

ARTICLES

Determination of $\cdot\text{OH}$, $\text{O}_2^{\cdot-}$, and Hydroperoxide Yields in Ozone Reactions in Aqueous Solution[†]

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In ozone reactions in aqueous solutions, $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$ are often generated as short-lived intermediates and hydroperoxides are formed as labile or stable final products. Tertiary butanol reacts with ozone only very slowly but readily with $\cdot\text{OH}$. In the presence of dioxygen, formaldehyde is a prominent final product, $30 \pm 4\%$, whose ready determination can be used as an assay for $\cdot\text{OH}$. Although dimethyl sulfoxide reacts much more readily with ozone, its fast reaction with $\cdot\text{OH}$ which gives rise to methanesulfinic acid can also be applied for the determination of $\cdot\text{OH}$, at least in fast ozone reactions. The formation of $\text{O}_2^{\cdot-}$ can be assayed with tetranitromethane (TNM), which yields nitroform anion (NF^-) at close to diffusion-controlled rates. TNM is stable in neutral and acid solution but hydrolyzes in basic solution ($k = 2.7 \text{ M}^{-1} \text{ s}^{-1}$), giving rise to NF^- plus nitrate ion (62%) and CO_2 plus 4 nitrite ions (38%). TNM reacts with O_3 ($k = 10 \text{ M}^{-1} \text{ s}^{-1}$), yielding 4 mol of nitrate (plus CO_2) and 4 mol of O_3 are consumed in this reaction. NF^- reacts with O_3 ($k = 1.4 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$) by O-transfer. The resulting products, $(\text{NO}_2)_3\text{CO}^-$ and $(\text{NO}_2)_2\text{C}=\text{O}$, rapidly hydrolyze ($k > 10 \text{ s}^{-1}$), and most of the nitrite released is further oxidized by ozone to nitrate. In the case of slow ozone reactions, these reactions have to be taken into account; i.e. the NO_3^- yield has to be measured as well. For the determination of hydroperoxides, Fe^{2+} -based assays are fraught with considerable potential errors. Reliable data may be obtained with molybdate-activated iodide. The kinetics of this reaction can also be used for the characterization of hydroperoxides. Reactive hydroperoxides undergo rapid O-transfer to sulfides, e.g., $k(\text{HC}(\text{O})\text{OOH} + (\text{HOCH}_2\text{CH}_2)_2\text{S}) = 220 \text{ M}^{-1} \text{ s}^{-1}$, and the corresponding reaction with methionine may be used for their quantification (detection of methionine sulfoxide by HPLC). Distinction of organic hydroperoxides and H_2O_2 by elimination of the latter by reaction with catalase can often be used with advantage but fails with formic peracid, which reacts quite readily with catalase ($k = 1.3 \times 10^{-3} \text{ dm}^3 \text{ mg}^{-1} \text{ s}^{-1}$). Some examples of $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$ formation in ozone reactions are given.

Introduction

Ozonolysis is gaining importance in drinking water and wastewater processing. In arid countries, where drinking water resources are scarce, it is widely used in the so-called reclamation process, where wastewater is processed in several steps for reuse as drinking water. Besides acting as an oxidant, it is a very good disinfectant that copes readily with viruses and

bacteria.^{1,2} In many aspects, it can hence substitute chlorine. Obviously, the chlorination byproducts such as trihalomethanes, which limit the use of chlorine, are not formed upon ozonolysis, but there must be also unwanted byproducts which have not yet been elucidated in detail.^{2,3}

Surprisingly little is known at present about the reactions of ozone in aqueous solutions, and a detailed knowledge of these reactions is a prerequisite for any further evaluation of a wider application of ozone, especially in the reclamation technology.

In the case of simple olefins, the Criegee mechanism⁴ is practically strictly followed; i.e. 1 mol of carbonyl compound and 1 mol of α -hydroxyhydroperoxide are formed per mol of ozone.⁵ In these reactions, no free radicals are generated.

On the other hand, in the reaction of ozone with amines, including the chelators NTA and EDTA, a nonnegligible pathway proceeds via $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$ radicals as intermediates.⁶ An example where $\cdot\text{OH}$ formation becomes the only process is the reaction of H_2O_2 with ozone. This reaction has found quite

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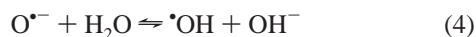
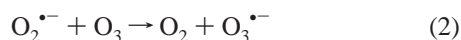
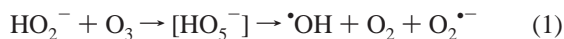
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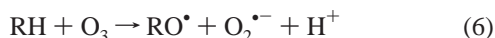
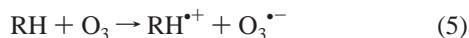
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some interest considering its potential to eliminate ozone-refractory compounds in drinking water processing with the help of the highly reactive $\bullet\text{OH}$ radical (for reviews see, e.g., refs 7 and 8; for compilations of ozone and $\bullet\text{OH}$ rate constants see refs 9 and 10, respectively).

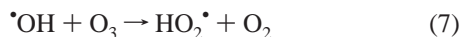
At low pH, where H_2O_2 predominates ($\text{p}K_{\text{a}}(\text{H}_2\text{O}_2) = 11.6$), the reaction is slow ($\leq 0.01 \text{ M}^{-1} \text{ s}^{-1}$,¹¹ $k = 0.036 \text{ M}^{-1} \text{ s}^{-1}$),¹² and in neutral solutions the reaction is mainly governed by the fast reaction of HO_2^- in equilibrium ($k = 5.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$).¹¹ The initiation step may proceed via a short-lived adduct (a hydropentoxide anion) which decomposes into $\bullet\text{OH}$, O_2 , and $\text{O}_2^{\bullet-}$ (reaction 1). The subsequent reaction of $\text{O}_2^{\bullet-}$ with ozone is very fast (reaction 2, $k = 1.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$).^{13,14} The ozonide radical anion is only stable at very high pH (equilibrium 3, $k_3 = 2.1 \times 10^3 \text{ s}^{-1}$, $k_{-3} = 3.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$).¹⁵ Due to the fast protonation of $\text{O}^{\bullet-}$ by water (equilibrium 4; $\text{p}K_{\text{a}}(\bullet\text{OH}) = 11.8$),¹⁰ equilibrium 4 is rapidly drawn to the left at neutral pH ($k_4 \approx 10^8 \text{ s}^{-1}$). As a consequence, $\bullet\text{OH}$ is formed at $\text{pH} \geq 7$ approximately at the same rate as $\text{O}_3^{\bullet-}$ decays (reaction 3). In acid solutions and in neutral solution in the presence of buffer, $\text{O}_3^{\bullet-}$ is protonated and $\bullet\text{OH}$ formation is caused via the short-lived HO_3^{\bullet} radical.¹³



The reaction of ozone with organic substrates can lead to $\text{O}_3^{\bullet-}$ (by electron transfer, reaction 5) and to $\text{O}_2^{\bullet-}$ (by an addition/elimination process, reaction 6). Both processes lead to the formation of $\bullet\text{OH}$ (cf. reactions 2–4).



The situation can become very complex at low substrate concentrations, since $\bullet\text{OH}$ reacts rapidly with ozone (reaction 7, $k = 1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$)⁹ and thus can initiate a chain reaction with $\text{HO}_2^{\bullet}/\text{O}_2^{\bullet-}$ as intermediates (cf. equilibrium 8, $\text{p}K_{\text{a}}(\text{HO}_2^{\bullet}) = 4.8$).¹⁶ This chain reaction may lead to an unwanted self-destruction of ozone.



For a better understanding of ozone reactions in water, $\bullet\text{OH}$ and $\text{O}_2^{\bullet-}$ yields have to be known. For monitoring $\bullet\text{OH}$ formation, one approach is to follow the consumption of an added ozone refractory compounds.^{17,18} This procedure has the advantage that the low additive concentration does not essentially alter the progress of the reaction, but it has also the disadvantage that the ensuing reactions of the $\bullet\text{OH}$ radical are not effectively suppressed.

