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The Arrhenius Parameters for the Reactions of $N(2^4S_{3/2})$ with Halogen Molecules

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The temperature dependence of the rate constants for the reactions of ground-state atomic nitrogen with halogens were measured by means of a pulse radiolysis-resonance absorption technique. The rate constants for iodine and bromine were well expressed by the following Arrhenius expressions below 410 K: $k(N+I_2)=1.1\times10^6 \exp(-1170/T)$; $k(N+Br_2)=1.1\times10^5 \exp(-1490/T)$, in units of $m^3\ mol^{-1}\ s^{-1}$. The rate constant for the reaction with chlorine was found to be $1.1\times10^3\ m^3\ mol^{-1}\ s^{-1}$ at 411 K. Below this temperature, the rate constants for $N+Cl_2$ were too small to be measured. The preexponential factors for the I_2 and Br_2 reactions were found to be much smaller than the semiempirically calculated ones. These small preexponential factors suggest that the reactions between $N(^4S)$ and halogens proceed via nonadiabatic routes.

Ground-state atomic nitrogen, $N(2^4S_{3/2})$, is unreactive to stable molecules which do not have unpaired electrons. For example, the rate constants for the reactions of atomic nitrogen with unsaturated hydrocarbons are too small to be measured by ordinary techniques,[1,2] although ground-state atomic hydrogen and oxygen react with unsaturated hydrocarbons once in every ten or one hundred gas kinetic collisions at room temperature.[3,4] The situation is similar in the cases of inorganic species with even-numbered electrons, such as oxygen, ozone, and phosphine.[5,6] The halogen molecules are not exceptions. In the 1960's Phillips and his co-workers measured the rate constants for the reactions of $N(^4S)$ with halogens near room temperature and found that they are several orders of magnitude smaller than that for gas kinetic collisions.[7,8] In our recent work, we also measured the rate constant for the reaction with molecular iodine at 302 K and found it to be $2.4\times10^4\ m^3 mol^{-1}\ s^{-1}$.[1] The slow reaction rates for the addition of $N(^4S)$ to unsaturated hydrocarbons have been explained by the concept of the simple spin-conservation rule.[1] However, the unreactiveness to halogens, as well as to oxygen and ozone,[5] cannot be explained by this concept, because there are spin-allowed and energetically accessible exit channels—for example, the formation of triplet-state nitrogen halide and atomic halogen. In other words, there must be large potential barriers or entropies of activation for these exit channels. Therefore, in order to ascertain why $N(^4S)$ is unreactive, it is necessary to determine the preexponential factors and the activation energies separately. In the present work, we measured the temperature dependence of the rate constants for the reactions of $N(^4S)$ with chlorine, bromine, and iodine, by employing a pulse-radiolysis resonance-absorption technique. The preexponential factors were then compared with those predicted by the semiempirical LEPS (London-Eyring-Polanyi-Sato) and BEBO (Bond Energy-Bond Order) calculations.

Experimental

The experimental apparatus and the procedure were similar to those described in previous publications.[1,9] Atomic nitrogen was produced by the irradiation of a pulsed electron beam generated by a Febetron 706 apparatus. The pseudo-first-order decay in the concentration of $N(^4S)$ atoms was measured by means of the resonance absorption around 120 nm. The temperature of the reaction vessel was controlled by winding it with a nichrome heater or by introducing cold nitrogen gas from boiling liquid nitrogen into the surrounding copper tubing. A temperature controller (Sanyo Rikagaku SR-4000) was used to reduce the fluctuation in temperature within ±2 K. The relationship between the gas temperature in the chamber and the temperature of the outside wall of the chamber was measured prior to the experiments, and the gas temperature for each run was estimated by measuring the wall temperature with a copper-constantan thermocouple. The halogen pressures were measured with a capacitance manometer (MKS Baratron). After measuring the halogen pressure, an excess amount of nitrogen gas was introduced into the vessel. In general, considerable care is required in the measurement of the gas pressure when the temperature of the reaction zone and that of the pressure gauge are different. Under the conditions of viscosity flow, normally when the pressure is over 100 Pa, the pressure at the gauge, P_0, agrees with that at the reaction zone, P. On the other hand, under the conditions of molecular flow, below 0.1 Pa, the ratio of the pressure at the reaction zone to that at the gauge, P/P_0, is equal to the square root of the ratio of the temperature of the reaction zone, T, to that of the gauge, T_0. In the present experiments, the pressures of halogens were in the intermediate region: 0.8—4.0 Pa for I_2 and 3—20 Pa for Br_2 and Cl_2. In other words, P should be between P_0 and $P_0(T/T_0)^{1/2}$. Therefore, at high temperatures and at low pressures, the error in the estimation of the pressures should be around 10 %. However, since the above error decreases with the increase in the pressure, the error in the estimation of the second-order rate constants as well as the Arrhenius parameters should be much smaller than this. Therefore, the rate constants were estimated with using P_0 without corrections.

