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Kinetic Isotope Effects in the Catalytic Synthesis of Ammonia

S. R. LOGAN AND J. PHILP

From the Department of Chemistry, University of Strathclyde, Glasgow, C. 1., Scotland

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A reanalysis of the data of Ozaki, Taylor, and Boudart on the H/D isotope effect in ammonia synthesis does not support their conclusion that the surface is covered chiefly by NH radicals. The evidence is shown to be more consistent with the presence of N atoms on the surface combined with the action of a H/D kinetic isotope effect in the dissociative adsorption of nitrogen. The magnitude of this enhancement factor, about 3.8 at room temperature, is that to be expected for the participation of an adsorbed H atom in the slow step of the dissociative chemisorption of nitrogen molecules.

INTRODUCTION

From studies of the kinetics of ammonia synthesis and of the deuterium kinetic isotope effect, Ozaki, Taylor, and Boudart (*1*) (OTB) concluded that the predominant species on the catalyst surface is not the adsorbed nitrogen atom but the imine radical. The unexpectedness of this situation, for which, since it is thermodynamically unfavorable, OTB could only postulate a kinetic explanation, merits a reexamination of the evidence in its favor.

The experiments were performed with stoichiometric mixtures of N_2 and H_2 or D_2 over doubly promoted iron catalysts using a flow technique. The total pressure was normally 1 atm and, with one exception, the catalyst temperature was in the range 251–302°C. Initially the data were analyzed by the simple equation of Temkin and Pyzhev (*2*)

$$y_A{}^{2\alpha+1} = (2\alpha + 1)C/v \qquad (1)$$

where y_A represents 2×10^3 times the mole fraction of ammonia in the gas leaving the catalyst bed; v, the flow rate (in liters at STP/hr); and α and C are constants. The plots of log y_A against log $(1/v)$ gave acceptably straight lines, but it was seen that the Temkin parameter α did not have the same value for all runs. However, the decrease from 0.7 or 0.8 in runs where the efficiency was high was notable only in the case of the one run at 218°C, where α was found to be 0.4.

This behavior was previously demonstrated (*3*) to arise under such conditions that the simplified form of the isotherm used in the derivation of Eq. (1) is no longer valid. These conditions are realized in ammonia synthesis when the efficiency is low, so that the ambient pressure of NH_3 is very much less than the equilibrium pressure, but they do not arise in ammonia decomposition. The more correct isotherm for the fraction of surface sites occupied by N atoms and the expression for the rate of adsorption, r, are given in Eqs. (2) and (3),

$$\theta = (2/f) \ln \{1 + K_0(\mathrm{NH_3})/(\mathrm{H_2})^{1.5}\} \qquad (2)$$

$$r = k_0(\mathrm{N_2}) \exp(-g\theta) \qquad (3)$$

where the parentheses denote partial pressures of the species enclosed; f and g are the constants used by Brunauer, Love, and Keenan (*4*) (BLK) to denote the extent of the variation, over elements of the surface, of the heat of adsorption and the activation energy of adsorption of nitrogen molecules; and the ratio g/f is equal to the Temkin parameter α. Also, k_0 denotes the rate constant for nitrogen adsorption and K_0 the equilibrium constant for the surface equilibrium

$$\mathrm{NH_3} \rightleftharpoons \mathrm{N_a} + \tfrac{3}{2}\mathrm{H_2}$$

both on the elements of surface with the highest heat of adsorption, q_0.

Equations (2) and (3) lead to Eq. (4) for the rate of ammonia synthesis

$$\frac{d\,(\mathrm{NH_3})}{dt} = 2r = \frac{2k_0(\mathrm{N_2})}{\{1 + K_0(\mathrm{NH_3})/(\mathrm{H_2})^{1.5}\}^{2\alpha}} \tag{4}$$