In the present study, we follow a different approach. The addition of a large excess of tertiary butanol which readily reacts with $\bullet\text{OH}$ (cf. reactions 10 and 11, $k_{10,11} = 6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$)¹⁰ but is practically inert against ozone ($k = 1 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$)¹⁹ and $3 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$)²⁰ allows us to scavenge all $\bullet\text{OH}$ and to

follow the reaction by measuring one of the ensuing products, formaldehyde (for details see below). Alternatively, dimethyl sulfoxide (DMSO) may be used as $\bullet\text{OH}$ scavenger (cf. reaction 21). Methanesulfinic acid is the measured product. This approach is limited to highly ozone-reactive substrates, since DMSO itself reacts with ozone with a rate constant of $8.2 \text{ M}^{-1} \text{ s}^{-1}$.⁹

The formation of $\text{O}_2^{\bullet-}$ is readily detected by its fast reaction with tetranitromethane (TNM, reaction 9, $k = 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$)²² by measuring the formation of the nitroform anion, $\text{C}(\text{NO}_2)_3^-$ (NF^- , $\epsilon(350\text{nm}) = 15\,000 \text{ M}^{-1}\text{cm}^{-1}$), a common technique in peroxy radical chemistry²³ but also applied to ozone chemistry.²⁴



In the present paper, it will be shown that in ozone reactions the latter assay is not as straightforward as in peroxy radical chemistry, and the rapid reactions of ozone with NF^- as well as NO_2^{\bullet} (a further product) have to be taken into account. Furthermore, the characterization and quantification of hydroperoxides which are common products in ozone reactions will be reported, and a number of ozone reactions will be described, where $\bullet\text{OH}/\text{O}_2^{\bullet-}$ play an important role.

Although our prime aim is a better understanding of the reactions that prevail in drinking water processing, some of our data must also be helpful for the elucidation of ozone reactions in clouds.

Experimental Section

Ozone was generated with a dioxygen-fed ozonator (Philaqua Philoz 04, Gladbeck). The ozone content of the aqueous ozone stock solutions was determined spectrophotometrically using ϵ -(260nm)^{25,26} = $3300 \text{ M}^{-1} \text{ cm}^{-1}$. Solutions were made up in Milli-Q-filtered (Millipore) water. Formaldehyde was determined by the Hantzsch method.²⁷ In this assay, 2 mL of reagent (0.2 mL of acetylacetone, 3 mL of acetic acid, and 25 g of ammonium acetate in 100 mL of water) are mixed with 5 mL of the sample, heated for 30 min at 50°C in the dark. The absorbance at 412 nm is read ($\epsilon = 7530 \text{ M}^{-1} \text{ cm}^{-1}$). Alternatively, formaldehyde can be determined by HPLC of its 2,4-dinitrophenylhydrazone.²⁸ Here, 0.2 mL of a 9 mM solution of 2,4-dinitrophenylhydrazine in acetonitrile is mixed with 0.1 mL of 1 M perchloric acid in acetonitrile and 1.7 mL of the sample. After standing for 45 min in the dark, the solution is chromatographed on a C-18 reversed phase column with acetonitrile/water (1:1). This method is reported to be generally applicable for the determination of aldehydes and ketones, but it failed to give reliable results in the $\text{H}_2\text{O}_2/\text{O}_3$ /tertiary butanol system (see below). An assignment of the various aldehydes and ketones in a reaction mixture can be done by gas chromatography/mass spectrometry.²⁹ The most prominent peaks of the mass spectra (CH5, Finnigan MAT) of the 2,4-dinitrophenylhydrazones of the carbonylic products that arise from the oxidation of tertiary butanol are as follows. Formaldehyde-2,4-DNPH. MW: 210. m/z (%): 210 (58), 180 (18), 152 (8), 122 (17), 106 (9), 91 (25), 89 (26), 79 (100), 63 (99), 51 (64). Acetone-2,4-DNPH. MW: 238. m/z (%): 238 (100), 222 (6), 208 (6), 181 (38), 152 (36), 122 (24), 115 (35), 105 (20), 91 (34), 79 (86), 59 (86). 2-Hydroxy-2-methylpropionaldehyde-2,4-DNPH. MW: 268. m/z (%): 268 (28), 253 (3.5), 225 (31), 203 (7), 183 (9), 164 (13), 148 (5), 59 (81), 55 (83) 43 (100).

Nitrite/nitrate and methanesulfinate/methanesulfonate were analyzed by ion chromatography (Dionex DX-100; AS-14; eluent, $4.75 \times 10^{-4} \text{ M Na}_2\text{CO}_3/4.63 \times 10^{-4} \text{ M NaHCO}_3$).³⁰

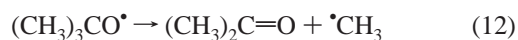
For the study of the destruction of H_2O_2 and formic peracid, 10 μL of catalase (from beef liver, Boehringer Mannheim) was added per 10 mL of sample. Formic peracid was generated by the ozonolysis of an aqueous solution 1,2-dichloroethene (cf. ref 5).

To follow the reaction of H_2O_2 with iodide, the absence of dioxygen had to be ensured. Deoxygenated solutions were placed into a spectrophotometric quartz cell which could be further purged with argon (cf. ref 31), but the inlet tube did not fully reach the bottom for the analyzing light of the UV spectrophotometer (Lambda 16, Perkin-Elmer) to pass through the cell. A serum cap allowed the injection of small amounts of reactants. The reactions of hydroperoxides with aqua- Fe^{2+} have been monitored at 305 nm ($\epsilon = 2095 \text{ M}^{-1} \text{ cm}^{-1}$) and those with $\text{Fe}(\text{CN})_6^{4-}$ at 420 nm ($\epsilon = 1020 \text{ M}^{-1} \text{ cm}^{-1}$).

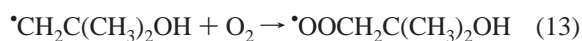
Stopped-flow experiments were carried out using a Biologic SFM3 setup. Conductance changes were measured with a conductometer (CDM3, Radiometer).

Results and Discussion

Tertiary Butanol System. Hydroxyl radicals react with tertiary butanol by abstracting an H-atom mainly from carbon (95%) and, to a much lesser extent, from oxygen (reactions 10 and 11).³² The tertiary butoxyl radical rapidly decomposes by β -fragmentation into acetone and a methyl radical (reaction 12, $k = 1.4 \times 10^6 \text{ s}^{-1}$,³³ cf. also ref 34).



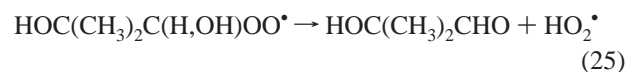
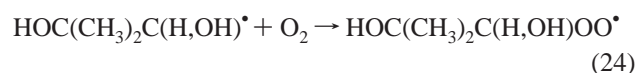
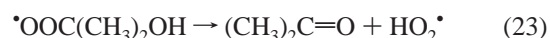
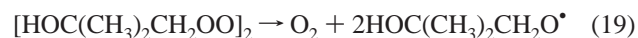
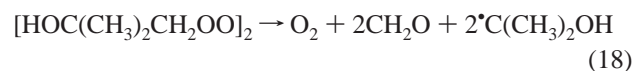
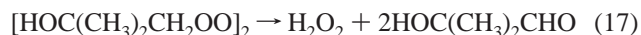
In the presence of dioxygen, the alkyl radicals add dioxygen, yielding the corresponding peroxy radicals (reactions 13 and 14). As with other simple alkyl radicals,^{23,35} the rate of these reactions must be close to diffusion controlled ($k \approx 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$).



The chemistry of methylperoxy radical has been investigated in some detail,³⁶ but since it plays only a minor role here, it will no longer be discussed.

The alkyl peroxy radicals decay bimolecularly, whereby a tetroxide is formed as a short-lived intermediate (reaction 15; for a review on peroxy radical reaction in aqueous solution see ref 23). In the case of the tertiary-butanol-derived peroxy radicals,³⁷ reaction 16 leads to dioxygen, 2-methyl-2-hydroxypropanol, and 2-methyl-2-hydroxypropanal, while reaction 17 gives rise to hydrogen peroxide and 2 mol of 2-methyl-2-hydroxypropanal. These reactions are concerted processes and do not proceed via free radical intermediates. The third reaction pathway leads to the formation of 2 mol of formaldehyde, 1 mol of dioxygen, and 2 mol of 2-hydroxyprop-2-yl radicals in a concerted reaction (cf. ref 38; reaction 18). The same products may be formed via oxyl radicals (reactions 19 and 20). The 2-hydroxyprop-2-yl radical readily adds to dioxygen (reaction 22), and this reaction is followed by a fast elimination of $\text{HO}_2\cdot$ (reaction 23, $k = 650 \text{ s}^{-1}$).³⁹ In competition with the β -fragmentation reaction 20, the 1,2-H-shift reaction 21 may also occur, although recently suggested⁴⁰ to be at the most minor in

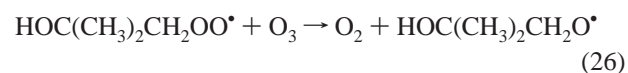
comparison to reaction 20. If reaction 21 contributes, it would lead to the formation of 2-hydroxy-2-methylpropanal and $\text{HO}_2\cdot$ (reactions 24 and 25).



