May, 1987] © 1987 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 60, 1641—1643 (1987) 1641

The Reaction of $N(2^4S_{3/2})$ with Hydrogen Halides and Deuterium Iodide

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(Received December 4, 1986)

The bimolecular rate constants for the reactions of ground state atomic nitrogen with hydrogen halides and deuterium iodide were measured by employing a pulse radiolysis-resonance absorption technique. As for the reactions of hydrogen iodide and deuterium iodide, the temperature dependence was also measured; it was found that the rate constants were well expressed by the following Arrhenius expressions: $k(N+HI)=(3.6\pm0.6)\times10^5 \exp[-(1530\pm50)/T]$; $k(N+DI)=(1.0\pm0.4)\times10^5 \exp[-(1460\pm130)/T]$, in units of $m^3\,mol^{-1}\,s^{-1}$. The preexponential factors for these reactions are much smaller than the semiempirically calculated ones. These small preexponential factors suggest that these reactions proceed non-adiabatically. The rate constants for hydrogen bromide and hydrogen chloride were found to be very small.

Recently, we have reported the Arrhenius parameters for the reactions of ground-state atomic nitrogen with halogen molecules.[1] The preexponential factors for these reactions were found to be much smaller than those for the analogous reactions of atomic hydrogen and oxygen or those predicted by the semiempirical calculations. It was also found that the preexponential factor increases with the increase in the molecular weight. In order to explain these experimental results, we proposed that the potential barrier for the adiabatic route on the quartet surface is very high and that the major route of the reaction is a non-adiabatic one via a doublet surface. If this hypothesis is true, the preexponential factors for the $N(^4S)+HI$ and DI reactions should also be small, although the production of NH (or ND) and I is spin-allowed and exothermic. In order to check this hypothesis, we have performed experiments with HI and DI. As for the reaction of $N(^4S)+HBr$, Milton and Dunford have reported the bimolecular rate constant to be $2\times10^4\,m^3\,mol^{-1}\,s^{-1}$ at 313 K.[2] They considered that the formation of NH and Br is almost thermoneutral, but recent measurement of the heat of the formation of NH suggests that the reaction is $55\,kJ\,mol^{-1}$ endothermic,[3] and the rate constant they obtained seems to be too large. Although the formation of NH and Cl is unquestionably endothermic in the reaction of $N(^4S)+HCl$, it is not certain if the production of NCl and H is also endothermic, since the NCl bond energy is not known precisely.[4] In the present work, we have measured the rate constants for the reactions of $N(^4S)$ with hydrogen halides and deuterium iodide at various temperatures.

Experimental

The experimental apparatus and the procedures were the same as those reported in a previous paper.[1]

The HI and DI were synthesized from H_2 or D_2 (both Takachiho Kako) and I_2 (Koso Chemical Co.) in the presence of platinized asbestos and were used after repeated trap-to-trap distillations. In order to estimate the isotopic purity of DI, it was photolyzed by the light from a high-pressure mercury lamp; the ratio of D_2 to HD was measured mass-spectrometrically. Since the absorption coefficient of HI is a little larger than that for DI,[5] the HI content must have been overestimated. The initial content of HI was 7%; it increased gradually during the storage, until it was 13% when the experiments were over. Then, all the data for DI were corrected by assuming that it contained 10% of HI. The HBr was separated from its aqueous solution (Wako Pure Chemical Industries) and used after repeated trap-to-trap distillations. The HCl was the product of the Takachiho Kako Co. and was used without further purification.

Results

The decay rate of $N(^4S)$ increased linearly with the increase in the pressure of HI or DI; it also increased with the temperature of the system, while it was independent of the total pressure at a given pressure of HI. On the other hand, in the cases of HBr and HCl, the decay rate did not show any marked dependence on the partial pressures of these gases. In other words, the rate constants for the reactions of $N(^4S)$ with HBr and HCl are too small to be measured by the present technique. From the least-squares slopes of the linear relationships between the decay rates and the pressures of HI and DI, the bimolecular rate constants can be determined. As has been discussed in the previous paper, the apparent rate constants determined from these slopes are considered to be twice the rate constants for the reactions of $N(^4S)$ with HI and DI.[1] This is because one of the products of the reaction, NH or ND, is considered to react with $N(^4S)$ once again very rapidly. The rate constant for the reaction of N and NH (ND) should be of the same order as those for the N+OH, N+CN, and $N+NH_2$ reactions.[6] It should be noted that the formation of NI and H (D) is highly endothermic. Table 1 summarizes the rate

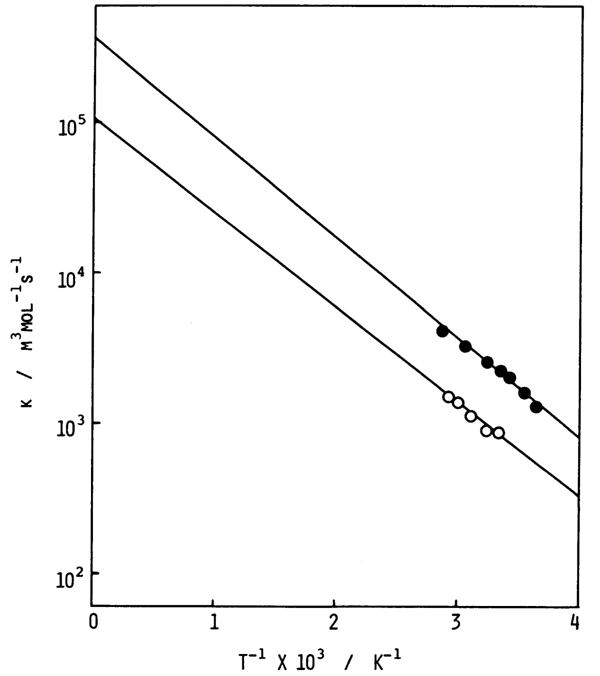

Fig. 1. Arrhenius plots for the reactions of N+HI(●) and N+DI(○).

