Calculations of the Rate Constants for the HX+NO $\rightleftharpoons$ HNO+X Reactions (X=H, F, Cl, Br, and I)

Tetsuo HIGASHIHARA

Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda-machi, Hiroshima 730

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The rate constants for these hydrogen-transfer reactions:

$$HX+NO \rightleftharpoons HNO+X \quad (X=H, F, Cl, Br, \text{and } I)$$

have been calculated by means of the transition-state theory combined with the BEBO method over the temperature range of 250—4000 K. The calculated rate constants were then compared with the experimental kinetic data.

There have been many attempts to estimate the rate constants theoretically for bimolecular reactions; these attempts have been, for example, collision theories, the transition-state theory combined with the BEBO or LEPS method, trajectory calculation, and so on. Although the bond energy-bond order (BEBO) method is an empirical one, this method has many advantages: calculations are easy, there are no parameters which need to be adjusted for each reaction, and the predicted activation energies are generally in good agreement with the experimental kinetic data.

In this study, in order to clarify the effect of the difference in X on the rate constants for these reactions:

$$HX + NO \rightleftharpoons HNO + X \quad (X=H, F, Cl, Br, \text{and } I),$$

the rate constants for these reactions were calculated by using the transition-state theory combined with the BEBO method. The rate constants for these reactions:

$$H_2 + NO \longrightarrow HNO + H \quad (1)$$

$$HCl + NO \longrightarrow HNO + Cl \quad (3)$$

$$HBr + NO \longrightarrow HNO + Br \quad (4)$$

$$HI + NO \longrightarrow HNO + I \quad (5)$$

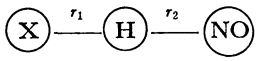
have been determined by Ando and Asaba[1] for Reaction 1 in shock waves, by Higashihara *et al.*[2,3] for Reactions 3 and 4 in shock waves, and by Holmes[4] for Reaction 5 in a static system. The rate constant of Reaction −1:

$$H + HNO \longrightarrow H_2 + NO \quad (-1)$$

has also been determined by several groups[5] by using various experimental methods over a wide temperature range. Although many kinetic data have thus been accumulated, there have been no theoretical studies for these reactions. Therefore, it is also interesting to try to explain these kinetic data consistently with a theory.

Calculations

The following linear three-atom model was used for the calculations of the BEBO potential energy curve:



The detailed procedures of calculations were summarized by Johnston (Ref. 6b, p. 339). It should, however, be noted that the following two points were modified in this calculation. First, the new Pauling constant, 0.28, which was evaluated by Gillion,[7] was used instead of 0.26 in Eq. I:

$$r = r_s - 0.28 \ln m \text{ (or } n), \quad (I)$$

where the subscript s denotes the length of a single bond and where m (or n) is the bond order of H–N (or X–H). Second, the new f value, 0.45,[7] in the Sato anti-Morse function (Eq. II) was used instead of 0.25:

$$V_{tr} = f\{D_e(1+e^{-\beta(r-r_s)})^2-1\}, \quad (II)$$

where β is the Morse parameter. All the molecular parameters necessary for the calculations are sum-

TABLE 1. MOLECULAR PARAMETERS

	D_0 / kcal mol^{-1}	ν / cm^{-1}	D_e / kcal mol^{-1}	r_s / Å	g	I / 10^{40} g cm	F / 10^8 N Å^{-1}	p	β / Å^{-1}
H-H	103.27	4405.3	109.4	0.74	1	0.46	5.74	1.069	—
H-F	134.6	4138	140.5	0.92	1	1.335	9.59	1.034	—
H-Cl	102.1	2989	106.4	1.27	1	2.64	5.16	0.948	—
H-Br	86.7	2649	90.5	1.42	1	3.316	4.12	0.897	—
H-I	70.6	2309	73.9	1.61	1	4.284	3.12	0.800	—
N-O	—	1903.6	—	—	2, 2	16.55	—	—	—
H-NO	48.6	3596	53.74	1.063	1	643.3[a]	7.1	0.984	1.794
F-NO	54.94	766	56.03	1.52	—	—	2.79	—	1.891
Cl-NO	37.15	605	38.01	1.95	—	—	1.92	—	2.024
Br-NO	27.8	542	28.57	2.14	—	—	2.06	—	2.278
I-NO	19.53	440	20.16	2.3	—	—	1.44	—	2.265

