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Pressure and Temperature Dependence of the Rate of Reaction between CN Radicals and NO over the Range 99 $\leqslant T/\mathrm{K} \leqslant$ 450

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Pulsed laser photolysis, laser-induced fluorescence experiments have been performed on the kinetics of reaction between CN radicals and NO. The measurements cover a range of temperature ($99 \leqslant T/\mathrm{K} \leqslant 450$) and total pressure {at 296 K, 5–400 Torr [1 Torr = (101 325/760) Pa]; at other temperatures, a smaller range}. Two methods were employed to extract rate constants in the limit of low and high pressure and their temperature dependences from the experimental results. Comparison of the values of the low-pressure rate constants derived from experiment with calculated values suggests that levels derived, in zeroth order, from the excited S_1 and T_1 electronic states mix with those in the ground S_0 state thereby contributing to the density of NCNO states in the region of the CN + NO dissociation limit and hence to the rate of association in the limit of low pressure.

The photochemical dissociation of nitrosyl cyanide, NCNO, to CN and NO has attracted considerable attention in recent years. Absorption in the weak $\pi^* \leftarrow n$ electronic absorption system ($\tilde{A}\,^1A'' \leftarrow \tilde{X}\,^1A'$) between *ca.* 500 and 885 nm is followed by internal conversion into vibrational levels of the electronic ground state above or just below the dissociation limit. Wittig and co-workers[1–4] have studied the CN rovibrational distributions produced by photolysis over a range of wavelengths and of NCNO samples both at room temperature and cooled in a supersonic jet. *Inter alia*, their results have established[2] that the dissociation energy corresponds to $17\,085 \pm 5\ \mathrm{cm^{-1}}$ and that there is no maximum of electronic potential energy along the dissociation pathway leading to $\mathrm{CN(X\,^2\Sigma^+) + NO(X\,^2\Pi_i)}$. Khundkar *et al.*[5] have monitored the photodissociation of NCNO in 'real time' using picosecond photofragment spectroscopy. Microcanonical state-to-state rate constants have been obtained for excitations of different energy, and these results have been compared with those from detailed calculations[6] using a form of unimolecular reaction rate theory invoking a highly flexible transition state.

The availability of the detailed experimental results has prompted several high-quality, *ab initio* quantum calculations[7,8] on the NCNO potential-energy surfaces which correlate with CN + NO in their ground electronic states. These confirm the experimental result that the lowest potential surface falls monotonically as CN and NO approach. The calculations also indicate, as Fig. 1 shows, that there are two excited electronic states, T_1 and S_1 ($\equiv \tilde{A}\,^1A''$) which are bound with respect to the $\mathrm{CN(^2\Sigma^+) + NO(X\,^2\Pi_i)}$ dissociation limit, but that there are well defined maxima along the dissociation paths of minimum energy from these states.

The reverse association reaction of CN and NO has been less studied than the photochemical dissociation. In 1981, when the available kinetic data were reviewed, Baulch *et al.*[9] found themselves unable to make recommendations owing to the paucity of, and disagreement about, the experimental results. Since then, three studies employing pulsed photolysis to generate CN radicals and time-resolved laser-induced fluorescence (LIF) to follow their decays have been reported,[10–12] including one study from our own laboratory. However, the results of those investigations are very limited in terms of the ranges of temperature and total pressure that were covered and are also, in some respects, contradictory. These earlier data are considered further in the Discussion section of this paper.

In the work reported here, we have extended our earlier experiments on the CN + NO reaction by measuring rate constants over a wider range of total pressure, up to 400 Torr at 296 K, and at several temperatures down to 99 K. As in our previous studies[12–15] of the rates of reactions of the CN radicals, the radicals were generated by photolysis of NCNO using the frequency-doubled output of a Nd : YAG laser ($\lambda = 532$ nm), and relative concentrations of $\mathrm{CN}(v = 0)$ were measured at a number of selected delays after the photolysis pulse, by measuring the strength of LIF signals generated by tuning a pulsed dye laser to a line in the (0,0) band of the $\mathrm{B\,^2\Sigma^+–X\,^2\Sigma^+}$ system of CN at 388.3 nm.

