Reexamination of the Quenching of NO⁺ Vibrations by $O_2(a \ ^1\Delta_g)$

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The quenching of vibrationally excited NO⁺ by $O_2(a \ ^1\Delta_g)$ has been examined using the monitor ion technique and chemical generation of $O_2(a \ ^1\Delta_g)$. In contrast to previous results which showed that the rate constant was much larger than for ground state O_2 , this study finds that the rate constant for quenching is below the detection limit (<10⁻¹¹ cm³ s⁻¹) of this experiment. The previous experiments produced $O_2(a \ ^1\Delta_g)$ in a discharge, which would also produces O atoms. We found that the monitor ion CH₃I⁺ reacts with O atoms to produce CHIOH⁺. This is the likely cause of error in the previous experiments.

Introduction

To resolve a discrepancy in the rate constants for O⁻ and O₂⁻ reacting with O₂($a^{1}\Delta_{g}$), we have developed a new technique for studying ion-molecule reactions with electronically excited oxygen.¹ The technique relies on (1) an emission cell calibrated to the PSI standard for absolute intensity using a NIST traceable blackbody source and (2) a chemical generator for producing O₂($a^{-1}\Delta_{g}$).² Both previous measurements of the reactions produced O₂($a^{-1}\Delta_{g}$) in a microwave discharge.^{3,4} To our surprise, we found that both previous measurements of the rate constants for the reactions were incorrect and that the O⁻ reaction also proceeded through a previously undiscovered charge transfer channel. The new results are important in modeling the ratio of electrons to negative ions in the upper atmosphere.

Since that time, we have exploited the technique to study the general reactivity of ions with $O_2(a \ ^1\Delta_g)$.^{1,2,5–7} In these studies, it was shown that the excitation energy often promoted otherwise endothermic processes such as charge transfer and electron detachment. A particularly unique example is that energy transfer from $O_2(a \ ^1\Delta_g)$ to $OH^-(H_2O)_{1,2}$ results in the dissociation of a H_2O ligand. An extensive study of the reactivity of $O_2(a^{-1}\Delta_2)$ with anions has been carried out; good agreement was found for the six organic ion reactions that had been previously studied.⁸ Positive ion reactions have been more challenging since the method produces about ~80% O₂(X ${}^{3}\Sigma_{g}$) and, unless extreme caution is taken, H₂O is also introduced into the flow tube. Both of these species are much more reactive with cations than with anions, leading to several competing reactions occurring simultaneously. We have also succeeded in evaluating several charge transfer reactions with $O_2(a \ ^1\Delta_2)$ and found that no concrete correlation emerges when these rate constants are compared with the analogous measurements with $O_2(X^{3}\Sigma_{o})$.

The vibrational quenching of NO⁺(v) by O₂($a^{-1}\Delta_g$) has not been reexamined with this new technique. This reaction had been studied elsewhere by the monitor ion technique,⁹ and in that study it was found that O₂($a^{-1}\Delta_g$) quenched NO⁺ vibrations much more rapidly ($k = 3 \pm 2 \times 10^{-10}$ cm³ s⁻¹) than $O_2(X {}^{3}\Sigma_g) (k = 2 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}).^{10}$ The $O_2(a {}^{1}\Delta_g)$ was produced in a microwave discharge, and its concentration was not measured. The fraction of $O_2(a {}^{1}\Delta_g)$ produced was estimated to be 5–15% and it was assumed that no other reactive oxygen species (O, $O_2(v)$, O_3) were involved. For these reasons, we have decided to re-examine the kinetics of this quenching reaction, and the results are reported here. In the process, we have also identified a potentially complicating reaction involved in the previous measurements and report on that chemistry as well.

