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Reaction of Peroxyl Radicals with Ozone in Water

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The reactivity of alkylperoxyl radicals and $-O_3SOO^\bullet$ toward ozone was investigated. The peroxyl radicals were produced by steady-state γ-radiolysis in the presence of O_3. The rate constants were extracted from the decay rate of ozone measured during the irradiation. The rate constants vary between 7×10^3 and 2×10^5 M^{-1} s^{-1} and there is a trend of increasing rate constant with electron-withdrawing substituent. Quantum chemical computations support a mechanism, according to which formation of an alkyl trioxide radical is the rate-determining step. This is followed by rapid expulsion of O_2 to yield the alkoxyl radical. Conceivably, the alkyl trioxide radical is preceded by an extremely unstable alkyl pentoxide radical in equilibrium with the reactants.

Introduction

During the past decade ozone has found a number of important technical applications. A powerful oxidant, it has been utilized, inter alia, for pulp bleaching and for water purification. In atmospheric chemistry ozone has for a long time been considered as an utmost important chemical.[1] Gas phase chemists have therefore endeavored ever since to determine rate constants for reaction with ozone of conceivable reactants. By means of such rate constants numerical simulations are being made in order to establish the fate of stratospheric ozone. Alkylperoxyl radicals, most notably the methylperoxyl radical, $CH_3OO^\bullet$, frequently form in the gas phase. The latter arises during $^\bullet OH$ radical initiated oxidation of methane. Not surprisingly, the gaseous reaction between $CH_3OO^\bullet$ and O_3 has been investigated[2] but found to be as slow as ca. 10^4 M^{-1} s^{-1}. The same reaction was also examined in CCl_4 solvent. The rate constant was found[3] only slightly higher than in the gas phase, i.e., 3×10^4 M^{-1} s^{-1}. In the polar solvent H_2O, the rate constant for reaction of alkylperoxyl radicals with O_3 could be both lower and higher than in nonpolar solvents. It should be mentioned that, to our knowledge, no reaction between O_3 and alkylperoxyl radicals in water has been reported. On the other hand, given that in all ozone-based technical processes alkylperoxyl radicals are unavoidable intermediates, this reaction is, at least potentially, important. Specifically, *tert*-butyl alcohol or acetic acid have often been used in the past as hydroxyl radical scavengers[4,5] in ozone-based processes, or during the measurement[6,7] of rate constants of O_3 reacting with various substrates in aqueous solution. In such systems, which always contain excess O_2 as well, a primary alkylperoxyl radical is formed, whose reactivity, if any, with ozone may modify the outcome of the process or distort the value of the derived rate constant. With the above points in mind we have measured in the present work the rate constant for reaction of ozone with a number of alkylperoxyl radicals, as well as with $^-O_3SOO^\bullet$.

Experimental Section

Pulse radiolysis was performed at ambient temperatures utilizing doses of 2−30 Gy/pulse, corresponding to 1.2×10^{-6} to 1.8×10^{-5} M radicals. The 4.6 MeV linear accelerator is characterized by a full width at half-maximum of 8 ns and a beam current of 4 A. The computerized optical detection system with a time resolution of ca. 10 ns has been described elsewhere.[8] In all experiments a monochromator bandwidth of 2.5 nm was used. The relative dose/pulse was monitored by scintillation of an optical fiber placed in front of the cell. The light signal from the fiber was calibrated against an aerated 10^{-2} M KSCN solution taking[9] $G\epsilon = 2.3 \times 10^{-3}/J^{-1}$ M^{-1} cm^{-1} at 500 nm.

γ radiolysis was performed in an AECL ^{60}Co γ-source. Dose rates were determined by means of a Fricke dosimeter. The ozone decay was measured spectrophotometrically at 255 nm. Comparing irradiated and unirradiated (blank) samples compensated for the self-decay of ozone.

Ozone was freshly prepared for each experimental series. O_2 gas was allowed to flow through a microwave discharge ozonizer, the outgoing gas being led into an aqueous 10^{-2} M $HClO_4$ solution. After ca. 5 min ozonolysis was discontinued and the absorbance of the solution at 255 nm was measured, utilizing $\epsilon(\text{ozone})_{255nm} = 3250$ M^{-1} cm^{-1}. This number was determined spectrophotometrically by measuring at 302 nm the absorbance of Fe^{3+} obtained after oxidation of Fe^{2+} by O_3 in acid solution. Typical ozone concentrations achieved during ozonolysis were in the vicinity of 10^{-4} M. Formaldehyde was analyzed according to a modified version of the Hanzsch method.[10]