In an element, dx, of the catalyst bed we have

$$d\,(\mathrm{NH_3}) = 2r\,dt = 2r\frac{PV}{v}dx = \frac{PV}{v}\frac{2k_0(\mathrm{N_2})}{\{1 + K_0(\mathrm{NH_3})/(\mathrm{H_2})^{1.5}\}^{2\alpha}}dx \tag{5}$$

where P is the total pressure in atm; V is the volume (in liters) of the gas space in the catalyst bed; and v is the flow rate in liters at STP/hr. This equation may be more conveniently written as

$$d\,(\mathrm{NH_3}) = \frac{Pk_1}{v\{1 + a_1(\mathrm{NH_3})\}^{2\alpha}}dx \tag{6}$$

where k_1 has been substituted for $2k_0(\mathrm{N_2})$ V and a_1 for $\mathrm{K_0/(H_2)^{1.5}}$. Integrating and applying the boundary conditions that at $x = 0$, $(\mathrm{NH_3}) = 0$ and at $x = 1$, $(\mathrm{NH_3}) = Py_\mathrm{A}/\ 2 \times 10^3$, we obtain Eq. (7)

$$(1 + a_2Py_\mathrm{A})^{(2\alpha+1)} - 1 = \frac{(2\alpha + 1)a_2Pk}{v} \tag{7}$$

where $a_2 = a_1/2 \times 10^3$ and $k = 2 \times 10^3\,k_1$.

If the simpler expression for θ were used which neglects the term unity in Eq. (2), then Eq. (8) results

$$y_\mathrm{A}{}^{(2\alpha+1)} = \frac{(2\alpha + 1)a_2Pk}{v(a_2P)^{(2\alpha+1)}} \tag{8}$$

Comparison with Eq. (1) shows that $C = k/(a_2P)^{2\alpha}$ and as k is proportional to $(\mathrm{N_2})$ and a_2 to $(\mathrm{H_2})^{-3/2}$ and both these partial pressures are proportional to P, C should be proportional to $P^{1+\alpha}$.

Since their results indicated that C was approximately proportional to $P^{1.2}$, OTB considered that the low-pressure runs provided evidence of the inapplicability of Eq. (1) under the conditions used. However, in employing the more complete Temkin-Pyzhev equation (7), these authors used only the value $\alpha = 1$. This corresponds either (as they showed) to a uniform surface or to a heterogeneous one of the type considered by BLK but with no variation in the activation energy of desorption. But the OTB experiments, like other studies of ammonia synthesis on doubly promoted iron catalysts, indicated that the value of α obtained by the use of Eq. (1) is always less than unity, no matter how high the efficiency: also, in ammonia decomposition experiments $(1 - \alpha)$ was found to be about 0.3 for a catalyst of this type (*5*). Thus the assumption that $\alpha = 1$ seems unjustified both on specific and on general grounds.

It was decided to reinvestigate the application of the complete Temkin-Pyzhev equation to the OTB results, using a more reasonable value for α and a properly objective method of determining the parameters a and k.

ANALYSIS OF DATA

On account of the complex nature of Eq. (7) and of the apparent character of the errors in the observations, standard methods are not applicable to determine the parameters a and k. To find, for an assumed value of α, the values in best agreement with the experimental results, the following procedure was used.

Equation (7) may be rewritten as

$$ay_\mathrm{A} = \left[\frac{ak(2\alpha + 1)}{v} + 1\right]^{1/(2\alpha+1)} - 1 \tag{9}$$

where $a = a_2P$.

By taking a trial value for the product ak and putting into Eq. (9) the pairs of values for y_A and $1/v$, there was obtained for each of n points a value of a. The mean, $\bar{a}$, of this set, $a_1, a_2, \ldots, a_n$, and $\bar{k}$, equal to $ak/\bar{a}$, were then taken as approximations to the two values with the product equal to the trial ak which best fitted the experimental results.

Since there would appear to be more experimental difficulty in accurately measuring y_A then $1/v$, it was assumed that significant experimental errors were present only in the y_A values. The fairly uniform scatter of the points on the log–log plots of OTB is in accord with the expected characteristics of these measurements, that errors of a certain fraction rather than of a certain absolute magnitude would be of equal probability at all y_A values. Thus the proper criterion of agreement with the line given by certain values of $\bar{a}$ and $\bar{k}$ is given by the parameter S

$$S = \left\{\sum_{1}^{n}\left(\frac{y_A - y'}{y_A}\right)^2\right\}^{1/2}$$

where y' is the value obtained by substituting $\bar{a}$, $\bar{k}$, and $1/v$ in Eq. (9). Calculations were performed on the ICT 1905 computer to determine $\bar{a}$, $\bar{k}$, and S for a number of values of ak, thus to find the values of these parameters which best fit the data.

