LOW-TEMPERATURE NO⁺ ION-MOLECULE REACTIONS IN A NITRIC OXIDE EXPANSION

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The absolute three-body association rate constant for the reaction $NO^+ + 2 NO \rightarrow (NO)_2^+ + NO$ and an upper limit to the charge transfer rate constant for the reaction $NO^+ + (NO)_2 \rightarrow (NO)_2^+ + NO$ were measured in a supersonic expansion near 4 K using a new free jet flow technique. The observed third-order rate constants, k_3 , show temperature dependence near 4 K which can be adequately explained by the expression: $k_3(T) = 7.2 \times 10^{-30} (T/300)^{-2.7} \text{ cm}^6$ molecule⁻² s⁻¹. This expression appears to hold over the temperature range from 430 to 4 K. An upper limit to the charge transfer rate constant is observed to be $4.3 \times 10^{-9} \text{ cm}^2$ molecule⁻¹ s⁻¹ based on estimates of $(NO)_2$ concentrations in the jet at several stagnation pressures.

1. Introduction

In this communication, we present the preliminary results of rate measurements of the three-body association reaction of nitric oxide ion,

$$NO^+ + 2 NO \rightarrow (NO)_2^+ + NO, \qquad (1)$$

occurring within the core of a pure NO supersonic jet. We also report the observation of the concurrent bimolecular charge transfer reaction,

$$NO^{+} + (NO)_{2} \rightarrow (NO)_{2}^{+} + NO$$
, (2)

with the nitric oxide dimer.

The study of the rates of ternary ion-molecule association reactions are particularly important since they show inverse temperature dependence given by

$$k_3 = zT^{-m}, \tag{3}$$

where z and m are constants for a given reaction. The value of m for a variety of such reactions has been found to vary from 0.4 to 4.2 [1]. An accepted mechanism for the reaction can be summarized as follows:

$$A^{+} + B \xrightarrow[k_{b}]{k_{b}} (AB)^{+*} \xrightarrow{\beta k_{c}[M]} (AB)^{+} .$$
 (4)

The first step of the reaction is the bimolecular

formation of a transient collision complex. This complex can subsequently decompose to give the reactants or, in the presence of a third body, can undergo a collision to give a stable molecular ion. The parameter β is a measure of the effectiveness of the third body to stabilize the intermediate complex. Within the steady state approximation, the overall third-order rate constant is given by

$$k_{3} = \frac{\beta k_{a} k_{c}}{k_{b} + \beta k_{c} [M]}.$$
(5)

The low-pressure limit is then

$$k_3 = \frac{\beta k_a k_c}{k_b}.$$
 (6)

With only a few exceptions, the studies of ternary association reactions have been limited to temperatures above 80 K. Measurements of rate coefficients at much lower temperatures are important in two regards. First, they will provide important mechanistic detail for these reactions at the limit of Treaching 0 K. Secondly, these lower temperatures closely resemble the temperatures of interstellar clouds and the rate constants could give insight into the radiative association processes which may be active in molecular synthesis within these clouds.

Most of the information regarding the low-tem-

0 009-2614/88/\$ 03.50 © Elsevier Science Publishers B.V. (North-Holland Physics Publishing Division) perature ternary association dynamics is available for the following reactions:

$$N_2^+ + N_2 + N_2 (He) \rightarrow N_4^+ + N_2 (He)$$
, (7)

$$O_2^+ + O_2 + O_2 \rightarrow O_4^+ + O_2$$
. (8)

Selected ion drift tube (SIFT), variable-temperature ion drift tube (DT) and low-energy drift tube techniques as well as the new CRESU technique have been used to obtain information about these two reactions [2-5]. The DT technique extended the lowtemperature limit to 40 K, whereas the CRESU technique has been used to study the above reactions down to 20 K.

The temperature dependence of reaction (1) has been studied over the range of 200-450 K by a lowenergy drift technique [6]. The value of m was found to be 2.7, whereas theory has predicted 2.0. No detailed study of this reaction has been reported below 200 K. Our results now extend this temperature range to near 4 K and support the continuity of the observed high-temperature dependence to this limit.

