermometers	Variable	$< \pm 1^{\circ}$
H		Variable	± 2 %

where P_{SH} = Pressure of CH_3SiH_3 in calibrated volume (Section 3.2.2)
P_{SD} = Pressure of CH_3SiD_3 in the mixing volume
P_{D_2} = Pressure of deuterium in the mixing volume
V_{RV} = Volume of the reaction vessel
V_{MV} = Volume of the mixing volume
V_{SH} = Volume between taps T9, 10, and 11 (Fig. 3.3)
T_{RV} = Temperature of the reaction vessel when in slush baths at or below 273 K
H = Measured peak height in a mass spectrum

uncertainty due to the errors in its constituents being of opposite sign to each other). Appendix B describes a method whereby the deuterium content, Ø, of a mixture can be determined directly from the mass spectrum; hence the initial value of the ratio CH_3SiH_3 : CH_3SiD_3 can be determined more accurately and thus better values can be calculated for $d_{0\infty}$, $d_{3\infty}$, and $d_{03\infty}$.

The effect of an error in the measurement of a pressure or of a volume is to change the quantity of material introduced into the reaction vessel, and hence to modify the calculated value of the specific rate. The number of moles, n, admitted to the reaction vessel are given by equation 4.16,

$$n = (P_{SH}+P_{SD}) \times V_{MV} x V_{RV}/T_M/T_{RV}/(V_{MV}/T_M+V_{RV}/T_{RV}) \qquad (4.16)$$

where Tm is the temperature of the mixing volume. The error, n/n, in the number of moles admitted is given by equation 4.17.

$$\frac{\Delta n}{n} = \frac{\pm\Delta P_{SH}}{P_{SH}} \frac{\pm\Delta P_{SD}}{P_{SD}} \frac{\pm\Delta T_{RV}}{T_{RV}} \frac{\pm\Delta T_M}{T_M} \pm \frac{\Delta V_{RV}}{V_{RV}} \pm \frac{\Delta V_{MV}}{V_{MV}} \qquad (4.17)$$

Substitution of values applicable to mutual exchange in a 0.30 l vessel at 273 K result in an error of up to 12 %. Smaller errors in the number of moles of methylsilane admitted apply for exchange with molecular deuterium.

Errors in the measurement of peak heights in the mass spectrum cause uncertainties in the values of d_0 and d_3 of ± 2 %.

Another source of inaccuracy lies in the calculation of the rate coefficients, $k_{\emptyset}$, k_{0}, and k_{03} from the appropriate function plots (see equations 4.4, 4.5, and 4.7). The first points in these graphs are uncertain because, experimentally, a finite time is required for the reaction mixture initially to leak into the mass spectrometer. Spurious non-linearity as $\emptyset \longrightarrow \emptyset_{\infty}$, and as $d_{03} \longrightarrow d_{03\infty}$ have been mentioned above.

For many reactions the function plots were non-linear; in many cases other considerations allowed this curvature to be attributed to poisoning of the surface by the reaction. In these cases a rate coefficient was estimated from the initial slope of the curve. In general, rate coefficients for unpoisoned reactions are judged to be uncertain to less than ± 5 % and those for poisoned reactions to be less than ± 10 %.

SECTION 5

RESULTS

5.1 Results Obtained using Molybdenum Films

5.1.1 Adsorption of CH_3SiH_3

Adsorption of CH_3SiH_3 on molybdenum has been investigated on one film deposited and used at 195 K, and on four films deposited and used at 273 K. The adsorption isotherms obtained are shown in Figure 5.1. The surface uptake, which was measured in terms of micromoles mg^{-1} (see Section 3.4.2), the composition of the chemisorbed layer, and of the gas phase, for complete surface coverage by CH_3SiH_3 for each film are shown in Table 5.1.

To the film prepared at 195 K further additions of CH_3SiH_3 were made after the first standing pressure of CH_3SiH_3 had been detected. The temperature was then raised to 273 K and more additions of CH_3SiH_3 made. These two sets of results are shown in Table 5.1.

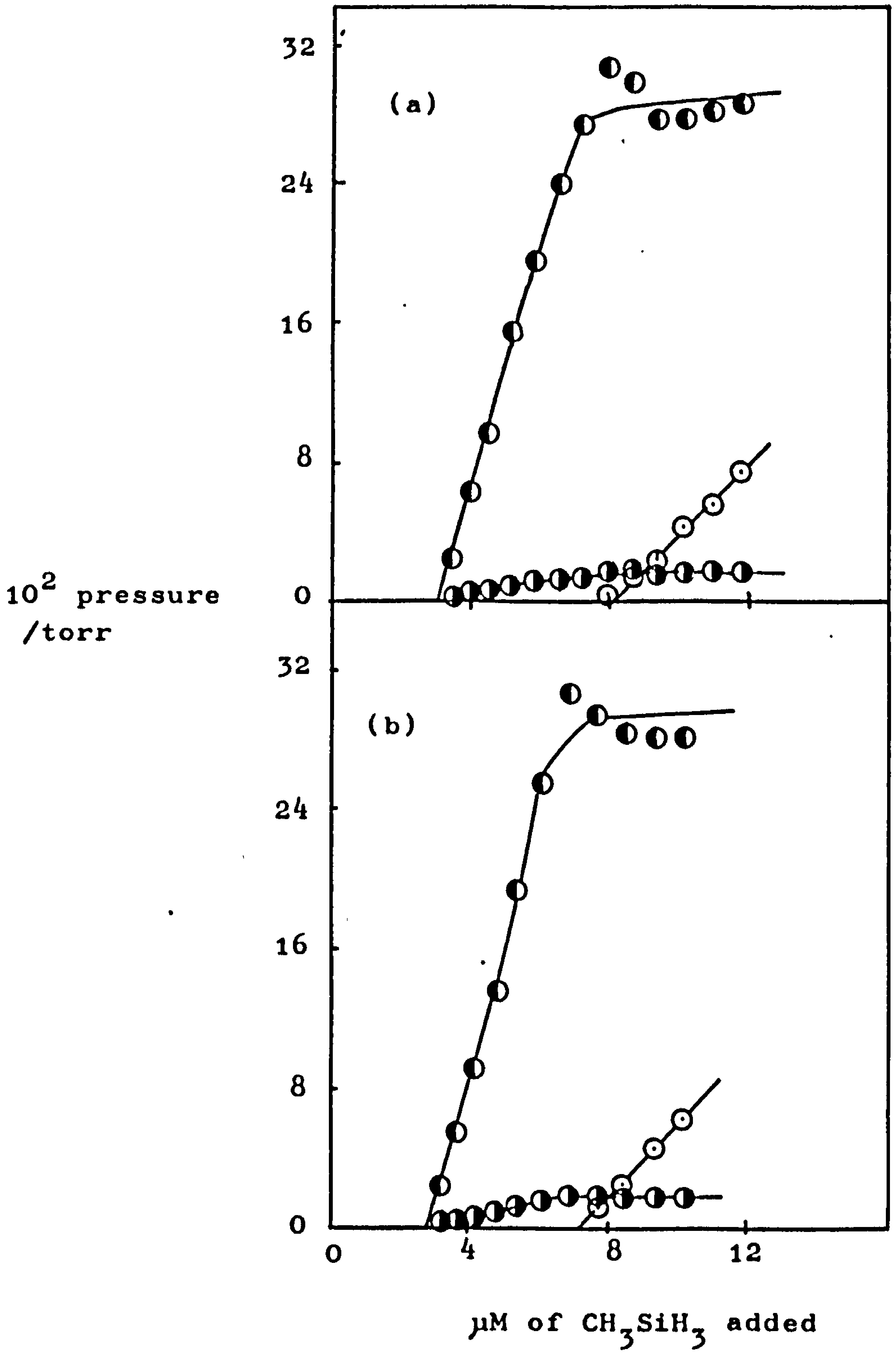


Figure 5.1.1 Chemisorption of CH_3SiH_3 on molybdenum at 273 K: (a) film wt. = 7.1 mg; (b) film wt. = 15.8 mg

Legend:- ⊙ CH_3SiH_3, ◐ H_2, ◑ CH_4

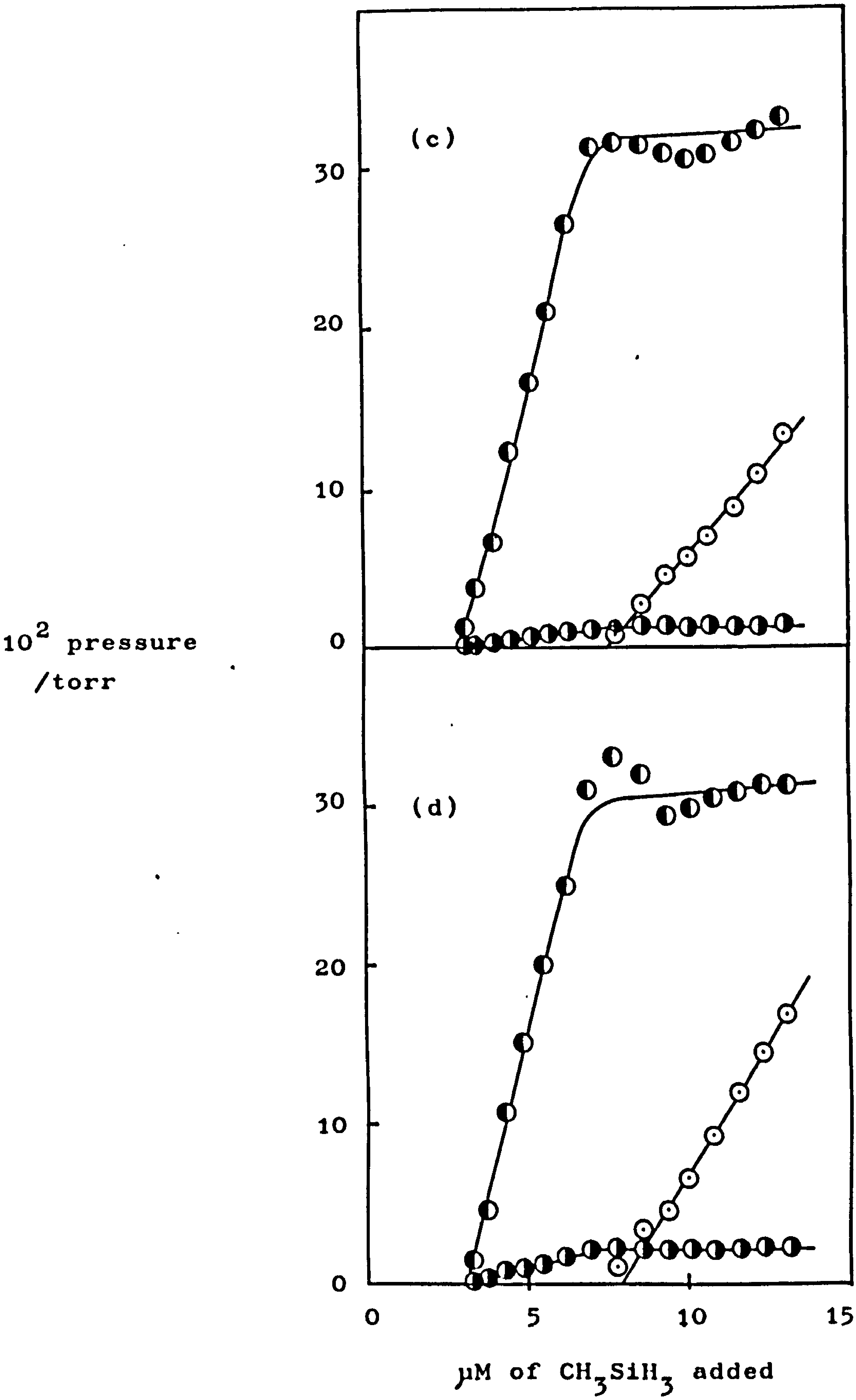


Figure 5.1.2 Chemisorption of CH_3SiH_3 on molybdenum at 273 K: (c) film wt. = 25.0 mg; (d) film wt. = 16.5 mg.

Legend:- ⊙ CH_3SiH_3, ◐ H_2, ◐ CH_4

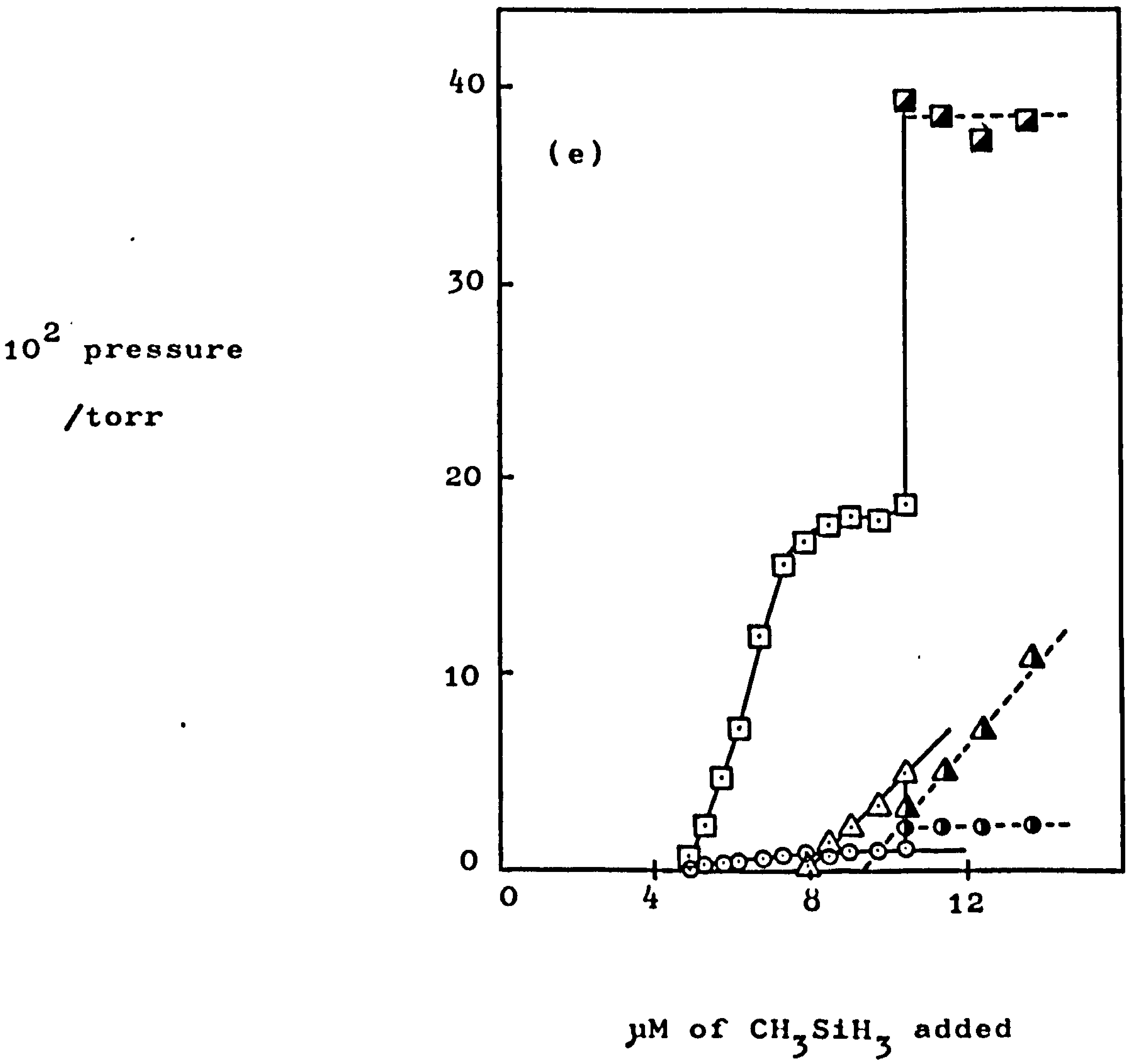


Figure 5.1.3 Chemisorption of CH_3SiH_3 on molybdenum: (e) film wt. = 15.4 mg.

Legend:-

△ CH_3SiH_3 at 195 K ▲ CH_3SiH_3 at 273 K

⊡ H_2 at 195 K ◩ H_2 at 273 K

⊙ CH_4 at 195 K ◐ CH_4 at 273 K

Table 5.1 Adsorption of CH_3SiH_3 on molybdenum

Volume of reaction vessel = 0.30 l

Film weight	Temp.	Surface uptake /micromoles mg^{-1}	Relative composition of chemisorbed layer			Gas phase composition [a]	
/mg	/K		C	: Si	: H	n_{H_2}	n_{CH_4}
7.1	273	0.47	0.95	1.00	4.25	0.77	0.05
15.8	273	0.46	0.94	1.00	4.04	0.86	0.06
25.0	273	0.47	0.96	1.00	3.97	0.94	0.04
16.5	273	0.47	0.94	1.00	3.97	0.88	0.06
Mean	273	0.47	0.95	1.00	4.06	0.86	0.05
15.4	195[b]	0.51	0.98	1.00	4.95	0.48	0.02
	273[c]	0.57	0.96	1.00	3.83	0.98	0.05

[a] n_{H_2} and n_{CH_4} are the number of moles of hydrogen and of methane evolved per mole of CH_3SiH_3 adsorbed at complete surface coverage as defined in Section 3.4.2

[b] See Figure 5.1 (e); open symbols

[c] See Figure 5.1 (e); half filled symbols

5.1.2 Self exchange and products of decomposition

Experiments designed to determine whether self exchange occurred on molybdenum films were carried out at 195, 273 and 323 K. No exchange was observed initially. Hydrogen and methane were detected in the gas phase (Table 5.2). The isotopic composition of each product is shown in Table 5.2.

Table 5.2 Reaction of CH_3SiD_3 on molybdenum:isotopic composition (%) of hydrogen and of methane formed by the decomposition of CH_3SiD_3.

Volume of reaction vessel = 0.30 l

Initial partial pressure of CH_3SiD_3 in the reaction vessel = 1.0 ± 0 1 torr

Film no.	Film weight /mg	Temp. /K	Time /ks	Hydrogen H_2	HD	D_2	Methane CH_4	CH_3D	CH_2D_2	CHD_3	CD_4
1	21.6	195	2.3	12	24	64	27	73	0	0	0
		293[a]	3.6	7	31	62	13	50	29	8	0
2	15.8	195	1.4	16	30	54	19	71	10	0	0
		293[b]	4.7	9	33	58	20	50	14	9	7
3[d]	16.5	273	0.5	-	-	-	30	70	0	0	0
		350[c]	6.4	-	-	-	30	44	21	4	0

[a] Temperature attained after 3.0 ks

[b] Temperature attained after 4.2 ks

[c] Temperature attained after 0.9 ks

[d] Mass spectra not recorded for hydrogen.

Upon raising the temperature from 195 to 293 K and from 273 to 350 K self exchange commenced. Mass spectra of methylsilane before and after the change of temperature are shown in Table 5.3. The yields of hydrogen and of methane increased significantly and their new isotopic compositions are shown in Table 5.2. Dimethylsilane (principally $(CH_3)_2SiD_2$) was also detected. The percentages of each substance detected in the gas phase before and after the temperature change are shown in Table 5.4.

Table 5.3 Reaction of CH_3SiD_3 on molybdenum:variation of the mass spectrum with time on warming the vessel from 195 to 293 K (films 1 and 2) and from 273 to 350 K (film 3). For other experimental details see Table 5.2

Film no.	Film weight /mg	Temp. /K	Time /ks	% ion current per *m*/*e* value[a]				
				43	44	45	46	47
1	21.6	195	0.0	4.9	6.6	51.4	6.4	30.7
		195	2.9	5.1	7.3	50.9	6.9	29.8
		293[b]	3.4	5.6	9.3	48.7	8.6	27.8
		293	3.6	5.9	10.8	47.4	9.7	26.2
		293	4.7	6.5	12.7	46.0	11.0	23.8
2	15.8	195	0.0	4.2	6.4	52.1	6.5	30.8
		195	4.1	4.4	6.6	52.2	6.3	30.5
		293[c]	4.6	4.7	8.0	50.3	7.8	29.2
		293	5.0	4.9	9.0	49.5	8.7	27.9
		293	13.3	5.6	11.4	47.2	10.6	25.3
3	16.5	273	0.0	3.2	6.1	51.2	7.8	31.7
		273	0.5	3.8	6.1	50.2	7.6	32.3
		350[d]	6.4	4.2	12.1	45.3	11.1	27.3
		350	18.0	5.2	12.0	44.7	11.3	26.8

[a] % ion current = 0.0 for *m*/*e* = 48 for all spectra

[b] Temperature attained after 3.0 ks

[c] Temperature attained after 4.2 ks

[d] Temperature attained after 0.9 ks

Table 5.4 Reaction of CH_3SiD_3 on molybdenum:variation of the composition of the gas phase with time on warming the vessel from 195 to 293 K (films 1 and 2) and from 273 to 350 K (film 3). For other experimental details see Table 5.2.

Film no.	Film weight /mg	Temp. /K	Time /ks	Composition of the gas phase / %			
				Hydrogen	Methane	Methyl-silane	Dimethyl-silane
1	21.6	195	2.3	32	3	65	0
		293[a]	3.6	54	10	34	2
2	15.8	195	1.4	31	4	65	0
		293[b]	4.7	53	10	35	2
3[d]	16.5	273	0.5	-	10	90	0
		350[c]	6.4	-	17	71	12

[a] Temperature attained after 3.0 ks
[b] Temperature attained after 4.2 ks
[c] Temperature attained after 0.9 ks
[d] Mass spectra not recorded for hydrogen.

5.1.3 Mutual exchange and products of decomposition

Exchange between CH_3SiH_3 and CH_3SiD_3 over molybdenum was examined at 195 and 273 K (Tables 5.5 and 5.6). Reaction was rapid at both temperatures. The rate at 195 K decreased slowly when a series of exchanges was carried out using a single film. For a series of runs at 273 K the rate of exchange decreased drastically. However, any given run exhibited first order behaviour during the course of reaction both at 195 and at 273 K.

Small amounts of hydrogen and of methane were detected and the consequent gas phase composition is shown in Table 5.7.

Table 5.5 Molybdenum catalysed mutual exchange: specific rates at 195 K

Volume of reaction vessel = 0.30 l

Film no.	Film weight /mg	Run no.	Initial partial pressure in the reaction vessel/ torr		k_{03}[a] /nM $s^{-1}mg^{-1}$
			CH_3SiH_3	CH_3SiD_3	
1	14.5	1	0.68	0.66	19.9
		2	0.86	0.84	18.8
		3	0.87	0.89	18.7
		4	0.89	0.87	18.5
		5	0.92	0.92	17.5
		6	1.62	1.59	15.4
		7	1.62	1.60	14.5
		8	0.89	0.89	10.1
		9[b]	1.23	1.25	3.5
		10[b]	0.99	0.97	0.9
2	18.8	3	0.87	0.87	16.3
		4	0.87	0.83	15.9
3	20.0	3	0.89	0.92	15.4
4	15.9	3	0.89	0.89	15.2
5	16.9	3[c]	1.00	0.98	11.1
		4[c]	1.00	0.96	9.8
		5[b]	1.05	1.07	5.3
6	8.2	1[d]	0.18	0.18	13.1

[a] As defined in Section 4.2

[b] Temperature of the reaction vessel = 290 K

[c] Mixture contained deuterium (10.3 torr)

[d] Film prepared under u.h.v. conditions; volume of reaction vessel = 0.48 l.

Table 5.6 Molybdenum catalysed mutual exchange: specific rates at 273 K

Volume of reaction vessel = 0.30 l

Film no.	Film weight /mg	Run no.	Initial partial pressure in the reaction vessel/torr		k_{03}[a] /nM $s^{-1}mg^{-1}$
			CH_3SiH_3	CH_3SiD_3	
7	15.9	1	0.83	0.87	34.8
8	13.4	1	1.08	1.14	13.0
9	13.6[b]	1	1.28	1.33	10.4
10	13.2	1	0.91	0.98	11.5
11	12.0	1	1.10	1.20	5.0
12	17.9	1	0.91	0.96	13.3
		2	0.91	0.96	0.5
13	12.7	1	0.91	0.96	5.0
14	12.4	1	0.92	1.90	15.0
15	12.9	1	1.50	0.77	20.4
16	10.5	1	0.91	0.96	20.1
		2	0.91	0.96	1.5
		3	0.91	0.96	0.5
17	11.9	1	1.00	1.10	14.9
		2	1.00	0.96	3.6
		3	0.91	0.96	3.0
Mean		1	1.03	1.11	14.9

[a] As defined in Section 4.2

[b] Volume of reaction vessel = 1.00 l

Table 5.7 Molybdenum catalysed mutual exchange: composition of the gas phase due to decomposition of methylsilane on the surface of the film. For other experimental details see Tables 5.5 and 5.6.

Film no.	Temp. /K	Run no.	Composition of the gas phase / %						
			Hydrogen			Methane			Methyl-silane
			H_2	HD	D_2	CH_4	CH_3D	CH_2D_2	
1	195	1	8	9	3	1	0	0	79
	195	2	5	4	1	0	0	0	90
	195	3	5	5	1	0	0	0	89
	195	4	5	4	1	0	0	0	90
	195	5	4	3	1	0	0	0	92
	195	6	4	3	1	0	0	0	92
3	195	3	5	4	1	0	0	0	90
10[a]	273	1	6	8	3	2	1	1	79

[a] Trace amounts of dimethylsilane were detected.

5.1.4 Exchange with molecular deuterium

The exchange of protium in methylsilane with gaseous deuterium has been catalysed by molybdenum films at 195, 273 and 300 K.

Mixtures consisting of CH_3SiD_3 and deuterium were used to determine the activity of protium bonded to carbon for exchange. Negligible activity for exchange was found at 195, 273 and 300 K. Exchange was observed at the above temperature for the exchange of protium for deuterium in CH_3SiH_3. Therefore the rates of exchange determined were for protium bonded to silicon.

Linear function plots of $\ln(d_o - d_{o\infty})$ and of $\ln(\phi_\infty - \phi)$ against time (see Section 4) were obtained for reactions at 195 K. However, a series of runs using a single film showed marked decreases of activity from run to run. At 273 and 300 K the corresponding function plots were non-linear presumably due to poisoning. Examples of the function plots obtained at 195 and 273 K are shown in Figure 5.2. Values of the specific rates and of the multiplicity, M, of exchange are shown in Tables 5.8 - 5.11.

The order of reaction in deuterium at 273 K by the initial rate method was determined by use of results in Tables 5.9 and 5.10. The value obtained was 0.6 ± 0.2.

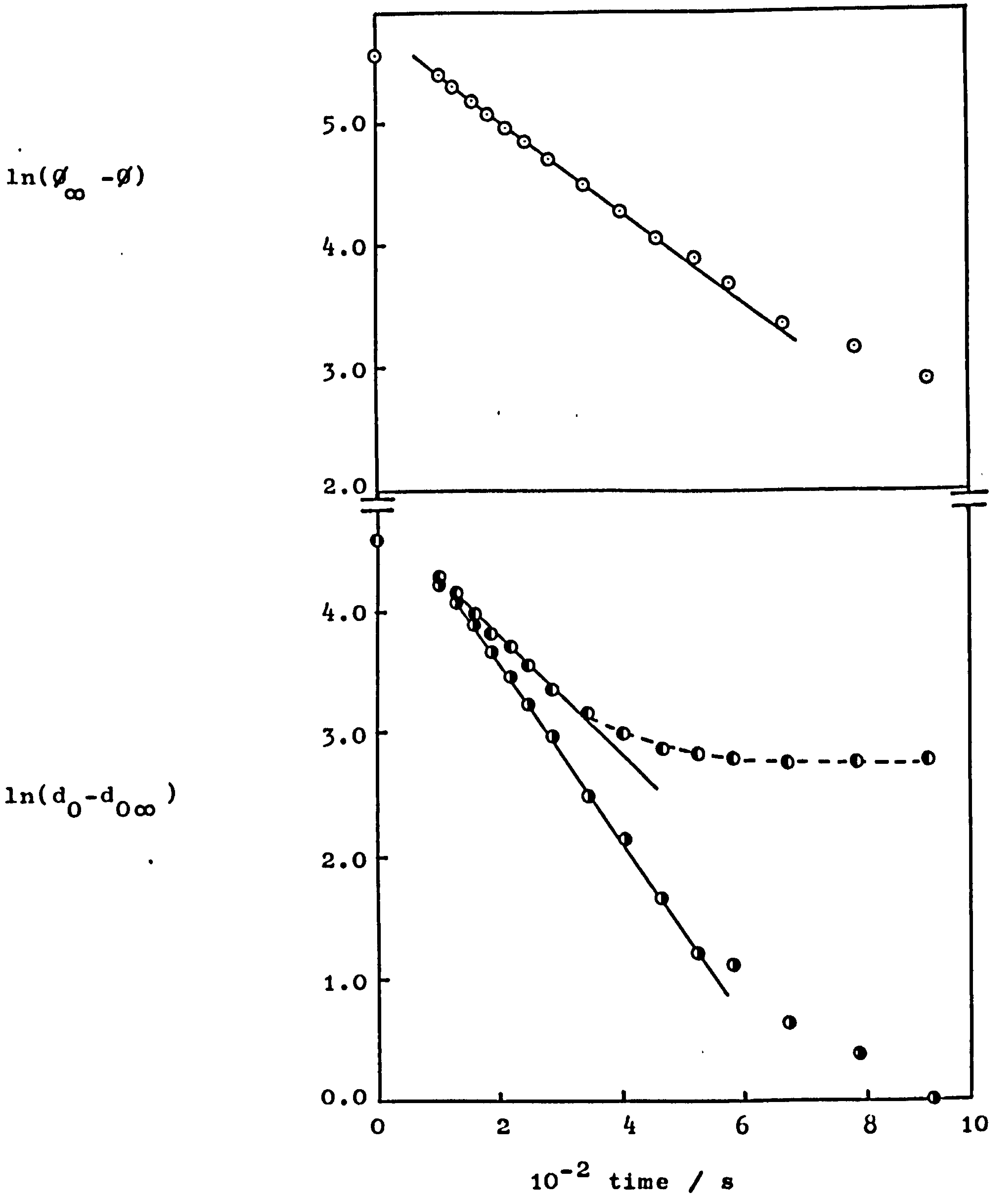


Figure 5.2.1 Exchange with molecular deuterium catalysed by molybdenum at 195 K: film no. 3, run no. 1.

Legend:- ⊙ gives k_ϕ, ◑ gives k_0^{I}, ◐ gives k_0^{III}

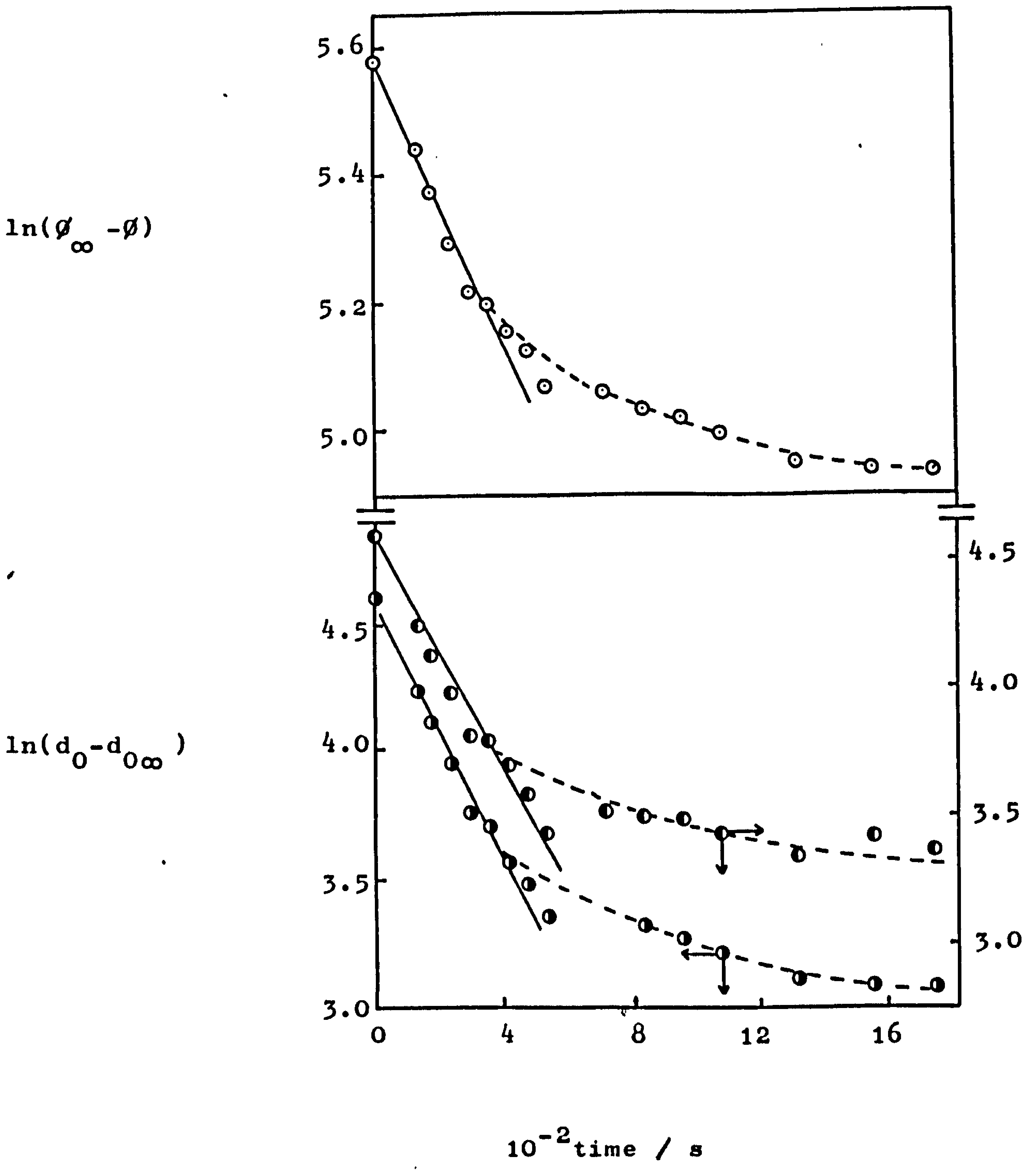


Figure 5.2.2 Exchange with molecular deuterium catalysed by molybdenum at 273 K: film no. 12

Legend:- ⊙ gives k_ϕ, ◐ gives k_0^{I}, ● gives k_0^{III}

Table 5.8 Molybdenum catalysed exchange of CH_3SiH_3 with deuterium:specific rates, k_ϕ and k_0[a], and values of the multiplicity, M[a], at 195 K.

Volume of reaction vessel = 0.30 l

Initial pressure of CH_3SiH_3 in reaction vessel = 1.0 ± 0.1 torr

Initial pressure of deuterium in reaction vessel = 9.9 ± 0.1 torr

Film no.	Film weight /mg	Run no.	k_ϕ /nM $s^{-1}mg^{-1}$	k_0/nM $s^{-1}mg^{-1}$			M		
				k_0^{I}	k_0^{II}	k_0^{III}	M^{I}	M^{II}	M^{III}
1	22.7	1	14.6	6.4	-	9.5	2.3	-	1.5
		2	3.3	2.7	3.1	2.8	1.2	1.1	1.2
2[b]	18.8	1	10.2	5.1	-	7.6	2.0	-	1.3
		2	0.19	0.14	0.15	0.14	1.4	1.3	1.4
		5	0.15	0.12	0.13	0.13	1.3	1.2	1.2
3[b]	20.0	1	11.4	6.0	-	8.2	1.9	-	1.4
		2	0.29	0.25	0.30	0.24	1.2	1.0	1.2
		4	0	0	0	0	-	-	-
		4[c]	3.1	2.3	-	2.7	1.3	-	1.1
		4[d]	1.9	0.68	1.7	1.5	2.8	1.1	1.3
4[b]	15.9	1	7.9	5.3	-	6.7	1.5	-	1.2
		2	0.53	0.53	0.53	0.49	1.0	1.0	1.1
		4	0	0	0	0	-	-	-
		4[c]	2.4	2.1	2.4	2.4	1.1	1.0	1.0
5[b]	16.9	1	9.6	5.9	-	7.1	1.6	-	1.4
		2	0.16	0.16	0.16	0.16	1.0	1.0	1.0
Mean		1	10.7	5.7	-	7.8	1.9	-	1.4

[a] Superscripts I, II, and III are defined in Section 4.3

[b] Mutual exchange carried out on corresponding film in Table 5.5

[c] Temperature raised to 290 K

[d] Gradient changed after 600 s at 290 K.

Table 5.9 Molybdenum catalysed exchange of CH_3SiH_3 with deuterium:specific rates, k_{ϕ} and k_0[a], and values of the multiplicity, M[a], at 273 K

Volume of reaction vessel = 1.00 l

Initial pressure of CH_3SiH_3 in reaction vessel = 1.0 ± 0.1 torr

Initial pressure of deuterium in reaction vessel = 10.6 ± 0.1 torr

Film no.	Film weight /mg	k_{ϕ} /nM $s^{-1}mg^{-1}$	k_0/nM $s^{-1}mg^{-1}$			M		
			k_0^{I}	k_0^{II}	k_0^{III}	M^{I}	M^{II}	M^{III}
6	11.6	8.4	7.8	8.4	8.3	1.1	1.0	1.0
7[b]	12.7	13.6	11.6	-	9.1	1.2	-	1.5
8	11.7	9.6	7.8	-	7.5	1.2	-	1.3
9	11.0	7.0	7.3	6.7	7.2	1.0	1.0	1.0
10	11.2	10.0	8.9	9.2	9.1	1.1	1.1	1.1
11	13.7	11.4	6.5	-	8.0	1.8	-	1.4
12	19.8	8.1	6.7	-	6.9	1.2	-	1.2
13	13.1	5.9	5.2	-	5.5	1.1	-	1.1
Mean		9.3	7.7	8.1	7.7	1.2	1.1	1.2

[a] Superscripts I, II, and III are defined in Section 4.3

[b] Volume of reaction vessel = 0.30 l

Table 5.10 Molybdenum catalysed exchange of CH_3SiH_3 with molecular deuterium (relatively low partial pressure): specific rates, $k_\emptyset$ and k_0[a], and values of the multiplicity, M[a], at 273 K

Volume of reaction vessel = 1.00 l

Initial pressure of CH_3SiH_3 in reaction vessel = 1.0 ± 0.1 torr

Initial pressure of deuterium in reaction vessel = 2.8 ± 0.1 torr

Film no.	Film weight /mg	$k_\emptyset$ /nM $s^{-1}mg^{-1}$	k_0/nM $s^{-1}mg^{-1}$			M		
			k_0^{I}	k_0^{II}	k_0^{III}	M^{I}	M^{II}	M^{III}
14	15.7	3.9	3.4	3.8	3.7	1.1	1.0	1.1
15	10.6	3.2	2.8	3.0	3.3	1.1	1.1	1.0
16	11.5	4.8	4.6	4.7	4.7	1.0	1.0	1.0
Mean		4.0	3.6	3.8	3.9	1.1	1.1	1.0

[a] Superscripts I, II, and III are defined in Section 4.3

Table 5.11 Molybdenum catalysed exchange of CH_3SiH_3 with molecular deuterium: specific rates, $k_\emptyset$ and k_0[a], and values of the multiplicity, M[a], at 300 K

Volume of reaction vessel = 1.00 l

Initial pressure of CH_3SiH_3 in reaction vessel = 1.0 ± 0.1 torr

Initial pressure of deuterium in reaction vessel = 11.7 ± 0.1 torr

Film no.	Film weight /mg	$k_\emptyset$ /nM $s^{-1}mg^{-1}$	k_0/nM $s^{-1}mg^{-1}$			M		
			k_0^{I}	k_0^{II}	k_0^{III}	M^{I}	M^{II}	M^{III}
17	15.9	8.6	6.2	-	7.3	1.4	-	1.2
18	12.8	12.8	10.8	-	12.4	1.2	-	1.0
19	17.7	14.0	10.0	-	11.9	1.4	-	1.2
Mean		11.8	9.0	-	10.5	1.3	-	1.1

---

[a] Superscripts I, II, and III are defined in Section 4.3

5.2 Results Obtained for Tungsten Films

5.2.1 Adsorption of CH_3SiH_3

Adsorption of CH_3SiH_3 on tungsten has been investigated on four films deposited and used at 273 K. The adsorption isotherms are shown in Figure 5.3. The surface uptake, the composition of the chemisorbed layer, and of the gas phase for complete surface coverage by CH_3SiH_3 for each film are shown in Table 5.12.

Table 5.12 The adsorption of CH_3SiH_3 on tungsten at 273 K

Volume of reaction vessel = 0.30 1

Film weight /mg	Surface uptake /micromoles mg^{-1}	Relative composition of chemisorbed layer C	: Si	: H	Gas phase composition[a] n_{H_2}	n_{CH_4}
9.1	0.23	0.98	1.00	4.88	0.52	0.02
12.2	0.23	0.96	1.00	4.84	0.50	0.04
18.3	0.19	0.96	1.00	4.48	0.68	0.04
21.3	0.31	0.96	1.00	4.60	0.62	0.04
Mean	0.24	0.97	1.00	4.70	0.58	0.04

[a] n_{H_2} and n_{CH_4} are the number of moles of hydrogen and of methane evolved per mole of CH_3SiH_3 adsorbed at complete surface coverage.