In competition with the unimolecular reaction 25, the peroxy radicals $\text{HOC}(\text{CH}_3)_2\text{C}(\text{H},\text{OH})\text{OO}\cdot$ may undergo bimolecular decay processes, leading to, e.g., the formation of 2-hydroxy-2-methylpropionic acid.⁴¹ Thus, the product yields will vary somewhat with the experimental conditions, notably the rate of radical generation.

The yields of the main products, formaldehyde, acetone, 2-hydroxy-2-methylpropanal, and 2-methyl-2-hydroxypropanol, have been determined in the radiolytic study.³⁷ However, the formation of considerable amounts of $\text{HO}_2\cdot/\text{O}_2^{\cdot-}$ in this system which also interact with the tertiary-butanol-derived peroxy radicals prevents a quantitative comparison with the present system, where any $\text{O}_2^{\cdot-}$ formed in the course of the tertiary-butanol-derived peroxy radicals are immediately converted into further $\cdot\text{OH}$ by ozone (cf. reactions 2–4). The regeneration of $\cdot\text{OH}$, however, does not lead to an efficient chain reaction because of the two competing pathways 16 and 17.

It has been recently shown that the tertiary-butanol-derived peroxy radicals react with ozone in competition with their bimolecular decay.⁴⁰ This leads to the formation of oxyl radicals (reaction 26) and consequently to an increase in the yields of formaldehyde and 2-hydroxy-2-methylpropanal (cf. reactions 20, 21, and 25).⁴¹



Reaction 26 is slow ($k = 1.8 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$)⁴⁰ and has to compete with the bimolecular decay of the tertiary-butanol-derived peroxy radicals ($2k = (8 \pm 2) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$).³⁷ Moreover, alkyl radical also reacts with ozone at a rate comparable to that of dioxygen.⁴² This reaction gains in importance at high $[\text{O}_3]/[\text{O}_2]$ ratios. Details have been discussed elsewhere.⁴¹

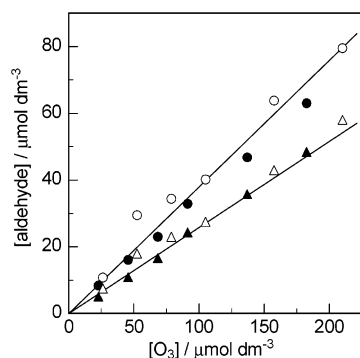


Figure 1. Formation of formaldehyde (▲, △) and 2-hydroxy-2-methylpropanal (●, ○) in the reaction of ozone with H_2O_2 (0.5 mM) in the presence of tertiary butanol (10 mM). Closed and open symbols are from two sets of experiments.

In the radiolytic system, the formaldehyde yield was found to be $\sim 25\%$ of $\cdot\text{OH}$, and the ratio of the 2-hydroxy-2-methylpropanal and formaldehyde yields was ~ 1.5 .³⁷ We have now determined the formaldehyde and 2-hydroxy-2-methylpropanal yields in the ozone/hydrogen peroxide/tertiary butanol system (variation of $[\text{H}_2\text{O}_2] = 0.5$ mM and 1 mM; [tertiary butanol] = 10 and 20 mM, respectively). According to our experience, yield data in ozone reactions are fraught with a somewhat higher intrinsic error (poorer dose yield plots, poorer day-to-day reproducibility) than radiolytic yield data. Because of the importance of these data for establishing an $\cdot\text{OH}$ probe in ozone reactions, we have measured these yields many times, and we obtain $30 \pm 4\%$ for the formaldehyde yield and a value of 1.3–1.4 for the 2-hydroxy-2-methylpropanal-to-formaldehyde ratio (cf. Figure 1).

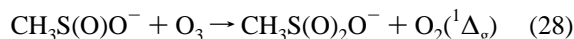
We have also tried to quantify the other carbonylic products, acetone as 2,4-dinitrophenylhydrazone. It turns out that the method reported by Lipari and Swarin²⁸ allows an accurate determination of the aldehydes but fails to determine acetone adequately in this mixture of carbonylic products (its yield comes out too low with respect to the formaldehyde yield). When the reagent concentration is raised 3-fold (a further increase would impede the quantification of 2-methyl-2-hydroxypropanal due to an overlap with the tail of the reagent peak), formaldehyde and acetone yields approach one another, but even with this improvement the method is not recommended for quantification of acetone in our system.

However, for the quantification of $\cdot\text{OH}$ formation in ozone reactions by its scavenging with tertiary butanol it usually suffices to determine the formaldehyde yield formed in reactions 18 and 20 by the fast Hantzsch method.²⁷ If colored products or educts interfere with this assay, one always can use HPLC of the 2,4-dinitrophenylhydrazones as discussed above.

Dimethyl Sulfoxide System. In the reaction of $\cdot\text{OH}$ with dimethyl sulfoxide (DMSO), methanesulfonic acid is formed in 92% yield (reaction 27).²¹



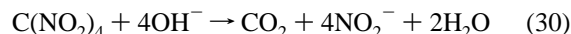
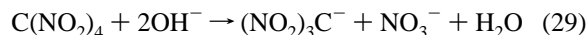
Methanesulfonic acid is readily detected by ion chromatography (see Experimental Section) or by a sensitive spectrophotometric assay.⁴³ The use of DMSO as $\cdot\text{OH}$ scavenger in ozone reactions has the disadvantage that DMSO reacts reasonably fast with ozone ($k = 8.2 \text{ M}^{-1} \text{ s}^{-1}$), and also the product of reaction 27, the methanesulfinate ion, is rapidly further oxidized by ozone to methanesulfonate in an O-transfer reaction (reaction 28, $k = 2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$),⁴⁴ with singlet dioxygen $\text{O}_2(^1\Delta_g)$ as the other product.^{44,45}



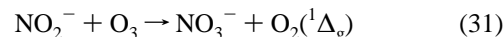
This and other side reactions are of little consequence when ion chromatography is used to assay the formation of methanesulfonic acid, since methanesulfonic acid elutes nearby (see Experimental Section), and their combined yields allow conclusions as to the yield of $\cdot\text{OH}$ formation. It will be shown below that the determination of methanesulfonic acid is a prerequisite for the exact determination of $\cdot\text{OH}$ yields in ozone reactions by the DMSO method. In fact, major parts of the methanesulfonic acid formed may undergo autooxidation, possibly induced by peroxy radicals (see below).

Tetranitromethane/Nitroform Anion System. For the use of tetranitromethane as an $\text{O}_2^{\cdot-}$ scavenger in ozone reactions, it is of importance to know the ozone rate constants with TNM and that with the primary product, the nitroform anion (NF^-). Moreover, the reaction products of ozone with TNM and NF^- may also react with ozone, and for this reason these products and their yields must be known as well. To generate NF^- , the hydrolysis of TNM is the most convenient method. However, in the literature there are conflicting reports as to the products.^{46,47} This required a reinvestigation of the hydrolysis of TNM which is reported next.

Hydrolysis of Tetranitromethane. TNM is stable in acid and neutral solutions but hydrolyzes quite rapidly in basic solutions.^{46,47} While the earlier study⁴⁶ reports that the hydrolysis takes two routes, an OH^- -attack at nitrogen which yields the NF^- and nitrate (reaction 29) and an OH^- -attack at carbon which leads to the formation of CO_2 and nitrite (reaction 30), in ref 47 only the former route is considered.



For the present study, it was most important to know to which extent reaction 30 takes place, because in this reaction nitrite is formed which reacts very fast with ozone by O-atom transfer (reaction 31, $k = 3.7 \times 10^5$,⁴⁸ $(3.5\text{--}4.0) \times 10^5$,⁴⁹ and $6.08 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$,⁵⁰ for the formation of $\text{O}_2(^1\Delta_g)$, see ref 45).