2. Experimental

2.1. Experimental technique

Our experimental technique, used to obtain absolute ion-molecule rate constants below 10 K, has been briefly discussed in an earlier report [7]. The rate coefficients are determined by monitoring the temporal composition of a reactant ion packet produced in the core of a supersonic expansion. This ion packet is sampled by a mass spectrometer which translates parallel to the expansion flow axis. A schematic of the experimental apparatus is shown in fig. 1. A free jet of 200 µs duration is obtained by expanding nitric oxide through a flat nozzle of 0.03 cm diameter. The stagnation pressure was varied from 2.3 atm ($P_0d = 52.4$ Torr cm) to 5.3 atm ($P_0d = 120.8$ Torr cm). The stagnation temperature was maintained at 298 K. At 2.6 cm below the nozzle, along the flow axis, the center of the gas pulse was irradiated with a 15 ns laser pulse at a wavelength of 381.8 nm. At this photon energy, NO undergoes resonant three-photon ionization through the



Fig. 1. Schematic of the free jet flow reaction zone. BV, pulsed beam valve; RP, pulsed ion repeller plate; L, laser-focusing lenses; AP, ion acceptance aperture plate; MS, ion-focusing optics and TOF mass spectrometer; TF, mass spectrometer translation flange.

 $C^{2}\Pi(v=0)$ state yielding predominantly NO⁺ X $\Sigma^{1}(v=0)$ [8,9].

After the ion packet has traveled with the jet for a time t under field-free conditions the ions are repelled out of the beam and into a time-of-flight mass analyzer by application of a pulsed extraction field. The mass analyzer rests perpendicular to the flow axis and can translate parallel to this axis for up to a distance of 50 cm from the nozzle. The reaction time is determined by the time needed for the ion packet to flow from the ionization region to the repeller zone. A study of the ion intensities and mass distribution as a function of analyzer position then yields a complete time history of the traveling ion packet. Collisional fragmentation of the ion clusters during the extraction process was found to be negligible at the 100 V/cm extraction fields used. Identical mass distributions were observed at fields ranging from 60 to 160 V/cm. Above 160 V/cm minor fragmentation of heavier cluster ions was observed to occur.

2.2. Flow analysis

Currently, reasonably accurate expressions are available for the calculation of flow properties of a supersonic beam [10-15]. We are mainly concerned with the variation of the density of the free jet as a

function of the distance from the nozzle along the flow axis, the terminal temperature in the jet core, and the effects of cluster formation and condensation on the temperature of the beam. Since the distance between the nozzle and the point where kinetic monitoring begins is about 200 nozzle diameters, the flow is adequately described as free molecular. Therefore, to a good approximation the parallel translational and rotational temperatures will have reached their terminal values. The perpendicular temperature does continue to drop with distance; however, in this study we have approximated the local temperature as being that in the parallel direction. In a future study, the errors implicit in this approximation will be discussed in detail. The ionization process, which leads to a fractional ionization of less than 10^{-5} , is assumed not to influence the basic flow dynamics of the beam. Under these conditions, the density of the beam is given by

$$n = n_0 \frac{d^2}{(z_0 + vt)^2} \left[\frac{1}{2} (\gamma - 1) A(\gamma)^2 \right]^{-1/(\gamma - 1)}, \qquad (9)$$

where γ is the ratio of the heat capacities, d is the nozzle diameter and n_0 is the stagnation density. The quantity $A(\gamma)$, a dimensionless flow parameter, is equal to 3.65 for $\gamma = 1.4$. The distance to the ionization region from the nozzle is given by z_0 and ν denotes the bulk flow velocity of the beam, which is directly measured in our experiment. The reaction time t can be evaluated from ν and the relative location of the mass spectrometer with respect to the nozzle.

The terminal translational temperature parallel to the flow axis is given by

$$T_{t} = T_{0} [1 + 0.5(\gamma - 1)M_{t}^{2}]^{-1}, \qquad (10)$$

where T_0 is the stagnation temperature and M_t is the terminal Mach number

$$M_{t} = F(\gamma) \left(\frac{K_{\rm no}}{\epsilon}\right)^{-(\gamma-1)/\gamma}, \qquad (11)$$

and K_{no} is the Knudsen number, which is the ratio of mean free path to the nozzle diameter at the nozzle throat. The quantity ϵ denotes the collision effectiveness in the jet, which is the maximum fractional change of mean random velocity per collision. The value of $F(\gamma)$ as a function of γ can be calculated [13]. The value of ϵ is obtained by determining the rotational temperature of the molecular beam under the experimental conditions. For a diatomic molecule this rotational temperature can be related to ϵ as follows

$$\epsilon^{2\gamma(\gamma-1)} = \frac{T_{i}(\epsilon=1)}{T_{rot}}.$$
 (12)

