Table 1. Energetics (kcal/mol) involved in gas phase reactions of $CH_2=CHR$ with CH_3O^- and $CH_3O^- \cdot H_2O$

(kcal/mole)	$CH_2=CHCN$			$CH_2=CHCHO$			$CH_2=CHNO_2$		
Reaction	$\Delta H°$	$\Delta G°$	ΔG^*	$\Delta H°$	$\Delta G°$	ΔG^*	$\Delta H°$	$\Delta G°$	ΔG^*
1	-5.6	-7.2	3.5	-12.7	-13.6	6.7	-27.6	-28.6	4.9
2	-37.3	-27.2	5.6	-39.6	-28.7	4.1	-63.2	-52.2	5.2
3	-19.7	-20.9	12.1	-26.4	-26.8	10.9	-47.9	-48.7	7.9
1S	6.1	5.6	5.3	-1.1	-0.7	9.4	-15.9	-15.7	3.4
2S	-20.8	-16.6	5.3	-23.2	-18.5	5.0	-46.7	-41.8	4.6

$\Delta H° = \Delta H_f(P) - \Delta H_f(R)$; $\Delta G° = \Delta G_f(P) - \Delta G_f(R)$; $\Delta G^* = \Delta G_f(TS) - \Delta G_f(RC)$.

but subsequently rotate out-of-plane to form tetrahedral complexes in addition reactions (2 and 3).

(2) The reactions of substituted ethylenes ($CH_2=CHR$) with a bare methoxide are all exothermic, the exothermicity being the greatest in the β-addition reaction.

(3) Although the β-addition (reaction 2) is the most exothermic process, the excess energy is carried by the adduct alone so that it becomes extremely unstable.

(4) The solvate water removes part of the excess energy in the β-addition of monosolvated methoxide to render the reaction product.

(5) The hydride transfer (3) is the most unfavorable process due to the highest energy barrier.

(6) The α-H^+ abstraction of acrylonitrile becomes endothermic by hydrating the methoxide ion so that the gas phase reaction will not be observed.

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Temperature Dependence of the Vibration-Vibration Energy Transfer in the Deexcitaion of NO(2) by NO(0)

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The temperature dependence of the vibrational relaxation of NO(=2) by NO(v=0) has been investigated over the temperature range 100-3000K. We have assumed that the deexcitation of NO(2) by NO(0) undergoes vibration-to-vibration (VV) energy exchange with the transfer of the energy mismatch ΔE through rotation (R) and translation(T). The relaxation rate constants are calculated by solving the time-dependent Schrödinger equation. The sum of V-V,T, and V-V,R contributions shows very weak temperature dependence and is in reasonable agreement with observed data over the temperature range 300-3000K.

Introduction

The vibrational relaxation of NO has been studied by a variety of techniques. Most of these studies have involved the measurements of the relaxation rate constant of NO(v=1)[1-4] by a variety of collision partners. However, a few investigators have studied the self-relaxation of NO(v=2).[1,5-8] In this paper, we have considered the rate con-

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stants, k_e for deactivation of NO(v = 2) by NO.

$$NO(v=2)+NO(v=0)\xrightarrow{k_e}2NO(v=1)-28cm^{-1} \quad (1)$$

There have been no reported measurements of the temperature dependence of k_e. The rate constants was measured only at the room temperature and at very high temperature. Futhermore, the scatter of k_e is large. Glänzer[7] measured k_e behind shock-heated NO and found k_e to be $2\times10^{-12}cm^3$ $molecule^{-1}s^{-1}$ independent of temperature from 2000 to 3000K. Stephenson[1] used an infrared-laser-induced uppumping technique to measure k_e which is about $3\times10^{-12}cm^3molecule^{-1}s^{-1}$. Macdonald and Sopchyshyn[8] measured k_e over the range 220-470K by UV absorption spectrophotometry and their results are about a factor of two smaller than those of Stephenson. No results for the decay of NO(V = 2) are reported below 293K. Thus, if these results are combined, k_e is almost independent of temperature from 300 to 3000K.

