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The Exchange of Deuterium with Methanol over Raney Nickel Catalyst and the Effect of Certain Nitro Compounds upon the Exchange

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Deuterium gas exchanges slowly with liquid methanol over Raney nickel catalyst at 35°. The reaction is zero order with respect to deuterium pressure and has a low activation energy. The influences of catalyst weight, catalyst treatment, and of the presence of certain nitro compounds have been studied. Since active Raney nickel can liberate hydrogen directly, a method for determining the origin of hydrogen which undergoes exchange with the deuterium gas has been developed. It has been shown that the exchanged hydrogen does originate from the hydroxyl hydrogen of methanol. The results are discussed in the light of the mechanism of catalytic exchange and catalytic hydrogenation reactions.

The catalytic exchange of deuterium gas with alcohol vapors over various catalyst films has been reported previously.[1] Nickel catalyst was found to be the least active for the exchange. Several deuterium exchange reactions involving hydrogenation solvents and catalysts have been studied.[2–4]

Since the kinetics for the hydrogenation of various nitro compounds in alcohol solvent using Raney nickel catalyst has been studied previously,[5] a study of the catalytic deuterium exchange reactions for similar systems was undertaken to determine whether there are kinetic correlations and whether the mechanism could be better understood.

Experimental

Materials.—Raney nickel was prepared in several batches by a method described previously.[6] Drum grade synthetic methanol was fractionally distilled in an 8-foot Vigreux column, and constant-boiling cuts were collected at a reflux ratio of 10:1.

Nitrobenzene, aniline, nitroethane, nitromesitylene, β-nitrostyrene and 2-nitro-1-butene were prepared and purified as in earlier work.[2,7] Deuterium gas was obtained from the Stuart Oxygen Co. Electrolytic hydrogen was obtained from the National Cylinder Gas Co. The deuterium and hydrogen were passed through a trap cooled with liquid nitrogen immediately before use. Heavy water of greater than 99.5% purity was obtained from the Liquid Carbonic Co.

Deuterated methanol was prepared by acid-catalyzed equilibrations of 25 ml. of methanol with four successive 25-ml. portions of heavy water each followed by slow fractional distillation. No hydrogen could be detected in the sample gas resulting after treating the heavy methanol with deuterium gas and Raney nickel catalyst. A minimum purity of the CH_3OD of 99.5% may be calculated by use of the experimental value, 1.81, for the equilibrium constant of the reaction $D_2O + CH_3OH \rightarrow CH_3OD + HOD$.[8]

Exchange Apparatus and Procedure.—The exchange apparatus and procedure were similar to those described in previous work.[3] Raney nickel while wet with methanol was added to the desired volume of methanol with a calibrated glass tube. After the exchange reaction was completed, the nickel was collected upon a tared fritted funnel under an atmosphere of carbon dioxide, dried in a vacuum desiccator, and weighed under a carbon dioxide atmosphere.

Analyses.—The analytical apparatus was similar to that described earlier.[3] However, the effusiometer used to analyze hydrogen and deuterium incorporated a glass effusion pinhole bulb which could be evacuated. A glass pinhole system for effusiometry has been described previously.[9,10] Effusions were carried out at 35 ± 0.2°. Calculations were similar to those in earlier work.[3]

When hydrogen may be liberated directly from the catalyst as well as by exchange with methanol, more data are required for a calculation of percentage exchange with the methanol. The difference in pressure readings before and after the exchange run was measured. The final reading will always be the sum of $P_{D_2(i)}$, the initial deuterium pressure reading, and the increase in pressure due to hydrogen liberated from the catalyst itself. All readings were taken for the same volume and temperature. An expression for calculation of percentage exchange was derived

$$\%\ \text{exchange} = 100 = [100 \pm \%\ H_2]\left[\frac{P_{H_2(1)}}{P_{D_2(i)}} + 1\right]$$

where

$$\%\ H_2 - \frac{t_{D_2}{}^2 - t_{X_2}{}^2}{t_{D_2}{}^2 - t_{H_2}{}^2}(100)$$

as defined previously[3] $P_{H_2(1)}$ is the increase in pressure during the run, and $P_{D_2(i)}$ is the initial gas (deuterium) pressure.