TABLE 1

Comparison of Parameters Obtained for Eq. (9) with $\alpha = 1$

Run No.	T (°C)	P (atm)	Gas	OTB parameters a	k	$10^2 S$(OTB)	"Best fit" parameters a	k	$10^2 S_{\min}$
8	251°	1	D_2	0.87	34.5	1.26	0.87	34.5	1.26
7	251°	1	H_2	2.40	33.3	3.05	2.74	40.1	2.86
6	278°	1	D_2	0.76	92.6	4.22	1.27	196	2.55
5	278°	1	H_2	2.07	91.8	2.46	2.47	121	2.21
4	302°	1	D_2	0.64	187	2.82	0.72	222	2.64
1	302°	1	H_2	1.70	182	2.62	1.65	175	2.60
1A	302°	2/3	H_2	1.70	118	3.40	1.34	82.3	3.14
3A	302°	1/3	H_2	2.14	61	5.30	1.22	24.6	4.40
3	302°	1	D_2	0.63	127	3.18	0.50	90.4	2.74
2	302°	1	H_2	1.73	128	1.58	1.66	120	1.58
2A	302°	2/3	H_2	1.60	84	3.60	2.47	174	2.08
4A	302°	1/3	H_2	2.02	44	2.14	1.48	27.1	1.12

Initially, this procedure was applied to the OTB data using $\alpha = 1$. The results, summarized in Table 1, show that the OTB parameters are not always those which give the best fit and in several cases the minimum value of S, ($S_{\min}$) is very considerably less than the S value of the OTB parameters. Since the latter were presumably derived by finding the value of a giving the best linearity in the plot of a function of y_A against $1/v$, some discrepancies are to be expected. The most notable one, however, is that by the present procedure close agreement is not always found between the k values for corresponding runs with H_2 and D_2. This suggests that the choice made by the previous treatment may not always have been fully objective.

Table 2 shows the results obtained when the present method was applied with α put equal to 0.8. From the results at the highest efficiencies it appears that this value best describes the catalyst behavior under the conditions used. The actual value is not crucial to the argument, since the use of 0.75 at this stage leads qualitatively to the same conclusions.

This treatment makes it clear that the lower value of α is in better accord with the data. In almost all cases, the values of S in Table 2 are less than those in Table 1. The only exceptions are the cases where with $\alpha = 0.8$ there appear to be no finite values of a and k which give a minimum in S: this could well be due to the presence of a "wild point" among the results. Undoubtedly the values of all parameters are a function of the actual results quoted and similar treatment of a set obtained by repeating the same experiments could not be expected to lead to identical values.

However, this analysis provides no support for the view that under the same conditions k_H and k_D are equal. From all four pairs of experiments, the former is found to be larger by an appreciable factor.

TABLE 2

PARAMETERS OBTAINED FOR EQ. (9) WITH $\alpha = 0.8$

Run No.	T (°C)	$\bar{a}$ (Range)	$\bar{k}$ (Range)	$10^2 S_{\min}$	$(\bar{a}_H/\bar{a}_D)_T$	$(\bar{k}_H/\bar{k}_D)_T$
9	218°	1.77 (1.51–1.87)	8.5 (8.0–8.8)	0.65	—	—
8	251°	1.73 (1.55–1.9)	49.1 (43–55)	1.08	5.8 (3.8–10.7)	2.6 (1.5–6.3)
7	251°	10.1 (7.2–16.6)	129 (81–270)	2.86		
6	278°	15.4 (4.9–≫32)	3903 (830–$\gg 10^4$)	2.47	20 (<0.5–≫100)	24 (<0.1–≫250)
5	278°	305 (14.5–≫500)	94,100 (830–$\gg 2 \times 10^5$)	2.06		
4	302°	3.91 (2.7–7.3)	1280 (590–3400)	2.52	9.6 (1.0–≫30)	7.3 (0.23–>50)
1	302°	37.5 (7.4–≫70)	9340 (770–$\gg 3 \times 10^4$)	2.50		
3	302°	1.72 (1.1–2.6)	268 (140–500)	2.34	>200	>1000
2	302°	>400 —	$>3 \times 10^5$ —	<2.6		
1A	302°	6.43 —	397 —	3.14	—	—
3A	302°	7.53 —	173 —	4.00	—	—
2A	302°	>500 —	$>3 \times 10^5$ —	<2.5	—	—
4A	302°	12.7 —	315 —	0.84	—	—

The reliability of this conclusion may be gauged from the ranges of these $\bar{k}$'s lying between the S values representing an increase by a factor of $[(n-1)/(n-2)]^{1/2}$ over $S_{\min}$. This range may be very large if $\bar{k}$ is large but is proportionately smaller when $\bar{k}$ is small. The last column of Table 2 indicates that the smaller values of $\bar{k}_H/\bar{k}_D$ are the more reliable.

