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Temperature dependence of the oxide ion/ozone reaction in the gas phase

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Abstract

Rate coefficient and branching fraction data were determined for the gas phase reaction of $O^- + O_3$ over the temperature range 123–500 K using the temperature variable selected ion flow tube technique. The reaction rate coefficient is large and relatively insensitive to temperature; reaction takes place on every collision. In contrast, the product distributions are sensitive to temperature. Charge transfer is the major reactive pathway (≥67%) at all temperatures, and its importance increases with increasing temperature. Atom transfer, forming $O_2^- + O_2$, constitutes approximately 33% of the products at 123 K. The temperature dependence of the branching fraction explains an apparent discrepancy between product data from room temperature flow tube experiments and low energy beam experiments. A reaction mechanism is proposed to qualitatively explain the product branching fraction temperature dependence.

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1. Introduction

Reactions of negative ions with ozone play key roles in the ion chemistry of the stratosphere and D-region of the ionosphere. Previous research revealed that O^- and O_2^- are ions formed early in the negative ion reaction scheme [1,2]. The reaction of oxide ion with ozone is among the most efficient reactions of this ion with atmospheric species [1,2]. This reaction is likely even more important in high energy/temperature air plasmas because high concentrations of ozone are formed and electron attachment to ozone forming oxide ion is efficient [3–6].

Ion chemistry also plays a role in the radar and optical characteristics of hypersonic vehicles [7]. Recent investigations of this chemistry have focused on a number of chemical systems including reactions of a variety of negative ions with ozone [8]. The present work extends these investigations by providing the first study of the temperature dependence of the oxide ion/ozone reaction. These data are important for determining the role this reaction plays in the stratosphere, lower ionosphere and higher temperature hypersonic vehicle wake environments. These data also provide insights into the origin of discrepancies between results from low energy beam and room temperature flow tube experiments recently identified in the literature [8,9].

2. Experiment

Experiments were performed with the temperature variable selected ion flow tube at the Air Force Research Laboratory that has been described in detail previously [10,11]. Briefly, O^- ions were formed from O_2 in a remote moderate pressure ion source. The ions of interest were mass-selected and injected into the reaction flow tube through a Venturi inlet. These ions were carried down the length of the flow tube by a fast flow of helium buffer gas with total pressure of

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0.4 torr and flow rate of 12 std. L/min. Neutral reactants were added to the flow tube through stationary inlets located 35 and 50 cm from the end of the flow tube. A small fraction of the ions in the flow tube was sampled through a 0.2 mm sampling orifice located at the tip of a nosecone at the terminus of the flow tube. These ions were analyzed with a quadrupole mass filter and detected with a particle multiplier.

Branching fractions of ionic products were determined from a plot of the product ion fraction (branching fraction) versus reactant neutral concentration. The nascent product fraction is the extrapolated value at zero concentration. Limits on the branching fraction for electron detachment channels were determined from the attenuation of the ion current to the nosecone as a function of neutral reactant flow and from the attenuation of the total ion signal with neutral reactant flow under low resolution conditions [12,13]. (Use of electron scavengers, such as CCl_4 and SF_6, was precluded by the combination of competing reactions forming and destroying the characteristic anions as well as rapid diffusion of electrons to the walls of the flow tube. Since this reaction channel comprised, at most, a small percent of the overall reaction efficiency, these complications made use of this technique impractical.) Rate coefficients were determined from the relative attenuation of the reactant ion signal with reactant neutral concentration under pseudo first order conditions (i.e., $[O_3] \gg [O^-]$).

The reactant ozone was formed, characterized, and delivered to the flow tube with our on-line source [8]. Ozone was created in a commercial ozonizer and introduced into the flow tube through a stationary inlet. The ozone concentration in the oxygen flow (∼5%) was determined accurately and continuously from an in-line absorption measurement just prior to introduction into the flow tube. Importantly, reaction between oxide ion and the co-flow of O_2 is energetically prohibited in our experimental temperature range [14,15]. Ozone concentrations in the flow tube were varied from 0.7 to 5×10^{11} cm^{-3}.

