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Isotope Exchange Rates. I. The Homogeneous Reaction between Deuterium and Ammonia

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The thermal isotope exchange reaction between deuterium and ammonia (highly diluted with argon) was investigated behind reflected shocks in a single-pulse shock tube. The temperature range covered was 1300–1700°K. The reaction orders with respect to ammonia and deuterium, as well as the total reaction order, were determined. The exchange rate was found to be approximately unit order with respect to deuterium and argon, and zero order with respect to ammonia. From the known rates of dissociation of D₂ it is evident that the reaction does not proceed via a three-center atomic displacement intermediate. A mechanism based on the vibrational excitation of deuterium molecules by argon as the rate-determining step is proposed.

Introduction

The kinetics of homogeneous, rather than catalytic, isotope exchange reactions in the gas phase has been the subject of a relatively small number of investigations. In the case of exchange reactions involving the hydrogen isotopes, measurement of the exchange rates between D₂ and H₂,^{1,2} HCl,^{3,4} and NH₃⁵ were reported. The method employed, in general, consisted of heating the reaction vessel and its contents in an electric furnace and removing small samples of the reaction mixture, at selected time intervals, for isotopic analysis.

(1) A. and L. Farkas, *Proc. Roy. Soc. (London)*, **A152**, 152 (1935).

(2) G. Boato, G. Careri, A. Cimino, E. Molinari, and G. G. Volpi, *J. Chem. Phys.*, **24**, 783 (1956).

(3) P. Gross and H. Steiner, *ibid.*, **4**, 165 (1936).

(4) H. Steiner and S. K. Rideal, *Proc. Roy. Soc. (London)*, **A173**, 503 (1939).

(5) A. Farkas, *J. Chem. Soc.*, 26 (1936).

Unavoidably, in this procedure the hot vessel walls participate to some degree in the reaction.

The exchange between H₂ and D₂ was shown by both groups of investigators^{1,2} to follow a total three-halves order, with an activation energy of 59.8 kcal./mole. It was shown to be essentially homogeneous and an atom displacement chain mechanism was proposed. However, there remained some ambiguity as to the extent of participation of the walls in the initial formation of the chain-carrying deuterium and hydrogen atoms. In the earlier study¹ it was assumed that the chain-carrying species were produced in a homogeneous gas phase reaction, *i.e.*, the thermal dissociation of molecular hydrogen. In the later investigation,² it was assumed that the dissociation was wall catalyzed. This postulate was introduced because an early theoretical calculation² showed that the homogeneous dissociation step is extremely slow. Since then the rate of dissociation of hydrogen was measured,⁶ and it was demonstrated that the reaction proceeded too slowly to account for the measured rate of exchange.²

The exchange reaction between D₂ and HCl was found to proceed by two parallel mechanisms, a bimolecular (four-center) reaction with an activation energy of 57.1 kcal./mole and a surface-catalyzed radical chain reaction.^{3,4}

The kinetics of the exchange reaction between ammonia and deuterium was investigated over the temperature range 680–780° at pressures of 10–400 mm.⁵ The order of the reaction with respect to deuterium was found to be larger than unity and with respect to ammonia, much smaller than unity. Here also an atomic

(6) (a) E. A. Sutton, *J. Chem. Phys.*, **36**, 2923 (1962); (b) J. P. Rink, *ibid.*, **36**, 1398 (1962).

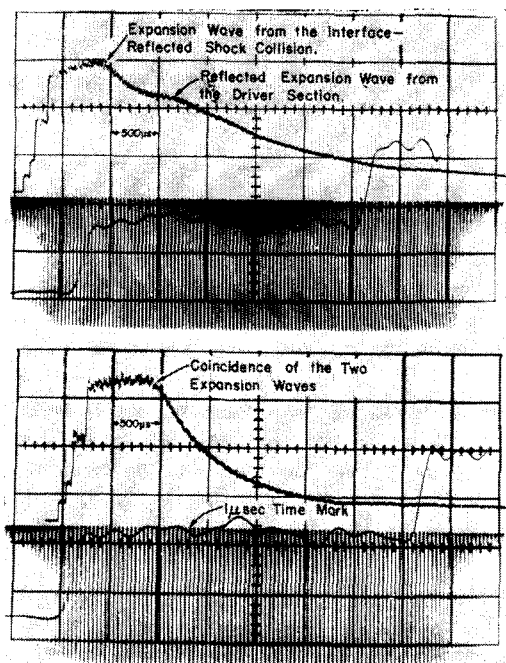


Figure 1. Pressure records for the "untuned" (upper trace) and "tuned" (lower trace) shock tube, as recorded with the two piezoelectric gauges connected in series.

displacement chain mechanism was proposed, in which the first step was the *homogeneous* gas phase dissociation of the deuterium molecule into atoms, while the rate-determining step was assumed to be: $D + NH_3 \rightarrow NH_2D + H$. This occurs $1/30-1/40$ as fast as the step $H + D_2 \rightarrow HD + D$. The over-all apparent activation energy was found to be 62 kcal./mole of which 52 kcal./mole, half of the dissociation energy of D_2 , was attributed to the dissociation step, with the remaining 10 kcal./mole being attributed to the activation energy of the rate-determining step. However, the calculated dependence of the rate on the ammonia concentration does not agree well with the experimental results, assuming that the dissociation step was sufficiently rapid (now proved invalid).

