adsorption by not more than about 1.0 kcal. Assuming a symmetrical potential energy barrier, this means that ΔH^* for adsorption will increase by about 0.5 kcal. when the pressure increases tenfold, and at $-100°$ the value of k is reduced by $10^{0.6}$. Under these conditions $(1 - \theta)^2 k$ therefore varies as $p^{-0.4} \times p^{-0.6}$, *i.e.*, as p^{-1}. The rate is therefore independent of p, *i.e.*, the kinetics are zero order.

A consideration of the reaction along these lines, taking into account the pressure variations of $1 - \theta$ and k, therefore leaves no difficulty in connection with the orders of reaction of close to zero that were observed experimentally. The variation in $(1 - \theta)^2 k$ that was deduced above represents the highest that is to be expected, so that under certain conditions the order will be higher. Smaller variations in $(1 - \theta)^2 k$ are to be expected the higher is θ, *i.e.*, at lower temperatures or higher pressures. It would therefore be predicted that the order will tend to increase at lower temperatures or higher pressures and this appears to be the case.

The plausibility of this interpretation of the reaction may be checked by an order of magnitude calculation of the rate at $-100°$ and a pressure of 1 mm. The rate is given by eq. (10) of the previous paper[15] and it will be assumed that $f_{\ddagger} = f_a$. The partition function for parahydrogen is 3.4×10^{23} at this temperature. The surface is about 90% covered, so that the concentration of bare single sites, c_s, is equal to $L(1 - \theta) = 10^{14}$ sites per sq. cm.; the coördination number s is assumed to be 4. Using these values the rate of the conversion is calculated to be

$$v = 6.0 \times 10^{18}\, e^{-E_1/RT} \text{ molecules cm.}^{-2} \text{ sec.}^{-1}$$

This is consistent with the experimental value of 2.1×10^{18} if there is a small activation energy.

(15) K. J. Laidler, THIS JOURNAL, **57**, 318 (1953).

This conclusion is to be contrasted with that of Couper and Eley[11] who, as discussed in the preceding paper,[15] employ an incorrect equation for calculating the absolute rate.

It may be concluded from the above that there is no major difficulty in interpreting the conversion on the basis of the Bonhoeffer–Farkas mechanism.

The Rideal Mechanism.—It does not seem possible to account for the results on the basis of the Rideal mechanism, as has also been concluded by Trapnell. If the reaction occurred between an adsorbed atom and a molecule in the gas phase the rate would be proportional to θkp. Now since the surface is fairly fully covered θ varies only very slightly with p, so that θkp varies approximately as $p^{-0.6} \times p = p^{0.4}$. It therefore is not possible to interpret on this basis the experimental orders which are close to zero. A lower pressure dependence may be obtained by assuming the hydrogen molecule to be adsorbed in a van der Waals layer, but the coverage in the second layer has to be quite considerable. Such a high coverage is not reasonable in view of the low adsorption heats for a van der Waals layer.

Absolute rate calculations also render this type of mechanism unlikely. The rate is now found to be $10^{20}\, e^{-E/RT}$ and this requires an activation energy of about 1.5 kcal. for agreement with the data. This is too low for this type of mechanism, involving the dissociation of a hydrogen molecule by interaction with an adsorbed hydrogen atom; a value of 7 kcal. applies to the reaction $H + p\text{-}H_2 \rightarrow o\text{-}H_2 + H$ even when the reacting atom is free and the Rideal mechanism should require a value at least as great as this.

The author is much indebted to Dr. B. M. W. Trapnell for valuable discussions and suggestions in connection with this paper.

MOLECULAR KINETICS AND MECHANISM OF METHANE-DEUTERIUM EXCHANGE REACTIONS ON NICKEL

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The data of Kemball on the methane–deuterium exchange on evaporated nickel are discussed, mechanisms are formulated, and absolute rate equations derived. CH_3D is considered to be formed from adsorbed CH_3 and D, and the rate of production of CH_3D is shown to be approximately equal to the rate of adsorption of methane as methyl radicals. CH_2D_2, CHD_3 and CD_4 are considered to be formed by reaction between adsorbed methylene radicals and adsorbed deuterium atoms, and a treatment is given for the relevant statistical factors. Calculated rates for all four processes are in excellent agreement with the experimental ones.

Introduction

The object of the present paper is to consider recent data on the surface-catalyzed exchange reactions between methane and deuterium, to propose definite mechanisms, to formulate expressions for absolute rates, and to check the mechanisms by means of rate calculations.