3. Results and discussion

Two different product ions were observed for this reaction. Based on the mass-to-charge ratios observed, mass balance and energetic constraints, the operative reaction channels are shown below with associated reaction enthalpies.

	ΔH_{rxn} (kJ/mol) [14,15]
$O^- + O_3 \rightarrow O_3^- + O$	−62
$O^- + O_3 \rightarrow O_2^- + O_2$	−295

Enthalpy values assume that reactant and products are in their ground electronic states. Reactive detachment is at most a minor product channel in this reaction. Based on our measurements, we place an upper limit of ≤20% for reactive detachment, a limit that reflects the precision of nosecone current measurements, uncertainty of mass and diffusional discriminations, and the high reactivity of ozone with trace impurities in the system.

The product branching fraction data over the 123–500 K temperature range are listed in Table 1. The 296 K branching fractions are in agreement with our previous determination [8]. At all temperatures, charge transfer is the major product, accounting for at least 67% of the products. Fig. 1 compares the ratio of O_2^-/O_3^- with temperature. The line in the graph

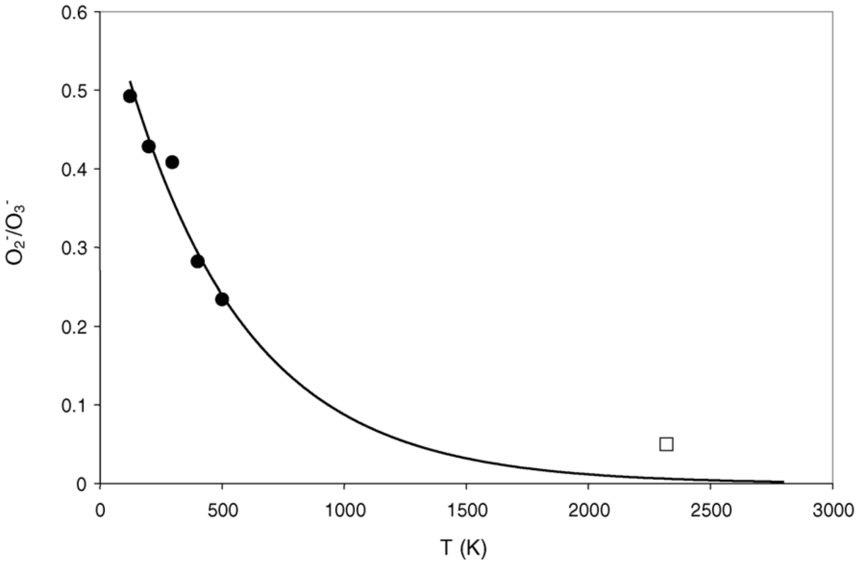

Fig. 1. Ratio of O_2^- to O_3^- product branching fraction as a function of temperature. Solid circles (●) are from this thermal flow tube work and the solid line is an exponential fit to these data. Open square (☐) is from the low energy beam experiment of Lifshitz et al. [9] and is located at an effective temperature corresponding to the collision energy reported.

Table 1
Branching fractions for product channels of $O^- + O_3$ as a function of temperature

Temperature (K)	$O_3^- + O$[a]	$O_2^- + O_2$[a]
123	0.67	0.33
200	0.70	0.30
296	0.71	0.29
400	0.78	0.22
500	0.81	0.19

[a] Relative uncertainty in ionic product branching fraction is 0.05.

is an exponential fit to the data. These data indicate that reaction will proceed almost exclusively by charge transfer at high temperatures. Importantly, these data also suggest that the apparent discrepancy between branching fractions reported for 0.3 eV collision energies by Lifshitz et al. ($O_2^-/O_3^- = 0.05$) [9] and those reported in the recent room temperature thermal investigation [8] as well as this work arises from differences in collision energies. We do not attach any significance to the fact that the beam result does not fall exactly on the fit to our data because the fit is empirical and the extrapolation is over an enormous temperature range.