All of the above investigations suffer from the drawback that the influx of thermal energy is through the walls of the reaction vessels. It is not surprising that the walls participate in the kinetic processes. This is particularly critical for exchange reactions, because the homogeneous production of the atoms is far too slow to account for the observed rate of exchange. The major advantage of the shock tube technique is the homogeneous heating of the gas, allowing the walls of the reaction vessel to remain cold. This heating is extremely rapid (10^{-3} sec.) and dwell times are very short (500–800 μ sec.), such that no significant heat transfer to the walls can occur. Thus any reaction studied is certainly homogeneous and not wall catalyzed. The potential of this method for studying isotope exchange reactions was recently realized, and the exchanges between D_2 and H_2 ,⁷ between D_2 and HCl ,⁸ and between D_2 and C_2H_2 ⁹ were investigated in a shock tube.

The present study is a reinvestigation of the ammonia-

deuterium exchange, employing the single-pulse shock tube technique.¹⁰ The total and individual reaction orders, as well as the over-all activation energy, were determined. It will be shown that the reaction in the presence of argon is neither simple bimolecular nor a radical chain. Alternative mechanisms will be presented and discussed.

Experimental

Apparatus. The exchange reaction between D_2 and NH_3 was studied in a single-pulse shock tube, 1-in. i.d., of Pyrex tubing. Details were given in an earlier publication,¹⁰ wherein the principles of the method were discussed. Temperatures behind the reflected shocks were computed from recorded incident shock speeds using the three conservation equations, the ideal gas equation of state, and the gas composition. Shock speeds were obtained by recording the time interval required for the incident shock wave to travel between two high frequency pressure transducers; for calibration 1- μ sec. time marks were superimposed on the oscilloscope traces. Additional details were given in previous publications.¹¹ Errors in temperature around 1500°K. were $\pm 25^\circ K.$, and dwell times could be read to within 10%. There may be systematic errors in the temperatures of -10 to $-25^\circ K.$,^{11b} but these should not affect estimation of the activation energy.

The first few experiments were run with a mixture of D_2 , NH_3 , and argon, using hydrogen for the driver gas. However, when mixtures of similar concentrations of D_2 in argon, but without ammonia, were shock heated, some exchange was observed. It was suspected that this was due to reaction between the hydrogen driver and the D_2 in the mixed "entropy interface." We had to discard the first few series of runs and henceforth used He for the driver gas. This eliminated the small amount of exchange reaction found in the absence of ammonia.

Since the tube was tuned for the pair Ar- H_2 ,¹⁰ it had to be retuned for the pair Ar-He. Figure 1 shows two runs performed with He as driver. In the upper trace, before retuning, the reflected expansion wave from the driver section came in too late, and one observes two successive cooling processes. In the lower trace, the driver section was shortened, and the two processes appear simultaneously. The cooling rate with He as driver, as shown in Figure 1b is approximately $10^6^\circ K./sec.$ at around 1500°K.

Gas Analysis. Samples of the shocked gas were taken from the end block of the driven section and were analyzed with a C.E.C. Model 21-401 mass spectrometer. Ratios of $[HD]_t$ to $[D_2]_0$ were determined, where $[D_2]_0$ is the initial deuterium concentration and $[HD]_t$ is the concentration of HD in the quenched shocked mixture. In principle, the extent of reaction can be computed either from the above ratio or from measurement of the ratio $[NH_2D]_t/[NH_3]_0$. However, since the concentration of the ammonia in the gas mixture was around 1%, its absorption on the walls of the ionization chamber prevented us from making an accurate analysis of this ratio. In addition, the background of water in the mass spectrometer made the de-

(10) A. Lifshitz, S. H. Bauer, and E. L. Resler, Jr., *J. Chem. Phys.*, **38**, 2056 (1963).

(11) (a) A. Lifshitz, H. F. Carroll, and S. H. Bauer, *ibid.*, **39**, 1661 (1963); (b) W. Tsang, *ibid.*, **40**, 1498 (1964).

(7) E. Ossa, S. H. Bauer, S. C. Tsang, and W. Tsang, in preparation.

(8) C. M. Sadowski, K. S. Addecott, and S. H. Bauer, in preparation.

(9) K. Kuratani and S. H. Bauer, *J. Am. Chem. Soc.*, **87**, 150 (1965).

termination of NH_2D unreliable. The peak heights at $m/e = 18$ were approximately as expected and gave no indication of the possible production of H_2O owing to unsuspected air leaks. Thus, in all cases rate constants were computed from the ratio $[\text{HD}]_t/[\text{D}_2]_0$. The sensitivity of the mass spectrometer towards HD and D_2 , was found from experiments using samples of the pure gases to be the same to within 1%.

The use of He as driver introduced some difficulty in the analysis of D_2 at $m/e = 4$, owing to the presence of small amounts of driver gas in the shocked samples. The mass spectrometer used could not separate the He and D_2 peaks. The ratio $[\text{HD}]_t/[\text{D}_2]_0$ was, therefore, computed indirectly in the following manner (the Ar^{2+} peak served as a reference peak). First, the ratio D_2 to Ar^{2+} in the unshocked gas mixture was determined. Then, the HD to Ar^{2+} ratios in the shocked samples were determined, and the quantities $[\text{HD}]_t/[\text{D}_2]_0$ were thus obtained by dividing the $[\text{HD}]_t/[\text{Ar}^{2+}]$ ratios by the $[\text{D}_2]_0/[\text{Ar}^{2+}]$ ratio.

Materials. The argon used was Matheson pure grade listed as 99.998%. The deuterium was Matheson pure grade and was found to contain approximately 0.5% H as HD. The ammonia was Matheson anhydrous pure grade listed as 99.99% pure. All materials were used without further purification. The shock tube was pumped down to about 1×10^{-4} mm. with a diffusion pump (liquid nitrogen trap) before filling, and the shock was triggered immediately after filling. Since the leak rate was less than $1 \mu/\text{min.}$, in the worst case, contamination by atmospheric oxygen was reduced to less than 10^{-3} of the hydrogen present.

