Rate Constants of the Reaction of the Hydrated Electron and Hydroxyl Radical with Ozone in Aqueous Solution

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Absolute rate constants for the reaction of the hydrated electron and hydroxyl radical with ozone in aqueous solution have been determined by using pulse radiolysis techniques. The rate constant, $k(e_{aq}^- + O_3) = (3.60 \pm 0.14) \times 10^{10}$ dm^3 mol^{-1} s^{-1}, was measured in the pH range 4.1–6.05 by following the decay of e_{aq}^- at 600 nm. The rate constant $k(OH\cdot + O_3) = (3.02 \pm 0.25) \times 10^9$ dm^3 mol^{-1} s^{-1}, was obtained by a competition method at pH 6.7 with acetate ions as the OH· radical scavengers. The ozone concentration for both studies varied from 0.05×10^{-3} to 0.50×10^{-3} mol dm^{-3}.

Introduction

The interaction of ozone with photochemically produced free radicals has been studied extensively in the gas phase[1] because of the importance of ozone in atmospheric chemistry and the potential environmental hazards of its depletion in the stratosphere. On the other hand, the free-radical reactions of aqueous ozone have not been studied even though ozone has been postulated by a number of authors[2-8] as an unstable reaction product during the radiolysis of alkaline oxygenated solutions. The OH· radical also forms during the alkali-catalyzed decomposition of O_3 solutions,[9] and it is one of the propagation radicals in the resulting chain decomposition of O_3.[10] The assumed reactions of the hydrated electron and the OH· radical with O_3 are

$$e_{aq}^- + O_3 \rightarrow O_3^-\cdot \quad (1)$$

$$OH\cdot + O_3 \rightarrow HO_2\cdot + O_2 \quad (2)$$

The ozonide ion, a possible product of reaction 1, is a prominent species observed in irradiated alkaline O_2 solutions. However, under these conditions $O_3^-\cdot$ forms by reaction of $O^-\cdot$ with O_2, producing the well-known strong band centered at 430 nm.[11] Electron transfer from a number of negative ions is proposed as a mechanism to account for ozone formation in electron-irradiated solutions.[3-5,7,12] But even the formation of O_3 and its participation in this mechanism are open to question.[13] The goal of our studies is to provide rate constants of reactions 1 and 2 so that the thermal, photolytic, and radiolytic behavior of O_3 in aqueous solution may be better understood.

Experimental Section

Materials and Techniques. Ozone. The preparation and storage of O_3 at −78 °C on silica gel has been described.[14] For the measurements of the reaction with e_{aq}^-, ozone solutions, as free as possible from CO_2 and O_2, were desired to avoid possible competition reactions since e_{aq}^- reacts rapidly with these molecules. For these experiments the O_2 was pumped off the silica gel at low pressure and the O_2 and O_3 were further eluted from the gel by He and condensed in a liquid-N_2 trap. After collection of about 1 g of O_3, the trap was gradually warmed and the O_3 vaporized while a slow stream of He was flowing at atmospheric pressure. This gaseous mixture was then passed into a 100-mL syringe containing 20 mL of cooled 0.01 mol dm^{-3} acetic acid. After 20–40 cm^3 of the O_3 gas was added to the syringe, the O_3 flow was stopped and the O_3 solution was shaken until absorption of the gas was complete. The undissolved gas was ejected and the solution was immediately diluted 25-fold in syringes and stored in ice water. This procedure produced solutions essentially free of CO_2 and O_2 initially and about 0.0004 mol dm^{-3} in O_3 and acetic acid. Acetic acid is an excellent inhibitor of O_3 decomposition in aqueous solutions.[9]

For the OH· radical measurements, O_3 was eluted from the silica gel by CO_2 and passed directly into the 100-mL syringe at a stage in the elution when the O_3 was being rapidly desorbed.[14] This procedure minimizes contamination by CO_2.

Reagents. Acetic acid and sodium acetate were of AnalaR grade and used without further purification. Carbonate-free sodium hydroxide was prepared by the dropwise addition of degassed water into a 100-mL syringe containing 2–4 g of metallic sodium. The air in the syringe was displaced by helium that flowed continuously into the syringe during the water addition. After dissolution of the sodium, more water was added to produce a 2.0 mol dm^{-3} NaOH solution.

