

## The Exchange of Hydrogen Between Methane and Deuterium Oxide Over Nickel

A. METCALFE AND D. E. VICKERS

*Chemistry Department, University of Canterbury, Christchurch, New Zealand*

Received February 9, 1973

The exchange of hydrogen between methane and heavy water over finely divided nickel catalysts has been observed to proceed by two distinct mechanisms; by a single atom exchange over clean nickel surfaces and by exchange of two atoms over surface contaminated by oxygen.

### INTRODUCTION

It has been observed (1) that transition metal catalysed deuterium exchange between aliphatic hydrocarbons and deuterium gas occurs with greater ease with the increasing size of the C-atom chain; the effect is attributed to increasing strength of adsorption of hydrocarbons in the order  $\text{CH}_4 \ll \text{C}_2\text{H}_6 < \text{C}_3\text{H}_8 < \text{C}_4\text{H}_{10}$ . It has also been reported that exchange between methane and  $\text{D}_2\text{O}$  over nickel occurs less readily than with  $\text{D}_2$  at 457 K and 528 K (2). The very strong adsorption of water at the catalyst surface is believed to leave very few "active sites" upon which the competing hydrocarbon may be adsorbed, especially at the lower temperature.

The object of the present work was to investigate more fully the kinetics and mechanism of  $\text{CH}_4/\text{D}_2\text{O}$  exchange.

### EXPERIMENTAL

#### *Catalyst Preparation*

High specific area nickel catalysts were prepared by leaching a 50 wt% nickel-aluminum alloy with aqueous sodium hydroxide (3). After preparation, the finely divided catalyst material was stored under de-aerated distilled water until use in order to retard oxidation, and water removed only after transfer of catalyst to the vacuum system. Surface areas of catalysts, after poisoning by CO to suppress pyro-

phoric activity, were determined by volumetric  $\text{N}_2$  adsorption at 77 K using BET (4) analysis.

#### *Apparatus and Technique*

The reaction system was an all-glass construction around which reaction gases were pumped by a double action displacement pump with an electromagnetically driven, iron-filled piston. Reaction gases were circulated through a  $\text{D}_2\text{O}$  saturator held at constant temperature and passed through the reactor containing the nickel catalyst. Flow of the finely divided catalyst throughout the system was prevented by a coarse glass sinter fitted in the exit port of the reactor and small magnetic traps to retain the finest dust. The reactor was immersed in an electrically heated pot-furnace maintained to within  $\pm 0.5^\circ\text{C}$ . Pressure measurements within the system were measured using a silica bourdon-tube manometer. The reaction system was connected through high vacuum greaseless stopcocks to the gas storage and sampling systems, and to a conventional high-vacuum system in which pressure measurements were made using an ionization gauge. The catalyst chamber and heavy water saturator could be outgassed independently of each other. The procedure adopted for carrying out a kinetic study is outlined as follows:

The wet catalyst was transferred to the reactor and the system sealed: water vapor

from the catalyst was removed by pumping and the temperature raised to about 600 K until a pressure of  $10^{-6}$  Torr was attained. The catalyst was then reduced for 24 hr at 600 K with 1 atm high-purity hydrogen (from electrolysis of water through a palladium-silver osmosis membrane). During this stage of catalyst preparation, about 5 ml of deuterium oxide were admitted to the saturator by sublimation under continuous pumping. The catalyst temperature was then adjusted to some suitable value within experimental range and outgassed until the pressure fell below  $10^{-6}$  Torr. The reactor was then connected to the reaction system and the  $D_2O$  saturator allowed to come to a chosen temperature and it too connected in the reaction circuit and the pressure of  $D_2O$  in the system measured. About 1 atm of 90% Argon, 10% methane was admitted to the reaction system, its pressure measured and the circulation pump started. Gas samples (100 ml at 10 Torr) were removed periodically for analysis on an A.E.I. MS902 mass spectrometer.

The volume of the reaction system was determined by expansion of gas from a known volume, into the system and found to be 1012  $cm^3$ .

### Analytical

The estimation of relative amounts of the different isotopic species of methane in a mixture by means of a mass spectrometer was based on the assumption that the probability of ionization of the species is not affected by the number of H or D atoms in the molecule (1).

Allowances were made for the formation of fragmentary ions when these had the same mass as molecule ions of less highly deuterated products. Corrections were made to each peak of masses 16-20 using published data (5), confirmed by fragmentation ratios obtained locally for  $CH_4$  and  $CH_3D$  under identical conditions used for experimental analyses.

Corrected peak heights of masses 16-20 were used to estimate fraction of isotopic species present in a reaction product.