Preparation of Mixtures. Mixtures of deuterium, ammonia, and argon were prepared in the following way. First a mixture of a known ratio of deuterium to ammonia was prepared in a 1-l. flask by filling it with a known pressure of ammonia, cooling it with liquid nitrogen, and then admitting deuterium to the desired pressure. This mixture served later as the source for most of the runs of the desired ammonia to deuterium ratio. A fraction of this mixture was later transferred to a 12-l. bulb at the required pressure, and the argon was added to a total pressure of 1 atm. The sample was left overnight for mixing before use in the shock tube.

Results

In the first series of experiments, shocks were run at a constant temperature, but with varying compositions, in order to establish the order of the reaction with respect to ammonia and deuterium. Shock speeds vs. temperature curves were computed for the following three compositions (%).

	Ammonia	Deuterium	Argon
A	0.75	0.75	98.5
B	0.75	3	96.25
C	3	0.75	96.25

The uniform shock temperature for all the runs in this series was obtained by using the same diaphragm (1-mil Mylar film) and varying slightly the driven gas pressure, according to the specific heat of the shocked sample (the higher the specific heat, the lower the pressure used), over pressure range 95–105 mm. Owing to some irreproducibility in the bursting of the diaphragm, only about half of the shocks were close enough in

temperature to serve for determining the reaction orders. The average temperature obtained in this series of experiments was $1380 \pm 25^\circ\text{K.}$, and space-average dwell times were around 700 $\mu\text{sec.}$ These data are summarized in Table I. The temperatures behind the reflected shocks are listed in column 2, the equivalent pressures ($P_1 \times \rho_3/\rho_1$) in column 3, and values of $[\text{HD}]_t/[\text{D}_2]_0$ in column 4.

Table I. Dependence of Yield Ratio on the Initial Concentrations of Ammonia and Deuterium (in Excess Argon)^a

Run no.	$T_s, ^\circ\text{K.}$	Equiv. pressures, $P_1(\rho_3/\rho_1)$, mm.	$[\text{HD}]_t/[\text{D}_2]_0$
A			
1	1365	570	0.041
2	1365	563	0.068
3	1350	558	0.046
4	1383	563	0.054
5	1390	568	0.040
6	1383	567	0.060
7	1350	559	0.052
8	1370	508	0.044
9	1390	509	0.046
			Average
			Av. dev.
B			
10	1380	555	0.047
11	1355	537	0.071
12	1355	552	0.065
13	1370	552	0.056
14	1355	550	0.047
15	1355	578	0.045
16	1355	586	0.050
			Average
			Av. dev.
C			
17	1375	529	0.051
18	1365	542	0.042
19	1350	600	0.036
20	1405	496	0.035
21	1405	496	0.037
			Average
			Av. dev.

^a A = 0.75% NH_3 , 0.75% D_2 , and 98.5% Ar; B = 0.75% NH_3 , 3% D_2 , and 96.25% Ar; C = 3% NH_3 , 0.75% D_2 , and 96.25% Ar.

Groups A and B serve to establish the order of reaction with respect to D_2 . For the very low conversions of D_2 to HD observed around 1380°K. (a few per cent), the back reaction can be neglected, and the simple relation shown in eq. 1 can be used for deducing the order. The equilibrium constant for

$$\frac{\Delta[\text{HD}]_t}{\Delta t} = k[\text{NH}_3]_0^n[\text{D}_2]_0^m \quad (1)$$

exchange is 6. The ratios $[\text{HD}]_t/[\text{D}_2]_0$ in groups A and B, where the ammonia concentration is the same, varies little over a fourfold change in $[\text{D}_2]_0$, indicating a first-order rate law with respect to D_2 . Using eq. 1, one may now compare the ratios from sets A and C. To within the limits of experimental error, these $[\text{HD}]_t/[\text{D}_2]_0$ ratios are equal, indicating a zero-order dependence on the ammonia over the range of concentrations covered.

This observation was most unexpected. A question arose whether $[\text{NH}_2\text{D}]_t/[\text{NH}_3]_0$ is equal to $[\text{HD}]_t/[\text{D}_2]_0$. Since this could not be checked directly by the mass

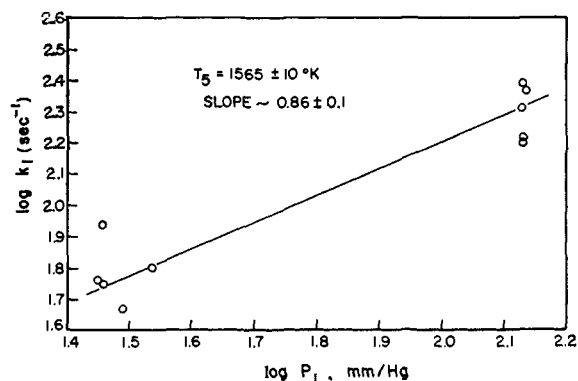


Figure 2. The effect of total pressure on the rate constant for fixed T_5 and the composition 0.75% D_2 and 0.75% NH_3 , to establish its dependence on the argon concentration.

spectrometric or v.p.c. analytical devices at our disposal, we ran several isotopic exchange experiments of similar compositions with D_2 and hydrogen sulfide instead of ammonia. There it is possible to determine mass spectrometrically the ratio of HDS to H_2S in the shocked samples, in addition to the ratio of HD to D_2 . Ratios $[HDS]_t/[H_2S]_0$ were computed from the peaks at $m/e = 34$ and 35 , after taking into account the contribution of H_2S^{33} to $m/e = 35$.