Solutions. All solutions were prepared by using O_2-free, Millipore-filtered water the quality of which corresponds to triply quartz-distilled water. The stock O_3 solutions were stored in 50–100-mL syringes, diluted, mixed with buffer, and transferred into the quartz irradiation cells by means of the "syringe technique".[15,16] The optical path

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[*] Award of the Alexander von Humboldt-Stiftung, 1979–1980. Address correspondence to this author at the following address: 2115 Hart Road, Port Angeles, WA 98362.

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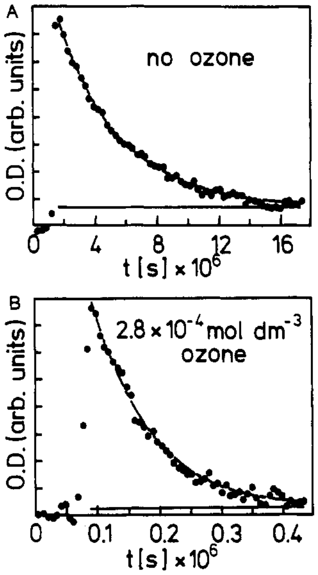

Figure 1. Decay of the optical signal at 600 nm observed on pulse irradiation of solutions containing (A) no ozone (upper trace) and (B) 2.8 × 10^{-4} mol dm^{-3} ozone (lower trace) in the same matrix. The solid line represents the computer fit of the first-order decay kinetics and the appropriate base line (1-cm cell, 5-ns pulse, 500 rd).

length of the cell was 1 cm. Oxygen had previously been removed from this cell by purging with argon and by filling and emptying the cell twice with the test solution. The O_3 concentration was calculated from the absorbance of the solution at 260 nm where ϵ_{260} = 3300 mol^{-1} dm^3 cm^{-1}.[14] A second measurement was made on the solution remaining in the syringe at the completion of the irradiation.

Pulse Radiolysis. A 4-MeV Van de Graaf accelerator with pulse lengths between 5 and 50 ns and doses varying from 300 to 1000 rd per pulse was used throughout this work. The optical detection system has already been described.[17] Each experiment was repeated at least 3 times with fresh solution, and the results were averaged. In the case of the unstable O_3-acetate solutions where the irradiations were completed in less than 5 min, the experiments were repeated until satisfactory agreement was found between the half-lives of the three samples measured. Pure matrix solutions, i.e., degassed, O_2-free containing low concentrations of acetic acid or acetate in the experiments with e_{aq}^- or OH· radical, respectively, were used as reference solutions and for dosimetric purposes. The data were recorded on a transient digitizer and displayed as absorption vs. time curves on a Tektronix 4010 screen. The evaluation of yields and rate constants was performed by using a PDP 11/40 computer. The program structure has been described.[18]

Results and Discussion

Reaction of e_{aq}^- with O_3. The rate constant of this reaction was determined from the first-order decay constant of e_{aq}^- absorbance for acetate-buffered solutions. Figure 1 shows typical decay curves of the optical absorption at 600 nm after a 5-ns (500-rd) electron pulse. Curve 1A is observed in the absence of ozone, and curve 1B in the presence of 2.8 × 10^{-4} mol dm^{-3} ozone (in both cases the solid line represents the best first-order fit). For these experiments the O_3 concentrations were varied in the range 68.5 × 10^{-6}–525 × 10^{-6} mol dm^{-3} (see Table I). In Table I the first three O_3 solutions were prepared from a 0.0114 mol dm^{-3} stock solution; the last five O_3 solutions were prepared from a 0.0143 mol dm^{-3} solution. We consider that our rate constant calculated from these five solutions provides our best value. From these data we obtain a rate constant of (3.60 ± 0.14) × 10^{10} dm^3 mol^{-1} s^{-1} for reaction 1.

TABLE I: Rate Constant for Reaction of the Hydrated Electron with Ozone in Aqueous Solution

10^6 × [ozone], mol dm^{-3}	10^6 × [oxygen],[a] mol dm^{-3}	pH	10^9 × $t_{1/2}$, s	$10^{-10}k(e_{aq}^- + O_3)$, dm^3 mol^{-1} s^{-1}
00.0		5.30	5000	
68.5	21.3	5.30	211.0	4.19
197.6	53.1	5.63	92.7	3.27
282.7	71.9	4.84	56.9	3.82
111.5	8.1	5.37	157.8	3.80
278.2	7.0	5.80	67.8	3.48
230.6	88.9	5.76	82.8	3.57
503.0	125.5	4.1	33.0	3.70
525.2	69.4	6.05	35.1	3.44

[a] Estimated O_2 concentration (see text).