Results and Discussion

General Background to the Present Work. In the aqueous solutions the ionizing radiation initially produces three radicals with their yields in parentheses: OH radicals (2.9×10^{-7} mol/J), hydrated electrons, e^-_{aq} (2.9×10^{-7} mol/J), and hydrogen atoms, $H^\bullet$ (6×10^{-8} mol/J). In very acidic solutions e^-_{aq} is rapidly converted into $H^\bullet$ atoms (eq 1).[11] In all experiments the solutions contain a mixture of O_2 and O_3, where O_2 is at least in a 10-fold excess over O_3. Consequently, the following

$$e^-_{aq} + H^+ \rightarrow H^\bullet \qquad k_1 = 1.9 \times 10^{10}\ M^{-1}\ s^{-1} \qquad (1)$$

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reactions are of interest, their rate constants having been taken from ref 11:

$$O_2 + e^-_{aq} \rightarrow O_2^{\bullet -} \qquad k_2 = 1.9 \times 10^{10}\ M^{-1}\ s^{-1} \tag{2}$$

$$O_2 + H^{\bullet} \rightarrow HO_2^{\bullet} \qquad k_3 = 2.0 \times 10^{10}\ M^{-1}\ s^{-1} \tag{3}$$

$$HO_2^{\bullet} \rightleftarrows O_2^{\bullet -} + H^+ \qquad pK_a(HO_2^{\bullet}) = 4.8$$

$$O_3 + O_2^{\bullet -} \rightarrow O_3^{-\bullet} + O_2 \qquad k_4 = 1.6 \times 10^{9}\ M^{-1}\ s^{-1} \tag{4}$$

$$O_3^{-\bullet} + H^+ \rightarrow OH^{\bullet} + O_2 \qquad k_5 = 5 \times 10^{10}\ M^{-1}\ s^{-1} \tag{5}$$

$$HO_2^{\bullet} + O_3 \rightarrow OH^{\bullet} + 2O_2 \qquad k_6\ \text{slow} \tag{6}$$

It can be seen that, due to the high values of k_2, k_3, *and* k_4, e^-_{aq} and $H^{\bullet}$ will ultimately consume O_3 to produce $OH^{\bullet}$ radicals. This reaction sequence may, however, be inhibited at very low pH, provided k_6 is sufficiently small. The rate constant of reaction 6, k_6, was shown by pulse radiolysis to be immeasurably small.[12] In our γ-radiolysis experiments at pH 0 we found the rate of decay of O_3 ca. twice as high as would be expected assuming k_6 to be insignificant. Without correcting for ionic strength effects, we derive $k_6 = 2.5 \times 10^4\ M^{-1}\ s^{-1}$. Nevertheless, as most experiments in this work are conducted at pH $\geq$ 2, the exact value of k_6 is inconsequential. At the high dose rates employed during pulse radiolysis and when no other substrate is present, the OH radical disappears mainly in second-order radical−radical reactions. In particular, at the ozone concentrations employed (less than 10^{-4} M) reaction 7 with a relatively low rate constant[11] will be of minor importance. However, in the presence of millimolar amounts of added precursors of alkyl radicals, their reaction with OH will be dominant.

$$O_3 + OH^{\bullet} \rightarrow HO_2^{\bullet} + O_2 \qquad k_7 = 1 \times 10^{8}\ M^{-1}\ s^{-1} \tag{7}$$

Reactivity of Alkylperoxyl Radicals. In the present work the OH radical was brought to react with compounds of the general form $R_1R_2R_3CH$ according to the following scheme:

$$R_1R_2R_3CH + {}^{\bullet}OH \rightarrow R_1R_2R_3C^{\bullet} + H_2O \tag{8}$$

$$R_1R_2R_3C^{\bullet} + O_2 \rightarrow R_1R_2R_3COO^{\bullet} \tag{9}$$

When at least one of the R groups, say R_3, is OH, the peroxyl radical $R_1R_2(OH)COO^{\bullet}$ will expel,[13] more or less rapidly, a superoxide radical anion according to

$$R_1R_2(OH)COO^{\bullet} \rightarrow R_1R_2C{=}O + O_2^{\bullet -} + H^+ \tag{10}$$

Whenever reaction 10 operates, the $O_2^{\bullet -}$ ion will attack O_3, giving rise to a chain reaction through reactions 4 and 8−10. The expulsion of $O_2^{\bullet -}$ from $R_1R_2(OH)COO^{\bullet}$ is catalyzed by both OH^- and general bases such as HPO_4^{2-}. This explains our finding that during pulse radiolysis of solutions containing methanol and 0.1 M $HPO_4^{2-}/H_2PO_4^-$ a very rapid bleaching of O_3 was observed, corresponding to almost complete destruction of the O_3 present.

Neither the reactions of the peroxyl radical of methanol ($CH_2(OH)OO^{\bullet}$) nor that of *tert*-butyl alcohol ($CH_3C(CH_3)(OH)CH_2OO^{\bullet}$) with O_3 could be observed by pulse radiolysis. This was deduced from our observations that around pH 1 neither the rate nor the yield of O_3 bleaching, ascribed to reaction 4, was modified upon introduction of methanol or *tert*-butyl alcohol into O_2/O_3 containing solutions. All the other alkylperoxyl radicals tested in this work proved inert as well toward O_3 on the pulse-radiolytic scale.

