REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)* 30-11-2009	**2. REPORT TYPE** REPRINT	**3. DATES COVERED** *(From - To)*

4. TITLE AND SUBTITLE
Dissociative excitation transfer in the reaction of $O_2(a^1\Delta_g)$ with $OH^-(H_2O)_{1,2}$ clusters

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
61102F

6. AUTHOR(S)
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5d. PROJECT NUMBER
2303

5e. TASK NUMBER
HP

5f. WORK UNIT NUMBER
A1

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory
29 Randolph Road
Hanscom AFB MA 01731-3010

8. PERFORMING ORGANIZATION REPORT NUMBER

AFRL-RV-HA-TR-2009-1112

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

YM(S)

20091207048

12. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for Public Release; Distribution Unlimited

13. SUPPLEMENTARY NOTES
REPRINTED FROM: J. CHEM. PHYS., V. 131, 094303(2009) Copyright: 2009 Am. Inst. of Phys.
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14. ABSTRACT

Rate constants for the dissociation of $OH^-(H_2O)$ and $OH^-(H_2O)_2$ by transfer of electronic energy from $O_2(a^1\Delta_g)$ were measured. Values of 1.8×10^{-11} and 2.2×10^{-11} cm^3 $molecule^{-1}$ s^{-1}, respectively, at 300 K were derived and temperature dependences were obtained from 300 to 500 K for $OH^-(H_2O)$ and from 300 to 400 K for $OH^-(H_2O)_2$. Dissociative excitation transfer with $OH^-(H_2O)$ is slightly endothermic and the reaction appears to have a positive temperature dependence, but barely outside the uncertainty range. In contrast, the reaction of $OH^-(H_2O)_2$ is exothermic and appears to have a negative temperature dependence. The rate constants are analyzed in terms of unimolecular rate theory, which suggests that the dissociation is prompt and is not affected by collisions with the helium buffer gas. © *2009 American Institute of Physics.* [doi:10.1063/1.3212839]

15. SUBJECT TERMS
Temperature dependence Rate constants Excited oxygen Dissociation

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON** A.A. Viggiano
a. REPORT UNCLAS	**b. ABSTRACT** UNCLAS	**c. THIS PAGE** UNCLAS	SAR		**19b. TELEPHONE NUMBER** *(include area code)*

THE JOURNAL OF CHEMICAL PHYSICS **131**, 094303 (2009)

Dissociative excitation transfer in the reaction of $O_2(a^1\Delta_g)$ with $OH^-(H_2O)_{1,2}$ clusters

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(Received 13 May 2009; accepted 5 August 2009; published online 4 September 2009)

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I. INTRODUCTION

In recent years, we have studied the reactions of $O_2(a^1\Delta_g)$ with a variety of anions in a selected ion flow tube (SIFT).[1–5] In these experiments, $O_2(a^1\Delta_g)$ and $O_2(X^3\Sigma_g^-)$ were produced in a chemical reaction[6,7] and the concentration of $O_2(a^1\Delta_g)$ was monitored by light emission, which was calibrated against an absolute standard.[8] Ionic reactants were present in much lower concentration, such that pseudo-first-order conditions were always established. The presence of electronic ground state oxygen does not pose a problem as long as the particular reaction with $O_2(X)$ is sufficiently slow compared to the analogous reaction with $O_2(a)$. This condition is easily verified by experiments with pure ground state O_2.

In our previous studies, we found numerous examples in which the electronic excitation energy of $O_2(a^1\Delta_g)$ is available for driving chemical reactions. Several Penning-type electron detachment reactions were observed, including those of O_2^-, SO_2^-, and HO_2^-.[3] The electronic excitation of O_2, in general, was found to efficiently drive charge transfer.[3] A particularly interesting example was the reaction with O^-, where the endothermic charge transfer channel was not detected in previous flowing afterglow studies,[7,9] but was observed in SIFT experiments and found to increase with temperature.[4]