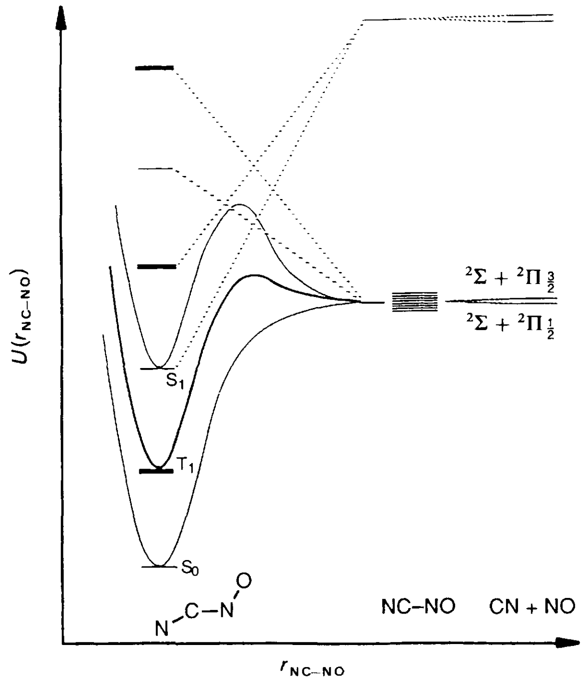

Fig. 1 Schematic potential-energy diagram showing correlations between the bound electronic states of NCNO and $\mathrm{CN(X\,^2\Sigma^+) + NO(X\,^2\Pi_i)}$

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Experimental

Our apparatus and our experimental and analytical procedures have been described in detail elsewhere.[12,14] Briefly, reaction was initiated by photolysing NCNO in a gas mixture flowing through a tubular reactor. For experiments at sub-ambient temperatures, a doubly jacketed reaction cell was employed.[14] The inner jacket contained coolant and the outer jacket was evacuated. To achieve temperatures of *ca.* 205 and 145 K, isopentane was circulated through the inner jacket and through an external Pyrex coil, which was immersed in either a solid CO_2–acetone mixture or liquid N_2. The lowest temperature of *ca.* 100 K was achieved using liquid N_2 directly as a coolant. The temperatures obtained were measured in separate experiments, in which an end-window from the cell was removed and replaced by an assembly that allowed a thermocouple to be inserted so that its junction was located in the region from which LIF was normally observed. Temperatures were then measured under the conditions of cooling, gas flow and total pressure that were used in the 'real' kinetics experiments.

NCNO was photolysed with a Nd : YAG laser (JK Lasers, system 2000) operating at 10 Hz. LIF from CN($v = 0$) was excited using a home-built dye laser pumped by a N_2 laser and observed 'off-resonance'; that is, an interference filter was used to transmit B–X(0,1) fluorescence at 421.6 nm and to discriminate against scattered laser light at 388.3 nm. The time delays between the photolysis and probe lasers were controlled by a microcomputer, which also accumulated the LIF signals.

The sources and procedures for purifying NCNO and Ar were the same as described previously.[12] NO was used from two sources (Cambrian Gases; CP grade, 99% pure; BOC, N2.8 grade, 99.8% pure) and introduced to the vacuum line through a coil immersed in an *n*-pentane slush. After subsequent trap-to-trap distillation between pentane slush and liquid N_2, it was further purified by distillation from a trap at a temperature just above 77 K by repeated applications of liquid N_2. This procedure, when carefully implemented, resulted in NO which did not show significant discoloration when frozen.

Results

In the presence of NO concentrations sufficient to ensure that removal of CN by reaction with NO dominated over diffusive loss,[12] the decays of LIF signals with time were fitted well by exponential curves yielding pseudo-first-order rate constants, k_{1st}. For particular conditions of temperature and total pressure, values of k_{1st} were measured for a number of concentrations of NO and second-order rate constants, k_{2nd}, determined from the gradient of a plot of k_{1st} *vs.* [NO]. Examples of such plots are shown in Fig. 2.