However, study of ozone consumption and product formation during γ-radiolysis clearly revealed that reaction 11 does occur, if relatively slowly. For a correct analysis of the γ-radiolysis

$$R_1R_2R_3COO^{\bullet} + O_3 \rightarrow R_1R_2R_3CO^{\bullet} + 2O_2 \tag{11}$$

results one has to account for the fate of the alkoxyl radical, $R_1R_2R_3CO^{\bullet}$, the product of reaction 11. The following reactions summarize the possibilities.

$$R_1R_2HCO^{\bullet} \rightarrow {}^{\bullet}CR_1R_2OH \tag{12}$$

If at least one of the substituents, e.g., R_3, is H, a rapid 1,2 H-shift[14] (reaction 12) can take place to yield a carbon-centered reducing radical. This radical will undergo more or less rapidly reactions 9 and 10, followed by reaction 6. The net result is that two O_3 molecules will be consumed for every alkylperoxyl radical.

$$R_1R_2R_3CO^{\bullet} \rightarrow R_1^{\bullet} + R_2R_3CO \tag{13}$$

The alkoxyl radical can suffer a so-called β-cleavage[15] to yield a smaller molecule and a new radical, e.g., $R_1^{\bullet}$. R_1 must, however, not be $H^{\bullet}$. Clearly R_1 will immediately react with O_2 in reaction 9 to yield $R_1OO^{\bullet}$. Then, depending on the nature of R_1, reactions 10 and 4 may or may not occur. In the former case, we shall again observe two O_3 molecules consumed for every initial $R_1R_2R_3COO^{\bullet}$ radical present. The $R_1OO^{\bullet}$ radicals derived from the initial $R_1R_2R_3COO^{\bullet}$ radicals studied in this work will eventually give rise to an $O_2^{\bullet -}$ species through reaction 10 and hence result in the consumption of two O_3 per peroxyl radical. In conclusion, whether via reaction 12 or 13 or a combination of the two, each alkylperoxyl radical will consume two O_3. Finally, it should be mentioned that additional $O_2^{\bullet -}$ can be generated even in the absence of reaction 10. This occurs if a peroxyl radical produces some $O_2^{\bullet -}$ as a product during its self-combination in reaction 14. For most peroxyl radicals studied in this work the yield of $O_2^{\bullet -}$ in the combination process is reported in the literature.[16−18] When calculating steady-state concentrations of alkylperoxyl radicals, we set the rate constant of second-order termination equal to $2k_{14}(1 - \alpha)$ where α is the fraction of $O_2^{\bullet -}$ produced.

$$2R_1R_2R_3COO^{\bullet} \rightarrow \text{some } O_2^{\bullet -}/HO_2^{\bullet} + \text{other products} \tag{14}$$

$O_2^{\bullet -}$ as Chain Carrier. The $O_2^{\bullet -}$-mediated chain consumption of O_3 via reactions 4, 8, 9, 11, and 12 or 13 followed by reaction 10 will operate in all peroxyl radical systems. To check $O_2^{\bullet -}$ as a chain carrier, we scrutinized the chain length in systems where the predominant radical present is $O_2^{\bullet -}/HO_2^{\bullet}$. This was achieved by subjecting to γ-radiolysis substrates whose peroxyl radicals, $R_1R_2R_3COO^{\bullet}$, are known rapidly to generate $O_2^{\bullet -}/HO_2^{\bullet}$ in reaction 10. This is especially true for $CO_2^{\bullet -}$, formed from formic acid, where no intermediate peroxyl radical has been observed. Table 1 presents the chain lengths of O_3 consumption with different substrates mainly at pH 2. If no other reactions beyond 8, 9, 10, and 4 were operating, we would expect the chain length to be given by $k'_4[O_3]_{av}/2k[HO_2]_{ss}$. Here, k'_4 is the effective rate constant at the relevant pH and

TABLE 1: Chain Lengths of Ozone Consumption during γ-Irradiation of Aqueous Solutions Containing Initially 0.06−0.08 mM O_3, 1.3 mM O_2 in the Presence of Different Substrates at mM Concentrations

substrate	chain length	pH	dose rate
theory	≈250	2	0.098
formic acid	16.7	2	0.098
ethylene glycol	11.5	3	0.098
2-propanol	6.7	2	0.098
ethanol	3.9	2	0.098
ethanol	4.9	≈6[a]	0.098
methanol	1.0	2	0.098
methanol	0.9[b]	2	0.098
methanol	4.5	2	0.0061

[a] Unbuffered solution. [b] The chain length was derived from the measured CH_2O yield.