Table 1. Rate Constants for the Reactions of N(^{4}S) with Hydrogen and Deuterium Halides

Reactant	T/K	$k\times10^{-3}$/m^3 mol^{-1} s^{-1}
HI	348	4.18±0.39
	327	3.30±0.45
	308	2.54±0.07
	298	2.23±0.11
	292	2.04±0.15
	282	1.61±0.13
	274	1.31±0.07
DI	341	1.46±0.10
	333	1.35±0.08
	322	1.09±0.08
	309	0.87±0.08
	299	0.86±0.09
HBr	376	<0.8
HCl	377	<0.6

Table 2. Experimental and Semiempirically Calculated Arrhenius Parameters for the Reactions of N(^{4}S) with HI and DI

Reactant	E_a/kJ mol^{-1}	$A\times10^{-5}$/m^3 mol^{-1} s^{-1}			
	exp$^{a)}$	exp$^{a)}$	LEPS$^{b)}$	BEBO$^{c)}$	BEBO$^{d)}$
HI	12.7±0.4	3.6±0.6	680	120	140
DI	12.1±1.1	1.0±0.4	680	110	130

a) Experimental value; b) Sato parameter=0.053; c) C_1=4.13, C_2=0.28; d) C_1=3, C_2=0.303.

Table 3. Arrhenius Parameters Calculated by the BEBO Method

Reaction	C_1	C_2	E_a/kJ mol^{-1}	$A\times10^{-5}$/m^3 mol^{-1} s^{-1}
N+HI	3	0.28	8.4	230
	4.13	0.28	12.7	120
	3	0.303	12.7	140
N+DI	3	0.28	8.5	210
	4.13	0.28	13.1	110
	3	0.303	13.9	130

constants determined in this way at various temperatures. The rate constants for HI and DI are well expressed by the Arrhenius expressions. This is shown in Fig. 1, while the Arrhenius parameters are listed in Table 2.

The semiempirical LEPS and BEBO calculations were performed to evaluate the preexponential factors for the reactions of N(^{4}S) with HI and DI. The procedure for the LEPS calculation was the same as that described in the previous paper.[1)] The Sato parameter was adjusted to give the activation energy experimentally obtained for the N+HI reaction. As for the BEBO calculation, in the previous work the factor of the anti-Morse function, C_1, according to the notation by Singleton and Cvetanović,[7)] was parametrized and adjusted to give the experimental activation energy. In the present work, not only this factor, but also the Pauling constant, C_2, were parametrized. A similar procedure has been employed by Brown and Smith in the calculation of the rate constant for the O+DCl and DBr reactions.[8)] When C_1 was adjusted, C_2 was fixed at 0.28, the recommended value by Gilliom, while, when C_2 was adjusted, C_1 was fixed at 3 considering that atomic nitrogen is a quartet. The rest of the calculational procedure was the same as that reported previously.[1)] The results are shown in Tables 2 and 3. The calculations for the N+DI reaction were performed by using the same parameters as those for the N+HI reaction.

Discussion

As has been discussed in the previous paper, the reactions of N(^{4}S) with halogen molecules are considered to proceed non-adiabatically via doublet surfaces.[1)] In the present cases, the experimentally obtained preexponential factors for the N+HI and DI reactions were also found to be much smaller than those for the analogous reactions of H and O atoms[7,9)] or than the results of the semiempirical LEPS and BEBO calculations, as is shown in Table 2. In general, the agreement between the experimentally obtained Arrhenius parameters and the semiempirically calculated ones is not very good, even in the simple systems, such as H+HX and O+HX, where

HX stands for hydrogen halides.[7,8,10,11] Three-dimensional trajectory calculations are necessary for a quantitative discussion.[12] However, the present disagreement between the experimental and the calculated preexponential factors is outstanding. This discrepancy suggests that these reactions involve transitions between potential surfaces of different multiplicities. Correlation diagrams similar to that presented in the previous paper for the N+halogens systems may also be drawn in the present cases.[1] The preexponential factor for the N+HI reaction was found to be around one-third of that for the N+I_2 reaction. This is also consistent with the above consideration that the reactions are not adiabatic, because in the N+I_2 system, a stronger spin-orbit coupling is expected and the spin-conservation rule is considered to hold less rigorously. The isotope effect observed in the preexponential factors for HI and DI may be attributed to the difference in the probabilities of crossing from a quartet surface to a doublet surface, since the semiempirical calculations predict no large isotope effect.

The extremely slow reaction rates for HBr and HCl are consistent with the thermodynamical predictions. The formation of NH and halogen atoms from these molecules is endothermic. The production of NCl and H from N(^{4}S) and HCl may also be endothermic. The rate constant reported by Milton and Dunford for the N+HBr reaction seems to be erroneous.[2] Their method, a diffusion-flame technique, is too indirect for quantitative measurements. Moreover, their reported value for the N+C_2H_4 reaction has not been confirmed in a recent work.[13]

From the present results, together with those of our recent work,[1,13] it can be concluded that N(^{4}S) atoms are very inert to stable molecules with even-numbered electrons. This inertness can be attributed to the conservation of the spin-angular momentum. In most practical systems at moderate temperatures, such as discharge-flow systems, the decay of N(^{4}S) is governed by the reactions with the molecules with odd-numbered electrons, such as free radicals. In the absence of such active species, the only decay process is the termolecular or heterogeneous recombination reaction between atomic species.

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