After completion of the hydrolysis of TNM, we find $[\text{NO}_3^-]/[\text{NO}_2^-] = 0.4$ and an NF^- yield of 62%, in good agreement with the earlier report.⁴⁶ In this context, the rate of TNM hydrolysis was redetermined by following the build-up of NF^- as a function of the OH^- concentration. In these experiments, the OH^- concentration was always in large excess over the TNM concentration (ensuring first-order kinetics), and from the data shown in Figure 2 a rate constant of $k = 0.27 \text{ M}^{-1} \text{ s}^{-1}$ is obtained. The reported⁴⁷ value of $0.4 \text{ M}^{-1} \text{ s}^{-1}$ (at 25°C) is in reasonable agreement with our data (for a compilation of rate constants determined in the present study, see Table 1).

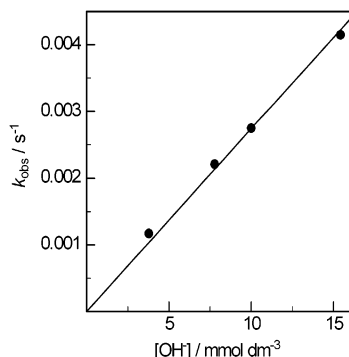
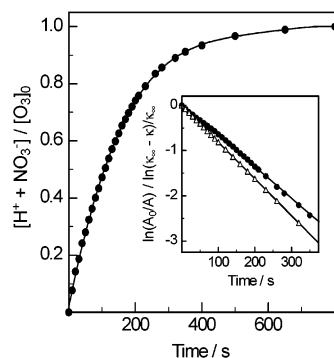
Reaction of Tetranitromethane with Ozone. TNM reacts slowly with ozone. The reaction has been followed spectrophotometrically at 260 nm as well as by changes in conductance as a function of time (Figure 3). From these data, rate constants of $k = 10.2$ (conductometry) and $9.9 \text{ M}^{-1} \text{ s}^{-1}$ (spectrophotometry) are calculated. Their mean value of $10 \text{ M}^{-1} \text{ s}^{-1}$ is given in Table 1.

This rate constant is low when compared with many other ozone rate constants, but noticeably higher than the one with tertiary butanol mentioned above and in the range of rate

TABLE 1: Compilation of Rate Constants ($\text{M}^{-1} \text{s}^{-1}$) Determined in the Present Study and Related Values Taken from the Literature

reaction	k	ref
$\text{C}(\text{NO}_2)_4 + \text{OH}^- \rightarrow \text{products}$	0.27 (20 °C)	this work
	0.4 (25 °C)	47
$\text{C}(\text{NO}_2)_4 + \text{O}_3 \rightarrow \text{products}$	10	this work
$\text{C}(\text{NO}_2)_3^- + \text{O}_3 \rightarrow \text{products}$	1.4×10^4	this work
$(\text{NO}_2)_2\text{C}=\text{O} + \text{H}_2\text{O} \rightarrow 2\text{HNO}_2 + \text{CO}_2$	$> 10 \text{ s}^{-1}$	this work
$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \text{OH}^-$	48 (18 °C)	this work
	60 (25 °C)	51
$\text{Fe}^{2+} + \text{HOCH}_2\text{OOH} \rightarrow \text{Fe}^{3+} + \text{HOCH}_2\text{O}\cdot + \text{OH}^-$	39 (18 °C)	this work
$\text{Fe}^{3+} + t\text{-BuOOH} \rightarrow \text{Fe}^{3+} + t\text{-BuO}\cdot + \text{OH}^-$	13 (18 °C)	this work
$\text{HC}(\text{O})\text{OOH} + (\text{HOEt})_2\text{S} \rightarrow \text{HC}(\text{O})\text{OH} + (\text{HOEt})_2\text{SO}$	220	this work
$\text{HC}(\text{O})\text{OOH} + \text{HOEtSSEtOH} \rightarrow \text{HC}(\text{O})\text{OH} + \text{HOEtS}(\text{O})\text{SEtOH}$	10	this work
$\text{HC}(\text{O})\text{OOH} + 2\text{Fe}(\text{CN})_6^{4-} \rightarrow \text{HC}(\text{O})\text{OH} + 2\text{Fe}(\text{CN})_6^{3-} + 2\text{H}^+$	4.3	this work
$\text{HC}(\text{O})\text{OOH} + \text{catalase} \rightarrow \text{products}$	$(1.3 \times 10^{-3})^a$	this work
$\text{H}_2\text{O}_2 + \text{I}^-/\text{molybdate-activated} \rightarrow \text{I}_3^-$	2.1	5
$\text{H}_2\text{O}_2 + \text{I}^- \rightarrow \text{I}_3^-$	very slow	52
	1.8×10^{-3}	this work
$\text{HC}(\text{O})\text{OOH} + \text{I}^-/\text{molybdate-activated} \rightarrow \text{I}_3^-$	1.7×10^3	5
$\text{HC}(\text{O})\text{OOH} + \text{I}^- \rightarrow \text{I}_3^-$	1.7×10^3	this work
$\text{HOCH}_2\text{OOH} + \text{I}^-/\text{molybdate-activated} \rightarrow \text{I}_3^-$	2.6×10^{-2}	5
$\text{CH}_3\text{CH}(\text{OH})\text{OOH} + \text{I}^-/\text{molybdate-activated} \rightarrow \text{I}_3^-$	0.39	5
$(\text{CH}_3)_2\text{C}(\text{OH})\text{OOH} + \text{I}^-/\text{molybdate-activated} \rightarrow \text{I}_3^-$	1.5×10^{-4}	5
5-hydroperoxy-5-methylhydantoin + $\text{I}^- \rightarrow \text{I}_3^-$	7.5	53

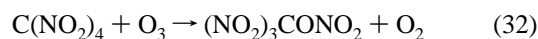
^a In units of $\text{dm}^3 \text{mg}^{-1} \text{s}^{-1}$.

**Figure 2.** Hydrolysis of tetranitromethane at 20 °C. Rate of nitroform formation as a function of the OH^- concentration.**Figure 3.** Reaction of ozone ($7.2 \times 10^{-5} \text{ M}$) with tetranitromethane ($6.7 \times 10^{-4} \text{ M}$) as a function of time as followed by the buildup of conductance, starting at pH 5. Inset: first-order plot of these data (●) and of data (Δ), where the rate of reaction was followed by the decay of the 260 nm absorption of ozone ($[\text{O}_3] = 4.5 \times 10^{-5} \text{ M}$; [tetranitromethane] = $8.2 \times 10^{-4} \text{ M}$) at pH 3.

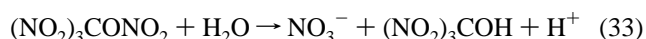
constants of H-abstraction reactions of saturated compounds having activated C–H functions or olefins deactivated by electron-withdrawing substituents. Thus, this reaction deserves some further comments.

In the reaction of TNM with ozone, 4 mol of ozone is consumed and 4 mol of nitrate ion is formed ($\text{C}(\text{NO}_2)_4 + 4\text{O}_3 + 2\text{H}_2\text{O} \rightarrow 4\text{HNO}_3 + 4\text{O}_2 + \text{CO}_2$). This is shown by

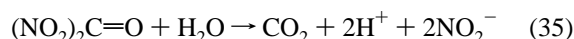
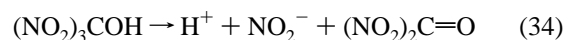
conductance measurements (Figure 3) and by ion chromatography. The formation of NF^- is not observed, and nitrite yields are very small ($< 2\%$ of nitrate). It is tentatively suggested that this reaction proceeds by a bipolar addition of ozone at nitrogen. The subsequent elimination of dioxygen may be followed by a rearrangement into trinitromethyl nitrate (reaction 32).



Nitrate is a better leaving group than nitrite, and it is expected that $(\text{NO}_2)_3\text{CONO}_2$ hydrolyzes (reaction 33) much faster than $\text{C}(\text{NO}_2)_4$ (for its hydrolysis see above).



The trinitromethanol thus formed immediately loses nitrous acid (reaction 34) (HCl release from trichloromethanol occurs within less than a few microseconds),⁵⁴ and the hydrolysis of dinitro carbon monoxide (reaction 35) will also be fast.



