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On the Mechanism of the Decomposition of Acidic O_3 Solutions, Thermally or H_2O_2-Initiated

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Thermal or hydrogen peroxide initiated decomposition of acidic aqueous ozone is described as a chain process propagated by OH and O_2^-/HO_2 radicals. In the absence of H_2O_2 added, the chain is initiated by surface-catalyzed formation of H_2O_2. Surface-dependent formation of H_2O_2 is experimentally verified. Since homogeneous radical−radical reactions are much too inefficient to account for the termination, a heterogeneous chain termination is strongly suggested. Without addition of H_2O_2 no dependence of the decay on the surface-to-volume ratio could be observed. However, on initial addition of H_2O_2 in amounts sufficient for homogeneous initiation to prevail, the rate of O_3 decay becomes proportional to the surface of the reaction vessel. These findings strongly suggest that the decomposition of acidic aqueous O_3 is governed by initiation and termination processes occurring at the reaction-vessel surface, while its apparent appearance of a homogeneous solution-phase reaction results from the counteractive nature of these two processes.

Introduction

The mechanism of aqueous ozone decomposition has been studied for decades, and the free-radical chain-reaction characteristics of the self-decomposition reaction of aqueous ozone is generally accepted.[1] Well established is also the alkali-catalyzed decomposition, initiated by OH^-

$$O_3 + OH^- \rightarrow HO_2^- + O_2 \qquad (1)$$

and that OH, HO_2/O_2^- radicals are the chain-propagating species.[1,2] In γ-ray-initiated decomposition of acidic ozone[3] the chain-initiating species are the H atom and the hydroxyl radical and the propagating radicals the same as in alkaline solutions. These radicals are also involved in the chain-termination process. The reactions are

$$OH + OH \rightarrow H_2O_2 \qquad (2)$$

$$OH + HO_2 \rightarrow H_2O + O_2 \qquad (3)$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad (4)$$

Under a low-intensity generation of the initiating free radicals,[3] these three termination reactions are insufficient to account for the experimentally observed chain lengths. However, on the assumption that termination takes place predominately on an "impurity" in the γ-ray initiation experiments, the ozone-decay data could be accounted for.[3]

The assumed "impurities" may influence the chain termination, but it was difficult to deduce the real mechanism, since the assumed minute amount of "impurities" had to provide a constant k_c of about 800 s^{-1} to explain the measured chain lengths and to give good reproducibility of the γ-ray experiments.[3] These demands of a constant micromole "impurity" with a high rate constant is hard to conceive.

Although the initiation reactions of the alkali and γ-ray-induced decomposition of ozone have been established, such is by no means the case for the thermal decomposition of acidic ozone solutions. In acid (pH 0−4) solutions the decay of ozone is much faster than predicted from the OH^- initiation. It has been suggested that ozone can produce radicals in a reaction with water molecules,[4,5] and later it has been proposed that the O atom formed by the thermal dissociation of ozone reacts with water, producing two OH radicals:[1]

$$O + H_2O \rightarrow 2OH \qquad (5)$$

However, this mechanism has been considered inadequate and a recent idea is that the recombination reaction

$$O + O_2 \rightarrow O_3^* \qquad (6)$$

creates ozone in an excited electronic state capable of decomposing water into initiating radical species.[6] Hydrogen peroxide has previously been shown to be an important trace product in aqueous ozone decomposition.[6−8] The purpose of the present work is to study the role of H_2O_2 in the acidic ozone decomposition process in order to explore further the nature of the initiating and terminating species and their reactions.

Experimental Section

Preparation and storage of millimolar O_3 stock solutions have been previously described.[9] Ozone stock solutions were also prepared from diluted O_3 gas samples stored in syringes in the dark at 0 °C.[1] Special care was taken to avoid the effects of impurities on the decomposition of ozone solutions. All glassware made of borosilicate glass was baked at 450 °C for 4 h after cleaning and preconditioned by flushing with O_3 solutions of the corresponding acidity before use.