The present study examines whether the electronic excitation energy of $O_2(a^1\Delta_g)$ can be used to dissociate ionic clusters. Cluster bond strengths[10] are often in the range of the electronic excitation energy of $O_2(a^1\Delta_g)$ (94.29 kJ mol^{-1} or 0.9773 eV, at 0 K). In the present work, we have studied reactions of $O_2(a^1\Delta_g)$ with $OH^-(H_2O)$ and $OH^-(H_2O)_2$ for which the energies for dissociating one hydroxide-water bond are[11] 113 and 75 kJ mol^{-1}, respectively, at 298 K, i.e., of the order of the excitation energy of O_2. We have indeed observed dissociative excitation energy transfer such as in reaction (1a),

$$OH^-(H_2O) + O_2(a^1\Delta_g) \rightarrow OH^- + H_2O + O_2(X^3\Sigma_g^-). \quad (1a)$$

In analyzing the derived rate constants over the range of 300–500 K, the question arises as to the nature of the mechanism. Reaction (1a) begins as a capture process whose rate constant is easily estimated from ion-quadrupole capture theory.[12] We discuss the possibility of whether the reaction then proceeds sequentially,

$$OH^-(H_2O) + O_2(a^1\Delta_g) \rightarrow OH^-(H_2O)^* + O_2(X^3\Sigma_g^-), \quad (1b)$$

$$OH^-(H_2O)^* \rightarrow OH^- + H_2O, \quad (1c)$$

$$OH^-(H_2O)^* + M \rightarrow OH^-(H_2O) + M, \quad (1d)$$

or whether the formation of OH^- can be considered as a prompt process without the possibility of collisional stabilization of $OH^-(H_2O)^*$. Mechanisms (1b)–(1d) may be understood as a chemical activation process and analyzed in the framework of unimolecular rate theory,[13] provided that the energy partitioning in process (1b) can be characterized. Improved knowledge of the molecular properties of $OH^-(H_2O)$ clusters (see e.g., Refs. 14 and 15) is helpful for estimating dissociative lifetimes of $OH^-(H_2O)^*$.

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0021-9606/2009/131(9)/094303/6/$25.00

II. EXPERIMENTAL TECHNIQUE

Our measurements were made in a SIFT, which has been described in detail previously.[4,16] $OH^-(H_2O)_{1,2}$ cluster ions were produced in an external moderate-pressure ion source, mass selected, and injected into the flow tube through a Venturi inlet. The ions were carried downstream by the helium buffer gas and $O_2(a^1\Delta_g)$ was added to the flow at 59 cm from a sampling orifice. At the end of the reaction flow tube, the bulk of the gas was pumped away by a Roots-type blower and a small amount was sampled through a nose cone aperture. The ions were extracted into a quadrupole mass spectrometer and detected by a discrete dynode particle multiplier. The source produces hot $OH^-(H_2O)_n$ clusters (cooled by the helium buffer) and the injection energy is above thermal, both of which lead to dissociation in the initial collisions with the He buffer. Therefore, in order to produce optimum cluster signals, we injected larger clusters and allowed them to dissociate to the desired cluster ion. To produce the $n=1$ cluster, $n=2$ was injected, resulting in $>90\%$ dissociation to form the singly solvated ion, with a small amount of OH^- comprising the bulk of the remaining signal. To produce $n=2$, all high mass clusters were injected and adequate $n=2$ signals were obtained, with larger signals of $n=1$. The presence of the smaller clusters did not affect rate constant determinations but complicated product observations as discussed below.

The technique used to generate and monitor $O_2(a^1\Delta_g)$ concentrations has been described before in detail.[2,4] Briefly, a Cl_2/He mixture was bubbled through a mixture of $4.04M$ KOH and H_2O_2 (35% w/w) in water, held at 253 K by a recirculating chiller. The reaction