2.3. Kinetic analysis

In addition to the termolecular mechanism we also observed bimolecular charge transfer to the neutral van der Waals' dimer of NO. Previous studies have shown that the concentration of the dimer can be as high as 3% in the beam at the condensation limit $(P_0d=78\pm4$ Torr cm), where P_0 is the stagnation pressure [16]. Thus, we had to include both of the competing processes,

$$NO^{+} + 2 NO \xrightarrow{k_3} (NO)_2^{+} + NO, \qquad (13)$$

$$NO^+ + (NO)_2 \xrightarrow{\sim} (NO)_2^+ + NO$$
, (14)

k-

in our kinetic treatment. The differential rate law can be written as

$$\frac{d[NO^{+}]}{dt}$$

= $-k_{3}[NO^{+}][NO]^{2} - k_{2}[NO^{+}][(NO)_{2}]$
+ $[NO^{+}]F(t)$, (15)

where the last term describes the drop in ion density due to physical expansion. Ion diffusion is expected to be minor and is ignored in this treatment. Now we write $[(NO)_2] = f[NO]$ and rearrange the above equation to yield

$$\frac{d[NO^+]}{[NO^+]}$$

= $-k_3[NO]^2 dt - k_2 f[NO] dt + F(t) dt$. (16)

The quantity f denotes the fraction of the dimer in the beam and is treated as independent of time. This is justified in the molecular flow region of the jet. Substitution of eq. (9) into (16) for the NO density followed by integration leads to

$$\ln\left(\frac{[NO^{+}]_{r,t}}{[NO^{+}]_{r,t=0}}\right) = k_{3} \frac{s^{2}}{3v(z_{0}+vt)^{3}}$$
$$= k_{2}f\frac{s}{v(z_{0}+vt)} + \int_{0}^{t} F(t) dt + R, \qquad (17)$$

where

$$s = [NO]_0 d^2 [\frac{1}{2} (\gamma - 1) A(\gamma)^2]^{-1/(\gamma - 1)},$$

and R is a constant. The subscript r stands for the condition where k_3 and k_2 are non-zero. If k_3 and k_2 are assumed to be zero, then the pure expansion condition gives (with the subscript u to denote this situation)

$$\ln\left(\frac{[\text{NO}^+]_{u,t}}{[\text{NO}^+]_{u,t=0}}\right) = \int_0^t F(t) \, \mathrm{d}t \,. \tag{18}$$

Subtraction of eq. (18) from eq. (17) yields

$$\ln\left(\frac{[\mathrm{NO}^+]_{\mathrm{r},t}}{[\mathrm{NO}^+]_{\mathrm{u},t}}\right) = \frac{k_3 s^2}{3v(z_0 + vt)^3} + \frac{k_2 fs}{v(z_0 + vt)} + R.$$
(19)

The quantity $[NO^+]_{r,t}/[NO^+]_{u,t}$ can be replaced by the fraction of NO⁺ to the total ion density at time *t* in the packet. This last step assumes that the diffusional loss of all the species from the ion packet is independent of mass. We denote

$$I^+ = \frac{I_1}{\Sigma I_i},\tag{20}$$

where I_i is the intensity of the (NO)_i⁺ ion mass signal and *i* is found to range from 1 to 6 under our experimental conditions. With this substitution we obtain

$$\ln I^{+} = \frac{k_3 s^2}{3v(z_0 + vt)^3} + \frac{k_2 fs}{v(z_0 + vt)} + R.$$
 (21)

Values of k_3 and $k_2 f$ are obtained by fitting the data to the above equation using a non-linear numerical fitting routine.

3. Results and discussion

The analysis of the REMPI spectrum of the ${}^{2}\Pi_{1/2}$ band up to $J - \frac{1}{2} = 7$ indicates a Boltzmann distri-



Fig. 2. A qualitative example of the temporal dependence of the ion mass distribution. The vertical axis represents the normalized fraction of each ion as a function of reaction time observed at $P_0d=81$ Torr cm.

bution for the low J levels. The population of higher J levels decreases more slowly than expected from a Boltzmann distribution. This has been observed for NO expansions in Ar and He buffer gasses as well [17]. The observed rotational temperatures yield a value for ϵ of 0.06, which suggests a fairly low collision effectiveness of pure NO expansions. A similar low ϵ value has been obtained for SF₆ [18].