The water was triply distilled and treated with O_3 solutions in 5-L flasks. A better reproducibility was achieved by this pretreatment. $HClO_4$ from G.F. Smith was used without further purification. H_2O_2 was prepared by irradiation of oxygen-

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TABLE 1: Initial Rate Constants for Decomposition of a 100 μM O_3 Solution at pH 2 and 22 °C with Various Amounts of H_2O_2 Added Measured in Different Reaction Vessels

		$k \times 10^5$ s^{-1}					
	surface	$[H_2O_2] \times 10^6$ M					
reaction vessel	cm^2	0	7.5	23.0	31.2	50.0	100
25-mL syringe	70	1.7	2.7				
100-mL syringe	155	1.4	3.3	8.0	10.8	15.1	23.0
250-mL flask	223	1.3	3.8				
500-mL flask	350	1.6	4.7			28.5	
1-L flask	530	1.5	6.0	17.5	29.0	35.4	72.5
2-L flask	880	1.5	8.5	27.2	47.5	68.5	
5-L flask	1620	1.4	11.2	46.1			

saturated neutral or pH 2 solutions by γ-rays. By this method, pure H_2O_2 without stabilizer of (1−2) × 10^{-3} M was obtained.

The decomposition studies without H_2O_2 added were performed in 100-mL all-glass syringes covered with Al foil in order to prevent decomposition by laboratory light. The syringes were wrapped in plastic bags and kept at constant temperature in a water bath. At suitable times, the O_3 concentration was measured spectrophotometrically using the absorption at 260 nm. An extinction coefficient of 3300 dm^3 mol^{-1} cm^{-1} [10] was used to calculate the O_3 concentration. The H_2O_2 does not interfere with the O_3 determination.

Before analysis of H_2O_2, the O_3 was removed by purging the solution with Ar or O_2 for 5 min. After 1−2 min, more than 95% of the O_3 was removed, and after 5 min of purging, no ozone could be detected. Purging tests with known concentrations of H_2O_2 and O_3 have shown no significant loss of H_2O_2.

The H_2O_2 concentration was determined by the oxidation of Fe^{2+} in 0.4 M H_2SO_4.[11] The absorption of the ferric sulfate complex was measured in 5-cm cells at 304 nm and the H_2O_2 concentration calculated using an extinction coefficient of 2200 M^{-1} cm^{-1}.[11]

To evaluate the importance of possible wall reactions, the O_3 decomposition rates with and without H_2O_2 added were measured at ambient temperature in different sizes of reaction vessels with surface-to-volume ratios from 325 to 3300 cm^2/L. The vessels were 25- and 100-mL all-glass syringes and $^1/_4$-, $^1/_2$-, 1-, 2-, and 5-L measuring flasks. The syringes were Summit British Made with grounded barrels and pistons, and measuring flasks were German Scherf Präzision or Schott made of Duran and Pyrex England. The kinetics of O_3 decay was found to be independent of the nature of the glass surface or brand; even coating with paraffin did not changed the kinetics significantly.

The surface of each of the flasks was calculated as part of a sphere with a truncated cone and is listed in Table 1. The calculated surfaces are 10−20% higher than those of the corresponding spheres.

Like in our previous studies on O_3 decomposition in aqueous acidic solutions,[1,6] we have treated the data as initial first-order kinetics taken over approximately the first half-life. Although the thermal decomposition of acidic O_3 solutions is a chain reaction, the change in the initial rate expressed as a first-order rate constant has proved to be a reliable measure of the effect of various concentrations, pH, and temperatures.[1,6]

The kinetics measured over approximately one half-life of the O_3 decomposition deviates from first-order only within the overall accuracy of our experiments (±20%). When H_2O_2 is added to the acidic O_3 solutions, the determination of the initial first-order rate constant is even better determined, since the linearity may be extended to 1.5−2 half-lives.