The values of k_{2nd} were found to depend strongly on both temperature and total pressure. In this investigation, we have carried out experiments at pressures 5–400 Torr of Ar at room temperature, 296 ± 2 K, and over more limited ranges of pressures at other temperatures. Experimental effects set some limits on the range of T, p that could be investigated. Thus the strong negative temperature dependence of the reaction and the difficulties of working at high total pressure mean that, at higher temperatures, it is difficult to make reactive removal of CN significantly greater than diffusive loss. We have previously reported an approximate value for k_{2nd} of $(5 \pm 3) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 771 K and 30 Torr and argued that this observation provides strong evidence that, at the pressures and temperatures of our experiments, reaction between CN and NO proceeds entirely by association, *i.e.*,

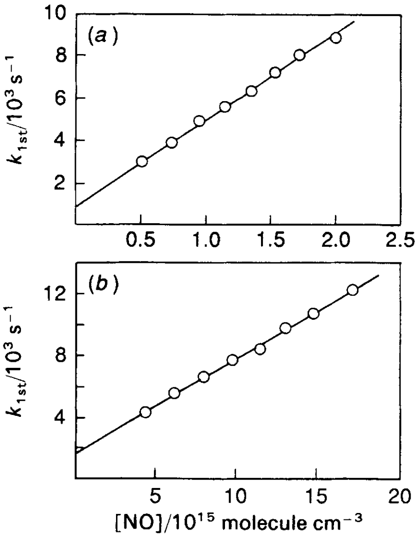

Fig. 2 Examples of the variation of pseudo-first-order rate constants for loss of CN with the concentration of NO: (*a*) total pressure = 5 Torr, T = 104 K, and (*b*) total pressure = 10 Torr, T = 296 K

$$CN + NO(+M) \rightarrow NCNO(+M); \quad \Delta H^\circ_0 = -204.3 \text{ kJ cm}^{-1}$$

with negligible contribution arising from the highly exothermic production of CO and N_2:

$$CN + NO \rightarrow CO + N_2; \quad \Delta H^\circ_0 = -635.8 \text{ kJ mol}^{-1}$$

At the lowest temperatures used in our experiments, in which liquid N_2 was employed as coolant, total pressures were limited to 10 Torr. When the total pressure was raised further, very high levels of scattered laser light resulted, making useful observations of LIF impossible. It appears that the enhanced light scattering was due to the onset of NCNO condensation in the gas phase.

Table 1 summarises the experimental details in the present set of experiments and lists the values of k_{2nd} that have been obtained. For completeness, we include, in brackets, the rate constants obtained in our earlier work.[12]

Calculations

As expected for an association reaction between two diatomic free radicals, the second-order rate constants given in Table 1 are neither independent of the total gas density [M], nor linearly dependent on [M]: that is the kinetics are in the fall-off region. Therefore it is necessary to use a model of the kinetics in order to extract values for the rate constants in the limit of high (k^∞) and low (k^0) pressure. To achieve this aim, we have adopted two methods, both based on the factorisation method of Troe and co-workers[16,17] which is now widely used to extrapolate rate data in the fall-off region in order to find k^∞ and k^0. According to this method, reduced rate constants are given as the product of three terms:

$$k_1/k_1^\infty = F^{LH}F^{sc}F^{wc} \tag{1}$$

where F^{LH} is the reduced Lindemann–Hinshelwood rate constant,

$$F^{LH} = (k^0[M]/k^\infty)/(1 + k^0[M]/k^\infty) \tag{2}$$

and F^{sc} and F^{wc} are broadening factors which allow for the energy dependence of the microcanonical rate constants for dissociation and for weak collision effects, respectively. The factor F^{sc} is a function of the ratio $k^0[M]/k^\infty$ and modified

Table 1 Summary of the experiments and of the second-order rate constants derived for the reaction of CN and NO [CN(v = 0) + NO]