One particular thing about NO is that it can form a dimer, and the NO dimer has a dissociation energy of 1.6kcal/mole[9] giving intermolecular interaction which is stronger than those due to purely dispersive van der Waals interactions between the ordinary molecules and being of the same order of magnitude as those for the hydrogen halide dimers. Thus, in order to describe the NO-NO collision adequately, it is necessary to have a collision model which takes into account the presence of strong attractive forces.[10] Near room temperature, the attractive forces can cause the colliding molecules to stay close to each other for a sufficiently long time, which then, in turn, provides ample time for the molecules to relax.

In process (1), there can be two possible pathways for the supply of the energy mismatch[11]: one is the transfer of ΔE by local translation, which is confined to the vicinity of the equilibrium separation, and the other is by rotation. These two energy transfer pathways of the V-V step can be classified as V-V, T and V-V,R mechanism, respectively. In this paper, we shall show the calculation of the deactivation rate constant k_e over 100-3000K introducing both pathways.

V-V,T Energy Transfer

In near-resonant VV energy exchange processes, the major portion of vibrational energy is rapidly redistributed among vibrational modes of the colliding molecules. Then, the energy mismatch ΔE is transfered to or supplied by other modes such as translation or rotation. In the collision of two NO molecules, due to the strong attraction, the translational motion is confined to the region where the attraction is strong. This motion, which may be referred to as "local translation," is quite efficient in transferring ΔE, but the direct contribution of rotation to the transfer of ΔE, is not important at lower temperatures.[11(a),(b)] When temperature increases, however, this energy transfer mechanism becomes less important.[11(a),(b)] We now have to recognize the direct participation of the rotational motion in transferring ΔE. Therefore, the V-V energy process can be described in terms of both V-V,T and V-V,R mechanisms; the former is of major importance at lower temperatures, while the participation of the V-V,R pathway becomes important relative to the former at higher temperatures.

For the collision of two nitric-oxide molecules, the potential energy of the interaction is assumed to be a Morse type composed of four atom-atom interactions. We shall denote the relative separation between molecules 1 and 2 by r; the counterclockwise angle between the molecular axis of 1 and r by θ_1 and that of 2 and r by θ_2. The four atom-atom distances are defined by representing molecules 1 and 2 by $N_{(1)}$–$O_{(1)}$ and $N_{(2)}$–$O_{(2)}$ as follows: we express the distance between $N_{(1)}$ and $N_{(2)}$ by r_1, between $N_{(1)}$ and $O_{(2)}$ by r_2, between $O_{(1)}$ and $N_{(2)}$ by r_3, and between $O_{(1)}$ and $O_{(2)}$ by r_4. For the relative separation which is significantly larger than the equilibrium bond length d, these atom-atomdistances may be approximated as

$$\begin{aligned} r_{1,2}&=r-\gamma_1(d+x_1)\cos\theta_1\pm\gamma_{1,2}(d+x_2)\cos\theta_2\\ r_{3,4}&=r+\gamma_2(d+x_1)\cos\theta_1\pm\gamma_{1,2}(d+x_2)\cos\theta_2 \end{aligned} \quad (2)$$

where x_i is the vibrational amplitude of the ith molecule, $\gamma_1=m_O/(m_N+m_O)$ and $\gamma_2=m_N/(m_N+m_O)$, m's being the atomic masses. The overall potential energy can then be expressed in the form