In group A (0.75% H_2S and 0.75% D_2), the $[HD]_t/[D_2]_0$ ratios were found to be equal, to within experimental error, to the values of $[HDS]_t/[H_2S]_0$. In group B (0.75% H_2S and 3.0% D_2), the ratios $[HDS]_t/[H_2S]_0$ were four times larger than $[HD]_t/[D_2]_0$. Similarly, in group C (3% H_2S and 0.75% D_2), the $[HDS]_t/[H_2S]_0$ ratios were one-fourth as large as the $[HD]_t/[D_2]_0$ values. These observations confirm to some extent the method of reduction of the ammonia-exchange data, which relies only on the $[HD]_t/[D_2]_0$ values, as well as demonstrate that for the H-D exchange with H_2S the reaction order is approximately unity with respect to D_2 and zero order with respect to H_2S . Since the $D_2 + H_2S$ results are preliminary, no further details will be given in this paper.

In the next series of experiments, shocks were run to check on any possible dependence of the rate of ammonia-deuterium exchange on the argon concentration. Since argon is the major component ($\sim 98\%$) of the mixture, its concentration cannot be changed without generating a new gas-dynamic situation; its contribution to the reaction rate can only be obtained from the total reaction order. This was estimated by running shocks at different total pressures at a fixed composition and temperature. Experimentally, the ratio of P_4/P_1 (driver to driven pressure) was fixed and the diaphragm thickness was chosen according to P_4 ; P_1 was varied from 29 to 136 mm. and diaphragms from 0.5- to 2-mil Mylar film were used. First-order rate constants were computed for these experiments, from the integrated form of the equation

$$k_* t = -\ln \left[1 - \frac{[D_2]_0 [HD]_t}{[HD]_{eq} [D_2]_0} \right] \quad (2)$$

where $k_* = k_1 + k_{-1}$. At these temperatures $K_{eq} = 6$ for the exchange reaction

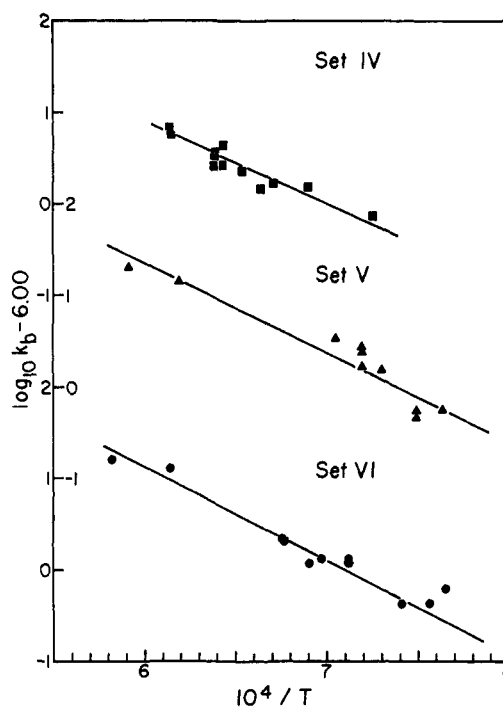
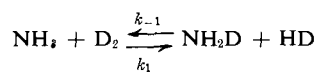


Figure 3. Three sets of data in which the logarithm of the bimolecular rate constant was plotted against the reciprocal temperature to deduce the corresponding activation energies.

and $k_* = k_1[D_2]_0/[HD]_{eq}$. Since the peak intensity of H_2^+ in the mass spectrum never exceeded its background magnitude, the reaction $NH_2D + HD \rightarrow NHD_2 + H_2$ amounted to less than a few per cent of the total conversion. This argues for a negligible correction due to the reverse reaction of the first exchange step. Nevertheless, eq. 2 was used, and k_1 values were computed for the various samples.¹² Since k_1 may depend on the argon density, $\log k_1$ was plotted against the logarithm of the total density (essentially, the argon concentration); the slope of this plot should give the reaction order with respect to argon. Figure 2 shows the experimental results. It is obvious that there is a considerable effect of the argon concentration on the values of k_1 , the slope being 0.86 ± 0.1 . Thus, to within the experimental error, the rate of exchange is given by the expression

$$\frac{\Delta(HD)}{\Delta t} = k_b[D_2][Ar] \quad (3)$$

In Table II a complete summary of the data is presented, grouped as to composition, in sequence of recording. There is much more internal consistency among runs obtained on 1 day than between sets taken weeks apart. Hence, to estimate the activation energy we plotted three curves (Figure 3a-c) for the three most recent sets of runs. Least-square analyses of the sets give 36.4 ± 3.9 , 41.9 ± 4.4 , and 35.2 ± 6.8 kcal./mole for E_a in the expression: $k_b = AT^{1/2} \exp(E_a/RT)$, cc.

(12) For ratios of $(NH_3)_0/(D_2)_0$ equal to 1, 0.25, and 4, values of $(D_2)_0/(HD)_{eq}$ were 1.408, 4.21, and 1.053, respectively. Thus, for these three samples, eq. 2 takes on the forms

$$\begin{aligned} 1.408k_1t &= -\ln [1 - 1.408(HD)_t/(D_2)_0] \\ 4.21k_1t &= -\ln [1 - 4.21(HD)_t/(D_2)_0] \\ 1.053k_1t &= -\ln [1 - 1.053(HD)_t/(D_2)_0] \end{aligned}$$

The argon concentration $[Ar]_s = P_1(\rho_s/\rho_1)(1/RT)_s$; $k_b = k_1/[Ar]_s$.