The exchange reactions between methane and deuterium have recently been the object of careful experimental study by Kemball,[1] who used evaporated nickel surfaces. He measured the rates of formation of CH_3D, CH_2D_2, CHD_3 and CD_4, and determined an activation energy for each process. All of the rates were found to be proportional to the first power of the methane pressure. The rate of formation of CH_3D is inversely proportional to the square root of the deuterium pressure, while the rates of formation of CH_2D_2, CHD_3 and CD_4 are inversely proportional to the first power of the deuterium pressure. As suggested by Kemball, this result implies that the methyl radicals do not

(1) C. Kemball, *Proc. Roy. Soc. (London)*, **B207**, 539 (1951).

TABLE I

RATES OF FORMATION OF CH_2D_2, CHD_3 AND CD_4 AT 500°K.

		Rate (molecules mg.$^{-1}$ sec.$^{-1}$ × 10^{-12})								
		CH_2C_2			CHD_3			CD_4		
P_{D_2} (mm. 0°)	P_{CH_4}	Calcd. (E = 32.0)	Calcd. (E = 33.0)	Obsd.	Calcd. (E = 32.0)	Calcd. (E = 33.0)	Obsd.	Calcd. (E = 32.0)	Calcd. (E = 33.0)	Obsd.
2.49	12.4	220	88	96	1260	380	340	2380	700	780
4.85	3.26	6	2.4	1.7	82	25	30	440	130	130
4.85	9.69	58	23	22	340	100	130	1100	440	460
14.4	3.20	0.8	0.3	0.4	18	5	5	140	40	36

rapidly undergo exchange with adsorbed deuterium atoms, but merely add on atoms to form CH_3D. The other deuterated methanes must then be formed in another manner, and the simplest hypothesis is that they are produced from adsorbed CH_2 radicals. Kemball has in fact produced evidence for two kinds of equilibria, one probably involving adsorbed CH_3 and the other adsorbed CH_2.

The exchange mechanisms formulated in the present paper are considerably more explicit than those of Kemball, but our discussion is, except in a few details, consistent with his. The general approach to the problem is similar to that given for the parahydrogen conversion.[2] The exchange processes occurring on the surface, *i.e.*, the production of absorbed CH_3D from adsorbed CH_3 and D and of adsorbed CH_2D_2, CHD_3 and CD_4 from adsorbed CH_2 and D, are considered to occur rapidly, the slow process in each case being the desorption of the products from the surface. Adsorption equilibrium, apart from exchange, is assumed to be established rapidly, and the concentrations of adsorbed CH_3 and CH_2 will therefore be calculated from the equilibrium expressions. The rate of removal of CH_3 from the surface, equal to the rate of adsorption of methane as CH_3, controls the rate of production of CH_3D, the proportionality factor being the statistical weight expressing the probability that an adsorbed CH_3 will pick up a D rather than an H. Similarly the rates of production of CH_2D_2, CHD_3 and CD_4 are controlled by the over-all rate of desorption of CH_2, which is initially equal to the rate of adsorption of methane as CH_2; the proportionality factors are now the statistical factors for the uptake of two, three and four deuterium atoms, respectively.

In the present formulation of the kinetic expressions the notation is the same as in previous publications.[2-6]

Formation of CH_3D.—Methyl radicals, hydrogen atoms and deuterium atoms are assumed to be adsorbed on single surface sites, and the rate of formation of CH_3D is the rate with which adsorbed CH_3 and D are desorbed together from the surface. The equilibria for deuterium adsorption may be written as

$$\frac{1}{2}D_2 + S \rightleftarrows S\text{-}D \qquad (I)$$

The equilibria involving H_2 and HD may be neglected since initially D_2 predominates. The surface is sparsely covered by methane and well covered by deuterium, so that the concentration of bare sites is given by the equations

$$L = c_S + c_{a'} \qquad (1)$$

and

$$c_{a'}/c_S = K'c_{g'}^{1/2} \qquad (2)$$

where the prime indicates deuterium. These equations give rise to

$$c_S = \frac{L}{1 + K'c_{g'}^{1/2}} \qquad (3)$$

$$\simeq L/K'\, c_{g'}^{1/2} \qquad (4)$$

for full coverage.