The sources and purities of N_2, He, I_2, and Cl_2 were the same as those reported previously.[1,9] Br_2 was separated from its aqueous solution (Koso Chemical Co.) and used after repeated trap-to-trap distillation and drying with P_2O_5.

Results

Evaluation of the Arrhenius Parameters. Figure 1

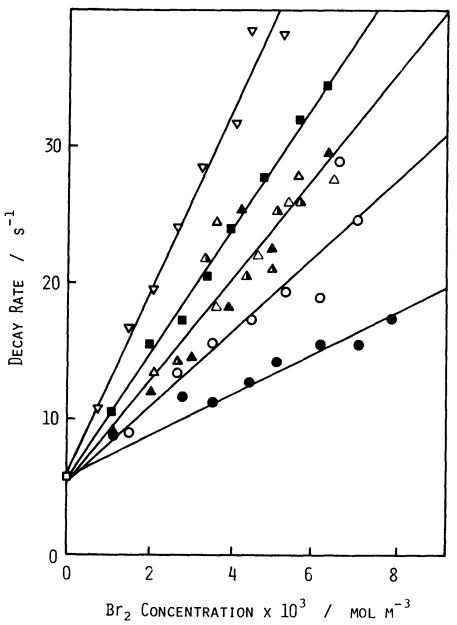

Fig. 1. The decay rate of N(⁴S) as a function of the Br_2 concentration. The temperatures and the total pressures are 410 K and 93 kPa(▽), 387 K and 93 kPa(■), 365 K and 93 kPa(▲), 365 K and 53 kPa(▲), 365 K and 133 kPa(△), 330 K and 93 kPa(○), and 293 K and 93 kPa(●). The symbol □ stands for the average of 24 runs measured in the absence of halogens.

illustrates the dependence of the pseudo-first-order decay rates of N(⁴S) on the Br_2 concentration at several temperatures. As has been observed for the N+I_2 reaction,[1] no total pressure dependence could be observed in this case, either. This suggests that termolecular processes are not important. Similar linear relationships could also be obtained for the cases of I_2 and Cl_2. The intercepts of such linear plots correspond to the decay in the absence of halogens. This value was found to be temperature-independent and to be 6.2± 1.7 s^{-1} (average of 24 runs). In a previous paper, we reported this value to be 3.2 s^{-1}.[1] This change is due to the difference in the reaction vessel. The decay of N(⁴S) in the system of pure nitrogen is considered to be the sum of the homogeneous and heterogeneous recombination of atomic nitrogen. The rate for the homogeneous loss is supposed to be independent of the size of the reaction vessel, while that for the heterogeneous loss may depend on the size. In the present work, we used a smaller vessel in order to obtain better temperature control; this may be the cause of the difference. It should be noted that the room temperature experiments with iodine showed that the slope of the plots was independent of the size of the reaction vessel.