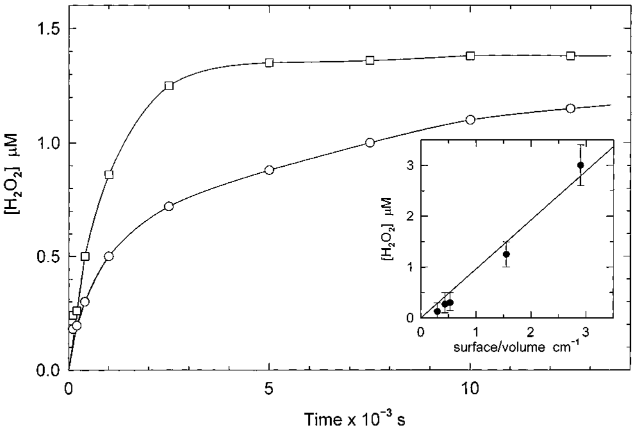

Figure 1. H_2O_2 formation during the decay of acidic ozone solutions in 100-mL syringes at 31 °C, pH 2, and oxygen-saturated: (○) 167 μM O_3 and (□) 790 μM O_3. Ozone half-life is 1.8 × 10^4 and 6 × 10^3 s, respectively. Inset: H_2O_2 plateau concentrations in 5-, 2-, and 1-L flasks and 100- and 25-mL syringes as a function of surface-to-volume ratio.

Results

Formation of H_2O_2. Small amounts (1−2 μM) of hydrogen peroxide are formed as a result of O_3 decomposition in 100-mL glass syringes at 31 °C, pH 2 (Figure 1). Initially, H_2O_2 forms rapidly with a rate proportional to the O_3 decay. Then the formation slows down until the H_2O_2 concentration eventually reaches a plateau at about one half-life of the O_3 decomposition. After ∼80% O_3 has decomposed, the H_2O_2 concentration diminishes slightly. This behavior is analogous to the formation of H_2O_2 in O_3 decomposition in acetic acid solutions,[6] the only difference being that the H_2O_2 concentrations in this study (without acetic acid) are much lower. The H_2O_2 plateau occurred at 1.2−1.4 μM H_2O_2 at 31 °C, and the change in initial formation rate during the course of the O_3 decomposition is consistent with a simultaneous formation and consumption of H_2O_2 with rates proportional to the O_3 concentration. Figure 1 shows an example where H_2O_2 was measured during decay of 167 and 790 μM O_3 in an oxygen-saturated (∼10^{-3} M O_2) solution at pH 2 and 31 °C. The half-lives of the two O_3 solutions were 1.8 × 10^4 and 6 × 10^3 s, respectively. The H_2O_2 concentration plateau is rather independent of the initial O_3 concentration and of pH, but it depends on the temperature, since a 400 μM O_3 solution gave a H_2O_2 plateau of 1.0, 1.3, and 2.1 μM H_2O_2 at 22, 31, and 45 °C, respectively. Also, reaction vessels of different sizes gave different H_2O_2 concentrations—the larger the vessel, the less H_2O_2 was detected—and in the largest flasks, the accuracy of the H_2O_2 measurement is low with the applied analytical method (the detection limit is $[H_2O_2] \approx 1 \times 10^{-7}$ M).

Effect of Added H_2O_2. When H_2O_2 was added to an acidic O_3 solution in a l00-mL syringe, the initial first-order decomposition rate of O_3 increased with increasing H_2O_2 concentration. The first-order half-life of O_3 decay in a 100 μM O_3 solution, pH 2 at 31 °C, increases linearly with H_2O_2 added (Figure 2 inset). The H_2O_2 concentration was followed during the course of the O_3 decomposition, and Figure 2 shows that the initial formation of H_2O_2 is prominent even up to ∼10 μM H_2O_2 added, but at higher H_2O_2 concentrations, as the consumption