The values in Table I have been corrected for pH and for O_2 content. Oxygen impurity arises from two sources: (1) O_2 present during the O_3 saturation process and (2) O_2 originating from the decay of O_3. Column 2 of Table I provides our estimate of the amount present at the time of the irradiation. These calculations were made as follows. The original O_2 content was derived from the partial pressure of O_3 and O_2 present at the time of saturation. The solubility of O_3 at 0 °C was taken as 0.022 mol dm^{-3} (atm of O_3)$^{-1}$.[19] The O_2 content of decayed solutions was calculated from O_3 in the solution by assuming the following stoichiometry: $2O_3 \rightarrow 3O_2$.

Interesting is the fact that $k(e_{aq}^- + O_3)$ is about twice $k(e_{aq}^- + O_2)$ which has a diffusion-controlled rate constant[20] of 1.9 × 10^{10} dm^3 mol^{-1} s^{-1}. Our rate constant is also higher than one calculated from the Smoluchowski equation[21,22] when reasonable values for $D(O_3)$ and $r(O_3)$ are assumed. Since experimental values for these quantities are unavailable, we calculate $r(O_3)$ by using our $k(e_{aq}^- + O_3)$ = 3.6 × 10^{10} dm^3 mol^{-1} s^{-1}. The sum of the radii, $r = r(e_{aq}^-) + r(O_3)$, may be calculated from the Smoluchowski equation in the form

$$r = 1000k(e_{aq}^- + O_3)/(4\pi DN) \qquad \text{(I)}$$

where $D = D(e_{aq}^-) + D(O_3)$, $D(e_{aq}^-)$ = diffusion constant of e_{aq}^-, $D(O_3)$ = diffusion constant of O_3, and N = Avogadro's number.

Using $D = 7.0 \times 10^{-5}$ cm^2 s^{-1} for the sum $D(e_{aq}^-) + D(O_3)$ (ref 21) and $k = 3.6 \times 10^{10}$ dm^3 mol^{-1} s^{-1}, we derive a value of $r = 6.8 \times 10^{-8}$ cm from eq I. Since $r(e_{aq}^-)$ is 2.5 × 10^{-8} cm, this gives an exceptionally high $r(O_3)$ of 4.3 × 10^{-8} cm, an indication that electron tunneling may be a feature of this reaction.[22] Abnormally high reaction rates have been observed for a number of e_{aq}^- reactions with neutral molecules[23] that form stable or transitory negative ions; examples are NO, CS_2, CCl_4, and I_2. The ozone may be

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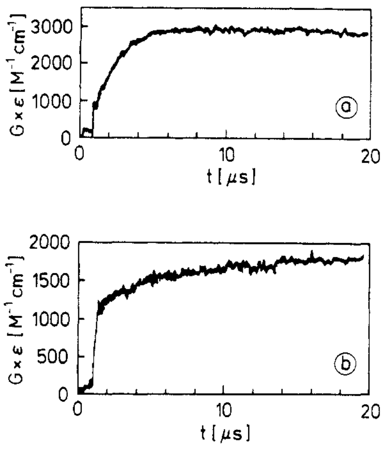

Figure 2. Formation of the acetate radical ion at 350 nm on pulse irradiated 0.01 mol dm^{-3} sodium acetate solutions containing 0.0025 mol dm^{-3} nitrous oxide: (a) no ozone; (b) 5.39 × 10^{-4} mol dm^{-3} ozone.

added to this group of compounds since the ozonide ion has been observed to be a product of the e_{aq}^- reaction at pHs as low as 7.5.[23]

Reaction of OH· with O_3. Attempts to measure the rate constant of reaction 2 by direct observation of the transient $HO_2\cdot$ radical failed because of the strong overlapping optical absorption bands of the $HO_2\cdot$, $O_2^-\cdot$, and O_3. Since ozone shows a high reactivity with many inorganic and organic compounds, the choice of a suitable competing OH· radical scavenger is difficult. Acetic acid, however, is an excellent, relatively inert stabilizer of aqueous O_3 solutions; thus, the acetate ion was selected as a competitive solute. The observations were carried out on the transient 350-nm band of the acetate radical ion formed by reaction 3. The

$$OH\cdot + CH_3COO^- = H_2O + \dot{C}H_2COO^- \qquad (3)$$

half-life of O_3 in a solution containing 0.01 mol dm^{-3} acetate ion buffered at pH 7.0 is about 20 min. Consequently, the experiments were carried out promptly after mixing the stabilized O_3 solution with the acetate buffer (see Experimental Section for details).