$[O_3]_{av}$ is the average ozone concentration during irradiation, in the range 30−40 μM. $2k$ signifies the rate constant of self-combination of $HO_2/O_2^{\bullet-}$ at the pH in question.

$$2HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \tag{15}$$

$$HO_2^{\bullet} + O_2^{\bullet-} \rightarrow HO_2^{-} + O_2 \tag{16}$$

At pH 2 $2k$ has been determined to be[19] 1.92×10^6 M^{-1} s^{-1}. Similarly, at this pH, the effective rate constant of reaction 4 is given by $k_4' = k_4\,(10^{-pH}/(10^{-pH} + 10^{-4.8})) = 2.5 \times 10^6$ M^{-1} s^{-1}. $[HO_2]_{ss}$ is the steady-state concentration of HO_2 and can be calculated from the relationship $P = 2k[HO_2]^2_{ss}$, where $P =$ is the rate of production of radicals. Hence the theoretical chain length is calculated to be ca. 250. Table 1 contains the measured chain lengths. As can be seen, the experimental chain length of HCOOH makes up less than 10% of the theoretical figure. In our O_3/O_2 mixture about 5−10% of the $CO_2^{\bullet-}$ is expected to react with O_3. Were this reaction mainly an oxygen atom rather than an electron transfer, it would constitute a termination step and thus rationalize the shortness of the chain. Alternative terminators could be transition metal impurities. For the other substrates in Table 1 well-known reactions such as hydrogen abstraction from methyl groups by $OH^{\bullet}$ (2-propanol, ethanol) or a relatively slow expulsion of $O_2^{\bullet-}$ from the peroxyl radical derived from ethylene glycol account for the short chain length. The entries for methanol are quite interesting. In this system reaction 10 is rate-determining, as evidenced by published rate constants.[20,21] First we note that dose rate variation implies second-order termination in radicals. Thus, virtually all radicals undergoing combination reactions are alkylperoxyl radicals, $CH_2(OH)OO^{\bullet}$, and the termination reaction must be reaction 14. Furthermore, the chain length of ozone consumption and that of CH_2O formation are almost equal. CH_2O forms in reaction 10, while virtually no CH_2O is produced in reaction 14. From these findings and using the steady-state approximation described above and $2k_{14}(HOCH_2OO)$[22] $= 2.1 \times 10^9$ M^{-1} s^{-1}, we calculate $k_{10} = 10$ s^{-1} for methanol, a value that is equal to the highest upper limit given in the literature.[20] This shows that termination by way of $O_2^{\bullet-}$ does not effect the chain length. The overall conclusion, drawn from Table 1 and the methanol experiments, is that limitations due to the $O_2^{\bullet-}$ chain are unimportant unless the alkylperoxyl radical gives rise to a chain length ≫1.

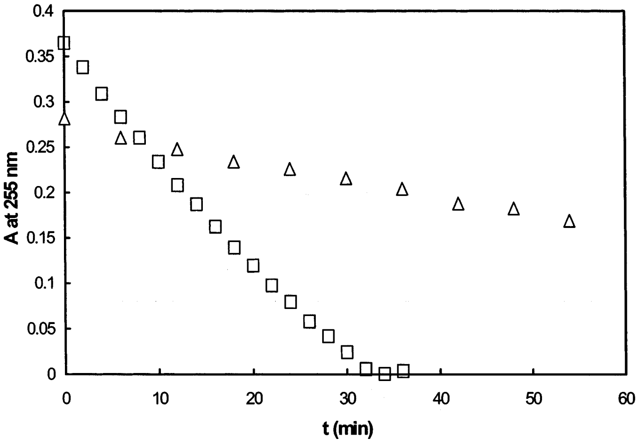


Figure 1. Decay of the absorbance at 255 nm upon γ-radiolysis of an aqueous solution containing initially 10 mM 2-methyl, 2-propanol, 0.11 mM O_3, and 1.3 mM O_2. Dose rate: (△) 0.0077 Gy/s; (□) 0.096 Gy/s.

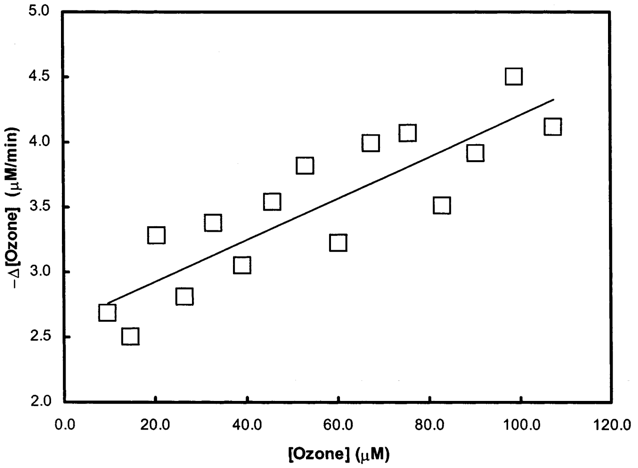


Figure 2. Data from Figure 1 plotted according to eq 17. Dose rate: (□) 0.096 Gy/s.