Nitrite is then readily oxidized by ozone (reaction 31). The fact that practically no nitrite is observed after completion of the reaction is a strong indication that the bona fide intermediate $(\text{NO}_2)_3\text{CONO}_2$ must have hydrolyzed quite rapidly, faster than the time required for the completion of the reaction, which was 12 min in the above experiment. This also requires that the lifetime of $(\text{NO}_2)_2\text{C}=\text{O}$ must be short (see below).

Reaction of the Nitroform Anion with Ozone. In the preparation of NF^- by the hydrolysis of TNM, nitrite is a major product which reacts very fast with ozone (see above). Hence, for the determination of the rate constant of ozone with the NF^- , nitrite could be destroyed most conveniently by ozonolysis. The remaining nitrite concentration was $\sim 3\%$ of that of NF^- . Using the stopped-flow technique, the decay of NF^- at 350 nm was followed in the presence of a large excess of ozone (Figure 4), and from such data a rate constant of $k = 1.4 \times 10^4 \text{ M}^{-1} \text{s}^{-1}$ is obtained.

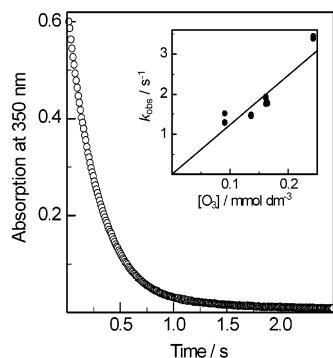
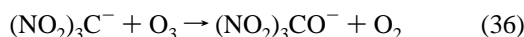


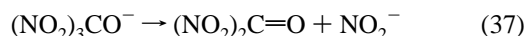
Figure 4. Reaction of ozone (2.4×10^{-4} M) with the nitroform anion (2×10^{-5} M) as followed by the decay of the nitroform anion at 350 nm in a stopped-flow experiment. Inset: plot of k_{obs} vs the ozone concentration ([nitroform anion] = 2×10^{-5} M).

This value is ~ 30 times lower than the rate constant of ozone with nitrite (in agreement with a stationary ratio of $[\text{NF}^-]/[\text{NO}_2^-] \approx 30$ observed upon ozonolysis of NF^-). This has a bearing on the determination of the $\text{O}_2^{\cdot-}$ yield by following the yield of NF^- formation. This aspect will be discussed below.

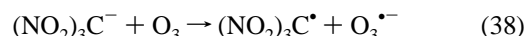
It is suggested that the reaction of ozone with the NF^- proceeds by O-atom transfer (reaction 36).



This reaction is followed by a rapid release of nitrite (reaction 37 followed by the hydrolysis of $(\text{NO}_2)_2\text{C}=\text{O}$, reaction 35, see above).



An alternative pathway, the reaction by electron transfer (reaction 38), can be excluded.



This reaction would give rise to $\text{O}_3^{\cdot-}$ and thus to $\cdot\text{OH}$. The formation of $\cdot\text{OH}$ can be readily detected by the formation of methanesulfinic acid in the presence of DMSO (see above). The absence of methanesulfinic (and its oxidation product methanesulfonic acid) indicates that reaction 38 does not take place.

The lifetime of the bona fide intermediates $(\text{NO}_2)_3\text{CO}^-$ and $(\text{NO}_2)_2\text{C}=\text{O}$ must be indeed very short. According to the proposed mechanism, ozonolysis of NF^- leads to the formation of 3 mol of NO_2^- , but 3 mol of NO_3^- and no NO_2^- are detected after the completion of the reaction. The stoichiometry of the reaction (as followed by conductance and optical measurements) is 4 mol of ozone/mol of NF^- . Thus, NO_2^- released in reactions 37 and 35 is immediately oxidized to NO_3^- . This requires that these hydrolyses (i.e. release of nitrite which subsequently reacts very rapidly with ozone) are much faster than the reaction of NF^- with ozone under such conditions. The first step, reaction 34, will certainly be very fast, typically in the microsecond time range (cf. the release of HCl from geminal chlorohydrins).^{54–56} In analogy with phosgene, the resulting $(\text{NO}_2)_2\text{C}=\text{O}$ is expected to hydrolyze on the subsecond time scale (reaction 35). Due to the much stronger electron-withdrawing properties of the $-\text{NO}_2$ substituent compared to the $-\text{Cl}$ substituent, one even may suspect that reaction 35 is faster than the hydrolysis of phosgene under such conditions ($k \sim 10 \text{ s}^{-1}$).^{54,57} Indeed, if the hydrolysis of $(\text{NO}_2)_2\text{C}=\text{O}$ were as slow as that of phosgene, considerable amounts of NO_2^- should have been found after ozonolysis.

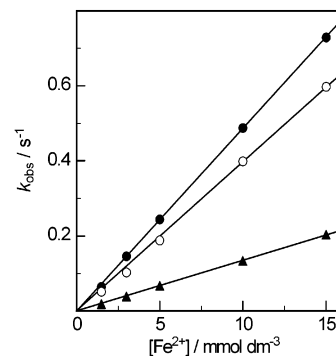
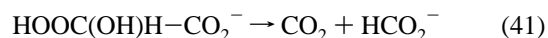
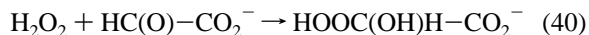
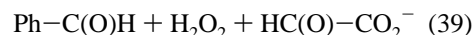
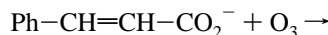


Figure 5. Rate of reaction of Fe^{2+} in 0.1 M H_2SO_4 with H_2O_2 (●) hydroxymethylhydroperoxide (○), and tertiary butylhydroperoxide (▲) at 18 °C as a function of the Fe^{2+} concentration. The kinetics of the reaction was followed by stopped-flow.

Detection of Hydroperoxides. In ozone reactions, hydroperoxides are common products. They are sometimes only very short-lived, too short-lived to be detectable by a peroxide assay, and their formation can only be inferred from the final products.⁵⁸ However, there is a wide span of hydroperoxides that are stable for seconds, minutes, or “forever”. Hydrogen peroxide is such a long-lived hydroperoxide, but it may react with an ozonolysis product, and then it can fade away even on the time scale of typical analytical procedures. A case in point is the ozonolysis of cinnamic acid.⁵⁸ Here, benzaldehyde, hydrogen peroxide (via an α -hydroxyhydroperoxide that is too short-lived to be detected), and glyoxylic acid are the products (reaction 39).⁵⁸ The latter two react with one another (reaction 40), and the hydroperoxide thus formed decomposes into formic acid and carbon dioxide (reaction 41).



For any mechanistic study, a material balance is a prerequisite. Hence for the study of ozone reactions, reliable assays for hydroperoxides which allow their quantitative determination are required. In the following, some established assays will be discussed and some new ones presented.

Fe(II)-Based Assays. Aqua- Fe^{2+} is known to reduce H_2O_2 and organic hydroperoxides. For H_2O_2 , the rate constant is $\sim 60 \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C.⁵¹ The rate of reaction is strongly temperature dependent,⁵¹ and our value of $48 \text{ M}^{-1} \text{ s}^{-1}$ determined at 18 °C (● in Figure 5) agrees very well with these data. The rate constant of the reaction of hydroxymethylhydroperoxide (produced in the reaction of 1,1-dichloroethene with ozone; cf. ref 5) with Fe^{2+} is not much slower ($k = 39 \text{ M}^{-1} \text{ s}^{-1}$; ○ in Figure 5). Noticeably slower is the reaction with tertiary butylhydroperoxide ($k = 13 \text{ M}^{-1} \text{ s}^{-1}$; ▲ in Figure 5), but these differences are too small for the characterization of a given hydroperoxide based on its kinetics with aqua- Fe^{2+} .

This ready reaction of Fe^{2+} with hydroperoxides has often been used for their quantification (e.g., refs 59 and 60), but the question has to be asked, whether one can rely on such data.