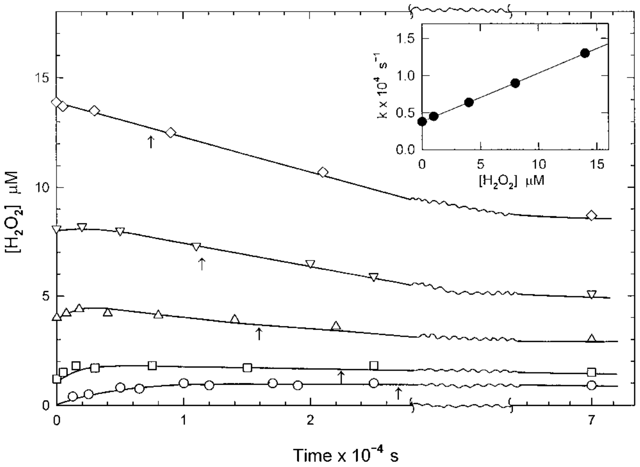

Figure 2. H_2O_2 formation and decay during decomposition of acidic O_3 solutions at 31 °C, pH 2 and 100 μM O_3 solution oxygen-saturated in 100-mL syringes: (○) without H_2O_2 added; (□) 1 μM H_2O_2; (△) 4 μM H_2O_2; (▽) 8 μM H_2O_2; (◇) 14 μM H_2O_2 added. ↑ indicates the half-life of O_3. Inset: Rate constant of initial O_3 decomposition as a function of initial H_2O_2 concentration.

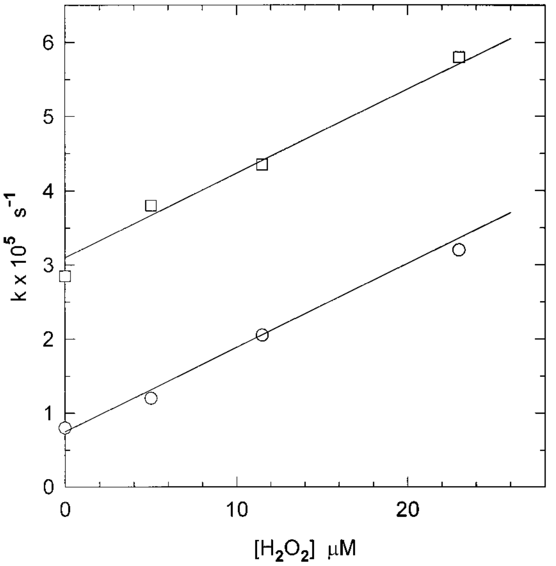

Figure 3. Effect of addition of 5.0, 11.5, and 23 μM H_2O_2 on the rate of O_3 decay in oxygen-saturated (1.2×10^{-3} M) and oxygen-depleted (less than 10% of the O_3 concentration) solutions at 31 °C, pH 1, and 76−84 μM O_3: (○) oxygen-saturated and (□) oxygen-depleted solutions.

of H_2O_2 during the O_3 decay becomes more pronounced, this feature vanishes.

The increase in O_3 decomposition rate by H_2O_2 addition is identical in oxygen depleted (initially less than 10% oxygen relative to O_3) and O_2 saturated at low concentrations of H_2O_2. Figure 3 shows an example of a 75 μM O_3 solution, pH 1 and 31 °C in 100-mL syringes, with 5, 11.5, and 23 μM H_2O_2 added.

On addition of larger amounts of H_2O_2, comparable to or higher than the initial ozone concentrations, the rate of decomposition of O_3 in O_2-saturated solutions maintains proportionality to the H_2O_2 concentration (Figure 4). For fixed initial concentrations of H_2O_2 added, there is a proportionality between the decomposition rate and the O_3 concentration; that is, addition of 100 μM H_2O_2 to 100, 230, and 375 μM O_3 solutions at pH 2 and 22 °C in syringes results in $k_{ini} = 3.7 \times 10^{-5}$, 8.0×10^{-5}, and 14.9×10^{-5} s^{-1}, respectively (Figure 4 inset).