Experimental Section

The monitor ion^{11–13} and O₂($a^{1}\Delta_{g}$) production techniques^{1,2} are thoroughly described in the literature. Here we describe them briefly. The experiments described here were carried out in a selected ion flow tube (SIFT)¹⁴ incorporating a monitor ion inlet.¹³ NO⁺(v) ions were produced in a moderate pressure ion source from NO. The ions were mass selected and injected into the flow tube through a Venturi inlet. The extent of vibrational excitation was controlled both by the conditions in the ion source and by the injection energy. Higher injection energies resulted in more excitation. In these experiments we found an injection energy of 70 eV to be optimal because it produced significant excitation but little NO⁺ fragmentation. A helium buffer carried the ions down the tube and thermalized the translational and rotational, but not vibrational, degrees of freedom. Ions were sampled at the end of the flow tube through a pinhole orifice in the nose cone, mass analyzed by a quadrupole mass filter, and detected by a discrete dynode multiplier. $O_2(a \ ^1\Delta_g)$ was added 59 cm from the sampling orifice. Two centimeters before the sampling orifice a monitor gas was added to convert vibrationally excited NO⁺ into other ions. We used two monitors that react with various excited states at different rates.^{15–17} The simplest chemistry occurs with CH₃I as the monitor since it does not cluster to any vibrational state of NO⁺. For v = 1-4, the rate constants for the monitor reaction,

$$NO^{+}(v) + CH_{3}I \rightarrow CH_{3}I^{+} + NO$$
(1)

are 2, 9, 13, and 14×10^{-10} cm³ s⁻¹, respectively. In addition, CH₃I quenches NO⁺(v) vibrational excitation with rate constants equal to 14 and 7 × 10⁻¹⁰ cm³ s⁻¹ for v = 1 and 2, respectively.

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Therefore, $NO^+(v = 1)$ was monitored but not as efficiently as higher states. For that reason, we also used C_2H_5I as a monitor,

$$NO^{+}(v) + C_{2}H_{5}I \rightarrow C_{2}H_{5}I^{+} + NO$$
 (2)

The rate constants for reaction 2 are 0.4, 7.3, 11.2, 16, and 16×10^{-10} cm³ s⁻¹, for v = 0-4, respectively.¹⁶ Quenching of NO⁺(v) is less important than for CH₃I, with rate constants of 7 and 8 × 10⁻¹⁰ cm³ s⁻¹, for v = 1 and 2. All rate constants refer to measurements made at low pressures in an ICR. Under the SIFT conditions, NO⁺ is observed to cluster to C₂H₅I but not to CH₃I. However, we do not know if that applies to all states or just v = 0. Thus, the monitor ion chemistry can be complex with C₂H₅I.

The $O_2(a \ ^1\Delta_g)$ generator and detector have been described in detail elsewhere.⁶ Cl₂ was bubbled through a basic solution of hydrogen peroxide to produce both ground and excited states of O₂, that is, $O_2(X \ ^3\Sigma_g)$ and $O_2(a \ ^1\Delta_g)$, as shown by eq 3.

$$H_2O_2 + Cl_2 + 2KOH \rightarrow O_2(X {}^3\Sigma_g \text{ and } a {}^1\Delta_g) + 2 KCl + 2 H_2O$$
 (3)

100% of the Cl₂ reacted to form one of the states of O₂. This reaction is a well-known source of $O_2(a \ ^1\Delta_g)^{18,19}$ and has been used to create a chemical O_2/I_2 laser (COIL).²⁰ Water was collected in a trap submerged in a methanol—liquid nitrogen slush maintained at -60 to -70 °C. $O_2(a \ ^1\Delta_g)$ emissions at 1270 nm were monitored in a calibrated cell to determine its concentration.¹ Using this technique, mainly He, $O_2(X \ ^3\Sigma_g)$, and $O_2(a \ ^1\Delta_g)$ entered the SIFT. The fraction of O_2 as $O_2(a \ ^1\Delta_g)$ in the current experiments varied from 12–16%.

We also performed two other experiments to look for interferences in the monitor technique. In the first, the reaction of CH₃I⁺ with O was studied since the experiment performed by Dotan et al.⁹ relied on a discharge method to generate O₂($a^{1}\Delta_{g}$). O atoms are a known product in such a discharge. For that experiment, the O₂($a^{1}\Delta_{g}$) inlet was replaced with an inlet incorporating a microwave discharge. We produced O atoms in the conventional manner.²¹ N₂ was discharged to produce N atoms, and NO was added downstream in the side arm. The reaction of N atoms with NO produced O and N₂. In a second experiment, the reactivity of CH₃I⁺, C₂H₅I⁺, and NO⁺(C₂H₅I) with O₂($a^{1}\Delta_{g}$) was determined. For that measurement, we moved the alkyl iodide addition 30 cm upstream of the O₂($a^{1}\Delta_{g}$) was added.