Table II. Summary of Kinetic Data

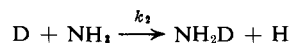
Set ^a	P ₁ , mm.	T ₀ , °K.	ρ ₀ /ρ ₁	[Ar] ₀ , mole/cc. × 10 ⁸	(HD) ₀ / (D ₂) ₀	Dwell time, μsec.	k _b × 10 ⁻⁶ , cc. mole ⁻¹ sec. ⁻¹
I	34.5	1565	5.875	1.085	0.035	790	4.20
	37.5	1565	5.875	1.176	0.013	790	1.41
	31	1575	5.90	0.979	0.024	750	3.31
	28	1635	6.00	0.898	0.045	740	6.98
II	28	1575	5.90	0.882	0.030	760	4.55
	80	1325	5.32	2.278	0.032	940	1.53
	72	1338	5.35	2.059	0.016	720	1.09
	66	1365	5.40	1.904	0.031	740	2.23
	61	1390	5.475	1.786	0.026	720	2.06
	120	1338	5.35	3.433	0.018	720	0.73
	102	1358	5.39	2.941	0.040	720	1.94
III	155	1430	5.575	4.620	0.070	790	2.02
	178	1390	5.475	5.214	0.057	770	1.48
	135	1555	5.85	4.225	0.121	760	4.10
	29	1565	5.875	0.909	0.047	760	7.00
IV	29	1555	5.85	0.909	0.030	770	4.35
	136	1565	5.875	4.272	0.102	770	3.35
	135	1565	5.875	4.240	0.114	800	3.65
	135.5	1555	5.85	4.240	0.086	800	2.70
	135.5	1565	5.875	4.257	0.082	790	2.58
	29	1630	6.00	0.930	0.048	760	7.00
	29	1625	5.95	0.925	0.040	760	5.85
	62	1380	5.475	1.813	0.012	880	0.76
	55	1450	5.625	1.652	0.020	780	1.57
	82	1530	5.80	2.540	0.045	800	2.28
	82	1490	5.71	2.534	0.033	780	1.72
	84.5	1505	5.75	2.599	0.030	790	1.49
	V	102	1335	5.35	2.92	0.010 ₅	760
104		1335	5.35	2.97	0.013	790	0.56
96		1308	5.275	2.71	0.011 ₇	760	0.57
94		1370	5.40	2.72	0.034	790	1.50
93		1390	5.475	2.72	0.036	830	1.64
94		1390	5.475	2.75	0.049	760	2.42
93		1418	5.55	2.76	0.068	760	3.39
93		1390	5.475	2.72	0.053	740	2.73
94		1615	5.975	3.00	0.253	740	14.1
93		1690	6.125	3.05	0.354	770	20.8
93		1322	5.625	2.71	0.009 ₃	800	0.43
VI	92	1350	5.675	2.70	0.009	800	0.43
	82.5	1405	5.825	2.49	0.024 ₉	820	1.21
	83	1405	5.825	2.49	0.026 ₆	840	1.29
	83	1405	5.825	2.49	0.023 ₈	800	1.18
	84	1308	5.555	2.41	0.011 ₁	740	0.63
	83	1480	6.010	2.57	0.043 ₁	770	2.23
	83	1435	5.920	2.53	0.025	760	1.32
	83	1480	6.010	2.57	0.043	760	2.23
	83	1630	6.375	2.72	0.233	740	13.2
	83	1720	6.575	2.81	0.277	730	16.0

^a Sets I-V were run with 0.75% D₂ and 0.75% NH₃; set VI was run with 0.75% D₂ and 3% NH₃.

mole⁻¹ sec.⁻¹. The corresponding A factors are 1.06 × 10¹⁰, 1.74 × 10¹¹, and 0.90 × 10¹⁰, respectively.

The Reaction Mechanism

The reaction rate was found to be independent of the ammonia concentration. Hence, the rate-controlling step is not the formation of a bimolecular four-centered transition state. Indeed, the rate is controlled by collisions between D₂ and Ar. It may appear at first that the rate is determined by a homogeneous dissociation of D₂ into atoms, followed by a fast reaction with the ammonia



the argon serving as the third body for the first step. This mechanism is ruled out by the following considera-

tions. The rate of the homogeneous dissociation of deuterium molecules into atoms has been measured by several investigators⁶ using shock tube techniques. The rate constant for dissociation in the presence of argon, at around 1400°K., was found to be 8.75 × 10⁻² cc. mole⁻¹ sec.⁻¹. On the other hand, k_b, which appears in footnote 12, is much higher at 1400°K. and is approximately equal to 2 × 10⁶ cc. mole⁻¹ sec.⁻¹; i.e., it is seven to eight orders of magnitude higher. In other words, the number of deuterium atoms formed is seven orders of magnitude smaller than the number of NH₂D molecules formed over the same time interval. Thus the dissociation process cannot be the first step with the exchange as the second step.

The presence of a chain mechanism, as suggested by Farkas,⁵ can also be ruled out.