## RESULTS AND DISCUSSION

### Rate Constants

The disappearance of light methane was observed to be zero order in deuterium oxide pressure and first order in  $CH_4$ . The first order rate constants  $k_1$  (1) for disappearance of  $CH_4$  were calculated from Eq. (1)

$$-\log_{10}[(x - x_\alpha)/(x_0 - x_\alpha)] = kt(x_0 - x_\alpha)/2.303, \quad (1)$$

where  $x$ ,  $x_0$  and  $x_\alpha$  are the fraction of  $CH_4$  at times  $t$ ,  $t = 0$  and  $t = \alpha$ , respectively. Since the total amount of  $D_2O$  in the system (0.25 mole) was much larger than the amount of methane, it was reasonable to assume that the concentration of methane at equilibrium is very small, irrespective of the values of the equilibrium constants for exchange of deuterium between methane and water, and hence  $x_\alpha \simeq 0$ .

The rate constants  $k_\phi$  (1) for incorporation of deuterium into methane were also calculated using Eq. 2

$$d\phi/dt = k(1 - \phi/\phi_\alpha), \quad (2)$$

where  $\phi = x_1 + 2x_2 + 3x_3 + 4x_4$  and  $x_1, x_2, x_3, x_4$  represent the fraction of methane

TABLE 1

Run	Temp (K)	$P_{D_2O}^a$	$P_{CH_4}^a$	$k_1(\text{hr}^{-1})$	$k_\phi(\text{hr}^{-1})$	$k_\phi/k_1$
1	496	13	44	41.9	45.3	1.08
2	495	6	44	40.7	43.3	1.06
3	543	13	74	82.5	87.5	1.07
4	543	6	73	84.0	89.1	1.06
5	563	13	66	129.0	134.0	1.03
6	563	6	67	130.0	136.5	1.05
7 <sup>b</sup>	558	13	74	18.9	36.9	1.95
8 <sup>b</sup>	558	6	74	19.1	37.6	1.94
9 <sup>b</sup>	542	13	75	7.6	15.7	2.06
10 <sup>b</sup>	542	6	74	7.5	15.0	2.00
11	569	13	75	130.5	135.7	1.04
12	569	6	75	127.9	131.7	1.03
13	562	13	79	107.2	121.1	1.13
14 <sup>b</sup>	542	13	79	8.1	16.3	2.01
15	513	13	52	60.19	65.0	1.08
16	513	6	53	63.3	64.6	1.02

<sup>a</sup> Pressure in Torr.

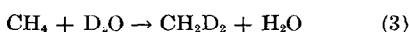
<sup>b</sup> Catalyst not reduced between runs after outgassing at 600 K.

present in the system as  $\text{CH}_4$ ,  $\text{CH}_3\text{D}$ ,  $\text{CH}_2\text{D}_2$ ,  $\text{CD}_3\text{H}$  and  $\text{CD}_4$ , respectively.

The ratios  $k_\phi/k_1$  represent the mean number of hydrogen atoms replaced by deuterium in a molecule of methane during the initial stages of the exchange. This data together with values of  $k_1$ ,  $k_\phi$  are presented in Table 1 for a series of runs between 490 K and 570 K.

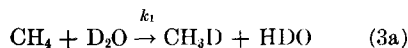
It is interesting to observe in Table 1 the division of kinetic parameters into two classes.

(a) Oxidized surfaces for which  $k_\phi/k_1 \simeq 2$ , and over which the exchange appears to proceed by a double deuterium substitution mechanism.



Product distribution curves are displayed in Fig. 1 for such a catalyst.

(b) Reduced surfaces for which  $k_\phi/k_1 \simeq 1$ , and over which the exchange appears to proceed by a single substitution mechanism.



and subsequently

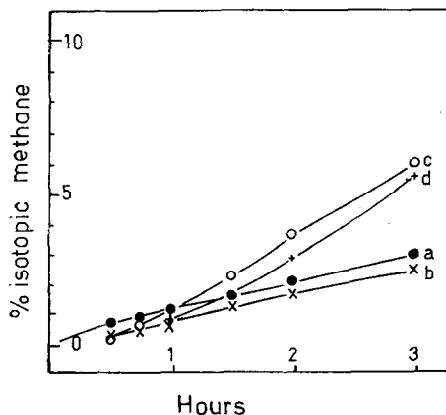
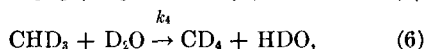


FIG. 1. Product distribution for  $\text{CH}_4/\text{D}_2\text{O}$  exchange over oxidized nickel at 542 K. (a)  $\text{CH}_3\text{D}$ ; (b)  $\text{CH}_2\text{D}_2$ ; (c)  $\text{CHD}_3$ ; (d)  $\text{CD}_4$ .