$$H_2O_2 + Cl_2 + 2KOH \rightarrow O_2(a)/O_2(X) + 2KCl + 2H_2O \tag{2}$$

is a well known source of $O_2(a^1\Delta_g)$,[6,7] e.g., it has been used to create chemical O_2/I_2 lasers.[17] Before use, the mixture was degassed by pumping. A second continuous flow of helium was used to prevent freezing of the mixture. Working at low temperature accomplished three objectives. First, low temperatures prevented the decomposition of hydrogen peroxide in the highly exothermic reaction. Second, the vapor pressure of the aqueous solution was lowered, minimizing water contamination. Third, the highest yields of $O_2(a^1\Delta_g)$ occurred at low bath temperatures. Cl_2 is quantitatively consumed in reaction (2) while a mixture of $O_2(a^1\Delta_g)$ and $O_2(X^3\Sigma_g^-)$ is produced. The total O_2 flow rate then equals the Cl_2 flow rate within the accuracy of our measurements. At the exit of the bubbler, the gas mixture consisted of O_2 in the two electronic states, He, and H_2O. It was confirmed by chemical ionization mass spectrometry that no Cl_2 remained. A second trap, held at −70 °C, removed the H_2O so that only $O_2(a^1\Delta_g)$, $O_2(X^3\Sigma_g^-)$, and He remained in the flow. An emission cell monitored the weak $O_2(a^1\Delta_g \rightarrow X^3\Sigma_g^-)$ 0-0 transition at 1270 nm. The light passed through a narrow-band interference filter and was directed onto a cooled InGaAs detector through a fiber-optic cable. The relative emission rates were established on an absolute basis by previous calibration with an absolute $O_2(a^1\Delta_g)$ concentration such as described in Ref. 2. The outside of the inlet was gold-coated to prevent charge buildup from the unipolar swarm of ions in the SIFT.

Flow rates of $O_2(a^1\Delta_g)$ were determined as follows. The fractional abundance of $O_2(a^1\Delta_g)$ in the emission cell was simply the ratio of the $O_2(a^1\Delta_g)$ concentration determined from the emission measurement to the total gas concentration in the cell determined by measuring the total pressure. Multiplying the total gas flow rate by the fractional abundance then directly gave the $O_2(a^1\Delta_g)$ flow needed for the derivation of the bimolecular rate constants from the measured pseudo-first-order rate constants. The fraction of $O_2(a^1\Delta_g)$ in the overall O_2 flow was determined from this measurement and the measured ratio of the Cl_2 flow (assumed to correspond completely to O_2) to the total He flow. Typical $O_2(a^1\Delta_g)/O_2$ fractions in our experiments were 10%–25%.[1–5]

Normally, in this type of experiment, the Cl_2 flow would be varied and the decline in the primary ion signal would be measured in order to determine pseudo-first-order rate constants. However, this procedure could not be applied with the cluster ions. That method required about 10 min for each run and small changes in the primary ion signals due to drift prevented the decline from being determined accurately. Instead, primary and product ions were monitored by peak stepping on a computer based strip chart. The Cl_2 flow was turned on and off in approximately 1 min intervals. The primary ion on/off count rate was combined with the previously measured reaction time and concentration of $O_2(a^1\Delta_g)$ to obtain the reaction rate between two measurement points. We tested this technique by flowing an O_2/He mixture through the bubbler and found that within experimental error, the corresponding rate constants for the reaction $O_2^- + O_2(a^1\Delta_g)$ agreed with literature values.[4]

The observation of a m/z 61 ion indicated a further complication of the experiment. This ion is presumably HCO_3^-, which is formed rapidly by reaction (3) below:[18]

$$OH^-(H_2O)_n + CO_2 \rightarrow HCO_3^- + nH_2O. \tag{3}$$

The source of the CO_2 is unknown. Replenishing the KOH/H_2O_2 mixture did not change the observation of this product, nor did changing Cl_2 mixture containers. A correction of up to approximately 30% for the presence of CO_2 was made, based on the relative count rates in the experiments. The flow of CO_2 was on the order of 1% of the O_2 flow. We have not observed CO_2 in our previous experiments because those rate constants were much larger than the values reported here and, therefore, the small impurity was much less important. CO_2 would also not react with many of the ions in previous studies.[1–5] In our typical SIFT experiments, uncertainties of ±15% and ±25% were quoted for relative and absolute rates, respectively. Due to the problems with precise determination of $O_2(a)$ concentrations, low depletion of the