$$U(r_1,r_2,r_3,r_4)=\frac{1}{4}\sum_{i=1}^{4}U(r_i) \quad (3)$$

where $U(r_i)=D\{\exp[(r_{ie}-r_i)/a]-2\exp[(r_{ie}-r_i)/2a]\}$, D and a being potential constants. Here r_i's are the equilibrium values of r_i's, and they can be obtained from Eq. (2) by setting $x_1=x_2 0$, $\theta_1=\theta_{1e}$, and $\theta_2=\theta_{2e}$. It is important to notice the introduction of the factor $\frac{1}{4}$ in Eq. (3). The introduction is made because the overall interaction energy is constructed through the molecular field which is characterized by D and a. If $\theta_1=\theta_{1e}$ and $\theta_2=\theta_{2e}$, the additive potential would become four times the center of mass interaction

$$U(r)=D\{\exp[(r_e-r)/a]-2\exp[(r_e-r)/2a]\},$$

where r_e is the equilibrium value of r. This indicates that at other orientation angles the additive model of atom-atom interactions will lead to the potential which is effectively four times the "true" interaction energy. Therefore, to obtaine U(r) which describes the relative motion, we need to introduce the factor $\frac{1}{4}$ in Eq.(3). Of course, if all r_i's were assumed independently from each other with a_i and D_i, the factor should not appear in the potential.[12] We assume that the N-N, N-O, and the O-O interactions are identical.

On the other hand, in V-V, T mechanism the effect of direct participation of the rotational motion will not be included; instead, we shall use an orientation-averaged interaction potential to include the effect of molecular rotations on the VV processes. Then the orientation-averaged potential is[13]

$$\bar{U}(r,x_1,x_2)=\frac{1}{4}\int_0^\pi\int_0^\pi U(r,\theta_1,\theta_2,x_1,x_2)\sin\theta_1\sin\theta_2\,d\theta_1\,d\theta_2 \quad (4)$$

where, because $r_i=r_i(r,x_1,x_2,\theta_1,\theta_2)$ as shown by Eq.(2), the overall potential can be represented by $U(r_1,r_2,r_3,r_4)=U(r,x_1,x_2,\theta_1,\theta_2)$. Performing integrations, the interaction potential describing the relative separation can then be written in the form

$$\bar{U}_0=D^*[\exp(\frac{r_e^*-r}{a})-2\exp(\frac{r_e^*-r}{2a})], \quad (5)$$

where, $$D^*=D\frac{4[\sinh(Q_1/2)/Q_1+\sinh(Q_2/2)/Q_2]^4}{[\sinh Q_1/Q_1+\sinh Q_2/Q_2]^2}$$

and $Q_{1,2}=\gamma_{1,2}d/a$, and r_e^* is the new equilibrium value of r after rotation-averaging. The energy representing the coupling of two vibrational modes is

$$\bar{U}_{12} = D^*\left[f\exp\left(\frac{r_e^* - r}{a}\right) - g\exp\left(\frac{r_e^* - r}{2a}\right)\right]\frac{x_1 x_2}{a^2} \qquad (6)$$

where

$$f = \left[\frac{\cosh Q_1(1-\tanh Q_1/Q_1) + \cosh Q_2(1-\tanh Q_2/Q_2)}{\sinh Q_1/Q_1 + \sinh Q_2/Q_2}\right]^2$$

$$g = \frac{a^2}{2d^2}\left[\frac{\cosh(Q_1/2)(1-2\tanh(Q_1/2)/Q_1) + \cosh(Q_2/2)(1-2\tanh(Q_2/2)/Q_2)}{\sinh(Q_1/2)/Q_1 + \sinh(Q_2/2)/Q_2}\right]^2.$$

Equation (5), which describes the relative motion of colliding molecules, is a simple form of the Morse potential function with the well depth now reduced to D^* due to the averaging effect of molecular orientations. We express x_1x_2 in terms of boson operators $(a_i^\dagger\ a_i)$ as $x_1x_2 = (\hbar/2M_1\omega_1)^{\frac{1}{2}}(\hbar/2M_2\omega_2)^{\frac{1}{2}}(a_1^\dagger + a_1)(a_2^\dagger + a_2)$, where M_i and ω_i are the reduced mass and the angular frequency of molecule i, respectively. Equation (6) can then be written as $\bar{U}_{12}(r, x_1, x_2) = F(r)(a_1^\dagger + a_1)(a_2^\dagger + a_2)$.