Experimental Calculations and Results

Preliminary experiments indicated that the rate of exchange of deuterium gas with methanol for a shaking rate of 270 cycles per minute was proportional to the weight of Raney nickel catalyst added, provided this did not exceed 300 mg. Therefore, all exchange measurements were made under these conditions. In general, the percentage exchange was determined three times under any set of experimental conditions, and the recorded values are the average of these.

The percentage exchange per minute per unit weight of catalyst decreased linearly with an increase in initial deuterium pressure (total pressure less vapor pressure of methanol) as shown in Fig. 1. The order of the exchange reaction with respect to deuterium pressure is thus zero order, and it is pseudo zero order with respect to methanol concentration, since this material is present in considerable excess. Zero-order rate constants were calculated from the equation

$$k = \frac{P_{H_2}}{tw} = \frac{P_{D_2} \times \%\ \text{exchange}}{100tw}$$

where P_{H_2} and P_{D_2} are the pressures of hydrogen and deuterium, t is the time, w is the weight of catalyst, and the percentage exchange is determined in

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(1) J. R. Anderson and C. Kemball, *Trans. Faraday Soc.*, **51**, 966 (1955).

(2) H. A. Smith and E. L. McDaniel, THIS JOURNAL, **77**, 533 (1955).

(3) L. E. Line, B. Wyatt and H. A. Smith, *ibid.*, **74**, 1808 (1952).

(4) E. L. McDaniel and H. A. Smith, "Advances in Catalysis," Academic Press, Inc., New York, N. Y., 1957, Vol. IX, p. 76.

(5) H. A. Smith and W. C. Bedoit in P. H. Emmett, "Catalysis," Reinhold Publishing Corp., New York, N. Y., 1955, Vol. III, p. 149.

(6) W. C. Bedoit, "Studies of Raney Nickel Catalysts," Master's Thesis, The University of Tennessee, 1948, Appendix.

(7) H. A. Smith and W. C. Bedoit, *J. Phys. Colloid Chem.*, **55**, 1085 (1951).

(8) H. Kwart, L. P. Kuhn and E. L. Bannister, THIS JOURNAL, **76**, 5998 (1954).

(9) Atomic Energy Commission Research Development Report, O.R.N.L.-2997, Series A, July 13, 1956 (Declassified).

(10) D. A. Lee, *Anal. Chem.*, **30**, 1296 (1958).

the effusion apparatus. Table I shows that the rate constants calculated in this manner agree reasonably well when deuterium pressures above 500 mm. are employed. Below this pressure there is probably insufficient deuterium present to maintain the surface coverage required for zero-order kinetic behavior. The zero-order constants in Table I should be corrected for the volume (53 ml.) of gas in the system in order to compare them with constants obtained in different systems. The value of the rate constant corrected in this manner becomes 2.9 l. mm. min.$^{-1}$ g.$^{-1}$ at 35°.

TABLE I

ZERO-ORDER RATE CONSTANTS FOR DEUTERIUM-METHANOL EXCHANGE OVER RANEY NICKEL AT 35°

P_0,[a] mm.	P_{H_2},[b] mm.	Catalyst wt., g.	$k_{1.0}$, mm. min.$^{-1}$ g.$^{-1}$
323	85.2	0.232	36.7
403	97.9	.220	44.5
507	49.8	.096	51.9
761	122.5	.200	61.3
799	119.9	.221	54.3
897	76.3	.146	52.3
181	77.3	.147	52.6
		Av.	54.5[c]

[a] Corrected for vapor pressure of methanol. [b] After 10 min. shaking time. [c] Neglecting first two values.

The zero-order expression for the exchange reaction predicts a straight line when P_{H_2} is plotted *versus* reaction time. Figure 2 shows that the plot is linear for the exchange to about 42% reaction. The points represent individual runs for the given times. A single run cannot be followed analytically by the effusion method, since the gases are lost upon analysis.

Exchange runs were carried out at four temperatures to determine the apparent activation energy. A plot of log $k_{1.0}$ *versus* $1/T$ is shown in Fig. 3. The apparent activation energy is 3500 cal. per mole.