The rate of adsorption of methane as methyl radicals is

$$v = c_g c_S \frac{kT}{h}\frac{f_\ddagger}{F_g f_S} e^{-\epsilon_0/kT} \qquad (5)$$

$$= \frac{c_g}{c_{g'}^{1/2}}\frac{L}{K'}\frac{kT}{h}\frac{f_\ddagger}{F_g f_S} e^{-\epsilon_0/kT} \qquad (6)$$

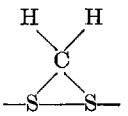
$$= \frac{c_g}{c_{g'}^{1/2}} L \frac{kTf_\ddagger}{h}\frac{F_{g'}^{1/2}}{F_g f_{a'}} e^{-(\epsilon_0+\epsilon)/kT} \qquad (7)$$

since $K' = (f_{a'}/F_{g'}^{1/2}f_S)e^{\epsilon/kT}$ where ϵ is the energy of adsorption at 0°K. per deuterium atom. The treatment is seen to account correctly for the pressure dependence of the rate. This equation essentially gives the rate of desorption of CH_3D, since the probability that an adsorbed CH_3 will pick up a deuterium atom is close to unity on account of the high surface coverage by deuterium atoms.

Equation (7) has been applied to Kemball's data, taking $f_\ddagger$ and $f_{a'}$ as unity, and L as 13.6 × 10^{16} sites per milligram of catalyst, this value having been determined directly by Kemball. The partition functions were calculated from the free energy values given in the National Bureau of Standards tables. The value of 24.75 kcal. was used for E_0 $[=N(\epsilon_0 + \epsilon)]$, being obtained from the experimental value of 24.0 kcal. by the addition of 3/4 RT. At 500°K. and deuterium and methane pressures of 2.49 mm. and 12.4 mm. the calculated rate is found to be 1.3 × 10^{14} molecules mg.$^{-1}$ sec.$^{-1}$, as compared with an experimental rate of 1.9 × 10^{14}. At pressures of 14.4 and 3.20, respectively, the calculated rate is 1.3 × 10^{13}, the observed 1.5 × 10^{13} molecules mg.$^{-1}$ sec.$^{-1}$. The agreement is seen to be very satisfactory.

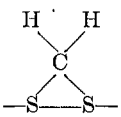
Formation of CH_2D_2, CHD_3, CD_4.—In addition to being adsorbed as methyl radicals it must be assumed that methane is also adsorbed as methylene radicals, which are presumably attached to two surface sites

(2) K. J. Laidler, THIS JOURNAL, **57**, 320 (1953).
(3) K. J. Laidler, *Disc. Faraday Soc.*, **8**, 47 (1950).
(4) K. J. Laidler, THIS JOURNAL, **55**, 1067 (1951).
(5) K. J. Laidler, S. Glasstone and H. Eyring, *J. Chem. Phys.*, **8**, 667 (1940).
(6) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941.



Whereas adsorbed methyl radicals can only add deuterium atoms, methylene radicals can undergo rapid surface exchange and be desorbed as CHD_3 and CD_4 as well as CH_2D_2.

The initial equilibria are



$$CH_4 + S_2 \rightleftharpoons -S-S- + H_2 \qquad \text{(II)}$$

and

$$\tfrac{1}{2}D_2 + S \rightleftharpoons S\text{-}D \qquad \text{(III)}$$

The methylenes only sparsely cover the surface, so that eq. (4) again gives the concentration of single sites. The concentration of dual sites is equal to $^1/_2\ sc_S^2/L$, where s is the coördination number, so that

$$c_{S_2} = \tfrac{1}{2}sL/K'^2c_{g'} \qquad (8)$$

The rate of adsorption of methane in the form of methylene is given by

$$v = c_g c_{S_2} \frac{kT}{h} \frac{f_\ddagger}{F_g f_{S_2}} e^{-\epsilon_0/kT} \qquad (9)$$

$$= \tfrac{1}{2}s\frac{c_g}{c_{g'}} \frac{L}{K'^2} \frac{kT}{h} \frac{f_\ddagger}{F_g f_{S_2}} e^{-\epsilon_0/kT} \qquad (10)$$

$$= \tfrac{1}{2}s\frac{c_g}{c_{g'}} L \frac{kT}{h} \frac{f_\ddagger f_S^2 F_{g'}}{f_{a'}^2 F_g f_{S_2}} e^{-(\epsilon_0+2\epsilon)/kT} \qquad (11)$$

Equation (11) also gives the total rate of desorption of CH_2 in the form of the various methanes, and is seen to give the correct pressure dependence for the formation of CH_2D_2, CHD_3 and CD_4. To obtain the rates of formation of these, eq. (11) must be multiplied by suitable statistical factors, as follows. It is assumed that surface equilibration is established rapidly compared with the rates of desorption. Let q be the probability of a deuterium atom being picked up, and $1 - q$ the probability of a hydrogen atom being picked up. Then the relative probabilities that an adsorbed CH_2 will form CH_2D_2, CHD_3 and CD_4 are $6(1 - q)^2q^2$, $4q^3(1 - q)$ and q^4. Kemball has listed experimental values of $q/(1 - q)$ and these are used in the following calculations; the theoretical interpretation of q is given in the Appendix.