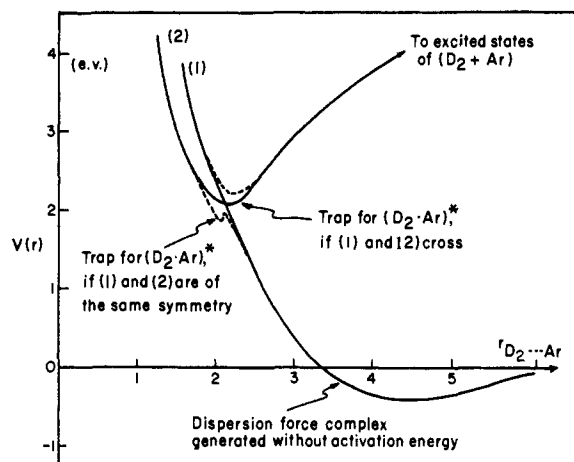
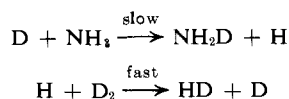


Figure 4. Possible potential energy functions for the formation of electronically excited complexes between argon and deuterium. The dispersion-type complex (in the ground electronic state) is exemplified by the rare gas-hydrogen halide complex reported by Rank and co-workers (D. H. Rank, *et al.*, *J. Chem. Phys.*, **37**, 2511 (1962)).



In the first place the extremely long chain which is required to account for the observed rate of exchange should show a dependence on the ammonia concentration, contrary to our observations. There is, however, a much stronger argument which excludes the possibility of a long chain. Knowing the maximum concentration of deuterium atoms in the reaction mixture, one may ask whether enough collisions can occur between these atoms and ammonia during the experimental dwell time to account for the observed extent of reaction. The maximum concentration of atoms which can be present in the reaction mixture is the one which can be generated by the homogeneous dissociation process during the 700- μ sec. dwell time. Its value at 1400°K. is about 10^{-15} mole/cc. (much below the equilibrium value). This may be estimated from the equation

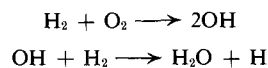
$$[\text{D}] = 2k_D[\text{D}_2][\text{Ar}](700 \times 10^{-6}) \quad (4)$$

where k_D is the rate constant for dissociation in the presence of argon⁶ in cc. mole⁻¹ sec.⁻¹. The above value for the concentration of deuterium atoms may then be inserted in the equation

$$\frac{d[\text{NH}_2\text{D}]}{dt} = k_2[\text{D}]_{\text{max}}[\text{NH}_3] \quad (5)$$

and a bimolecular rate constant, k_2 , estimated on the basis of a 5% conversion during 700 μ sec., *i.e.*, $0.05/(700 \times 10^{-6}) = 10^{-15}k_2$. This leads to $k_2 = 7 \times 10^{16}$ cc. mole⁻¹ sec.⁻¹. Since the atom displacement reaction has approximately 10 kcal./mole activation energy,⁵ k_2 must have a pre-exponential factor higher than 10^{18} cc. mole⁻¹ sec.⁻¹, which is far too high for a simple bimolecular process. This means that the mechanism which is represented by the rate law (eq. 5) is unacceptable. Further, the possibility that the H atoms are produced from the decomposition of ammonia is ruled out because of the zero-order depend-

ence on the ammonia concentration and the relatively large activation energy (≈ 78 kcal./mole) reported for the pyrolysis of NH_3 .¹³ An order of magnitude estimate of the maximum H-atom concentration which might have been produced from the largest possible O_2 contamination, based on the reactions

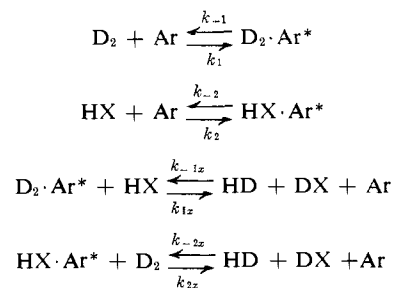


also led to an unacceptably low rate of HD production.

Having eliminated the two obvious mechanisms, we are forced to consider three alternate processes, each of which involves an unusual feature. With sufficient *ad hoc* assumptions, all reduce to the observed rate law. At this stage our choice of the third process is based on a subjective evaluation of the most acceptable model. Further obvious experiments are planned which may provide an objective basis for this choice.

A. Complex formation of exchange partners followed by selective quenching. One may impose the steady-state condition on the concentration of the complex and force agreement with eq. 3 by introducing the assumption that collisions of the complex with Ar are particularly effective for inducing exchange, whereas collisions with HX are especially effective for conversion to the original reactants. This is highly artificial.

B. Electronically excited complex formation with Ar (write HX for NH_3 , H_2S , HCl , etc.).



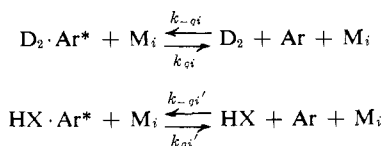
After eliminating three-body processes, impose the steady-state condition on $\text{D}_2 \cdot \text{Ar}^*$ and $\text{HX} \cdot \text{Ar}^*$.

$$\frac{d(\text{HD})}{dt} = k_{1x}(\text{HX}) \frac{k_1(\text{Ar})(\text{D}_2)}{k_{-1} + k_{1x}(\text{HX})} + k_{2x}(\text{D}_2) \frac{k_2(\text{Ar})(\text{HX})}{k_{-2} + k_{2x}(\text{D}_2)} \quad (6)$$

To force agreement with eq. 3 one must assume: (a) the second term is negligible in magnitude compared with the first, and (b) $k_{-1} \ll k_{1x}(\text{HX})$; for the activated species the exchange is very rapid. Then $d(\text{HD})/dt \rightarrow k_1(\text{D}_2)(\text{Ar})$. Since our data require that k_1 have as a factor $\exp(-40,000/RT)$, this complex could conceivably be generated, as indicated schematically in Figure 4, by the presence of the $V_2(r)$ potential curve. However, neglect of the second term in the full rate expression in a highly artificial assumption; indeed $\text{HX} \cdot \text{Ar}^*$ should be present in higher concentrations than $\text{D}_2 \cdot \text{Ar}^*$.

