

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

Albert A. Viggiano,<sup>1</sup> Anthony Midey,<sup>1,a)</sup> Nicole Eyet,<sup>2,b)</sup> Veronica M. Bierbaum,<sup>2</sup> and Jürgen Troe<sup>3,c)</sup>

<sup>1</sup>*Air Force Research Laboratory, Space Vehicles Directorate, 29 Randolph Rd., Hanscom Air Force Base, Massachusetts 01731-3010, USA*

<sup>2</sup>*Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309, USA*

<sup>3</sup>*Institut für Physikalische Chemie, Universität Göttingen, Tammannstrasse 6, D-37077 Göttingen, Germany and Max-Planck-Institut für Biophysikalische Chemie, D-37077 Göttingen, Germany*

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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  $1.8 \times 10^{-11}$  and  $2.2 \times 10^{-11}$   $cm^3$  molecule<sup>-1</sup> s<sup>-1</sup>, 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.

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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).<sup>1-5</sup> In these experiments,  $O_2(a^1\Delta_g)$  and  $O_2(X^3\Sigma_g^-)$  were produced in a chemical reaction<sup>6,7</sup> and the concentration of  $O_2(a^1\Delta_g)$  was monitored by light emission, which was calibrated against an absolute standard.<sup>8</sup> 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  $HO_2^-$ .<sup>3</sup> The electronic excitation of  $O_2$ , in general, was found to efficiently drive charge transfer.<sup>3</sup> A particularly interesting example was the reaction with  $O^-$ , where the endothermic charge transfer channel was not detected in previous flowing afterglow studies,<sup>7,9</sup> but was observed in SIFT experiments and found to increase with temperature.<sup>4</sup>

The present study examines whether the electronic exci-

tation energy of  $O_2(a^1\Delta_g)$  can be used to dissociate ionic clusters. Cluster bond strengths<sup>10</sup> are often in the range of the electronic excitation energy of  $O_2(a^1\Delta_g)$  (94.29 kJ mol<sup>-1</sup> 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<sup>11</sup> 113 and 75 kJ mol<sup>-1</sup>, 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),



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.<sup>12</sup> We discuss the possibility of whether the reaction then proceeds sequentially,



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,<sup>13</sup> 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  $OH^-(H_2O)^*$ .

<sup>a)</sup>Under contract to the Institute for Scientific Research, Boston College, Chestnut Hill, MA 02467.

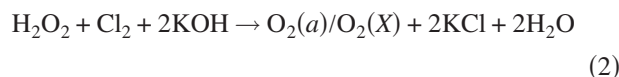
<sup>b)</sup>Present address: Department of Chemistry, Saint Anselm College, Manchester, NH 03102.

<sup>c)</sup>Author to whom correspondence should be addressed. Electronic mail: shoff@gwdg.de.

## II. EXPERIMENTAL TECHNIQUE

Our measurements were made in a SIFT, which has been described in detail previously.<sup>4,16</sup>  $\text{OH}^-(\text{H}_2\text{O})_{1,2}$  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  $\text{O}_2(a^1\Delta_g)$  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  $\text{OH}^-(\text{H}_2\text{O})_n$  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  $\text{OH}^-$  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  $\text{O}_2(a^1\Delta_g)$  concentrations has been described before in detail.<sup>2,4</sup> Briefly, a  $\text{Cl}_2/\text{He}$  mixture was bubbled through a mixture of 4.04M KOH and  $\text{H}_2\text{O}_2$  (35% w/w) in water, held at 253 K by a recirculating chiller. The reaction



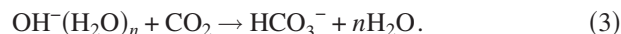
is a well known source of  $\text{O}_2(a^1\Delta_g)$ ,<sup>6,7</sup> e.g., it has been used to create chemical  $\text{O}_2/\text{I}_2$  lasers.<sup>17</sup> Before use, the mixture was degassed by pumping. A second continuous flow of helium was used to prevent freezing of the mixture. Working at low 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  $\text{O}_2(a^1\Delta_g)$  occurred at low bath temperatures.  $\text{Cl}_2$  is quantitatively consumed in reaction (2) while a mixture of  $\text{O}_2(a^1\Delta_g)$  and  $\text{O}_2(X^3\Sigma_g^-)$  is produced. The total  $\text{O}_2$  flow rate then equals the  $\text{Cl}_2$  flow rate within the accuracy of our measurements. At the exit of the bubbler, the gas mixture consisted of  $\text{O}_2$  in the two electronic states, He, and  $\text{H}_2\text{O}$ . It was confirmed by chemical ionization mass spectrometry that no  $\text{Cl}_2$  remained. A second trap, held at  $-70^\circ\text{C}$ , removed the  $\text{H}_2\text{O}$  so that only  $\text{O}_2(a^1\Delta_g)$ ,  $\text{O}_2(X^3\Sigma_g^-)$ , and He remained in the flow. An emission cell monitored the weak  $\text{O}_2(a^1\Delta_g \rightarrow X^3\Sigma_g^-)$  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  $\text{O}_2(a^1\Delta_g)$  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  $\text{O}_2(a^1\Delta_g)$  were determined as follows. The fractional abundance of  $\text{O}_2(a^1\Delta_g)$  in the emission cell was simply the ratio of the  $\text{O}_2(a^1\Delta_g)$  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  $\text{O}_2(a^1\Delta_g)$  flow needed for the derivation of the bimolecular rate constants from the measured pseudo-first-order rate constants. The fraction of  $\text{O}_2(a^1\Delta_g)$  in the overall  $\text{O}_2$  flow was determined from this measurement and the measured ratio of the  $\text{Cl}_2$  flow (assumed to correspond completely to  $\text{O}_2$ ) to the total He flow. Typical  $\text{O}_2(a^1\Delta_g)/\text{O}_2$  fractions in our experiments were 10%–25%.<sup>1–5</sup>