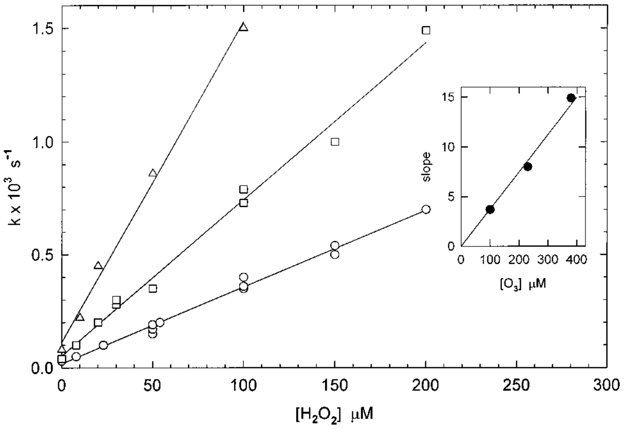

Figure 4. Initial first-order rate constants for decomposition of (○) 100, (□) 230, and (△) 350−400 μM O_3 as a function of $[H_2O_2]$ added, in 100-mL syringes at 25 °C, pH 2.0, and in O_2-saturated solutions. Inset: Initial rate constant divided by $[H_2O_2]$ (slopes) as a function of initial O_3 concentration.

Effect of Size of the Reaction Vessel. In our previous study,[1] we found no significant difference in the O_3 decomposition rate using various reaction vessels from 25-mL syringes to 5-L flasks. However, from the study with acetic acid solutions[6] there was an indication of some wall effects. In the present study on the H_2O_2 formation and steady-state concentration during the course of O_3 decay, there again are indications of an effect of reaction-vessel size, since the bigger the volume, the smaller the concentration of H_2O_2 that forms in initially hydrogen peroxide free O_3 solutions. Therefore, a more detailed study of the influence of the size of the reaction vessel was undertaken.

In this series of reaction vessels the variation in surface-to-volume ratio was about a factor of 10. We found no indication of wall effects in experiments without H_2O_2 added, since identical rates were obtained in all the vessels: $k_{ini} = (1.5 \pm 0.2) \times 10^{-5}$ s^{-1} for O_2-saturated solutions at pH 2 and 22 °C (Table 1). The variation in rates with O_3 and O_2 concentrations, pH 0−4, and temperature is, in all vessels, identical to the results previously obtained in 100-mL syringes.[1]

However, on addition of H_2O_2, the rates of O_3 decomposition were found to vary with the size of reaction vessels: the larger the vessel the higher the decomposition rate. This effect becomes more and more pronounced with higher amounts of H_2O_2 added. Table 1 presents the initial decay rates of a 100 μM O_3 solution measured in different reaction vessels, oxygen-saturated at pH 2 and 22 °C with various amounts of H_2O_2 added. A correlation of the measured initial rates with the surface-to-volume ratio of the different types of reaction vessels is nonlinear. When, however, the rates are plotted as a function of the surface area of each vessel, a fairly straight-line dependence is obtained. Figure 5 shows plots of the initial decomposition rates versus surface area for the experiments with and without addition of H_2O_2 (Table 1). When the slopes of the lines for various H_2O_2 concentrations in Figure 5, k_{ini}/surface, are plotted as a function of the H_2O_2 concentration, strict proportionality is found (Figure 5 inset).

Discussion

Decomposition of acidic ozone solutions involves chain reactions similar to those taking place in alkaline and neutral solutions. The radicals OH and O_2^-/HO_2 are the chain-carrying species in this process (Scheme 1).

SCHEME 1: Reaction Mechanism (k Is Rate Constant in $M^{-1}\ s^{-1}$)

$$O_3 \rightleftharpoons O + O_2 \qquad (7,-7)$$

$$\text{O or } O_3^* + H_2O \rightarrow 2OH \text{ or } H_2O_2 + O_2 \text{ (surface reaction)} \qquad (8)$$

$$OH + O_3 \rightarrow HO_2 + O_2 \quad k = 1.1 \times 10^8 \text{ (ref 9)} \qquad (9)$$

$$HO_2 + O_3 \rightarrow OH + 2O_2 \quad k < 10^4 \text{ (ref 9)} \qquad (10)$$

$$HO_2 \rightleftharpoons O_2^- + H^+ \quad K = 1.59 \times 10^{-5}\ \text{M (ref 12)} \qquad (11,-11)$$