From the slopes of the plots, such as are shown in Fig. 1, the rate constants could be obtained. In a previous paper, we proposed the following reaction scheme for the N_2+I_2 system in order to explain the nonlinear relationship between the decay rate of N(⁴S) and the I_2 pressure in the presence of ethene:[1]

Table 1. Rate Constants for the Reactions of N(⁴S) with Halogens

Reactant	T/K	$k\times10^{-4}$/m³ mol⁻¹ s⁻¹
I_2	410	6.28 ±0.45
	366	3.93 ±0.38
	325	2.95 ±0.17
	302	2.39 ±0.15[a]
	275	1.37 ±0.13
Br_2	410	0.330±0.010
	387	0.226±0.003
	365	0.182±0.010
	330	0.136±0.010
	293	0.070±0.003
Cl_2	411	0.105±0.013
	387	<0.07

a) Ref. 1.

$$N(^4S) + I_2 \longrightarrow NI(X^3\Sigma^-) + I, \quad (1)$$

$$N + NI \longrightarrow N_2(\text{or } N_2^*) + I, \quad (2)$$

$$NI + I_2 \longrightarrow NI_2 + I, \quad (3)$$

$$N + NI_2 \longrightarrow \text{Products}, \quad (4)$$

If NI and NI_2 are not reactive with N(⁴S), the apparent decay rate of N(⁴S) should agree with that for Reaction 1. However, it seems unreasonable to assume that Reactions 2 and 4 are slow. Their rate constants should be of the same order as those for the N+OH, N+CN, and N+NH_2 reactions, which have been measured to be very fast.[10] If NI and NI_2 react with N(⁴S) rapidly, the apparent decay rate should be twice that for Reaction 1. As has been mentioned in a previous paper, the addition of ethyne and 1,3-butadiene, which have been considered to be reactive with NI, to the N_2+I_2 system has halved the apparent decay rate of N(⁴S). This strongly suggests that Reaction 1 is rate-determining and that the apparent decay rate of N(⁴S) in the N_2+I_2 system can be regarded as twice that for Reaction 1. It should also be pointed out that the concentrations of NI and NI_2 are considered to be much less than that of N(⁴S) and that such processes as NI+NI may be neglected. Similar reaction mechanisms may also be assumed for the cases of Br_2 and Cl_2. As for the system of N_2+Cl_2, a reaction similar to Reaction 3, NCl+Cl_2→NCl_2+Cl, has been proposed by Combourieu et al.[11] Table 1 summarizes the rate constants for the reactions of N(⁴S) with halogens calculated by the least squares method at various temperatures. The error limits are the standard deviations. As for Cl_2, the reaction rates were too small to be measured precisely below 387 K. All the data for I_2 and Br_2 are well characterized by Arrhenius equations; the Arrhenius plots are shown in Fig. 2, together with the results of Phillips and his co-workers.[7,8] The Arrhenius parameters, as determined by the weighted least-squares method,[12] are listed in Table 2.

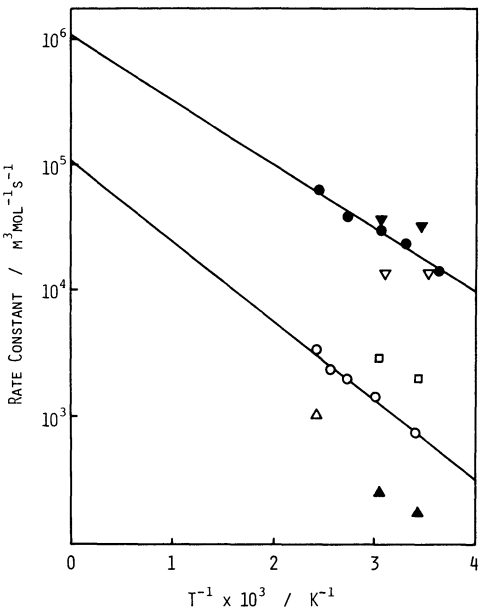

Fig. 2. Arrhenius plots for the reactions of N+I_2(●), N+Br_2(○), and N+Cl_2(△). Results reported by Phillips for N+I_2(▽), and by Grigor and Phillips for N+I_2(▼), N+Br_2(□), and N+Cl_2(▲) are also shown.[7,8]