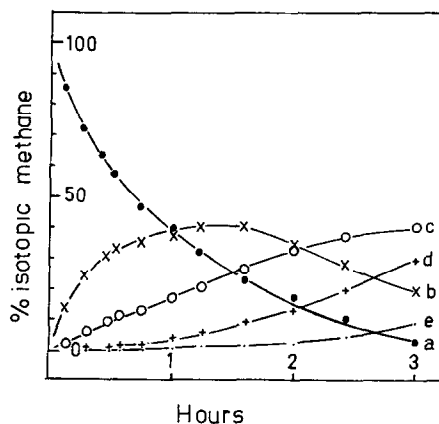


FIG. 2. Product distribution for  $\text{CH}_4/\text{D}_2\text{O}$  exchange over reduced nickel at 563 K. (a)  $\text{CH}_4$ ; (b)  $\text{CH}_3\text{D}$ ; (c)  $\text{CH}_2\text{D}_2$ ; (d)  $\text{CHD}_3$ ; (e)  $\text{CD}_4$ .

where  $k_1$ ,  $k_2$ ,  $k_3$ , and  $k_4$  represent the first-order rate constants for these processes. Figure 2 shows typical product distribution curves for the exchange over reduced catalysts.

The reactions 3a through 6 all display first order kinetics in the isotopic methane and the set of relations

$$\frac{d}{dt} [\text{CH}_{4-n}\text{D}_n] = k_{n+1} [\text{CH}_{5-n}\text{D}_{n-1}] - k_{n+2} [\text{CH}_{4-n}\text{D}_n]. \quad (7)$$

$\frac{d}{dt} [\text{CH}_{1-n}\text{D}_n]/[\text{CH}_{4-n}\text{D}_n]$  was plotted against  $[\text{CH}_{5-n}\text{D}_{n-1}]/[\text{CH}_{4-n}\text{D}_n]$  and the values of  $k_{n+1}$ ,  $k_{n+2}$  determined from the slopes and intercepts of the lines using the method of least squares for deuterium exchange over reduced nickel (Run 3 and 5) are displayed in Table 2.

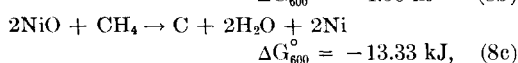
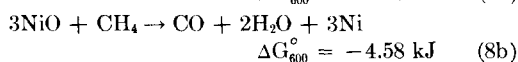
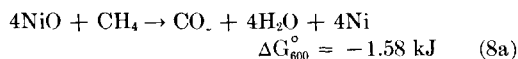
A naive statistical approach would suggest that the decreased rate be in simple proportion to the probability of removing an H atom from the isotopic species (calculated values Table 2). These figures are

TABLE 2

Run	Temp (K)	$k_2/k_1$	$k_3/k_1$	$k_4/k_1$
3	543	0.93	0.67	0.32
5	563	0.95	0.55	0.27
Calcd.	—	0.75	0.50	0.25

in surprisingly good agreement with the experimental data.

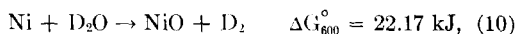
Equilibria in the Ni/D<sub>2</sub>O/CH<sub>4</sub> system: The distinction between catalysts which promote single or double substitution mechanisms appears to be the presence, or absence of oxygen contamination on the catalyst surface. This oxygen is removed by reduction in hydrogen at 600 K. The reduction of NiO by methane is favored by the standard Gibbs free energies of the processes:



where  $\Delta G_{600}^{\circ}$  have been calculated from data available in the literature (6), but the maintenance of a double substitution mechanism over oxidized nickel suggests that the exchange occurs more rapidly than the reduction. The oxygen dissociation pressure of Ni at 600 K obtained from



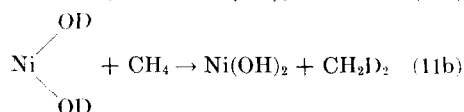
is about  $10^{-29}$  Torr, indicating that a 600 K oxygen gas in the system will be very strongly adsorbed in nickel surfaces. Even in the absence of molecular oxygen, NiO may be produced by the reaction



where  $-\log_{10}K_{600} = 1.93$ . If there are no other sources of D<sub>2</sub> and NiO in the system it is possible to estimate the total amount of D<sub>2</sub>O dissociated according to Eq. (10), and the amount of NiO also produced, for a system of approximately 1 liter capacity with a D<sub>2</sub>O pressure of 13 Torr some  $20.5 \times 10^{18}$  "molecules" of NiO are produced, and with a nickel surface area of 75 m<sup>2</sup> or about  $75 \times 10^{19}$  Ni atom sites it is estimated the maximum oxide coverage of the nickel due to reaction with deuterium oxide is about 3%. The amount of NiO produced depends only upon the capacity of the system and not upon the extent of nickel surface so that in systems of higher

capacity/surface area, surface oxide may well cover a major proportion of available surface. It is evident that in addition to those variations in the activity of Raney nickel which arise as a consequence of the preparation of the alloy and the structure and composition of the catalyst (7-9), the presence of extremely small amounts of contaminating oxygen on nickel may cause changes in the reaction mechanism of hydrogen exchange between methane and deuterium oxide from a single step to a single step to a multiple exchange mechanism.