One additional discrepancy remains unexplained. We determined that reactive detachment is at most a minor reaction channel over the 123–500 K temperature range while Lifshitz et al. [9] found that this reaction channel constituted 60% of the reactive collisions at 0.3 eV collision energy. At higher energies (3–20 eV), Fedchak et al. [16] report a smaller relative cross-section for reactive detachment as compared to charge transfer. Without additional data over a much wider temperature range (not accessible in our experiment) it is not possible to identify the reason these data differ.

The reaction rate coefficient is collisional throughout the 123–500 K temperature range, e.g., $k = 1.6\ (\pm 0.4) \times 10^{-9}\ \mathrm{cm^3\ s^{-1}}$ at 296 K and $k_{\mathrm{obs}}/k_{\mathrm{coll}} = 1.07$ based on the Su–Chesnavich equation for the collision rate coefficient [17,18]. The 296 K value is in excellent agreement with our previous room temperature determination [8] but is approximately a factor of three larger than the value reported at higher energy by Lifshitz et al [9]. Since the overall reaction rate coefficient is temperature independent, the change in the branching fractions with temperature indicates that the efficiency of the charge transfer reaction channel is increased at the expense of the atom transfer. Such competition is most easily explained if the two reaction channels are mechanistically linked. A reaction mechanism consistent with the data is shown below. Reaction is initiated by charge transfer and most of the complexes formed separate into isolated products. A small fraction of the initially formed charge-transfer complexes, however, go on to react further via O atom/ion transfer, ultimately forming dioxygen anion and neutral. Support for the stepwise formation of the atom transfer products is provided by the study of Fehsenfeld [19] that showed that $O_3^- + O \rightarrow O_2^- + O_2$ proceeds at room temperature. Further support is provided by recent work that explored the structure and photochemistry of O_4^-. Chertihin and Andrews [20] and Aquino et al. [21] have established that the ground state geometry of O_4^- is rectangular and the two O_2 moities evenly share the negative charge. The *trans* O_4^- planar structure that should be more easily formed from $O_3^- + O$, is only slightly higher in energy (∼37 kJ/mol) [20,21] and is expected to readily interconvert with the rectangular structure [20]. Sherwood et al. [22,23] found that O_4^- photodissociates exclusively and rapidly ($\leq$10 ps) into $O_2^- + O_2$ or to $2O_2 + e$ over a wide range of energies; no $O_3^- + O$ was observed. These data suggest that once atom transfer takes place in the reaction mechanism proposed above, the O_4^- immediately dissociates into $O_2^- + O_2$.

$$\begin{tikzcd}
O^- + O_3 \arrow[r] & {[O_3^- \bullet O]} \arrow[r] \arrow[d] & O_3^- + O \\
& {[O_4^-]} \arrow[r] & O_2^- + O_2
\end{tikzcd}$$

In this mechanism, the change in branching fraction with increasing temperature arises from a decrease in the lifetime of the charge transfer complex with increasing temperature; the charge transfer products separate before the atom/ion transfer can take place. The large fraction of collisions that form charge transfer products regardless of temperature (∼2/3 over our temperature range) may not be involved in this long-lived complex but rather may proceed by a direct or long-range charge transfer mechanism.

4. Conclusions

Reaction between oxide ion and ozone is efficient over the temperature range of 123–500 K. Product channels include charge transfer and atom transfer. At all temperatures, charge transfer is the dominant reactive channel and becomes increasingly important with increasing temperature. This temperature dependence explains the apparent discrepancy between low energy ion beam and room temperature flow tube experimental results. The product branching fraction temperature dependence is most easily explained by a common mechanism in which atom transfer products are formed from the initially formed charge transfer products.

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