Normally, in this type of experiment, the  $\text{Cl}_2$  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  $\text{Cl}_2$  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  $\text{O}_2(a^1\Delta_g)$  to obtain the reaction rate between two measurement points. We tested this technique by flowing an  $\text{O}_2/\text{He}$  mixture through the bubbler and found that within experimental error, the corresponding rate constants for the reaction  $\text{O}_2^- + \text{O}_2(a^1\Delta_g)$  agreed with literature values.<sup>4</sup>

The observation of a  $m/z$  61 ion indicated a further complication of the experiment. This ion is presumably  $\text{HCO}_3^-$ , which is formed rapidly by reaction (3) below:<sup>18</sup>



The source of the  $\text{CO}_2$  is unknown. Replenishing the KOH/ $\text{H}_2\text{O}_2$  mixture did not change the observation of this product, nor did changing  $\text{Cl}_2$  mixture containers. A correction of up to approximately 30% for the presence of  $\text{CO}_2$  was made, based on the relative count rates in the experiments. The flow of  $\text{CO}_2$  was on the order of 1% of the  $\text{O}_2$  flow. We have not observed  $\text{CO}_2$  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.  $\text{CO}_2$  would also not react with many of the ions in previous studies.<sup>1–5</sup> In our typical SIFT experiments, uncertainties of  $\pm 15\%$  and  $\pm 25\%$  were quoted for relative and absolute rates, respectively. Due to the problems with precise determination of  $\text{O}_2(a)$  concentrations, low depletion of the

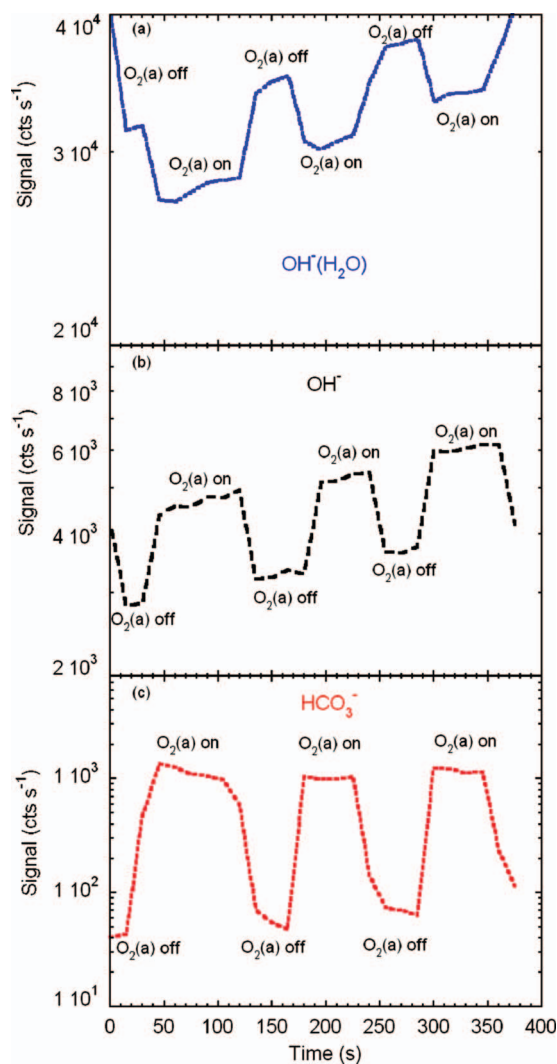


FIG. 1. Ion signals as a function of time for  $\text{OH}^-(\text{H}_2\text{O})$  reacting with  $\text{O}_2(a^1\Delta_g)$  (reaction 1a) at 400 K. (a)  $\text{OH}^-(\text{H}_2\text{O})$ , (b)  $\text{OH}^-$ , and (c)  $\text{HCO}_3^-$  due to  $\text{CO}_2$  impurity.

reactant ions, and the observed  $\text{CO}_2$  impurity background discussed above, we estimate  $\pm 30\%$  and  $\pm 40\%$  uncertainties of the presently measured rate constants.