Reactivity of $HOC(CH_3)_2CH_2OO^{\bullet}$. The (2-hydroxy-2-methyl-1-propyl)peroxyl radical is a prototypical primary peroxyl radical, which in the present work was investigated in detail with respect to its reactivity toward ozone. Figure 1 depicts the time course of ozone consumption in γ-irradiated ozone solutions containing 2-methyl-2-propanol at two dose rates. O_3 consumption during irradiation is partly due to the reduction of O_3 by $O_2^{\bullet-}$ according to reactions 1−6 and 14. As was discussed above, this rate is independent of the concentration of O_3. On the other hand, the rate of reaction 11 is proportional to $[O_3]$. The overall rate of O_3 consumption is described by eq 17. Figure 2 is a plot of eq 17, i.e., a rate versus $[O_3]$ plot. Here, G denotes

$$-d[O_3]/dt = GD + k_{exp}[O_3] \tag{17}$$

the sum of the yields of e^-_{aq} and $H^{\bullet}$, 3.4×10^{-7} M/J and the yield of $O_2^{\bullet-}$ in reaction 14, which according to ref 17 should be ca. 1.2×10^{-7} M/J. D is the dose rate with the value 0.098 J/s. Thus $GD = 4.6 \times 10^{-8}$ M/s. From the intercept in Figure 2 we calculate $G(H^{\bullet}+e^-_{aq}+O_2^{\bullet-}) = (4.6 \pm 0.3) \times 10^{-7}$ M/J, in excellent agreement with the expected value. Clearly, the intercept corresponds to the consumption of O_3 during initiation. The rate of initiation is given by intercept × 6.4/4.6 where 6.4×10^{-7} M/J is the total radiation chemical yield of radicals. The excess ozone consumption in the figure is due to the peroxyl radical destroying ozone. From the figure it is seen that the chain length of the peroxyl radical mediated ozone consumption at all ozone concentrations is below 1. As this value is so much smaller than the $O_2^{\bullet-}$ mediated chain length (see Table 1), termination is achieved exclusively by the alkylperoxyl radical. This was found to be the case with all peroxyl radicals presented in Table 2.

TABLE 2: Rate Constants of Peroxyl Radicals Reacting with Ozone (k_{11} or k_{21}) and Parameters Used for Their Calculation[a]

peroxyl	$10^{-7}G(O_2^-)$, J/kg	$2 \times 10^{-8}\,k_{14}$, $M^{-1}\,s^{-1}$	pH	k_{11}, $M^{-1}\,s^{-1}$
$OOCH_2CO_2^-$	3.9[b]	1.5[b]	4.6	7.8×10^3
$OOCH_2CO_2H$[g]	3.9[b]	>1.5[c]	0	$\geq 2.7 \times 10^4$
$OOCHClCO_2^-$	3.9[b]	1.5[c]	2	1.6×10^4
$OOCH_2COCH_3$	3.4[e]	8[e]	2	$\geq 7.3 \times 10^4$
$OOCH_2C(CH_3)_2(OH)$	4.6[d]	8[d]	2	1.8×10^4
$^-O_3SOO^\bullet$	0	4.4[f]	1.8	1.6×10^5 (k_{21})

[a] Substrate concentrations varied from 1 to 20 mM. [b] Reference 16. [c] See text. [d] Reference 17. [e] Reference 18. [f] $2k_{24}$ taken from ref 32. [g] pK_a = 2.1.[33]

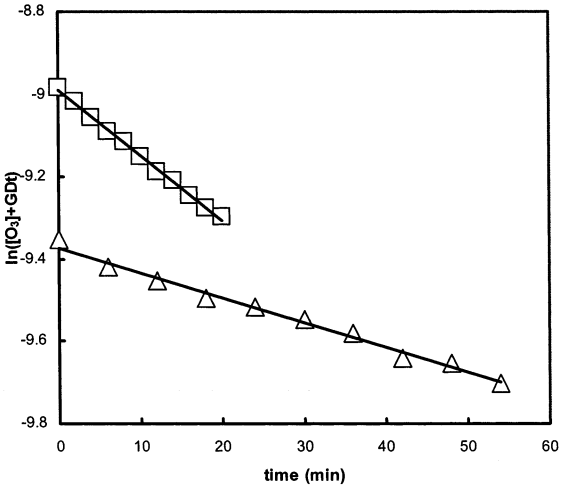


Figure 3. Data from Figure 1 plotted according to eq 19. Dose rate: (□) 0.096 Gy/s; (△) 0.0077 Gy/s.