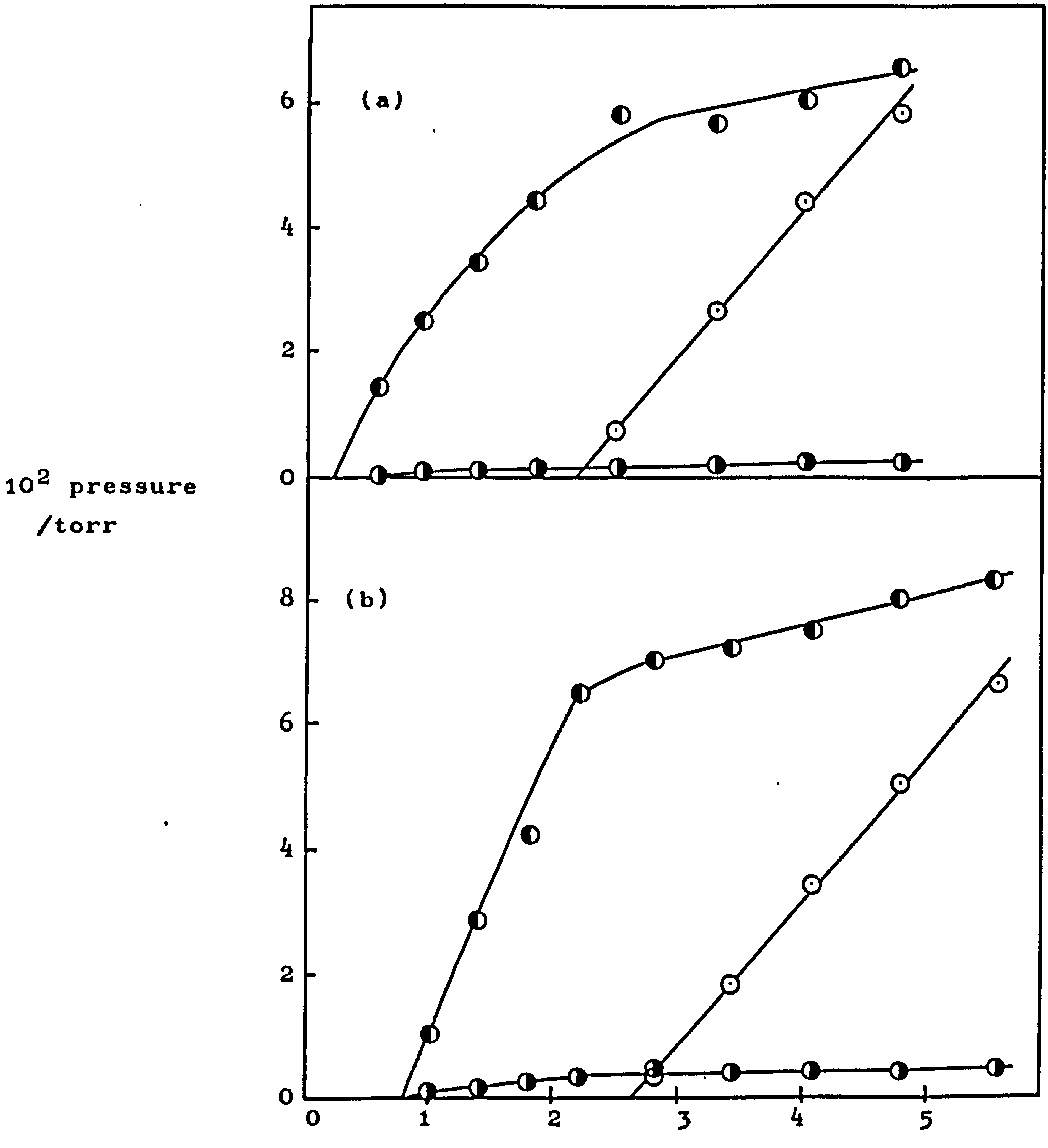


Figure 5.3.1 Chemisorption of CH_3SiH_3 on tungsten at 273 K: (a) film wt. = 9.1 mg; (b) film wt. = 12.2 mg.

Legend:- ⊙ CH_3SiH_3 , ◐ H_2 , ◑ CH_4 .

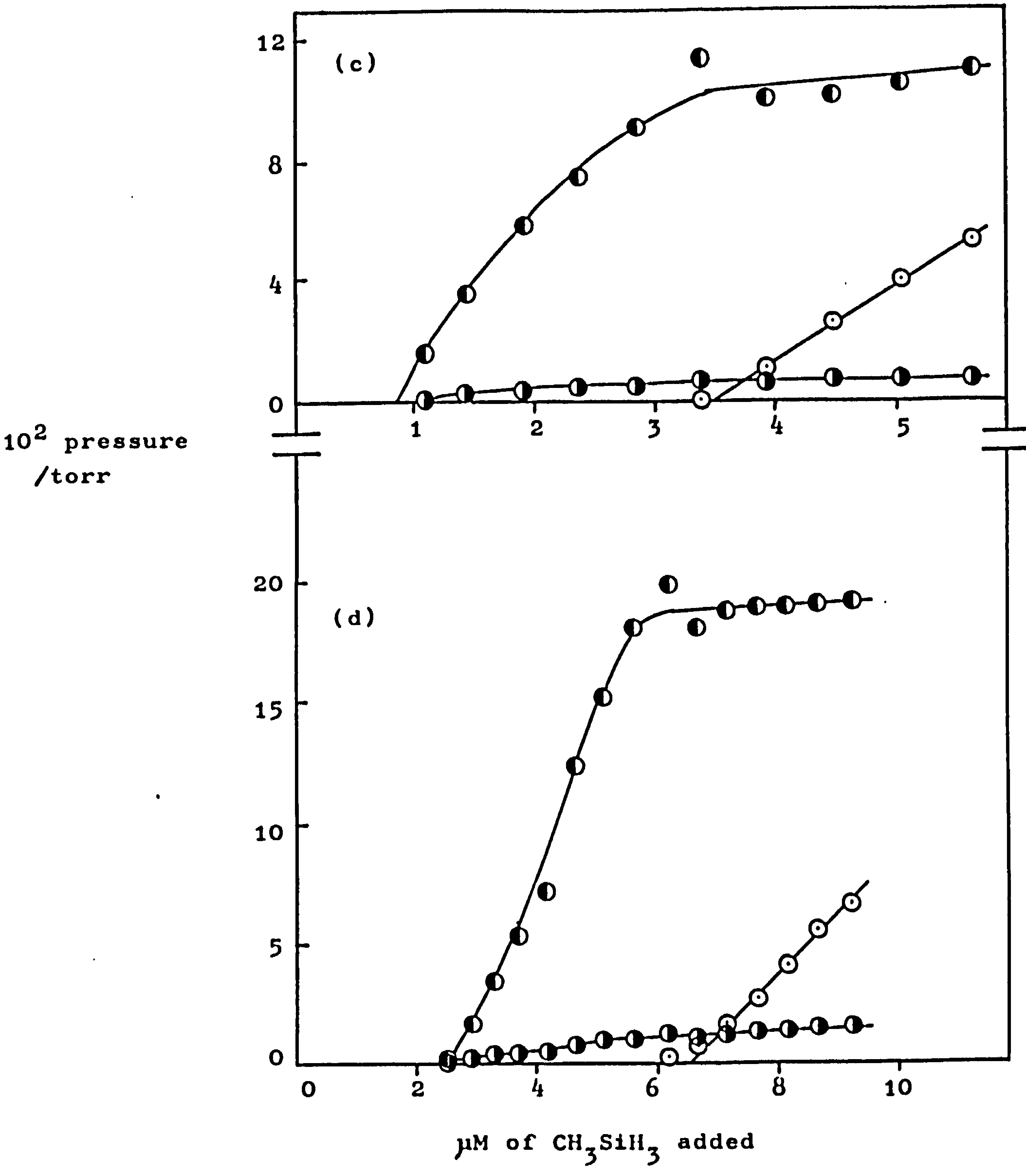


Figure 5.3.2 Chemisorption of CH_3SiH_3 on tungsten at 273 K: (c) film wt. = 18.3 mg; (d) film wt. = 21.3 mg.

Legend:- ⊙ CH_3SiH_3, ◐ H_2, ◑ CH_4.

5.2.2 Self exchange and products of decomposition

Experiments designed to determine whether self exchange occurred on tungsten films were carried out in the range 195 to 340 K. No exchange was observed initially at 195 K (films 1 and 2) but a small degree of exchange was observed at 273 K (film 3). For reaction on each film, methane and hydrogen were detected in the gas phase and their isotopic compositions are shown in Table 5.13.

Raising the temperature of the reaction vessel from 195 to 293 K (films 1 and 2) resulted in the commencement of self exchange. Raising the temperature of the vessel from 273 to 340 K (film 3) resulted in further exchange taking place. The variation of the mass spectrum of methylsilane with time and temperature is shown in Table 5.14. The yields of hydrogen and of methane increased and their new isotopic compositions are shown in Table 5.13. Trace amounts of dimethylsilane were detected. The percentages of each substance detected in the gas phase before and after the increase of temperature are shown in Table 5.15.

Table 5.13 Reaction of CH_3SiD_3 on tungsten:isotopic composition (%) of hydrogen and of methane formed by the decomposition of CH_3SiD_3

Volume of reaction vessel = 0.30 l

Initial pressure of CH_3SiD_3 in reaction vessel = 1.0 ± 0.1 torr

Film no.	Film weight /mg	Temp. /K	Time /ks	Hydrogen			Methane				
				H_2	HD	D_2	CH_4	CH_3D	CH_2D_2	CHD_3	CD_4
1	24.0	195	1.5	21	45	34	41	47	12	0	0
		293[a]	2.4	12	38	50	35	55	10	0	0
		293	4.2	11	38	51	31	53	16	0	0
		293	10.8	12	38	50	33	44	13	7	3
2	30.5	195	1.5	20	40	40	31	44	25	0	0
		293[b]	3.1	9	32	59	26	52	22	0	0
		293	4.1	9	33	58	30	48	22	0	0
		293	10.8	11	35	54	24	41	25	6	4
3	17.4	273	1.5	13	38	49	37	47	16	0	0
		340[a]	2.6	12	39	49	29	45	16	7	3
		340	3.2	12	40	48	30	45	14	7	4
		340	6.0	11	41	48	29	39	16	9	7

[a] Temperature attained after 1.8 ks

[b] Temperature attained after 2.1 ks

Table 5.14 Reaction of CH_3SiD_3 on tungsten:variation of the mass spectrum of methylsilane with time on warming the vessel from 195 to 293 K (films 1 and 2) and from 273 to 340 K (film 3). For other experimental conditions see Table 5.13.

Film no.	Film weight /mg	Temp. /K	Time	% ion current per m/e value[a]				
				43	44	45	46	47
1	24.0	195	0.0	4.4	6.3	51.9	6.7	30.7
		195	1.5	4.5	6.1	52.4	6.4	30.6
		293[b]	2.4	4.7	6.7	51.7	6.9	30.0
		293	4.1	4.6	7.1	51.8	6.9	29.6
		293	10.8	5.0	7.6	51.3	7.5	28.6
2	30.5	195	0.0	4.5	6.6	51.7	6.6	30.6
		195	1.5	4.6	6.8	51.8	6.5	30.3
		293[c]	3.1	4.9	8.2	50.4	7.6	28.9
		293	3.9	4.8	8.3	50.1	8.0	28.8
		293	10.8	5.6	9.9	48.3	8.5	27.7
3	17.4	273	0.0	4.9	6.9	51.1	7.1	30.0
		273	1.5	5.1	7.7	51.1	7.7	28.4
		340[b]	2.2	5.3	8.7	49.8	8.5	27.7
		340	3.2	5.4	9.6	49.5	8.7	26.8
		340	10.8	6.1	10.6	47.9	9.9	25.5

[a] % ion current = 0.00 for m/e = 48 for all spectra

[b] Temperature attained at 1.8 ks

[c] Temperature attained at 2.1 ks

Table 5.15 Reaction of CH_3SiD_3 on tungsten:variation of the composition of the gas phase on warming the vessel from 195 to 293 K (films 1 and 2) and from 273 to 340 K (film 3). For other experimental conditions see Table 5.13.

Film no.	Film weight /mg	Temp. /K	Time /ks	Composition of the gas phase / %			
				Hydrogen	Methane	Methyl-silane	Dimethyl-silane
1	24.0	195	1.5	31	2	67	0
		293[a]	2.4	43	2	55	0
		293	4.2	42	3	55	0
		293	10.8	49	5	46	0
2	30.5	195	1.5	29	3	68	0
		293[b]	3.1	49	4	47	trace
		293	4.1	52	4	44	trace
		293	10.8	60	5	35	trace
3	17.4	273	1.5	55	5	40	0
		340[a]	2.6	62	5	33	trace
		340	3.2	62	5	33	trace
		340	6.0	65	5	29	1

[a] Temperature attained after 1.8 ks

[b] Temperature attained after 2.1 ks

5.2.3 Mutual exchange and products of decomposition

Exchange between CH_3SiH_3 and CH_3SiD_3 over tungsten was examined on films prepared and used at 195 and at 273 K (Tables 5.16 and 5.17). Exchange was rapid at both temperatures. A pronounced loss of activity was found for a series of runs on a single film at either 195 K or 273 K. However, any given run exhibited first order behaviour during the course of reaction. (These films were also used to study the exchange of CH_3SiH_3 with molecular deuterium, the results of which are contained in Section 5.2.4).

During mutual exchange a significant amount of methylsilane decomposed to hydrogen and methane. The resulting composition of the gas phase is shown in Table 5.18.

Table 5.16 Tungsten catalysed mutual exchange:specific rates at 195 K

Volume of reaction vessel = 0.30 l

Film no.	Film weight /mg	Run no.	Initial partial pressure in the reaction vessel /torr		k_{03}[a]
			CH_3SiH_3	CH_3SiD_3	/nM $s^{-1}mg^{-1}$
1	22.6	2	0.88	0.87	12.2
		3[b]	0.88	0.89	4.70
		4[b]	0.92	0.87	2.23
		5	0.90	0.87	1.30
2	25.9	3	0.90	0.96	10.4
3	23.8	1	1.00	0.99	13.1
		2	1.00	1.02	11.3
		3	1.01	0.99	8.60
		4	1.01	1.02	6.68
		5	1.03	0.99	3.78
		6[c]	0.89	0.87	1.04

[a] As defined in Section 4.2

[b] Mixture contained deuterium (10.1 torr)

[c] Temperature of reaction vessel = 290 K

Table 5.17 Tungsten catalysed mutual exchange: specific rates at 273 K

Volume of reaction vessel = 0.30 l

Film no.	Film weight /mg	Run no.	Initial partial pressure in the reaction vessel /torr		k_{03}[a] /nM $s^{-1}mg^{-1}$
			CH_3SiH_3	CH_3SiD_3	
4	13.9	1	0.91	1.06	17.7
5	15.1	1	0.95	1.06	18.1
6	23.8	1	0.84	0.89	9.95
		2	0.84	0.89	8.03
		3	0.84	0.89	6.40
		4	0.85	0.90	4.88
		5	0.84	0.89	3.14
Mean		1	0.90	1.00	15.3

[a] As defined in Section 4.2

Table 5.18 Tungsten catalysed mutual exchange: composition of the gas phase due to decomposition of methylsilane on the surface of the film. For other experimental details see Tables 5.16 and 5.17

Film no.	Temp. /K	Run no.	Composition of the gas phase / %					
			Hydrogen			Methane		Methylsilane
			H_2	HD	D_2	CH_4	CH_3D	
3	195	2	5	4	1	1	trace	89
		3	6	5	1	1	1	86
		4	6	5	trace	1	trace	88
6	273	1	9	11	3	2	1	74
		2	6	5	1	1	trace	87
		3	6	5	1	1	trace	87
		5	4	3	trace	1	trace	92

5.2.4 Exchange with molecular deuterium

The exchange of protium in methylsilane with gaseous deuterium has been catalysed by tungsten films at 195 and at 273 K.

Mixtures consisting of CH_3SiD_3 and deuterium were used to determine the activity of protium bonded to carbon for exchange at 195 and at 273 K. Negligible exchange occurred. Exchange was observed at the above temperatures for the exchange of protium for deuterium in CH_3SiH_3. Therefore the rates of exchange determined were for protium bonded to silicon.

For experiments at 195 and at 273 K the function plots of $\ln(\emptyset_{\infty} - \emptyset)$ and of $\ln(d_o - d_{o\infty})$ against time were non-linear, presumably due to poisoning (examples are shown in Figure 5.4) and hence the specific rates were determined from the initial slope. Values of specific rates and of the multiplicity, M, are shown in Tables 5.19 and 5.20.

Table 5.19 Tungsten catalysed exchange of CH_3SiH_3 with deuterium:specific rates, k_ϕ and k_0[a], and values of the multiplicity, M[a], at 195 K.

Volume of reaction vessel = 0.30 l

Initial pressure of CH_3SiH_3 in reaction vessel = 1.0 ± 0.1 torr

Initial pressure of deuterium in reaction vessel = 10.1 ± 0.1 torr

Film no.	Film weight /mg	Run no.	k_ϕ /nM $s^{-1}mg^{-1}$	k_0/nM $s^{-1}mg^{-1}$			M		
				k_0^I	k_0^{II}	k_0^{III}	M^I	M^{II}	M^{III}
1[b]	22.6	1	0.28	0.26	0.27	0.27	1.08	1.04	1.04
		6	0.04	0.02	0.03	0.03	2.00	1.33	1.33
		6[c]	0.12	0.11	0.11	0.13	1.09	1.09	1.00
2[b]	25.9	1	0.72	0.64	0.74	0.70	1.13	1.00	1.03
		2	0.04	0.02	0.03	0.02	1.00	1.33	2.00
		4	0	0	0	0	-	-	-
		4[c]	0.65	0.57	0.66	0.66	1.14	1.00	1.00

[a] Superscripts I, II, and III are defined in Section 4.3.

[b] Mutual exchange carried out on corresponding film in Table 5.16

[c] Reaction vessel warmed to 290 K

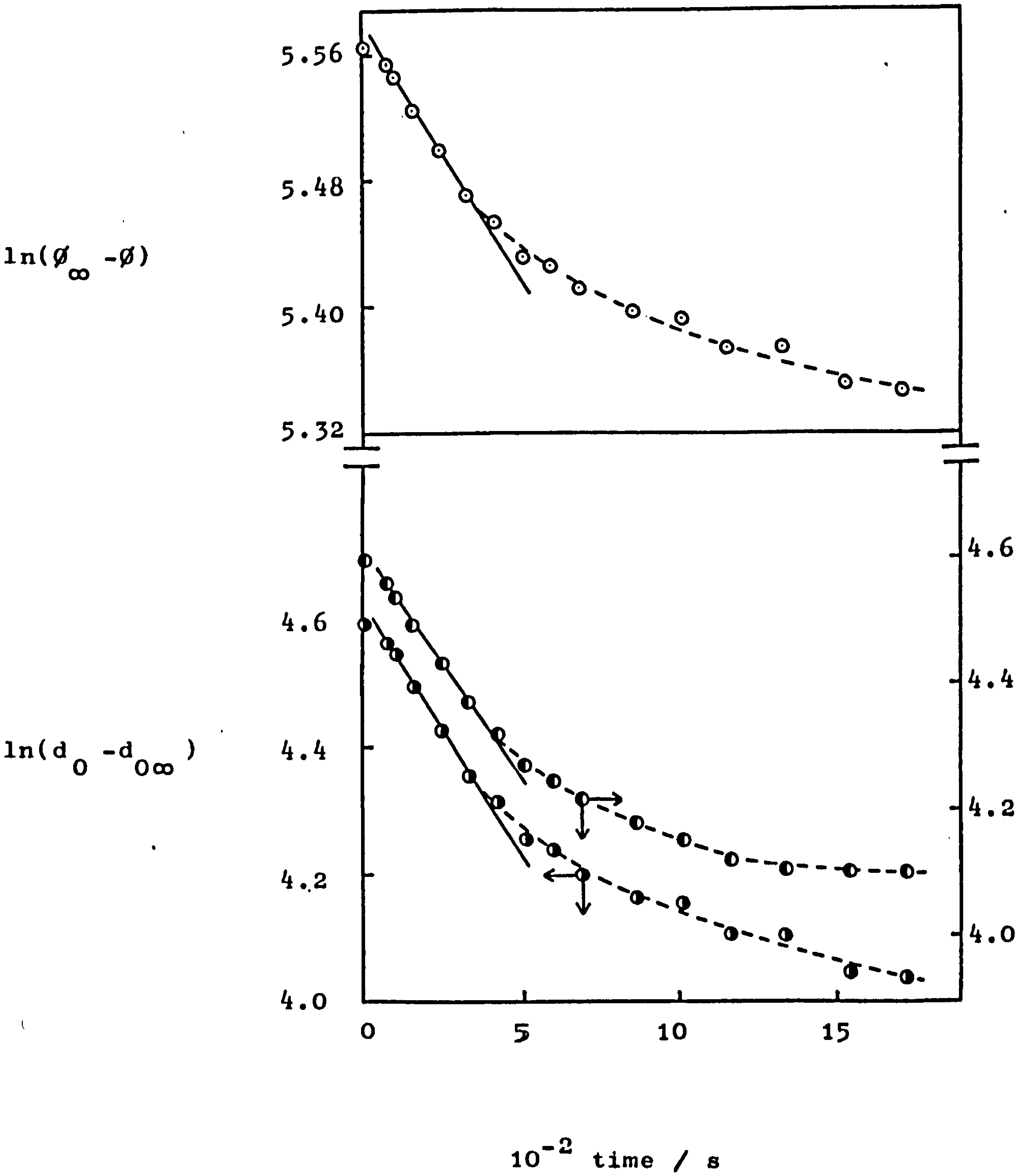


Figure 5.4.1 Exchange with molecular deuterium catalysed by tungsten at 195 K: film no. 2, run no. 1

Legend:- ⊙ gives k_ϕ , ◐ gives k_0^{I} , ◑ gives k_0^{II} and k_0^{III}

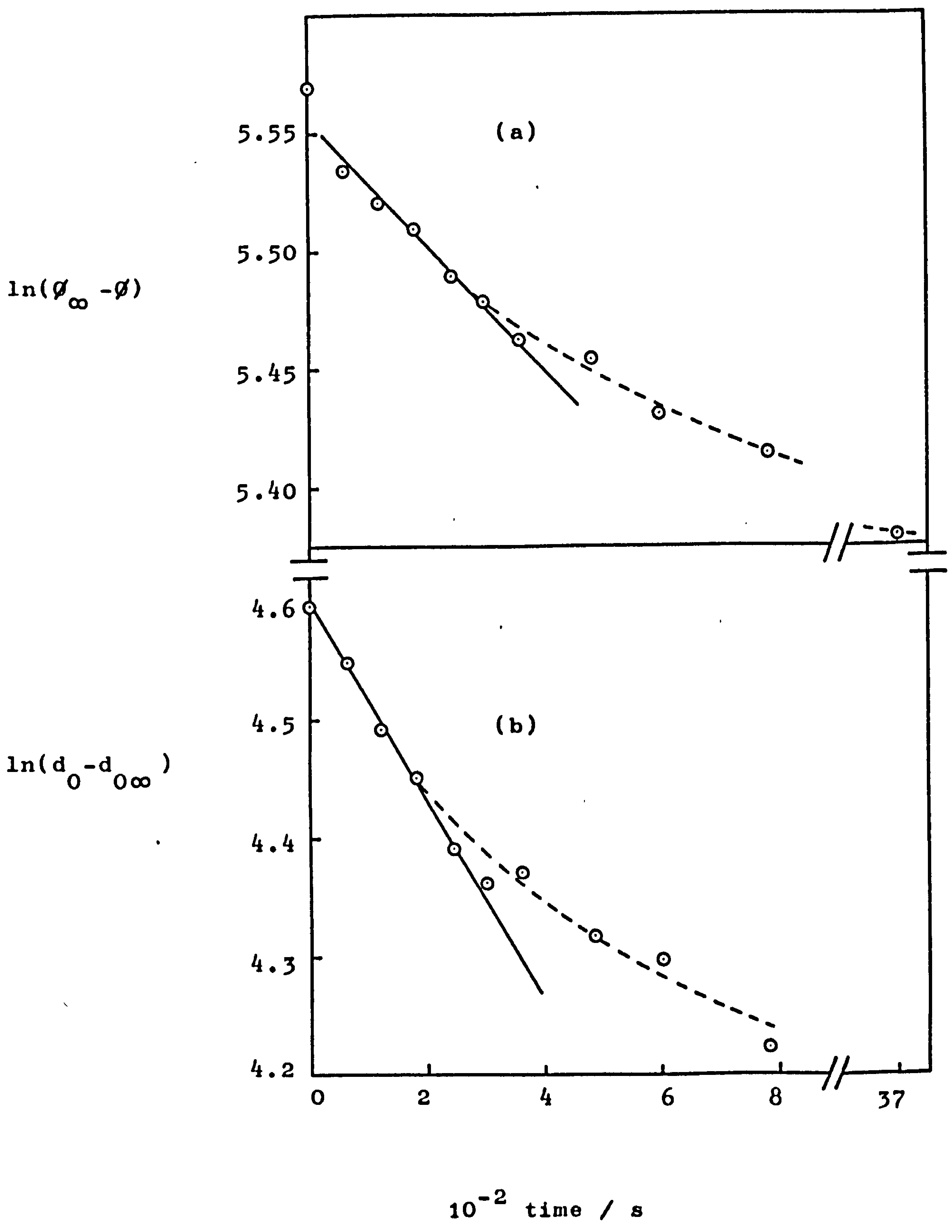


Figure 5.4.2 Exchange with molecular deuterium catalysed by tungsten at 273 K: film no. 5, run no. 1.

Legend:- graph (a) gives k_{ϕ}, graph (b) gives k_0^I .

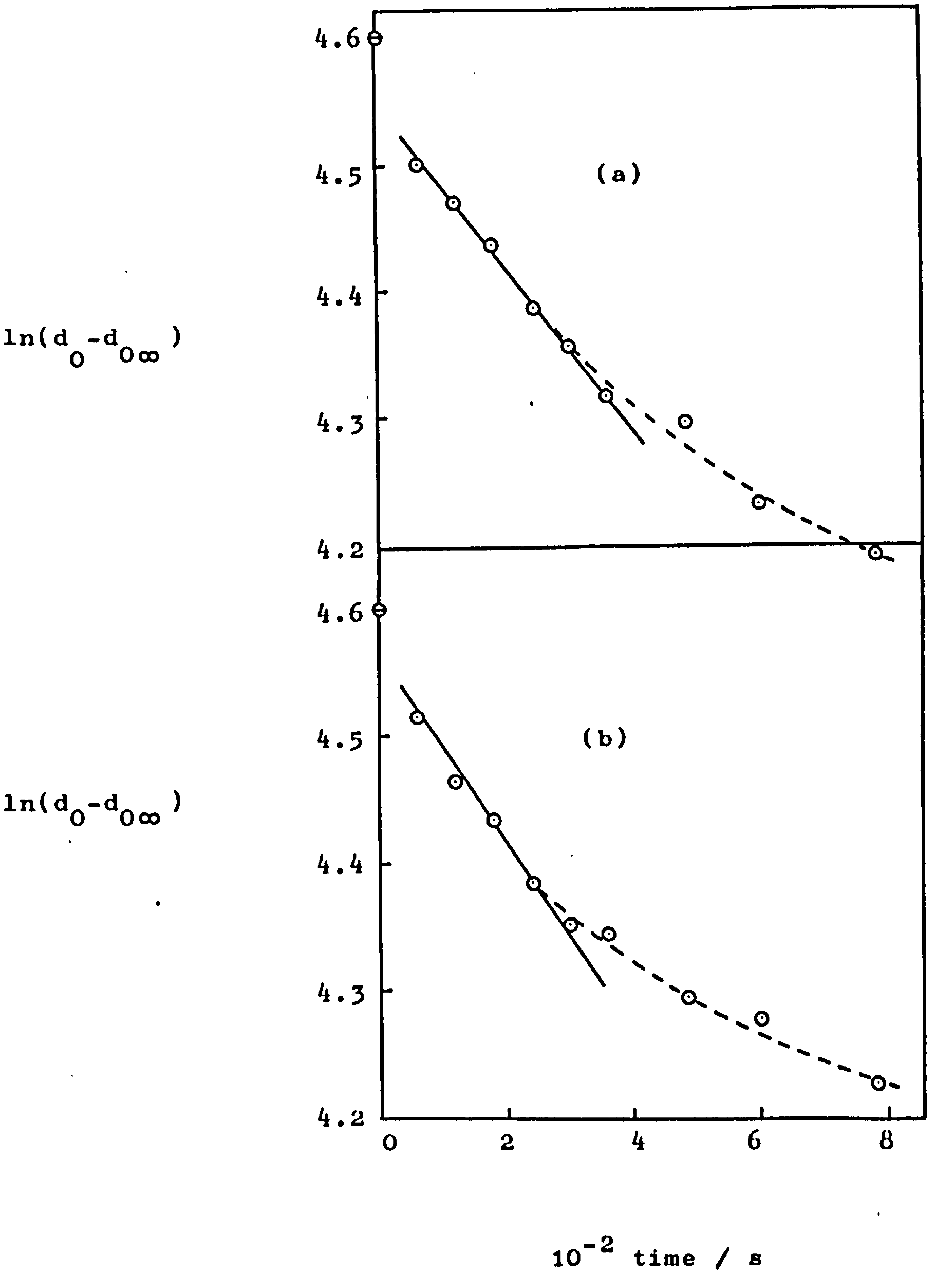


Figure 5.4.3 Exchange with molecular deuterium catalysed by tungsten at 273 K: film no. 5, run no. 1.

Legend:- graph (a) gives k_0^{II}, graph (b) gives k_0^{III}.

Table 5.20 Tungsten catalysed exchange of CH_3SiH_3 with deuterium:specific rates, k_ϕ and k_0[a], and values of the multiplicity, M[a], at 273 K

Volume of reaction vessel = 1.00 l

Initial pressure of CH_3SiH_3 in reaction vessel = 1.0 ± 0.1 torr

Initial pressure of deuterium in reaction vessel = 10.6 ± 0.1 torr

Film no.	Film weight /mg	Run no.	k_ϕ /nM $s^{-1}mg^{-1}$	k_0/nM $s^{-1}mg^{-1}$			M		
				k_0^{I}	k_0^{II}	k_0^{III}	M^{I}	M^{II}	M^{III}
3	19.5	1	2.50	1.90	2.50	2.50	1.32	1.00	1.00
4	14.5	1	4.70	4.35	-	4.55	1.08	-	1.03
5	16.1	1	2.75	2.80	2.45	2.55	1.00	1.12	1.06
6	17.2	1	5.25	3.10	-	4.30	1.69	-	1.22
7	30.3	1	0.75	0.65	0.75	0.75	1.15	1.00	1.00
Mean			3.20	2.55	1.90	2.95	1.25	1.04	1.08

[a] Superscripts I, II, and III are defined in Section 4.3

5.3 Results Obtained for Rhodium Films

5.3.1 Adsorption of CH_3SiH_3

Adsorption of CH_3SiH_3 on rhodium has been investigated on four films prepared and used at 273 K. The adsorption isotherms are shown in Figure 5.5. The surface uptake, the composition of the chemisorbed layer and of the gas phase at complete surface coverage by CH_3SiH_3 for each film are shown in Table 5.21.

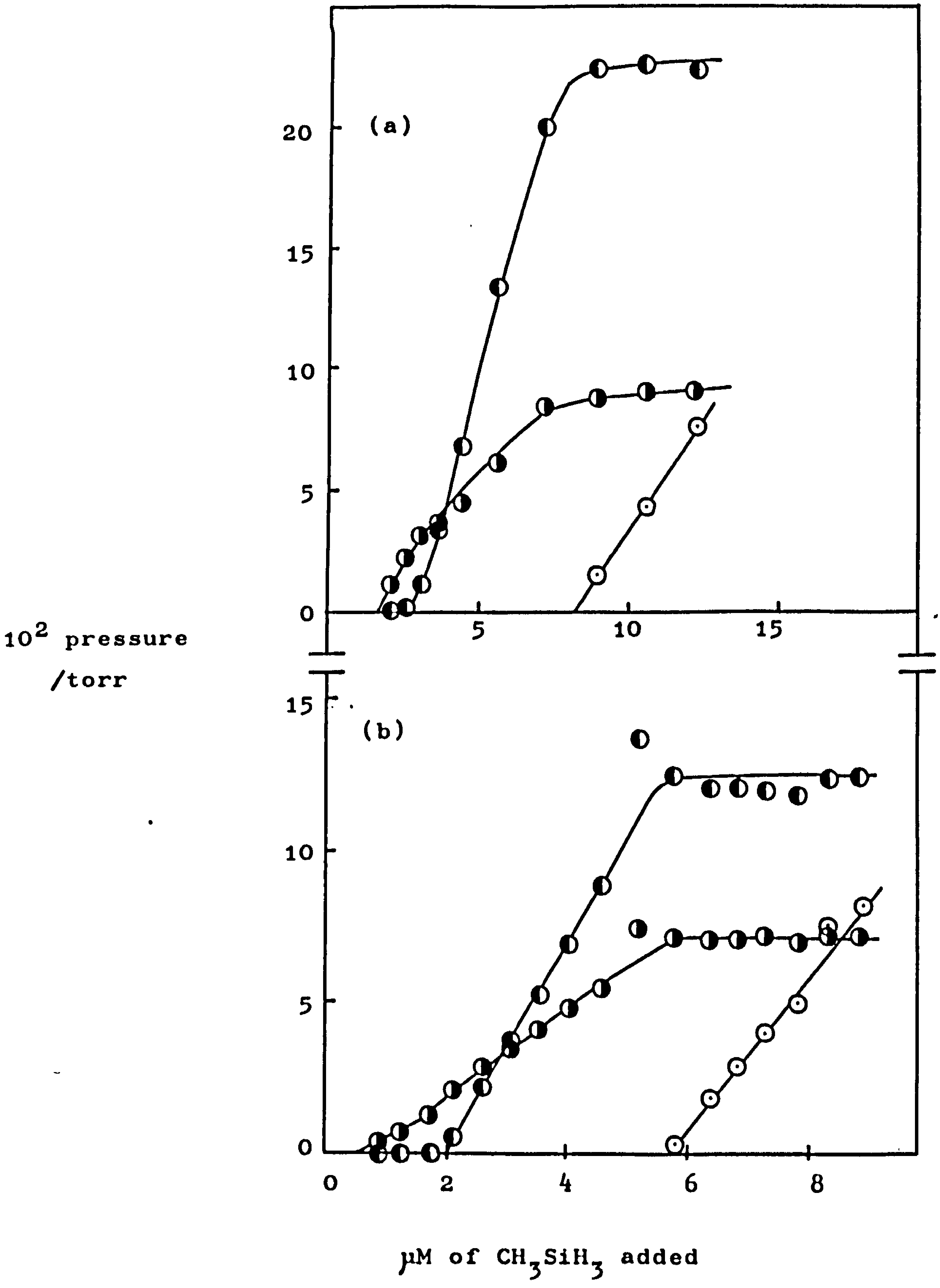


Figure 5.5.1 Chemisorption of CH_3SiH_3 on rhodium at 273 K: (a) film wt. = 26.9 mg; (b) film wt. = 17.6 mg.

Legend:- ⊙ CH_3SiH_3, ◐ H_2, ◑ CH_4 .

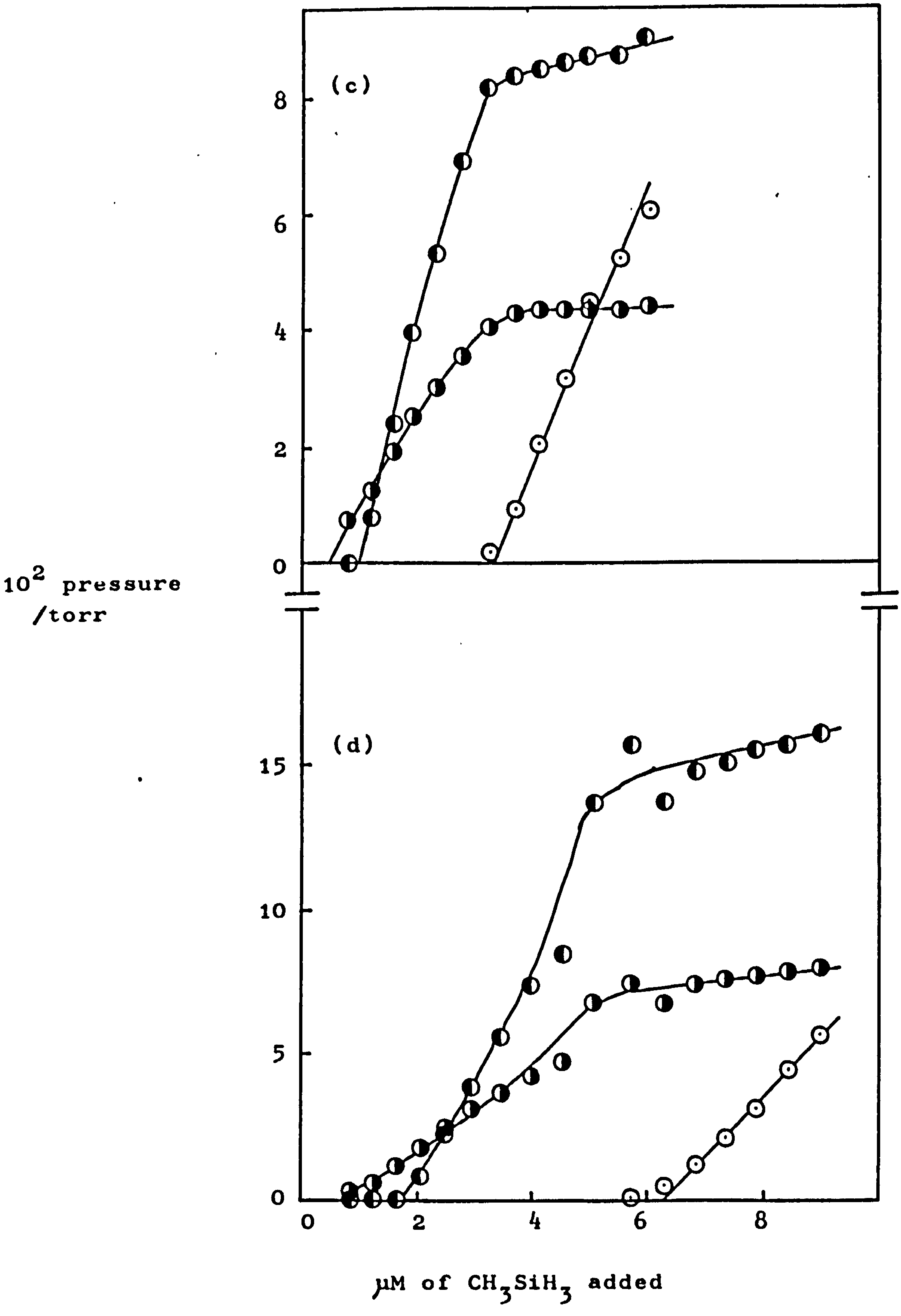


Figure 5.5.2 Chemisorption of CH_3SiH_3 on rhodium at 273 K: (c) film wt. = 8.8 mg; (d) film wt. = 15.7 mg.

Legend:- ⊙ CH_3SiH_3, ◐ H_2, ◑ CH_4.

Table 5.21 The adsorption of CH_3SiH_3 on rhodium at 273 K

Volume of reaction vessel = 0.30 l

Film weight /mg	Surface uptake /micromoles mg^{-1}	Relative composition of the chemisorbed layer			Gas phase composition[a]	
		C	Si	H	n_{H_2}	n_{CH_4}
26.9	0.31	0.77	1.00	4.16	0.46	0.23
17.6	0.31	0.71	1.00	3.86	0.49	0.29
8.8	0.38	0.73	1.00	3.82	0.55	0.27
15.7	0.39	0.74	1.00	3.88	0.54	0.26
Mean	0.35	0.74	1.00	3.94	0.51	0.26

[a] n_{H_2} and n_{CH_4} are the number of moles of hydrogen and of methane evolved per mole of CH_3SiH_3 adsorbed at complete surface coverage.

5.3.2 Self exchange and products of decomposition

Experiments designed to determine whether self exchange occurred on rhodium films were carried out at 195, 273 and 323 K. No exchange was observed initially. Hydrogen and methane were detected in the gas phase and the isotopic compositions of each are shown in Table 5.22.

Upon raising the temperature of the film self exchange commenced. The consequent variations of the mass spectrum of methylsilane with time are shown in Table 5.23. The yields of hydrogen and of methane increased after the change of temperature and their new isotopic compositions are shown in Table 5.22. Dimethylsilane (principally

$(CH_3)_2SiD_2$) was also detected. The percentage of each substance in the gas phase before and after the change of temperature are shown in Table 5.24

Table 5.22 Reaction of CH_3SiD_3 on rhodium:isotopic composition (%) of hydrogen and of methane formed by the decomposition of CH_3SiD_3

Volume of reaction vessel = 0.30 l

Initial pressure of CH_3SiD_3 in reaction vessel = 1.0 ± 0.1 torr

Film no.	Film weight /mg	Temp. /K	Time /ks	Hydrogen			Methane				
				H_2	HD	D_2	CH_4	CH_3D	CH_2D_2	CHD_3	CD_4
1	52.0	195	1.8	8	20	72	19	66	13	2	0
		293[a]	3.6	6	30	64	21	55	8	7	9
		293	5.4	7	35	58	20	56	8	7	9
2	46.5	195	2.0	6	22	72	11	73	8	3	5
		293[a]	3.6	6	34	60	24	53	8	7	8
		293	9.5	15	44	41	22	48	12	10	8
3	16.3	195	1.7	21	40	39	31	38	31	0	0
		293[b]	2.0	20	38	42	23	59	18	0	0
		293	18.0	24	43	33	25	59	12	4	0

[a] Temperature attained after 2.4 ks

[b] Temperature attained after 1.8 ks

Table 5.23 Reaction of CH_3SiD_3 on rhodium: variation of the mass spectrum of methylsilane with time on warming the vessel from 195 to 293 K (films 1 to 3) and from 273 to 350 K (film 4). For other experimental details see Table 5.22.

Film no.	Film weight /mg	Temp. /K	Time /ks	% ion current per m/e value[a]				
				43	44	45	46	47
1	52.0	195	0.0	4.7	6.9	51.4	7.3	29.7
		195	2.3	5.3	7.5	50.7	7.5	29.0
		293[b]	2.5	5.6	9.4	49.5	8.4	27.1
		293	2.7	7.3	11.8	46.9	9.8	24.2
		293	3.2	10.5	16.0	41.7	10.4	21.4
2	46.5	195	0.0	5.4	8.0	51.2	7.1	28.3
		195	1.8	5.5	9.0	49.3	7.8	28.4
		293[b]	2.6	6.2	9.5	50.1	7.7	26.5
		293	3.0	16.0	23.1	34.8	8.7	17.4
3	16.3	195	0.0	4.4	6.2	52.2	6.4	30.8
		293[c]	18.0	4.4	7.1	51.4	6.8	30.3
4	3.8	273	0.0	4.6	7.4	51.4	6.9	29.7
		350[c]	12.7	4.8	8.8	49.6	8.3	28.4

[a] % ion current = 0.00 for m/e = 48 for all spectra

[b] Temperature attained after 2.4 ks

[c] Temperature attained after 1.8 ks

Table 5.24 Reaction of CH_3SiD_3 on rhodium: variation of the composition of the gas phase on warming the vessel from 195 to 293 K. For other experimental details see Table 5.22

Film no.	Film weight /mg	Temp. /K	Time /ks	Composition of gas phase / %			
				Hydrogen	Methane	Methyl-silane	Dimethyl-silane
1	52.0	195	1.8	60	13	27	0
		293[a]	3.6	59	38	3	trace
		293	5.4	57	42	0	1
2	46.5	195	2.0	54	13	33	0
		293[a]	3.6	59	40	1	trace
		293	9.5	46	54	0	0
3	16.3	195	1.7	23	4	73	0
		293[b]	2.0	22	3	75	0
		293	18.0	18	6	76	0

[a] Temperature attained after 2.4 ks
[b] Temperature attained after 1.8 ks

5.3.3 Mutual exchange and products of decomposition

Exchange between CH_3SiH_3 and CH_3SiD_3 over rhodium has been investigated at 195 and at 273 K (Tables 5.25 and 5.26). Rapid exchange was observed at both temperatures. For a series of runs on a single film at 195 K the rate of exchange decreased markedly for each successive run. At 273 K a similar series of runs exhibited a greater loss of activity with increasing run number. First order behaviour was observed at

195 K, but at 273 K slight curvature was observed in the function plot of $\ln(d_{03}-d_{03_\infty})$ against time (examples are shown in Figure 5.6).