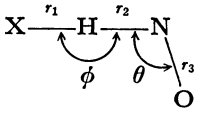
a) 10^{120} (g cm)^3.

marized in Table 1. The bond-order index (p or q) was calculated from this equation:

$$p(\text{or } q) = 0.28 \ln (D_e/D_x)/(r_x - r_s), \quad \text{(III)}$$

where D_x and r_x are the bond strength and the length of the corresponding noble gas molecule respectively. The BEBO properties of the activated complexes calculated by using this model are summarized in Table 2. In the case of the HI–NO reaction, the maximum value of the potential energy did not exist. In this case, the distance of H–I in the activated complex was assumed to be the same as the He–Kr Lennard-Johnes internuclear distance, and from this distance the bond orders, m and n, were calculated.

The vibrational frequencies of the activated complexes were calculated according to the method of the ***GF*** matrix by using the following model:



As is shown in Table 2, the bond order of H–N (m) in the activated complex is nearly unity in all cases. This means that the bond angle of H–N–O and the bond length of N–O in the complex may be nearly the same as those of the HNO molecule. Then, $\theta = 108.5°$ and $r_3 = 1.211$ Å, values which are the same as those of the HNO molecule, were assumed. The **G** matrix was constructed according to this model from Table, 7-4 of Ref. 8 (p. 135). The force constants used for each activated complex are listed in Table 3. The values of F_{33} and F_θ in this table are the same as those used by Brown and Pimentel[9] in the calculations of the vibrational frequencies of the HNO molecule.[10] The values of F_{11}, F_{22}, F_{12}, and F_ϕ were calculated by means of the three-atom BEBO method according to the procedures of Ref. 6b. The rest of the interaction force constants were assumed to be 0. The calculated vibrational frequencies are listed in Table 3 for each activated complex. In this table, the moments of inertia, I, of the activated complex and the activation energies, E_0 of the forward and backward reactions are also listed for each activated complex. Though the bending-force constant of H–N–O in the activated complex was assumed to be the same as that of the HNO molecule, this force constant might be appreciably affected by X. Therefore, the vibrational analysis was also carried out using a value one-half the normal F_θ value. The results of the calculations shown in the parentheses of Table 3 indicate that the change in the value of F_θ does not affect the vibrational frequencies very much.

Table 2. Properties of activated complexes calculated from the three-atom BEBO model

	n	m	r_1 / Å	r_2 / Å	V^{*} a) / kcal mol^{-1}
H-H-NO	0.028	0.972	1.741	1.071	56.89
F-H-NO	0.019	0.981	2.030	1.068	88.1
Cl-H-NO	0.008	0.992	2.622	1.065	53.01
Br-H-NO	0.002	0.998	3.160	1.064	36.77
I-H-NO	0.0004	0.9996	3.8	1.063	20.16

a) V^* is the maximum value of the potential energy.

The rate constants were calculated according to this familiar expression from the transition-state theory:

$$k = (kT/h)(Q^*/Q_{\text{react.}}) \exp(-E_0/RT), \quad \text{(IV)}$$

where Q^* and $Q_{\text{react.}}$ are the partition functions of the activated complex and the reactants respectively and where E_0 is the theoretical activation energy.