Table 2 also shows much higher ratios $\bar{a}_H/\bar{a}_D$ than were obtained by OTB, with values of about 5 being quite probable in all cases. Thus the evidence of these results is fully consistent with a_H/a_D being of the magnitude to be expected from an N-covered surface and with k_H being greater than k_D. The consequences of this situation may be more conveniently considered by reference to Eq. (8), which is an acceptable approximation when the product of a and k is very large, since $(2\alpha+1)$ and v both lie close to unity. Except for Run 9, which has no H_2 counterpart and so is not involved in these comparisons, the values

TABLE 3

CALCULATION OF k_H/k_D FROM EQ. (10)

Run No.	T (°C)	I	K_H/K_D[a]	$\left(\frac{I_H}{I_D}\right)^{2.6}\left(\frac{K_H}{K_D}\right)^{1.6} = \frac{k_H}{k_D}$	$RT \ln(k_H/k_D)$ (cal/mole)
1	302°	5.20	4.16	1.99	786
4	302°	9.59			
2	302°	4.46	4.16	1.98	780
3	302°	8.24			
5	278°	3.50	4.61	2.40	956
6	278°	6.40			
7	251°	2.16	5.22	2.77	1057
8	251°	4.05			

[a] Reference (*6*).

of $\bar{a}$ and $\bar{k}$ in Table 2 show that this approximation is justifiable.

From Eq. (8) we have

$$(2\alpha + 1) \log y_{\mathrm{A}} = \log \left(\frac{1}{v}\right) + \log \frac{(2\alpha + 1)k}{(a_2P)^{2\alpha}} \tag{10}$$

which shows that $k/a^{2\alpha}$ may be calculated from I, the y_{A} value at $1/v = 1$. Since a is proportional to K_0 and the ratio $(K_0)_{\mathrm{H}}/(K_0)_{\mathrm{D}}$ is equal to the ratio $K_{\mathrm{H}}/K_{\mathrm{D}}$ of the equilibrium constants for dissociation of NH_3 and ND_3 [which has recently been determined (*6*) and agrees with that calculated (*1*) from partition coefficients] the ratio $k_{\mathrm{H}}/k_{\mathrm{D}}$ may be calculated from the OTB data, as shown in Table 3. These values lie close together and are well within the range to be expected from the previous analysis by the use of Eq. (7).

TABLE 4
CALCULATION OF THE PRESSURE DEPENDENCE OF k_0

Run No.	P (atm)	I	$I^{2.6}P^{-1.8}$	∴ Ratio
1	1	5.20	72.7	1.0
1A	2/3	4.41	90.4	1.0:1.24
3A	1/3	2.92	94.4	1.0:1.30
2	1	4.46	48.7	1.0
2A	2/3	4.07	73.7	1.0:1.51
4A	1/3	2.65	73.0	1.0:1.50

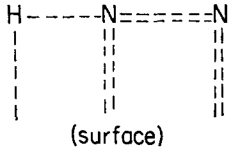
In regard to the variable pressure runs, the quantity whose log is the last term in Eq. (10) is proportional, at constant temperature and for the same catalyst, to $k_0P^{1+\alpha}$. Evaluation of the intercepts thus permits the determination of the dependence on total pressure of k_0, as shown in Table 4.

DISCUSSION

This reanalysis of the data of Ozaki, Taylor, and Boudart has led to the conclusion that the ratio whose value differs from that anticipated is $k_{\mathrm{H}}/k_{\mathrm{D}}$, not $a_{\mathrm{H}}/a_{\mathrm{D}}$. Thus their experimental evidence supports the view that the major species on the surface is the adsorbed N atom and asserts that there is a kinetic isotope effect in the dissociative adsorption of nitrogen, depending on whether the "hydrogen" is H_2 or D_2. This implies that a hydrogen atom is (or is in some cases) involved in this step.