On the other hand, the relative motion of two individual molecules in the loosely bound complex is local translation, which is restricted to the vicinity of r_e^*. An approximate form of the interaction potential describing this motion can be derived as $\bar{U}(r) = -D^* + D^*[(r_e^* - r)/2a]^2 + \ldots$, *i.e.*, we can fit $\bar{U}(r)$ to the quadratic form $\frac{1}{2}\chi(r_e^* - r)^2$, χ being $D^*/2a^2$. From the equation of motion written in the form $t = (\mu/2)^{\frac{1}{2}}\int_{r_0}^{r}[E - \frac{1}{2}\chi(r_e^* - r)^2]^{-\frac{1}{2}}dr$, we obtain the trajectory as $r(t) = r_e^* - 2a(E/D^*)^{\frac{1}{2}}\cos[D^*/2\mu)^{\frac{1}{2}}(t/a)]$, where μ is the reduced mass of the collision system and r_0 is the root of $E - \frac{1}{2}\chi(r_e^* - r)^2 = 0$. This equation is an oscillatory function of time describing a snarled trajectory of the back-and-forth type motion for local translation in the neighborhood of r_e^* for long-lived collisions. Thus, $F(r)$ can now be expressed as a time-dependent function F(t):

$$F(t) = \frac{D^*\hbar}{2a^2(M_1M_2\omega_1\omega_2)^{1/2}}\left[f\exp\left(\frac{r_e^* - r(t)}{a}\right) - g\exp\left(\frac{r_e^* - r(t)}{2a}\right)\right]$$

For 2,0→1,1 V-V transition, the energy exchange probability expression can be obtained in the form[13]

$$P_{2,0}^{1,1}(E) = 2\sin^2 G\ \cos^2 G\ ;\ G = \hbar^{-1}\int F(t)\exp(i\Delta\omega t)dt \qquad (7)$$

where E is the initial collision energy and the energy mismatch $\Delta E = \hbar\Delta\omega$ is $(E_2 + E_0) - (E_1 + E_1)$, and ω_i's are given by $\hbar\omega_1 = E_2 - E_1$ and $\hbar\omega_2 = E_1 - E_0$, the energy levels E_v being derived from spectroscopic measurements. In terms of $F(t)$ given above, we obtain

$$\hbar^{-1}\int_{-\infty}^{\infty}F(t)\exp(i\Delta\omega t)dt = \frac{D^*}{2a^2(M_1M_2\omega_1\omega_2)^{\frac{1}{2}}}\left[2\pi a\left(\frac{2\mu}{D^*}\right)^{\frac{1}{2}}\right] \times \left\{\frac{f}{2\pi}\int_{\phi_1}^{\phi_2}(\cos n\phi + i\sin n\phi)\exp\left[2\left(\frac{E}{D^*}\right)^{\frac{1}{2}}\cos\phi\right]d\phi - \frac{g}{2\pi}\int_{\phi_1}^{\phi_2}(\cos n\phi + i\sin n\phi)\exp\left[\left(\frac{E}{D^*}\right)^{\frac{1}{2}}\cos\phi\right]d\phi\right\}. \qquad (8)$$