During the course of reaction a significant amount of methylsilane decomposed on the surface of the film to yield hydrogen and methane. The resulting composition of the gas phase is shown in Table 5.27.

Table 5.25 Rhodium catalysed mutual exchange: specific rates at 195 K

Volume of reaction vessel = 0.30 l

Film no.	Film weight /mg	Run no.	Initial partial pressure in the reaction vessel /torr		k_{03}[a] /nM $s^{-1}mg^{-1}$
			CH_3SiH_3	CH_3SiD_3	
1	12.1	1	0.89	0.95	24.9
		2	0.90	0.96	11.8
		3	0.90	0.96	4.51
		4	0.89	0.95	1.40
		5	0.89	0.95	1.90
		5[b]	0.89	0.95	12.5
2	9.8	1	0.88	0.95	27.2
		2	0.90	0.96	9.70
		3	0.89	0.96	4.76
		4	0.86	0.92	3.30
		5	0.90	0.96	2.40
		5[b]	0.90	0.96	13.8
		6[c]	0.88	0.94	2.65
Mean		1	0.89	0.95	26.1

[a] As defined in Section 4.2

[b] Reaction vessel warmed up to 290 K

[c] Reaction vessel at 290 K

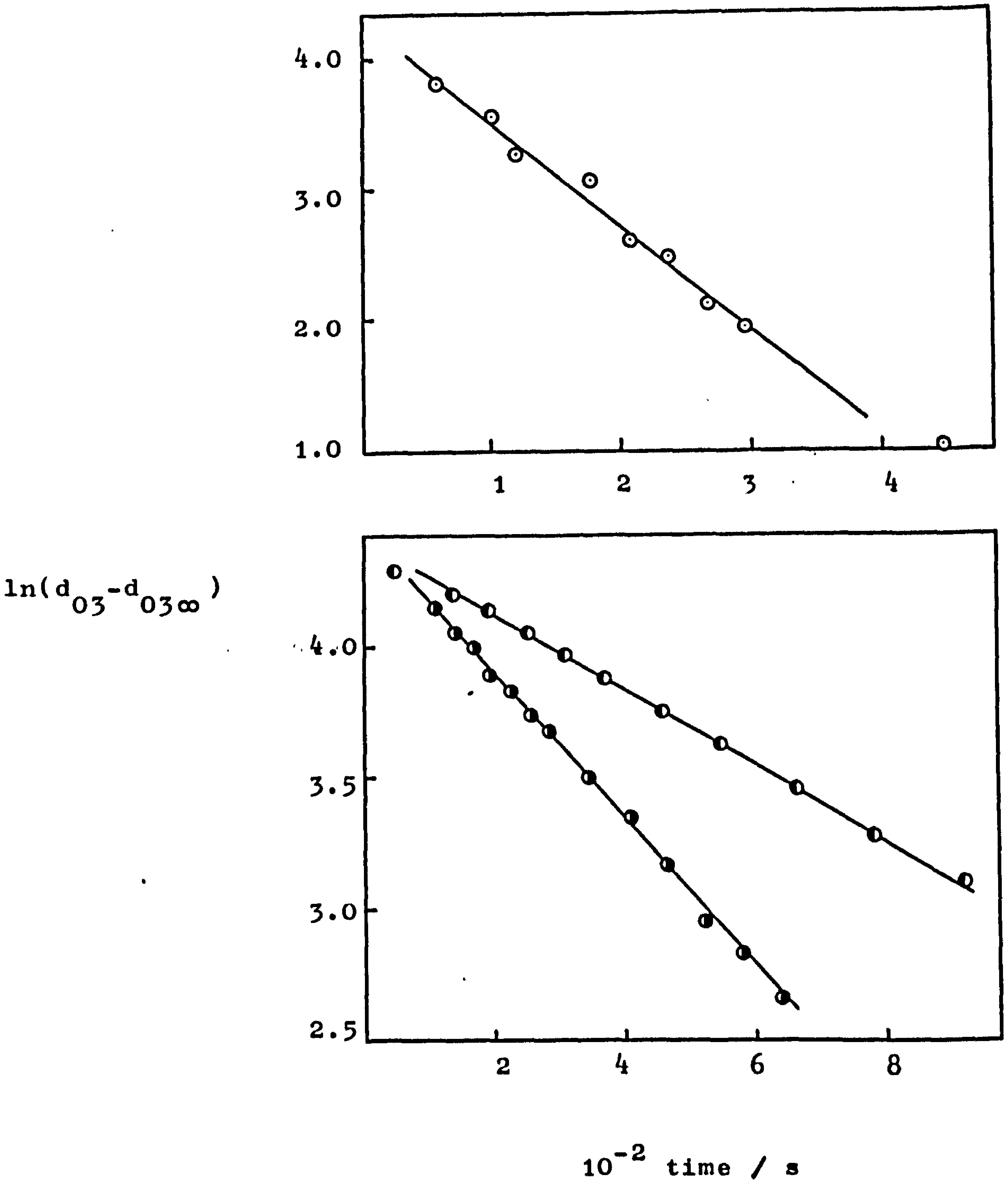


Figure 5.6.1 Mutual exchange catalysed by rhodium at 195 K: film no. 2.

Legend:- ⊙ run no. 1 , ◑ run no. 2 ,

◐ run no. 3 .

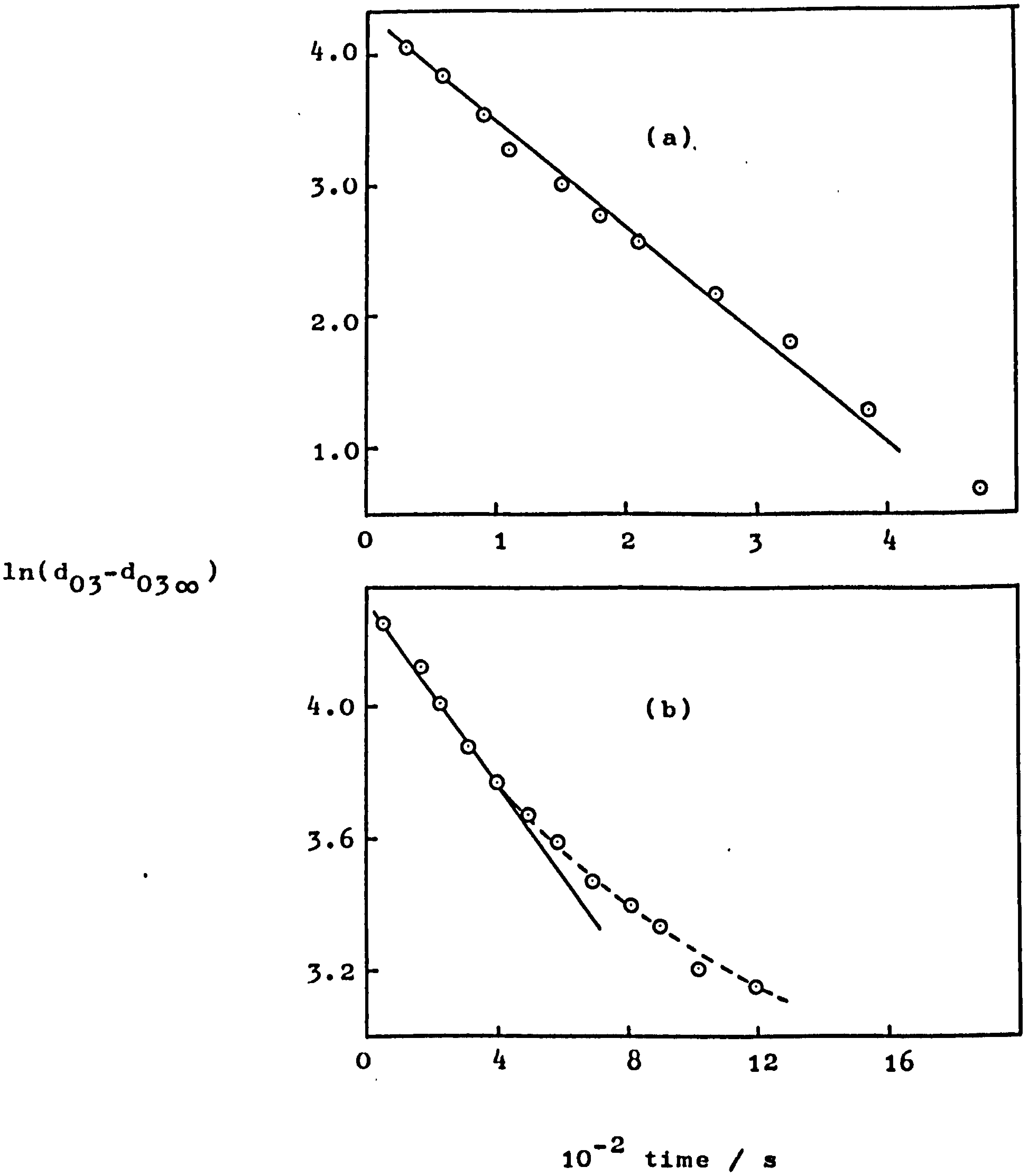


Figure 5.6.2 Mutual exchange catalysed by rhodium at 273 K: film no. 12.

Legend:- (a) run no. 1 , (b) run no. 2 .

Table 5.26 Rhodium catalysed mutual exchange: specific rates at 273 K

Volume of reaction vessel = 1.00 l

Film no.	Film weight /mg	Run no.	Initial partial pressure in the reaction vessel /torr		k_{03}[a] /nM $s^{-1}mg^{-1}$
			CH_3SiH_3	CH_3SiD_3	
3[b]	17.8	1	1.04	0.92	5.14
		2	2.00	2.02	0.79
4	14.0	1	1.26	1.34	14.1
5	11.3	1	1.28	1.37	8.60
6	21.5	1	1.08	1.14	11.1
7	18.9	1	1.20	1.27	5.90
8	6.3	1	1.26	1.30	6.95
9	12.1	1	0.95	1.00	1.10
10	5.5	1	0.95	1.00	5.35
11[b]	5.1	1	0.91	0.96	35.6
12[b]	12.3	1	0.81	0.87	14.4
		2	0.82	0.88	2.40
		3	0.79	0.85	0.88
Mean		1	1.07	1.11	10.8

[a] As defined in Section 4.2

[b] Volume of reaction vessel = 0.30 l

Table 5.27 Rhodium catalysed mutual exchange: composition of the gas phase due to decomposition of methylsilane on the surface of the film. For other experimental details see Table 5.25

Film no.	Temp. /K	Run no.	Composition of the gas phase / %						
			Hydrogen			Methane			Methyl-silane
			H_2	HD	D_2	CH_4	CH_3D	CH_2D_2	
1	195	1	7	7	1	3	2	trace	80
2	195	1	7	6	trace	3	2	1	81
	195	2	5	3	1	1	trace	trace	90
	290	5	4	4	1	3	1	0	87

5.3.4 Exchange with molecular deuterium

The exchange of methylsilane with gaseous deuterium has been catalysed by rhodium films at 195 and 273 K.

Mixtures consisting of CH_3SiD_3 and deuterium were used to determine the activity of protium bonded to carbon for exchange at 195 and at 273 K. Negligible exchange was found. Exchange was observed for the above temperatures for the exchange of hydrogen for deuterium in CH_3SiH_3. Therefore the rates of exchange determined were for protium bonded to silicon.

At 195 K the function plots of $\ln(\phi_\infty - \phi)$ and of $\ln(d_0 - d_{0\infty})$ against time were approximately linear. At 273 and 303 K the above function plots were non-linear presumably due to poisoning. Examples of the function plots obtained are shown in Figure 5.7. Values of the specific rates and of the multiplicity, M, are shown in Tables 5.28 - 5.30.

Table 5.28 Rhodium catalysed exchange of CH_3SiH_3 with deuterium:specific rates, k_{ϕ} and k_0[a], and values of the multiplicity, M[a], at 195 K

Volume of reaction vessel = 0.30 l

Initial pressure of CH_3SiH_3 in reaction vessel = 1.0 ± 0.1 torr

Initial pressure of deuterium in reaction vessel = 10.3 ± 0.1 torr

Film no.	Film weight /mg	Run no.	k_{ϕ} /nM $s^{-1}mg^{-1}$	k_0/nM $s^{-1}mg^{-1}$			M		
				k_0^{I}	k_0^{II}	k_0^{III}	M^{I}	M^{II}	M^{III}
1	17.9	1	12.8	6.20	-	8.85	2.06	-	1.45
		2	0.88	0.84	0.84	0.86	1.04	1.04	1.02
		2[b]	6.60	1.35	-	5.20	-	-	1.27
2	25.0	1	14.2	6.20	-	6.15	2.29	-	2.30
		2	2.20	2.00	2.10	2.20	1.10	1.05	1.00
		3	0.31	0.27	0.28	0.29	1.15	1.11	1.07
		3[b]	10.0	2.55	-	5.90	-	-	1.69
Mean		1	13.5	6.20	-	7.50	2.18	-	1.80

[a] Superscripts I, II, and III are defined in Section 4.3

[b] Reaction vessel warmed to 290 K

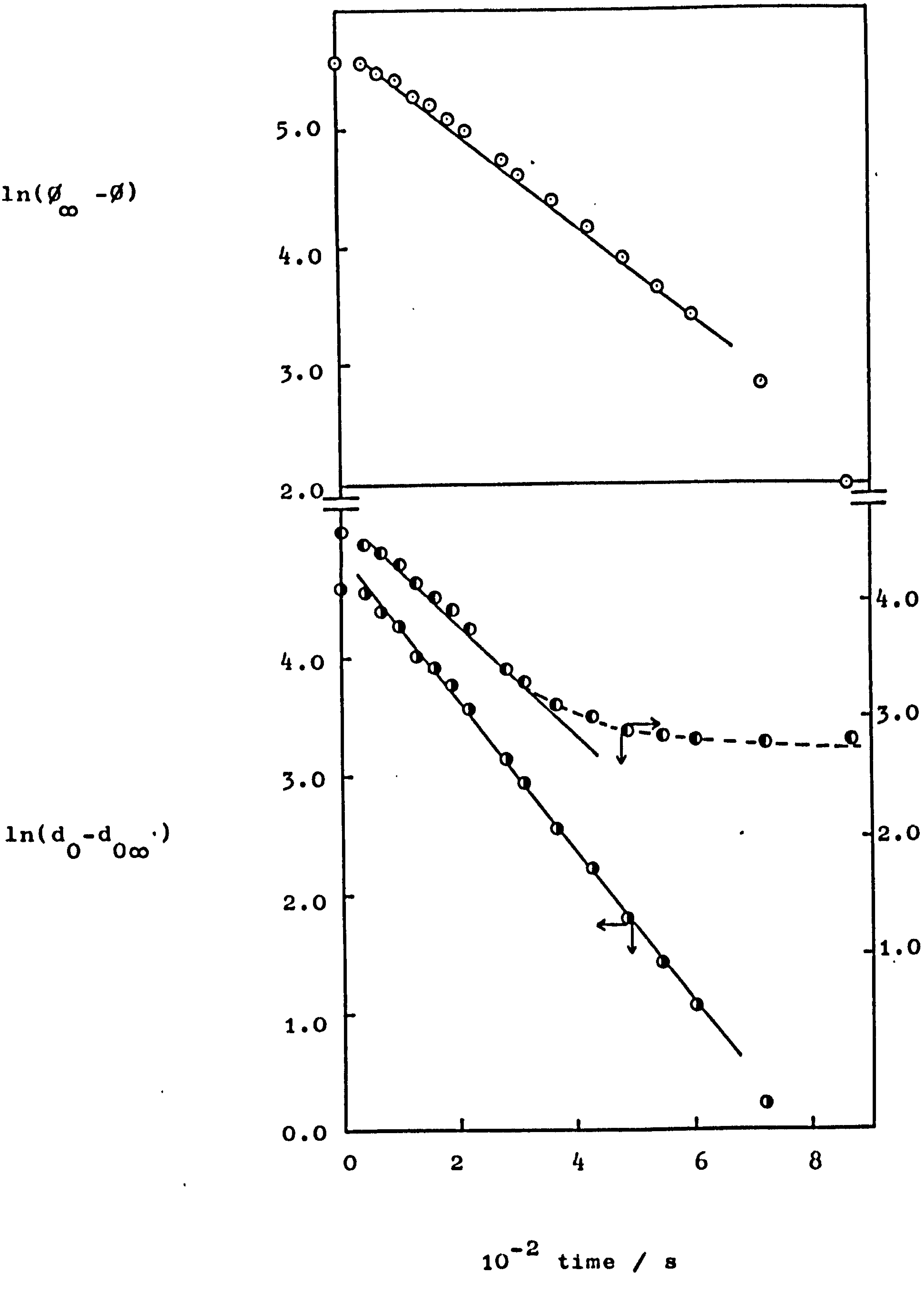


Figure 5.7.1 Exchange with molecular deuterium catalysed by rhodium at 195 K: film no. 1, run 1.

Legend:- ⊙ gives k_ϕ, ◐ gives k_0^I, ◑ gives k_0^{III}.

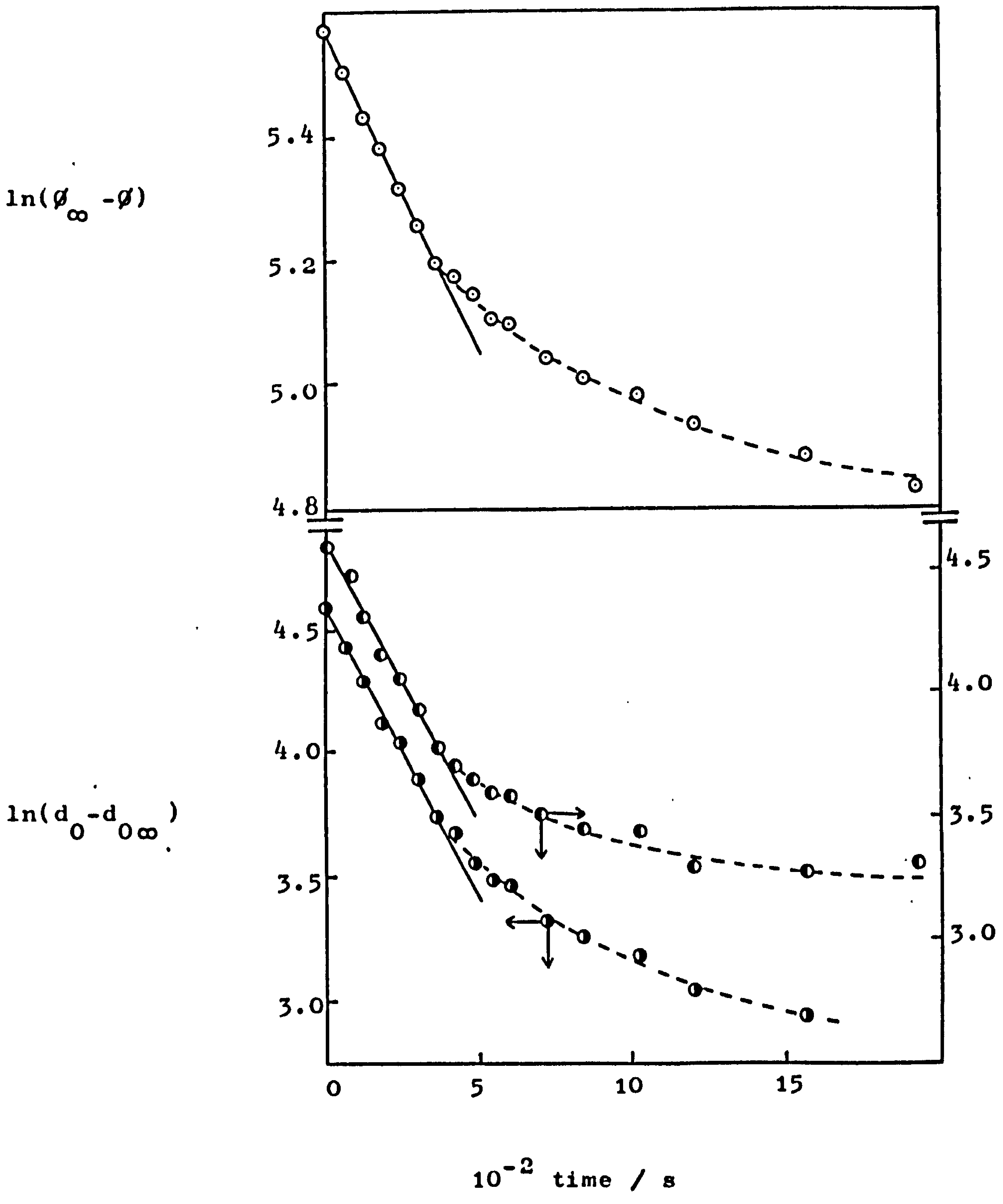


Figure 5.7.2 Exchange with molecular deuterium catalysed by rhodium at 273 K: film no. 7, run no. 1.

Legend:- ⊙ gives k_{ϕ}, ◐ gives k_0^{I}, ○ gives k_0^{III}.

Table 5.29 Rhodium catalysed exchange of CH_3SiH_3 with deuterium: specific rates, k_ϕ and k_0[a], and values of the multiplicity, M[a], at 273 K

Volume of reaction vessel = 1.00 l

Initial pressure of CH_3SiH_3 in reaction vessel = 1.0 ± 0.1 torr

Initial pressure of deuterium in reaction vessel = 10.6 ± 0.1 torr

Film no.	Film weight /mg	Run no.	k_ϕ /nM $s^{-1}mg^{-1}$	k_0/nM $s^{-1}mg^{-1}$			M		
				k_0^{I}	k_0^{II}	k_0^{III}	M^{I}	M^{II}	M^{III}
3	15.2	1	3.85	3.80	-	3.70	1.01	-	1.04
4	16.7	1	11.7	9.25	9.95	9.95	1.26	1.18	1.18
5	3.3	1	14.7	10.3	-	12.3	1.43	-	1.20
6	15.4	1	5.40	4.90	-	5.20	1.10	-	1.04
7	19.5	1	7.90	6.65	-	7.10	1.19	-	1.11
8	11.9	1	4.85	3.95	-	4.00	1.23	-	1.21
Mean		1	8.07	6.48	9.95	7.04	1.25	1.18	1.15

[a] Superscripts I, II, and III are defined in Section 4.3

Table 5.30 Rhodium catalysed exchange of CH_3SiH_3 with deuterium:specific rates, k_ϕ and k_0[a], and values of the multiplicity, M[a], at 303 K

Volume of reaction vessel = 1.00 l

Initial pressure of CH_3SiH_3 in reaction vessel = 1.1 ± 0.1 torr

Initial pressure of deuterium in reaction vessel = 11.7 ± 0.1 torr

Film no.	Film weight /mg	Run no.	k_ϕ /nM $s^{-1}mg^{-1}$	k_0/nM $s^{-1}mg^{-1}$			M		
				k_0^I	k_0^{II}	k_0^{III}	M^I	M^{II}	M^{III}
9	13.4	1	5.10	4.30	-	4.80	1.19	-	1.06
10	15.0	1	6.80	6.80	-	6.45	1.00	-	1.05
11	20.2	1	11.4	8.30	-	8.90	1.37	-	1.28
12	13.2	1	6.05	4.50	-	4.35	1.34	-	1.39
13	12.6	1	12.2	9.65	-	11.3	1.26	-	1.08
14	18.8	1	4.25	3.65	-	4.15	1.16	-	1.02
Mean		1	7.63	6.19	-	6.66	1.23	-	1.15

---

[a] Superscripts I, II, and III are defined in Section 4.3

5.4 Results Obtained for Nickel Films

5.4.1 Adsorption of CH_3SiH_3

Adsorption of CH_3SiH_3 on nickel has been investigated on four films prepared and used at 273 K. The adsorption isotherms are shown in Figure 5.8. The surface uptake, the composition of the chemisorbed layer, and of the gas phase at complete surface coverage by CH_3SiH_3 for each film are shown in Table 5.31.

Table 5.31 The adsorption of CH_3SiH_3 on nickel at 273 K

Volume of reaction vessel = 0.30 l

Film weight /mg	Surface uptake /micromoles $\cdot mg^{-1}$	Relative composition of the chemisorbed layer C	: Si	: H	Gas phase composition[a] n_{H_2}	n_{CH_4}
7.1	0.28	0.83	1.00	3.68	0.82	0.17
15.8	0.15	0.86	1.00	4.02	0.71	0.14
25.0	0.12	0.81	1.00	3.78	0.73	0.19
13.4	0.19	0.76	1.00	3.66	0.69	0.24
Mean	0.19	0.81	1.00	3.79	0.74	0.19

[a] n_{H_2} and n_{CH_4} are the number of moles of hydrogen and of methane evolved per mole of CH_3SiH_3 adsorbed at complete surface coverage.

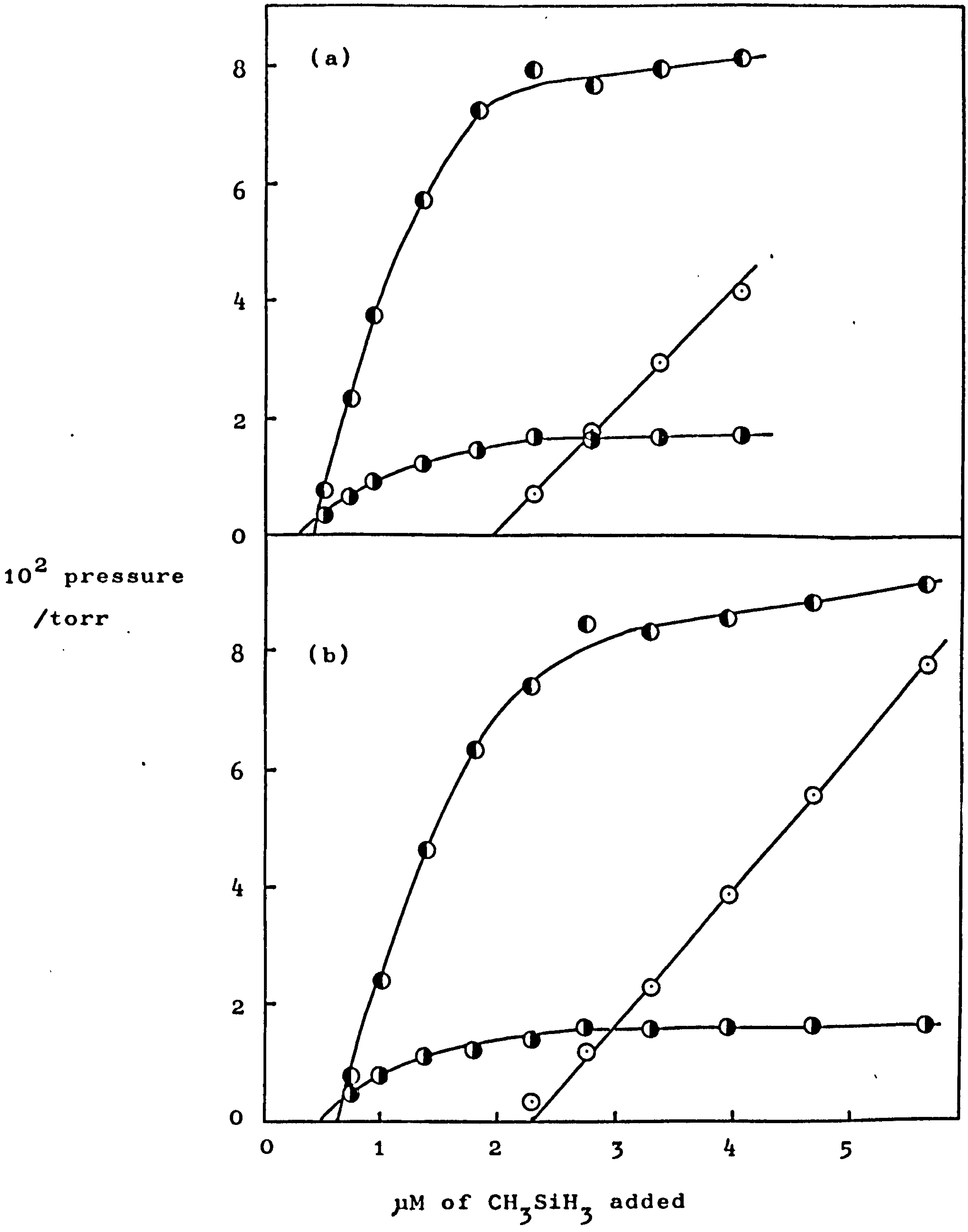


Figure 5.8.1 Chemisorption of CH_3SiH_3 on nickel at 273 K:
(a) film wt = 7.1 mg; (b) film wt. = 15.8 mg.

Legend:- ⊙ CH_3SiH_3, ◐ H_2, ◑ CH_4.

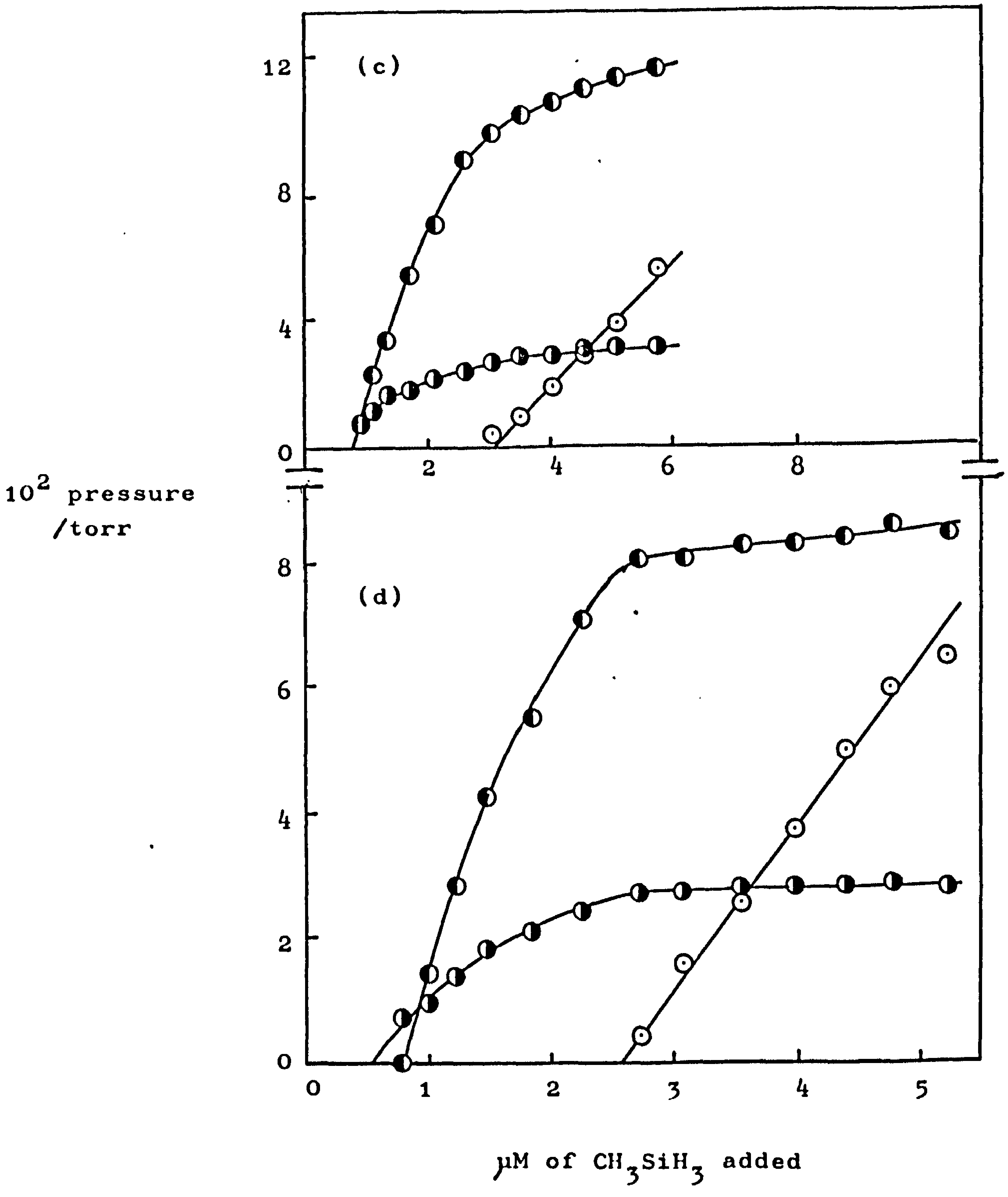


Figure 5.8.2 Chemisorption of CH_3SiH_3 on nickel at 273 K: (c) film wt. = 25.0 mg; (d) film wt. = 13.4 mg.

Legend:- ⊙ CH_3SiH_3, ◐ H_2, ◑ CH_4.

5.4.2 Self exchange and products of decomposition

Experiments designed to determine whether self exchange occurred on nickel films were carried out for the temperature range of 195 to 293 K. No exchange was observed initially at 195 K. Hydrogen and methane were detected in the gas phase and the isotopic compositions of each are shown in Table 5.32.

Raising the temperature of the reaction vessel from 195 to 293 K caused exchange to commence. The consequent variations in the mass spectrum of methylsilane with time are shown in Table 5.33. The yields of hydrogen and of methane increased after the change of temperature and dimethylsilane (principally $(CH_3)_2SiD_2$) was also detected. The yields of each substance in the gas phase before and after the change of temperature are shown in Table 5.34 and the new isotopic compositions of hydrogen and of methane are shown in Table 5.32.

Table 5.32 Reaction of CH_3SiD_3 on nickel: isotopic composition (%) of hydrogen and of methane formed by the decomposition of CH_3SiD_3

Volume of reaction vessel = 0.30 l

Initial pressure of CH_3SiD_3 in reaction vessel = 1.0 ± 0.1 torr

Film no.	Film weight /mg	Temp. /K	Time /ks	Hydrogen			Methane				
				H_2	HD	D_2	CH_4	CH_3D	CH_2D_2	CHD_3	CD_4
1	77.0	195	1.8	11	31	58	23	50	27	0	0
		293[a]	2.6	11	21	68	23	64	13	0	0
		293	4.6	8	23	69	19	64	13	1	3
2	28.5	195	1.7	5	27	68	22	54	22	2	0
		293[a]	3.2	7	23	70	18	64	13	2	3
		293	5.3	7	25	68	18	63	13	2	4

[a] Temperature attained after 2.1 ks

Table 5.33 Reaction of CH_3SiD_3 on nickel: variation of the mass spectrum of CH_3SiD_3 with time on warming the vessel from 195 to 293 K. For other experimental details see Table 5.32

Film no.	Film weight /mg	Temp. /K	Time /ks	% ion current per m/e value[a]				
				43	44	45	46	47
1	77.0	195	0.0	4.7	5.8	51.9	6.3	31.3
		195	2.0	5.3	5.9	51.7	6.3	30.8
		293[b]	2.5	5.0	6.1	51.6	6.6	30.7
		293	4.5	5.6	6.7	50.9	6.8	30.0
2	28.5	195	0.0	4.3	6.0	52.1	6.7	30.9
		195	1.9	4.5	6.0	51.6	6.7	30.5
		293[b]	3.2	5.4	7.4	51.0	7.0	29.2
		293	5.4	5.7	7.7	49.9	7.5	29.2

[a] % ion current = 0.00 for m/e = 48 for all spectra

[b] Temperature attained after 2.1 ks

Table 5.34 Reaction of CH_3SiD_3 on nickel:variation of the composition of the gas phase on warming the vessel from 195 to 293 K. For other experimental details see Table 5.32

Film no.	Film weight /mg	Temp. /K	Time /ks	Composition of the gas phase / %			
				Hydrogen	Methane	Methyl-silane	Dimethyl-silane
1	77.0	195	1.8	18	8	74	0
		293[a]	2.6	25	10	64	1
		293	4.6	29	14	55	2
2	28.5	195	1.7	29	8	63	0
		293[a]	3.2	48	15	35	2
		293	5.3	51	17	30	2

[a] Temperature attained after 2.1 ks

5.4.3 Mutual exchange and products of decomposition

Exchange between CH_3SiH_3 and CH_3SiD_3 over nickel has been investigated on films prepared and used at 195 and at 273 K. Exchange was rapid at both temperatures (Tables 5.35 and 5.36). Activity for exchange decreased for each successive run on a film at 195 or at 273 K. Generally, first order behaviour was observed.

During the course of each reaction significant amounts of methylsilane decomposed on the surface of the film to yield hydrogen and methane. The resulting composition of the gas phase is shown in Table 5.37.

Table 5.35 Nickel catalysed mutual exchange: specific rates at 195 K

Volume of reaction vessel = 0.30 l

Film no.	Film weight /mg	Run no.	Initial partial pressure in the reaction vessel /torr		k_{03}[a] /nM $s^{-1}mg^{-1}$
			CH_3SiH_3	CH_3SiD_3	
1	17.2	2	0.96	0.99	12.0
		2[b]	0.96	0.99	1.70
2	10.0	1	0.95	0.99	27.9
		2	0.95	1.00	8.25
		3	0.98	1.00	3.10
		4	0.96	1.00	2.65
		4[c]	0.96	1.00	13.7
		5[c]	1.28	1.31	13.1
3	34.2	1	0.95	0.98	8.95
		2	0.96	0.98	8.25
		3	0.93	0.90	5.15
		4	0.90	0.92	3.45
		5	0.92	0.95	2.25
		6[c]	0.95	0.95	1.65
		7[c]	0.93	0.91	0.34
4	28.3	1	0.88	0.94	10.5
		2	0.87	0.93	9.55
		2[b]	0.87	0.93	6.95
		3	0.93	0.99	5.95
		3[b]	0.93	0.99	1.10
		4	0.88	0.94	7.00
		5	0.84	0.90	5.80
		6	0.85	0.91	4.70
Mean		1	0.93	0.97	∿15

[a] As defined in Section 4.2

[b] Gradient of function plot altered

[c] Vessel at 290 K.

Table 5.36 Nickel catalysed mutual exchange: specific rates at 273 K

Volume of reaction vessel = 0.30 l

Film no.	Film weight /mg	Run no.	Initial partial pressure in the reaction vessel /torr		k_{03}[a] /nM $s^{-1}mg^{-1}$
			CH_3SiH_3	CH_3SiD_3	
5	6.9	1	0.99	1.00	23.4
6	6.8	1	1.99	1.02	27.5
		2	2.03	1.00	4.20
		3	1.92	0.92	2.60
7	16.5	1	1.04	1.00	10.80
		2	1.05	1.00	5.15
		3	1.05	1.02	2.75
		4	1.02	0.96	2.00
		5	1.00	0.96	1.15
Mean		1	1.34	1.01	20.6

[a] As defined in Section 4.2

Table 5.37 Nickel catalysed mutual exchange: composition of the gas phase due to decomposition of methylsilane on the surface of the film. For other experimental details see Table 5.35

Film no.	Temp. /K	Run no.	Composition of the gas phase / %					
			Hydrogen			Methane		Methyl-silane
			H_2	HD	D_2	CH_4	CH_3D	
2	195	1	7	7	2	1	trace	83
	290	4	7	8	2	1	trace	82
	290	5	8	7	2	1	trace	82
3	195	1	10	10	4	2	1	73
	195	2	8	6	1	1	trace	84
	195	3	8	6	2	1	trace	83
	195.	4	8	6	1	1	trace	84
	195	5	6	5	1	1	trace	87
	290	6	11	12	4	4	2	66
	290	7	7	6	2	1	trace	84

5.4.4 Exchange with molecular deuterium

The exchange of methylsilane with gaseous deuterium has been catalysed by nickel films at 195, 273 and 300 K.

No exchange took place at the above temperatures for reaction mixtures consisting of CH_3SiD_3 and deuterium, hence it was demonstrated that protium bonded to carbon did not exchange in the temperature range used. At 195, 273 and 300K exchange was observed in reaction mixtures consisting of CH_3SiH_3 and deuterium. Therefore the rates of exchange determined were for protium bonded to silicon.

At 195, 273 and 300 K function plots of $\ln(\phi_\infty - \phi)$ and of $\ln(d_0 - d_{0\infty})$ against time were non-linear presumably due to poisoning. Examples of the function plots obtained are shown in Figure 5.9. Values of specific rates and of the multiplicity, M, are shown in Tables 5.38 - 5.40.