### III. RESULTS

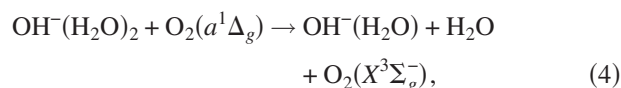
Figures 1(a)–1(c) show typical  $\text{OH}^-(\text{H}_2\text{O})$ ,  $\text{OH}^-$ , and  $\text{HCO}_3^-$  on-off signals for an experiment, respectively, where  $\text{OH}^-(\text{H}_2\text{O})$  was the dominant primary ion in the flow tube. The presence of  $\text{OH}^-$  with no added  $\text{O}_2(a^1\Delta_g)$  is due to breakup in the injection process. The experiment was performed at 400 K. When  $\text{O}_2(a^1\Delta_g)$  was introduced, the  $\text{OH}^-(\text{H}_2\text{O})$  signal decreased by about 20%. The  $\text{O}_2(a^1\Delta_g)$  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  $\text{OH}^-(\text{H}_2\text{O})$  decay were the reasons for using the on/off method instead of measurements changing the reactant concentration. While  $\text{OH}^-(\text{H}_2\text{O})$  signals decreased upon switching  $\text{O}_2(a^1\Delta_g)$  on,  $\text{OH}^-$  and  $\text{HCO}_3^-$  increased, indicating that

TABLE I. Rate constants for  $\text{OH}^-(\text{H}_2\text{O})$  and  $\text{OH}^-(\text{H}_2\text{O})_2$  with  $\text{O}_2(a^1\Delta_g)$  as a function of temperature.

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

dissociative excitation transfer occurs. This general behavior was observed at all experimental temperatures between 300 and 500 K.

Measurements of the reaction between  $\text{O}_2(a^1\Delta_g)$  and  $\text{OH}^-(\text{H}_2\text{O})_2$ , i.e.,



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

We have also examined the reaction of  $\text{O}_2(a^1\Delta_g)$  with  $\text{OH}^-$ ,



The reaction is endothermic ( $\Delta H = +38.7 \text{ kJ mol}^{-1}$ ).<sup>19</sup> Apparent rate constants of  $3(\pm 1) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  were obtained with a small negative temperature coefficient. However, in our experiment, vibrationally excited  $\text{OH}^-$  has been observed previously<sup>20</sup> such that reactions with  $\text{OH}^-(v > 0)$  may have influenced the observations. A single vibrational quantum is enough to make the reaction energetically possible. The fact that  $\text{O}_2^-$  was observed in these experiments, however, confirms the occurrence of reaction (5). Furthermore, the reaction of  $\text{O}_2^-$  with  $\text{O}_2(a^1\Delta_g)$  efficiently produces electrons,<sup>4</sup> making the analysis even more complicated. For these reasons, we refrain from recommending a value for  $k_5$ . The experiments with hydrated  $\text{OH}^-$  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.<sup>16,18,20</sup> The hydrated  $\text{OH}^-$  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

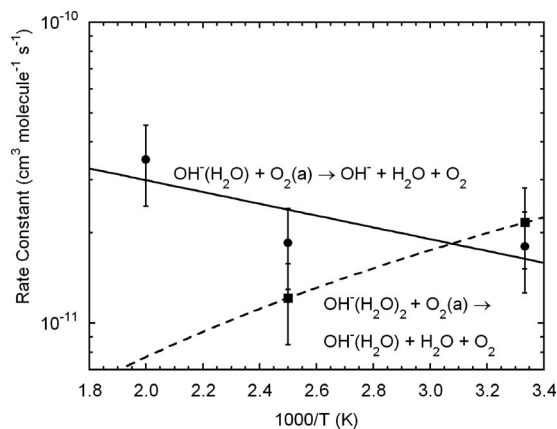


FIG. 2. Rate constants for the reactions of  $\text{OH}^-(\text{H}_2\text{O})$  and  $\text{OH}^-(\text{H}_2\text{O})_2$  with  $\text{O}_2(a^1\Delta_g)$  as a function of inverse temperature. The lines are least-squares fits to the Arrhenius power law fits and are only intended to guide the eye.