The slope, k_{exp}, is related to k_{11}, the rate constant of reaction 11, by

$$k_{exp} = 2k_{11}[HOC(CH_3)_2CH_2OO^\bullet]_{ss} \tag{18}$$

$[HOC(CH_3)_2CH_2OO^\bullet]_{ss}$ signifies the steady-state concentration of the alkylperoxyl radical. As each alkylperoxyl radical consumes two O_3 molecules (see above) the factor 2 was included into the equation. Whenever the rate of ozone consumption is low, the data tend to display much scatter and hence the integrated eq 19 provides more accurate results. In

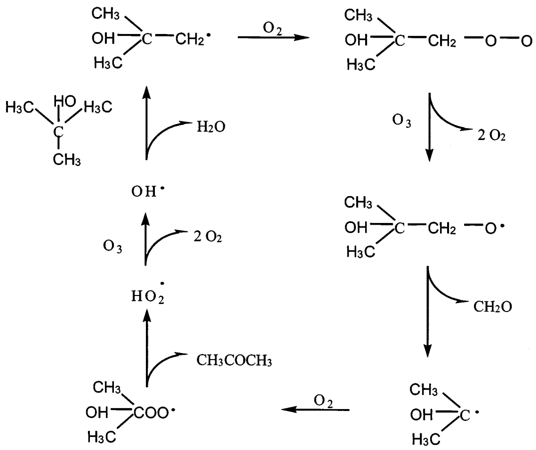
$$\ln([O_3]_{corr}) = \ln[O_3]^\circ + k_{exp}t \tag{19}$$

eq 19 $[O_3]_{corr} = [O_3] + GDt$ and $[O_3]^\circ$ is the initial ozone concentration. Figure 3 presents such plots of the data in Figure 1. As expected, the value of k_{exp}, taken from the slope of Figure 3 (upper curve), is the same as that from Figure 2. Dose rate variation affects the steady-state concentration of $[HOC(CH_3)_2CH_2OO^\bullet]_{ss}$. If the termination of the radicals occurs mainly via second-order recombination we obtain eq 20. Here, $G_R = 6.4$

$$[HOC(CH_3)_2CH_2OO]_{ss} = (G_RD/2k'_{14})^{1/2} \tag{20}$$

$\times 10^{-7}$ M/J, is the yield of alkylperoxyl radicals, D is the dose rate, while k'_{14} denotes k_{14} multiplied by the fraction that does *not* yield $O_2^{\bullet -}$, in the range of ca. 70%. The lower graph of Figure 3 differs from the upper one in that the dose rate, D, in the former plot is lower by a factor of 12. k_{exp} is found to vary by a factor of 2.5, close to 3.5, the expected value. This confirms that the alkylperoxyl radicals do destroy ozone according to reaction 11.

SCHEME 1



Product analysis sheds further light on the nature of reaction 11. During ozone decomposition in irradiated *tert*-butyl alcohol solutions, we measure the formaldehyde yield per ozone consumed, $[CH_2O]/[O_3]^\circ = 0.40 \pm 0.05$. Now it is known that in reaction 14 ca. 30% CH_2O forms, which was thought to derive from an alkoxyl radical formed in the process. Allowing for this CH_2O yield and for that part of ozone consumption that does not occur in reaction 11, i.e., reactions 1, 4, and 14, we calculate that reaction 11 gives rise to $[CH_2O]/[O_3]_o = 1.08 \pm 0.18$. This finding implies that, within experimental uncertainty, the alkoxyl radical formed in reaction 11 undergoes quantitative β-scission, reaction 13, to yield CH_2O and $(HO)((CH_3)_2)C^\bullet$. After reacting with O_2, the latter radical expels $O_2^{\bullet -}$ in reaction 10. Of course, $O_2^{\bullet -}$ destroys an additional O_3 in reaction 4. The net result is thus two O_3 destroyed and one CH_2O formed for every reaction 11 that occurs, as is reflected by the factor 2 in eq 18.

For summarizing the various pathways of the $HOC(CH_3)_2CH_2OO$ radical reacting with ozone, we present Scheme 1.

We have performed additional experiments with a number of alkylperoxyl radicals. Like in Figure 3 the results were plotted according to eq 19. The extracted rate constants, k_{11}, and all pertinent parameters are compiled in Table 2. Some comments are in order. In our calculations we have assumed k_{14} for $^\bullet OOCHClCO_2^-$ and $^\bullet OOCH_2CO_2H$ to be equal to that for $^\bullet OOCH_2CO_2^-$. As $^\bullet OOCH_2CO_2H$ is neutral, we feel that its k_{14} should be close to that of $^\bullet OOCH_2COCH_3$. Thus the derived k_{11} for the former should be a lower limit. The fate of the acetonylalkoxyl radical is not known. Pulse and γ radiolysis[18] on the acetonylperoxyl radical system produce substantial amounts of formaldehyde but almost no $O_2^{\bullet -}$. It was assumed that the acetyl radical formed in high yield. If these products derive from an intermediate acetonylalkoxyl radical, the assumption of a stoichiometric factor of 2 may not be valid, in which case k_{11} may be twice as high as the value in Table 2.