To ascertain whether only the hydroxyl hydrogen of methanol was involved for the exchange reactions, the following experiments were carried out. An exchange run using 10 ml. of heavy methanol (CH_3OD) and 53 ml. of deuterium gas at 799 mm. for 10 minutes and at 35° gave no detectable exchange. This is evidence that the hydrogen originates neither from the catalyst nor from the hydrogen atoms attached to the carbon of methanol. Another run using 10 ml. of heavy methanol (CH_3OD) and 53 ml. of hydrogen gas at 35° gave an exchange (9.99% exchange per gram per minute) which is comparable to that obtained using ordinary methanol with deuterium. Thus, it was concluded that only the hydroxyl hydrogen of methanol is involved in the exchange reaction with deuterium.

Deuterium gas exhibits an average of 71.1% exchange per gram of catalyst for 10 minutes using pure methanol. This value was adopted for the standard catalyst; see Table II. Various concentrations of nitromesitylene, nitroethane, β-nitrostyrene, nitrobenzene and 2-nitro-1-butene were used to determine their effect upon the deuterium-methanol exchange. The reactions were carried out for 10 minutes at 35.0° with an initial deuterium pressure of 799 mm. Catalyst weights were less than 300 mg. in order to have equilibrium amounts for the shaking rates.

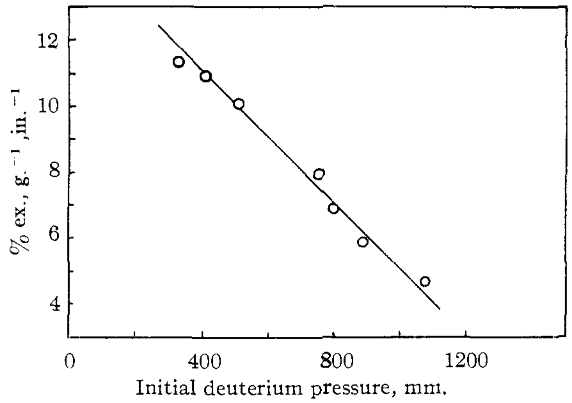

Fig. 1.—The effect of initial deuterium pressure upon the methanol–deuterium exchange reaction.

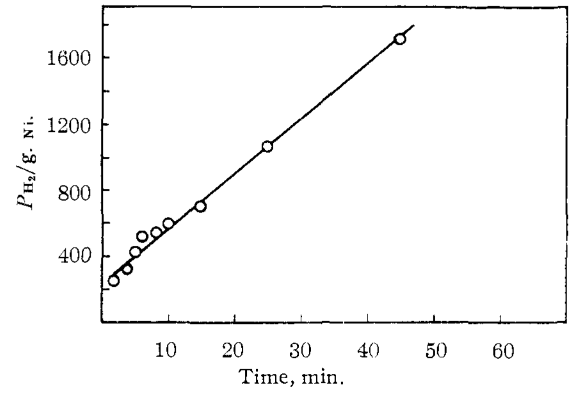

Fig. 2.—Zero-order plot for deuterium–methanol exchange.

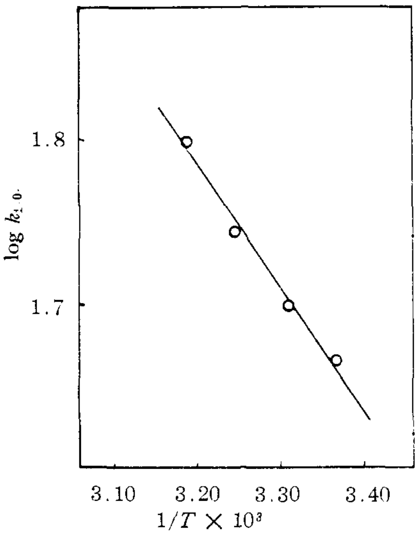

Fig. 3.—Activation energy plot for deuterium–methanol exchange.

Table II shows that the higher concentrations of all of the compounds except nitromesitylene prevented the exchange. The nitromesitylene solution gave a value for the percentage exchange almost equal to that obtained with pure methanol. There was no significant decrease for concentrations as great as 0.27 mole per liter. The minimum may be due to poisoning of the catalyst by the small quantity of amine formed during the exchange, and the plateau at higher concentrations may be due to appreciable adsorption of the nitro compound which would displace the amine.