From the translational trajectory, the period of local translation is $T = 2\pi a(2\mu/D^*)^{\frac{1}{2}}$. In the time interval of $-\frac{1}{2}$T to $\frac{1}{2}$T, local translation undergoes one period of the back-and-forth motion transferring ΔE, so we replace the integration limits (ϕ_1, ϕ_2) by $(-\frac{1}{2}T, \frac{1}{2}T)$, which correspond to $(-\pi, \pi)$ in the integration. The result is

$$\hbar^{-1}\int_{-\infty}^{\infty}F(t)\exp(i\Delta\omega t)dt = \frac{D^*}{2a^2(M_1M_2\omega_1\omega_2)^{\frac{1}{2}}}\left[2\pi a\left(\frac{2\mu}{D^*}\right)^{\frac{1}{2}}\right] \times [fI_n(2z) - gI_n(z)] \qquad (9)$$

where $z = (E/D^*)^{\frac{1}{2}}$ and the order of the Bessel functions appearing in the last bracket is $n = \Delta\omega a(2\mu/D^*)^{\frac{1}{2}}$. Note that the integrals containing $\sin n\phi$ vanish. To obtain the thermal-average probability, we shall replace the collision energy in Eq.(9) by the symmetrized energy $\{[E(1-b^2/r^{*2}) - \hbar|\Delta\omega|]^{\frac{1}{2}} + [E(1-b^2/r^{*2})]^{\frac{1}{2}}\}^2$, where b is the impact parameter and r^* is a constant distance in the most important region of energy exchange. With the introduction of the energy symmetrization and impact parameter, we define the average of $P_{2,0}^{1,1}(E,b)$ over E and b as

$$P_{2,0}^{1,1}(T) = \frac{1}{\pi r^{*2}(kT)^2}\int_0^{r^*}2\pi b\ db\int_{\hbar|\Delta\omega|}^{D^* + \hbar|\Delta\omega|}EP_{2,0}^{1,1}(E, b)\exp(-E/kT)dE. \qquad (10)$$

V-V,R Energy Transfer

As the molecule NO(2) deexcites to NO(1), the quantum $\hbar\omega_1 = E_2 - E_1$, is released, and it is taken up by NO(0) in its upward change to NO(1). In the latter change, however, the energy needed is $\hbar\omega_2 = E_1 - E_0$, which is larger than $\hbar\omega_1$ because of the vibrational anharmonicity. We expect rotation-to-vibration energy conversion within the same molecule (molecule 2) balancing the energy difference between these two quanta, *i.e.*, ΔE, to be more efficient over the energy conversion between the rotation of molecule 1 and the vibration of molecule 2. We thus construct the coupling potential which represents the interaction between the θ_1-averaged oscillator (molecule 1) and the rovibrator (molecule 2); the coupling potential then has the functional dependence of $U_{12}(r, \theta_2, x_1, x_2)$. From the θ_1 average of Eq.(3) at $r = r_e^*$, we obtain[10(a)]

$$\bar{U}_0(r, \theta_2) = D^*\left\{\frac{2Q_1}{[\sinh Q_1 + (\gamma_1/\gamma_2)\sinh Q_2]}\exp(-Q_1\cos\theta_2) - \frac{2Q_1}{[\sinh(Q_1/2) + (\gamma_1/\gamma_2)\sinh(Q_2/2)]}\exp(-Q_1\cos\theta_2/2)\right\}$$
$$= A\ \exp(-Q_1\cos\theta_2) - B'\exp\left(-\frac{Q_1}{2}\cos\theta_2\right) \qquad (11)$$

It should be noted that when Eq.(11) is further averaged over θ_2 without imposing the restriction that $r = r_e^*$, the result of course reduces to Eq.(5) obtained above for the V-V,T process. Similarly, the coupling potential at $r = r_e^*$ is[10(a)]

$$\bar{U}_{12}(\theta_2, x_1, x_2) = -D^{**}\left(\frac{\gamma_1}{a}\right)^2\left\{\phi_1\exp(-Q_1\cos\theta_2) - \phi_2\exp\left(-\frac{Q_1}{2}\cos\theta_2\right)\right\} \times \cos\theta_2 x_1 x_2 \qquad (12)$$

where,

$$D^{**} = \left(\frac{8D}{Q_1}\right)\frac{[\sinh\frac{Q_1}{2} + (\gamma_1/\gamma_2)\sinh\frac{Q_2}{2}]^4}{[\sinh Q_1 + (\gamma_1/\gamma_2)\sinh Q_2]^2}$$