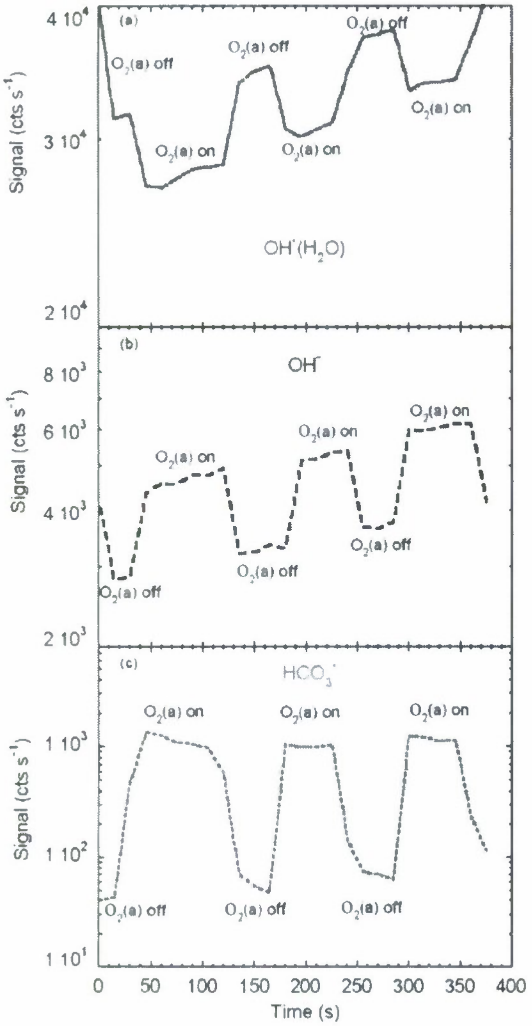

FIG. 1. Ion signals as a function of time for $OH^-(H_2O)$ reacting with $O_2(a^1\Delta_g)$ (reaction 1a) at 400 K. (a) $OH^-(H_2O)$, (b) OH^-, and (c) HCO_3^- due to CO_2 impurity.

reactant ions, and the observed CO_2 impurity background discussed above, we estimate ±30% and ±40% uncertainties of the presently measured rate constants.

III. RESULTS

Figures 1(a)–1(c) show typical $OH^-(H_2O)$, OH^-, and HCO_3^- on-off signals for an experiment, respectively, where $OH^-(H_2O)$ was the dominant primary ion in the flow tube. The presence of OH^- with no added $O_2(a^1\Delta_g)$ is due to breakup in the injection process. The experiment was performed at 400 K. When $O_2(a^1\Delta_g)$ was introduced, the $OH^-(H_2O)$ signal decreased by about 20%. The $O_2(a^1\Delta_g)$ flow was turned on and off three times during a period of about 400 s. Figure 1 shows that there was a long term drift of the ion signals. This drift and the small amount of $OH^-(H_2O)$ decay were the reasons for using the on/off method instead of measurements changing the reactant concentration. While $OH^-(H_2O)$ signals decreased upon switching $O_2(a^1\Delta_g)$ on, OH^- and HCO_3^- increased, indicating that dissociative excitation transfer occurs. This general behavior was observed at all experimental temperatures between 300 and 500 K.

TABLE I. Rate constants for $OH^-(H_2O)$ and $OH^-(H_2O)_2$ with $O_2(a^1\Delta_g)$ as a function of temperature.

Temperature (K)	Rate constant (cm^3 molecule^{-1} s^{-1})	Rate constant (cm^3 molecule^{-1} s^{-1})
	$OH^-(H_2O)$ (10^{-11})	$OH^-(H_2O)_2$ (10^{-11})
300	1.8	2.2
400	1.9	1.2
500	3.5	⋯

Measurements of the reaction between $O_2(a^1\Delta_g)$ and $OH^-(H_2O)_2$, i.e.,

$$OH^-(H_2O)_2 + O_2(a^1\Delta_g) \rightarrow OH^-(H_2O) + H_2O + O_2(X^3\Sigma_g^-), \tag{4}$$

could only be performed up to 400 K because the initial concentrations of $OH^-(H_2O)_2$ could not be produced in sufficient quantity at 500 K. For $OH^-(H_2O)_2$, appreciable amounts of $OH^-(H_2O)$ were present before reaction and the occurrence of reaction (1a) prevented observation of the $OH^-(H_2O)$ produced by reaction (4).

We have also examined the reaction of $O_2(a^1\Delta_g)$ with OH^-,

$$OH^- + O_2(a^1\Delta_g) \rightarrow O_2^- + OH. \tag{5}$$

The reaction is endothermic ($\Delta H = +38.7$ kJ mol^{-1}).[19] Apparent rate constants of $3(\pm 1) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} were obtained with a small negative temperature coefficient. However, in our experiment, vibrationally excited OH^- has been observed previously[20] such that reactions with $OH^-(v>0)$ may have influenced the observations. A single vibrational quantum is enough to make the reaction energetically possible. The fact that O_2^- was observed in these experiments, however, confirms the occurrence of reaction (5). Furthermore, the reaction of O_2^- with $O_2(a^1\Delta_g)$ efficiently produces electrons,[4] making the analysis even more complicated. For these reasons, we refrain from recommending a value for k_5. The experiments with hydrated OH^- cluster ions will, in all likelihood, not suffer from nonthermal populations. Many years of experience show that the He buffer equilibrates vibrations in triatomic (usually) and larger ions (always) much more rapidly than in diatomic ions. In hundreds of reactions studied, the curvature typical of excited states is not present for polyatomic systems.[16,18,20] The hydrated OH^- cluster ions, therefore, are assumed to enter the reaction zone in thermal energy distributions.