Furthermore, the rate constants of Reactions 1, 2, 3, 4, and 5 were calculated by using the simple collision theory to check the reliability of the observed kinetic data. The molecular diameters of the reactants

Table 3. Properties of activated complexes

	H-H-N-O	F-H-N-O	Cl-H-N-O	Br-H-N-O	I-H-N-O
F_{11} a)	−0.0194	−0.0738	−0.0202	−0.0021	0.0010
F_{22} a)	6.9516	7.0304	7.0726	7.0726	7.100
F_{12} a)	0.0201	0.1377	0.0572	0.0142	0.0028
F_ϕ a)	0.0853	0.1068	0.0339	0.0083	0.0017
F_{33} a)	10.54	10.54	10.54	10.54	10.54
F_θ a)	0.52 (0.26)	0.52	0.52 (0.26)	0.52	0.52
ν_1(N-H)$_s$ b)	3523.8 (3523.6)	3506.0	3566.5 (3566.4)	3595.3	3604.2
ν_2(N-O)$_s$ b)	1598.3 (1588.4)	1530.4	1532.7 (1520.9)	1533.6	1536.0
ν_3(H-N-O)$_b$ b)	1098.3 (883.1)	942.3	988.8 (737.1)	949.9	945.5
ν_4(X-H-N)$_b$ b)	245.6 (216.8)	607.4	89.6 (84.9)	58.2	21.2
ν_5 b)	167.0i (196.9i)	103.1i	27.5i (27.8i)	18.9i	2.4
ν_6(X-H-N)$_b$ b)	620.6 (620.6)	619.2	322.5 (322.5)	152.0	66.0
I_A c)	8.528	13.859	14.50	18.91	15.18
I_B c)	27.688	222.49	423.91	729.57	985.52
I_C c)	36.22	236.36	438.413	748.58	1000.7
E_{of} d)	58.0	89.8	55.5	39.25	22.96
E_{ob} d)	2.4	2.68	0.88	0.04	0.0

a) 10^8 N Å^{-1}. b) cm^{-1}. c) 10^{40} g cm. d) kcal mol^{-1}.

Table 4. Rate constants calculated from the simple collision theory

		M.D.[a] / Å	Rate expression[b] / $cm^3\ mol^{-1}\ s^{-1}$	Steric factor
1)	H_2+NO	2.93	$k=2.1\times10^{13}\ T^{1/2}\exp(-54.6\ kcal/RT)$	2.6×10^{-2}
2)	HF+NO	3.0	$k=8.4\times10^{12}\ T^{1/2}\exp(-86.0\ kcal/RT)$	(7.1×10^{-3})
3)	HCl+NO	3.36	$k=8.0\times10^{12}\ T^{1/2}\exp(-53.5\ kcal/RT)$	6.4×10^{-2}
4)	HBr+NO	3.41	$k=7.0\times10^{12}\ T^{1/2}\exp(-38.1\ kcal/RT)$	9.1×10^{-2}
5)	HI+NO	4.12	$k=8.1\times10^{12}\ T^{1/2}\exp(-22.0\ kcal/RT)$	1.6×10^{-3}

a) Molecular diameter of HX. The molecular diameter of NO was assumed to be 3.5 Å. b) The activation energy was assumed to be the same as the standard enthalpy change of the reaction.

and the calculated rate constants are listed in Table 4. The last column of this table shows the steric factor which was obtained from a comparison of the calculated rate constant with the experimental one at the middle temperature of each experiment. The steric factor of Reaction 2 was determined by comparison with the calculated value by using the transition-state theory combined with the BEBO method, since there are no rate data for this reaction. In general, the steric factors for abstraction reactions lie in the 0.01—0.1 range. As is shown in Table 4, the steric factors for these reactions (except for that for Reaction 5) lie in this range; this fact indicates that the observed rate constants are reasonable.

Discussion

As is shown in Table 2, in all the activated complexes the bond order of H–N (n) is very large compared with that of X–H (n). This trend is always observed in the cases of large endothermic or exthothermic reactions, it can be ascribed to the large contribution of the bonding term compared with that of the repulsive one. The bond order, n, gradually decreased as X changed from F to I because of the decrease in the triplet repulsion energy.