Table 5.38 Nickel catalysed exchange of CH_3SiH_3 with deuterium:specific rates, k_ϕ and k_0[a], and values of the multiplicity, M[a], at 195 K

Volume of reaction vessel = 0.30 l
Initial pressure of CH_3SiH_3 in reaction vessel = 0.9 ± 0.1 torr
Initial pressure of deuterium in reaction vessel = 10.2 ± 0.1 torr

Film no.	Film weight /mg	Run no.	k_ϕ /nM $s^{-1}mg^{-1}$	k_0/nM $s^{-1}mg^{-1}$			M		
				k_0^{I}	k_0^{II}	k_0^{III}	M^{I}	M^{II}	M^{III}
1[b]	17.2	1	0.60	0.60	0.55	0.58	1.00	1.09	1.03
		3	0.06	0.05	0.06	0.06	1.20	1.00	1.00
		3[c]	2.25	2.00	2.15	2.25	1.13	1.05	1.00
2	13.6	1	0.18	0.18	0.15	0.16	1.00	1.20	1.13
		2	0	0	0	0	-	-	-
		2[c]	1.70	1.55	1.65	1.70	1.10	1.03	1.00

[a] Superscripts I, II, and III are defined in Section 4.3

[b] Mutual exchange carried out on corresponding film in Table 5.35

[c] Reaction vessel warmed to 290 K

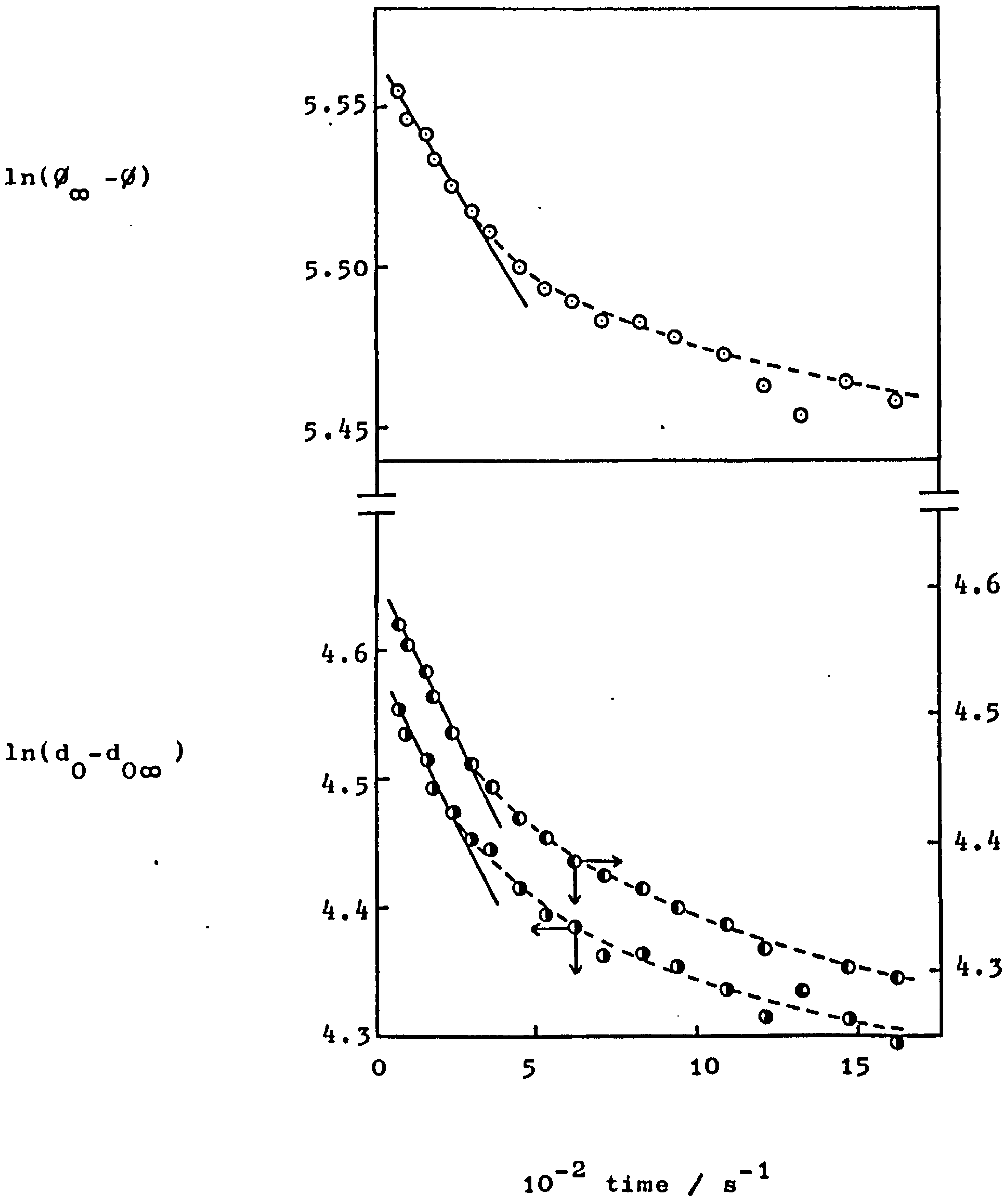


Figure 5.9.1 Exchange with molecular deuterium catalysed by nickel at 195 K; film no. 1, run no. 1.

Legend:- ⊙ gives $k_ø$, ◐ gives k_0^{I}, ◑ gives k_0^{II} and k_0^{III}

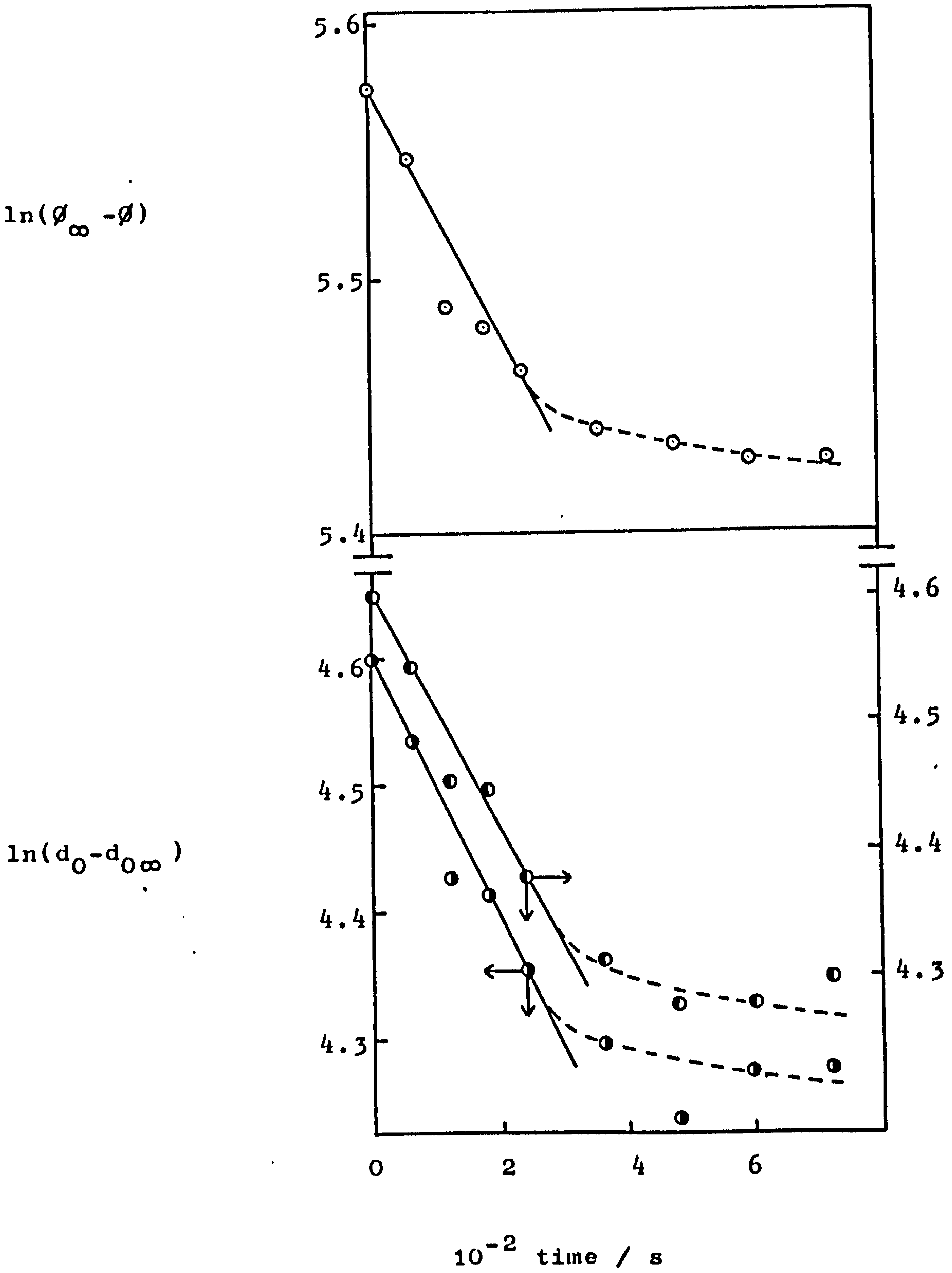


Figure 5.9.2 Exchange with molecular deuterium catalysed by nickel at 273 K: film no. 5, run no. 1.

Legend:- ⊙ gives k_ϕ, ◐ gives k_0^{I}, ◑ gives k_0^{III}.

Table 39 Nickel catalysed exchange of CH_3SiH_3 with deuterium:specific rates, k_ϕ and k_0[a], and values of the multiplicity, M[a], at 273 K

Volume of reaction vessel = 0.30 l

Initial pressure of CH_3SiH_3 in reaction vessel = 1.0 ± 0.1 torr

Initial pressure of deuterium in reaction vessel = 11.0 ± 0.1 torr

Film no.	Film weight /mg	Run no.	k_ϕ /nM $s^{-1}mg^{-1}$	k_0/nM $s^{-1}mg^{-1}$			M		
				k_0^{I}	k_0^{II}	k_0^{III}	M^{I}	M^{II}	M^{III}
3	7.5	1	3.15	2.50	2.90	2.60	1.26	1.09	1.21
4	11.2	1	1.25	1.25	1.25	1.20	1.00	1.00	1.04
5	8.8	1	2.35	1.55	-	1.90	1.52	-	1.24
6	12.3	1	2.85	2.35	-	2.65	1.21	-	1.08
7	8.5	1	1.55	1.45	1.55	1.60	1.07	1.00	1.00
Mean		1	2.25	1.80	1.90	2.00	1.25	1.03	1.13

---

[a] Superscripts I, II, and III are defined in Section 4.3

Table 5.40 Nickel catalysed exchange of CH_3SiH_3 with deuterium:specific rates, k_ϕ and k_0[a], and values of the multiplicity, M[a], at 300 K

Volume of reaction vessel = 0.30 l

Initial pressure of CH_3SiH_3 in reaction vessel = 1.0 ± 0.1 torr

Initial pressure of deuterium in reaction vessel = 10.7 ± 0.1 torr

Film no.	Film weight /mg	Run no.	k_ϕ /nM $s^{-1}mg^{-1}$	k_0/nM $s^{-1}mg^{-1}$			M		
				k_0^{I}	k_0^{II}	k_0^{III}	M^{I}	M^{II}	M^{III}
8	3.7	1	1.95	1.50	-	1.55	1.30	-	1.26
9	10.8	1	2.70	2.55	2.65	2.60	1.06	1.02	1.04
10	9.5	1	2.00	1.85	-	1.85	1.08	-	1.08
11	17.8	1	2.50	2.35	2.45	2.50	1.06	1.02	1.00
Mean		1	2.30	2.05	2.55	2.15	1.12	1.02	1.07

[a] Superscripts I, II, and III are defined in Section 4.3

5.5 Results Obtained for Gold Films

5.5.1 Adsorption of CH_3SiH_3

Adsorption of CH_3SiH_3 on gold has been investigated on four films prepared and used at 273 K. The adsorption isotherms are shown in Figure 5.10. The surface uptake, the composition of the chemisorbed layer,

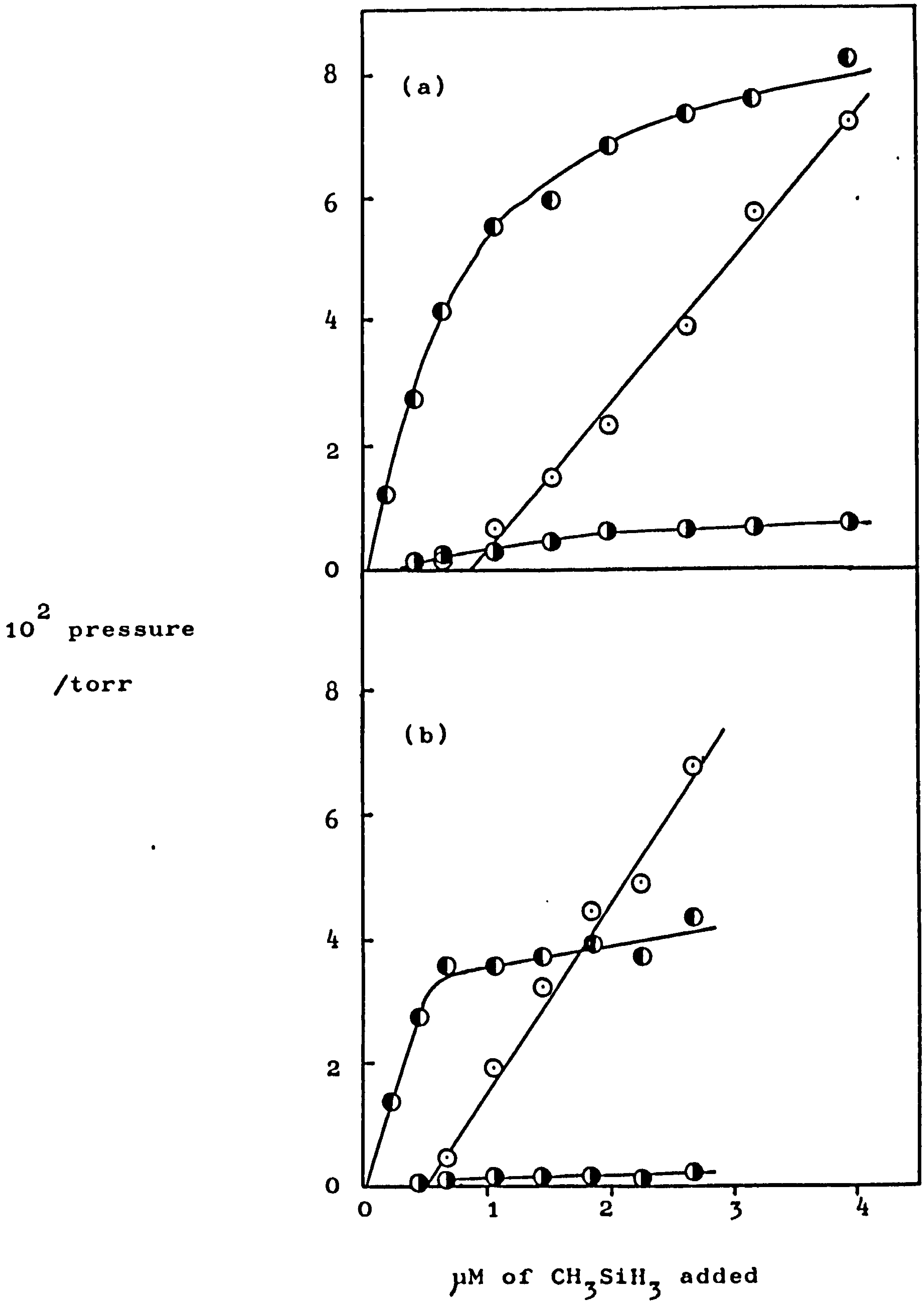


Figure 5.10.1 Chemisorption of CH_3SiH_3 on gold at 273 K: (a) film wt. = 52.0 mg; (b) film wt. = 32.9 mg.

Legend:- ⊙ CH_3SiH_3, ◐ H_2, ◑ CH_4.

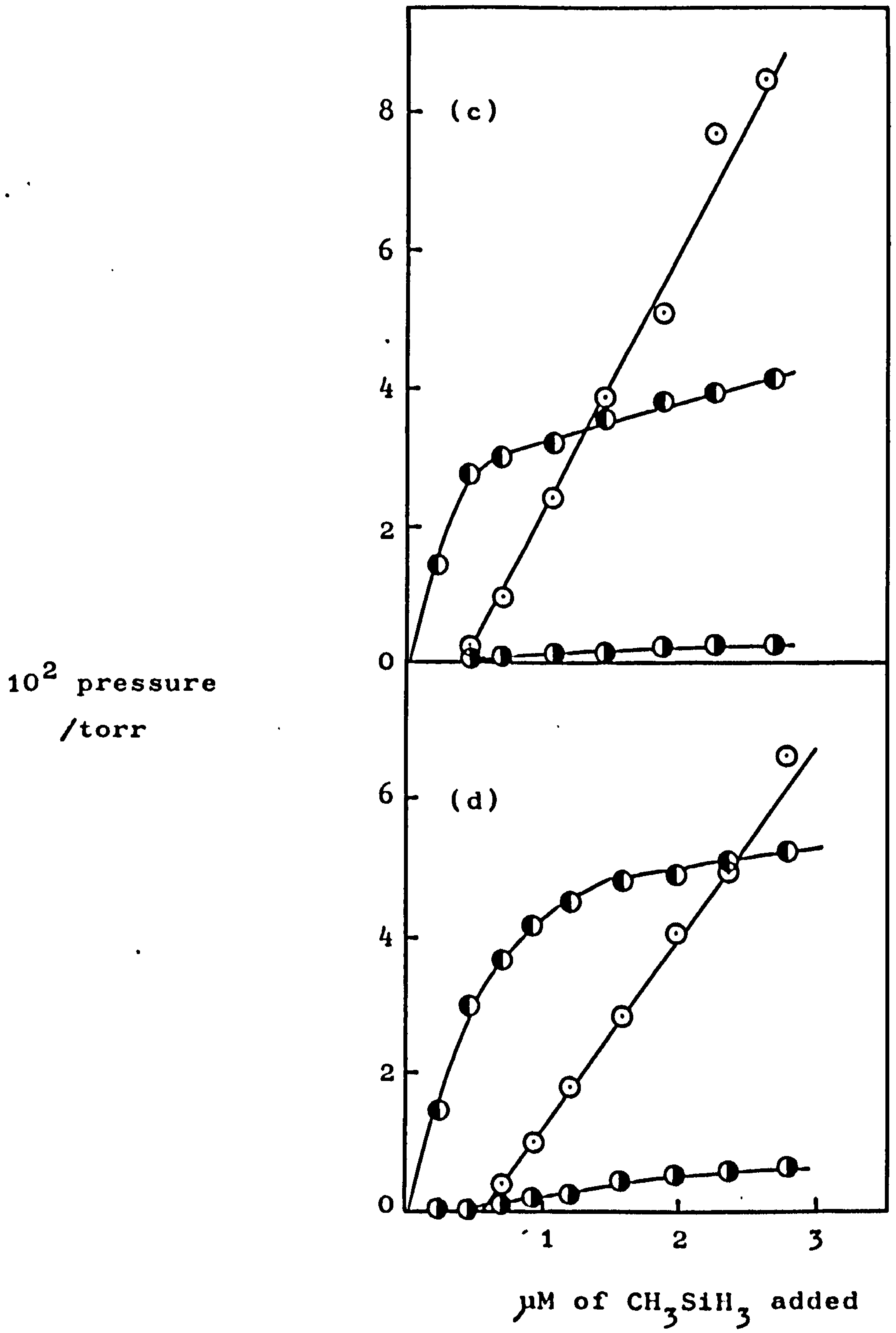


Figure 5.10.2 Chemisorption of CH_3SiH_3 on gold at 273 K: (c) film wt. = 7.9 mg; (d) film wt. = 63.4 mg.

Legend:- ⊙ CH_3SiH_3, ◐ H_2, ◑ CH_4.

and of the gas phase at complete surface coverage by CH_3SiH_3 for each film are shown in Table 5.41.

Table 5.41 The adsorption of CH_3SiH_3 on gold at 273 K

Volume of reaction vessel = 0.30 l

Film weight /mg	Surface uptake /micromoles mg^{-1}	Relative composition of the chemisorbed layer C	: Si	: H	Gas phase composition[a] n_{H_2}	n_{CH_4}
52.0	0.018	0.93	1.00	3.24	1.24	0.07
32.9	0.016	0.94	1.00	3.10	1.33	0.06
7.9	0.055	0.94	1.00	3.02	1.37	0.06
63.4	0.0088	0.96	1.00	3.36	1.24	0.04
Mean	0.024	0.94	1.00	3.16	1.30	0.06

[a] n_{H_2} and n_{CH_4} are the number of moles of hydrogen and of methane evolved per mole of CH_3SiH_3 adsorbed at complete surface coverage.

5.5.2 Self exchange and products of decomposition

Experiments designed to determine whether self exchange occurred on gold films were carried out for the temperature range of 195 - 273 K. No exchange was observed. Traces of hydrogen and of methane were detected. Increasing the temperature of the reaction vessel from 195 to 290 K and from 273 to 340 K did not result in the commencement of exchange.

5.5.3 Mutual exchange

Exchange between CH_3SiH_3 and CH_3SiD_3 over gold has been investigated on films prepared and used at 195, 245 and 273 K. Films were prepared under high vacuum and ultra-high vacuum conditions. Exchange was rapid at each of these temperatures (Tables 5.42 and 5.43). For a series of runs at 195 K little activity was lost from run to run, but raising the temperature to 273 K resulted in a pronounced loss of activity. First order behaviour was observed for all reactions.

5.5.4 Exchange with molecular deuterium

Gold did not catalyse this reaction in the range 195 to 350 K.

Table 5.42 Gold catalysed mutual exchange:specific rates for films prepared under u.h.v. conditions.

Volume of reaction vessel = 0.48 l

Film no.	Film weight /mg	Run no.	Temp. /K	Initial partial pressure in the reaction vessel /torr		k_{03}[a] /nM $s^{-1}mg^{-1}$	k_{03}[a] /nM s^{-1}
				CH_3SiH_3	CH_3SiD_3		
1	18.1	1	195	0.22	0.22	7.75	140
		2	195	0.22	0.22	13.1	237
		3	195	0.22	0.22	11.8	214
		4	195	0.23	0.23	15.9	288
		5	195	0.22	0.22	14.3	259
		6	195	0.21	0.21	15.8	286
		7	273	0.25	0.25	0.09	1.60
		8	273	0.22	0.22	0.03	0.54
2	<1	1	195	0.15	0.15	-	116
		2	195	0.15	0.15	-	8.5
		3	195	0.15	0.15	-	84.2
		4	195	0.16	0.16	-	13.4
3	4.3	1	245	0.22	0.22	42.7	184
		2	245	0.22	0.22	43.6	187
		3	245	0.24	0.24	30.7	132
		4	273	0.24	0.24	8.1	34.8
		5	273	0.25	0.25	2.1	9.0
		6	273	0.22	0.22	0.58	2.5

[a] As defined in Section 4.2

Table 5.43 Gold catalysed mutual exchange:specific rates for films prepared under conditions of high vacuum.

Volume of reaction vessel = 0.30 l

Film no.	Film weight /mg	Run no.	Temp. /K	Initial partial pressure in the reaction vessel /torr		k_{03}[a] /nM $s^{-1}mg^{-1}$	k_{03}[a] /nM s^{-1}
				CH_3SiH_3	CH_3SiD_3		
4	55.0	1	195	0.94	1.02	5.35	294
		2	195	0.97	1.00	5.25	288
		3	195	0.96	0.99	5.05	278
		4	195	0.89	1.06	5.15	283
		5	195	1.03	0.96	5.40	297
		6	195	0.92	0.96	5.60	308
		7	195	0.98	1.03	5.10	281
5	103.4	1	273	0.81	0.87	2.15	222
6	100.4	1	273	0.81	1.00	2.65	266
7	37.0	1	273	0.96	0.96	4.15	154

[a] As defined in Section 4.2

SECTION 6

DISCUSSION

6.1 Interpretation of the Adsorption Studies

Adsorption of CH_3SiH_3 has been studied on each of the metals used in this investigation and the results are summarized in Table 6.1.

Table 6.1 Composite results of the adsorption of CH_3SiH_3 at 273 K

Metal	Surface uptake /micromoles mg^{-1}	Literature values of surface area (Mo = 100)	Empirical composition of chemisorbed layer[a] C	: Si	: H	Gas phase composition[b] n_{H_2}	n_{CH_4}
Mo	0.47	100	0.95	1.00	4.06	0.86	0.05
W	0.24	54	0.97	1.00	4.70	0.58	0.04
Rh	0.35	43	0.74	1.00	3.94	0.51	0.26
Ni	0.19	18	0.81	1.00	3.79	0.74	0.19
Au	0.024	-	0.94	1.00	3.16	1.30	0.06

[a] Composition determined at complete surface coverage (as defined in Section 3.4.2)

[b] n_{H_2} and n_{CH_4} are the number of moles of hydrogen and of methane evolved per mole of CH_3SiH_3 adsorbed at complete surface coverage (as defined in Section 3.4.2).

For all the metals studied substantial decomposition of CH_3SiH_3 occurred at the surface of each film; hydrogen was always the principal product of this decomposition and methane a minor product. Silane and higher silanes were never detected in the gas phase, thus it would appear that silicon residues are very strongly adsorbed. This in turn suggests that chemisorbed methylsilane may be bonded to the surface principally through the silyl group and this is confirmed by studies of self exchange (see Section 5; Tables 5.2, 5.13, 5.22 and 5.32). Indeed, at 273 K and above the deuterium content of hydrogen evolved from the decomposition of CH_3SiD_3 was well over 50 %.

Roberts and Ross (45) have reported that substantial C-Si bond cleavage occurred when tetramethylsilane was chemisorbed on iron and on tungsten films; a similar result is reported here for methylsilane. In the present work, methane evolution was rapid until a standing pressure of methylsilane became detectable, after which such methane as was formed, was formed slowly. Substantial methane formation also occurred during ethane chemisorption on rhodium at 300 K (52), but the time period involved was a matter of hours. On other metals at about 273 K little or no methane was formed from the cracking of ethane (53,54). From this comparison it appears (i) that the C-Si bond in methylsilane is more readily broken than the C-C bond in ethane and (ii) in methylsilane adsorption, carbonaceous residues are readily displaced during further adsorption of methylsilane.

The relative yields of the products of decomposition varied from metal to metal (Table 6.1). With the exception of gold the first few admissions of methylsilane resulted in no measurable standing pressure, that is no pressure greater than 5 x 10^{-3} torr. Methane was the first substance detected in the gas phase when either nickel or rhodium films were used. Hydrogen was detected after one or two additional doses of CH_3SiH_3 had been admitted. This observation is in keeping with methane being less strongly adsorbed than hydrogen, which has been demonstrated by the positive order in methane and negative order in deuterium obtained for methane-deuterium exchange (18). Therefore at this stage, dehydrogenation and cracking of CH_3SiH_3 result in competition for surfaces sites between protium and carbonaceous groups, and consequently the less strongly adsorbed species are displaced. Over all the metals studied an increase in the amount of CH_3SiH_3 added was accompanied by an increase in the ratio of hydrogen to methane formed. After the first appearance of a standing pressure of CH_3SiH_3 there was little further evolution of hydrogen and of methane. Thus these products are formed by decomposition of CH_3SiH_3 as the surface is being covered, and not by a continuous process of cracking. Figures 5.1, 5.3, 5.5, 5.8 and 5.10 show that cleavage of the carbon-silicon bond occurs much more easily on nickel and rhodium than on the other metals investigated.

Surface areas relative to molybdenum (Mo = 100) have been obtained by various authors for most transition metals. These surface areas have been summarized by Baron and the mean values calculated are quoted in Table 6.1 (25). Reasonable agreement exists between values obtained in the present work and mean literature values. The relatively high values obtained for rhodium and nickel indicate that species formed by adsorption of CH_3SiH_3 occupy fewer sites than on molybdenum and on tungsten and hence a greater surface uptake could occur. Gold had a small surface uptake which was in keeping with the small surface areas determined for copper and for silver by adsorption of krypton (55,56).

Clean metal films and films on which methylsilane had been adsorbed were studied by X-ray diffraction to determine whether any bulk silicide was formed. However, the results obtained were inconclusive and hence are not presented here.

6.2 Species Formed by the Adsorption of Silanes

Surface species may be physically adsorbed or chemisorbed. Physically adsorbed methane and deuterium are usually written thus:

(6.1)

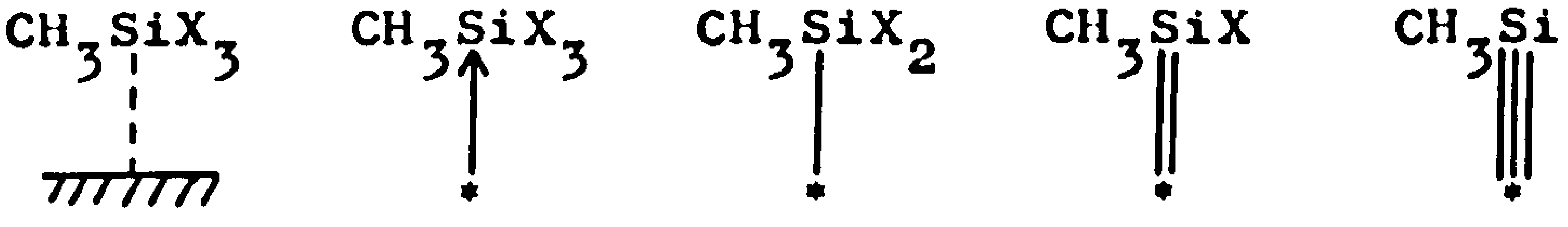
Chemisorbed species may be associatively or dissociatively adsorbed. e.g. (A) is a representation of associatively adsorbed ethylene and (B) is dissociatively adsorbed ethane.

(A) (B)

(6.2)

The mechanism of a reaction depends on the types of adsorbed species present. Mechanisms may in principle involve chemisorbed species only (Langmuir mechanisms) or they may involve the reaction of chemisorbed species with physically adsorbed molecules (Rideal-Eley mechanisms). The types of adsorbed species formed by the adsorption of silanes, and the mechanisms of the reactions they undergo, may be described by the above conventions. However, other and new possibilities attend the adsorption and reaction of silanes and these are described in this section with special reference to methylsilane.

CH_3SiX_3 (where X is H or D) may provide three distinct types of adsorbed state: (i) a physically adsorbed state (I), (ii) an associatively chemisorbed state (II), or (iii) dissociatively chemisorbed states (III), (IV), and (V).



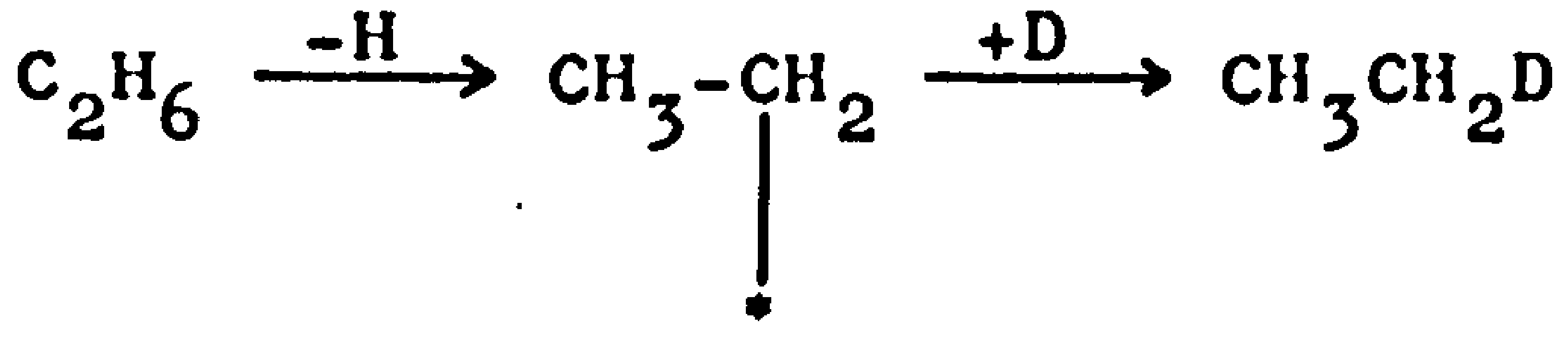
(I) (II) (III) (IV) (V)

(6.3)

Species (I), (III), (IV), and (V) have analogues in the adsorption of alkanes, but (II) does not. Rapid exchange between CH_3SiH_3 and CH_3SiD_3 has been detected over gold catalysts (see Section 5.5.3), whereas alkane adsorption on gold has not been reported, and even exchange between C_6H_6 and C_6D_6 does not occur (25). Thus it is necessary to propose a method whereby methylsilane can adsorb readily at gold surfaces so that the observed exchange may be understood. The formation of the adsorbed state (II) is both consistent with the known chemistry of silicon, and is a key to the understanding of the catalytic activity of gold for exchange in methylsilane. Once (II) is admitted as an adsorbed state on gold, it is only logical to assume that it may be formed at the surfaces of the earlier transition metals.

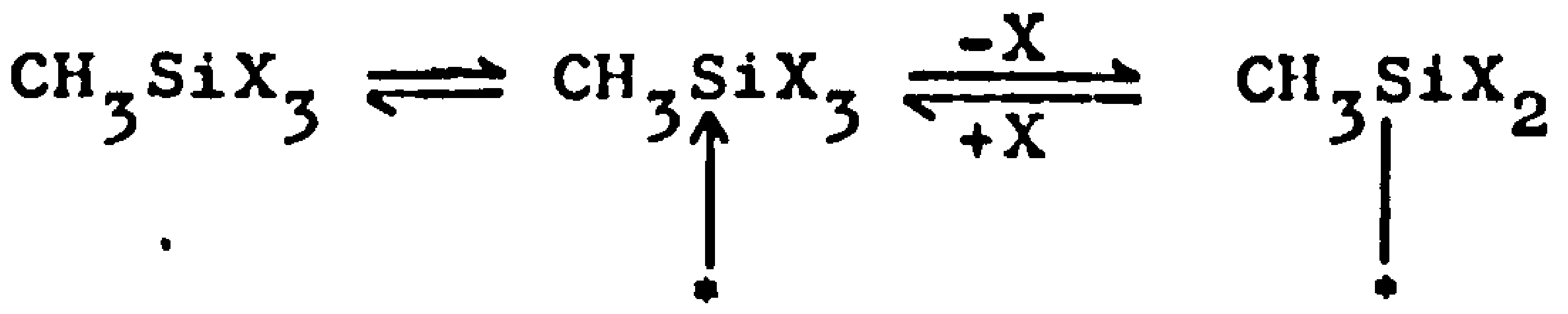
With respect to (II), it is proposed that a coordinate bond can be formed by overlap of a filled d-orbital of a surface metal atom with vacant d-orbitals of silicon. It is well-known that the coordination number of silicon may exceed four. For example, tetrachlorosilane is easily hydrolysed via the formation of a pentacoordinate species, whereas carbon tetrachloride is resistant to hydrolysis because the coordination number cannot exceed four. In (III), (IV), and (V) a contribution from the coordinate bond may be present but no attempt is made to express this in the formulae of such species.

The introduction of species (II) in a sense blurs the distinction between Rideal-Eley and Langmuir mechanisms since methylsilane adsorbed as (I) or (II) may not be readily distinguished. An important implication of species (II) is that processes which provide stepwise exchange in alkanes e.g.:



$$C_2H_6 \xrightarrow{-H} CH_3\text{-}\underset{\underset{*}{|}}{CH_2} \xrightarrow{+D} CH_3CH_2D \qquad (6.4)$$

may lead to multiple exchange in methylsilane, because the molecule undergoing exchange may remain associatively adsorbed, thus:



$$CH_3SiX_3 \rightleftharpoons \underset{\underset{*}{\uparrow}}{CH_3SiX_3} \underset{+X}{\overset{-X}{\rightleftharpoons}} \underset{\underset{*}{|}}{CH_3SiX_2} \qquad (6.5)$$

where X = H or D.

6.3 Exchange and Decomposition of Methylsilane over Gold

Rapid mutual exchange in methylsilane over gold catalysts is the most remarkable result obtained in the present work. Therefore, the results for exchange using gold catalysts are discussed before those obtained using other catalysts.

6.3.1 Self exchange at constant temperature

The adsorption studies have demonstrated that CH_3SiH_3 is dissociatively chemisorbed on gold, whereas under similar conditions alkanes are not, and that C-Si bond cleavage occurs (Table 5.41). Admission of CH_3SiD_3 to a gold film at either 195 or 273 K led to no intramolecular rearrangement of H or D, therefore there was no self exchange. Thus the initial chemisorption does not appear to involve dissociation of both C-H and Si-D bonds.

6.3.2 Mutual exchange

Specific rates for mutual exchange are shown in Tables 5.42 and 5.43, and examples of plots of $\ln(d_{03}-d_{03_\infty})$ against time are shown in Figure 6.1. Rapid exchange occurred between CH_3SiH_3 and CH_3SiD_3 at 195, 245, and 273 K. Under comparable conditions self exchange had not been observed. Therefore, protium bonded to silicon readily exchanges with deuterium bonded to silicon, and species active for exchange are bonded to the surface via silicon and not via carbon. The gold films produced were not however capable of catalysing the exchange $H_2 + D_2 \rightleftharpoons 2HD$, thus demonstrating that mutual exchange was not catalysed by impurities in gold. This is the first rapid protium-deuterium exchange over gold to be reported.

Explanations of the following are offered below:

(i) rapid mutual exchange occurs, but for alkanes no analogous reaction is observed;

(ii) specific rates show little variance from run to run at 195 and 243 K, but specific

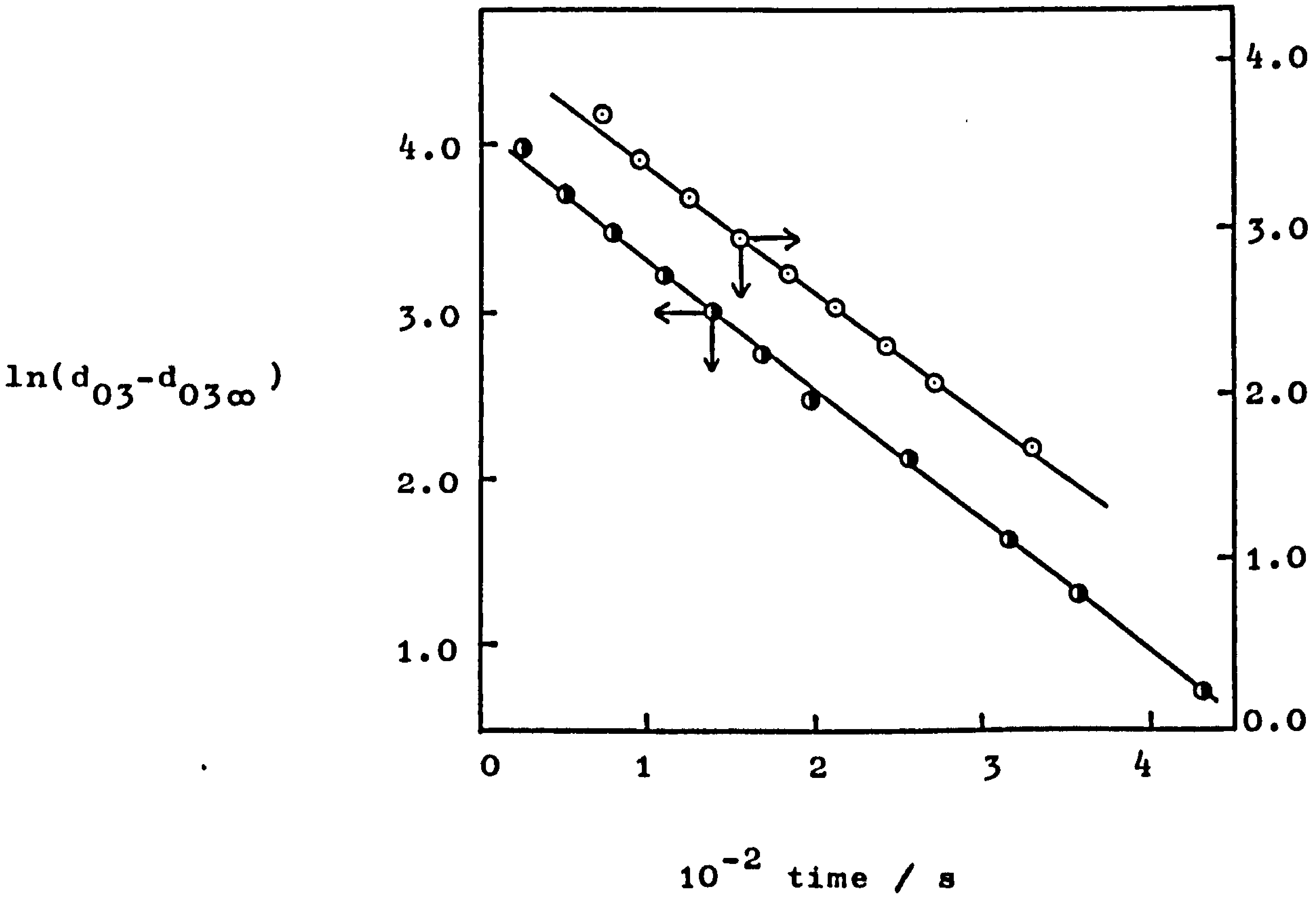


Figure 6.1 Mutual exchange catalysed by gold at 195 K: film no. 4.

Legend:- ⊙ run no. 1 , ◐ run no. 5 .

rates decrease on warming the reactor to 273 K;

(iii) exchange has an ill-defined temperature dependence.

For exchange to occur at least one of the reactants must be chemisorbed at the surface of the catalyst. Item (i) above is readily explained by supposing that methylsilane is able to chemisorb at a gold surface, whereas alkanes cannot. Alkanes and silanes are structurally analogous to each other, but results obtained show that methylsilane must have a different bonding capability with gold, Species that may be formed at gold surfaces are discussed in Sections 6.2 and 6.3.4.

On films 1, 3, and 4 (Tables 5.42 and 5.43) little variation was observed in the specific rates at constant temperature from run to run. On film number 2 at 195 K marked variations in specific rates from run to run were observed. However, this film was ultra-thin (its appearance being a purplish tint on the walls of the vessel) and thus its susceptibility to poisoning may have differed from that of films of more usual weight.

Kemball has discussed the stability of adsorbed species formed by adsorption of alkanes on metal catalysts (36). Three temperature regions were proposed and these are shown in Table 6.2.

Table 6.2 Sequence of events on raising the temperature for metal catalysts with alkanes

Temperature region	Nature of adsorbed species	Type of catalysis
A	Reversibly formed, stable to breakdown	Exchange occurs
B	More strongly adsorbed, formation not readily reversible	Exchange becomes poisoned
C	Intermediates for other reactions	Breakdown or rearrangement occurs

(Temperature region C is higher than region B which in turn is higher than region A). These are only generalisations, and thus overlap may occur. This classification may be used to clarify the variations in specific rates from run to run referred to in item (ii) above. At 195 and 243 K adsorbed species probably correspond to those of region A. Thus evacuation of the reactor causes reversibly adsorbed species to be desorbed and pumped away. The initial adsorption of methylsilane resulted in evolution of hydrogen and of methane, and thus adsorbed hydrogen may recombine with dissociated methylsilane or with other adsorbed hydrogen atoms to be pumped away from the surface during evacuation.

Admission of a fresh reaction mixture appears to result in the re-establishment of the original concentrations of those species that participate in mutual exchange. Thus, no variation in specific rates occurred from run to run.