Table I summarizes our results for reactions (1a) and (4) and Fig. 2 illustrates their temperature dependence. Reaction (1a) appears to have a small positive temperature coefficient, while reaction (4) has a small negative temperature coefficient, both being in the range $k \propto T^{\pm 2}$. However, the uncertainty of our data prevents accurate determination of temperature dependences. On the other hand, we can conclude

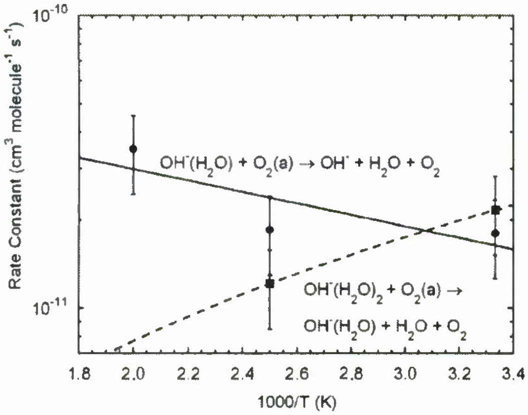

FIG. 2. Rate constants for the reactions of $OH^-(H_2O)$ and $OH^-(H_2O)_2$ with $O_2(a^1\Delta_g)$ as a function of inverse temperature. The lines are least-squares fits to the Arrhenius power law fits and are only intended to guide the eye.

with certainty that the rate constants have absolute values of the order of 2%–5% of the Langevin rate coefficients. We further discuss these observations in Sec. IV.

IV. DISCUSSION

At this stage, it is not possible to provide a unique analysis of the measured rate constants. First, the energetics of reactions (1a) and (4) are still relatively uncertain. Second, only little can be said about the potential energy surfaces of the spin-forbidden processes without doing extensive quantum-chemical calculations. Therefore, only qualitative considerations are addressed in the following discussion.

The enthalpy ΔH^o_{298} of reaction (1a) is between +10.3 and +18.7 kJ mol^{-1}.[10,11,19,21–23] Thus, this process is endothermic, while reaction (4) with ΔH^o_{298} between -19.0 and -20.7 kJ mol^{-1} is exothermic. This difference in the energetics does not appear to strongly influence the absolute values of k_{1a} and k_4 as derived from our experiments. One may be tempted to see a slightly positive temperature coefficient in Fig. 2 for the endothermic process (1a), in contrast to a slightly negative temperature coefficient for the exothermic process (4). However, this observation is barely outside the uncertainty limits of our measurements. On the other hand, the Boltzmann factor $\exp(-\Delta H/RT)$ for reaction (1a) at 400 K is between 0.004 and 0.05, i.e., it is not orders of magnitude smaller than unity, such that its contribution to k_1 does not dominate over the other factors included in the rate constant.

In the following discussion, we provide estimates of rate parameters for the reaction. An upper limit may be estimated by ion-quadrupole (and ion-induced dipole) capture theory,[12,24] which provides ratios of capture rate constants, k_{cap}, and Langevin rate constants, k_L. The latter is given by $k_L = 8.76 \times 10^{-10}$, 7.13×10^{-10}, and 6.53×10^{-10} cm^3 molecule^{-1} s^{-1} for $O_2(a^1\Delta_g) + OH^-(H_2O)_{0-2}$, respectively, with a calculated polarizability[24] for $O_2(a^1\Delta_g)$ of $\alpha = 1.56 \times 10^{-24}$ cm^3; this value is nearly equal to that for $O_2(X^3\Sigma_g^-)$ of $\alpha = 1.58 \times 10^{-24}$ cm^3. For symmetry reasons, one may assume that the quadrupole moment of $O_2(a^1\Delta_g)$ is not too different from that of $O_2(X^3\Sigma_g^-)$, i.e., it should be of the order of -0.4×10^{-26} esu cm^2. For this value, ion-quadrupole capture theory[13,24] gives an increase in the capture rate constant by only a few percent over the ion-induced dipole capture value of k_L. Capture rate constants for reactions (1a) and (4) thus are close to k_L, i.e., about a factor of 30–40 larger than our measured rate constants.