temperature/K	number of measurements	P/Torr	range of [NO]/10^{15} molecule cm^{-3}	$k_{2nd}/10^{-13}$ cm^3 molecule^{-1} s^{-1}
(450	8	30	12.4–59.8	3.8 ± 0.4[a])
296	8	5	4.1–15.6	4.27 ± 0.55
296	8	10	4.4–17.3	6.10 ± 0.38
(295.5	7	10	3.7–10.1	6.00 ± 0.40)
297	7	20	5.4–18.6	10.5 ± 0.8
(294.5	7	30	0.6–2.5	14.7 ± 1.8)
(294.5	9	30	4.2–30.5	14.2 ± 1.0)
298	8	50	4.0–24.8	20.4 ± 1.4
297	8	100	2.7–15.9	32.7 ± 2.0
297	7	200	1.2–7.8	52.0 ± 2.0
296	8	400	1.4–8.5	79.9 ± 4.6
205	8	10	0.5–2.0	17.4 ± 1.4
205	8	20	0.6–4.1	27.1 ± 1.4
205	8	50	1.5–10.1	52.8 ± 2.8
147	9	10	3.0–21.8	34.8 ± 1.8
147	7	10	0.4–2.9	34.8 ± 2.6
145	8	20	0.8–5.8	59.6 ± 3.2
140	7	50	1.2–6.3	128 ± 10
104	8	5	0.5–2.0	40.5 ± 2.6
99	8	10	0.6–4.3	73.4 ± 5.9

[a] Errors equivalent to $\pm 2\sigma$ including an estimate of systematic errors.

Kassel parameters (S_K, B_K)[16] and (S_T, B_T),[17] whereas F^{wc} depends on $k^0[M]/k^\infty$ and β_c, the collision efficiency of the third body M.

In the first set of calculations, the room temperature values of k_{2nd} were fitted to calculated fall-off curves to yield values of $k^0(298)$ and $k^\infty(298)$. It was then assumed that the temperature dependence of k^∞ could be expressed in the form $k^\infty(T) = k^\infty(298)\ (T/298)^n$ with $n = -0.30$. This value of n was obtained[12] by measurements on the relaxation of CN(v = 1) by NO over the temperature range 295–761 K. The rates of both processes, association in the limit of high pressure and vibrational relaxation, are likely to be determined by the rate of formation of energised NCNO collision complexes so their absolute rates should be very similar.[18] Recent high-pressure experiments by Hippler *et al.*[19] have confirmed the essential correctness of this proposition. Having obtained estimates of k^∞ at other temperatures, values of F^{sc} and F^{wc} appropriate to the conditions of our experiments could be estimated and hence values of k^0 determined.

To fit the room temperature data and hence find $k^0(298)$ and $k^\infty(298)$, estimates were needed for the effective Kassel parameters, S_K and B_K, and for the collision efficiency, β_c. S_K is defined by the equation

$$S_K = 1 + T\ \mathrm{d}\ln Q^\dagger/\mathrm{d}T \qquad (3)$$

where $Q^\dagger$ is the partition function for the transition-state species. In order to evaluate S_K from this equation, and to obtain preliminary estimates of k^∞, we carried out calculations according to the simplified statistical adiabatic channel model (SSACM) of Troe.[20] The rate constant k^∞ is expressed in the normal transition-state theory form but the degrees of freedom in the transition state are separated into conserved oscillators, disappearing oscillators, and those contributing to the centrifugal barrier. The details of the calculations are given elsewhere;[21] they yielded values of $k^\infty(T)$ of 1.41×10^{-11}, 1.65×10^{-11} and 1.76×10^{-11} cm^3 molecule^{-1} s^{-1} at 100, 298 and 450 K, respectively, and a value of S_K of 3.86 at 296 K. Having found S_K, B_K was calculated to be 55.2 according to the equation[16]

$$B_K = [(S_K - 1)/(s - 1)][(E_0 + a(E_0)E_z/kT] \qquad (4)$$

where $s = 6$ is the total number of oscillators in NCNO, E_0 and E_z are the dissociation energy and zero-point energy of NCNO, and $a(E_0)$ is the Whitten–Rabinovitch parameter. With β_c assumed to equal 0.2, values of F^{sc} and F^{wc} could be calculated using eqn. (76) and (79) in ref. (16). The room-temperature data (k, [M]) were then fitted using a non-linear least-squares computer program which treated k^0 and k^∞ as completely adjustable parameters which were varied until χ^2, the 'sum of squares', was minimised. This procedure yielded

$$k^0(296) = (2.6_1 \pm 0.17) \times 10^{-30}\ \mathrm{cm^6\ molecule^{-2}\ s^{-1}} \qquad (5a)$$

$$k^\infty(296) = (3.7 \pm 0.45) \times 10^{-11}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}} \qquad (5b)$$

where the errors quoted correspond to $\pm 1\ \sigma$ as generated by the fitting program. The experimental data and the fitted fall-off curve as displayed in Fig. 3.