Figure 1 compares the calculated rate constants with the experimental ones for Reaction 3. The rate constants were calculated by using two different values of F_θ, since one can not precisely estimate the effect of the X–H bond in the activated complex on the value of F_θ. The solid and dash-dot lines in Fig. 1 show the rate constants calculated by using values of $F_\theta=0.52\times10^{-8}$ and $F_\theta=0.26\times10^{-8}$ N/Å respectively. Thus, the calculated rate constants were not sensitive to the values of F_θ. The circles in this figure are the rate constants determined by Higashihara *et al.*[2] and are compatible with the theoretical values.

Figure 2 compares the experimental rate constants (broken lines) with the theoretical ones (solid lines) for Reactions 1, 4, and 5. The experimental con-

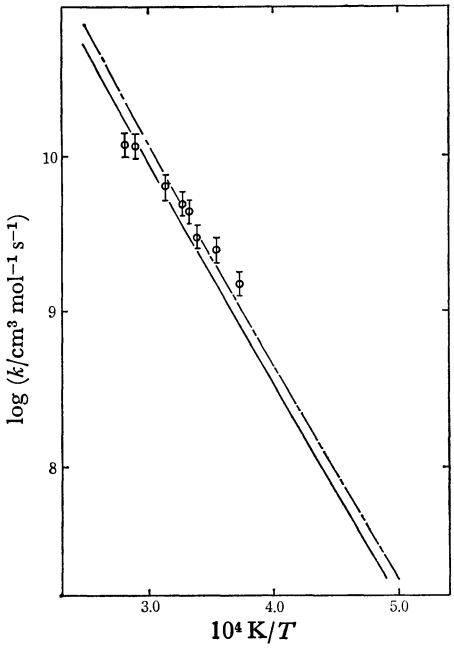


Fig. 1. Comparisons of the calculated and experimental rate constants for the reaction HCl+NO→HNO+Cl. Solid and dash-dot lines represent the calculated rate constants by using $F_\theta=0.52\times10^{-8}$ and $F_\theta=0.26\times10^{-8}$ N/Å, respectively. Circles are the experimental rate constants determined by Higashihara *et al.*[2] The error bars represent ±25% maximum uncertainty.

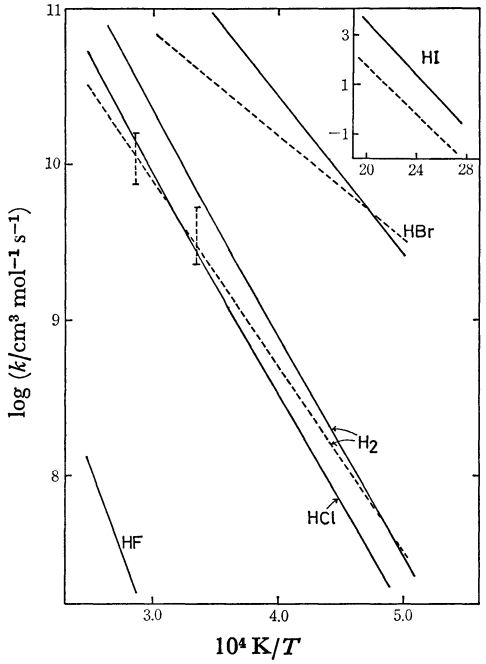


Fig. 2. Comparisons of the calculated rate constants (solid lines) with the experimental ones (broken lines) for the reactions HX+NO→HNO+X. Experimental rate constants are summarized in Table 5.