In the following, we qualitatively discuss the possible reasons why reactions (1a) and (4) could have similar and roughly temperature independent rate coefficients k which are markedly below the capture rate constants k_{cap} in spite of having quite different reaction enthalpies. We employ the formulation of statistical rate theory for complex-forming bimolecular reactions such as elaborated in Ref. 25. Considering a process $A+B \Leftrightarrow AB^* \rightarrow C+D$, we denote the entrance bottleneck for formation of AB^* by the subscript a and the exit bottleneck from AB^* leading to the products $C+D$ by the subscript b. Both bottlenecks may be classified as either "loose" or "rigid" transition states. That is, an exit transition state b may be formed by a "central barrier." For this reaction scheme, the second-order rate constant can be expressed by[25]

$$k = \frac{k_B T}{h} \left(\frac{Q_{AB}}{Q_A Q_B} \right)_{\text{el,trans}} \left(\frac{1}{Q_A Q_B} \right)_{\text{vibrot}} Q^*_{AB} \tag{6}$$

with

$$Q^*_{AB} = \sum_{J=0}^{\infty} (2J+1) \int_0^{\infty} \frac{dE}{k_B T} \exp\left(-\frac{E}{k_B T} \right) W_a(E,J) \times \left[\frac{W_b(E,J)}{W_a(E,J) + W_b(E,J)} \right]. \tag{7}$$

The Q_i denote the relevant partition functions of A, B, and AB^*, while the $W_i(E,J)$ are effective numbers of states (or cumulative reaction probabilities) at the entrance and exit of the complex AB^*, respectively, as a function of the energy E and total angular momentum J. The term within the bracket at the right hand side of Eq. (7) corresponds to the probability that the complex AB^* proceeds to the products $C+D$ rather than backdissociates to $A+B$. In the case of spin-allowed passage through the bottlenecks a and b, the $W_i(E,J)$ are obtained by state counting. If a or b correspond to spin-forbidden processes, the $W_i(E,J)$ are given by sums over channel-specific transmission coefficients.

As we do not have knowledge about the reaction path potential at this stage, only qualitative considerations about the properties of k can be made. When the reaction rate constant approaches the capture rate constant, then $W_b(E,J) \gg W_a(E,J)$; under these conditions, the bracket in Eq. (7) assumes the value of unity and Eq. (7) approaches

$$Q^*_{AB,\text{cap}} = \sum_{J=0}^{\infty} (2J+1) \int_0^{\infty} \frac{dE}{k_B T} \exp\left(-\frac{E}{k_B T} \right) W_a(E,J). \tag{8}$$

If k is found to be considerably smaller than k_{cap}, such as is the case here, the term within the bracket in Eq. (7) must be smaller than unity and $W_b(E,J) \ll W_a(E,J)$. Then,

$$Q^*_{AB} = \sum_{J=0}^{\infty} (2J+1) \int_0^{\infty} \frac{dE}{k_B T} \exp\left(-\frac{E}{k_B T}\right) W_b(E,J) \tag{9}$$

and

$$k/k_{\text{cap}} \approx \frac{\sum_{J=0}^{\infty} (2J+1) \int_0^{\infty} \frac{dE}{k_B T} \exp\left(-\frac{E}{k_B T}\right) W_b(E,J)}{\sum_{J=0}^{\infty} (2J+1) \int_0^{\infty} \frac{dE}{k_B T} \exp\left(-\frac{E}{k_B T}\right) W_a(E,J)}. \tag{10}$$

For an endothermic process with a threshold energy E_0, $W_b(E,J)$ is different from zero only at $E > E_0$ such that k includes a factor $\exp(-E_0/k_B T)$. At 300 K, for reaction (1a) this would amount to 1/60, if $\Delta H^o_{298} = +10.3$ kJ mol^{-1}, and 1/1800, if $\Delta H^o_{298} = +18.7$ kJ mol^{-1}. The two possibilities denote the uncertainty limits of ΔH^o_{298} (for simplicity $\Delta H^o_{298} \approx E_0$ is taken). Therefore, even if the weighted average over the bracket in Eq. (7) is not much smaller than unity, the experimental value of $k/k_{\text{cap}} \approx 1/30$ to 1/40 could only be accommodated by the lower limit of the endothermicity of reaction (1a), see above.