$$\phi_1 = \frac{(\cosh Q_1 + \cosh Q_2)}{[\sinh Q_1 + (\gamma_1/\gamma_2)\sinh Q_2]^2}$$

$$-\frac{1}{Q_1[\sinh Q_1+(\gamma_1/\gamma_2)\sinh Q_2]}$$

$$\phi_2=\frac{1}{4}\left\{\frac{(\cosh\frac{Q_1}{2}+\cosh\frac{Q_2}{2})}{[\sinh\frac{Q_1}{2}+(\gamma_1/\gamma_2)\sinh\frac{Q_2}{2}]^2}-\frac{2}{Q_1[\sinh\frac{Q_1}{2}+(\gamma_1/\gamma_2)\sinh\frac{Q_2}{2}]}\right\}$$

The trajectory $\theta_2(t)$ may be determined from the rotational equation of motion written in the form

$$\frac{d\theta_2}{dt}=\left\{\left(\frac{2}{I}\right)[E_r-\bar{U}_o(\theta_2)]\right\}^{\frac{1}{2}} \tag{13}$$

where E_r is the initial rotational collision energy and I is the moment of inertia. The approximation $r=r_e^*$ which we introduced above to write $\bar{U}_o(\theta_2)$ represents the situation that the relative motion is "frozen" at r_e^*, which we think is responsible when there is a strong attractive interaction between the collision partners. An integration of Eq.(13) for $\bar{U}_o(\theta_2)$ given by Eq.(11) has been shown elsewhere with the result[14,15].

$$\exp\left(-\frac{1}{2}Q_1\cos\theta_2\right)=\frac{\alpha_0}{i}\left(\frac{2I}{A'}\right)^{1/2}\frac{1}{t-i\tau} \tag{14}$$

Here,

$$\tau=\left(\frac{\pi I}{2}\right)^{\frac{1}{2}}\sum_{i=0}^{\infty}\frac{\Gamma(\frac{1}{2}+i)}{\Gamma(1+i)}\frac{a_i}{E_r^{\frac{1}{2}+i}},$$

with

$$\alpha_0=\frac{1+\alpha}{Q_1};\ \alpha_{\frac{1}{2}}=-\frac{\alpha_0}{2A'^{\frac{1}{2}}}\left(B'+\frac{\beta}{1+\alpha}\right);$$

$$\alpha_1=\frac{\alpha_0(2B'\beta+\delta)}{2A'(1+\alpha)};$$

$$\alpha_{\frac{3}{2}}=-\frac{\alpha_0}{16A'^{\frac{3}{2}}}\left(B'^3+\frac{3B'^2\beta+6B'\delta}{1+\alpha}\right);$$

$$\alpha_2=\frac{\alpha_0 B'^2\delta}{4A'^2(1+\alpha)};\ \cdots\cdots\cdots\cdots$$

$$\alpha=\frac{9}{2Q_1^2}\left(1+\frac{4}{3Q_1^2}\right);\ \beta=\frac{22}{Q_1^2}\left(1+\frac{24}{11Q_1^2}\right)A';$$

$$\delta=\frac{34}{Q_1^2}\left(1+\frac{72}{17Q_1^2}\right)A'^2.$$

From Eqs.(12) and (14), with the contour integration

$$\int_{-\infty}^{\infty}\frac{\exp(i\Delta\omega t)}{(t-i\tau)^n}dt=[2\pi(i\Delta\omega)^n/\Delta\omega\,\Gamma(n)]\exp(-\Delta\omega\tau),$$

we find

$$\hbar^{-1}\int_{-\infty}^{\infty}F(t)\exp(i\Delta\omega t)\,dt=\frac{2\pi\gamma_1^2\phi_1\Delta\omega\alpha_0^2ID^{**}}{a^2(M_1M_2\omega_1\omega_2)^{1/2}A'}\left\{1-\frac{\phi_2}{\phi_1}\left(\frac{A'}{2I}\right)^{\frac{1}{2}}\frac{1}{\alpha_0\Delta\omega}\right\}\exp(-\Delta\omega\tau) \tag{15}$$