For a normal hydrogen isotope effect the ratio $k_{\mathrm{H}}/k_{\mathrm{D}}$ is expected to increase as the temperature decreases, but the increase to be seen from the fifth column of Table 3 is rather too large. A relevant factor here is that the approximation involved in Eq. (8) becomes less valid the lower the efficiency, so that the ratio would be less reliable at lower temperatures. Thus the difference in the activation zero-point energies probably lies closer to the lower end of the range obtained from these $k_{\mathrm{H}}/k_{\mathrm{D}}$ ratios, and may be about 800 cal/mole (280 cm^{-1}), which means that at room temperature this ratio would be 3.8.

The transition state (TS) of this reaction could be envisaged as follows:



In the expression for the enhancement ratio, in Eq. (11),

$$\frac{k_{\mathrm{H}}}{k_{\mathrm{D}}} \simeq \exp \left\{ -\frac{hc}{2kT} \left[\sum^{2} (\bar{\nu}_i{}^{\ddagger}{}_{(\mathrm{H})} - \bar{\nu}_i{}^{\ddagger}{}_{(\mathrm{D})}) - \sum^{3} (\bar{\nu}_i{}^{\mathrm{H}} - \bar{\nu}_i{}^{\mathrm{D}}) \right] \right\} \tag{11}$$

there are three noncancelling modes in the reactants (one stretching and two bending of an adsorbed H atom) and two such in the TS. Since the two partial bonds to the H atom in the TS above are from dissimilar atoms, a high degree of asymmetry is likely, and the N--H stretching mode may approximate to movement along the reaction coordinate. If the effective force constants in the two remaining modes are taken as half those in the normal H-metal and N-H bonds, then the noncancelling frequencies in the TS may be assumed to be $3000/\sqrt{2}$ cm^{-1} (H--metal stretching) and

$1600/\sqrt{2}$ cm^{-1} (N--H bending) and those in the reactants 3000 cm^{-1} (H– metal stretching) and 1000 cm^{-1} (H– metal bending). These values lead to a ratio at 300°K of about 3.6, which indicates that a kinetic isotope effect of the magnitude shown in Table 3 is quite conceivable.

Measurements of amounts of gas adsorbed during catalytic reactions (*7*) have been cited as showing that although the presence of hydrogen increases the rate of nitrogen adsorption there is no kinetic isotope effect in this process. On the other hand, it is reported that ND_3 is produced faster than NH_3 from adsorbed nitrogen. While the reports of these experiments are rather too vague to permit the accuracy and significance of the results to be estimated, it may be pointed out that these assertions would not necessarily conflict with the conclusions above, if the adsorbed nitrogen were undissociated. However, this situation would be difficult to reconcile with the mutual effect of H_2 and N_2 on the amount adsorbed.

If a step determining the rate of adsorption of nitrogen may involve an adsorbed H atom, there is no longer any reason to expect k_0 to be independent of pressure, since it will be a function of the surface concentration of H atoms adjacent to an adsorption site. The manner in which this might depend on pressure is difficult to predict, but an inverse relationship can easily be envisaged. While the experimental results seem to support this, no clear pattern can be detected from Table 4. These results, which OTB found anomalous both by their first interpretation (rejected partly for this reason) and by their second, remain a puzzle.

REFERENCES

1. Ozaki, A., Taylor, H. S., and Boudart, M., *Proc. Roy. Soc. (London)*, **A258,** 47 (1960).
2. Temkin, M., and Pyzhev, V., *Acta Physicochim.* **12,** 327 (1940).
3. Temkin, M., and Kiperman, S., *Zh. Fiz. Khim.* **21,** 927 (1947); Kiperman, S., and Granovskaya, V. Sh., *Zh. Fiz. Khim.* **26,** 1615 (1952).
4. Brunauer, S., Love, K. S., and Keenan, R. G., *J. Am. Chem. Soc.* **64,** 751 (1942).
5. Love, K. S., and Emmett, P. H., *J. Am. Chem. Soc.* **63,** 3297 (1941)
6. Schultz, G., and Schaefer, H., *Ber. Bunsenges. Physik Chem.,* **70,** 21 (1966).
7. Tamaru, K., *Trans. Faraday Soc.* **59,** 979 (1963); *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam. 1964,* p. 664.