Kinetic data were obtained for reactions occurring in jets produced at three distinct stagnation pressures, 2.3, 4.1 and 5.3 atm. From the above analysis we calculate terminal parallel temperatures of 6.1, 4.5 and 3.8 K, respectively, for the cores of these jets. The temporal dependence of the mass distribution in the ion packet for one set of expansion conditions is shown in fig. 2. The consecutive growth of the ion clusters indicates a dominant step-wise three-body association process in the beam. We find good agreement of our results with the rate expression (21) as seen from fig. 3. The experimental results for the two reactions are summarized in table 1 along with the calculated temperature, T(calc), obtained using eqs. (10) through (12). The observed rate constant for the three-body association process, k_3 , is found to vary over the effective temperature range of the study. The values of k_3 calculated using eq. (3) with m=2.7 suggested for this reaction at temperatures above 200 K are also shown [6]. Included in this table are the k_2 values we obtain using the dimer mole fractions given by Golomb et al. for these stagnation pressures [16].



Fig. 3. A plot of the best fit of the experimental data to the rate equation (21), at $P_0 = 5.3$ atm.

3.1. Ternary association reaction

The observed ternary association rate contants show inverse temperature dependence, which can be adequately explained by the value of m=2.7 suggested for this reaction by van Koppen et al. [6]. Fig. 4 shows this measured dependence of k_3 from 450 to 3.9 K. This result supports recent theories which predict that for reactions studied in the quasi zero pressure regime, the inverse temperature law (1) should hold as long as there is no rotational collapse of the neutral reactant to the lowest rotational level ("rotational freezing") [4,19-25]. For molecules like NO with low rotational constants, this latter condition may be achieved only near 0 K. The CRESU technique has supported the inverse temperature dependence of the association reaction of N_2^+ , reaction (7), down to 20 K [5]. The study of the association reaction of O_2^+ , reaction (8), by the CRESU technique has shown deviation from the inverse

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Fig. 4. A plot of the termolecular rate coefficients, k_3 , for reaction (1) versus temperature. The solid points are the values from ref. [6]. The open circles are the values from this study. The solid line represents the high-temperature-fitted rate coefficient expression; $k_3 = 7.2 \times 10^{-30} (T/300)^{-2.7} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$.

temperature law; however, this result was inconclusive since the rate constants measured were only lower limits to the true values. The drift tube studies at temperatures down to 45 K, on the other hand, have shown that considerable deviations from the inverse temperature dependence of the rate constant occur for both of the above reactions, the deviation being quite marked for reaction (8) [2]. Further, a study of the same reactions with He as the third body using a similar technique has shown that the steepness of the temperature dependence reduces considerably at low temperatures [3]. A sufficient explanation for the above deviations is not available. It has been suggested that these deviations may be a result of cluster fragmentation, which might lead to low values of k_3 for these reactions.

It is important to note that the rate constants are extremely sensitive at these low temperatures. The

P_0 (atm)	T(calc) (K)	$k_3(\text{obs})^{a}$	$k_3(\text{calc})^{a,b}$	$k_2 f(\text{meas})^{c}$	$k_2(\text{est})^{\text{c,d}}$
2.3	6.1	3.0	2.7	0.01	4.8
4.1	4.5	7.4	6.0	0.086	3.9
5.3	3.8	12	9.5 (6.1–15)	0.080	4.4

^{a)} In 10^{-25} cm⁶ molecule⁻² s⁻¹, estimated error 25%.

^{b)} Using m = 2.7 from ref. [6]. The values in parentheses indicate the range.

^{c)} In 10⁻⁹ cm³ molecule⁻¹ s⁻¹.

^{d)} Upper limit to k_2 based on the observations in ref. [16].

The results of numerical fitting to the rate equation (21)

Table 1

previously reported error in the value of $m (\pm 0.1)$ can lead to fairly large error limits for the rate constant. For example, in table 1, we have given the upper and lower limits to the rate constant imparted by this error, computed for the lowest temperature of our study.