$$H_2O_2 + O_3 \rightarrow OH + HO_2 + 2O_2 \quad k = 0.025 \text{ (ref 6)} \qquad (12)$$

$$O_2^- + O_3 \rightarrow O_3^- + O_2 \quad k = 1.5 \times 10^9 \text{ (ref 13)} \qquad (13)$$

$$O_3^- + H^+ \rightarrow OH + O_2 \quad k = 9 \times 10^9 \text{ (ref 14)} \qquad (14)$$

$$OH + OH \rightarrow H_2O_2 \quad k = 6 \times 10^9 \text{ (ref 15)} \qquad (2)$$

$$OH + HO_2 \rightarrow H_2O + O_2 \quad k = 7 \times 10^9 \text{ (ref 11)} \qquad (3)$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \quad k = 8 \times 10^5 \text{ (ref 12)} \qquad (4)$$

The initiation process for the thermal decomposition has previously been shown to be controlled by the dissociation equilibrium reaction of ozone (reaction 7,−7).[1] This reaction requires an intermediate species that is capable of producing the chain-propagating radicals, OH and O_2^-/HO_2, from water. It has been suggested that this could be either the oxygen atom[1] or an electronically excited ozone molecule[6] created by the recombination reaction of the oxygen atom and oxygen molecule. Although there is little doubt that the thermal dissociation reaction of ozone is the precursor for the initiation mechanism in acid solution, it may be questioned how this reaction results into the propagating water radicals.

The formation of H_2O_2 during the course of the ozone decomposition in acid media and the different rates obtained for the O_3 destruction by H_2O_2 addition in various sizes of reaction vessels add some new aspects to the mechanism of the thermal decomposition of ozone in acidic solution.

We interpret our experimental results in terms of a mechanism, where H_2O_2 (reaction 8) is formed at the surface as a result of the O_3 dissociation[1] (reaction 7) followed by a reaction with O_3 to form the water radicals OH and HO_2 (reaction 12). The formation of H_2O_2 is in accordance with the observations by Heikes et al.[7,8] who measured H_2O_2 generation from bubbling ozonized air through water in glass impingers and concluded that their results contradicted a mechanism that includes the reaction $O_3 + OH^-$. The mechanism assumed for explaining their results involved surface chemistry at the impinger walls. They suggest that O_3 absorbs at glass-surface sites and that in contact with liquid water it hydrolyzes or by molecular dissociation forms water radicals that subsequently yields H_2O_2. By desorption, H_2O_2 may then react in the bulk solution.

Our observations of the vessel-size-dependent rate of O_3 decomposition by addition of H_2O_2 imply that the termination of the chain destruction of O_3 has to be surface-related too. The initiation of the chain is, in the case of H_2O_2 addition, due to a homogeneous reaction in the bulk solution between hydrogen peroxide and O_3 (reaction 12). If the termination reaction also should be homogeneous, either by radical−radical reaction or by reaction with a bulk "impurity", we would observe the same rate of decomposition in all vessels. However, the surface dependence of the chain-decomposition rates shows clearly that a heterogeneous termination predominates while the contribution of a homogeneous radical−radical termination is negligible in all our experiments.