Table 2. Arrhenius Parameters for the Reactions of N(⁴S) with I_2 and Br_2

Reactant	$A\times10^{-6}$/m³ mol⁻¹ s⁻¹	E_a/kJ mol⁻¹
I_2	1.08 ±0.26	9.7±0.6
Br_2	0.110±0.029	12.4±0.8

Semiempirical Calculations of the Preexponential Factors. The LEPS and BEBO calculations were performed. The general procedures for these calculations have been reviewed by Johnston.[13] In the LEPS calculation, Sato's empirical parameters were adjusted to give the experimental activation energies. The Morse parameters were evaluated from the molecular constants listed in the table of Huber and Herzberg, except for NI.[14] As for those of NI, since the molecular constants were not listed in that table, they were extrapolated from the NF/NCl/NBr series. For a given Sato parameter, the calculated activation energy was the lowest at the linear symmetric configuration in both cases. The force constants for the bending vibrations at the transition states were calculated to be in the order of 10^3 J mol^{-1} rad^{-2}. As has been discussed by Mayer et al., the conventional transition state theory should not be used to calculate the rate constants when the bending force constant is less than 10^4 J mol^{-1} rad^{-2}, because the amplitude of the vibration becomes too large.[15,16] Therefore, the rate constants were evaluated by the hard-sphere collision treatment.[15,16] From the Arrhenius plots of the calculated rate constants from 280 to 420 K, the preexponential factors were estimated to be 2.5×10^8 and 2.4×10^8 m^3 mol^{-1} s^{-1} for the N+I_2 and N+Br_2 reactions respectively.

As for the BEBO calculation, many modifications of its original form have been presented.[16-21] Mayer et al. have demonstrated that the anti-Morse function for the repulsion potential must be modified for reactions which involve transfers of atoms other than hydrogen.[17] It has also been suggested that the anti-Morse function should be scaled in some cases.[16-18] In the present work, we not only employed the modification by Mayer et al., but also parametrized the factor of the anti-Morse function to give the experimentally obtained activation energy. The modification to change the Pauling constant, which has been proposed by Gilliom,[20] was also employed, but it was found to have little effect on the final results. The molecular constants of the noble gas clusters which originate from the recent crossed molecular beam-scattering experiments and which are recommended by Bérces and Dombi[22] were used for the calculation. The conventional transition-state theory with unit transmission coefficients was employed to evaluate the preexponential factors. The results are 6.0×10^7 m^3 mol^{-1} s^{-1} in the cases of both N+I_2 and N+Br_2.

Both of the semiempirical calculations predict the presence of early potential barriers, loose transition states, and, consequently, fairly large preexponential factors for the reactions of N(⁴S) with halogens.

Discussion

Comparison with Literature Values. Figure 2 compares the present results with those of Phillips and his co-workers.[7,8] In Ref. 7, Phillips has mentioned that he performed the experiments on N+I_2 under conditions in which the homogeneous loss of NI is negligible and that the rate constant for Reaction 1 is 1.4×10^4 m^3 mol^{-1} s^{-1} at room temperature. However, the rate constant cited from this paper by Grigor and Phillips (Ref. 8) is 3.3×10^4 m^3 mol^{-1} s^{-1}. We cannot judge which is more reliable. Therefore, both results are plotted in Fig. 2. At any rate, the present results are not greatly different from those of Phillips. Phillips estimated the activation energy for N+I_2 to be around 0.3 kJ mol^{-1}. This value is much smaller than the present one, and we think their temperature range, 283—323 K, is too small to estimate activation energies. As for Cl_2, the very small rate constants reported by Grigor and Phillips near room temperature are consistent with the present results if the activation energy is in the order of 10 kJ mol^{-1}. In this case, the preexponential factor for N+Cl_2 should be less than that for Br_2. The unreactiveness of N(⁴S) to Cl_2 has also been reported by Iannuzzi and Kaufman.[23] The rate constants for N+Br_2 obtained in the present work are much smaller than those reported by Grigor and Phillips. We have no idea of how to account for this discrepancy.