The finer details of the temperature dependences of k are determined by the details of the ratio $W_b(E,J)/W_a(E,J)$. It is known that in the case of rigid central barriers and exothermic reactions, k may decrease from a value near unity at very low temperatures to a minimum and then increase again with increasing temperature. (See, for example, the results for the reaction $CH_4 + O_2^+$ as discussed in Refs. 25 and 26.) One might imagine such a behavior for the exothermic reaction (4), if the apparent absence of a temperature dependence is attributed to the transition from a negative to a positive temperature coefficient of k near its minimum value. The central barrier then may possibly, but not necessarily, be formed by the singlet-triplet transition range of the potential. The similarity of the observed ratios k/k_{cap} of 1/30 to 1/40 in reactions (1a) and (4), in spite of their different energetics, nevertheless remains surprising and suggests that the two reactions have considerably different characters of their exit bottlenecks b. Beyond these qualitative arguments, not much can be speculated without knowledge of the respective reaction path potentials.

In the present experiments the disappearance of $OH^-(H_2O)$ and the formation of OH^- were studied. Therefore, the question arises whether OH^- can always be considered as a prompt product, or whether $OH^-(H_2O)^*$ from excitation transfer can also be collisionally stabilized without formation of OH^-. This possibility was outlined by mechanisms (1b)–(1d) given above. In order to answer this question, the energy content of $OH^-(H_2O)^*$ formed in Eq. (1b) must be determined and the dissociative lifetimes of $OH^-(H_2O)^*$ must be estimated. We do the latter by employing simplistic rigid RRKM (Rice-Ramsperger-Kassel-Marcus) theory. Using the harmonic frequencies of $OH^-(H_2O)$ from Ref. 27 (207, 328, 453, 570, 1321, 1608, 1729, 3814, and 3864 cm^{-1}), an $OH^-{-}H_2O$ bond energy of 100 kJ mol^{-1}, the frequency 570 cm^{-1} as the reaction coordinate, and identifying the activated complex with ground state frequencies, we obtain a threshold rate constant $k(E = E_0) \approx 5 \times 10^8$ s^{-1} and an increase in the specific rate constant for dissociation $k(E)$ by a factor of 10 over an energy range of about 9 kJ mol^{-1}. Although one expects marked anharmonicity of the vibrations in $OH^-(H_2O)$ [and even more so in $OH^-(H_2O)_2$], this $k(E)$ should be a lower limit, as rigid RRKM theory is likely to underestimate $k(E)$ for the present system. Therefore, any $OH^-(H_2O)^*$ produced by reaction (1b) with an energy larger than the bond energy (~ 100 kJ mol^{-1}) should dissociate promptly under our conditions via reaction (1c) without the opportunity for collisional stabilization via reaction (1d). $OH^-(H_2O)$ at 300 K contributes an average vibrational energy of 3.7 kJ mol^{-1} into reaction (1b). If this energy together with the electronic excitation energy (94.29 kJ mol^{-1}) of $O_2(a^1\Delta_g)$ was statistically distributed over the products of reaction (1b), there would be sufficient energy for dissociation, and a majority of $OH^-(H_2O)^*$ would dissociate promptly. One comes to the same conclusion by considering the absolute values of k_{1a} discussed above. These values are so large relative to the capture rate constants that the major part of the reaction must result in disappearance of $OH^-(H_2O)$ and appearance of OH^-, without much collisional deactivation of $OH^-(H_2O)^*$ from reaction (1b). We, therefore, conclude that the electronic excitation energy of $O_2(a^1\Delta_g)$ in reaction (1a) must predominantly be available for dissociation of $OH^-(H_2O)$.

ACKNOWLEDGMENTS

We would like to acknowledge Bill McDermott, Terry Rawlins, and Steve Davis who provided numerous helpful suggestions on how to work with $O_2(a^1\Delta_g)$. This work was supported by the United States Air Force Office of Scientific Research (AFOSR) under Project No. 2303EP4 and Grant Award No. FA8655-09-3001. A.J.M. was supported by the Boston College under Contract No. FA8718-04-C-0006. N.E. and V.M.B. were supported by the National Science Foundation under Grant No. CHE-0647088.

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