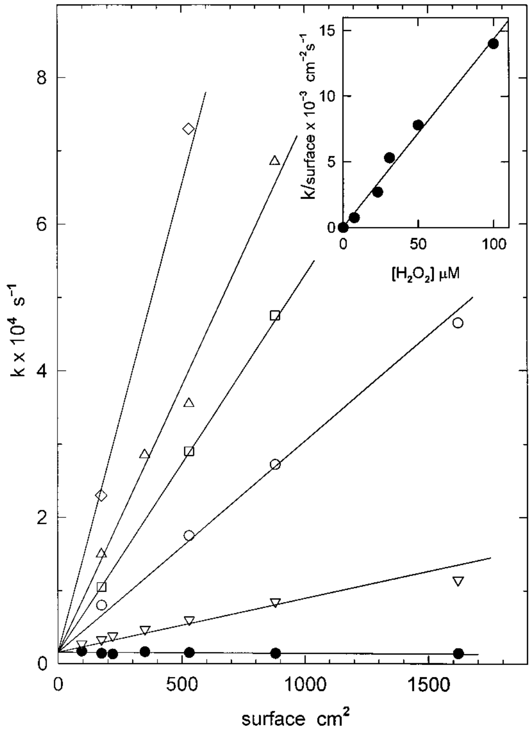

Figure 5. Initial first-order rate constant for decomposition of a 100 μM O_3 solution at 22 °C and pH 2.0 containing various amounts of H_2O_2 as a function of the surface area of the different reaction vessels: (●) without H_2O_2; (▽) 7.5 μM H_2O_2; (○) 23 μM H_2O_2; (□) 31 μM H_2O_2; (△) 50 μM H_2O_2; (◇) 100 μM H_2O_2. Inset: Initial first-order rate constant for O_3 decomposition divided by the surface area (slopes) as a function of added H_2O_2 concentration.

The importance of heterogeneous termination is illustrated by comparison of the calculated initial rate constants with those experimentally observed for experiments with H_2O_2 added (Table 2). The calculated values were obtained by numerical integration of the reactions in Scheme 1, reactions 2−4, and 9−14 (thus, only the homogeneous radical−radical reactions accounted for the termination). As can be seen in Table 2, the calculated values exceed by far those obtained experimentally: for the 100-mL syringes factors of 25−50 were obtained and for the larger vessels factors of 10−20 were obtained. Our calculations also show that steady-state concentrations of the chain-carrying radicals OH and O_2^-/HO_2 are on the order of $10^{-14}-10^{-12}$ M.

On the other hand, calculated rate constants would match the experimentally obtained rate constants by addition of a hypothetical termination reaction with surface sites to Scheme 1

$$OH + X(S) \rightarrow P \qquad (15)$$

in analogy to the "impurity" invoked to interpret the γ-irradiation-initiated O_3 decay.[3]

The values of k_c of reaction 15 necessary to match experimental rates of decay are given in Table 2. The k_c decreases with the size of the vessel but is independent of the initial H_2O_2

TABLE 2: Calculated Values of Initial Rate Constants, k_{ini}, with H_2O_2 Initiation and Homogeneous Radical−Radical Termination (Reactions 2−4 and 9−14) and Calculated k_c for Radical−Surface Termination (Reaction 15) Included To Match Experimentally Observed Decomposition Rates of a 100 μM O_3 Solution at pH 2 and 22 °C with Various Amounts of H_2O_2 Added Measured in Different Reaction Vessels

	$k \times 10^5$ s^{-1}				
	$[H_2O_2] \times 10^6$ M				
	7.5	23.0	31.2	50.0	100
calcd k_{ini}	120	250	320	380	500

	calcd k_c, s^{-1}					
	$[H_2O_2] \times 10^6$ M					
reaction vessel	7.5	23.0	31.2	50.0	100	k_c, V/s
100-mL syringe	125	145	150	160	155	98
250-mL flask	110					122
500-mL flask	90			85		125
1-L flask	65	65	70	65	70	125
2-L flask	50	45	45	47		107
5-L flask	40	30				108
				ave		115 ± 20

concentration. The k_c of 150 obtained for 100-mL syringes is in excellent agreement with k_c of 100−200 s^{-1} used in modeling of our γ-irradiation experiments.[3] When values of k_c are divided by the corresponding ratio of the surface to the volume, a constant value of 115 ± 20 s^{-1} cm is obtained for all reaction vessels. These results are strong indications of a surface-related heterogeneous termination mechanism in O_3 decay.

With the termination reaction catalyzed by the surface of the vessel, we can expect a rate of O_3 decay that would be proportional to the surface area of the vessel. The larger the volume the relatively smaller is the surface, and a higher rate may be expected. Our results are in good agreement with this assumption, as exhibited in Figure 5, where the initial rates of O_3 decomposition are plotted as a function of the surface area of the various reaction vessels. When the slopes in Figure 5 are plotted versus the corresponding H_2O_2 concentrations (Figure 5 inset), a straight line is obtained showing the proportionality between the initial rates and $[H_2O_2]$ added.