TABLE II

THE EXCHANGE OF DEUTERIUM GAS OVER RANEY NICKEL CATALYST WITH CERTAIN METHANOL SOLUTIONS

Concn., mole/l.	% ex. g.$^{-1a}$	Concn., mole/l.	% ex. g.$^{-1a}$
0 (pure MeOH)	71.1^b	β-Nitrostyrene	
Nitromesitylene		0.0129	47.8
0.0134	40.4	.0587	14.1
.0198	48.1	.0971	7.36
.0454	65.6	.1553	0
.0454	63.7	.2279	0
.0705	64.5	Nitrobenzene	
.0935	60.8	0.0257	17.7
.0992	57.5	.0514	11.5
.1674	60.8	.0771	0
.2710	63.7	.1285	0
.2710	67.2	2-Nitro-1-butene	
.2710	63.2	0.0169	19.2
Nitroethane		.0338	0
0.0340	35.3	.0676	0
.0680	19.4		
.1020	4.34		
.1360	0		

[a] For 10 minutes reaction time. [b] Average of seven determinations, each representing three analyses.

Discussion

The kinetic behavior of the catalytic hydrogenation of nitro compounds in ethanol solution over Raney nickel catalyst is first order with respect to hydrogen pressure and zero order with respect to the hydrogen acceptor. This is found for both aromatic and aliphatic nitro compounds, and is in contrast to the behavior over platinum catalyst with acetic acid solvent. In the latter case, the hydrogenation of the aromatic nitro compounds is also first order with respect to hydrogen pressure and zero order with respect to the nitro compound; but for nitroparaffins, the kinetic behavior is reversed, in that the reduction is zero order with respect to the hydrogen pressure and first order with respect to the acceptor.

The exchange experiments with deuterium gas and acetic acid in the presence of platinum and with deuterium gas and methanol in the presence of Raney nickel reflect these differences. In the first situation, aromatic nitro compounds when added in small quantities prevent the exchange,[2] while aliphatic nitro compounds do not.[3] For experiments with deuterium gas and methanol over nickel, both aliphatic and aromatic nitro compounds prevent the exchange. Thus, both hydrogenation and exchange experiments indicate strong adsorption of both nitroparaffins and aromatic nitro compounds on the nickel surface. Presumably these, when present in appreciable concentrations, exclude the methanol from the catalyst surface, thus preventing the exchange reaction.

The situation occurring with nitromesitylene is unusual, in that it does not prevent the exchange. It is well known that the methyl substituents prevent resonance between the nitro group and the benzene ring, and this influences such properties as dipole moments[11] and Raman spectra,[12] thus making the compound behave somewhat more as a nitroparaffin than as an aromatic nitro compound. This is evidenced in the hydrogenation of nitromesitylene over platinum in acetic acid solution.[7] However, since nitroparaffins and aromatic nitro compounds influence the exchange of deuterium with methanol over Raney nickel, one would expect that the nitromesitylene would suppress the exchange reaction. The reason for its behavior is not clear unless there may be some unexpected exchange of deuterium with the nitromesitylene itself.

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[12] R. H. Saunders, M. J. Murray and F. F. Cleveland, *ibid.*, **63**, 3121 (1941).

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Studies on the Mechanism of Clemmensen Reduction. I. The Kinetics of Clemmensen Reduction of *p*-Hydroxyacetophenone

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The kinetics of the reduction of *p*-hydroxyacetophenone with zinc amalgam and hydrochloric acid has been studied at 60°. Except in the initial stage, the reaction is first order with respect to the ketone. Chloride ion and zinc concentration have a predominant effect on the rate, whereas the effect of the potential of the zinc amalgam or hydrogen ion concentration is small. The effect of polyvinyl alcohol on the rate and on the potential of zinc amalgam are reported. The apparent energy of activation of the reaction is 5.1 kcal./mole. A hypothesis on the mechanism of this reaction is presented.

Clemmensen reduction is widely employed in organic syntheses,[1] but the mechanism of the reaction is not yet established. The present work has been undertaken in order to solve this problem.

Steinkopf and Wolfram studied the Clemmensen reduction of benzophenone, acetophenone, esters of keto acids and benzaldehyde.[2] The mechanism

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[1] E. L. Martin, "Organic Reactions," Vol. 1, edited by R. Adams, John Wiley & Sons, Inc., New York, N. Y., 1942, p. 155.

[2] W. Steinkopf and A. Wolfram, *Ann.*, **430**, 113 (1923).