TABLE 5. KINETIC DATA OBTAINED EXPERIMENTALLY FOR THE HX+NO⇌HNO+X REACTIONS

		Rate constant $cm^3\ mol^{-1}\ s^{-1}$	Temperature range/K	Method	Reference
1)	H_2+NO	$k=10^{13.5}\exp(-55.2\ kcal/RT)$	2000—3500	Shock Tube	1) Ando and Asaba
3)	HCl+NO	$k=10^{13.2}\exp(-50.2\ kcal/RT)$	2650—3850	Shock Tube	2) Higashihara *et al.*
4)	HBr+NO	$k=10^{12.8}\exp(-30\ kcal/RT)$	2000—3300	Shock Tube	3) Higashihara *et al.*
5)	HI+NO	$k=10^{11.43}\exp(-22\ kcal/RT)$	368— 523	Static Sys.[a]	4) Holmes
−1)	H+HNO	$k\geqq 3\times10^{10}$	226— 294	Disch. Flow[b]	5a) Clyne and Thrush
		$k=(6\pm3)\times10^{12}$	1600—2000	Flame	5b) Bulewicz and Sugden
		$k\leqq(2.7\pm0.6)\times10^{10}$	296	Disch. Flow[b]	5c) Lambert
		$k=6\times10^{10}-6\times10^{11}$	300	Static Sys.[a]	5d) Kohout and Lampe
		$k=(4.8\pm1.2)\times10^{12}$	2000	Flame	5e) Halstead *et al.*
		$k=(2.3\pm1.1)\times10^{12}$	2177	Flame	5f) Smith
		$k\geqq 9.63\times10^{11}$	298	Disch. Flow[b]	5g) Washida *et al.*
		$k=3.0\times10^{11}\ T^{1/2}\exp(-2.4\ kcal/RT)$	—	Estimated	5h) Nicolet
		$k=1.4\times10^{11}\ T^{1/2}$	—	Estimated	5i) Lordi *et al.*
		$k=7\times10^{13}\exp(-3.0\ kcal/RT)$	—	Estimated	5j) Wilde *et al.*

a) Static system. b) Discharge flow system.

ditions and techniques for the data cited in this figure are summarized in Table 5. Unfortunately, there are no rate data for Reaction 2: HF+NO→HNO+F. For Reactions 1 and 4, the agreement between the experiment and theory seems to be reasonable in the temperature ranges within which experiments were carried out. The calculated rate constant for Reaction 5 is greater by about two orders in magnitude than that observed. This is the only example of a large difference between the experimental and theoretical rate constants.

As is listed in Table 5, there are many data for Reaction −1 obtained over the wide temperature range from room temperature to 2177 K by using various experimental techniques. Therefore, this reaction is very suitable for use in testing the application of the BEBO method to the group of reactions considered here. Baulch *et al.*[12] recommended in their data book a value of $k=4.8\times10^{12}\ cm^3\ mol^{-1}\ s^{-1}$ at 2000 K based on the data of Halstead and Jenkin.[5e] At room temperature they suggested that a value of $k\geqq3\times10^{10}\ cm^3\ mol^{-1}\ s^{-1}$ determined by Clyne and Thrush[5a] was likely. Recently, Ando and Asaba[1] determined the rate constant for the $H_2+NO\rightarrow HNO+H$ reaction at 3000 and 3500 K by using a shock-tube method. By combining their value of the rate constant with the equilibrium constant, the rate constant of Reaction −1 can be calculated. The value thus obtained is about one order larger than that recommended by Baulch *et al.* More recently, Washida *et al.*[5g] determined the lower limit for this reaction at room temperature as $k\geqq9.63\times10^{11}\ cm^3\ mol^{-1}\ s^{-1}$ by a method combining a photoionization mass spectrometer with a dischargeflow system. This value is also larger (by more than one order) than that of Clyne and Thrush. Thus, recent studies suggest that this reaction is very fast. Figure 3 shows a comparison of the experimental rate constants (broken lines and circles) with the theoretical ones (solid and dash-dot lines). It may be found from Fig. 3 that the theoretical rate constants are consistent with the recent rate data.