Results and Discussion

Reaction rate constants were measured by monitoring the signal intensity of CH₃I⁺ or C₂H₃I⁺ monitor ions as the flow of O₂($a^{-1}\Delta_g$) was turned on and off on an electronic strip chart. This technique has been used previously with good success.⁵ The CH₃I⁺ signal remained essentially constant as the O₂($a^{-1}\Delta_g$) was turned on or off (by adding Cl₂), indicating little quenching occurred. The intensity of the C₂H₅I⁺ signal showed a very small decrease, <5%. Quenching by O₂(X ${}^{3}\Sigma_{g}$) is slow and had little effect on the NO⁺ vibrational distribution.¹⁰ Upper limits of the rate constants for the disappearance of the monitor ions with O₂($a^{-1}\Delta_g$) are <2 × 10⁻¹¹ cm³ s⁻¹ for C₂H₅I⁺ and <8 × 10⁻¹² cm³ s⁻¹ for CH₃I⁺. These are essentially at our limit of detection for O₂($a^{-1}\Delta_g$) reactions. Data were also obtained in the normal manner, as a function of added O₂($a^{-1}\Delta_g$). They are consistent with the strip chart method, but instabilities in the ion signals

made determining very small slopes difficult, and this method was abandoned in favor of the former. The absence of a change in either monitor ion signal also indicates that the electronic energy from $O_2(a \ ^1\Delta_g)$ does not transfer to NO⁺ vibrational excitation. In that case, an increase in the monitor ion signal would have occurred with $O_2(a \ ^1\Delta_g)$ addition. There is the extremely unlikely possibility that the V-TR deexcitation exactly balances the E–V excitation.

The derived quenching rate constants are much smaller than those reported by Dotan et al., who found $k = 3 \pm 2 \times 10^{-10}$ cm³ s⁻¹, using CH₃I⁺ as the monitor.⁹ A rate as large as the lower limit $(10^{-10} \text{ cm}^3 \text{ s}^{-1})$ would be easy to measure in our apparatus. The two experiments were performed in a similar manner except that in the previous experiments the $O_2(a \ ^1\Delta_g)$ was generated by discharging O₂ rather than through a chemical reaction. The $O_2(a^{-1}\Delta_{\alpha})$ concentration in the Dotan et al. experiments was not measured but estimated based on previous experiments with $O_2(a^{1}\Delta_g)$. Our experience is that the estimated 5–15% conversion of $O_2(X^{3}\Sigma_g)$ to $O_2(a^{1}\Delta_g)$ in the discharge was reasonable;1 however, discharging O2 produces other species including O atoms. In previous experiments in our laboratory, when $O_2(a \ ^1\Delta_g)$ was made in a discharge with glass wool added to reduce the O atom concentration, we found that the fractions of $O_2(X^{3}\Sigma_g)$ converted to $O_2(a^{1}\Delta_g)$ and O were 9 and 1%, respectively.¹ Without the glass wool, the concentration of O atoms introduced into the flow tube would be larger. Therefore, O atoms may be expected to affect the chemistry. Comparison to quenching rates by other atoms shows that quenching of $NO^+(v)$ by O atoms is probably negligible.¹²

An alternative explanation for the apparent fast quenching rate in the Dotan et al. experiment is that O atoms could have reacted with the CH_3I^+ monitor. We have tested this possibility and have been able to confirm that a reaction occurs, as shown in eq 4, where the exothermicity was calculated using Gaussian 03 at the B3LYP/6-311++G(d,p) level of theory.^{22–24}

$$CH_3I^+ + O \rightarrow CHIOH^+ + H + \sim 220 \text{ kJ mol}^{-1}$$
 (4)

Unfortunately, the oxygen atoms affected our sampling efficiency and prevented rate constants from being derived. In the experiments of Dotan et al.⁹ a decline in the CH_3I^+ signal was observed when the discharge was turned on and was interpreted as being due to quenching. However, based on our observations, we believe the decline was actually due to reaction 4.