Calculations were made by eq. (11) and using Arrhenius activation energies of 32 and 33 kcal.; Kemball actually obtained values of 34, 31 and 31 kcal. for the three reactions but it seems highly probable that the same value should apply to each. The E_0 values used were obtained by subtracting $1/2\ RT$ from the Arrhenius values. The partition functions $f_\ddagger$, f_S, f_a and f_{S_2} were taken as unity, L as 13.6×10^{16} per mg. (as determined by Kemball) and s as 4. The agreement between calculated and observed values is seen from Table I to be extremely good when the value of 33 kcal. is used.

APPENDIX

Theory of the Statistical Factors.—The problem is primarily to calculate the concentration of adsorbed hydrogen atoms ($c_{a''}$) in terms of the concentrations of gaseous methane and deuterium. These hydrogen atoms arise from the adsorption of methane as methylene radicals, so that in addition to reactions (II) and (III) above the adsorption process

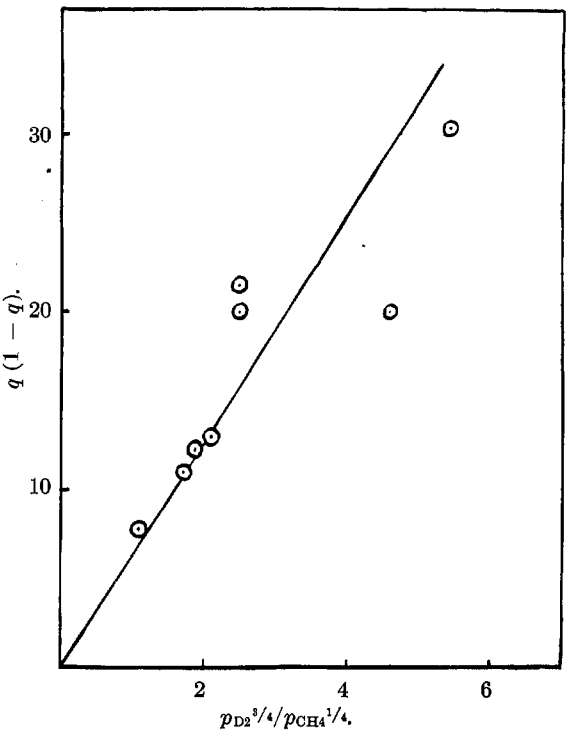


Fig. 1.—Plot of $q(1 - q)^{-1}$ *vs.* $p_{D_2}^{3/4}/p_{CH_4}^{1/4}$; *cf.* eq. (18).

$$\tfrac{1}{2}H_2 + S \rightleftharpoons S - H \qquad \text{(IV)}$$

must be considered. The equilibrium expressions corresponding to reactions (II) and (IV) are

$$c_a c_{g''}/c_g c_{S_2} = K \qquad (12)$$

and

$$c_{a''}/c_{g''}^{1/2}c_S = K'' \qquad (13)$$

c_{S_2} is given by eq. (8) above. Since an adsorbed methylene corresponds either to two adsorbed hydrogen atoms or to one gaseous hydrogen molecule it follows that

$$c_a = \tfrac{1}{2}c_{a''} + \frac{V}{S}c_{g''} \qquad (14)$$

where V is the gas volume and S the surface area. Equations (12), (13) and (14) give rise to

$$c_{a''}^4 + \frac{SK''^2L}{sV}c_{S_2}c_{a''}^3 - \frac{4SK''^4L^2K}{s^2V}c_g c_{S_2}^3 = 0 \qquad (15)$$

Consideration of the magnitudes of the quantities in this equation reveals that the second term can be neglected; hence

$$c_{a''} = \left[\frac{4SKK''^4L^2}{s^2V}c_g c_{S_2}^3\right]^{1/4} \qquad (16)$$

$$= \left[\frac{sSKK''^4L^5}{VK'^6}\right]^{1/4}\frac{c_g^{1/4}}{c_{g'}^{3/4}} \qquad (17)$$

Since $c_{a'}$ is essentially L, it follows that

$$\frac{q}{1 - q} = \frac{c_{a'}}{c_{a''}} = \left[\frac{VK'^6}{sSKK''^4L}\right]^{1/4}\frac{c_{g'}^{3/4}}{c_g^{1/4}} \qquad (18)$$

According to this a plot of $q(1 - q)^{-1}$ *vs.* $c_{g'}^{3/4}/c_g^{1/4}$ should be linear; such a plot is shown in Fig. 1, and it is seen that eq. (18) is consistent with the data.