Figure 2 illustrates the typical acetate radical ion formation traces obtained by using a 50-ns (875-rd) electron pulse. Figure 2a is for 0.01 mol dm^{-3} acetate; Figure 2b is for 0.01 mol dm^{-3} acetate plus 3.15 × 10^{-4} mol dm^{-3} ozone. Figure 3 shows the agreement between the experimental points obtained from the data of Figure 2 and the solid line which represents the first-order formation of the transient $\cdot CH_2COO^-$ ion. Noteworthy is the fact that two processes are exhibited in Figure 2, a and b. The more pronounced effect occurs in the solution containing O_3. Our rate constants are based on a first-order plot of the fast part of each curve (see Figure 3) which we attribute to the OH· radicals generated by the electron pulse and by the reaction of e_{aq}^- with N_2O or O_3. The slow secondary buildup of $\cdot CH_2COO^-$ may be due to delayed OH· radicals produced from $O_3^-\cdot$, $HO_3\cdot$, and/or $HO_4\cdot$ (see discussion below).

The scavenger plot of our data is shown in Figure 4. Here $(R_0 - R)/R$ is plotted as a function of the concentration ratio $[O_3]/[CH_3COO^-]$. R_0 is the maximum optical density of the 350-nm band in the absence of O_3 and R is the observed maximum at the designated $[O_3]$/[acetate ion] ratio on the graph. The O_3 concentrations vary from 0.041 × 10^{-3} to 0.314 × 10^{-3} mol dm^{-3}; the acetate concentrations are either 0.005 or 0.010 mol dm^{-3}. The nitrous oxide concentration is constant at 0.0025 mol dm^{-3} and converts most of e_{aq}^- into OH· radicals. The fraction not reacting with N_2O reacts with O_3 to produce $O_3^-\cdot$, an ion

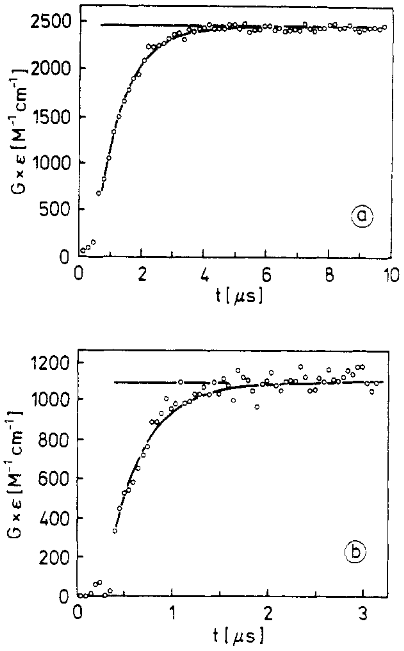

Figure 3. Formation of the acetate radical ion at 350 nm on pulse irradiation of solutions containing (a) no ozone and (b) 3.15 × 10^{-4} mol dm^{-3} ozone. The solid line represents the computer fit of the first-order buildup kinetics and the final base line.

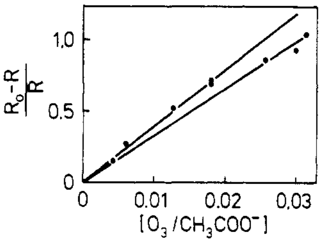

Figure 4. Pseudo-first-order plot for the reaction OH· + O_3 → products. The two solid lines represent the error limit in the determination of k(OH· + O_3). From the slopes a mean value of k(OH· + O_3) = 3.04 × 10^9 dm^3 mol^{-1} s^{-1} is derived (1-cm cell, 875 rd/50-ns pulse).

in rapid equilibrium with O_2, $O^-\cdot$, and OH·.[11] Therefore, it is equivalent to an OH· radical in our competition kinetics, which leads to a total OH· radical yield of $G = 6.0$. It was demonstrated by a kinetic simulation on a PDP 11/40 computer that the apparent rate constant will not be different if ozone converts e_{aq}^- into OH· radicals. If, however, the e_{aq}^--induced reduction of O_3 does not yield OH· radicals but leads to other, nonoxidizing products via

$$e_{aq}^- + O_3 \rightarrow \text{products} \qquad (4)$$

the $\cdot CH_2COO^-$ yield will be decreased, thus leading to a higher apparent rate constant for the reaction of ozone with OH·. The experimentally derived value of the rate constant of reaction 2 must thus be regarded as an upper limit for this rate constant.

