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ON THE HYDROGEN EXCHANGE BETWEEN DEUTERIUM AND AMMONIA CATALYZED BY EVAPORATED NICKEL FILM

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In the previous short note[1] it was shown that rapid hydrogen randomization in ammonia takes place in a mass spectrometer used for measurement, which invalidated any reaction mechanism[2,3] of catalyzed hydrogen exchange between deuterium and ammonia deduced from the distribution of deuteroammonias thus observed.

It was found, on the other hand, that the relative abundances of P_2, PD and D_2, where P or D denotes protium or deuterium respectively, were practically not affected by a mass spectrometer, providing hence a sound basis of analyzing the mechanism of the exchange. Table 1 reproduces the initial rate $V_0^{P_2}$, V_0^{PD} or $V_0^{D_2}$ of evolution of P_2, PD or D_2 respectively observed in the previous experiments with an evaporated nickel film[3], which were corrected for change of catalytic activity by multiplying observed values of $V_0^{P_2}$ *etc.* in the second or the third series by the ratio of the rate of a standard reaction conducted prior to the first series to the rate of the same standard reaction conducted prior to the latter series. The rate of the standard reaction was given by the amount of $[PD]/[D_2]$ in 3:1 mixture of D_2 and NP_3 at 44 mmHg total pressure observed at 100°C, 5 minutes after the latter mixture being brought into contact with the catalyst, where [PD] or $[D_2]$ is the concentration of PD or D_2. The y^D in Table 1 is the fraction of the number of adsorbed deuterium D(a) over the sum of the numbers of D(a) and adsorbed protium P(a), which was calculated by the relation derived in the previous paper ignoring isotopic difference[3] that

$$y^D = V_0^{PD}/(2V_0^{P_2} + V_0^{PD}). \qquad (1)$$

V_0^P in Table 1 is the initial increasing rate $100(2V_0^{P_2} + V_0^{PD})/2[H_2]$ of P atom percent in hydrogen gas, where H represents P and D.

TABLE 1. The Observed Initial Formation Rates of P_2 and PD, y^D, V_0^P, $V(I)$ and $V(I)/V(II)$.

No. of series	Partial pressure, mmHg		Reaction temp.	Initial formation rate, mmHg/min.			y^D	V_0^P	$V(I)$	$\frac{V(I)}{V(II)}$
	D_2	NP_3	°C	$V_0^{D_2}$	V_0^{PD}	$V_0^{P_2}$		%/min.	mmHg/min.	
1	33	11	100	−0.76	0.63	0.13	0.70	2.70	1.49	1.17
2	33	11	120	−1.42	1.22	0.21	0.75	4.94	3.25	1.50
3	100	10	100	−7.19	6.97	0.22	0.94	7.41	6.20	11.8

The results of Table 1 are now reexamined on the basis of a reaction scheme that

$$H_2 \overset{I}{\longrightarrow} 2H(a) \overset{II}{\longrightarrow} NH_3, \qquad (2)$$

where I is the step of hydrogen chemisorption and II that of exchanging H(a) with H in ammonia.

The total forward or backward rate of I balanced with each other, *i.e.* $V(I)$ is evaluated as given in the second last column of Table 1 from the values of $V_0^{D_2}$ and y^D by the relation

$$V(I) = V_0^{D_2} \Big/ \left\{(y^D)^2 - 1\right\},$$

which is the special case of the formation rate of D_2 given, ignoring the isotopic difference, as

$$V^{D_2} = V(I)\left\{(y^D)^2 - y^{D_2}\right\}$$

at the initial stage of the reaction, where $V^{D_2} = V_0^{D_2}$ and the mole fraction y^{D_2} of D_2 in hydrogen gas equals unity.

The steady state condition of P(a) is now given as

$$V(I)\left\{2y^{P_2} + y^{PD} - 2(1-y^D)^2 - 2y^D(1-y^D)\right\} + V(II)\left\{(1-y) - (1-y^D)\right\} = 0, \qquad (3)$$

where $V(II)$ denotes the total forward or backward rate of step II, y^{P_2} or y^{PD} the fraction of the number of P_2 or PD over the sum of those of P_2, PD and D_2 and y the atomic fraction of D in ammonia gas. It follows from (3) that

$$V(I)/V(II) = y^D/2(1-y^D) \qquad (4)$$

at the initial stage of the reaction, where y, y^{P_2} and y^{PD} are respectively zero. The values of $V(I)/V(II)$ calculated by (4) are shown in the last column in Table 1.

From values of V_0^P of the first and the second series in Table 1 the activation energy of the exchange reaction of 3:1 mixture of D_2 and NP_3 at 44 mmHg total pressure is evaluated as

$$E_{ex} = -R\partial \ln V_0^P / \partial(1/T) = 8.9 \text{ Kcal/mole}.$$

This value is in conformity with the activation energy deduced by KEMBALL[2] from the decreasing rate of NP_3 at the initial stage of its exchange reaction with D_2, where deuteroammonia formed was practically exclusively NP_2D; this decreasing rate may be identified with V_0^P, provided that NP_2D content was little affected by the mass spectrometric measurement. The activation energy of step I is determined from values of $V(I)$ as

$$E(I) = -R\partial \ln V(I)/\partial(1/T) = 11.5 \text{ Kcal/mole} \qquad (5)$$

in conformity with that obtained by HORIUTI and SUZUKI[4] for the chemisorption of hydrogen. It follows, on the other hand, from values of $V(I)/V(II)$ of the first and the second series in Table 1 that

$$E(I)-E(II) = -R\partial \ln \left\{ V(I)/V(II) \right\} /\partial(1/T) = 3.6 \text{ Kcal/mole}, \qquad (6)$$

hence with reference to (5)

$$E(II) = 7.9 \text{ Kcal/mole}.$$

It is deduced from the values $E(I)-E(II)$ and $V(I)/V(II)$ of series 1 and 2 that either I or II governs the rate of the present exchange reaction at lower or higher temperature respectively, which is in conformity with the conclusion arrived at in the previous paper[3]; for instance $V(I)/V(II)$ is evaluated as 3.92, 0.37 or 0.037 at 200°C, 0°C or −100°C respectively. It follows, on the other hand, from the large excess of D_2 that the temperatures, where step I governs the rate, should be remarkably low as compared with those in series 1 or 2, as seen from the values of $V(I)/V(II)$, 3.90 or 0.29 at 0°C or −100°C respectively as calculated similarly identifying the appropriate value of $E(I)-E(II)$ with that in series 1 and 2.

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