Comparison with the Semiempirically Calculated Values. As has been mentioned in the Results section, the agreement between the calculated and the observed

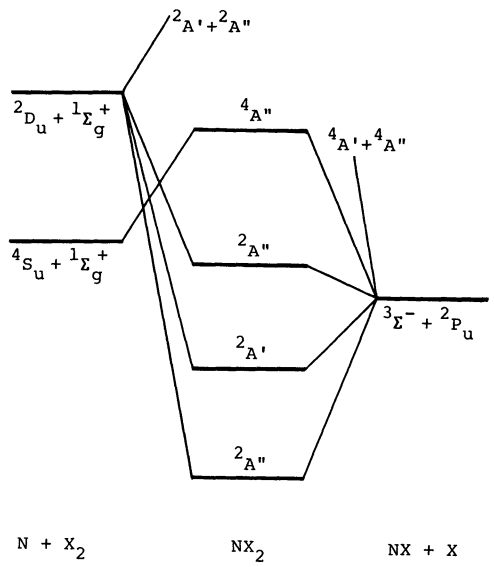

Fig. 3. Schematic correlation diagram connecting the states of $N+X_2$ and NX+X.

preexponential factors is very poor, especially for the $N+Br_2$ reaction. The experimental ones are two or three orders of magnitude smaller than the calculated ones. The LEPS method has originally been developed for the system of three hydrogen atoms.[24] Although the LEPS method has been applied to many systems, it is not necessarily accurate enough to evaluate the reaction rates, especially in the systems with p-electrons. The BEBO method has also been developed for the H-atom-transfer reactions. It is also questionable if the conventional transition-state theory is applicable.[25] However, the disagreement between the experimental and the calculated values seems beyond the uncertainty in the experiments or the calculations. In the next section, we would like to discuss the reason why.

Correlation between $N+X_2$ and NX+X. The reaction between $N(^4S)$ and X_2 (X represents halogen atoms) presumably proceeds via a collision complex, N-X-X, in the C_s symmetry. Although the LEPS calculation suggests that the transition state is collinear, this should not be considered to be conclusive, for the LEPS calculation predicts that the geometry of the transition state for the reaction of $N+O_2$ is also linear, while the more reliable ab initio calculations suggest that it is bent.[26] As is shown in Table 38 of Ref. 27, the ground state and the first and the second excited states of NF_2 in C_{2v} symmetry are doublets. By analogy with the case of NH_2, the energy of the lowest quartet state should be fairly high.[28] This situation will not change in the case of C_s symmetry, or in the cases of the other nitrogen dihalides. On the other hand, the intermediate state which can be correlated with $N(^4S)+X_2$ is a quartet. Therefore, under the assumption of weak spin-orbit coupling, there must be a crossing between the quartet and the doublet surfaces. A schematic correlation diagram is shown in Fig. 3. In such a case, the activation energy for the adiabatic route is very high; the only path to the product state, NX+X, is the non-adiabatic one via a doublet surface, and the preexponential factor should be much smaller than the theoretical one. On the other hand, under the approximation of strong spin-orbit coupling, the level crossings which appear in Fig. 3 are avoided and the reaction can proceed adiabatically. In conclusion, the extremely small preexponential factors for the $N+Br_2$ and $N+I_2$ reactions can be explained by considering that the reactions are non-adiabatic, while the increase in the preexponential factor from Br_2 to I_2 may be accounted for in terms of the increase in the degree of the spin-orbit interaction. The preexponential factors for the $N+Cl_2$ and $N+F_2$ reactions should be even smaller. Now, we are trying to measure the reaction rates for the N+HI reaction, which is also expected to have a small preexponential factor.

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