In principle, the stoichiometry of the reaction hydroperoxides with Fe^{2+} is simple; i.e. 1 mol of hydroperoxide may yield 2 mol of Fe^{3+} (reactions 42–45; $k_{44} \approx 3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$,⁶¹ $k_{45} \approx 3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$; cf. ref 10). For organic hydroperoxides, two pathways are conceivable, reactions 42 and 43, but only the

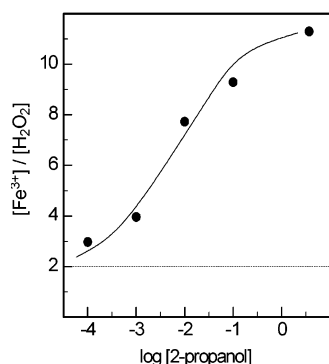
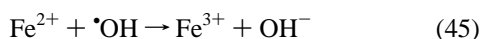
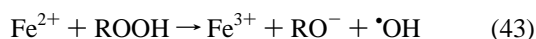
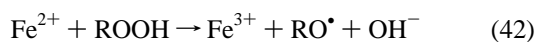


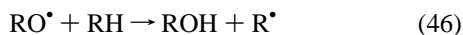
Figure 6. Reaction of H_2O_2 (varied between 0.2 and 2 mM) with Fe^{2+} (6 mM) in the presence of 2-propanol at pH 1.5. Formation of Fe^{3+} as a function of the 2-propanol concentration.

former route is taken in a one-electron reduction process.⁶² The reason for this is the much higher solvation energy of OH^- as compared to that of RO^- .



A system which seems to follow this sequence of reactions with practically no side reaction is the reaction of formic peracid with $\text{Fe}(\text{CN})_6^{4-}$. At pH ~ 3.7 the rate constant of this reaction is $4.3 \text{ M}^{-1} \text{ s}^{-1}$, and $\sim 1.9 \text{ mol}$ of $\text{Fe}(\text{CN})_6^{3-}$ and $\sim 0.9 \text{ mol}$ of formic acid are formed. These yields were independent of the $\text{Fe}(\text{CN})_6^{4-}$ concentration (0.4–4 mM) and were not affected by an addition of tertiary butanol. This indicates that no $\bullet\text{OH}$ are formed in this electron-transfer reaction (confirming the earlier⁶² conclusion) and that the $\text{HC}(\text{O})\text{O}^\bullet$ radical undergoes the otherwise very fast 1,2-H-shift (cf. reaction 48) only slowly if at all. The reason for this could be a resonance stabilization of the alkoxy radical by the carbonyl group.

Reaction 44 does not consider competing reactions. In reality, however, the RO^\bullet radicals are usually very short-lived and may react with the substrate RH (reaction 46, $k_{46} \approx 3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ for the *tert*-butoxyl⁶³ and the methoxyl⁶⁴ radicals with methanol), decompose by β -fragmentation (e.g., reaction 12, $k = 1.4 \times 10^6 \text{ s}^{-1}$),³³ or undergo an 1,2-H-shift^{65–67} when α -hydrogens are available (e.g., reaction 47). In water, the 1,2-shift reaction is also very fast, typically $\sim 10^6 \text{ s}^{-1}$.



In the presence of dioxygen, the alkyl radicals are rapidly converted into the corresponding peroxy radicals (reaction 48) which are subsequently reduced by Fe^{2+} into hydroperoxides (reaction 49).



Thus, a short chain reaction is induced. To exemplify this point, the formation of Fe^{3+} in the reaction of H_2O_2 with Fe^{2+} in the presence of 2-propanol is shown in Figure 6. Here, quantitative oxidation of Fe^{2+} by $\bullet\text{OH}$ is only achieved at high

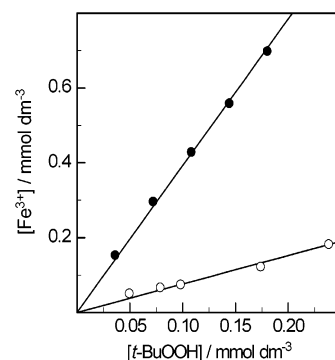


Figure 7. Formation of Fe^{3+} in the reaction of tertiary butylhydroperoxide with Fe^{2+} (3 mM) at pH 1.5 as a function of the tertiary butylhydroperoxide concentration in the presence of air (●) and in deoxygenated solution (○).

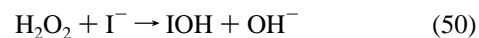
$[\text{Fe}^{2+}]/[\text{2-propanol}]$ ratios ($k(\bullet\text{OH} + \text{2-propanol}) = 1.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$),¹⁰ where the Fe^{3+} yield approaches the value $2\text{Fe}^{3+}/\text{H}_2\text{O}_2$.

When Fe^{2+} reacts with organic hydroperoxides, it is no longer guaranteed that even at low substrate concentrations 2 mol of Fe^{3+} are formed/(mol of hydroperoxide reacted). The reason for this is the occurrence of the fast unimolecular processes. An example is tertiary butylhydroperoxide. Here, 4 mol of Fe^{3+} are formed/(mol of hydroperoxide) in the presence of dioxygen, but only 0.8 mol of Fe^{3+} in its absence (Figure 7).

This low yield, which is even below unity, deserves a comment. The rapid fragmentation of the tertiary butoxyl radical (reaction 12) prevents a further oxidation of Fe^{2+} according to reaction 43. In reaction 12, methyl radicals are formed. They are capable of abstracting an H-atom from tertiary butylhydroperoxide (cf. $k(\bullet\text{CH}_3 + \text{H}_2\text{O}_2) = 2.7 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$).⁶⁸ This reaction consumes tertiary butylhydroperoxide, which thus is no longer capable of reacting with Fe^{2+} . The fast termination reactions of the methyl and tertiary butylperoxyl radicals will eliminate the latter before it can be reduced by Fe^{2+} to a major extent.

It is thus concluded that Fe^{2+} -based hydroperoxide assays, although most useful for their detection, are often not well-suited for their quantification (cf. also ref 69).

Iodide Assay. Iodide is known to react very slowly with hydrogen peroxide and many other hydroperoxides, but this reaction can be considerably speeded up by molybdate catalysis,⁷⁰ for example with H_2O_2 by 3 orders of magnitude (Table 1). Similar to the reaction of sulfides with hydroperoxides (see below), the reaction may proceed via a two-electron reduction process (nucleophilic substitution; reaction 50). The measured entity is I_3^- (reactions 51 and 52). To shift equilibrium 52 fully to the right side, high iodide concentrations are required.



The potential alternative to reaction 50, a one-electron-transfer process ($\text{H}_2\text{O}_2 + \text{I}^- \rightarrow \bullet\text{I} + \bullet\text{OH} + \text{OH}^-$), must not be considered, since this (and also the proton-assisted) reaction is endothermic by 31 kcal mol^{-1} (12 kcal mol^{-1} at pH 0; G. Merényi, private communication); i.e. side reactions involving $\bullet\text{OH}$ have not been considered.

An advantage of this assay is that the kinetics of the reaction varies considerably from hydroperoxide to hydroperoxide.⁵ This

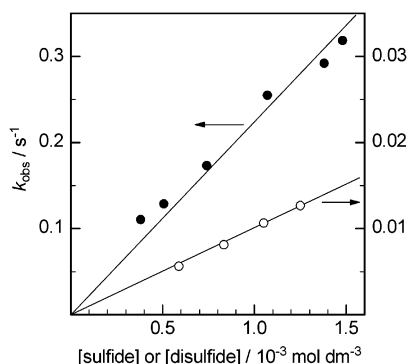


Figure 8. Rate of reaction of formic peracid with (HOCH₂CH₂)₂S (●) and HOCH₂CH₂SSCH₂CH₂OH (○) as a function of the sulfide/disulfide concentration. The kinetics were followed by the buildup of conductance due to the formation of formic acid.

can be used to characterize a given hydroperoxide, and if the rate constants of two hydroperoxides with this reagent differ significantly (\geq a factor of ~ 10), this assay can be used to quantify the yields of these hydroperoxides by a kinetic analysis.⁷¹ Rate constants for the reaction of some hydroperoxides that are often formed in the ozonolysis of olefinic compounds are given in Table 1. As can be seen from this table, the more reactive hydroperoxides such as formic peracid react with iodide also without molybdate catalysis.

Titanyl Sulfate Assay. It must be mentioned that the complexation of H₂O₂ by Ti(IV) in sulfuric acid solution that gives rise to a yellow color is often used for the determination of H₂O₂. However, the molar absorption coefficient is only low ($\epsilon(410\text{nm}) = 710 \text{ M}^{-1} \text{ cm}^{-1}$);^{72,73} i.e. the method is not very sensitive. Organic hydroperoxides give rise to this assay only after hydrolysis, which may be slow and incomplete due to competing reactions.⁷³ In favorable cases, however, the kinetics of this assay may also be used for the characterization of a given hydroperoxide.