$^-O_3SOO^\bullet$ Radical Reacting with O_3. Although the peroxysulfate radical, $^-O_3SOO^\bullet$, is not an alkylperoxyl radical, we thought it of interest to investigate its reactivity toward O_3. This peroxyl radical is an important chain carrier during the chain autoxidation of SO_2/sulfite in, e.g., atmospheric droplets. The radical was produced at pH 1.8 from 0.02 M peroxysulfate anion, $^-O_3SOOH$, in the presence of 1.3×10^{-3} M O_2 and ca. 10^{-4} M O_3. In this system all primary radicals eventually yield $^-O_3SOO^\bullet$, whose radiation chemical yield is thus 6.4×10^{-7}

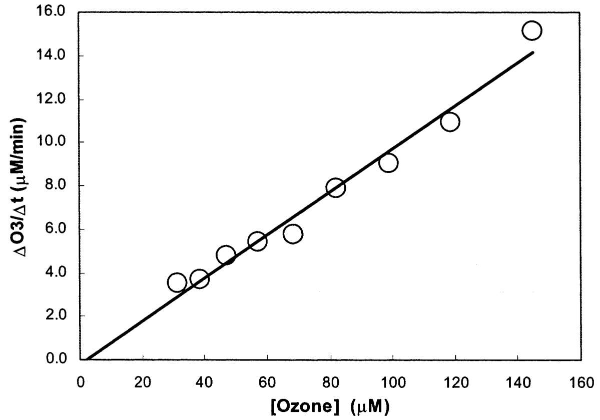


Figure 4. Rate of decay of ozone vs ozone concentration upon γ-radiolysis of an aqueous solution at pH 1.8 containing initially 0.02 M HSO_5^-, 1.3 × 10^{-3} O_2, and ca. 1.5 × 10^{-4} M O_3. Dose rate: 0.075 Gy/s.

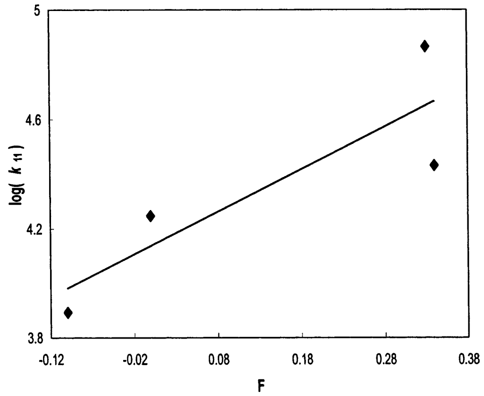


Figure 5. k_{11} plotted against the substituent field effect taken from ref 25.

mol/J. $^-O_3SOO^\bullet$ and $SO_4^{-\bullet}$ will then set up a chain reaction with O_3 as follows.

$$\mathrm{{}^-O_3SOO^\bullet + O_3 \rightarrow SO_4^{\bullet-} + 2O_2} \tag{21}$$

propagation

$$\mathrm{SO_4^{\bullet-} + {}^-O_3SOOH \rightarrow HSO_4^- + {}^-O_3SOO^\bullet} \qquad k_{22} = 1.0 \times 10^6\ \mathrm{M^{-1}\,s^{-1}}\ {}^{32} \tag{22}$$

$$\mathrm{2\,{}^-O_3SOO^\bullet \rightarrow 2SO_4^{\bullet-} + O_2} \qquad 2k_{23} = 4.2 \times 10^8\ \mathrm{M^{-1}\,s^{-1}}\ {}^{32} \tag{23}$$

termination

$$\mathrm{2\,{}^-O_3SOO^\bullet \rightarrow S_2O_8^{2-} + O_2} \qquad 2k_{24} = 4.4 \times 10^8\ \mathrm{M^{-1}\,s^{-1}}\ {}^{32} \tag{24}$$

We assume that the $SO_4^{-\bullet}$ radical is essentially unreactive toward O_3 in the present conditions. This is reasonable considering that the kindred $CO_3^{\bullet-}$ radical was shown to be inert toward ozone.[23,24] We can utilize eq 17, where $k_{\exp} = k_{21}[{}^-O_3SOO^\bullet]_{ss}$ and $[{}^-O_3SOO^\bullet]_{ss} = (G_RD/2k_{24})^{1/2}$. Note that here every peroxyl radical consumes only one O_3. Figure 4 shows a differential plot according to eq 17. The small intercept shows that no ozone is consumed by the primary radicals derived from water. The k_{21} value was extracted from the slope and is also presented in Table 2.