The limited experimental data at other temperatures were fitted by a similar procedure, but with only k^0 allowed to vary. As stated above, values of k^∞ were obtained from the room temperature value by assuming that their dependence on temperature was the same as that determined[12] for the rate constants for vibrational relaxation of CN(v = 1) by NO: *i.e.*, $k^\infty(T)$ was calculated from the expression:

$$k^\infty(T) = 3.7 \times 10^{-11}(T/298)^{-0.30}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}} \qquad (6)$$

Non-linear least-squares fitting of the data at the same, or closely similar, temperatures gave the value of k^0 displayed in

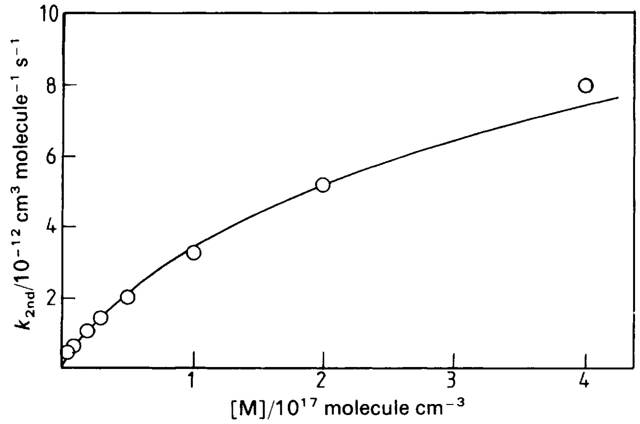

Fig. 3 Second-order rate constants at 296 ± 2 K fitted to fall-off curve calculated according to the first procedure described in the text

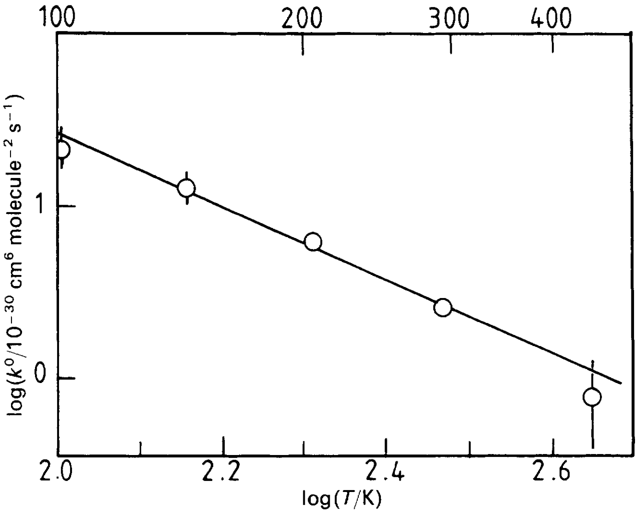

Fig. 4 log–log plot showing the variation with temperature of rate constants in the limit of low pressure calculated according to the first procedure described in the text; error bars (two standard deviations) are shown where they exceed the size of the points

Fig. 4. Within experimental error, they can be fitted to an expression of the form: $k^0(T) = A(T/298)^n$ with the values of A and n given in Table 2.

A problem with the procedure which has just been described is that S_K and k^∞ are not entirely independent parameters:[22] after all, S_K was derived from SSACM calculations which also predicted values of k^∞, but then k^∞ was allowed to vary. A procedure which avoids this inconsistency has been devised by Pilling and co-workers.[23] It also has the advantage that all the data, that is all values of k_{2nd} at any T[M], are fitted globally. We have also applied this method to find values of $k^0(T)$ and $k^\infty(T)$ from our experimental results.