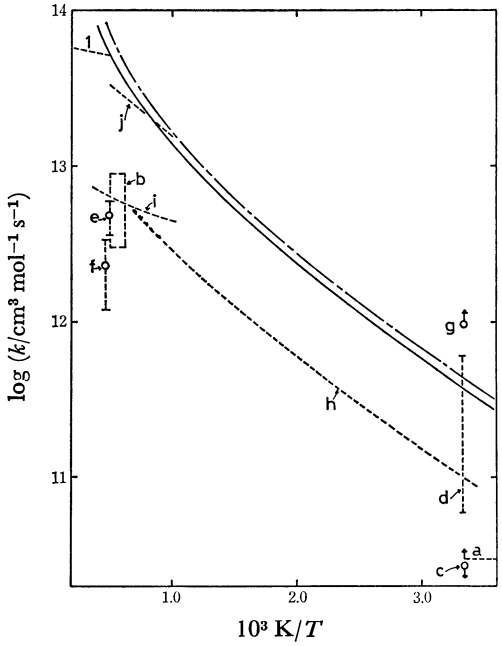


Fig. 3. Comparisons of the calculated rate constants (solid ($F_\theta=0.25\times10^{-8}$ N/Å) and dash-dot ($F_\theta=0.26\times10^{-8}$ N/Å) lines) with the experimental ones for the reaction $H+HNO\rightarrow H_2+NO$. The letters a—j and the number 1 represent the referencies indicated in Table 5.

There is a possibility of tunneling in the cases of hydrogen-transfer reactions at temperatures lower than 1000 K. Therefore, tunneling correction was considered for this reaction. If $u^*\leqq\pi$, where $u^*=h\nu_i/KT$, and $\pi V^*/h\nu_i>1$, where V^* is the maximum value of the potential energy, an approximate tunneling correction[6b] (this is generally known as a high-temperature approximation) is sufficient and the correction factor is given by

$$\Gamma^*_{ht}=0.5u^*/\sin(0.5u^*).$$

The value of Γ^*_{ht} for this reaction was calculated

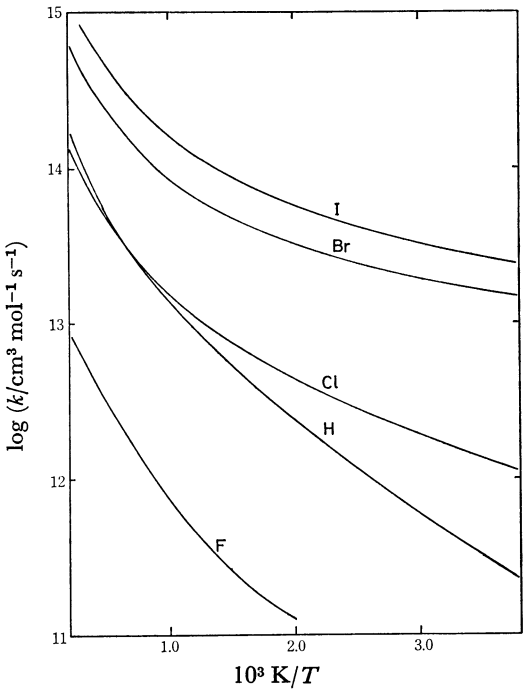


Fig. 4. Calculated rate constants for the reactions X+HNO→HX+NO.

to be 1.04 at 250 K. Thus, this effect was negligibly small and was not taken into account thereafter. Figure 4 shows the calculated rate constants for Reactions −1, −2, −3, −4, and −5. There are no rate data for any of these reactions except Reaction −1.