The mechanism whereby two hydrogen atoms are exchange over the oxidized surface probably involves processes of the type



The estimated dissociation pressure of bulk Ni(OH<sub>2</sub>) is extremely large ( $+\log_{10}K_{600} \simeq 3$ ) and it is expected that the surface concentration will be small and may account for the very low exchange rates over oxidized nickel.

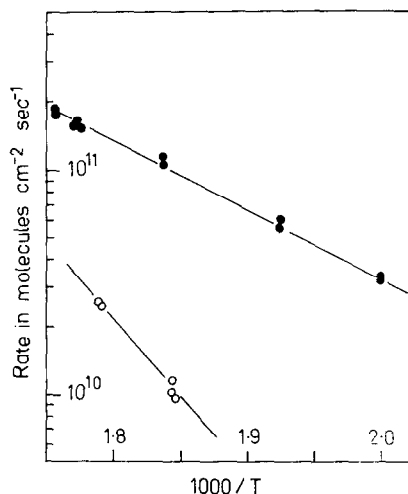


FIG. 3. Arrhenius plot for CH<sub>4</sub>/D<sub>2</sub>O exchange over nickel. ●, reduced nickel; ○, oxidized nickel.

The single substitution mechanism over reduced nickel appears to be first order in methane and zero order in D<sub>2</sub>O. The activation energy of this reaction obtained from the temperature coefficient of the first order constant for the disappearance of CH<sub>4</sub> (See Fig. 3) is 59.7 kJ mole<sup>-1</sup> (14.3 kcal mole<sup>-1</sup>) with a frequency factor  $B_m$  (10) of  $5.8 \times 10^{16}$  molecules cm<sup>-2</sup> sec<sup>-1</sup>; whereas the double substitution mechanism proceeds with an activation energy of about 137 kJ mole (32.7 kcal mole<sup>-1</sup>) and a frequency factor of the order of 10<sup>23</sup> molecules cm<sup>-2</sup> sec<sup>-1</sup>. It is possible that the single-step mechanism proceeds directly at the nickel surface between adsorbed methane and adsorbed deuterium oxide, although zero order kinetics in D<sub>2</sub>O at higher temperatures is surprising in view of the apparent instability of water monolayers on nickel at even modest temperatures (11). Probably the exchange reaction occurs between methane and the small amount of D<sub>2</sub> (estimated, 0.65 Torr) formed by reaction of D<sub>2</sub>O with Ni this may account for the exceptionally small value of  $B_m$  observed for this reaction.

## REFERENCES

1. KEMBALL, C., *Advan. Catal.* **11**, 223 (1959); *Proc. Roy. Soc.* **A207**, 539 (1951).
2. MORIKAWA, K., BENEDICT, W. S., AND TAYLOR, H. S., *J. Amer. Chem. Soc.* **58**, 1445 (1936).
3. MURRAY, RANEY, U. S. Patent 1,628,190. May (1927); COVERT, L. W., AND ATKINS, H., *J. Amer. Chem. Soc.* **54**, 4116 (1932).
4. EMMETT, P. H., BRUNAUER, S., AND TELLER, E., *J. Amer. Chem. Soc.* **60**, 309 (1938).
5. STENHAGEN, E., ABRAHAMSSON, S., AND McLAFTERTY, F. W., "Atlas of Mass Spectral Data." Interscience, New York, 1969.
6. "Selected Values of Thermodynamic Constants," U. S. Nat. Bureau Standards, Washington, D. C., 1952.
7. SASSOULAS, R., AND TRAMBOUZE, Y., *Bull. Soc. Chim.* **5**, 985 (1964).
8. FREEL, J., PIETERS, W. J. M., AND ANDERSON, R. B., *J. Catal.* **14**, 247 (1969); **16**, 281 (1970).
9. KOKES, R. J., AND EMMETT, P. H., *J. Amer. Chem. Soc.* **81**, 5032 (1959).
10. SOAPER, A., AND ELEY, D. D., *Disc. Faraday Soc.* **8**, 172 (1950).
11. SUHRMAN, R., HERAS, J. M., VISCIOLIO DE HERAS, L., AND WEDLER, G., *Z. Electrochem.* **68**, 511 (1964).