We also investigated the possibility of saturation of the three-body kinetics in the beam. As we have seen above, the low-pressure limit is achieved when

$$k_{\rm b} \gg k_{\rm c} \beta[\rm NO] , \qquad (22)$$

which is identical to

$$k_3[\text{NO}] \ll k_a \,. \tag{23}$$

Since bimolecular ion-molecule reactions often approach the capture rate, we can take k_a to be in the order of 1×10^{-9} cm³ molecule⁻¹ s⁻¹ calculated from the ADO model at 4 K. At the highest stagnation pressure and t=0 (this is the worst possible situation), it can be shown that $k_3[NO] \approx 0.04k_a$. Hence, we are justified in treating the kinetics with the low-pressure-limited model for k_3 .

3.2. Charge transfer reaction

In our experiment, we do not obtain a direct measure of the nitric oxide van der Waals' dimer concentration in the beam. The observation of the bimolecular charge transfer between (NO)⁺ and $(NO)_2$ can thus only lead to a measurement of the product of the rate constant k_2 and the local concentration of the dimer. Since neutral clustering is essentially frozen in the regions over which we observe ion chemistry, we assume that the local dimer concentration can be written as some fraction f of the local NO monomer concentration. Our measurements of the rate of reaction (14) then yield values for the product $k_2 f$ for various stagnation conditions. It was observed that this product decreases with increasing stagnation pressure. Assuming k_2 is a constant over this pressure range, this observation could be a result of a decreasing fraction of dimer density attributed to the onset of the condensation of the dimer in the isentropic region of the beam. This measurement, however, must only be taken as a qualitative one at this point until precise measurements of the dimer concentrations can be performed. Our results agree with the usual picture of condensation of van der Waals' clusters without monomer depletion [13]. The observed growth of the dimer cation at late stages of the experiment is found to contain a strong bimolecular component and must be largely due to the reactions

 $NO^+ + (NO)_3 \rightarrow (NO)_3^+ + NO$, (24)

$$(NO)_{2}^{+} + (NO)_{3} \rightarrow (NO)_{3}^{+} + (NO)_{2}.$$
 (25)

The observed rate of growth for the trimer ion is found to increase consistently with increasing stagnation pressure unlike the behaviour observed for reaction (14) and supports the argument for neutral dimer condensation towards higher clusters at the two larger stagnation pressures of this study. At the highest pressure used, our qualitative observations indicate a much larger tetramer concentration as well, as evidenced by tetramer cation growth. Quantitative rate determinations for the growth of these higher-order clusters were not attempted. Such measurements are complicated by the great uncertainties in both neutral concentrations and the velocity and internal energy distributions of species produced by chemical reactions within the beam. Using the fractions of van der Waals' dimer suggested by Golomb et al., the estimated value for k_2 is 4.3×10^{-9} cm³ molecule $^{-1}$ s $^{-1}$. This value is only an upper limit of k_{2} , since the true dimer mole fractions are probably greater than those reported by Golomb et al., due to the problem of cluster fragmentation in their experiment.

We assume that the molecule $(NO)_2$ has a polarizability twice that of NO. The dipole moment of $(NO)_2$ is calculated by considering this molecule to consist of two weakly perturbed NO molecules oriented in a cis fashion [26,27]. The use of the simple ADO model then predicts the rate of reaction (17) to be 2.6×10^{-9} cm³ molecule⁻¹ s⁻¹ at 4 K. A locked dipole model predicts an even greater value. This lends further support to our assignment of the van der Waals' charge transfer reaction and the suggestion that the k_2 value measured is an upper limit to the true rate constant.

4. Conclusion

We report the development of a new technique to study important gas-phase ion-molecule reactions at low temperatures. Three-body association processes have generally been considered responsible for the formation of neutral van der Waals' clusters in the hypersonic portion of free jets. We have shown that at sufficiently high stagnation pressures, three-body ionic association reactions can still occur in the free molecular core of these jets. The measured rate constant for the three-body association reaction of NO⁺ in general supports a strong temperature dependence down to low temperatures probed in this study. A concurrent bimolecular charge transfer process was also observed between NO⁺ and (NO)₂. Further work is in progress to study favorable third-order association reactions of other atmospherically relevant cations with a variety of neutrals under similar conditions.

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