At 273 K it is likely that many adsorbed species have the character of those found in temperature region B. These are more highly dehydrogenated and are therefore more firmly attached to the gold surface. Evacuation of the reactor results in reversibly adsorbed material being pumped away. Thus, further dehydrogenation of adsorbed species on the surface might occur because these species are no longer in equilibrium with the gas phase. Species formed by such a process will be more strongly attached to the surface and therefore are either less active or inactive for exchange. The disturbance of equilibrium between different adsorbed species by evacuation of the reactor is a likely reason for the decrease of values of specific rates from run to run at 273 K.

Temperature region C was not reached.

Interpretation of the ill-defined temperature dependence of gold-catalysed mutual exchange referred to in item (iii) above, is difficult. Most metals form porous films and consequently surface area is proportional to film weight.

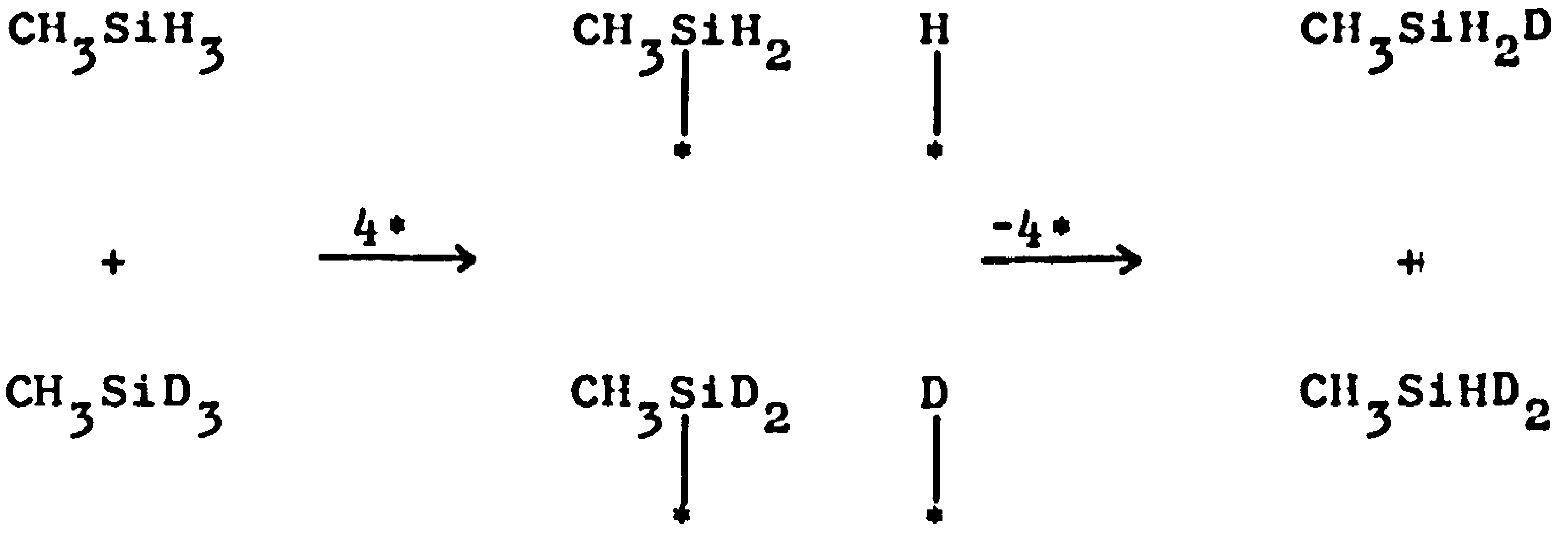
This may not be so for gold because it and other group IB metals sinter readily (57,58). Therefore specific rates are expressed both in the units $nMs^{-1}mg^{-1}$ and nMs^{-1}. The latter value assumes that the gold films produced were all of about the same geometric surface area. However, irrespective of the means of determining k_{03}, it is apparent that the rate of exchange does not obey the Arrhenius equation. Admission of a reaction mixture causes sites to be poisoned, and at higher temperatures more initial poisoning will occur (Table 6.2). The poisons are probably highly dehydrogenated residues of methylsilane, which occupy an increasing proportion of the surface as the temperature is increased and thus reduce the rates of exchange. However, sites still available for exchange are expected to be more active at higher temperatures in accord with the Arrhenius equation. Therefore over a range of 78° little alteration in specific rates occurred because these two effects compensated each other.

6.3.3 Exchange with molecular deuterium

Exchange did not occur when mixtures of CH_3SiH_3 and molecular deuterium were admitted to gold films at 195 and at 273 K, due to the well-known inability of molecular deuterium to chemisorb at gold surfaces at these temperatures. At about 400 K and above gold does exhibit weak activity for hydrogenation (<u>26</u>,<u>27</u>), and H_2-D_2 exchange has been detected in the temperature range of 573-773 K (<u>59</u>).

6.3.4 Mechanisms of mutual exchange

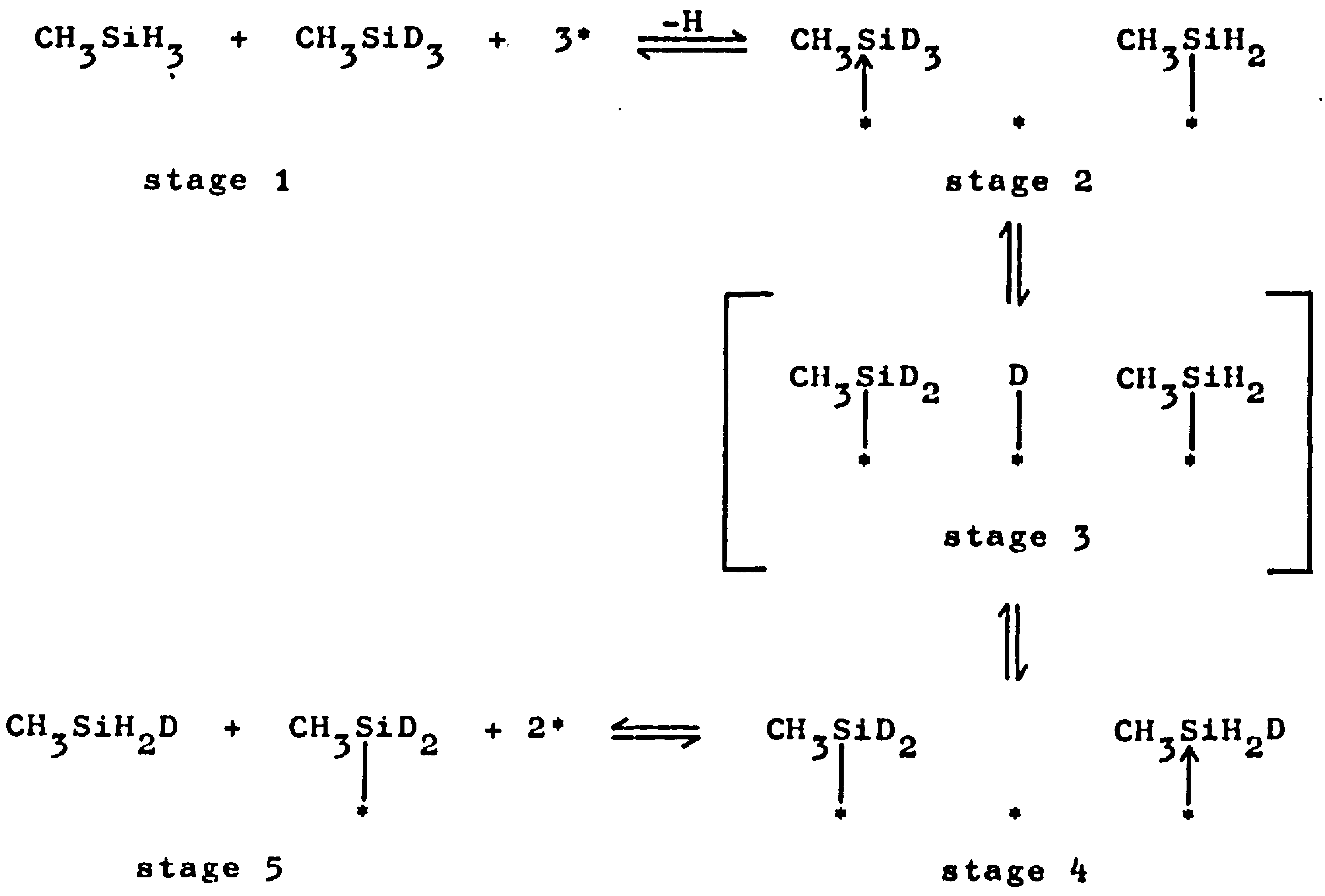
A mechanism is best described by use of as few intermediates as possible. The simplest mechanism whereby mutual exchange may be interpreted is by dissociation of methylsilane on the gold surface followed by its recombination and desorption, thus:



$$\begin{matrix} CH_3SiH_3 & & \underset{*}{CH_3SiH_2} & \underset{*}{H} & & CH_3SiH_2D \\ + & \xrightarrow{4*} & & & \xrightarrow{-4*} & + \\ CH_3SiD_3 & & \underset{*}{CH_3SiD_2} & \underset{*}{D} & & CH_3SiHD_2 \end{matrix}$$

<u>Mechanism 1 for Mutual Exchange</u> (6.6)

Only species (III) (Section 6.2) is used by mechanism 1. This mechanism can apparently describe mutual exchange on gold because the dissociative adsorption of methylsilane has already been demonstrated (Table 5.41). However, it is reasonable to suppose that adsorbed hydrogen atoms may combine with each other as well as with adsorbed methylsilane. Hydrogen that desorbs from a gold surface cannot be re-adsorbed. Therefore it is possible that as mutual exchange proceeds, the pool of adsorbed hydrogen diminishes and for this situation the function plots should be non-linear. Experimentally, linear function plots were obtained. Also, evacuation of the reactor might cause hydrogen to be pumped away from the surface, and thus specific rates would be expected to decrease from run to run. However, at 195 and at 243 K values of k_{03} do not vary from run to run. Therefore, either hydrogen atoms involved in exchange do not combine with each other on gold, or mutual exchange occurs by a somewhat different mechanism by which exchange can be achieved on a surface having a very low concentration of adsorbed protium and deuterium. A mechanism is shown in equation 6.7.



<u>Mechanism 2 for Mutual Exchange</u> (6.7)

This mechanism invokes the participation of both associatively and dissociatively adsorbed methylsilane (Species (II) and (III), Section 6.2). Passage from stage 2 to stage 4 constitutes an intermolecular hydrogen transfer. It is supposed that this transfer is rapid and thus exchange can take place without a substantial hydrogen pool being created at the surface.

Because it is probable that adsorbed hydrogen atoms formed by mechanism 1 may combine with each other as reaction proceeds, mechanism 2 appears to provide a more likely interpretation of mutual exchange. Poisoning of exchange by mechanism 2 caused by evacuation of the reactor is deemed to be due to dehydrogenation of species (III).

6.3.5 Products of decomposition and the effects of varying the temperature of a given reaction

Trace amounts of methane and of hydrogen were detected during self exchange and mutual exchange. The yield of hydrogen was very much greater than that of methane. When CH_3SiD_3 was sole reactant, methane evolved was principally CH_3D and hydrogen was principally D_2. This confirms that hydrogen lost during chemisorption is removed from the silyl group, and that methylsilane is chemisorbed via the silicon atom.

6.4 Exchange and Decomposition of Methylsilane over Molybdenum

6.4.1 Self exchange at constant temperature

Negligible self exchange occurred at 195 or at 273 K (Table 5.3) indicating that chemisorption of CH_3SiD_3 does not involve the dissociation of both C-H and Si-D bonds, or alternatively that such species are inactive to exchange under the conditions employed.

6.4.2 Mutual exchange

Specific rates for mutual exchange are shown in Tables 5.5 and 5.6 and examples of plots of $\ln(d_{03}-d_{03\infty})$ against time for these results are shown in Figure 6.2. As with gold, rapid exchange occurred at 195 and at 273 K, whereas negligible self exchange was observed under similar conditions. Consequently, only species bonded to the surface through silicon are able to take part in exchange for the temperature range studied.

Specific rates at 195 K decreased slightly from run to run, whereas at 273 K very pronounced decreases were observed, although the function plots were always linear. Arguments presented in Section 6.3.2 also apply here. The reaction was poisoned between runs. If poisoning had occurred as exchange took place, the function plots would have been curved. Loss of activity is associated with evacuation of the reactor. Weakly adsorbed

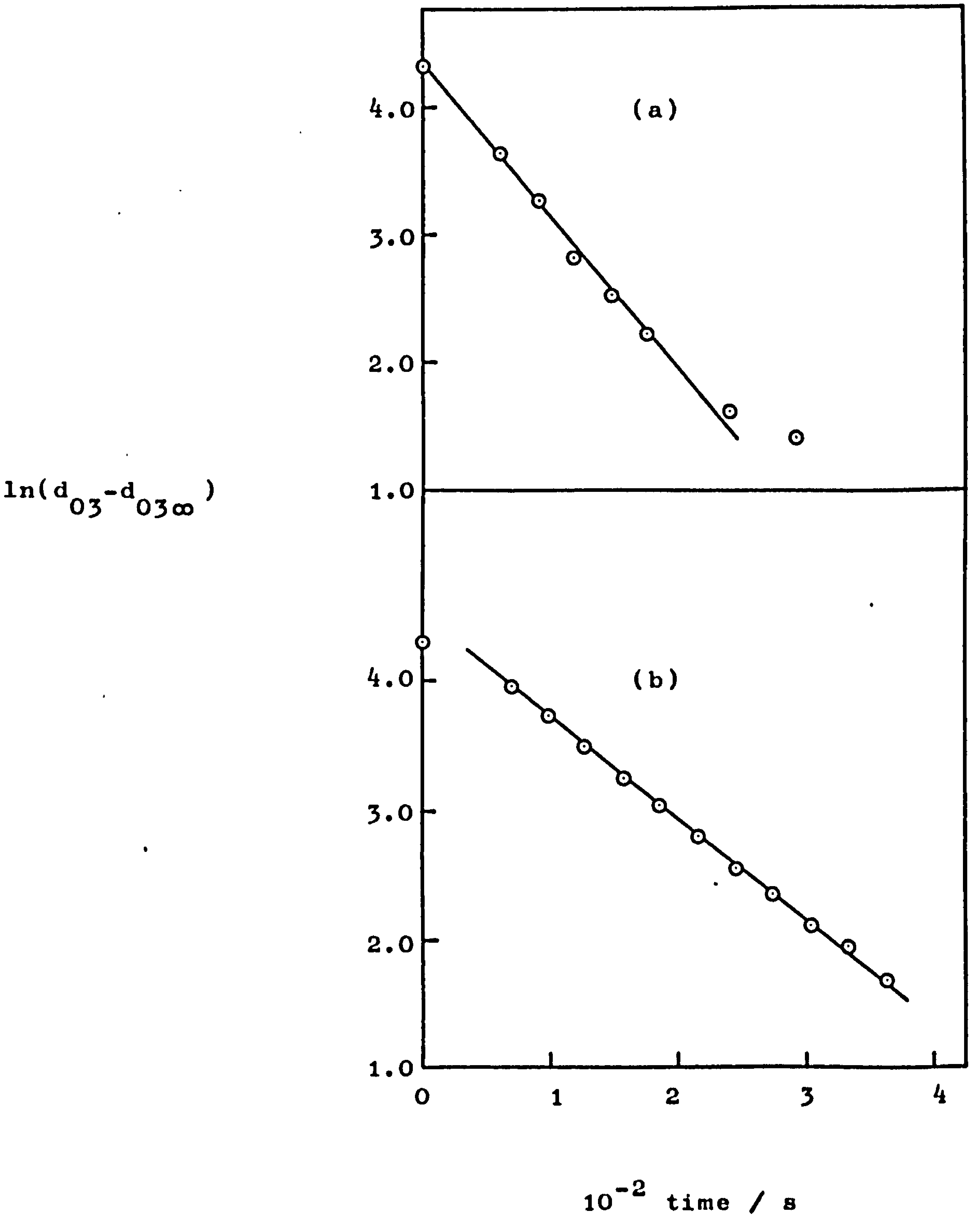


Figure 6.2.1 Mutual exchange catalysed by molybdenum at 195 K: film no. 1

Legend:- (a) run no. 1 , (b) run no. 5

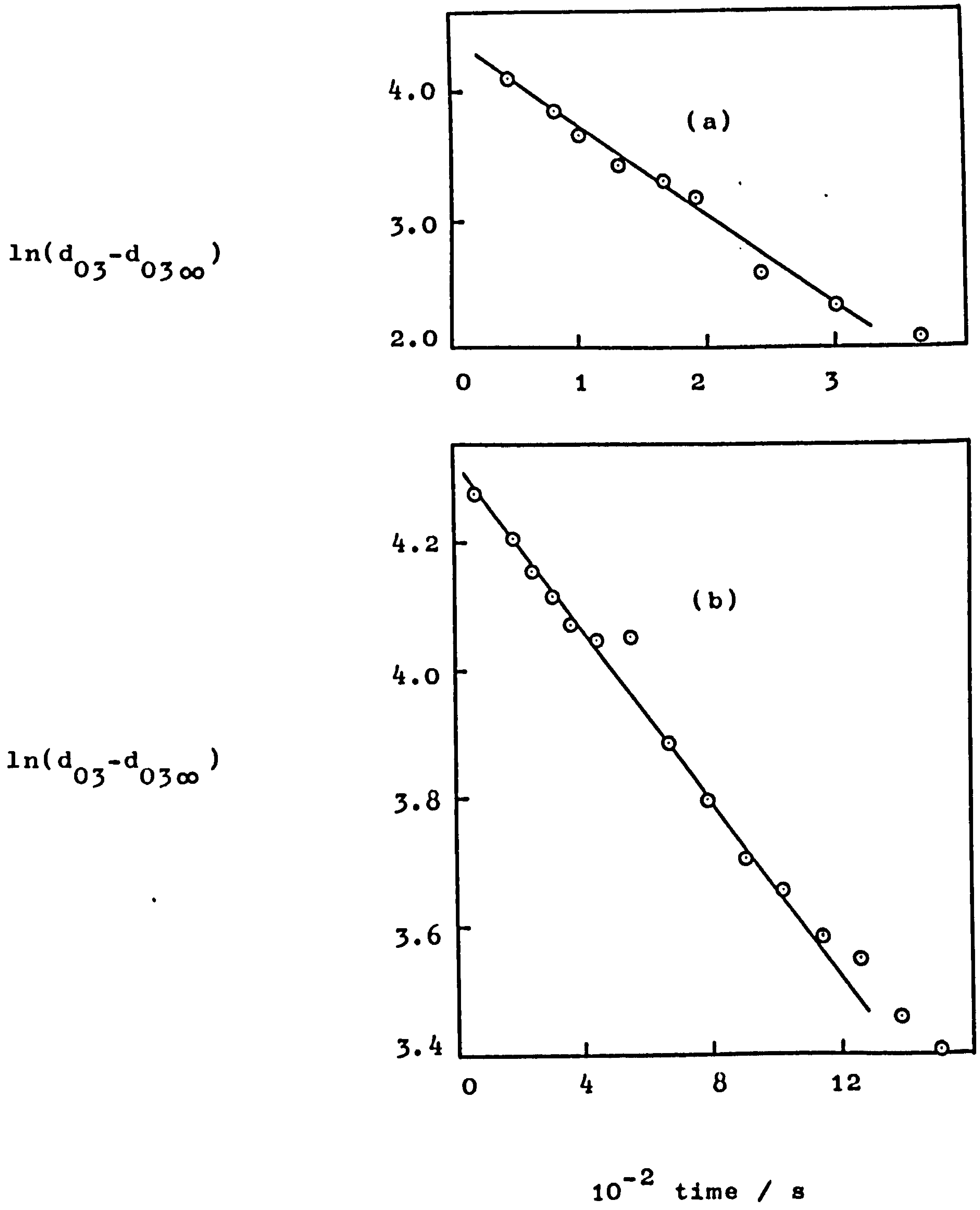


Figure 6.2.2 Mutual exchange catalysed by molybdenum at 273 K: film no. 17

Legend:- (a) run no. 1 , (b) run no. 2

material is pumped away from the surface during evacuation, and thus the equilibrium of species on the surface is disturbed. Conditions of disturbed equilibrium permit species that remain adsorbed to dehydrogenate further, and cleavage of carbon-silicon bonds may also occur. At 273 K this process of poisoning will be more severe than at 195 K, and thus loss of catalytic activity is greater. For the adsorption studies it was seen that increasing the temperature of the reactor from 195 to 273 K resulted in surface species becoming more dehydrogenated (Table 5.1). Therefore at higher temperatures species that are more extensively dehydrogenated are formed, and these act as poisons (Table 6.2).

Alternatively loss of activity from run to run might be explained as follows. Adsorption of methylsilane causes a pool of adsorbed hydrogen to be created. Mutual exchange might occur by means of this pool (see equation (6.6)). Suppose that evacuation at 195 K decreases the size of the pool slightly, whereas at 273 K much of this hydrogen pool may be pumped away. In this case, the size of the hydrogen pool would diminish from run to run, and the activity for mutual exchange would diminish accordingly. However, the isotopic composition in the gas phase should reflect that of the pool of adsorbed hydrogen, provided equilibrium is established; this is not the case (Table 5.7). Also, exchange with molecular deuterium differs from mutual exchange in respect of its behaviour towards poisons, which suggests that a pool of adsorbed hydrogen does not participate in mutual exchange.

The latter interpretation of the loss of activity requires a mechanism like that of equation 6.6 (Section 6.3.4). That the size of the hydrogen pool does not diminish during the course of reaction seems incongruous because hydrogen atom recombination would be expected to occur. Therefore the mechanism shown in equation 6.7 is preferred as the mechanism for mutual exchange and this mechanism is in keeping with the former interpretation of the loss of activity from run to run.

The variation between specific rates obtained on clean molybdenum films at 195 and 273 K was small, and thus mutual exchange showed little temperature dependence. Similar behaviour was observed for gold and hence the interpretation presented in Section 6.3.2 applies to the molybdenum catalysed reaction, that is, the extent of poisoning that occurred on admission of a mixture increased with increasing temperature. However, mutual exchange was very rapid, therefore it is possible that the reaction was diffusion controlled. However, the exchange $H_2 + D_2 \rightleftharpoons 2HD$ was studied qualitatively over molybdenum films at 195 K; the rate of exchange was more than ten times as fast as that for mutual exchange. Therefore, the temperature dependence of mutual exchange is not considered to be governed principally by diffusion.

6.4.3 Exchange with molecular deuterium

This section aims to provide a mechanism for exchange with molecular deuterium that is consistent with the following observations:

(i) exchange was observed in the silyl group of methylsilane but not in the methyl group;

(ii) at 195 K for a series of runs on a single film specific rates for exchange with molecular deuterium decreased drastically from run to run, although function plots exhibited good first order behaviour (Table 5.8 and Figure 5.2);

(iii) films that had lost their high activity for exchange with molecular deuterium at 195 K, still retained high activity for a series of runs involving mutual exchange;

(iv) values of the multiplicity, M, were greater than 1.0 for high values of k_{ϕ} and M = 1.0 when k_{ϕ} was small;

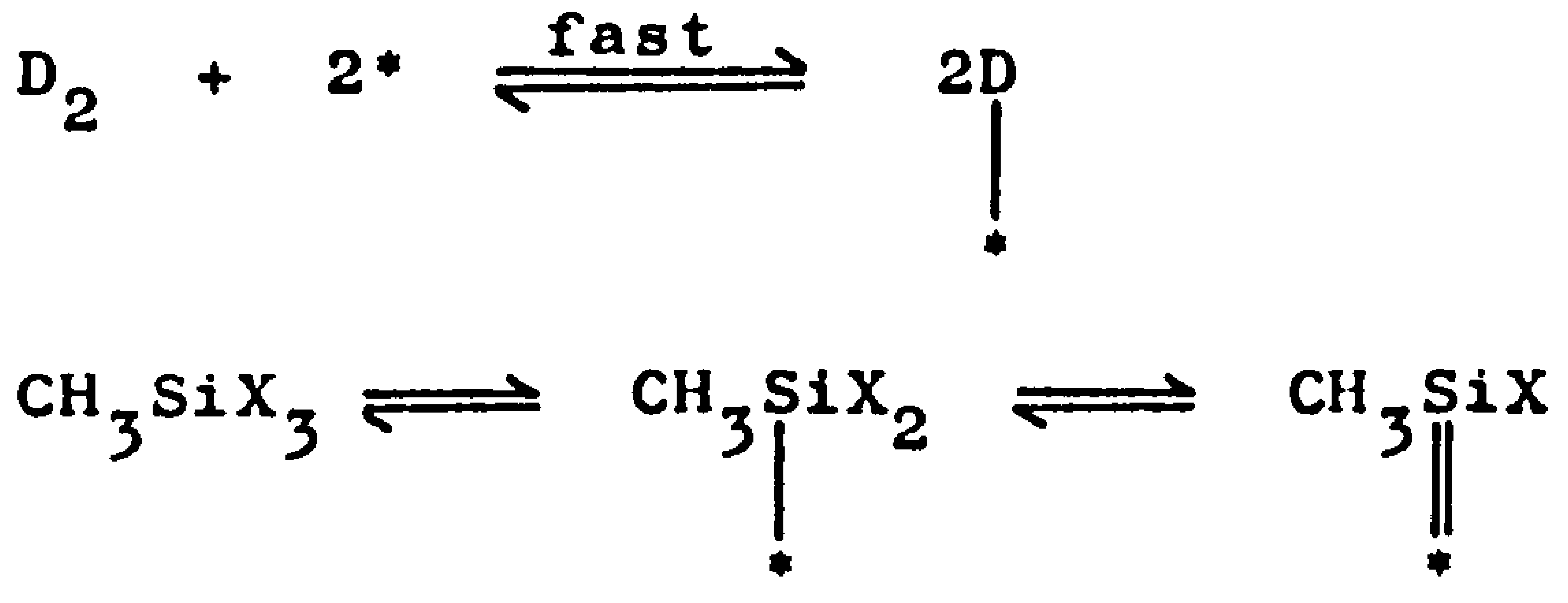
(v) at 273 K and above exchange with molecular deuterium was poisoned i.e. complete loss of activity occurred after 2 - 3 ks (ks = kilo-seconds) and function plots were curved. (Tables 5.9-5.11 and Figure 5.2).

Observation (i) arose from the absence of exchange when mixtures of CH_3SiD_3 and molecular deuterium were admitted to molybdenum films at 195, 273, and 300 K, whereas exchange did occur when mixtures of CH_3SiH_3 and deuterium were admitted under comparable conditions. This indicated that adsorbed species bonded to the surface via carbon are either absent or are inactive for exchange. Thus, all species formed from adsorption of methylsilane that are to be used in the mechanism to be proposed, were bonded to the surface via silicon only. The adsorbed species to be considered have been presented as (II), (III), and (IV) in Section 6.2.

Polycrystalline films were used for this work. Therefore, the surfaces used consisted of a mixture of low index and high index planes containing various dislocations (60). Methylsilane adsorption may occur at various surface sites. At sites of high coordination number situated in low index planes, weak adsorption is expected, whereas at sites of low coordination number in high index planes relatively strong adsorption may occur. Thus, methylsilane proceeds at an energetically heterogeneous surface, and any mechanism proposed to interpret the experimental observations (especially observation (iii)) has to consider the surface as having variable activity from one region to another.

The orders of reaction at 273 K were zero or negative with respect to methylsilane and 0.6 with respect to deuterium. The positive order for deuterium indicated that it was only weakly adsorbed. Adsorption of methylsilane resulted in the rapid evolution of hydrogen until the surface was saturated with methylsilane; this, and the zero or negative order in methylsilane, indicated that methylsilane was more strongly adsorbed than deuterium. It is proposed below that exchange with molecular deuterium occurs on sites where fairly strong adsorption of CH_3SiH_3 can take place.

Reaction of CH_3SiH_3 with molecular deuterium at 195 K over clean molybdenum films resulted in rapid multiple exchange (Table 5.8), whereas for subsequent runs over poisoned films, exchange was apparently stepwise. The proposed mechanism is shown in equation 6.8.



$$D_2 + 2{*} \overset{\text{fast}}{\rightleftharpoons} 2\underset{\underset{*}{|}}{D} \qquad (6.8a)$$

$$CH_3SiX_3 \rightleftharpoons CH_3\underset{\underset{*}{|}}{Si}X_2 \rightleftharpoons CH_3\underset{\underset{*}{\|}}{Si}X \qquad (6.8b)$$

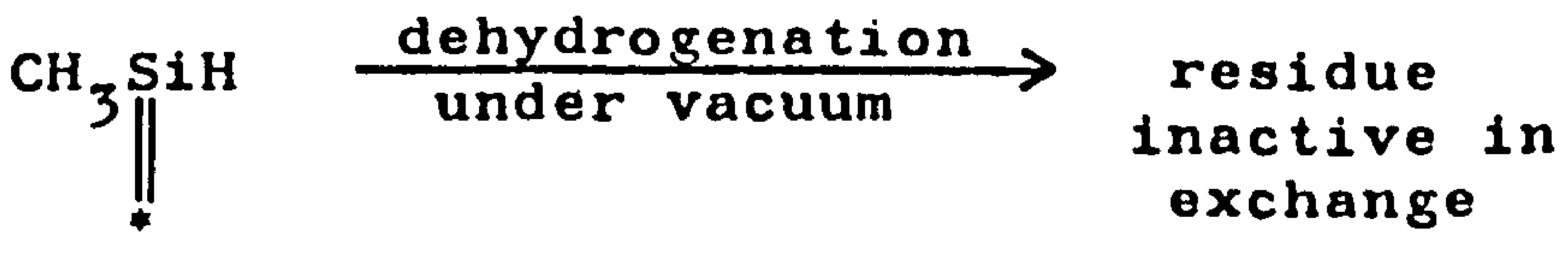
(where X = H or D)

(III) (IV)

Extensive multiple exchange occurs by rapid interconversion of (III) with (IV) before desorption to the gas phase. The first run at 195 K was unpoisoned during the course of reaction, indicating that none of the species in (6.8) is itself a surface poison.

The first run over a clean film produced a high yield of CH_3SiHD_2 and of CH_3SiD_3 as initial products, thus revealing that the steps in the conversion of adsorbed-CH_3SiX to gaseous methylsilane (6.8b) involved a high chance of the species acquiring a deuterium rather than a protium atom.

The second run on a film at 195 K was substantially slower (Table 5.8) and the multiplicity was close to unity (reasonable values of k_0^{II} were obtainable and such values could only be calculated when stepwise exchange occurred (Section 4.3)). The slower rate of the second and subsequent runs showed that, during evacuation of the reactor after run 1, some active species were retained on the surface and were converted into residues inactive for exchange (equation 6.9). It is proposed that the most severely dehydrogenated species in equation 6.8b is the one involved.



$$\underset{\underset{*}{\|}}{CH_3SiH} \xrightarrow[\text{under vacuum}]{\text{dehydrogenation}} \begin{array}{c}\text{residue}\\ \text{inactive in}\\ \text{exchange}\end{array} \qquad (6.9)$$

(IV)

On clean molybdenum films at 195 K the

exchange $H_2 + D_2 \rightleftharpoons 2HD$ was found to be fast. After exchange of methylsilane with molecular deuterium, admission of a mixture of CH_3SiH_3 with protium and deuterium resulted in very slow exchange in methylsilane. The exchange $H_2 + D_2 \rightleftharpoons 2HD$ was very much slower than it had been on the clean film, but was still very much faster than exchange in methylsilane. Therefore, not only is the rate of exchange in methylsilane impaired by the formation of inactive residues, but also the concentration of adsorbed deuterium is reduced. For the second and subsequent runs on a molybdenum film fewer vacant sites exist than on a clean film. On admission of a reaction mixture competition for the available sites occurs, and thus the hydrogen pool created is much smaller than that for the first run. Moreover, for the second and subsequent runs the M-value is reduced to a value nearer unity. (These reactions exhibit apparent stepwise exchange because good values of d_0 could be calculated by the method that yields k_0^{II} (Section 4.3)). This is not ascribed to a change of mechanism but to a lowering of the fraction of deuterium atoms in the hydrogen pool.

Observation (iii) is surprising and requires interpretation. If mutual exchange on the one hand and exchange with molecular deuterium on the other had been similarly poisoned, it would have been proposed that the relative proportions of species (II), (III), and (IV) were approximately the same at all regions of the surface. However, the fact to be accommodated by the mechanism is that the rate of mutual exchange varies slightly from run to run whereas exchange with molecular deuterium is drastically poisoned. Species undergoing mutual exchange are not affected by the presence of molecular deuterium (Table 5.8; film number 5). Also, mutual exchange occurs on surfaces that only had a small hydrogen pool in equilibrium with the gas phase for exchange with molecular deuterium. It is therefore necessary to propose that mutual exchange proceeds on one region of the surface (by equations 6.6 or 6.7, Section 6.3.4) and exchange with molecular deuterium occurs on another region by processes (6.8a) and 6.8b). For mutual exchange it is supposed that methylsilane is located at sites which permit weak adsorption only and deuterium, being less strongly adsorbed, does not chemisorb in these regions.

The proposal that the two types of exchange occur on different regions of the surface has an important implication. It implies that when the reactants were CH_3SiH_3 and molecular deuterium, exchange as shown by equations 6.6 or 6.7 was occurring (without isotopic differentiation) on one region while exchange by equations 6.8a and 6.8b was proceeding on another. Exchange by 6.6

or 6.7 creates a certain surface concentration of protium, a proportion of which may migrate across the boundary between regions and become involved in the CH_3SiH_3-D_2 exchange. During the first rapid reaction on a clean molybdenum surface the effect of protium migration is negligible because the deuterium pool is relatively large. However, for the second and subsequent runs over surfaces poisoned for the CH_3SiH_3-D_2 exchange, the rate of protium migration across the boundary of the two proposed regions may be considerable compared with the smaller amount of deuterium chemisorbed. The hydrogen pool becomes enriched with protium, and hence the value of the multiplicity M observed is reduced to about unity.

Observation (v) indicates that at 273 K and above poisoning of exchange with molecular deuterium occurs by a continuous process. It is proposed that dehydrogenation of (IV) (equation 6.9) can take place at 273 K without evacuation of the reactor. Similarly, under these conditions species (III) may also dehydrogenate to form poisons on sites used for exchange with molecular deuterium. At 273 K and above mutual exchange exhibited poisoning from run to run. Adsorption on the sites used for mutual exchange is probably weak and species (IV) is believed to be present in low concentrations. Pumping at 273 K probably causes species (III) to dehydrogenate to (IV) thus producing a poison.

Summary. The arguments presented in Section 6.4.2 and 6.4.3 provide a mechanism with the following major features.

1. Methylsilane adsorbs on an energetically heterogeneous surface.

2. Mutual exchange occurs by equation 6.6 or more probably by equation 6.7 at those regions of the surface where methylsilane is adsorbed weakly and where associatively adsorbed species and the first dissociatively adsorbed species (II) and (III) are the predominant intermediates.

3. Exchange of methylsilane with molecular deuterium occurs at those regions of the surface where adsorption is sufficiently strong for adsorbed-CH_3SiH to be formed. Adsorption of methylsilane must also occur in regions where deuterium may be dissociated into atoms (equation 6.8).

4. Because deuterium is more weakly adsorbed than methylsilane it is probably not adsorbed in regions where only mutual exchange can occur.

5. On evacuation of the reactor after the first run some adsorbed-CH_3SiH is converted to a permanent poison and fewer vacant sites are present than on the clean film. Admission of a fresh CH_3SiH_3-D_2 mixture results in competition for the available sites and a smaller deuterium pool is created. Hence the rate of exchange with molecular

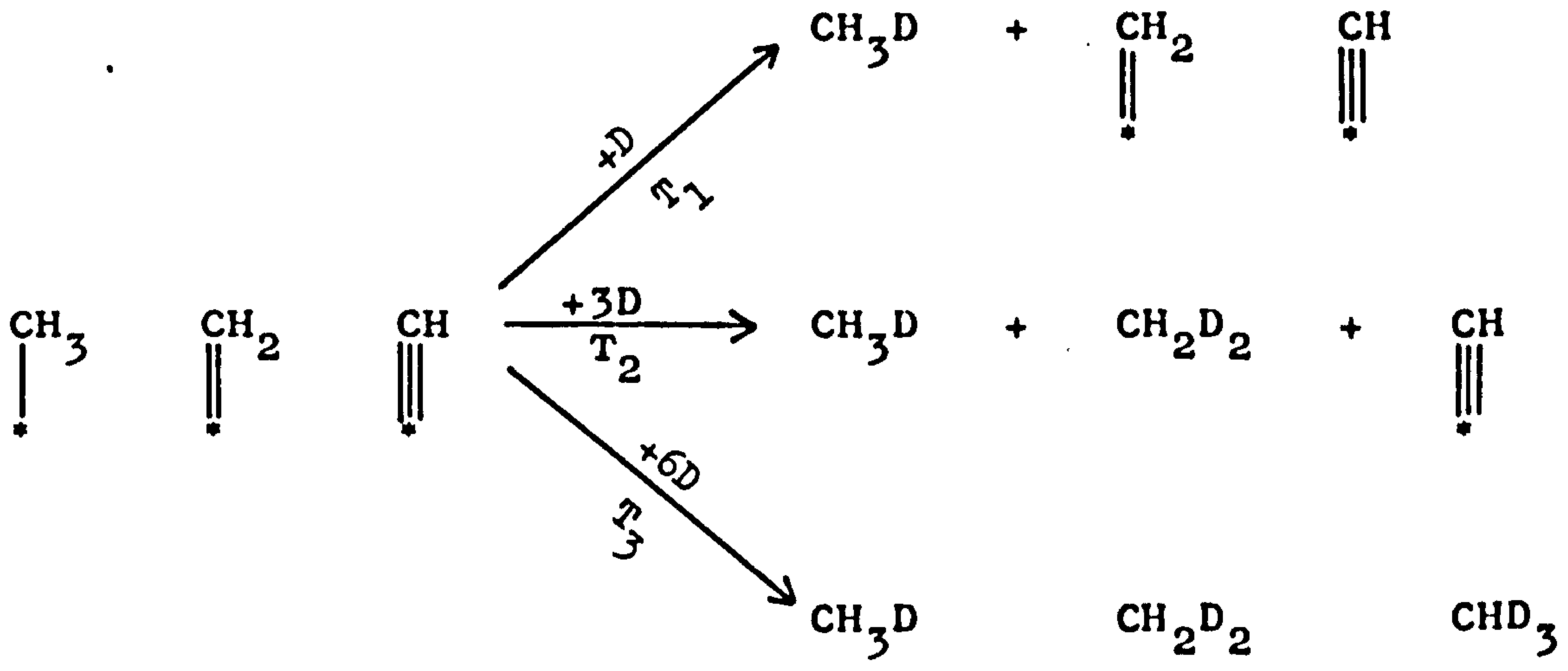
deuterium is greatly reduced, but mutual exchange, which occurs on other regions of the surface, is not affected. Exchange with molecular deuterium now proceeds with a lower value of M because part of the hydrogen pool arises not from the chemisorption of deuterium, but from migration of protium from regions of the surface that catalyse mutual exchange.

6.4.4 Products of decomposition and the effects of varying the temperature of a given reaction

The yield and isotopic composition of products formed from the decomposition of methylsilane during self exchange and mutual exchange at constant temperature did not vary substantially with time. Therefore hydrogen and methane are formed as initial products during dissociative chemisorption of methylsilane, and not from a process of continual cracking. This is in accord with the adsorption studies (Table 5.1 and Figure 5.1).

Increasing the temperature of the reactor had a marked affect on the composition of the gas phase when CH_3SiD_3 was the sole reactant (Tables 5.2 and 5.4). When the temperature was raised from 195 to 273 K the total yield of hydrogen increased by more than 50 %, but only slight variations in the isotopic composition were observed. This was probably due to increased dehydrogenation of chemisorbed methylsilane.

Over all the films studied, raising the temperature resulted in a major change in the isotopic composition of the methane evolved and a substantial increase in its total yield. The increase of temperature may have caused further cleavage of carbon-silicon bonds and additional hydrogenation of carbonaceous residues formed at lower temperatures. The alteration of the isotopic composition of methane and increased deuterium content was not due to methane-deuterium exchange, but more probably by progressive hydrogenation of the more highly dehydrogenated species shown in equation 6.10

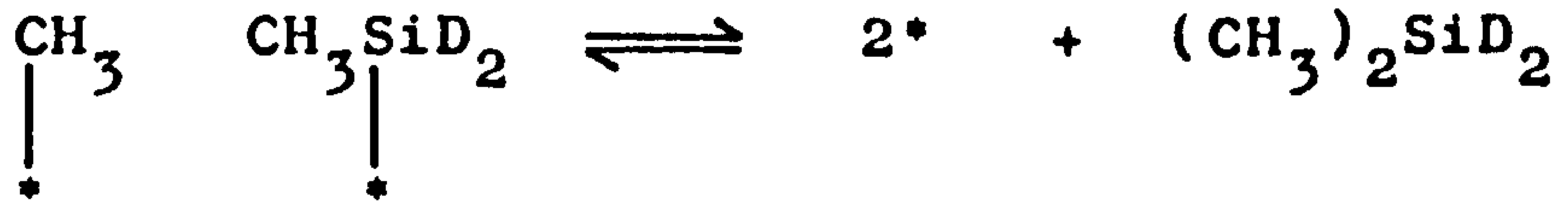


(6.10)

In equation 6.10 T_1 is the initial temperature, T_3 the final temperature, and T_2 an intermediate temperature. As the reactor is warmed, the concentration of adsorbed hydrogen is increased.

However, this increase is temporary, because some recombination occurs to give molecular hydrogen, and adsorbed hydrogen is also consumed by equation 6.10. Thus, soon after T_3 is attained, the hydrogen pool is consumed and reaction stops.