In this case an appropriate form of the thermal average V-V,R probability is

$$P_{2,0}^{1,1}(T)=(kT)^{-1}\int_0^{\infty}P_{2,0}^{1,1}(E_r)\exp(-E_r/kT)\,dE_r \tag{16}$$

where the E_r dependence of the probability is replaced by the symmetrized energy $[(E_r+\hbar|\Delta\omega|)^{\frac{1}{2}}+E_r^{\frac{1}{2}}]^2$. If the effect of translational motion is introduced, the probability would appear also as a function of E and b. In this case, additional integrations over E and b will have to be introduced, but the effect of translational motion is not expected to be important in the present V-V,R step.

Table 1. The calculated values of the V-V,T, V-V,R and the overall rate constants for NO(v=2) + NO(v=0) → 2NO(v=1)

Temp.	V-V,T	V-V,R	V-V,T+V-V,R
100	6.24(-13)[a]	7.87(-16)	6.25(-13)
200	6.49(-13)	1.44(-14)	6.63(-13)
300	5.20(-13)	4.94(-14)	5.69(-13)
400	4.11(-13)	1.01(-13)	5.12(-13)
500	3.32(-13)	1.58(-13)	4,89(-13)
700	2.30(-13)	2.81(-13)	5.11(-13)
1000	1.50(-13)	5.02(-13)	6.51(-13)
1500	8.83(-14)	9.11(-13)	9.99(-13)
2000	5.98(-14)	1.29(-12)	1.35(-12)
3000	3.39(-14)	1.93(-12)	1.96(-12)

[a] This means 6.24×10^{-13} cm^{3}molecule^{-1}s^{-1}.

Calculation and Discussion

The potential constants used to calculate energy exchange probabilities are D = 1.6 kcal/mol, a = 0.19Å.[9] The spectroscopic constants[16] $\omega_e=1904.405$, $\omega_e x_e=14.187$, and $\omega_e y_e=2.4\times10^{-2}$, all in cm^{-1}, are used to determine energy level spacings and the value of the energy mismatch ΔE. The equilibrium bond distance d is 1.15077Å. Once the energy exchange probabilities are known, the rate constants can be obtained from the gas kinetics as follows,[17]

$$\begin{aligned}k&=ZP(T)\\&=4.5708\times10^{-12}r^{*2}\left(\frac{T}{\mu}\right)^{1/2}P(T)\ \text{cm}^3/\text{molecule-sec}\end{aligned} \tag{17}$$

where Z is the collision number, r^* is the collision diameter in Å, and μ is the reduced mass in amu; we take $r^*=3.47$Å.

In Table 1, the calculated values of the V-V,T, V-V,R and the overall rate constants (i.e., V-V,T + V-V,R) are shown as a function of temperature. In this collision system, the endothermic energy mismatch ΔE is 28 cm^{-1} and the local translational motion can be effective in supplying this energy in the presence of strong attraction. The V-V,T reaction rate constant calculated at 300K is 5.2×10^{-13} cm^3 molecule^{-1}s^{-1}. But when the temperature increases to 1000K, V-V,T rate constant decreases to 1.49×10^{-13} cm^3 molecule^{-1}s^{-1}. When T = 2000 and 3000K, the V-V,T rate constants are 5.98×10^{-14} and 3.39×10^{-14} cm^{3}molecule^{-1}s^{-1}, respectively. Therefore, the V-V,T rate constant show considerable decrease as the temperature increases. On the other hand, the contribution of the rotational motion to the V-V,R rate constants show opposite trend, and they are, for example, 1.29×10^{-12} and 1.93×10^{-12} cm^{3}molecule^{-1}s^{-1} at T = 2000 and 3000K, respectively, which are much larger than the corresponding values of the V-V,T mechanism. We may therefore state that in the present collision system, the deexcitation of NO(2), over the range of 100-3000K, occurs through the V-V mechanism with the energy mismatch being supplied by rotation or translation and that the overall deexcitation rate constant can be expressed as the sum of V-V,T and V-V,R contribu-