A similar error would exist if the monitor ions reacted with $O_2(a \ ^1\Delta_g)$. In order to investigate this possibility, we injected NO⁺ and added either CH₃I or C₂H₅I 30 cm upstream of the $O_2(a \ ^1\Delta_g)$ inlet to produce CH₃I⁺ or C₂H₅I⁺ and NO⁺(C₂H₅I). Enough neutral reagent was introduced such that the chemistry was complete before $O_2(a \ ^1\Delta_g)$ addition, and this simulated the monitor situation more realistically than if the ions were injected from the source. None of the alkyl iodide ions were observed to react with $O_2(a \ ^1\Delta_g)$. Therefore, secondary reactions with $O_2(a \ ^1\Delta_g)$ could not cause an artifact.

The general description of quenching of ions by neutrals has been laid out by Ferguson.¹² Breifly, at thermal energies, the quenching generally involves formation of a long-lived complex followed by vibrational predissociation. Good, but not perfect, correlations between three-body association rate constants for v = 0 and vibrational quenching rate constants have been found. Calculations indicated that the predissociative lifetime was 10^{-9} to 10^{-10} s for many systems. These are based on assuming the complex for ground and excited state complexes form at the collisional rate and that the lifetime of the complex can be equated with the efficiency of the reactions.

 $O_2(X^{3}\Sigma_{e})$ does not quench NO⁺(v) effectively because the two molecules do not interact strongly, in part, because spin effects lead to a repulsive potential at long-range, instead of the more common attractive potential. This was confirmed in a previous study that showed that $NO^+(O_2)$ is not formed, even at 90 K,10 indicating a very weak bond. It was hypothesized that quenching by $O_2(a \ ^1\Delta_g)$, because it eliminates the spin effect problems, may result in an attractive interaction. The original results supported this idea. That is, $O_2(a \, {}^1\Delta_{\circ})$ quenched NO⁺(v) rapidly. However, when comparing the quenching rate constant to that found for other diatomics, one finds that the previously measured $O_2(a \ ^1\Delta_{\circ})$ value is inconsistent. The rate constants for NO⁺(v) quenching by the similar molecules, N₂ and CO, are 0.7 and 1.0×10^{-11} cm³ s⁻¹, ^{10,12} respectively. These are at least a factor of 30 slower than the previous value for $O_2(a)$ ${}^{1}\Delta_{g}$) and on the order of the upper limit reported here.

The previous work on collisional quenching discussed above¹² finds a distinct correlation between the quenching rate and that for three-body association to $NO^+(v = 0)$. With the molecular parameters of N₂, O₂($a^{-1}\Delta_{g}$), and CO being similar (vibrational frequencies are high enough to be negligible) the association rate should be roughly dependent on the bond strength of NO⁺-(X), where X = N₂, O₂($a^{1}\Delta_{g}$), CO. We calculated the bond strengths for X with G3 theory using the Gaussian 03²² suite of programs and found them to be 0.22, 0.30, and 0.21 eV for N₂, O₂($a^{-1}\Delta_{g}$), and CO, respectively. These values are the same within the error of the calculation and should indicate that the rates should be comparable. The quenching rate constants for N_2 and CO, are similar to detection limit for $O_2(a)$ $^{1}\Delta_{g}$) quenching. This may indicate that the $O_{2}(a^{1}\Delta_{g})$ quenching rate may be just below our limit and that it may still be substantially greater than that for $O_2(X^{3}\Sigma_g)$.

In summary, we have found that quenching of NO⁺(v) by O₂($a^{-1}\Delta_g$) is much slower than previously reported and potentially more consistent with what is expected based on polarizibilities. We tested several of the potential problems that may have occurred and found that the reaction of CH₃I⁺ with O atoms probably affected the previous results.

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