Destruction of H₂O₂ by Catalase. The destruction of H₂O₂ with the help of catalase is often a most useful tool for distinguishing between H₂O₂ and organic hydroperoxides. The addition of 10 μL of catalase to 10 mL of 0.1 mM H₂O₂ solution eliminates H₂O₂ in less than 2 s (the time required for adding catalase and subsequently molybdate-activated iodide), while organic hydroperoxides are typically not or only very little affected. For example, at a catalase concentration of 0.8 mg dm⁻³ methylhydroperoxide decays with a half-life of a day.³⁶ In contrast, we now have found that formic peracid is very rapidly destroyed by catalase ($k_{\text{obs}} = 1.2 \times 10^{-2} \text{ s}^{-1}$ at a catalase concentration of 8.9 mg L⁻¹, pH ~ 7). In the reaction with a sulfide (two-electron reductant), formic peracid is fully transformed into formic acid and with Fe(CN)₆⁴⁻ (one-electron reductant) to at least 90% (see above). In contrast, catalase treatment yields only little if any formic acid. This very surprising observation was not further investigated.

Oxidation of Sulfides and Disulfides by Reactive Hydroperoxides. Reactive hydroperoxides such as formic peracid and hydroperoxides of a similar reactivity are capable of oxidizing sulfides and disulfides by O-transfer (cf. reaction 53).



The reaction with formic peracid can be readily followed by conductance measurements, because formate ions and protons are liberated in this reaction ($\text{pK}_a(\text{formic peracid}) = 7.1$, $\text{pK}_a(\text{formic acid}) = 3.8$). The rate constant with the sulfide is considerably faster than that of the disulfide (cf. Figure 8 and

Table 1). The reaction with the sulfide can be used to reduce reactive organic hydroperoxides (a case in point is the ozonolysis of thymine).⁵³

Although they can be separated readily from their parent sulfides by HPLC, simple aliphatic sulfoxides do not have sufficiently strong absorptions at $\lambda > 200 \text{ nm}$ to use them for the quantitative determination of reactive hydroperoxides. The amino acid methionine also gives this reaction. Its corresponding sulfoxide absorbs more strongly in the UV, and, therefore, methionine can be used with advantage to quantify reactive hydroperoxides (see Experimental Section).

Factors To Be Taken into Account in the Determination of $\cdot\text{OH}$ in Ozone Reactions with the Tertiary Butanol/Formaldehyde Assay. It has been shown above that in the reaction of $\cdot\text{OH}$ with tertiary butanol the formation of formaldehyde is connected with the concomitant release of O₂^{•-}. Since the latter reacts rapidly with ozone giving rise to further $\cdot\text{OH}$, this additional source of formaldehyde has to be taken into account when the primary $\cdot\text{OH}$ yield is calculated from such data. In the above study, $\cdot\text{OH}$ was generated by the reaction of ozone with an excess of H₂O₂; i.e. it did not matter if any O₂^{•-} gave rise to $\cdot\text{OH}$ via its reaction with ozone or whether $\cdot\text{OH}$ formation was entirely due to the reaction of ozone with H₂O₂. However, in any other system, the formaldehyde yield will be higher than the above value of $(30 \pm 4\%)/(1 \text{ mol of primary } \cdot\text{OH})$ due to the short chain reaction. The relationship between the yield of the chain carrier forming reaction x and the total yield of chain reaction product (y) , $y = x/(1 - x)$, was established by solving the initial value problem of the set of ordinary differential equations, modeling the reaction mechanism and taking the limes to infinite time. Applied to our system, a correction factor of 0.48 ± 0.08 is obtained by which the measured formaldehyde yield has to be divided to arrive at the precursor $\cdot\text{OH}$ yield; i.e. as a rule of thumb one can take twice the formaldehyde yield.

When the initial $\cdot\text{OH}$ yield is high, ozone depletion due to the secondary formation of $\cdot\text{OH}$ in this assay can no longer be neglected and has to be taken into account in material balance calculations. Furthermore, when the rate of reaction of ozone with the substrate is very fast, O₂^{•-} released in the tertiary-butanol-derived peroxy radical reactions may no longer be able to react with ozone and thus the correction factor mentioned above may not have to be applied. A case in point may be *N,N,N',N'*-tetramethylphenylenediamine (cf. data in Table 2). In addition, when $\cdot\text{OH}$ formation in ozone reactions becomes a major process, there are always substrate radicals to be taken into account which will interact with the tertiary-butanol-derived peroxy radicals. This must have an influence on the formaldehyde yield. Whether this will lead to an increase or a decrease cannot be predicted. As a consequence, the tertiary butanol assay is an excellent tool for the detection of $\cdot\text{OH}$ in ozone reactions, but as its quantitative aspect is concerned, it is fraught with an error beyond the experimental one, especially when the formaldehyde ($\cdot\text{OH}$) yield is found to be high.

Formation of $\cdot\text{OH}$ in Ozone Reactions. It has been mentioned above that $\cdot\text{OH}$ may be formed in an electron-transfer process (reaction 5). This reaction always has to compete with other reactions of ozone. Thus, the differences in the reduction potentials of substrate and ozone are not expected to be a measure of the electron-transfer efficiency, although a larger difference will favor electron transfer and thus $\cdot\text{OH}$ formation. Most experiments reported here were carried out at pH ~ 7 . For assessing the reduction potential difference, one has to take the ozone reduction potential at pH 7. In the compilation of

TABLE 2: Reduction Potentials at pH 7 of Various Substrates,⁷⁴ Their Difference against the Reduction Potential of Ozone (1.01 V), Formaldehyde Yields in the Presence of Tertiary Butanol, and the Yields of •OH Calculated Therefrom

substrate	E^7/V	ΔE	CH ₂ O yield/%	OH yield/%
<i>N,N,N',N'</i> -tetramethylphenylenediamine	0.24	0.77	34	see text
<i>o</i> -phenylenediamine	0.34	0.67	14	30 ± 5
hydroquinone	0.45	0.56	20	43 ± 7
catechol	0.53	0.48	11	24 ± 4
Fe(CN) ₆ ³⁻	0.77	0.34		~70 ^a
<i>N,N</i> -diethylaniline	0.86	0.15	13	28 ± 5
phenol	0.86	0.15	11	24 ± 4
triethylamine ⁶	1.04			15
1,3,5-trimethoxybenzene	(1.23) ^b	(0.22) ^b	7.4	16 ± 2.5
	(1.27) ^b	(0.26) ^b		
iodide	1.28	0.27	<0.5	0
guanosine ⁴⁹	1.2981	0.28	0	0
1,4-dimethoxybenzene	1.3082	0.29	8.4	18 ± 3
1,2-dimethoxybenzene	1.4482	0.43	6.8	15 ± 2
adenosine	1.5681	0.55	20	43 ± 7
anisole	1.6282	0.61	4.1	9 ± 1.5
bromide	2.00	0.99	0	0

^a From experiments with DMSO. ^b Based on values in acetonitrile of 1.49 V vs SCE⁸³ and 1.25 V vs a silver electrode.⁸⁴

reduction potentials, a value of $E^7 = 1.8$ V is cited.⁷⁴ This value had been calculated⁷⁵ by taking $pK_a(\text{HO}_3^*) = 10.4$ from ref 76. Considering that the pK_a value of •OH is 11.9¹⁰ and that of HO_2^* is 4.8,¹⁶ it is very unlikely that the pK_a of the species richer by one oxygen atom, HO_3^* , should be as high as 10.4. Also for the corresponding parents, an increasing acidity $\text{H}_2\text{O} < \text{H}_2\text{O}_2 < \text{H}_2\text{O}_3$ has been calculated.⁷⁷ That the pK_a of HO_3^* must indeed be low has already been discussed by Czapski.⁷⁸ It is thus more reasonable to take the value $E(\text{O}_3^{\bullet-}/\text{O}_3) = 1.01$ V measured⁷⁹ at high pH also for experiments at pH 7. Thus, ozone is a rather weak one-electron oxidant. This low reduction potential does not allow the conclusion⁸⁰ that the Criegee mechanism for the reaction of ozone with olefins has to be revised and proceeds by an electron transfer in the first step, although the rate constants of the ozone reaction and the gas-phase ionization potentials of selected (electron rich) olefins correlate.⁸⁰ This correlation only reflects the electrophilic nature of ozone.