Mechanism of Reaction. The rate constants of O_3 reacting with the various alkylperoxyl radicals studied in this work are not very sensitive toward the nature of the alkyl group, all of them lying between 10^4 and 10^5 M^{-1} s^{-1}. Nevertheless, as clearly transpires from Figure 5, one can discern a trend in the response of the rate constant to the substituent on the alkyl group. As the figure presents $\log(k_{11})$ as a function of F, the modified Swain−Lupton constant,[25] it would appear that the more inductively electron withdrawing is the substituent, the larger is the rate constant. How is one to interpret this trend? First we note that the overall reaction 11 is extremely exothermic, with $\Delta H^\circ_{11} \approx -170$ kJ/mol. There can, however, be little doubt that the reaction does not occur in one step but proceeds at least via one intermediate, the alkyl trioxide radical, $ROOO^\bullet$, according to reactions 25 and 26. According to this model

$$\mathrm{ROO^\bullet + O_3 \rightarrow ROOO^\bullet + O_2} \tag{25}$$

$$\mathrm{ROOO^\bullet \rightarrow RO^\bullet + O_2} \tag{26}$$

reaction 25 should be the rate-determining step, followed by a very rapid expulsion of O_2 in reaction 26. The thermochemistry of reaction 25 is not known experimentally but has been estimated previously.[26,27] We also investigated this reaction by means of quantum chemical calculations, using the substituents, R = CH_3 and $CH_2C(O)H$. It was confirmed that the reaction proceeds in a two-step process according to eqs 25 and 26, with reaction 25 being the rate-determining step. The enthalpy of activation for reaction 25 was computed to be 54 kJ/mol at the G2X level. No significant substituent effect on the activation enthalpy was observed at this level of theory. However, the preexponential factor in reaction 11 can hardly exceed 10^{10} M^{-1} s^{-1}. Combining this value and the calculated enthalpy of activation yields a maximum k_{11} of ≈10 M^{-1} s^{-1}. There is thus a significant discrepancy between calculated and experimental k_{11}, the latter being 10^4 to 10^5 M^{-1} s^{-1}. In addition, it was found that the computational results are extremely sensitive to the method. Computations at the B3LYP/6-311+(3df,2p)//B3LYP/6-31+G* level gave the significantly lower activation enthalpy of 8.9 kJ/mol. This makes it difficult to predict the exact mechanism of reaction 25 by means of theory. Conceivably, there might exist a fleeting intermediate, $RO_5^\bullet$, in equilibrium with RO_2 and O_3 according to

$$\mathrm{RO_2^\bullet + O_3 \rightleftarrows [RO_5^\bullet] \rightarrow RO_3^\bullet + O_2}$$

If this assumed equilibrium is shifted to the right by electron-withdrawing substituents, the trend in Figure 5 can be rationalized.

Role of Peroxyl Radicals in Ozone Chemistry. The present work provides the first clear-cut evidence for the reaction of alkylperoxyl radicals with ozone in aqueous solution. We note that our aqueous values are in good agreement with the previously determined, if somewhat uncertain, gas phase value[2] for $CH_3OO^\bullet$. This suggests that the reaction is not subject to significant solvent effects. An important exception is the $HOO^\bullet$ radical. In the gas phase, reaction 6 is more rapid by ca. 2 orders of magnitude than our measured value in water. It has been shown[28,29] that reaction 6 in the gas phase is a hydrogen atom transfer, a reaction mode that is not possible with alkylperoxyl radicals (reaction 11). In hydrogen-bonding solvents hydrogen bonding between solvent and the hydrogen to be transferred has been shown[30] to slow the rate of the reaction by up to 2 orders of magnitude. Thus a rate constant of a few times 10^4 M^{-1} s^{-1} in water is to be expected. Even though we could demonstrate a substituent effect for alkylperoxyl radicals, it turns out to be slight. In atmospheric chemistry the alkylperoxyl radical with the most electron-withdrawing substituent should be $CF_3OO^\bullet$. Now, our rate constant for R = $^-O_2CCHCl$ reveals that an α-Cl atom has very little effect on the rate (see Table 2). From this comparison and assuming similar effects for Cl and F, we estimate k_{11} for $CF_3OO^\bullet$ to be no higher than ca. 10^5 M^{-1} s^{-1}. This agrees with a previously established[31] upper limit of 3×10^6 M^{-1} s^{-1} for this radical. In conclusion, our work confirms experimentally that alkylperoxyl radicals react with ozone fairly slowly. It would thus seem that this reaction is of negligible practical importance in atmospheric ozone chemistry. On the other hand, in many technical ozone-based aqueous processes, e.g., water purification, this reaction probably has to be considered for a quantitative description of the system. This becomes the more important the slower O_3 reacts with the primary substrates to be destroyed.

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