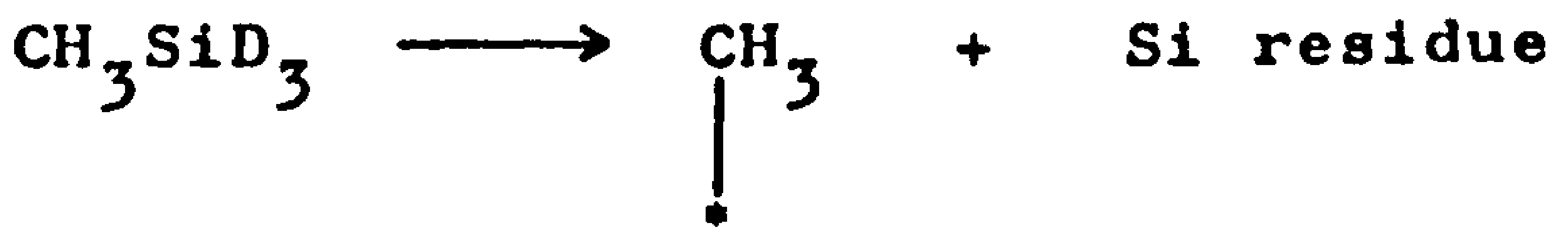
Besides increasing the yields of methane and of hydrogen, warming the vessel was also accompanied by the formation of dimethylsilane. When CH_3SiD_3 was the sole reactant dimethylsilane principally had the isotopic composition $(CH_3)_2SiD_2$. Equation 6.11 accounts for its formation, and warming of the reactor was necessary to produce a noticeable rate of reaction. Shortly after warming, the reaction was poisoned presumably by dehydrogenation of species (III).



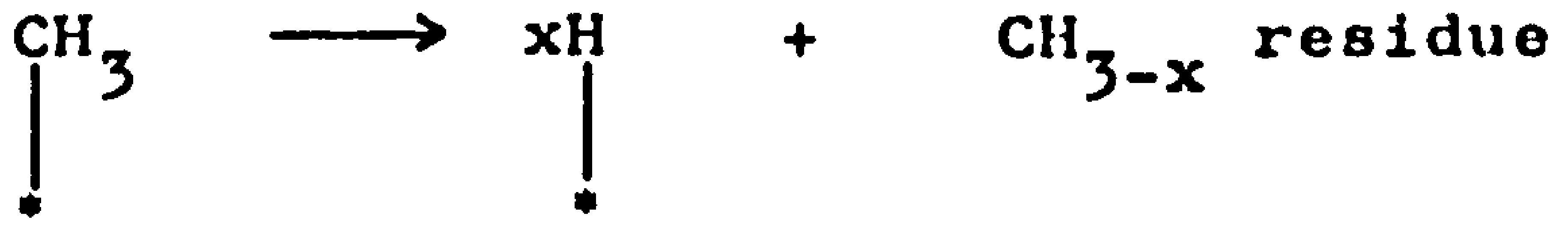
$$\underset{\ast}{\overset{|}{CH_3}} \quad CH_3\underset{\ast}{\overset{|}{Si}}D_2 \rightleftharpoons 2\ast + (CH_3)_2SiD_2 \qquad (6.11)$$

(III)

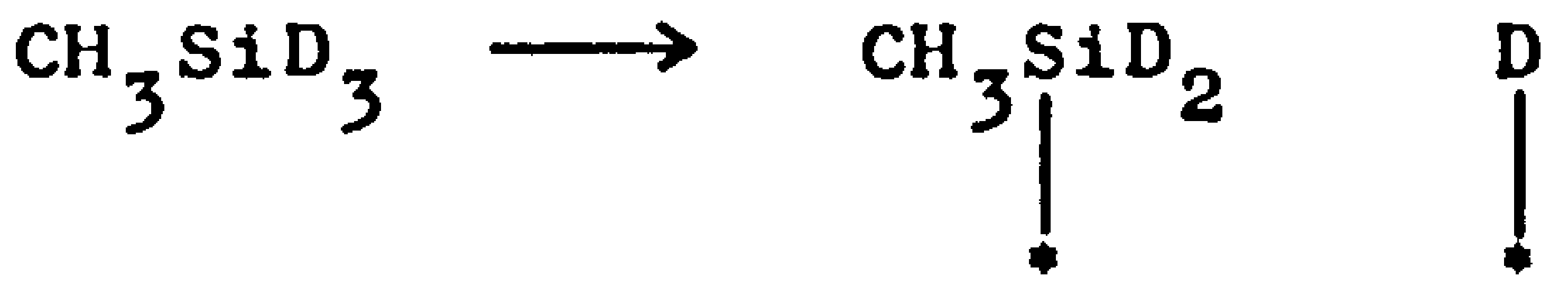
Finally, it was observed that by warming the vessel self exchange apparently occurred. However, the absence of an ion at m/e = 48 a.m.u., and the increased yields of ions at m/e = 43 and 44 a.m.u. indicated that protium entered the silyl group, but deuterium did not enter the silyl group. A mechanism for this exchange is set out schematically in equation 6.12. It is clear that exchange involved adsorbed protium evolved from the decomposition of CH_3SiD_3.



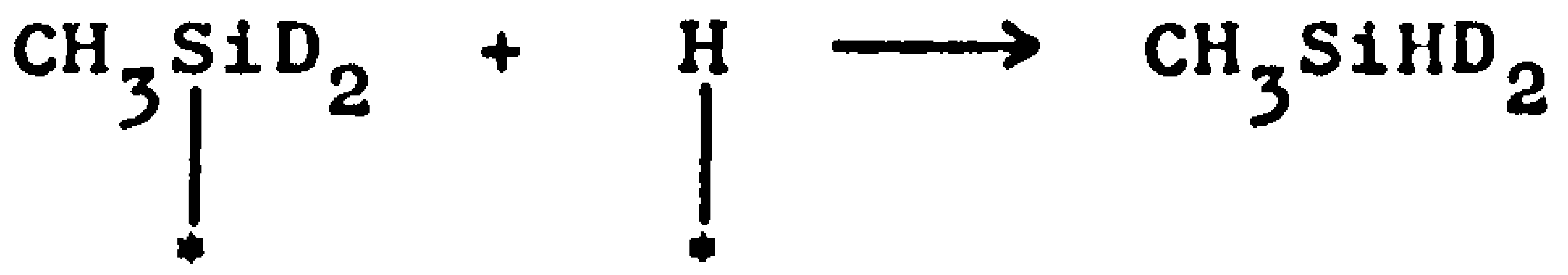
$$CH_3SiD_3 \longrightarrow \underset{*}{\underset{|}{CH_3}} + \text{Si residue} \qquad (6.12a)$$



$$\underset{*}{\underset{|}{CH_3}} \longrightarrow \underset{*}{\underset{|}{xH}} + CH_{3-x}\ \text{residue} \qquad (6.12b)$$



$$CH_3SiD_3 \longrightarrow \underset{*}{\underset{|}{CH_3SiD_2}} \quad \underset{*}{\underset{|}{D}} \qquad (6.12c)$$



$$\underset{*}{\underset{|}{CH_3SiD_2}} + \underset{*}{\underset{|}{H}} \longrightarrow CH_3SiHD_2 \qquad (6.12d)$$

6.5 Reactions of Methylsilane over Tungsten, Rhodium, and Nickel

Self exchange was not observed over any metal investigated. Results for mutual exchange and for exchange with molecular deuterium over tungsten, rhodium, and nickel are, in general, similar to those obtained over molybdenum, and it is proposed that, as with molybdenum, these two exchange reactions occur on different regions of the surface, mutual exchange occurring by equation 6.6 or 6.7, and exchange with molecular deuterium by equation 6.8.

Specific rates for mutual exchange and for exchange with molecular deuterium are summarized in Table 6.3; each of these results is for reaction over a clean film. The following observations can be made for the results at 195 K.

Table 6.3 Comparison of specific rates[a] for mutual exchange and exchange with molecular deuterium for first runs over Mo, W, Rh, and Ni

Metal	Temp. /K	Exchange with molecular deuterium $k_\emptyset$	k_0^I	M^I	Mutual exchange k_{03}
Mo	195	10.7	5.7	1.9	-
		-	-	-	16.5
	273	9.3	7.7	1.2	-
		-	-	-	14.9
W	195	0.50	0.45	1.1	-
		-	-	-	13.1
	273	3.2	2.5	1.3	-
		-	-	-	15.3
Rh	195	13.5	6.2	2.2	-
		-	-	-	26.1
	273	8.1	6.5	1.2	-
		-	-	-	10.8
Ni	195	0.39	0.39	1.0	-
		-	-	-	15.0
	273	2.2	1.8	1.2	-
		-	-	-	20.6

[a] Specific rates $k_\emptyset$, k_0^I, and k_{03} are expressed in units of nM $s^{-1}mg^{-1}$

(i) Mo, $k_{03} \overset{\sim}{>} k_{\phi}$

(ii) W, $k_{03} \gg k_{\phi}$

(iii) Rh, $k_{03} \overset{\sim}{>} k_{\phi}$

(iv) Ni, $k_{03} \gg k_{\phi}$

Where k_{03} and k_{ϕ} were comparable, that is over molybdenum and rhodium, multiple exchange was observed ($M^{I} \sim 2.0$). Under these conditions hydrogen migration from areas capable of catalysing mutual exchange was of little importance. However, over tungsten and nickel, k_{ϕ}, is small compared to k_{03}, and the multiplicity of exchange is approximately unity. Under these conditions much hydrogen migration may have occurred from regions that catalyse mutual exchange, and this may have caused the real value of the multiplicity to be lowered to unity; a value synonymous with stepwise exchange. The possibility that exchange may have been genuinely stepwise cannot be disregarded. Similar, effects were also observed at 273 K and above.

The following paragraphs discuss the reactions of methylsilane over tungsten, rhodium, and nickel in further detail, particularly in respect to the poisoning of the surface, and compare them with the same reactions over molybdenum and gold.

6.5.1 Mutual exchange

For the first run on a clean film of either tungsten, rhodium, or nickel, rapid mutual exchange was observed at 195 and at 273 K; specific rates were similar to those obtained over gold and over molybdenum. Specific rates at the above temperatures are summarized in Table 6.3, the full results being contained in Tables 5.16 and 5.17 (tungsten), 5.25 and 5.26 (rhodium), and 5.36 and 5.37 (nickel).

At 195 K specific rates decreased markedly from run to run over the above metals, although function plots were linear. Such behaviour on gold and on molybdenum was observed at 273 K, but not at 195 K. The losses of activity were not however as drastic as those observed for exchange with molecular deuterium at 195 K. As with molybdenum, it is believed that activity was lost between runs because evacuation disturbed the equilibrium of adsorbed species and those that remained (probably adsorbed-CH_3SiX_2) dehydrogenated to form poisons. This form of poisoning also occurred at 273 K, but with greater severity. Thus, the rate of exchange diminished from run to run, and for reasons argued in detail for reaction over gold and molybdenum, the mechanism is probably that which is shown in equation 6.7.

Certain features of mutual exchange over rhodium and over nickel require comment.

1. Rhodium. The specific rate of the first reaction over a rhodium film at 195 K was normally higher than that of the first reaction

on a film at 273 K. This inverse temperature dependence is probably due to methylsilane being more highly dehydrogenated at the higher temperature with the result that fewer sites are available for mutual exchange. This behaviour is similar to that of molybdenum, and unlike that of tungsten and nickel. At 273 K function plots of $\ln(d_{03}-d_{03\infty})$ against time (examples shown in Figure 5.6) exhibit slight departures from linearity. This indicates that adsorbed species (probably adsorbed-CH_3SiX_2, where X = H or D) dehydrogenate to form poisons by a continuous process. Continuous poisoning was not observed over molybdenum or gold.

2. Nickel. For certain runs over nickel films at 195 K the function plots exhibited a sudden diminution of gradient (Figure 6.3), i.e. rapid poisoning of the surface appeared to occur (Table 5.36). However, in the fourth reaction over film number 4, the gradient of the function plot obtained was similar to that obtained for the previous run before poisoning occurred, suggesting the existence of a type of reversible poisoning. However, no satisfactory interpretation of this phenomenon can be offered.

6.5.2 Exchange with molecular deuterium

Over tungsten, rhodium, and nickel at 195 and at 273 K exchange in methylsilane occurred in the silyl group but not in the methyl group; similar

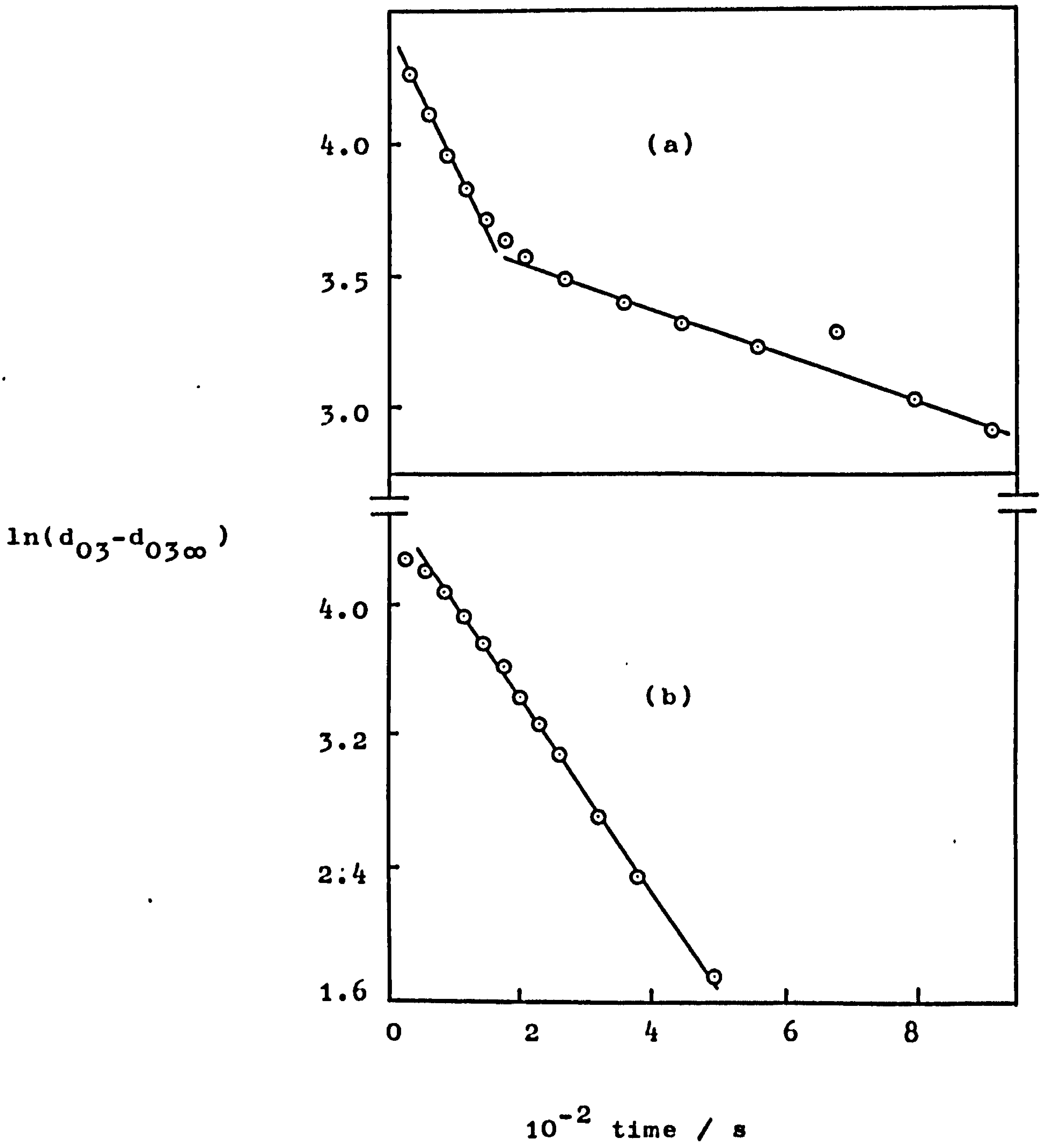


Figure 6.3.1 Mutual exchange catalysed by nickel at 195 K: film no. 4

Legend:- (a) run no. 3 , (b) run no. 4 .

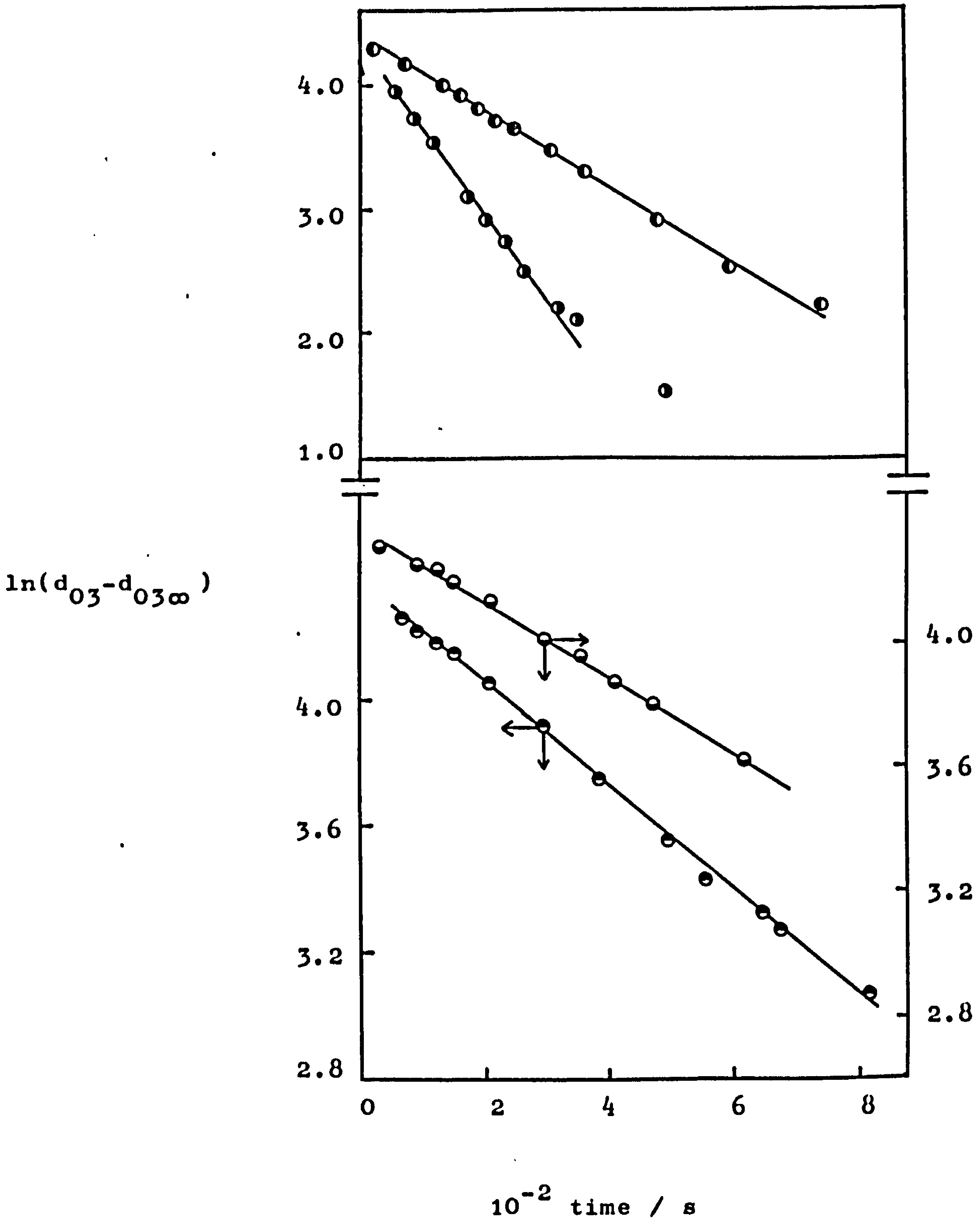


Figure 6.3.2 Mutual exchange catalysed by nickel at 273 K: film no. 7

Legend:- ◐ run no. 1 , ◐ run no. 2 ,

◒ run no. 3 , ◓ run no. 4 .

behaviour was observed for molybdenum. Specific rates for the first reaction on a film are summarized in Table 6.3, and the results are shown fully in Tables 5.19 and 5.20 (tungsten), 5.28, 5.29, and 5.30 (rhodium), and 5.38, 5.39, and 5.40 (nickel), and examples of the function plots are shown in Figures 5.4 (tungsten), 5.7 (rhodium), and 5.9 (nickel).

At 195 K function plots of $\ln(\phi_{\infty} - \phi)$ against time exhibited slight departures from linearity, which were most pronounced for tungsten; function plots were linear for molybdenum. However, like molybdenum, activity was drastically diminished from run to run for all the above metals. At 273 K all function plots were non-linear and exchange was completely poisoned after about 2 ks, although under similar experimental conditions function plots were linear for mutual exchange. Similar behaviour was observed over molybdenum.

For the first reaction on a clean film, a higher specific rate was obtained at 195 K than at 273 K over rhodium. As with molybdenum, this was due to poisoning being more severe at the higher temperature. Tungsten and nickel, however, exhibited a normal temperature dependence. In accordance with the well-known ability of rhodium to catalyse multiple exchange in alkanes, a high value of M^{I} was obtained at 195 K. Molybdenum, usually a stepwise exchange catalyst, exhibited similar behaviour. As with molybdenum it is proposed that exchange over tungsten, rhodium, and nickel occurred by equation 6.8, and hence multiple exchange was observed over rhodium. The interpretation of apparent stepwise exchange over nickel and tungsten was presented in the introduction to this section (Section 6.5).

6.5.3 Products of decomposition and the effects of varying the temperature of a given reaction

Hydrogen and methane were detected as initial products when mixtures for self exchange or for mutual exchange were admitted to either tungsten, rhodium, or nickel films at 195 and at 273 K. The yields of these products relative to each other varied from metal to metal, and at 273 K and above their relative yields were in accord with those obtained for the adsorption studies (Table 6.1).

Increasing the temperature of the reactor from 195 to 293 K when CH_3SiD_3 was the sole reactant had the following effects.

1. The percentage of hydrogen in the gas phase increased substantially for tungsten and nickel; similar behaviour was observed over molybdenum. As the reactor was warmed further dehydrogenation of methylsilane occurred. Over rhodium the percentage of hydrogen was unaltered.

2. A pronounced increase in the percentage

of methane in the gas phase was observed over each metal; similar behaviour was observed over molybdenum. This was due to increased breaking of C-Si bonds, and hydrogenation of adsorbed carbonaceous residues. The unchanged percentage of hydrogen in the gas phase over rhodium (see above) is occasioned by the increased consumption of hydrogen due to the very substantial formation of methane that occurred on warming.

3. Isotopic composition of hydrogen evolved over rhodium and nickel varied slightly as the reactor was warmed; similar behaviour was observed for molybdenum (Section 6.4.4). Thus the number of C-H bonds broken relative to Si-D bonds is independent of temperature. The percentage of deuterium in hydrogen evolved over tungsten increased as the reactor was warmed. This demonstrated that, at low temperatures, C-H bonds were broken more easily relative to Si-D bonds than at higher temperatures.

4. Over tungsten, rhodium, and nickel, the warming of the reactor resulted in the isotopic composition of methane being altered slightly, and the deuterium content being increased. Similar, but more pronounced, behaviour was observed for molybdenum (Section 6.4.4). As with molybdenum, these changes were probably due to hydrogenation of more severely dehydrogenated species, and not due to

methane-deuterium exchange (equation 6.10, Section 6.4.4).

5. Dimethylsilane, principally $(CH_3)_2SiD_2$, was evolved over tungsten, rhodium, and nickel. Equation 6.11 shows a simple mechanism where dimethylsilane may be formed over these metals and molybdenum.

6. Warming the reactor resulted in the apparent commencement of self exchange over each of the metals studied with the exception of gold. The interpretation of this exchange is the same as that originally expressed for molybdenum (Section 6.4.4), that is, adsorbed protium is present on the surface, due to decomposition of methylsilane, and this exchanges with deuterium in the silyl group. The mechanism of this exchange is shown schematically in equation 6.12.

6.6 Activity of Metals for Exchange in Methylsilane

6.6.1 Self exchange

In the temperature range of 195-340 K self exchange was not detected over any of the metals studied owing to the inability of adsorbed species containing both hydrogen and deuterium to undergo C-H bond fission.

6.6.2 Mutual exchange

The specific rates for mutual exchange at 195 and at 273 K over molybdenum, tungsten, rhodium, and nickel are shown in Table 6.3. From that table and from results obtained over gold films prepared under high vacuum (Table 5.4) the metals in the clean state can be ranked in order of decreasing activity for mutual exchange as follows:

$$\mathrm{Rh} > \mathrm{Mo} > \mathrm{Ni} > \mathrm{W} > \mathrm{Au} \quad \text{at 195 K and}$$
$$\mathrm{Ni} > \mathrm{W} > \mathrm{Mo} > \mathrm{Rh} > \mathrm{Au} \quad \text{at 273 K}$$

The extent of poisoning at the above temperatures varies from metal to metal. Consequently, the order of decreasing activity for mutual exchange is temperature dependent. All the metals studied exhibited high activity for exchange. However the surface uptake, which can be related to surface area, varies substantially from metal to metal with a very low value being obtained for gold. Thus if specific rates are converted into units that take surface uptake into account (nM s^{-1} (μM adsorbed)$^{-1}$), the order of decreasing activity at 273 K becomes:

$$\underset{(124)}{\mathrm{Au}} > \underset{(108)}{\mathrm{Ni}} > \underset{(64)}{\mathrm{W}} > \underset{(32)}{\mathrm{Mo}} > \underset{(31)}{\mathrm{Rh}}$$

This new order assumes that the proportion of the total surface area active for mutual exchange is the same for each metal. The high activity of gold is now apparent.

6.6.3 Exchange with molecular deuterium

Only gold was inactive for exchange with molecular deuterium. Specific rates for this exchange are summarized in Table 6.3. For clean films, activity decreases in the following order:

Rh > Mo > W > Ni at 195 K and
Mo > Rh > W > Ni at 273 K.

Once more, variations in the temperature dependence of poisoning causes differences in the order of catalytic activity at 195 and 273 K.

6.7 Reactions of Methylsilane and of some Simple Hydrocarbons

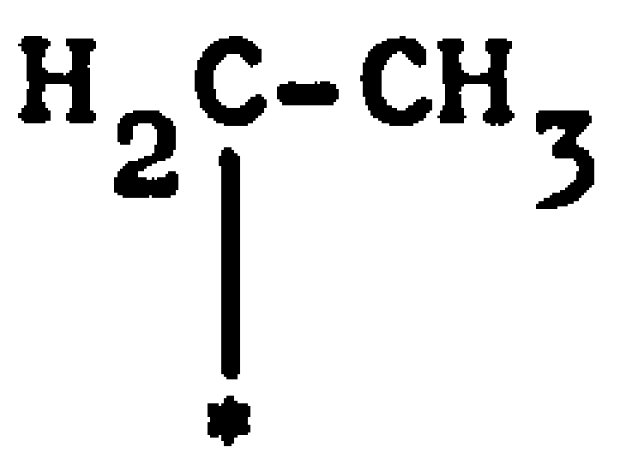
Methylsilane and ethane are compounds of similar structure. However, the electrons of the C-C bond are equally shared by the two carbon atoms, whereas in methylsilane the electrons of the C-Si bond are not equally shared. On the basis of Pauling's electronegativities for carbon and silicon (61), the bond is polarized thus:

$$\overset{\delta-}{H_3C} — \overset{\delta+}{SiH_3}$$

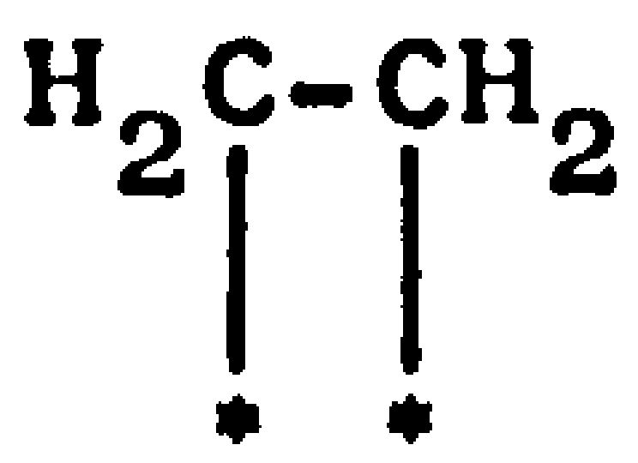
The C-Si and C-C bond dissociation energies are similar, being 359 kJ mole^{-1} (62) and 368 kJ mole^{-1} (63) respectively. The dissociation energy of the C-H bond in ethane is 410 kJ mole^{-1} (64) whereas that of the Si-H bond in methylsilane is 372 kJ mole^{-1} (65); the latter is moderately weaker than the former, and hence greater activity for exchange in the silyl group of methylsilane is to be expected. Despite superficial similarities, these two compounds exhibit different properties for adsorption and for exchange.

Ethane and other simple alkanes are usually more weakly adsorbed by transition elements than hydrogen. This has been demonstrated for the exchange of ethane with deuterium, the order of reaction being negative for deuterium and positive for ethane (19). However, methylsilane was strongly adsorbed on each of the metals studied, with rapid evolution of hydrogen accompanying adsorption. Also over molybdenum, exchange was shown to have a positive order of reaction with respect to deuterium, which is the reverse of the behaviour observed for exchange in ethane (19).

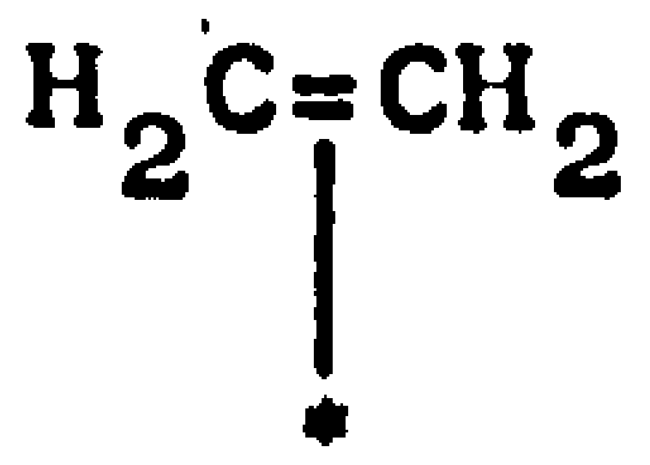
The complete absence of exchange in the methyl group is a remarkable feature of the present work. Multiple exchange in ethane occurs at both carbon atoms and involves the interconversion of (A) with (B) or (C), but in methylsilane exchange the formation of (D) or (E)


H_2C-CH_3

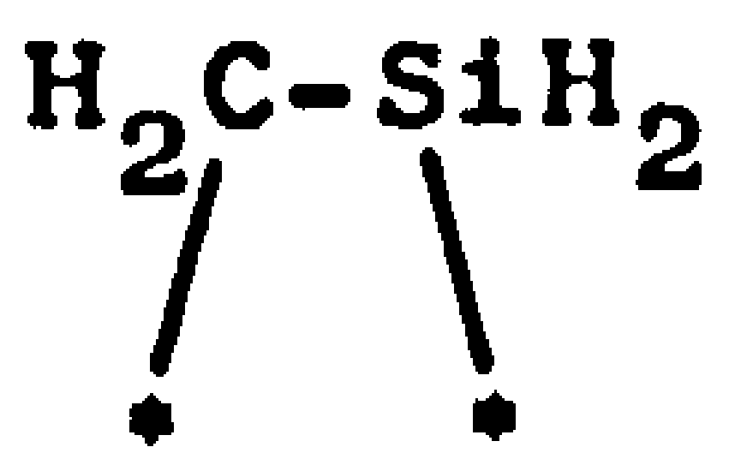
(A)


H_2C-CH_2

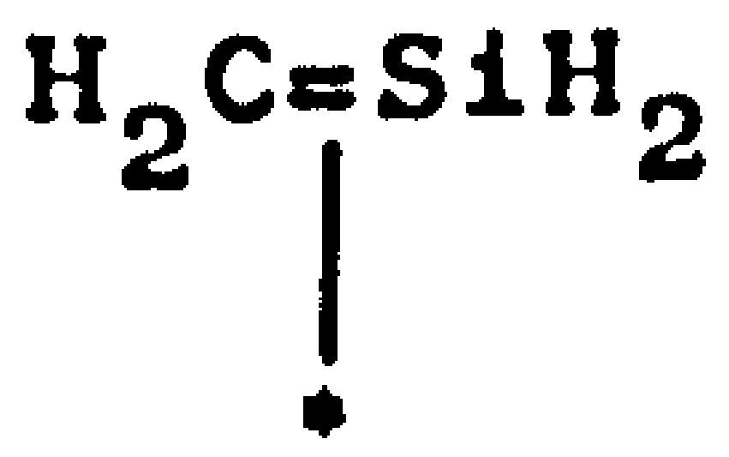
(B)


$H_2C=CH_2$

(C)


H_2C-SiH_2

(D)


$H_2C=SiH_2$

(E)

from adsorbed-CH_3SiH_2 either does not occur or provides unreactive species. Species (E) may be discounted because the carbon-silicon double bond has only just been reported and has been found to be very unstable (66). Species (D) is less easily dismissed, unless the bonding shown in (B) and (D) is simply a less satisfactory description than that in (C) or (E).

Because exchange is confined to the silyl group, exchange in methylsilane should perhaps be likened more to that of methane than ethane. However, mutual exchange and exchange with molecular deuterium in methylsilane proceed rapidly at much lower temperatures (about 100-200° lower) than the corresponding reactions in methane (18,29,37). The higher activity of methylsilane for exchange is due in part to the bond dissociation energy of Si-H in methylsilane being lower than that of C-H in methane. The strength of the silicon-metal bond is another factor that contributes to the high activity of methylsilane. As described in Section 6.2, the formation of a coordinate bond between filled *d*-levels of the metal atom and empty *d*-orbitals of silicon is probably important in producing strongly adsorbed species. Bonding of this sort is not possible for alkanes, and hence they are less strongly adsorbed. The types and strengths of bonding of adsorbed species determine the reactions that occur, the temperatures at which they occur, and the ease with which they may be poisoned.

Exchange of methylsilane with molecular deuterium at 273 K exhibited continuous poisoning over each of the metals studied (Mo, W, Rh, and Ni). Under conditions for which exchange occurred in methane and in ethane such poisoning was not observed (18,19,37); however, over rhenium exchange of ethane with deuterium was strongly poisoned at 273 K (67). Poisoning of methylsilane exchange was probably due to the ease with which highly dehydrogenated species could be formed, whereas for methane and for ethane such species were not readily formed because of their weaker adsorption.

It is of some interest that, in the process of hydrosilylation (41-44, 68), the silanes used normally have only one hydrogen atom bonded to silicon. Hydrosilylation proceeds without poisoning, and it seems probable that this is so because extensive dehydrogenation to form multiply bonded species which act as poisons cannot readily occur. Therefore methylsilane would probably prove to be unsuitable for hydrosilylation.

6.8 Conclusions

The exchange reactions presented in this thesis demonstrate that, on adsorption, the chemical reactivity of methylsilane is centred on the silicon atom. This arises because the Si-H bond has a lower bond dissociation energy than C-H, and because of the apparent inability for both carbon and silicon to form bonds to the surface simultaneously to give reactive species.

Adsorption of methylsilane is stronger relative to that of ethane. In part this stronger adsorption may be attributed to the metal forming coordinate bonds to silicon. It is believed that establishment of such bonds is of great importance for chemisorption of methylsilane on gold, and that associatively adsorbed species may possibly be formed.

Surfaces of evaporated metal films are energetically heterogeneous. Those regions on which methylsilane is least strongly adsorbed, and where adsorbed-CH_3SiX_2 is the only dissociatively adsorbed species, are active for mutual exchange. On regions where adsorption is stronger so that adsorbed-CH_3SiX_2 and -CH_3SiX are formed, and deuterium can dissociate, exchange of methylsilane with molecular deuterium occurs. Evacuation results in further dehydrogenation of dissociatively adsorbed species and thus the surface becomes poisoned for methylsilane exchange.

The extent of poisoning caused by evacuation is greater at 273 K and above than at 195 K, and for exchange with molecular deuterium poisoning occurs by a continuous process at the former temperature. Thus formation of surface poisons increases as the temperature is raised.

APPENDIX A

Preparation of CH_3SiD_3

CH_3SiD_3 was prepared by the action of $LiAlD_4$ on CH_3SiCl_3:

$$4CH_3SiCl_3 + 3LiAlD_4 \longrightarrow 4CH_3SiD_3 + 3LiCl + 3AlCl_3$$

A diagram of the apparatus is shown in Figure A.1.

About 0.5 g of $LiAlD_4$ was introduced into a 0.10 l three-necked flask, A, and approximately 30 to 40 ml of dibutyl ether were added. The apparatus was closed to the atmosphere, the flask and its contents were immersed in liquid air, and the apparatus was evacuated by means of a rotary pump. CH_3SiCl_3 (about 2 g) contained in flask B, was frozen in liquid air, and pumped. Tap T2 was closed when a vacuum of 0.05 torr or better was attained (Pirani gauge). Flask B was warmed to room temperature and CH_3SiCl_3 distilled into flask A; tap T1 was closed on completion of this procedure. Next, the cold-finger condenser, CF, was filled with an acetone-cardice slush, trap U1 was immersed in acetone-cardice slush, and trap U2 was immersed in liquid air. Flask A was pumped once more prior to it being warmed to 273 K.

The contents of flask A were agitated by use of a magnetic stirrer. After about 30 minutes reaction was virtually complete. CH_3SiD_3 was periodically pumped through traps U1 and U2 (care was taken to ensure that the contents of the flask A did not boil too vigorously).

Once complete reaction had occurred, tap T3 was closed, taps T4 and T5 opened, and as soon as a good vacuum was obtained, tap T6 was closed. Trap U2 was warmed up to room temperature and the pressure of the product measured on the manometer. The finger of the storage vessel S was cooled in liquid air to condense the product. The vessel was isolated from the line by closure of taps T4 and T5 and then transferred to the high vacuum apparatus where the CH_3SiD_3 was purified by trap to trap distillation, and used for exchange experiments.

Excess $LiAlD_4$ that remained in flask A was decomposed in the following manner. The apparatus was filled with nitrogen to a pressure of about half an atmosphere, a dilute solution of water in tetrahydrofuran (about 2 % water, v/v) was introduced into the dropping funnel, F, and added dropwise to the contents of the flask until evolution of deuterium ceased.

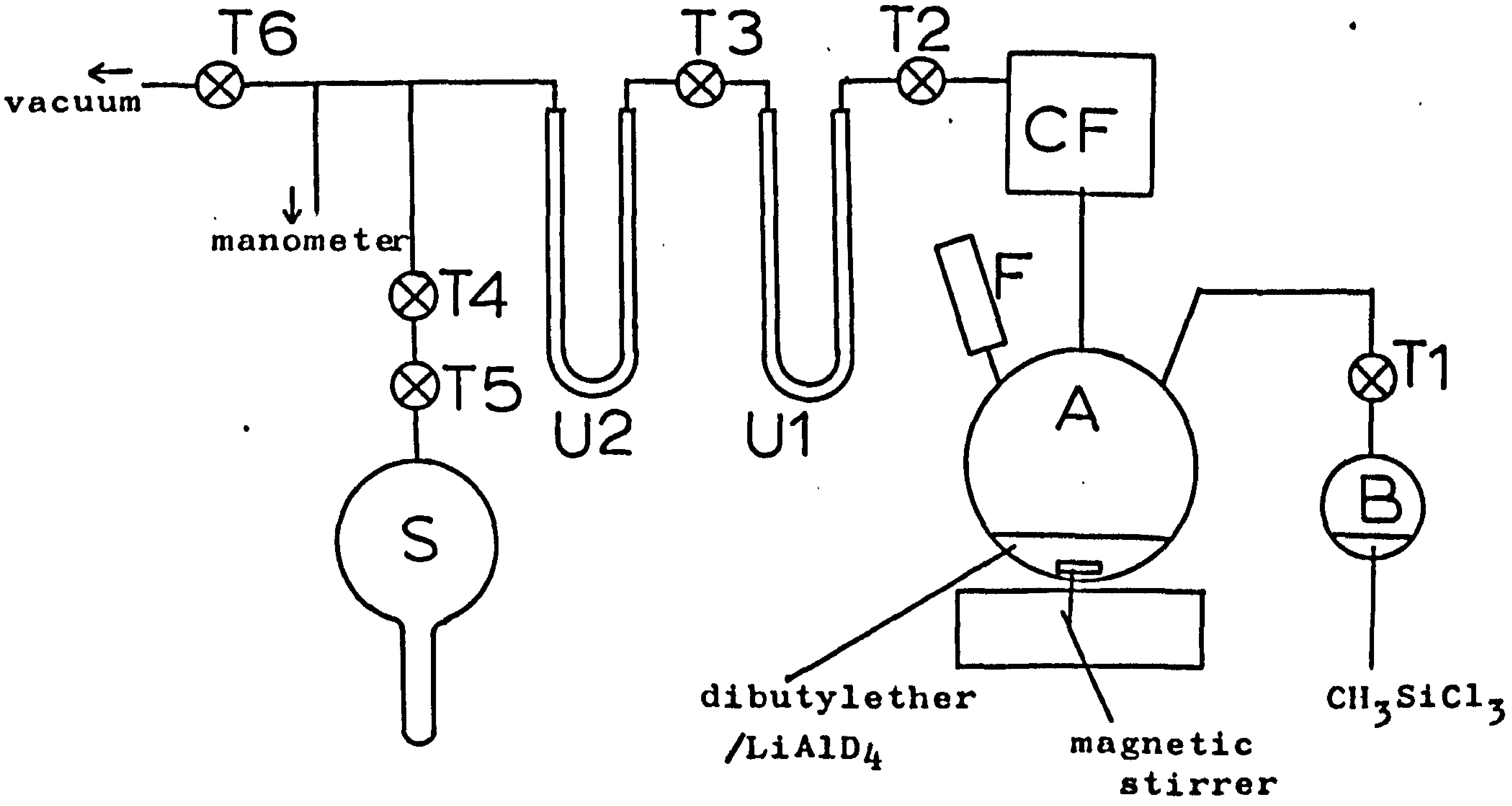


Figure A.1 Apparatus for the preparation of CH_3SiD_3

APPENDIX B

Mass Spectra of some Deuterium-labelled Methylsilanes and the Analysis of Mixtures.

Foreword.

A paper has been prepared on mass spectra and analysis of deuterium-labelled methylsilanes. An abbreviated version of this paper has been accepted for publication in the Canadian Journal of Chemistry. However, this appendix is devoted to the paper in its original and unabbreviated form.

Abstract

Positive ion mass spectra of CH_3SiH_3 and of CH_3SiD_3 ($m/e = 28 - 49$) in the range 12 - 70 eV are reported. The appearance potentials of the most abundant ions, and m*-values for four metastable ions formed from CH_3SiD_3 have been measured. Modifications to mechanisms of ion fragmentation are proposed.