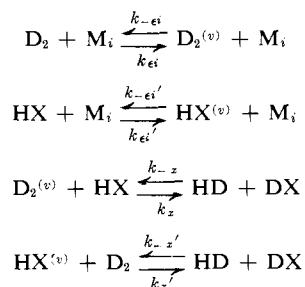
In an elaboration of this mechanism one may introduce selective quenching steps.

(13) T. A. Jacobs, *J. Phys. Chem.*, **67**, 665 (1963); H. E. Avery and J. N. Bradley, *Trans. Faraday Soc.*, **60**, 857 (1964).



This is a less strained, but is still largely an *ad hoc* mechanism, in which the very existence of $D_2 \cdot Ar^*$ type complexes is questioned.

C. Rate limited by vibrational excitation of one of the reactants.



Apply the steady-state condition on the concentrations of $D_2^{(v)}$ and $HX^{(v)}$, neglecting the reverse of the exchange step (low conversion limit).

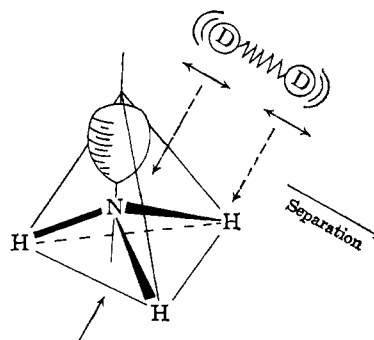
$$\frac{d(HD)}{dt} = \frac{k_x(D_2)(HX)\Sigma k_{ei}M_i}{k_x(HX) + \Sigma k_{-ei}M_i} + \frac{k_x'(D_2)(HX)\Sigma k_{ei}'M_i}{k_x'(D_2) + \Sigma k_{-ei}'M_i} \quad (7)$$

To force agreement with eq. 3 one must assume: (a) in the first term, $k_x(HX) \gg \Sigma k_{-ei}M_i$. This is merely the statement that for a sufficiently activated $D_2^{(v)}$, the reaction rate with HX is much faster than the de-excitation rate. This is not unexpected for diatomic molecules with appreciable vibrational relaxation times. (b) In the second term, $k_{-e2}'(HX) \gg [(k_x' + k_{-e3}'(D_2) + k_{-e1}'(Ar))]$. (c) In both terms, $k_{e1}(Ar) \gg [k_{e2}(D_2) + k_{e3}(HX)]$.

$$\frac{d(HD)}{dt} \rightarrow \left[k_{e1} + \frac{k_{e1}'k_x'}{k_{-e2}'} \right] (D_2)(Ar)$$

While assumption b seems artificial, one may argue that for the pairs $NH_3 + D_2$ and $H_2S + D_2$, it is likely that $k_x'k_{e1}'/k_{-e2}' \ll k_{e1}$ because of the small magnitude of k_x' ; *i.e.*, the rates of reaction between $NH_3^{(v)} + D_2$ and $H_2S^{(v)} + D_2$ are much smaller than between $D_2^{(v)} + NH_3$ and $D_2^{(v)} + H_2S$, respectively.

In the production of HD, species HNH_2 has a three-fold role. (i) Collisions between NH_3 and D_2 excite $D_2^{(v)}$. This provides a negligible contribution to the total rate of production of $D_2^{(v)}$ over the concentration range used in this experiment. (ii) Collisions between NH_3 and $D_2^{(v)}$ lead to exchange. This process (for $\nu > 5$) has a high cross section and hence is not rate limiting. (iii) Collisions between NH_3 and M_i produce $NH_3^{(v)}$. Such encounters probably are efficient, but the next step $NH_3^{(v)} + D_2$ appears to have a low-collision cross section. A partial explanation may lie in the geometric requirements for the four-center transition state.



Because of the large anharmonicity, in $D_2^{(5)}$ and $D_2^{(6)}$ there are peaks in the vibrational wave functions at an $r_{(D-D)}$ which match the mean value $\langle r_{(N-H)} \rangle$ in $NH_3^{(0)}$; conversely, excitation of either the symmetric or asymmetric stretching modes in NH_3 merely increases the disparity between the r_{N-H} values at which there are peaks in the $|\Psi_{NH_3}^{(v)}|^2$ function and $\langle r_{D-D} \rangle$ for $D_2^{(0)}$.

Another description of the exchange process is that the lifetime of the four-center transition state is too short to permit exchange to occur if the complex is generated by a hard collision between $D_2^{(0)}$ and $HX^{(0)}$, *i.e.*, when the necessary 40 kcal. of activation energy is localized in their relative energy of translation, as measured along their line of centers. However, a favorable transition state is generated when the required activation energy is present in the proper vibrational mode, while their relative kinetic energy is of the order kT .

Consequences of Mechanism C

The validity of $k_{e1}(Ar) \gg [k_{e2}(D_2) + k_{e3}(HX)]$ could have been checked if the relative relaxation times for vibrational excitation of D_2 by Ar, NH_3 , and D_2 were known. To date attempts to make direct measurements have failed, and the empirical relation developed by Millikan and White¹⁴ is not applicable. If one accepts the above inequality on the basis of our exchange rate data, one may argue that D_2 -Ar, D_2 - NH_3 , and D_2 - D_2 collisions are all highly efficient so that their relative contributions are approximately proportional to the relative concentrations of the colliders.