Contrary to the results with added H_2O_2, rates of the O_3 decomposition do not depend on the vessel size when no H_2O_2 is added (Table 1 and Figure 5). Moreover, filling 100-mL syringes with glass spheres or Rashig rings (in order to increase the surface-to-volume ratio) gave unchanged rates of O_3 decomposition, resulting, however, in higher formation of H_2O_2. Neither vigorous stirring nor coating of the surface with paraffin or silicone influenced significantly the observed rates.

Lack of the influence of coatings and different brands of the glassware indicates that trace substances leaching from the glass into acid solution have no influence on the observed O_3 decay. These observations are in agreement with the results of Heikes et al.,[7,8] who have shown that H_2O_2 is formed by aqueous ozone in impingers made of different materials. Also, the presence of ferric and cupric ions did not have any significant influence on the decay rate.

The kinetics observed with and without H_2O_2 added can only be explained if we assume that both the initiation reaction and the termination reaction are heterogeneous processes originating from the same source, that is, surface sites. In this case, both the initiation and termination of the chain will be proportional to the surface, and therefore, the decomposition of O_3 will behave as an apparent homogeneous process, although both reactions are heterogeneous. Thus, the observed decay rates should be independent of the vessel size.

Such a mechanism agrees well with our determinations of initially formed H_2O_2 where extremely small amounts of H_2O_2 were measured in the large (2−5 L) vessels (Figure 2). Therefore, reaction 12 (radical formation) is slower in larger vessels. By comparison of the surface area of a 100-mL syringe and that of the 5-L flask, the latter is about 10 times as large, whereas the volume of the two containers differs by a factor of 50. If we assume a constant production of H_2O_2 per surface area for the same initial O_3 concentration, we should expect 4−5 times less H_2O_2 in the 5-L flask, which is actually what was observed.

It has previously been shown[1,6] that the initiation of the O_3 chain decomposition is related to the O_3 dissociation (reaction 7). It is possible that the surface catalyzes either the oxygen atom or an excited O_3* molecule (from the recombination[6]) to react with water, creating OH radicals and/or H_2O_2 (reaction 8). Although the exact nature of the surface reactions is not known, formation of H_2O_2 seems to be most probable, since it is the only thermodynamically favorable bimolecular reaction capable of converting O_3 into a chain-initiating species. For the reaction $O_3 + H_2O = H_2O_2 + O_2$, $\Delta G° = -55.5$ kJ mol^{-1} is calculated.[16] By further reactions of H_2O_2 with O_3, the propagating radicals OH and HO_2 form and may diffuse into the bulk and react with O_3 . The termination reactions 2−4 (Scheme 1), too ineffective in the bulk, take place at the surface together with the reaction $OH + H_2O_2 \rightarrow HO_2$, which will decrease the chain-carrying radical concentration. The heterogeneous termination reactions make the termination more effective and the chain lengths much smaller and thus will render unnecessary the intervention of a hypothetical constant "impurity" reaction invoked to explain the chain lengths observed in the γ-radiolysis of acidic O_3 solutions.[3]

Conclusion

The O_3 chain decomposition in acidic solutions (pH 0−4) is initiated by the ozone equilibrium reaction 7,−7 and propagated by the radicals OH and O_2^-/HO_2. By comparison of decay kinetics of O_3 with and without H_2O_2 added in reaction vessels of various sizes, it is concluded that both the initiation and termination reactions are surface-catalyzed. Heterogeneous formation of H_2O_2 during the course of the O_3 decomposition was experimentally verified. It plays a crucial role in the chain initiation, forming the propagating radicals OH and O_2^-/HO_2 by reaction with O_3 (reaction 12). For the experiments with no H_2O_2 added within the applied range of surface-to-volume ratios, the effect of surface catalytic initiation manifested itself only in the concentration of H_2O_2 at the plateau while the rate of O_3 decomposition stayed invariant, indicating the compensating effect of the heterogeneous termination.

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