The limiting rate constants are cast in the form:

$$k^\infty(T) = A^\infty(T/298)^{n^\infty} \tag{7a}$$

and

$$k^0(T) = A^0(T/298)^{n^0} \tag{7b}$$

In this case, Keiffer *et al.*[23a] showed that for an association of two diatomic radicals to form a non-linear molecule, the effective Kassel parameter S_T is related to n^∞ by the equation:

$$S_T = n^\infty + 2 + \sum_i U_{\text{vib},i} kT \tag{8}$$

Table 2 Parameters describing the temperature-dependent rate constants in the limit of low and high pressure according to the form $k(T) = A(T/298)^n$

A^0/cm^6 molecule^{-2} s^{-1}	n^0	A^∞/cm^3 molecule^{-1} s^{-1}	n^∞
$(2.7 \pm 0.2) \times 10^{-30}$ [a]	-2.1 ± 0.2[a]	3.7×10^{-11} [a]	-0.30[a]
2.05×10^{-30} [b]	-2.1[b]	1.8×10^{-11} [b]	-0.5[b]
3.0×10^{-30} [c]	-2.3[c]	—	—

[a] Derived from the experimental data by the first fitting procedure described in the text, in which S_K was calculated at each temperature but $k^\infty(T)$ was calculated from $k^\infty(298)$ assuming $n^\infty = -0.3$. [b] Derived from the experimental data by the second fitting procedure described in the text, in which S_T and n^∞ were related by eqn. (8) and the best values of A^∞, n^∞, A^0 and n^0 were found by fitting the experimental data globally. [c] Calculated by the method of Troe[24] for association in the limit of strong collisions.

where $U_{\text{vib},i}$ is the vibrational energy of the ith radical reagent. The second Kassel-type parameter B_T at each temperature can be calculated using[17]

$$B_T = [(S_T - 1)/(s - 1)]^{1.6}\{[E_0 + a(E_0)E_z]/kT\} \tag{9}$$

Having found S_T and B_T, $F^{\text{sc}}_{\text{cent}}$ and F^{sc} at differet values of k^0[M]/k^∞can be calculated.

To estimate the second broadening factor, F^{wc}, some assumption must be made about β_c or about $\langle \Delta E \rangle_{\text{down}}$, the average energy transferred per collision in a downwards direction. For collisions between energised NCNO and Ar, we assumed that $\langle \Delta E \rangle_{\text{down}}$ was constant throughout the experimental temperature range and that

$$\beta_c = [\langle \Delta E \rangle_{\text{down}} / (\langle \Delta E \rangle_{\text{down}} + F_E kT)]^2 \tag{10}$$

where F_E is a factor which corrects for the energy dependence of the density of states above threshold.[24]

The above assumptions and equations were incorporated into a computer programme which found the values of A^0, n^0, A^∞ and n^∞ which minimised the sum of squares of the differences between $\ln(k_{2\text{nd, expt}})$ and $\ln(k_{2\text{nd, calc}})$. This procedure corresponds to minimising the fractional differences between the experimental and calculated values of the rate constants. Kinetic parameters which were obtained in this way are listed in Table 2. The standard deviation between the experimental rate constants and those calculated using the tabulated values of A^0, n^0, A^∞ and n^∞ amounted to 12%.

Even at the highest [M] used in the present series of experiments, $k^0[\text{M}] < k^\infty$, and at the lowest [M], $k^0[\text{M}] \approx 0.01\ k^\infty$. Under these circumstances, it is to be expected that the values of k^0 are better determined than those of k^∞. Troe[24] has described a formalism for calculating strong collision, limiting low-pressure rate constants, k^0_{sc}, which has been widely used and generally found to give agreement with experiment to within a factor of *ca.* 2.[18] For the present calculations, the molecular constants for NCNO, CN and NO were taken from ref. (5) and (24), and Lennard-Jones parameters for the intermolecular potential between NCNO and Ar were assumed to be the same as for C_2N_2 and Ar.[24] Limiting low-pressure rate constants, k^0_{sc}, were calculated for five temperatures in the range 100–450 K. They were very well fitted by the expression given above as eqn. (7*b*) and yielded the values of A^0 and n^0 given in the last column of Table 2.