The observed activation energy for the homogeneous exchange reaction is considerably lower than that expected were the rate-limiting step the formation of a four-centered transition state, for which $E_a \approx 0.28[(D_0)_{(A-A)} + (D_0)_{(B-B)}]$.¹⁵ The mechanism we favor implies that the activation energy for exchange must be available in an appropriate intramolecular mode. There are two other cases where a high specificity to the mode of excitation has been demonstrated. In the dissociation of diatomic molecules, the *a priori* probability for dissociation appears to be highest for the top-most vibrational level and declines exponentially with increasing distance below the dissociation limit.¹⁶ Also, in the ion-atom reaction, $He + H_2^+ \rightarrow HeH^+ + H$, which is endothermic to about 1.1 e.v., the rate appears to be independent of the relative kinetic energy of the reacting species,

(14) R. C. Millikan and D. R. White, *J. Chem. Phys.*, **39**, 3209 (1963), and private communications.

(15) J. O. Hirschfelder, *ibid.*, **9**, 645 (1941).

(16) P. V. Marrone and C. E. Treanor, CAL Report QM-1626-A-10, Feb. 1963, to DA-30-069-ORD-3443.

and is appreciable only for H_2^+ in vibrational states above the fifth level.¹⁷

Two points merit further discussion. Mechanism C as written is symbolic of a sequence of excitations in steps, from $\nu = 0$ to 6, followed by rapid depletion of the populations of states for $\nu \geq 6$. In such a system, the definition of a "rate constant" is not clear, since T_{vib} cannot be strictly defined. The measured activation energy is only approximately the height of that vibrational level which is filled to *nearly* the Boltzmann population. A complete analysis requires the solution of the coupled equations which express the rates of filling and depleting of the separate levels, say from $\nu = 0$ to 8, owing to vibrational energy transfer and exchange. Then one need not introduce the "steady-

(17) H. Von Koch and L. Friedman, *J. Chem. Phys.*, **38**, 1115 (1963); T. F. Moran and L. Friedman, *ibid.*, **39**, 2491 (1963); see also A. Weingartshofer and E. M. Clarke, *Phys. Rev. Letters*, **12**, 591 (1964).

state" approximation. A machine calculation of this model has been started.

The second question pertains to the distribution of the energy of activation (present in the supermolecule) among the reaction products. The postulate that the transition probability is high when the activation energy is localized as vibration in D_2 implies, by microscopic reversibility, that this excess energy will be carried away in the vibrational modes, but probably shared between the DX and HD. Furthermore, when the relative kinetic energy of the reactants is high, it is likely that the relative kinetic energy with which the products leave will also be high, although some redistribution with the vibrational modes will take place.

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Isotope Exchange Rates. II.^{1a} Mechanism of the Homogeneous Reaction between Acetylene and Deuterium^{1b}

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The homogeneous gas phase reaction between acetylene and deuterium was investigated in a shock tube over the temperature range 1300 to 1665°K. Incident shocks in samples highly diluted with argon (80–87%) were used; compression factors by the shock were in the interval 3.6 to 4.3 for initial total pressures (at 300°K.) of 23–110 mm. The rate of substitution of D for H was followed by recording the emission intensity in the infrared due to C_2HD (at 2555 cm^{-1}) and to C_2H_2 (at 3195 cm^{-1}). The total order for the substitution reaction was 1.24 ± 0.05 . It was demonstrated that $d(C_2HD)/dt \cong 2(d(C_2D_2)/dt) \cong -2/3(d(C_2H_2)/dt) = k(D_2)^{1.0}(C_2H_2)^{0.24}(Ar)^0$. A mechanism consistent with all the data involves two transient species: the complex $C_2H_2 \cdot D_2$, which is readily destroyed by collisions with C_2H_2 molecules, and $C_2H_2D_2^*$, which resembles a highly excited ethylene. The effective activation energy for the substitution reaction is 32.5 kcal./mole.

Introduction

One of the most intriguing facts which came to our attention during the course of our shock tube studies is the occurrence of unsuspected reactions which take place at high temperatures, but under conditions which heretofore had been assumed to be insufficiently severe for appreciable reactions to occur. One example, discussed in detail in this paper, is the reaction between acetylene and hydrogen at temperatures up to 1700°K.

(1) (a) A. Lifshitz, C. Lifshitz, and S. H. Bauer, *J. Am. Chem. Soc.*, **87**, 143 (1965); (b) presented before the Division of Fuel Chemistry, 145th National Meeting of the American Chemical Society, Philadelphia, Pa., 1964.

When one mixes acetylene and hydrogen at these temperatures, no change in the concentration of the acetylene can be detected for as long as 1 msec. During this interval, each acetylene molecule is subjected to an enormous number of collisions with argon (the ambient gas), acetylene, and hydrogen molecules. That the acetylene and hydrogen are actually involved in an extensive association reaction, but that the acetylene is rapidly replenished by the reverse processes, becomes evident when deuterium is used in place of hydrogen. The following special features of shock tube operation are thereby demonstrated: (a) the samples are heated very rapidly and homogeneously, and (b) it is possible to follow in time a sequence of steps for a selected reaction.

The heuristic rate expressions derived from these shock tube data permitted us to establish that the mechanism for H–D substitution in C_2H_2 differs significantly from that in NH_3 , H_2S , HCl , and H_2 . Further, selection between two plausible transition states



can be made on the basis of the relative amounts of C_2H_2 lost and of C_2HD and C_2D_2 generated.

Experimental

The Shock Tube. The studies described below were conducted in a stainless steel shock tube, 6 in. in