As is shown in Figs. 2 and 4, the rate constants for both the forward (Reactions 1, 2, 3, 4, and 5) and backward (Reactions −1, −2, −3, −4, and −5) reactions become larger as X changes from F to I. For the forward reactions, this trend may be attributed to two reasons. First, the activation energy becomes smaller as X changes from F to I. Second, as is shown in Table 3, the partition functions of the activated complexes, especially those of the rotation and X–H–N bending modes, become much larger as X changes from F to I, but those for the reactants do not change so much. On the other hand, for the backward reactions the activation energies do not differ very much. Therefore, the trend is mainly a result of the difference in the partition functions of the activated complexes, and is the reverse of that for the X+H_2→HX+H reactions,[6a] in which the rate constant becomes smaller as X changes from F to I, mainly because of the difference in the activation energy.

Conclusion

1. The rate constants determined experimentally for the HX+NO⇄HNO+X reactions were in fair agreement with those predicted by the transition-state theory combined with the BEBO method. Thus, the rate constants for analogous reactions may reasonably be calculated by this method.

2. For the temperature dependence, some difference between the experiment and theory exist. Apparently, more experimental data over a wide temperature range are necessary for all the reactions.

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References

1) H. Ando and T. Asaba, *Int. J. Chem. Kinet.*, **8**, 259 (1976).
2) T. Higashihara, K. Saito, and I. Murakami, *Bull. Chem. Soc. Jpn.*, **51**, 3426 (1978).
3) T. Higashihara, K. Saito, and I. Murakami, *Bull. Chem. Soc. Jpn.*, **51**, 3430 (1978).
4) J. L. Holmes, *Proc. Chem. Soc.*, **1962**, 75.
5) a) M. A. A. Clyne and B. A. Thrush, *Discuss. Faraday Soc.*, **33**, 139 (1962); b) E. M. Bulewicz and T. M. Sugden, *Proc. R. Soc. London, Ser. A*, **277**, 143 (1964); c) R. M. Lambert, *Chem. Commun.*, **1966**, 850; d) F. C. Kohout and F. W. Lampe, *J. Chem. Phys.*, **46**, 4075 (1967); e) C. J. Halstead and D. R. Jenkins, *Chem. Phys. Lett.*, **2**, 281 (1968); f) N. Y. Smith, *Combust. Flame*, **18**, 293 (1972); g) N. Washida, H. Akimoto, and M. Okuda, *J. Phys. Chem.*, **82**, 2293 (1978); h) N. Nicolet, *J. Geophys. Res.*, **70**, 679 (1965); i) J. A. Lordi and R. E. Mates, National Aeronautics and Space Administration, NASA CR-393 (1966); j) K. A. Wilde, *Combust. Flame*, **13**, 173 (1969).
6) a) H. S. Johnston and C. Parr, *J. Am. Chem. Soc.*, **83**, 2544 (1963); b) H. S. Johnston, "Gas Phase Reaction Rate Theory," Ronald, New York (1966).
7) R. D. Gillion, *J. Chem. Phys.*, **65**, 5027 (1976).
8) S. Mizushima and T. Shimanouchi, "Infrared Absorption and Ramman Effect," Kyoritsu Shuppan, Tokyo (1958).
9) H. W. Brown and G. C. Pimentel, *J. Chem. Phys.*, **29**, 883 (1958).
10) Although Brown and Pimentel did not give the value of F_{N-H}, the vibrational frequencies of the HNO molecule could be calculated by using F_{33}, F_θ, and F_{N-H} (7.1×10^{-8} N/Å) as 3590 (N–H stretching), 1558 (N–O stretching), and 978 cm^{-1} (H–N–O bending). These calculated frequencies are in good agreement with the observed frequencies (3596, 1562, and 1110 cm^{-1}).[11]
11) G. Herzberg, "Molecular Spectra and Molecular Structure," D. Van Nostrand Co., Prinston, N. J. (1967), Vol. III.
12) D. L. Baulch, D. D. Drysdale, D. G. Horne, and A. C. Lloyd, "Evaluated Kinetic Data for High Temperature Reactions," Butterworths (1973), Vol. 2. In this book, all the rate data for Reaction −1 are summarized except for the data of Washida *et al.*