A rate constant k(OH· + O_3) of (3.04 ± 0.25) × 10^9 dm^3 mol^{-1} s^{-1} is calculated from the data of Figure 4 by using a value of 8.5 × 10^7 dm^3 mol^{-1} s^{-1} for k(OH· + CH_3COO^-).[4] Our rate constant is 75-fold greater than the gas-phase value of 4.1 × 10^7 dm^3 mol^{-1} s^{-1} recommended by NASA (1979).[1] Because of the "cage effect" in solution, a 10-fold increase in rate constant over the gas-phase rate may be expected[25] and is found for the OH· radical reactions with H_2, D_2, and C_6H_6.[1] However, in reactions of OH· with $HO_2\cdot$,

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(25) E. F. Caldin, "Fast Reactions in Solution", Wiley, New York, 1964, p 282.

H_2O_2, and CH_4, the gas-phase rate is actually higher than the rate in water.[1,24]

The exceptionally high rate of reaction 2 in water relative to the gas phase may indicate that a rapid addition reaction occurs in aqueous solutions.

$$OH\cdot + O_3 \rightarrow HO_4\cdot \qquad (5)$$

While we are unable to decide the course of this reaction, our results indicate that the radical formed in reaction 5 is unable to react further with the acetate ion to produce its radical ion with a rate constant high enough to affect our measurements. It is possible, however, the $HO_4\cdot$ decomposes into $HO_2\cdot + O_2$ as observed in the gas phase. The dissociated form of $HO_2\cdot$, $O_2^-\cdot$, is known to react with O_3 with a rate constant of about 1×10^9 dm^3 mol^{-1} s^{-1} (ref 23) to form $O_3^-\cdot$ and subsequently an $OH\cdot$ radical. This sequence of reactions could explain the pronounced slow development of $\cdot CH_2COO^-$ after the initial rapid reaction (Figure 2b).

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Mechanism of the Hydroxide Ion Initiated Decomposition of Ozone in Aqueous Solution

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Stopped-flow experiments are reported on the OH^--catalyzed chain decomposition of ozone in the pH range 11–13. $O_3^-\cdot$ has been identified as a product by its 430-nm absorption band. Acetate and carbonate ions inhibit this reaction. In the carbonate-inhibited reaction, the radical anion $CO_3^-\cdot$ has been identified by its 600-nm absorption band. In this case an apparent second-order rate constant of 115 ± 40 dm^3 mol^{-1} s^{-1} has been obtained. Evidence is provided to support the reaction $OH^- + O_3 \rightarrow HO_2^- + O_2$ as the primary step. On this basis, $k(OH^- + O_3)$ equals 48 ± 12 dm^3 mol^{-1} s^{-1}. Some aspects of the overall reaction are discussed.

Introduction

The chemistry, as well as the biochemistry, of ozone has been of major interest for many scientists over the last century.[1-3] In water chemistry ozone is used as an environmentally satisfactory and potent oxidant for purification purposes.[4] Although highly reactive free radicals have been reported as intermediates in many ozone reactions, their detailed mode of action has not been revealed unambiguously.[5-9] The hydroxide ion induced decay of ozone, in particular, has been the subject of a number of studies.[7-18] Because of the rapidity and complexity of this reaction in alkaline solutions, an accurate determination of the ozone decomposition kinetics has been difficult to work out. The present investigation has been undertaken by using a time-resolved stopped-flow technique with a resolving time of about 1 ms.

Previous work has established the decomposition of ozone above pH 8 as a bimolecular process[13,16] with a rate given by

$$-d[O_3]/dt = k_1([O_3][OH^-]) \qquad (1)$$

However, there is considerable uncertainty regarding the value of k_1 for the overall decay of ozone, typically quoted values being 700 (ref 15) and 1500 (ref 17) dm^3 mol^{-1} s^{-1}.

The decay of ozone in solution appears to be a chain process involving the hydroxyl radical,[7-9] where the hydroxide ion is involved as an initiator. Thus, in reactions which involve ozone above a certain pH, the hydroxyl radical and other breakdown products of ozone, and not ozone itself, may be the oxidizing species, accelerating or decreasing the reaction rate. The idea that the hydroxyl radical may catalyze the decomposition of ozone is supported by the fact that ozone is reported to be more stable at high hydroxide ion concentrations,[19-21] where the hy-

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