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  $\Delta H_{298}^o$  of reaction (1a) is between +10.3 and +18.7  $\text{kJ mol}^{-1}$ .<sup>10,11,19,21–23</sup> Thus, this process is endothermic, while reaction (4) with  $\Delta H_{298}^o$  between –19.0 and –20.7  $\text{kJ mol}^{-1}$  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,<sup>12,24</sup> which provides ratios of capture rate constants,  $k_{\text{cap}}$ , and Langevin rate constants,  $k_L$ . The latter is given by  $k_L = 8.76 \times 10^{-10}$ ,  $7.13 \times 10^{-10}$ , and  $6.53 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for  $\text{O}_2(a^1\Delta_g) + \text{OH}^-(\text{H}_2\text{O})_{0-2}$ , respectively, with a calculated polarizability<sup>24</sup> for  $\text{O}_2(a^1\Delta_g)$  of  $\alpha = 1.56 \times 10^{-24} \text{ cm}^3$ ; this value is nearly equal to that for  $\text{O}_2(X^3\Sigma_g^-)$  of  $\alpha = 1.58 \times 10^{-24} \text{ cm}^3$ . For symmetry reasons, one may assume that the quadrupole moment of  $\text{O}_2(a^1\Delta_g)$  is not too different from that of  $\text{O}_2(X^3\Sigma_g^-)$ , i.e., it should be of the order of  $-0.4 \times 10^{-26} \text{ esu cm}^2$ . For this value, ion-

quadrupole capture theory<sup>13,24</sup> 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  $k_{\text{cap}}$  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  $A+B \rightleftharpoons AB^* \rightarrow C+D$ , 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<sup>25</sup>

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

with

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

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

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

If  $k$  is found to be considerably smaller than  $k_{\text{cap}}$ , 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,

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

and

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

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  $\Delta H_{298}^{\circ} = +10.3$  kJ mol<sup>-1</sup>, and 1/1800, if  $\Delta H_{298}^{\circ} = +18.7$  kJ mol<sup>-1</sup>. The two possibilities denote the uncertainty limits of  $\Delta H_{298}^{\circ}$  (for simplicity  $\Delta H_{298}^{\circ} \approx E_0$  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<sub>4</sub>+O<sub>2</sub><sup>+</sup> 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  $k/k_{\text{cap}}$  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<sup>-</sup>(H<sub>2</sub>O) and the formation of OH<sup>-</sup> were studied. Therefore, the question arises whether OH<sup>-</sup> can always be considered as a prompt product, or whether OH<sup>-</sup>(H<sub>2</sub>O)\* from excitation transfer can also be collisionally stabilized without formation of OH<sup>-</sup>. This possibility was outlined by mechanisms (1b)–(1d) given above. In order to answer this question, the energy content of OH<sup>-</sup>(H<sub>2</sub>O)\* formed in Eq. (1b) must be determined and the dissociative lifetimes of OH<sup>-</sup>(H<sub>2</sub>O)\* must be estimated. We do the latter by employing simplistic rigid RRKM (Rice-Ramsperger-Kassel-Marcus) theory. Using the harmonic frequencies of OH<sup>-</sup>(H<sub>2</sub>O) from Ref. 27 (207, 328, 453, 570, 1321, 1608, 1729, 3814, and 3864 cm<sup>-1</sup>), an OH<sup>-</sup>-H<sub>2</sub>O bond energy of 100 kJ mol<sup>-1</sup>, the frequency 570 cm<sup>-1</sup> 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<sup>-1</sup> 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<sup>-1</sup>. Although one expects marked anharmonicity of the vibrations in OH<sup>-</sup>(H<sub>2</sub>O) [and even more so in OH<sup>-</sup>(H<sub>2</sub>O)<sub>2</sub>], 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<sup>-</sup>(H<sub>2</sub>O)\* produced by reaction (1b) with an energy larger than the bond energy ( $\sim 100$  kJ mol<sup>-1</sup>) should dissociate promptly under our conditions via reaction (1c) without the opportunity for collisional stabilization via reaction (1d). OH<sup>-</sup>(H<sub>2</sub>O) at 300 K contributes an average vibrational energy of 3.7 kJ mol<sup>-1</sup> into reaction (1b). If this energy together with the electronic excitation energy (94.29 kJ mol<sup>-1</sup>) of O<sub>2</sub>(a<sup>1</sup>Δ<sub>g</sub>) was statistically distributed over the products of reaction (1b), there would be sufficient energy for dissociation, and a majority of OH<sup>-</sup>(H<sub>2</sub>O)\* 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<sup>-</sup>(H<sub>2</sub>O) and appearance of OH<sup>-</sup>, without much collisional deactivation of OH<sup>-</sup>(H<sub>2</sub>O)\* from reaction (1b). We, therefore, conclude that the electronic excitation energy of O<sub>2</sub>(a<sup>1</sup>Δ<sub>g</sub>) in reaction (1a) must predominantly be available for dissociation of OH<sup>-</sup>(H<sub>2</sub>O).

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