Methylsilane gives no parent ion and fragmentation is extensive. Analysis of mixtures containing CH_3SiX_3 (X = H or D) can be achieved at 18.0 ± 2.0 eV. Expressions representing the fragmentation spectra of CH_3SiH_2D and of CH_3SiHD_2 at 18.0 eV are obtained from the measured spectra for CH_3SiH_3 and CH_3SiD_3. Accurate analysis can be achieved of any sample containing two or three of these isotopically distinguishable methylsilanes, or of all four if the composition possesses a certain symmetry. The deuterium content can be determined for a sample of any composition.

Introduction

Mass spectrometric analysis of hydrocarbons in which some hydrogen atoms are exchanged for deuterium is widely practised, and isotope tracer studies have greatly advanced our understanding of hydrocarbon reactivity. By comparison, isotope exchange in silicon hydrides has been almost completely neglected, largely because of analytical difficulties associated with low or zero parent ion yields in the mass spectra.

The objects of the present work have been, first, to examine thoroughly the mass spectrum of CH_3SiD_3 which has not been reported before, and secondly, to validate a method of analysis for mixtures of deuterium-labelled methylsilanes. This analysis represents a difficult case, since the parent ion concentrations are zero and ion fragmentation considerable.

Experimental

Materials

CH_3SiH_3 was pure as supplied. CH_3SiD_3 was prepared by the reduction of methyltrichlorosilane with lithium aluminium deuteride in dibutyl ether solution at 273 K. Isotopic purity was $> 99\%$. The product contained less than 1% dimethylsilane as the only chemical impurity.

Apparatus and Methods

Mass spectra and appearance potentials were obtained using a Vacuum Generators Micromass 6 mass spectrometer. Source pressures were such (10^{-5} - 10^{-6} torr) that pressure-dependent reactions of ions were not observed. Appearance potentials were determined by the vanishing current method(1). Ionisation energy was varied in steps of 0.2 eV, and ion current intensities were measurable to ± 1 pA. The ionisation energy scale was calibrated by measurement of the ionisation potentials of helium, argon, and xenon. Mass spectra have been corrected for the natural abundance of ^{29}Si, ^{30}Si, and of ^{13}C.

An A.E.I. MS902 mass spectrometer was used for the examination of metastable ions.

Results

Figures 1 and 2 show the positive ion mass spectra of CH_3SiH_3 and of CH_3SiD_3 for various electron beam energies. The parent ions and ions of $m/e < 28$ were of negligible intensity under all conditions. The spectrum of CH_3SiH_3 at 70 eV agrees with a literature report(2). As expected, the extent of fragmentation increased with increasing electron beam energy, the fouth fragment (i.e. $CSiH_2^+$ from $CSiH_6$) being detected at 20 eV and above. It was thus necessary, for the purposes of analysis, to use a voltage lower than 20 eV in order to restrict fragmentation, but higher than 16 eV in order to maintain a sufficient total ion current (Figure 1a). 18.0 eV was chosen, and the spectra of both CH_3SiH_3 and CH_3SiD_3, together with the

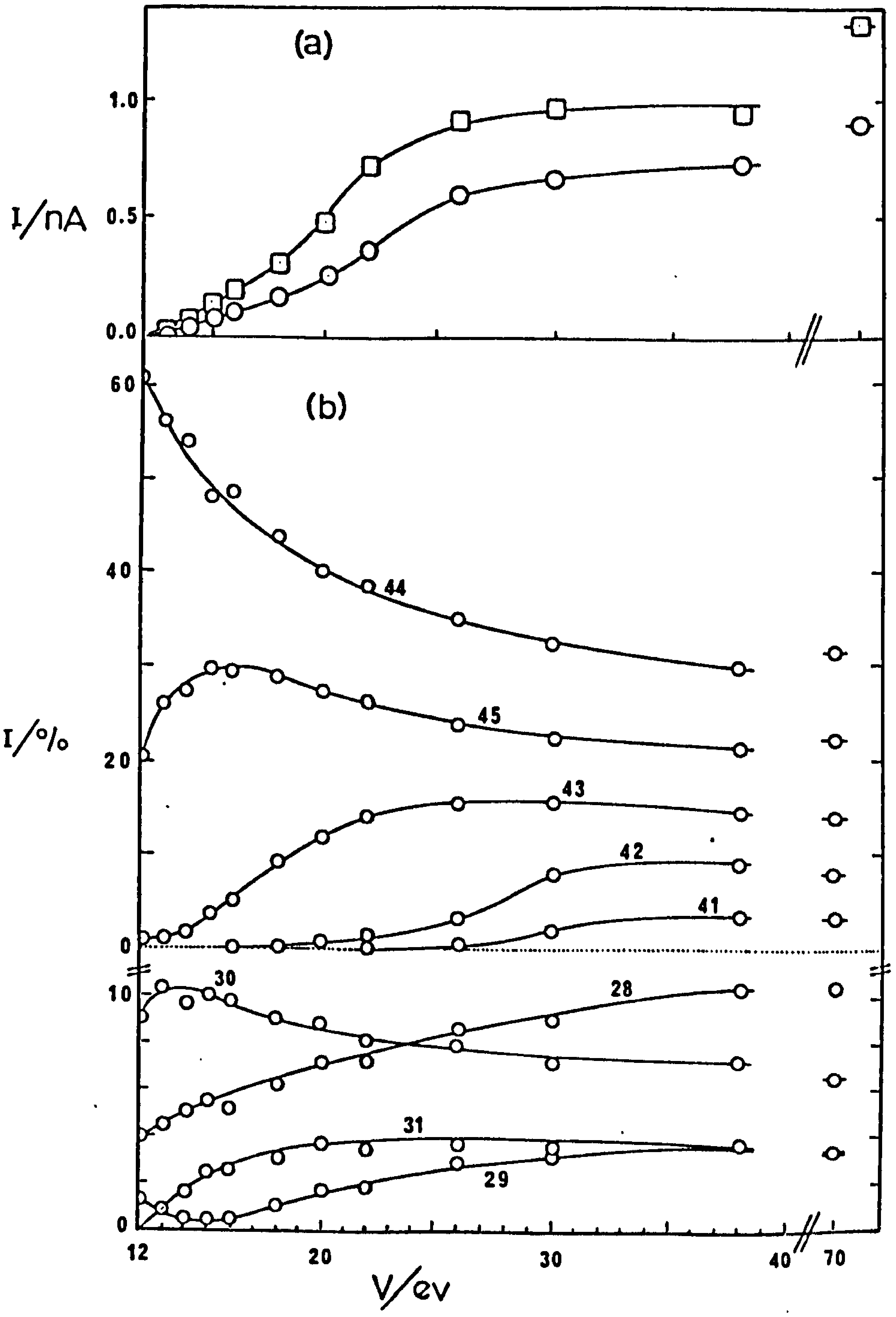


FIG. 1. (*a*) Ionisation efficiency curves for CH_3SiD_3 (squares) and for CH_3SiH_3 (circles).

(*b*) Mass spectra of CH_3SiH_3; variations of relative ion current, *I*, with ionisation energy, *V*.

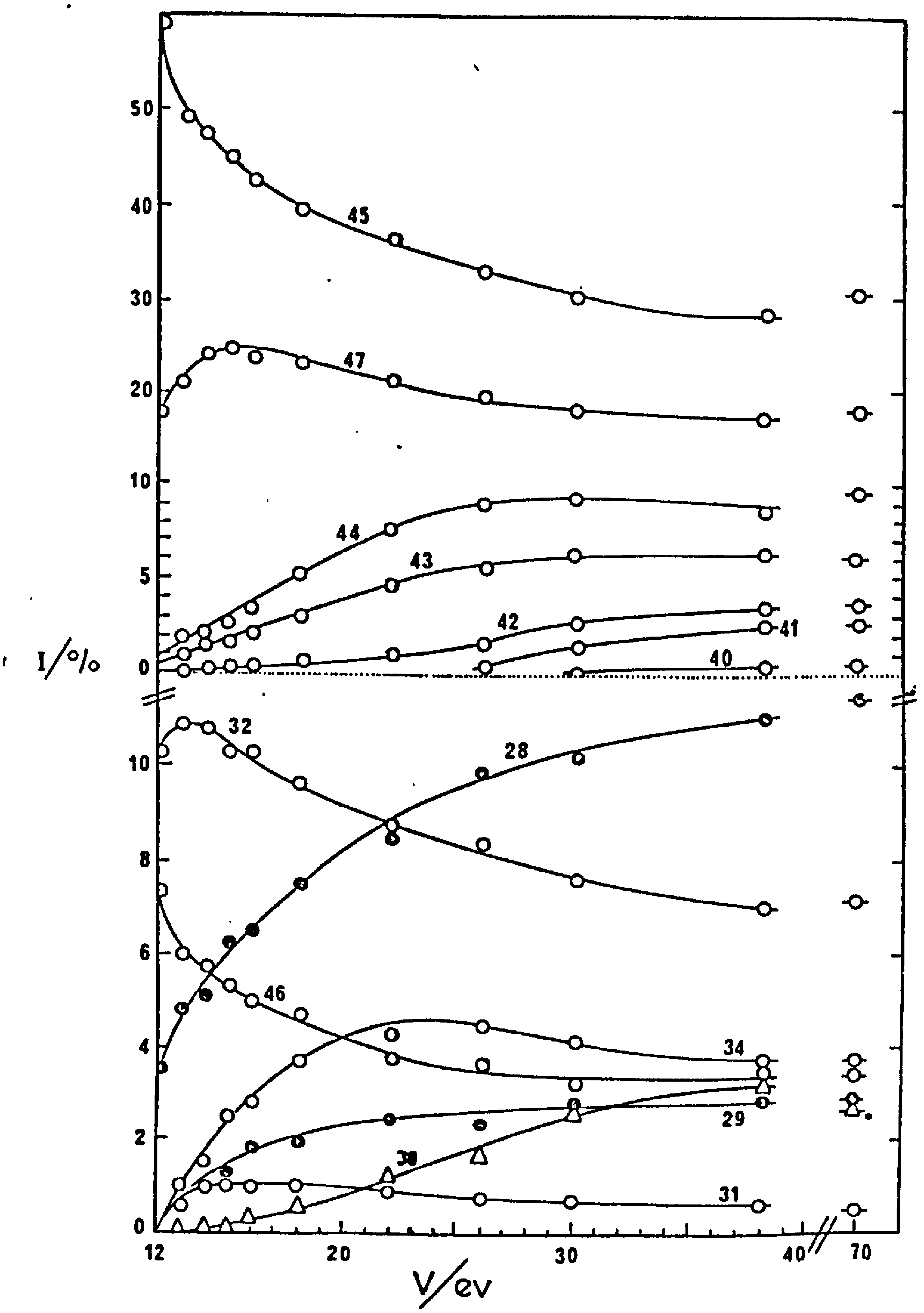


FIG. 2. Mass spectra of CH_3SiD_3; variations of relative ion current, *I*, with ionisation energy, *V*.

designation of the major contributing ions (see Discussion) are presented in Table 1.

Appearance potentials are recorded in Table 2. Breaks in the curves of ion current against ionisation potential reported by earlier workers (3) were not observed.

The mass spectrum of CH_3SiH_3 contains three peaks, corresponding to the decomposition of metastable ions, having $\underline{m}^*$-values of 41.1, 26.1, and 17.8 a.m.u.(2). We confirmed the presence of these ions, and observed four metastable transitions in the spectrum of CH_3SiD_3; $\underline{m}^*$-values and assignments are given in Table 3.

Discussion

Mechanisms of Fragmentation

The ions formed in greatest abundance from CH_3SiH_3 have been assigned the structures $CH_3SiH_2^+$, CH_3SiH^+, and CH_3Si^+ largely on the grounds that the dissociation energies of Si-H are generally lower than those of corresponding C-H bond, and that the ionisation potentials of silyl radicals are normally lower than those of the corresponding alkyl radicals. Potzinger and Lampe (3) assign the ion at $\underline{m}/\underline{e}$ = 45 in the spectrum of CH_3SiH_3 as $CH_3SiH_2^+$ in the neighbourhood of the appearance potential, with a contribution from $CH_2SiH_3^+$ above 12.9 eV where these authors report a break in the ionisation efficiency curve. The spectrum of CH_3SiD_3 (Table 1) confirms that the formation of $CH_3SiD_2^+$ is a favoured process. However, loss of protium from carbon to give the ion $CH_2SiD_3^+$ at $\underline{m}/\underline{e}$ = 48 was negligible under all conditions, and no break was evident in our ionisation efficiency curves. Thus, by analogy, the ion at $\underline{m}/\underline{e}$ = 45 in the spectrum of CH_3SiH_3 is almost entirely $CH_3SiH_2^+$ under all conditions.

Fragmentation of CH_3SiH_3 by loss of two atomic mass units (2 a.m.u.) to give CH_3SiH^+ in the neighbourhood of the appearance potential, with primary formation of $CH_2SiH_2^+$ above 12.4 eV has been proposed(3). Secondary formation

TABLE 1. Mass Spectra of CH_3SiH_3 and of CH_3SiD_3 at 18.0 eV

m/e	CH_3SiH_3		CH_3SiD_3	
	Ion current (%)	Major contributing ions[a]	Ion current (%)	Major contributing ions[a]
49			0.0	$(CSiH_3D_3^+)$
48			0.3	$CSiH_2D_3^+$
47			23.0	$CSiH_3D_2^+$
46	0.0	$CSiH_6^+$	4.7	$CSiH_2D_2^+$
45	28.4	$CSiH_5^+$	39.5	$CSiH_3D^+$
44	44.1	$CSiH_4^+$	5.2	$CSiH_2D^+$
43	9.2	$CSiH_3^+$	3.0	$CSiH_3^+$
42	0.3	$CSiH_2^+$	0.6	$CSiH_2^+$
41	0.0	$CSiH^+$	0.2	$CSiH^+$
40	0.0	CSi^+	0.0	CSi^+
34			3.7	SiD_3^+
33			0.1	$SiHD_2^+$
32			9.4	SiD_2^+
31	3.1	SiH_3^+	1.0	$SiHD^+$
30	8.9	SiH_2^+	0.5	SiD^+
29	1.0	SiH^+	1.9	SiH^+
28	6.2	Si^+	7.3	Si^+

[a] see Discussion

TABLE 2. Appearance potentials

CH_3SiH_3		CH_3SiD_3	
m/e	Appearance potential (eV)	m/e	Appearance potential (eV)
45	11.8 (11.80)[a]	47	11.8
44	11.3 (11.45)	46	11.4
43	12.8 (14.05)	45	11.5
31	12.5 (12.8)	44	11.4
30	11.7 (11.50, 11.62)	43	12.1
29	14.8	34	12.4
28	12.1	32	11.6
		28	11.8

[a] literature values(3,4) in parenthesis

TABLE 3. Values of $\underline{m}^{*a}$ for the decomposition of metastable ions formed from CH_3SiD_3

$\underline{m}^*$ observed (a.m.u.)	Proposed process	$\underline{m}^*$ expected^b (a.m.u.)
41.2	$CH_3SiD_2^+ \rightarrow CH_2SiD^+ + HD$	41.19
39.3	$CH_3SiD_2^+ \rightarrow CH_3Si^+ + D_2$	39.34
24.5	$SiD_2^+ \rightarrow Si^+ + D_2$	24.50
17.4	$CH_3SiD^+ \rightarrow Si^+ + CH_3D$	17.42

[a] $\underline{m}^* = (\underline{m}_{\text{product ion}})^2/\underline{m}_{\text{reactant ion}}$

[b] for the silicon isotope of mass 28

of $CH_2SiH_2^+$ may occur by intramolecular rearrangement of CH_3SiH^+, since resonance stabilisation would tend to render the process energetically favourable. These primary and secondary routes to $CX_2SiX_2^+$ (X = H or D) become distinguishable in the fragmentation of CH_3SiD_3 (equations 1 and 2).

$$[1] \quad CH_3SiD_3 \xrightarrow{-H_C,\ \ -D_{Si}} CH_2SiD_2^+$$

$$[2] \quad CH_3SiD_3 \xrightarrow{-2D_{Si}} CH_3SiD^+ \longrightarrow CH_2SiHD^+$$

Table 1 shows that the loss of four atomic mass units is more important by an order of magnitude than the loss of three. However, the ions at m/e = 45 and 46 in the spectrum of CH_3SiD_3 have virtually identical appearance potentials (Table 2) and rupture of the C–Si bond provides $SiHD^+$ at m/e = 31. Thus, a small but significant proportion of ions at m/e = 45 has the structure CH_2SiHD^+. Analogously, therefore, a small proportion of ions at m/e = 44 in the spectrum of CH_3SiH_3 has the structure $CH_2SiH_2^+$.

The same workers attribute ions of mass 43 formed from CH_3SiH_3 to the structure CH_3Si^+ (on admittedly slender grounds) with a contribution from CH_2SiH^+ above 15.5 eV. In the spectrum of CH_3SiD_3 the ion current at m/e = 44, ($CSiH_2D^+$) exceeds that at m/e = 43 ($CSiH_3^+$). Thus protium loss from carbon appears to have become important, although the situation is confused by the possibility that a proportion of these ions may have been formed in the ion source by secondary processes involving the decomposition of $CH_3SiD_2^+$ (Table 3).

The present work concurs with previous reports that the appearance potential of SiH_2^+ is lower than that of SiH_3^+; similarly, the appearance potential of SiD_2^+ is lower than that of SiD_3^+. The appearance potential of CH_3^+ from CH_3SiH_3 is 15.1eV (4). Thus the formation of SiH_2^+ occurs by the process shown in equation 3.

$$[3] \quad CH_3SiH_3 + e \longrightarrow SiH_2^+ + CH_4 + 2e$$

The formation of SiD_3^+ from CH_3SiD_3 shows that simple carbon-silicon bond cleavage occurs as a minor fragmentation reaction.

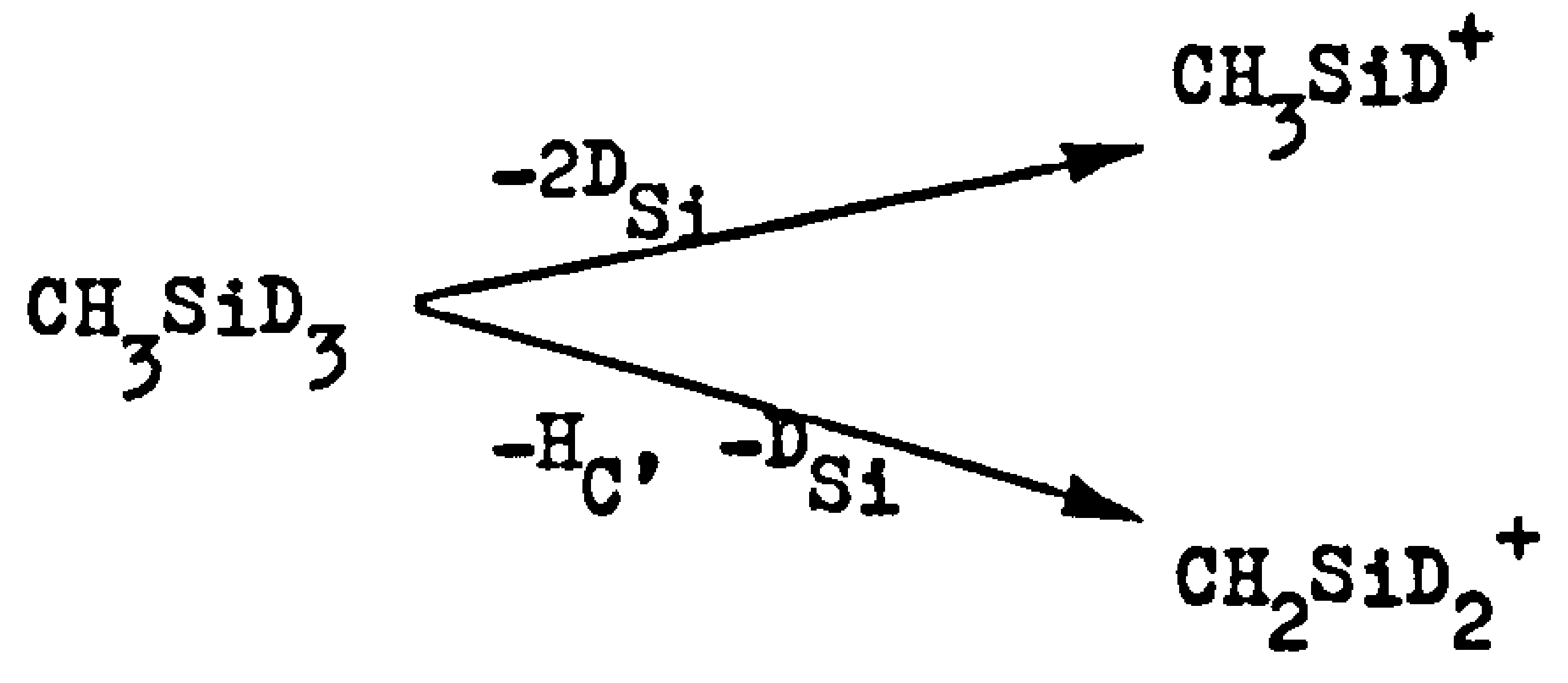
The metastable ions observed (Table 3) reveal that Si^+ originates in decompositions of CH_3SiX^+ and of SiX_2^+ (X = H or D). Such decompositions in the ion source are responsible for the ions at m/e = 28 reported in Table 1 and in Figures 1 and 2.

Analysis of Mixtures

The analysis of mixtures of deuterium-containing methylsilanes by positive ion mass spectrometry presents special difficulties because of the absence of parent ions and the complexity of fragmentation. The necessity of using low-voltage spectra for analytical purposes has been mentioned. In the method described below, the reported spectra of CH_3SiH_3 and of CH_3SiD_3 are used to obtain the fragmentation spectrum of CH_3SiH_2D and of CH_3SiHD_2. A set of equations is derived which describes the composition of each ion current over the m/e range 43-47 for the situation in which all four methylsilanes having protium or deuterium bonded to silicon are present together. Accurate information concerning mixture compositions can be obtained in certain cases, and the deuterium content of samples can be obtained in all cases. 1.

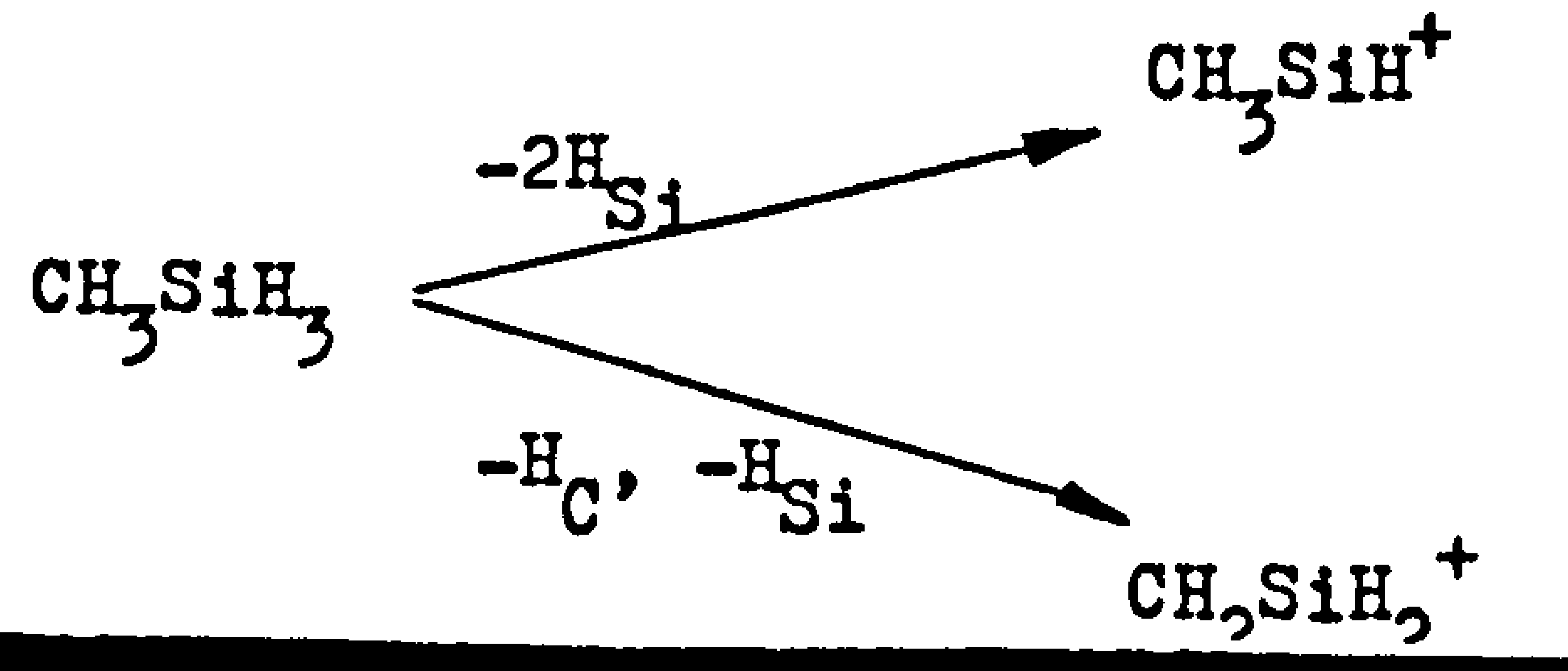
Fragmentation factors are defined as follows. The loss of one H atom bonded to silicon (H_{Si}) from CH_3SiH_3 is accorded the fragmentation factor X. (For example, X = 28.4 at 18.0 eV (Table 1)). Similarly, M represents the fragmentation of CH_3SiD_3 by loss of one deuterium atom.

Fragmentation of CH_3SiD_3 by loss of 2X (X = H or D) gives products distinguishable as to mass (equation 4), whereas the analogous fragmentation of CH_3SiH_3 does not (equation 5). $[CH_3SiH^+]/[CH_2SiH_2^+]$ is

[4]


fragmentation factor = P

fragmentation factor = N

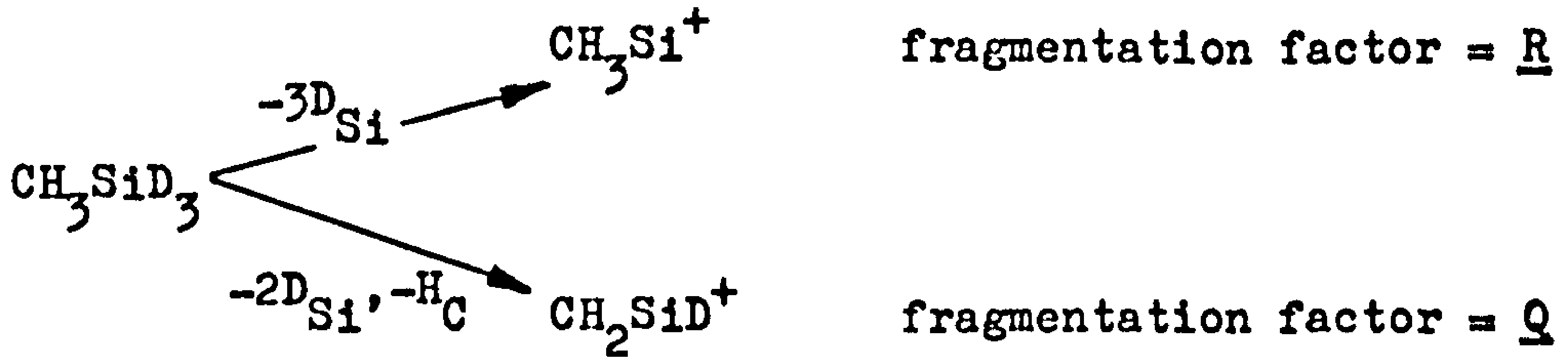
[5]


fragmentation factor = Y

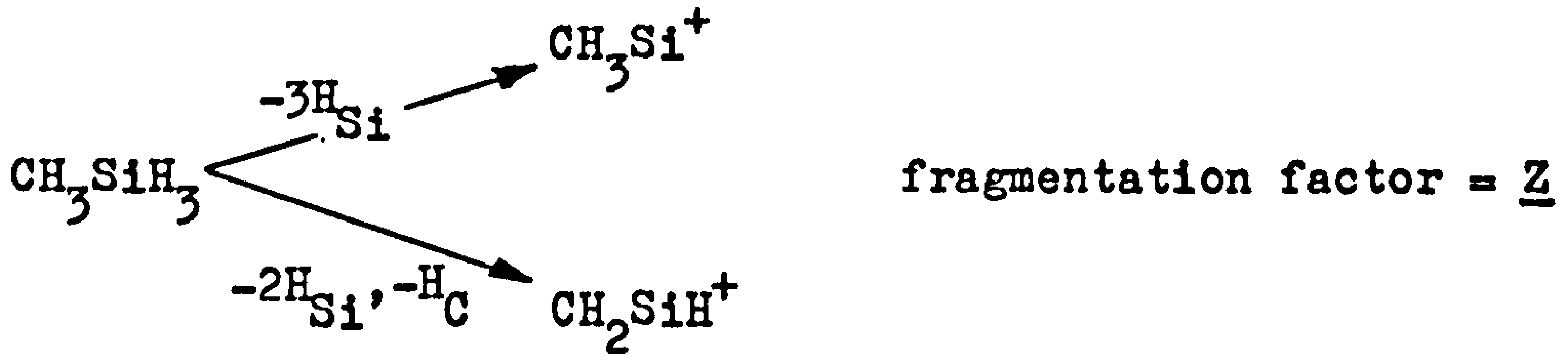
assumed equal to P/N.

Similarly, for fragmentation by overall loss of 3X (X = H or D) the factors are as described in equations 6 and 7 and it is assumed that $[CH_3Si^+]/[CH_2SiH^+] = R/Q$.

[6]



[7]



The fragmentation spectra of CH_3SiH_2D and of CH_3SiHD_2 below have been derived on the assumption that when H-atom loss occurs the relevant factor is that observed for the analogous process in CH_3SiH_3, and *mutatis mutandis* for D-atom loss.

CH_3SiH_2D

$$i_{46} = 2X/3$$
$$i_{45} = M/3 + 2NY/3(N + P) + PY/3(N + P)$$
$$i_{44} = N/3 + PY/3(N + P) + P/3 + QZ/3(Q + R)$$
$$i_{43} = QZ/3(Q + R) + Q/3 + R/3$$

CH_3SiHD_2

$$i_{47} = X/3$$
$$i_{46} = 2M/3 + NY/3(N + P)$$
$$i_{45} = 2N/3 + P/3 + PY/3(N + P)$$
$$i_{44} = P/3 + Q/3 + QZ/3(Q + R)$$
$$i_{43} = Q/3 + 2R/3 + RZ/3(Q + R)$$

Thus, the introduction into the mass spectrometer of a mixture containing CH_3SiH_3, CH_3SiH_2D, CH_3SiHD_2, and CH_3SiD_3 will result in ion currents the composition of which is:

[8a] $\underline{i}_{47} = \underline{a}_{1,1}[CH_3SiH_3] + \underline{a}_{1,2}[CH_3SiH_2D] + \underline{a}_{1,3}[CH_3SiHD_2] + \underline{a}_{1,4}[CH_3SiD_3]$

....

[8e] $\underline{i}_{43} = \underline{a}_{5,1}[CH_3SiH_3] + \underline{a}_{5,2}[CH_3SiH_2D] + \underline{a}_{5,3}[CH_3SiHD_2] + \underline{a}_{5,4}[CH_3SiD_3]$

where $\underline{a}_{\underline{x},\underline{y}}$ are arithmetical expressions involving $\underline{M},\underline{N},\underline{P},\underline{Q},\underline{R},\underline{X},\underline{Y}$, and $\underline{Z}$. Coefficients, $\underline{a}_{\underline{x},\underline{y}}$, derived from the mass spectra of CH_3SiH_3 and CH_3SiD_3 at 18 eV (Table 1) are given in Table 4.

Although the matrix [8] provides five equations containing four unknowns, equations for $\underline{i}_{43}$ and $\underline{i}_{44}$ can be generated from the remainder, and hence solutions in the general case are not obtainable. Nevertheless, solutions can be obtained, and hence useful analyses can be achieved, in the following special cases.

Case 1. Equations 8a, 8b, and 8c allow the composition of a mixture of any two or any three of the components CH_3SiX_3 (X = H or D) to be determined. For example, mass spectrometric analysis of a standard mixture containing 65.8 ± 1.0% CH_3SiH_3 and 34.2 ± 1.0% CH_3SiD_3 gave by use of equations 8 the composition 63.1% CH_3SiH_3 and 36.9% CH_3SiD_3. This is satisfactory agreement in view of the assumptions involved. Similarly, mixtures of CH_3SiH_3 with CH_3SiH_2D and CH_3SiHD_2 obtained by the stepwise exchange of CH_3SiH_3 with molecular deuterium catalysed by metals have been analysed in this way (5).

Case 2. Samples of deuterium-labelled methylsilane may arise by exchange reactions involving CH_3SiH_3 and CH_3SiD_3 as reactants. When the initial ratio of reactants is unity, the rate of formation of CH_3SiH_2D and of CH_3SiHD_2 will be equal, as will the rate of removal of each reactant. The number of unknowns is then reduced to two, equation 8a can be solved simultaneously, with 8b or 8c, and the remaining equation used as a check of the values obtained. Proportions (per cent) determined experimentally for a mixture initially containing 48.0% CH_3SiH_3 and 52.0% CH_3SiD_3 equilibrated over a molybdenum film at 195 K, with equilibrium proportions expected on a statistical basis shown in parenthesis, are: CH_3SiH_3, 11.9, (11.0); CH_3SiH_2D, 35.1, (35.9); CH_3SiHD_2, 38.2, (39.0); CH_3SiD_3, 14.8, (14.1).

TABLE 4. Coefficients $a_{x,y}$ for equations 8a-8e. (Ionisation energy = 18.0 eV)

	$a_{x,1}$	$a_{x,2}$	$a_{x,3}$	$a_{x,4}$
$a_{1,y}$	0.000	0.000	0.118	0.310
$a_{2,y}$	0.000	0.236	0.226	0.062
$a_{3,y}$	0.354	0.301	0.371	0.511
$a_{4,y}$	0.536	0.372	0.215	0.067
$a_{5,y}$	0.110	0.090	0.070	0.049

Finally, an important feature of this analysis is that the deuterium content, ϕ, of <u>any</u> sample containing CH_3SiX_3 (X = H or D) can be determined using equation 9 :

$$[9] \qquad \phi = \underline{i}_{46}/\underline{a}_{2,2} + \underline{i}_{47}(2.000 - \underline{a}_{2,3}/\underline{a}_{2,2})$$

where, following custom(6) ϕ = (% CH_3SiH_2D) + 2(% CH_3SiHD_2) + 3(% CH_3SiD_3). For example, Figure 3 shows the standard function plot(6) for the determination of the first order rate coefficient for the appearance of deuterium in methylsilane during exchange between CH_3SiH_3 and D_2 catalysed by an evaporated molybdenum film at 195 K. The figure shows linear behaviour to 85% conversion, whereas analysis under special case 1 was possible only as far as 20% conversion. Thus it is possible to undertake kinetic investigations of deuterium incorporation into methylsilane under conditions where neither special case illustrated above applies.

We thank the Science Research Council for the award of grants for the purchase of the mass spectrometers and of a maintenance grant (to D.I.B.).

References

1. F.H. FIELD and J.F. FRANKLIN. Electron Impact Phenomena. Academic Press, New York. 1957. p.28.
2. G.P. VAN DER KELEN, O. VOLDERS, H. VAN ONCKELEN, and Z. EECKHAUT. Zeit. fur Anorg. Allgem. Chem. 338, 106 (1965).
3. P. POTZINGER and F.W. LAMPE. J. Phys. Chem. 74, 587, 719 (1970).
4. W.C. STEELE, L.D. NICHOLS, and F.G.A. STONE. J. Am. Chem. Soc. 84, 4441 (1962).
5. D.I. BRADSHAW. Ph.D. thesis. University of Hull. 1975.
6. C. KEMBALL. Advan. Catalysis, 11, 223 (1959).

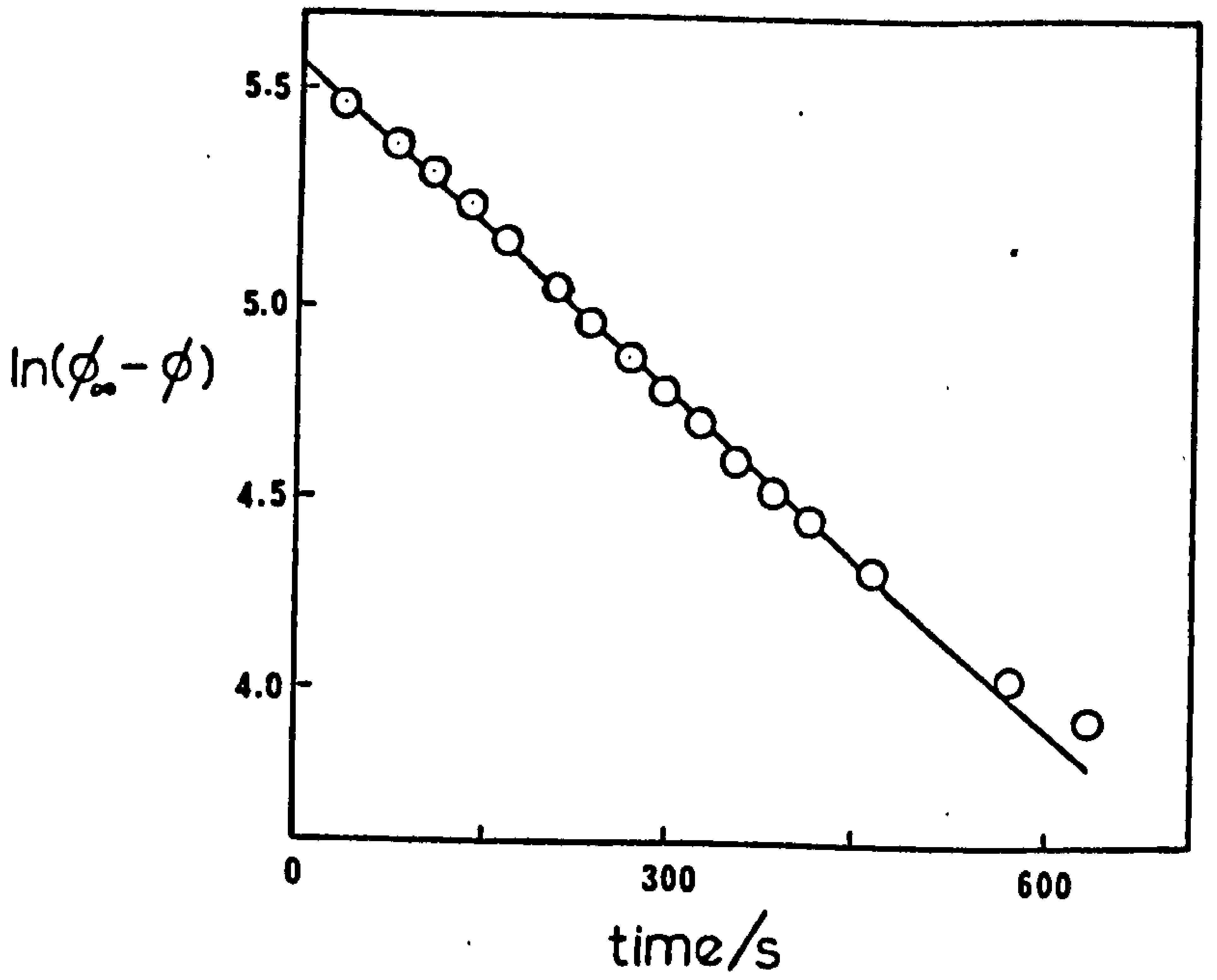


FIG. 3. First order exchange of protium for deuterium in the silyl group of CH_3SiH_3 catalyzed by an evaporated molybdenum film at 195 K. Film weight = 19 mg. Initial pressures of methylsilane = 1 torr and of deuterium = 10 torr. ϕ is defined in the text; ϕ_∞ is the value of ϕ at equilibrium.

APPENDIX C

COMPUTER PROGRAMS

Three computer programs have been written to analyse mass spectra obtained from mutual exchange reactions and from exchange reactions involving molecular deuterium. The programs are stored in following files.

(i) MUTUAL (8). This file provides a means of analysing mass spectra obtained for mutual exchange, and gives as output values of $\ln(d_{03}-d_{03\infty})$. The program makes corrections for the natural abundances of ^{13}C, ^{29}Si, and ^{30}Si.

(ii) D2 (6). This file provides a means of analysing mass spectra obtained for exchange with molecular deuterium. Values of $\ln(\emptyset_{\infty}-\emptyset)$ and of $\ln(d_{0}-d_{0\infty})$ are provided as output, and hence values of $k_{\emptyset}$, k_{0}^{I}, and k_{0}^{II} can be calculated from the gradients of the function plots. The program makes corrections for the natural abundances of ^{13}C, ^{29}Si, and ^{30}Si. Mass spectra, corrected for the presence of the above isotopes, are presented as output and certain results are entered into a newly-created file, which in turn may be used as a source of data for file KEM (18).

(iii) KEM (18). This file provides a means of analysing mass spectra obtained for exchange with molecular deuterium. Values of $\ln(d_0-d_{0\infty})$ are given in the output, and hence a value of k_0^{III} can be calculated from the function plot of $\ln(d_0-d_{0\infty})$ against time. Data for this program are read in from a file created by file D2 (6).

Files D2 (6) and KEM (18) are usually run in conjunction with each other thus:

```
JOB  jobname, :  username
HALGOL  *CR  D2 (6),  SV  D26B,  NORUN
****
JOB  jobname, :  username
HALGOL  *CR  KEM (18),  SV  KEM18B,  NORUN
****
JOB  jobname, :  username
HRUN  LO D26B, *CP RSLT, T1 50, VOL 1500, CONT
HRUN  LO KEM18B, *DATA RSLT, T1 200, VOL 1500
****
```

Files MUTUAL (8), D2 (6), and KEM (18) are listed below.