Discussion

In our earlier paper,[12] in which we reported more limited results on the CN + NO reaction, we compared our results to those of Lam *et al.*[10] and Li *et al.*[11] Both these groups analysed their results on the basis that the reaction occurred by independent second-order and third-order channels and made no allowance for fall-off behaviour in the pressure range of their room temperature experiments (5–22 Torr of Ar in one case,[10] 10–30 Torr of Ar in the other[11]). Consequently, from the intercept and gradient of plots of $k_{2\text{nd}}$ *vs.* [Ar], they claimed to determine rate constants for the bimolecular reaction leading to CO + N_2 and for the association reaction. Our work demonstrates unequivocally that the assumption that the association reaction is in its pure low-pressure regime is invalid and therefore that the values of k^0 derived by Lam *et al.*[10] and Li *et al.*[11] should be rejected. Furthermore, our results indicate that, at least at temperatures $\leqslant$500 K and total pressures above 5 Torr, reaction between CN and NO occurs by recombination, without significant contribution from the highly exothermic channel leading to CO + N_2.

The values of $k^0(298)$, A^0 and n^0 derived from the two analytical procedures that we have used are in quite good agreement. Furthermore, the dependence of k^0 on temperature, indicated by the values of n^0, also agrees well with that predicted by the calculations based on the Troe formalism.[24] However, the absolute values of the calculated rate constants seem rather low when it is remembered that the calculated values are for strong collisions, so that $k^0 = \beta_{c,Ar} k^0_{sc}$, and that $\beta_{c,Ar}$ for reactions of this kind is usually found to have values between 0.1 and 0.2, rather than 0.7 and 0.8 as would be indicated by a comparison of k^0 and k^0_{sc}.

A likely explanation for this discrepancy is that the bound S_1 and T_1 states contribute significantly to the density of states at energies corresponding to the CN + NO dissociation limit, and that this contribution has not been recognised in the calculations leading to values of k^0_{sc}. Smith[25] has considered the possible role of accessible, bound electronically excited states in association reactions of free radicals of different complexity, and recently Davies *et al.*[26] have obtained evidence for their participation in the combination of CH_3 radicals with NO. If the potential-energy surfaces for the S_1 and T_1 states are of the kind predicted by the *ab initio* calculations and represented in Fig. 1, then the situation in the case of the CN + NO association is somewhat different from the systems considered by Smith.[25] In those it was assumed that the potential-energy surfaces associated with the excited states, like that associated with the ground state, presented no potential barriers to the association of the two radicals. However, the theoretical calculations on NCNO indicate substantial barriers on the S_1 and T_1 surfaces. If correct, this means that the rate of formation of energised NCNO complexes, and therefore the rate of association of CN + NO in the limit of high pressure, will not be affected by the existence of the bound S_1 and T_1 states. However, if the rovibrational levels associated in the zeroth-order with these electronic states are mixed with those of the ground state, then the density of states will be increased accordingly and this will enhance the limiting low-pressure rate constant. The photochemical experiments of Wittig and co-workers[1–4] establish strong S_1–S_0 mixing. The rate of T_1–S_0 mixing would have to be as fast as redissociation of the NCNO complexes for the T_1 levels to make a significant contribution to the state density and k^0. Comparison of the values of k^0 derived from our experiments and the value of k^0_{sc} calculated from Troe's method and listed in the last column of Table 2 suggests that rapid mixing of zeroth-order T_1 and S_0 levels occurs.

As noted before,[12] the rate constants for relaxation of CN($v = 1$) by NO presumably correspond to those for complex formation. They are remarkably large given the fact that the spin and orbital degeneracies of CN and NO lead to two singlet and two triplet surfaces and, at room temperature, only *ca.* 16% of the collisions will occur on the ground-state surface. The absolute values of $k^\infty(298)$ given by the two fitting procedures differ by a factor of two and are both appreciably smaller (factors of two and four) than the corresponding rate constants for relaxation. These comparisons suggest that the transition-state structure is much looser than is predicted by the SSACM calculations. In addition, the results of investigations of other systems, which involve association and relaxation of OH radicals,[18,19] suggest that procedures of the type that we have used to fit data at total pressures well short of the high-pressure limit do underestimate the true values of k^∞. Consequently, the values of A^∞ and n^∞ listed in Table 2 should be used and interpreted with caution. They really represent parameters which can be used to estimate second-order rate constants in the pressure range of our experiments using the interpolation procedures that have already been described, rather than realistic estimates of the true rate constants for association in the limit of high pressure. Our conclusion is that the ways in which kinetic data in the fall-off region are fitted to yield the limiting low- and high-pressure rate constants may still require some refinement.

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