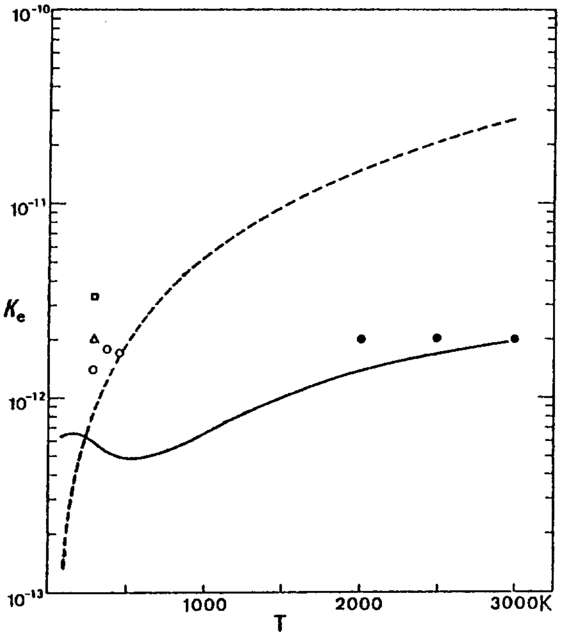

Figure 1. The temperature dependence of the vibrational energy transfer rate constant for NO(v=2)+NO(v=0)→2NO(v=1). The solid curve is calculated in this study. The dashed curve is obtained by SSH theory. Experimental data are taken from :□Ref. 1; △Ref. 6; ● Ref. 7; ○ Ref. 8.

tion.

The overall rate constants are plotted in Fig. 1 as a function of T over the range of 100-3000K. As the temperature increases the rate constant decreases. But the decrement is very weak and the rate constant decreases only slightly; from 100 to 500K it decreases from 6.25×10^{-13} to 4.89×10^{-13}cm^{3}molecule^{-1}e^{-1}. As the temperature continues to increase, however, the role of molecular attraction becomes less important. Furthermore, local translation, which is effective in causing V-V energy transfer at lower temperatures, is no longer the dominant motion. Whereas contribution of the rotational motion to the V-V process becomes more important relative to the translation. The rate constant thus increases with rising temperature. It increases slowly with rising temperature above 500K. From 500 to 3000K, the rate constant increases from 4.89×10^{-13} to 1.96×10^{-12}cm^{3}molecule^{-1}s^{-1}: That is, it increases at most by a factor of about 4.

In Fig. 1, there are also plotted the observed data and the result from other theoretical approach. The agreement between our calculated rate constants (the sum of V-V,T and V-V,R) and the observed ones is reasonable over the range of 2000-3000K, but up to 1000K our results are samll by a factor of 3-6. However, our results show a very weak temperature dependence for k_e over ther range of 100-3000K, in agreement with experiment. Whereas the results obtained by SSH theory[18] agree with the observed values at room temperature, but they become too large at high temperatures. Futhermore, these results show considerably strong temperature dependence over the range of 100-3000K.

Finally, the self-relaxation rate constant, k_e, for CO, N_2 and O_2 is an order of magnitude smaller than the corresponding self-relaxation rate constant for NO[19]. All four molecules have very similar vibrational frequencies, moments of inertia and reduced masses. This particularity of NO is due to the formation of dimer. Therefore, we suggest that the same mechanism of our approach is responsible when the colliding molecules form dimer, that is, when they have a strong attraction.

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