File MUTUAL(8)

```
'BEGIN'
'INTEGER'A,B,C,N,FRAG,NUMBER,SPECIES,J,DONE,BG,L,M,TWIT,
BIG,ASS,ZZ,LUMBER,EC,UN,G,SET,JJ;
'REAL'F1,F2,F3,S1,S2,DNO,SUM,F,R,Y0,Y1,Y2,Y3,K,RNO,Z,PD,PS,S3,
DE0,DE1,DE2,DE3,
DX,CONST,X1,X4;
'COMMENT'DONE = NO. OF SETS OF DATA TO BE READ.
          ASS IS AN ARBITRARY NUMBER AND IT
          REFERS TO AN ERASED SECTION OF
          PROGRAM (ASS USUALLY IS 10);
'COMMENT' RNO = RUN NO.
          SPECIES = CODE NO. FOR METAL UNDER
          INVESTIGATION(AN INTEGER).
          NUMBER = NO. OF SPECTRA OBTAINED FOR FILM
          UNDER INVESTIGATION;
DONE:=READ;
'FOR'JJ:=1'STEP'1'UNTIL'DONE'DO'
'BEGIN'
ASS:=READ;
RNO:=READ;
SPECIES:=READ;
NUMBER:=READ;
'BEGIN'
'ARRAY'X[1:7],DN,LDN,HN,LHN[1:NUMBER],I,ION[1:NUMBER,1:9],
TI[1:NUMBER],T[1:6],
II,OR[1:6,0:4],Y,DF[1:5];
```

Section A, see file D2(6)

```
Y[1]:=Y[4]:=0.0000;
J:=0;
'FOR'B:=1'STEP'1'UNTIL'NUMBER'DO'
'BEGIN'
DN[B]:=I[B,4]/II[3,2]+
      I[B,5]/II[4,3]*(2-II[3,3]/II[3,2]);
X4:=DN[B]/3;
X1:=100-X4;
PRINT(X1,2,3);PRINT(X4,2,3);        NEWLINE(1);
Y[1]:=Y[1]+X1;
Y[4]:=Y[4]+X4;
'END';
PS:=Y[1];
PD:=Y[4];
        DE0:=PS↑3;
        DE1:=3*PS↑2*PD;
        DE2:=3*PS*PD↑2;
        DE3:=PD↑3;
```

```
    SUM:=DE0+DE1+DE2+DE3;
    DE0:=DE0*100/SUM;
    DE1:=DE1*100/SUM;
    DE2:=DE2*100/SUM;
    DE3:=DE3*100/SUM;
    PRINT(DE0,3,3);
    PRINT(DE1,3,3);
    PRINT(DE2,3,3);
    PRINT(DE3,3,3);
    NEWLINE(5);
CONST:=Y[1]/Y[4];
'FOR'A:=1'STEP'1'UNTIL'4'DO'
  'FOR'B:=1'STEP'1'UNTIL'4'DO'
  OR[A,B]:=II[A,B];
'FOR'A:=2'STEP'1'UNTIL'4'DO'
'BEGIN'
  II[A,2]:=II[A,2]*CONST+II[A,3];
II[A,3]:=II[A,4];
II[A-1,1]:=II[A,1];
II[A-1,2]:=II[A,2];
II[A-1,3]:=II[A,3];
'END';
NEWLINE(5);
SPACE(4);
WRITE TEXT('('%%%%D0%%%%%%D1%%%%%%D2%%%%%%D3%%%')');
WRITE TEXT('('%%%%D0%%%%%%D1%%%%%%D2%%%%%%D3%%%')');
WRITE TEXT('('%LOGD03%%%LOGD0%%%%LOGD3%%%
%TIME%%')');
NEWLINE(1);
'FOR'B:=1'STEP'1'UNTIL'NUMBER'DO'
  'BEGIN'
'FOR'A:=1'STEP'1'UNTIL'3'DO'
II[A,0]:=I[B,A+2];
N:=3;
SOLVE(Y,II,N);
PRINT(B,2,0);
Y[4]:=Y[3];Y[3]:=Y[2];
Y[2]:=Y[3]*CONST;
'FOR'C:=1'STEP'1'UNTIL'4'DO'
PRINT(Y[C],2,2);
SUM:=0.0000;
'FOR'C:=1'STEP'1'UNTIL'4'DO'
SUM:=SUM+Y[C];
'FOR'C:=1'STEP'1'UNTIL'4'DO'
  'BEGIN'
Y[C]:=Y[C]/SUM*100;
PRINT(Y[C],2,2);
'END';
HN[B]:=Y[1]-DE0;
DN[B]:=Y[4]-DE3;
'IF'HN[B]+DN[B]'LT'0.001
'THEN'PRINT(LN(100),2,3)
'ELSE'
PRINT(LN(DN[B]+HN[B]),2,3);
```

```
'IF'HN[B]'LT'0.0001'THEN'HN[B]:=100;
LHN[B]:=LN(HN[B]);
'IF'DN[B]'LT'0.0001'THEN'DN[B]:=100.00;
LDN[B]:=LN(DN[B]);
PRINT(LHN[B],2,3);
PRINT(LDN[B],2,3);
PRINT(TI[B],2,2);
NEWLINE(1);
 'END';
PRINT(LN(PS/(PS+PD)*100-DE0),2,3);
PRINT(LN(PD/(PS+PD)*100-DE3),2,3);
PRINT(LN(100-DE0-DE3),2,3);
NEWLINE(1);
PRINT(PS/(PS+PD)*100-DE0,2,3);
PRINT(PD/(PS+PD)*100-DE3,2,3);
PRINT(100-DE0,2,3);
PRINT(100-DE3,2,3);
PRINT(100-DE0-DE3,2,3);
NEWLINE(5);
'FOR'A:=1'STEP'1'UNTIL'4'DO'
  'FOR'B:=1'STEP'1'UNTIL'4'DO'
  II[A,B]:=CR[A,B];
J:=J+1;
'IF'J=1'THEN'
  'BEGIN'PS:=PS-PS*2/100;
  'END';
'IF'J=2'THEN'
  'BEGIN'PS:=PS+PS*4/100;
  'END';
  'END';
'END';
'END';
'END'
****
```

File D2(6)

```
'INPUT'0=CR0
'OUTPUT'0=LP0
'OUTPUT'1=CP0
'BEGIN'
'INTEGER'A,B,C,N,FRAG,NUMBER,SPECIES,J,DONE,PG,L,M,TWIT,
PIG,ASS,ZZ,LUMBER,EQ,ON,G,SET;
'REAL'F1,F2,F3,S1,S2,DNU,SUM,P,R,Y0,Y1,Y2,Y3,K,RNU,Z,PD,FS,S3,
SIM0,SIM1,SIM2,SIM3,SSM0,SSM3,DE0,DE1,DE2,DE3,Z1,Z2,
GRAD2,GRAD3,DX,CONST,X1,X4,FSS,FDD;
SELECTINPUT(0);
SELECTOUTPUT(1);
DONE:=READ;
PRINT(DONE,2,0);NEWLINE(1);
SELECTOUTPUT(0);
'COMMENT'DONE = NO. OF SETS OF DATA TO
          BE READ.
          ASS IS AN ARBITRARY NUMBER AND
          IT REFERS TO AN ERASED SECTION OF
          PROGRAM (ASS USUALLY IS 10);
'COMMENT'RNO = RUN NO.
          SPECIES = CODE NO.FOR METAL UNDER INVESTIGATION
          (AN INTEGER).
          NUMBER=NO. OF SPECTRA OBTAINED FOR FILM
          UNDER INVESTIGATION;
'FOR'J:=1'STEP'1'UNTIL'DONE'DO'
'BEGIN'
ASS:=READ;
RNO:=READ;
SPECIES:=READ;
NUMBER:=READ;
'BEGIN'
'ARRAY'X[1:7],DN,LDN,HN,LHN,SSB[1:NUMBER],I,ION[1:NUMBER,1:9],
TI[1:NUMBER],T[1:6],F[1:8],IS[0:ASS,1:8],
II[1:6,0:4],Y[1:5],DR[1:5],
MM[1:6,0:4],DISTMEX[1:4];
'COMMENT' SOLVE IS A PROCEDURE FOR
          SOLVING SIMULATENEOUS EQUATIONS;

'COMMENT' START OF SECTION THAT ALSO APPEARS
          IN PROGRAM FOR MUTUAL EXCHANGE
          VIZ. SECTION A;

'PROCEDURE'SOLVE(Y,Q,N);
'VALUE'N,Q;'INTEGER'N;'ARRAY'Q,Y;
'BEGIN'
'INTEGER'I,R,C;'REAL'Z;
'FOR'I:=N-1'STEP'-1'UNTIL'1'DO'
  'FOR'R:=1'STEP'1'UNTIL'I'DO'
    'BEGIN'
    Z:=Q[R,I+1]/Q[I+1,I+1];
    'FOR'C:=0'STEP'1'UNTIL'I'DO'
    Q[R,C]:=Q[R,C]-Q[I+1,C]*Z;
    'END' OF R;
```

```
'FOR'K:=1'STEP'1'UNTIL'N'DO'
  'BEGIN'
  Z:=C[K,0];
  'FOR'I:=K-1'STEP'-1'UNTIL'1'DO'
  Z:=Z-Y[I]*C[K,I];
  Y[K]:=Z/C[K,K];
  'END' OF K;
'END' OF SOLVE;
'COMMENT' FRAG = NO. OF SPECTRA
          OF CH3SIH3 (FRAG. PATTERN).
          PIG = NO. OF SPECTRA OF
          CH3SID3 (FRAG.PATTERN).
          PD = PRESSURE OF DEUTERIUM IN MIXING
          VOLUME AT 77 K.
          PS = PRESSURE OF CH3SIH3 IN MIXING
          VOLUME AT 273 K;
FRAG:=READ;
PIG:=READ;
PD:=READ;
PS:=READ;
R:=280*PD/(77*PS);
WRITE TEXT('('METHYL%SILANE%%%%%%CH3SIH3')');NEWLINE(1);
WRITE TEXT('('SPECTRUM%NUMBER%IS')');
PRINT(RNO,2,3);
NEWLINE(1);
WRITE TEXT('('ATTEMPT%NUMBER%IS')');
PRINT(SPECIES,7,0);
NEWLINE(1);
P:=(R*2*3/(R*2+3))*100;
WRITE TEXT('('DEUTERIUM%:%SILANE%%=')');
PRINT(R,2,2);NEWLINE(1);
WRITE TEXT('('NO.%OFDEUTERIUMS%IN%100%MOLS.%=')');
PRINT(P,2,2);
NEWLINE(5);
SELECTOUTPUT(1);
PRINT(RNO,2,3);   PRINT(SPECIES,7,0);
PRINT(NUMBER,4,0);  PRINT(R,2,3);  NEWLINE(1);
PRINT(P,3,3);    NEWLINE(1);
SELECTOUTPUT(0);
S1:=4.70/92.21;    S2:=3.09/92.21;
S3:=1.11/98.89;
'COMMENT' X[A]=READ....READ IN ALL FRAG
          PATTERNS FOR CH3SIH3 (M/E=43TO 48 INC.);
          'FOR'A:=1'STEP'1'UNTIL'6'DO'
T[A]:=0.0000;
F1:=F2:=F3:=0.0000;
'FOR'B:=1'STEP'1'UNTIL'FRAG'DO'
  'BEGIN'
'FOR'A:=1'STEP'1'UNTIL'6'DO'
X[A]:=READ;
'FOR'A:=2'STEP'1'UNTIL'6'DO'
X[A]:=X[A]-X[A-1]*S3;
  X[2]:=X[2]-S1*X[1];
```

```
  'FOR'A:=3'STEP'1'UNTIL'6'DO'
      'BEGIN'
      X[A]:=X[A]-S1*X[A-1]-S2*X[A-2];
      'END' OF A;
  F1:=F1+X[3];
  F2:=F2+X[2];
  F3:=F3+X[1];
  SUM:=0.00;
  'FOR'C:=1'STEP'1'UNTIL'6'DO'
  SUM:=SUM+X[C];
      'FOR'C:=1'STEP'1'UNTIL'6'DO'
  PRINT(X[C]*10.00/SUM,2,2);
  NEWLINE(1);
  'END'OF FRAG;
'FOR'B:=1'STEP'1'UNTIL'PIG'DO'
  'BEGIN'
'COMMENT' X[A] = READ....READ IN ALL FRAG
          PATTERNS FOR CH3SID3(M/E = 43 TO 49 INC.);
'FOR'A:=1'STEP'1'UNTIL'7'DO'
X[A]:=READ;
'FOR'A:=2'STEP'1'UNTIL'7'DO'
X[A]:=X[A]-X[A-1]*S3;
  X[2]:=X[2]-S1*X[1];
  'FOR'A:=3'STEP'1'UNTIL'7'DO'
      'BEGIN'
      X[A]:=X[A]-S1*X[A-1]-S2*X[A-2];
      'END' OF A;
  'FOR'A:=1'STEP'1'UNTIL'6'DO'
  T[A]:=T[A]+X[A];
  SUM:=0.00;
  'FOR'C:=1'STEP'1'UNTIL'6'DO'
  SUM:=SUM+X[C];
  'FOR'C:=1'STEP'1'UNTIL'6'DO'
  PRINT(X[C]*10.00/SUM,2,2);
  NEWLINE(1);
  'END' OF PIG;
SUM:=0.00;
SUM:=F1+F2+F3;
F1:=F1/SUM;
F2:=F2/SUM;
F3:=F3/SUM;
SUM:=0.00;
'FOR'A:=1'STEP'1'UNTIL'6'DO'
SUM:=SUM+T[A];
'FOR'A:=1'STEP'1'UNTIL'6'DO'
T[A]:=T[A]/SUM;
'FOR'A:=1'STEP'1'UNTIL'NUMBER'DO'
'BEGIN'
TI[A]:=READ;
'COMMENT' TI[A] = TIME AT WHICH MASS
          SPECTRUM RECORDED;
'FOR'B:=1'STEP'1'UNTIL'7'DO'
ION[A,B]:=READ;
'END';
'COMMENT' ION[A,B]....READ IN MASS SPECTRUM
      CORRESPONDING TO TIME TI[A] (M/E = 43 TO 49 INC.);
```

```
'FOR'A:=1'STEP'1'UNTIL'NUMBER'DO'
'BEGIN'
  'FOR'B:=2'STEP'1'UNTIL'7'DO'
  ION[A,B]:=ION[A,B]-S3*ION[A,B-1];
'END';
'FOR'A:=1'STEP'1'UNTIL'NUMBER'DO'
  'BEGIN'
  ION[A,2]:=ION[A,2]-S1*ION[A,1];
  'FOR'B:=3'STEP'1'UNTIL'7'DO'
  ION[A,B]:=ION[A,B]-S1*ION[A,B-1]-S2*ION[A,B-2];
  'END' OF NUMBER;
WRITE TEXT('('%%%%PEAK%HEIGHTS%%%%')');
NEWLINE(1);
WRITE TEXT('('%%%43'('6S')'%44'('7S')'45'('7S')'46
'('7S')'47'('7S')'48'('7S')'49%%%%%%')');
NEWLINE(2);
'FOR'A:=1'STEP'1'UNTIL'NUMBER'DO'
'BEGIN'
SUM:=0.0000;
'FOR'B:=1'STEP'1'UNTIL'7'DO'
  'BEGIN'
I[A,B]:=ION[A,B];
SUM:=SUM+I[A,B];
  'END';
'FOR'B:=1'STEP'1'UNTIL'7'DO'
'BEGIN'
I[A,B]:=I[A,B]*100/SUM;
PRINT(I[A,B],3,2);
'END';.
SPACE(5);
PRINT(A,2,0);
SPACE(5);
PRINT(TI[A],3,2);
NEWLINE(2);
'END';
  NEWLINE(5);
II[1,1]:=F2;
II[1,2]:=(T[3]+F2*T[3]/(T[4]+T[3]))/3+F3*T[2]/3/(T[2]+T[1])
      +T[4]/3;
II[1,3]:=T[3]/3+(T[2]+T[2]*F3/(T[2]+T[1]))/3;
II[1,4]:=T[2];
II[2,1]:=F1;
II[2,2]:=T[5]/3+2*F2/3*T[4]/(T[4]+T[3])+F2/3*T[3]/(T[4]+T[3]);
II[2,3]:=2/3*T[4]+(T[3]+F2*T[3]/(T[4]+T[3]))/3;
II[2,4]:=T[3];
II[3,1]:=0.00;
II[3,2]:=2/3*F1;
II[3,3]:=2/3*T[5]+F2/3*T[4]/(T[4]+T[3]);
II[3,4]:=T[4];
II[4,1]:=0.00;
II[4,2]:=0.00;
II[4,3]:=F1/3;
II[4,4]:=T[5];
II[5,0]:=100;
II[5,1]:=1;
II[5,2]:=1;
```

```
II[5,3]:=1;
II[5,4]:=1;
NEWLINE(5);
  'FOR'A:=1'STEP'1'UNTIL'5'DO'
  'BEGIN'
  'FOR'B:=1'STEP'1'UNTIL'4'DO'
PRINT(II[A,B],2,5);
NEWLINE(1);
 'END';

'COMMENT' END OF SECTION A;

SELECTOUTPUT(1);
'FOR'A:=1'STEP'1'UNTIL'4'DO'
'BEGIN'
'FOR'B:=1'STEP'1'UNTIL'4'DO'
PRINT(II[A,B],2,5);
NEWLINE(1);
'END';
SELECTOUTPUT(0);
NEWLINE(1);
WRITE TEXT('('%%B%%%%%%DN%%%LN(PHI)%%COEFF%%%%%TIME%%%%%LN(D0)
%%%%D0%%%%%D1%%%%%%%%D2%%%%%%D3%%%%%%')');
NEWLINE(1);
'FOR'B:=1'STEP'1'UNTIL'NUMBER'DO'
'BEGIN'
DN[B]:=I[B,4]/II[3,2]+I[B,5]/II[4,3]*(2-II[3,3]/II[3,2]);
PRINT(B,2,0);
PRINT(DN[B],2,3);
'IF'DN[B]'GT'P'THEN'DN[B]:=0.00;
PRINT(LN(P-DN[B]),2,3);
PRINT(II[3,4]/II[3,2]+II[4,4]/II[4,3]*(2-II[3,3]/II[3,2]),1,3);
PRINT(TI[B],3,2);
SELECTOUTPUT(1);
'FOR'A:=1'STEP'1'UNTIL'7'DO'
  PRINT(I[B,A],3,3);
PRINT(TI[B],3,3);
PRINT(DN[B],3,3);   NEWLINE(1);
SELECTOUTPUT(0);
PSS:=300-DN[B];
PDD:=DN[B];
        DE0:=PSS↑3;
        DE1:=3*PSS↑2*PDD;
        DE2:=3*PSS*PDD↑2;
        DE3:=PDD↑3;
        SUM:=DE0+DE1+DE2+DE3;
        DE0:=DE0*100/SUM;
        DE1:=DE1*100/SUM;
        DE2:=DE2*100/SUM;
        DE3:=DE3*100/SUM;
        PRINT(LN(DE0),2,3);
        PRINT(DE0,3,2);
        PRINT(DE1,2,2);
        PRINT(DE2,2,2);
        PRINT(DE3,2,2);
'FOR'A:=1'STEP'1'UNTIL'4'DO'
DISTMEX[A]:=DE0*II[A,1]
            +DE1*II[A,2]+DE2*II[A,3]
            +DE3*II[A,4];
```

```
'FOR'A:=1'STEP'1'UNTIL'4'DO'
  PRINT(DISTMEX[A],2,2);
SSEP[B]:=0.00;
'FOR'A:=2'STEP'1'UNTIL'4'DO'
SSEP[B]:=SSEP[B]+(I[B,A+1]-DISTMEX[A])↑2;
SPACE(2);  PRINT(SSEP[B],2,2);
NEWLINE(1);
'END';
'FOR'A:=2'STEP'1'UNTIL'4'DO'
'FOR'B:=1'STEP'1'UNTIL'3'DO'
  MM[A-1,B]:=II[A,B];
NEWLINE(5);
SPACE(4);
WRITE TEXT('('%%%D0%%%%%%D1%%%%%%D2%%%%%%D3%%%')');
WRITE TEXT('('%%%D0%%%%%%D1%%%%%%D2%%%%%%D3%%%')');
NEWLINE(1);
Y[4]:=0.00;
'FOR'B:=1'STEP'1'UNTIL'NUMBER'DO'
  'BEGIN'
'FOR'A:=1'STEP'1'UNTIL'3'DO'
MM[A,0]:=I[B,A+2];
N:=3;
SOLVE(Y,MM,N);
PRINT(B,2,0);
'FOR'C:=1'STEP'1'UNTIL'4'DO'
PRINT(Y[C],2,2);
SUM:=0.0000;
'FOR'C:=1'STEP'1'UNTIL'4'DO'
'BEGIN'
'IF'Y[C]'LT'0.00'THEN'Y[C]:=0.00;
SUM:=SUM+Y[C];
'END';
'FOR'C:=1'STEP'1'UNTIL'4'DO'
  'BEGIN'
Y[C]:=Y[C]/SUM*100;
PRINT(Y[C],2,2);
'END';
HN[B]:=Y[1];
'IF'HN[B]'LT'0.0001'THEN'HN[B]:=100;
LHN[B]:=LN(HN[B]);
DN[B]:=Y[2]+2*Y[3];
'IF'P'LT'DN[B]'THEN'DN[B]:=0.0000;
LDN[B]:=LN(P-DN[B]);
PRINT(LHN[B],2,3);
PRINT(LDN[B],2,3);
PRINT(DN[B],2,2);
PRINT(TI[B],2,2);
NEWLINE(1);
Y[4]:=0.0000;
 'END';
PRINT(LN(P),2,3);
PRINT(LN(100.00),2,3);
NEWLINE(10);
  'END';
'END';
'END';
'END'
****
```

File KEM(18)

```
'BEGIN'
'COMMENT'THIS FILE IS RUN AFTER FILE
         D2(6).D2(6) CREATES A DATA FILE
         THAT SUPPLIES THIS FILE WITH THE
         REQUIRED DATA;

'INTEGER'A,B,C,J,DONE,NUMBER,SET,SPECIES,ALPHA,BETA,GAMMA,
COUNT,AB,N;
'REAL'SSPE,ESSPE,RNO,STEP,TOL,HH,DD,DNU,PHI,DDATA,M,SUM,
FAC2,FAC5,FAC10,
  A1,B1,G1,X0,X1,X2,X3,DN,DN1,DN2,FAC,F,SUM1,D,H,DADD;
'ARRAY'X[0:3],Z0,Z1,Z2,Z3,I[1:4],II[1:6,0:4],
CD0,CD1,CD2,CD3[1:3,0:3],Y0,Y1,Y2,Y3[1:4],XX,TX[0:3];
'COMMENT' DONE = NO. OF SETS OF DATA TO BE READ.
         ASS IS AN ARBITRARY NUMBER AND IT
         REFERS TO AN ERASED SECTION OF
         PROGRAM (ASS USUALLY IS 10).
         RNO = RUN NO.
         SPECIES = CODE NO. FOR METAL UNDER
         INVESTIGATION (AN INTEGER).
         NUMBER = NO. OF SPECTRA OBTAINED FOR
         FILM UNDER INVESTIGATION;
'COMMENT' DDATA = RATIO OF CH3SIH3 TO DEUTERIUM.
         DN = PHI INFINITY;
DONE:=READ;
'FOR'J:=1'STEP'1'UNTIL'DONE'DO'
'BEGIN'
RNO:=READ;
SPECIES:=READ;
NUMBER:=READ;
DDATA:=READ;
DN:=READ;
WRITE TEXT('('SPECTRUM%NUMBER%IS%')');PRINT(RNO,3,3);
NEWLINE(1);
WRITE TEXT('('ATTEMPT%NUMBER%IS%')');
PRINT(SPECIES,7,0);NEWLINE(1);
WRITE TEXT('('DEUTERIUM:CH3SIH3%=%')');
PRINT(DDATA,2,2);NEWLINE(1);
WRITE TEXT('('NUMBER%OF%DEUTERIUMS%IN%100%MOLS.%AT%
EQUILIB.%=%')');
PRINT(DN,3,2);NEWLINE(5);
'BEGIN'
'ARRAY'ION[1:NUMBER,1:7],TI[1:NUMBER];

'PROCEDURE'SOLVE(Y,C,N);
'VALUE'N,C;'INTEGER'N;'ARRAY'C,Y;
'BEGIN'
'INTEGER'I,K,C;'REAL'Z;
'FOR''I:=N-1'STEP'-1'UNTIL'1'DO'
  'FOR'K:=1'STEP'1'UNTIL'I'DO'
    'BEGIN'
    Z:=C[K,I+1]/C[I+1,I+1];
    'FOR''C:=0'STEP'1'UNTIL'I'DO'
    C[K,C]:=C[K,C]-C[I+1,C]*Z;
    'END' OF K;
```

```
'FOR'R:=1'STEP'1'UNTIL'N'DO'
   'BEGIN'
   Z:=Q[R,0];
   'FOR'I:=R-1'STEP'-1'UNTIL'1'DO'
   Z:=Z-Y[I]*Q[R,I];
   Y[R]:=Z/Q[R,R];
   'END' OF R;
'END' OF SOLVE;

'COMMENT' II[A,C] ARE COEFFICIENTS FOR
DESCRIBING MASS SPECTRUM OF METHYLSILANES;
'FOR'A:=1'STEP'1'UNTIL'4'DO'
'FOR'C:=1'STEP'1'UNTIL'4'DO'
II[A,C]:=READ;
ALPHA:=10.00;
BETA:=GAMMA:=0.00;
'FOR'B:=1'STEP'1'UNTIL'NUMBER'DO'
'BEGIN'
BSSPE:=0.00;
SET:=0;
STEP:=100.00;
TOL:=1.00;
X[0]:=100.00;
DD:=DDATA*100.00*2;
WRITE TEXT('('NUMBER%=%%')');
PRINT(B,2,0);         SPACE(5);
PRINT(DD,3,2);     SPACE(4);
HH:=0.00;
PRINT(P,2,0);          NEWLINE(1);
'COMMENT' IUN[B,C].....READ IN MASS SPECTRUM
          CORRESPONDING TO TIME TI[B](M/E=43 TO 49);
'FOR'C:=1'STEP'1'UNTIL'7'DO'
    IUN[B,C]:=READ;
'FOR'C:=3'STEP'1'UNTIL'5'DO'
    BSSPE:=BSSPE+IUN[B,C]↑2;
PRINT(BSSPE,4,2);     NEWLINE(1);
DNU:=0.00;
'COMMENT' TI[B] = TIME AT WHICH MASS
          SPECTRUM WAS RECORDED.
          PHI = DEUTERIUM CONTENT OF MASS SPECTRUM;
TI[B]:=READ;
PHI:=READ;
'IF'PHI'LT'70.0'THEN'
    'BEGIN'
    ALPHA:=10.00;BETA:=GAMMA:=0.00;
    'END';
X0:=X1:=X2:=X3:=0.00;
X[1]:=X[2]:=X[3]:=0.00;
AR;=0;
COUNT:=0;
'IF'PHI'GT'150'THEN'TOL:=1.18;
P:=0;
AGAIN:
  'IF'(PHI+5)'GT'DN'THEN''GOTO'NOSOL;

X[0]:=100.0;
X[1]:=X[2]:=X[3]:=0.00;
DNU:=0.00;
FAC:=0.01;
```

```
DD:=DDATA*100.00*2;
HH:=0.00;
FAC2:=FAC*2;
FAC5:=FAC*5;
FAC10:=FAC*10;
START:
'IF'DNU'GT'50'THEN'FAC:=FAC2;
 'IF'DNU'GT'150'THEN'FAC:=FAC5;
 'IF'DNU'GT'220'THEN'FAC:=FAC10;
H:=HH/(HH+DD);
D:=DD/(HH+DD);
QD0[1,0]:=1/(1+D*P);
QD0[1,1]:=1.0;
QD0[1,2]:=-0.5*H*P/(1+D*P);
QD0[1,3]:=0.0;
QD0[2,0]:=0.0;
QD0[2,1]:=-D*P/(1+0.5*P);
QD0[2,2]:=1.0;
QD0[2,3]:=-H*P/(1+0.5*P);
QD0[3,0]:=0.00;
QD0[3,1]:=0.00;
QD0[3,2]:=-0.5*D*P/(1+H*P);
QD0[3,3]:=1.00;
QD1[1,0]:=1/6/(1+D*P);
QD1[2,0]:=1/3/(1+0.5*P);
QD1[3,0]:=0.00;
QD2[1,0]:=0.00;
QD2[2,0]:=QD1[2,0];
QD2[3,0]:=QD1[1,0];
QD3[1,0]:=QD3[2,0]:=0.00;
QD3[3,0]:=1.00;
'FOR'A:=1'STEP'1'UNTIL'3'DO'
'FOR'C:=1'STEP'1'UNTIL'3'DO'
QD1[A,C]:=QD2[A,C]:=QD3[A,C]:=QD0[A,C];
N:=3;
'FOR'A:=1'STEP'1'UNTIL'3'DO'
'FOR'C:=0'STEP'1'UNTIL'3'DO'
'BEGIN'
QD1[A,C]:=QD1[A,C]*2;
QD2[A,C]:=QD2[A,C]*2;
'END';
SOLVE(Y0,QD0,N);
SOLVE(Y1,QD1,N);
SOLVE(Y2,QD2,N);
SOLVE(Y3,QD3,N);
SUM:=0.00;
SUM:=X[0]+X[1]+X[2]+X[3];
Z0[1]:=Y0[1]*H;
Z0[2]:=Y0[2]*H+Y0[1]*D;
Z0[3]:=Y0[3]*H+Y0[2]*D;
Z0[4]:=Y0[3]*D;
Z1[1]:=Y1[1]*H;
Z1[2]:=Y1[2]*H+Y1[1]*D;
Z1[3]:=Y1[3]*H+Y1[2]*D;
Z1[4]:=Y1[3]*D;
Z2[1]:=Y2[1]*H;
Z2[2]:=Y2[2]*H+Y2[1]*D;
```

```
Z2[3]:=Y2[3]*H+Y2[2]*D;
Z2[4]:=Y2[3]*D;
Z3[1]:=Y3[1]*H;
Z3[2]:=Y3[2]*H+Y3[1]*D;
Z3[3]:=Y3[3]*H+Y3[2]*D;
Z3[4]:=Y3[3]*D;
'FOR'A:=1'STEP'1'UNTIL'4'DO'
'BEGIN'
Y0[A]:=Z0[A];     Y1[A]:=2*Z1[A];
Y2[A]:=2*Z2[A];     Y3[A]:=Z3[A];
'END';
'FOR'A:=1'STEP'1'UNTIL'4'DO'
'BEGIN'
  Y0[A]:=Y0[A]*X[0]/SUM;
  Y1[A]:=Y1[A]*X[1]/SUM;
  Y2[A]:=Y2[A]*X[2]/SUM;
  Y3[A]:=Y3[A]*X[3]/SUM;
XX[A-1]:=Y0[A]+Y1[A]+Y2[A]+Y3[A];
'END';
SUM:=0.00;
'FOR'A:=1'STEP'1'UNTIL'4'DO'
SUM:=SUM+XX[A-1];
'IF'SUM'LT'0.000011'THEN'SUM:=1.00;
DN1:=DN2:=0.00;
'FOR'A:=0'STEP'1'UNTIL'3'DO'
'BEGIN'
XX[A]:=XX[A]*100/SUM;
DN2:=DN2+A*XX[A];
'END';
'FOR'A:=0'STEP'1'UNTIL'3'DO'
TX[A]:=X[A]*FAC;
SUM1:=0.00;
'FOR'A:=0'STEP'1'UNTIL'3'DO'
SUM1:=SUM1+TX[A];
'IF'SUM1'LT'0.00001'THEN'SUM1:=1.00;
'FOR'A:=0'STEP'1'UNTIL'3'DO'
'BEGIN'
TX[A]:=TX[A]*100/SUM1;
DN1:=DN1+A*TX[A];
'END';
'FOR'A:=0'STEP'1'UNTIL'3'DO'
X[A]:=X[A]-(TX[A]-XX[A])*SUM1/100;
DADD:=(DN2-DN1)*SUM1/100;
DD:=DD-DADD;
HH:=HH+DADD;
DNU:=X[1]+2*X[2]+3*X[3];
'IF'DNU'LT'PHI'THEN''GOTO'START;
AB:=AB+1;
'FOR'C:=1'STEP'1'UNTIL'4'DO'
I[C]:=0.00;
'FOR'C:=1'STEP'1'UNTIL'4'DO'
'FOR'A:=1'STEP'1'UNTIL'4'DO'
I[C]:=I[C]+X[A-1]*II[C,A];
SSPE:=0.00;
'FOR'C:=2'STEP'1'UNTIL'4'DO'
  SSPE:=SSPE+(IUN[B,C+1]-I[C])↑2;
SET:=SET+1;
```

```
'IF'SSPE'GT'BSSPE'THEN'
  'BEGIN'
COUNT:=COUNT+1;
  X[0]:=X0;X[1]:=X1;X[2]:=X2;X[3]:=X3;
ALPHA:=A1;BETA:=B1;GAMMA:=G1;
  'END';
'IF'SSPE'GT'BSSPE'THEN''GOTO'IT;
'IF'SSPE'LT'BSSPE'THEN'
  'BEGIN'
'IF'ABS(BSSPE-SSPE)'LT'0.015'THEN'AB:=10;
  BSSPE:=SSPE;
  'END';
'IF'SSPE'LT'TUL'THEN''GOTO'IT;
'IF'AB'GT'10'THEN''GOTO'IT;
'FOR'C:=0'STEP'1'UNTIL'3'DO'
  X[C]:=0.00;
X[0]:=100.00;
DNO:=0.00;
DD:=DDATA*100.00*2;
HH:=0.00;
'IF'COUNT'GT'3'THEN''GOTO'IT;

'IF'P'LT'1.0'THEN'P:=P+0.2
'ELSE'P:=P+0.4;
'GOTO'AGAIN;
    NOSOL:
  WRITE TEXT('('NO%SOLUTION')');
NEWLINE(1);
'GOTO''BYPASS;
IT:
PRINT(P,2,3);
'FOR'A:=0'STEP'1'UNTIL'3'DO'
PRINT(XX[A],2,3);
'IF'P'GT'3.5'THEN''GOTO'NOSOL;
NEWLINE(1);
WRITE TEXT('('BSSPE%=%')');
  PRINT(BSSPE,2,2);
  SPACE(5); PRINT(DD,3,2);PRINT(HH,3,2);PRINT(STEP,3,2);
PRINT(P,1,2);PRINT(DADD,2,3);
  NEWLINE(1);
NEWLINE(2);
WRITE TEXT('('I[C]%=%%')');
'FOR'C:=1'STEP'1'UNTIL'4'DO'
PRINT(I[C],2,2);
WRITE TEXT('('%%%%%%X[C]%=%%')');
'FOR'C:=1'STEP'1'UNTIL'4'DO'
PRINT(X[C-1],3,2);
NEWLINE(1);   SPACE(40);
SUM:=0.0000;
WRITE TEXT('('%%X[C]%=%')');
'FOR'C:=0'STEP'1'UNTIL'3'DO'
  SUM:=SUM+X[C];
'FOR'C:=0'STEP'1'UNTIL'3'DO'
  PRINT(X[C]/SUM*100.0,3,2);
  NEWLINE(2);
```

```
WRITE TEXT('('LN(D0)%=%')');
PRINT(LN(X[0]),2,3);
WRITE TEXT('('%%%TIME%=%')');
PRINT(TI[B],3,2);
  BYPASS:COUNT:=0;
NEWLINE(5);
  'END' OF NUMBER;
'END' OF BLOCK;
'END' OF DONE;
'END'
****
```

REFERENCES

1. G.C.A. Schuit and L.L. van Reijen, Adv.Catalysis, 10, 242 (1958).
2. D.O. Hayward and B.M.W. Trapnell, in "Chemisorption", Butterworths, London (1964).
3. D. Brennan and F.H. Hayes, Trans.Faraday Soc., 60, 589 (1964).
4. J.W. Geus, in "Chemisorption and Reaction on Metallic Films" (J.R. Anderson, ed.), Academic Press, London and New York, Vol. 1, p.327 (1971).
5. P.W. Selwood, J.Amer.Chem.Soc., 79, 4637 (1957).
6. M.L. Hair, in "Infrared Spectroscopy in Surface Chemistry", Marcel Dekker, New York (1967).
7. J.F. Harrod, R.W. Roberts, and E.F. Rissmann, J.Phys.Chem., 71, 343 (1967).
8. G. Blyholder and L.D. Neff, J.Phys.Chem., 66, 1464 (1962).
9. R.P. Eischens and W.A. Pliskin, Adv.Catalysis, 10, 1 (1958).
10. J. Fahrenfort and H.F. Hazebroeck, Z.phys.Chem. (Frankfurt), 29, 105 (1959).
11. A. Pentenero, Catal.Rev., 5, 199 (1971).
12. C.R. Brundle, Surface Sci., 48, 99 (1975).
13. W.N. Delgass, T.R. Hughes, and C.S. Fadley, Catal.Rev., 4, 179 (1970).
14. B.F. Lewis, M. Mosesman, and W.H. Weinberg, Surface Sci., 41, 142 (1974).

15. K.C. Campbell and S.J. Thomson, Progress in Surface and Membrane Science, 9, 163 (1975).

16. See ref. 25.

17. C. Kemball, Proc.Roy.Soc., A207, 539 (1951).

18. C. Kemball, Proc.Roy.Soc., A217, 376 (1953).

19. J.R. Anderson and C. Kemball, Proc.Roy.Soc., A223, 361 (1954).

20. C. Kemball, Proc.Roy.Soc., A223, 377 (1954).

21. C. Kemball and F.J. Wolf, Trans.Faraday Soc., 51, 1111 (1955).

22. R.L. Wilson and C. Kemball, J.Catal., 3, 426 (1964).

23. P. Kieran and C. Kemball, J.Catal., 4, 380 (1965).

24. J.R. Anderson and B.G. Baker, in "Chemisorption and Reaction on Metallic Films", (J.R. Anderson, ed.), Academic Press, London and New York, Vol. 2, p. 64 (1971).

25. K. Baron, Ph.D. Thesis, University of Hull (1971).

26. G.C. Bond, P.A. Sermon, G. Webb, D. A. Buchanan, and P.B. Wells, J.C.S. Chem.Comm., 444 (1973).

27. D.A. Buchanan and G. Webb, J.C.S. Faraday I, 71, 134 (1975).

28. D.R. Ramanarao, Ph.D. Thesis, University of Hull (1975).

29a. K. Morikawa, W.S. Benedict, and H.S. Taylor, J.Amer. Chem.Soc., 57, 592 (1935).

29b. K. Morikawa, W.S. Benedict, and H.S. Taylor, J.Amer. Chem.Soc., 58, 1445 (1936).

30. D.W. McKee and F.J. Norton, J.Phys.Chem., 68, 481 (1964).

31. D.W. McKee and F.J. Norton, J.Catal., 3, 252 (1964).

32. D.W. McKee, Trans.Faraday Soc., 61, 2273 (1965).

33. D.W. McKee and F.J. Norton, J.Catal., 4, 510 (1965).

34. D.W. McKee and F.J. Norton, J.Phys.Chem., 70, 525 (1966).

35. A. Frennet, G. Liennard, and G. Verhaegen, J.Res.Inst.Catal., Hokkaido Univ., 16, 115 (1968).

36. C. Kemball, Catal.Rev., 5, 33 (1971).

37. A. Frennet, Catal.Rev., 10, 37 (1974).

38. J.M. Cece and R.D. Gonzalez, J.Catal., 28, 260 (1973).

39. J.L. Carter, J.A. Cusumano, and J.H. Sinfelt, J.Phys.Chem., 70, 2257 (1966).

40. J.R. Anderson and R.J. Macdonald, J.Catal., 13, 345 (1969).

41. J.L. Speier, J.A. Webster, and G.H. Barnes, J.Amer.Chem.Soc., 79, 974 (1957).

42. V.A. Ponomarenko, G.V. Odabashyan, and A.D. Petrov, Doklady Akad. Nauk S.S.S.R., 131, 321 (1960).

43. J.W. Ryan and J.L. Speier, J.Amer.Chem.Soc., 86 895 (1964).

44. L.H. Sommer, J.E. Lyons, and H. Fujimoto, J.Amer.Chem.Soc., 91, 7051 (1969).

45. M.W. Roberts and J.R.H. Ross, J.C.S. Faraday I, 68, 221 (1972).

46. J.R.H. Ross, M.W. Roberts, and C. Kemball, J.C.S. Faraday I, 68, 914 (1972).

47. A.E. Finholt, A.C.Bond, K.E. Wilzbach, and H.I. Schlesinger, J.Amer.Chem.Soc., 69, 2692 (1947).

48. O. Beeck, A.E. Smith, and A. Wheeler, Proc.Roy.Soc., A177, 62 (1940).

49. H. v. Ubisch, Anal.Chem., 24, 931 (1952).

50a. G.C. Bond, in "Catalysis by Metals", Academic Press, London and New York, p. 188 (1962).

50b. See ref. 17.

51. C. Kemball, Adv.Catalysis, 11, 223 (1959).

52. R.W. Roberts, Trans.Faraday Soc., 58, 1159 (1962).

53. B.M.W. Trapnell, Trans.Faraday Soc., 52, 1618 (1956).

54. P.G. Wright, P.G. Ashmore, and C. Kemball, Trans.Faraday Soc., 54, 1692 (1958).

55. G.L. Kington and J.M. Holmes, Trans.Faraday Soc., 49, 417 (1953).

56. Y. Delaunois, A. Frennet, and G. Lienard, J.Chim.phys., 64, 572 (1967).

57. G.C. Bond, in "Catalysis by Metals", Academic Press, London and New York, p. 37 (1962).

58. D.O. Hayward and B.M.W. Trapnell, in "Chemisorption", Butterworths, London, p. 24 (1964).

59. R.J. Mikovsky, M. Boudart, and H.S. Taylor, J.Amer.Chem.Soc., 76, 3814 (1954).

60. J.R. Anderson and B.G. Baker, in "Chemisorption and Reactions on Metallic Films" (J.R. Anderson, ed.), Academic Press, London and New York, Vol. 2, p.1 (1971).

61. L.C. Pauling, "The Nature of the Chemical Bond", Cornell University Press, New York (1948).

62. W.C. Steele, L.D. Nichols, and F.G.A. Stone, J.Amer.Chem.Soc., 84, 4441 (1962).

63. J.A. Kerr, Chem.Rev., 66, 465 (1966).

64. D.M. Golden and S.W. Benson, Chem.Rev., 69, 125 (1969).

65. K. Obi, H.S. Sandhu, and O.P. Strausz, J.Phys.Chem., 76, 3911 (1972).

66. M.D. Curtis, J.Organomet.Chem., 60, 63 (1973).

67. D.I. Bradshaw, R.B. Moyes, and P.B. Wells, unpublished work.

68. C.S. Cundy, B.M. Kingston, and M.F. Lappert, Adv. Organomet.Chem., 11, 253 (1973).