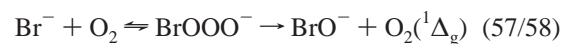
For a number of substrates, the formaldehyde yields in the presence of an excess tertiary butanol, the •OH yields calculated (see above) from these data, together with the substrate reduction potentials at pH 7 are given in Table 2.

Of the substrates compiled in Table 2, the compound with the lowest reduction potential is *N,N,N',N'*-tetramethylphenylenediamine. Although the reduction potential difference is as much as 0.77 V, and thus the only reaction to take place has been considered⁸⁵ to be electron transfer, it is not. As is evident from the 9% yield of singlet dioxygen, $\text{O}_2(^1\Delta_g)$, O-transfer competes.⁴⁵ A short-lived (zwitterionic) adduct to nitrogen is the likely precursor for both reaction channels. A tertiary amine with a higher reduction potential is triethylamine. Here, an adduct has also been assumed to be the primary product (reaction 54), but now the route to the *N*-oxide and singlet dioxygen (reaction 55) is the preferred pathway, and electron transfer (reaction 56) occurs with a much lower yield (Table 2).⁶

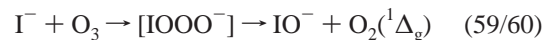


In this context, it may be worth mentioning that short-lived adducts are common in ozone chemistry. Cases in point are the

halide ions, bromide and iodide. Kinetic evidence for such an intermediate has been found with bromide which does not react very fast with ozone (reactions 57 and 58). Reaction 57 is close to isoenergetic, and thus the first step is even reversible.⁵⁰



The reaction of I^- with ozone is, however, very fast ($k = 1.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$),⁵⁰ and the endothermic electron transfer does not compete effectively (cf. Table 2) with O-transfer (reactions 59 and 60).

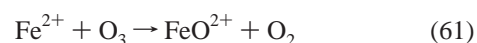


Support for a certain lifetime of such adducts comes from the $\text{O}_2(^1\Delta_g)$ yields in these systems. While with other systems, e.g. various sulfur- and nitrogen-containing compounds, $\text{O}_2(^1\Delta_g)$ yields are 100% when an O-transfer occurs; it is only 54% in the case of Br^- and 14% in the case of I^- .⁴⁵ This low $\text{O}_2(^1\Delta_g)$ yield is readily explained if the adducts (IOOO^- and BrOOO^-) are sufficiently long-lived to allow heavy-atom-assisted spin conversion and release of triplet (ground-state) dioxygen. This effect would be more pronounced with I^- than with the lighter Br^- , as observed.

The Criegee mechanism, followed by olefins, also involves a short-lived zwitterion, and there is now experimental evidence that under favorable conditions, e.g. in the case of maleic and fumaric acids, the zwitterion reverts again, thereby producing also the other isomer.⁸⁶

The preference of forming adducts rather than undergoing outer-sphere electron transfer is also given by the much stronger oxidant, the •OH radical ($E^7 = 2.73$ V),⁷⁴ and even in the very few cases, where electron transfer is observed (e.g., ref 87), short-lived adducts are not fully excluded.

It is reasonable to assume that short-lived trioxides are also intermediates in other O-transfer reactions and that they compete with electron transfer whenever this reaction is thermodynamically possible, e.g. in the case of aqua- Fe^{2+} (reaction 61, $k = 8.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$).⁸⁸



Although the reduction potential of $E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) = 0.77$ V would allow the electron-transfer reaction to occur in acid

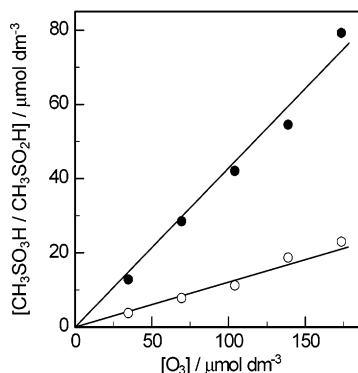


Figure 9. Ozonolysis of $\text{Fe}(\text{CN})_6^{4-}$ (1 mM) in the presence of DMSO (10 mM). Formation of methanesulfonic acid (●) and methanesulfinic acid (○) as a function of the ozone concentration.

solution ($\text{pH} \leq 4$), there is no indication that it takes place to a noticeable extent.⁸⁸ In agreement with this conclusion, in the presence of an excess of DMSO the yield of methanesulfinic acid and thus the $\cdot\text{OH}$ yield is only $10 \pm 5\%$ at $\text{pH} 4$. These measurements are fraught with a considerable error, since Fe^{2+} and SO_4^{2-} cause some problems in the determination of methanesulfinic acid by ion chromatography, and it was impossible to extend these measurements to lower pH values.

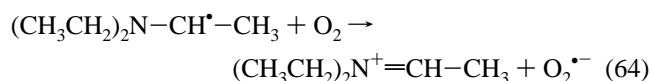
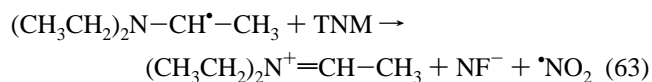
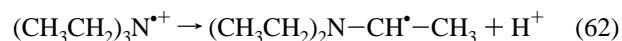
However, in contrast to aqua- Fe^{2+} , $\text{Fe}(\text{CN})_6^{4-}$ cannot accommodate a further ligand and has to react by electron transfer and/or by an oxidation of the ligand. The rate of reaction of $\text{Fe}(\text{CN})_6^{4-}$ with ozone was determined by competition with indigosulfonate using the stopped-flow setup for rapid mixing of an ozone solution with a solution containing $\text{Fe}(\text{CN})_6^{4-}$ and indigosulfonate at varying concentration ratios. Based on $k(\text{O}_3 + \text{indigosulfonate}) = 9.4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$,⁸⁹ we arrived at an ozone rate constant with $\text{Fe}(\text{CN})_6^{4-}$ of $1.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ (data not shown), a value close to that for aqua- Fe^{2+} . When ozone is reacted with $\text{Fe}(\text{CN})_6^{4-}$, $\text{Fe}(\text{CN})_6^{3-}$ is formed in 140% yield (as determined by UV spectrophotometry at 420 nm, $\epsilon = 1020 \text{ M}^{-1} \text{ cm}^{-1}$). Addition of DMSO halves this value, and methanesulfinic plus methanesulfonic acid are formed in a total yield of $\sim 60\%$ (Figure 9).

Reaction 27 has an efficiency of 92%. Correcting for this brings the $\cdot\text{OH}$ yield as determined by the DMSO assay to 65%. This value is in agreement with a value of $\sim 70\%$ as concluded from the oxidation of $\text{Fe}(\text{CN})_6^{4-}$. Thus, electron transfer with concomitant formation of $\cdot\text{OH}$ occurs in this system to an extent of only 65–70%. In competition to electron transfer, the ligand may have been oxidized, but experimental evidence for this is still lacking. The ratio of methanesulfinic acid to methanesulfonic acid remained constant when the DMSO concentration was varied between 0.01 and 0.1 M. We have recently shown that methanesulfinic acid reacts very fast with ozone ($k = 2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$), but it also undergoes a very fast $\cdot\text{OH}$ -induced chain reaction in the presence of dioxygen.⁴⁴ It has the uncommon peculiarity that its chain length does not depend on the substrate (methanesulfinic acid) concentration. It can be readily shown by computer-assisted modeling that under the prevailing experimental conditions the formation of methanesulfonic acid cannot be due to a reaction of methanesulfinic acid with ozone to a significant extent. The fact that the methanesulfinic to methanesulfonic acid ratio was not affected much by the DMSO concentration when varied from 0.01 to 0.1 M also excludes an $\cdot\text{OH}$ -induced chain reaction as a cause of the partial conversion of methanesulfinic acid into methanesulfonic acid. There was also an indication that other radicals, e.g. the methylperoxyl radical (formed in the reaction of the

methyl radical from reaction 27 with dioxygen), can induce this chain reaction albeit with a much slower rate.⁴⁴ We tentatively suggest that the observed partial conversion of methanesulfinic acid into methanesulfonic acid is due to a methylperoxyl-induced autoxidation. The formation of high yields of methanesulfonic acid besides methanesulfinic acid seems to be quite general, and this is also observed when probing with DMSO $\cdot\text{OH}$ -formation in the phenol/phenolate system.⁹⁰

Use of Tetranitromethane for the Detection of Superoxide in Ozone Reactions. When the ozone rate constant with the substrate is much lower than that with NF^- , the TNM assay when only based on the formation of NF^- may underestimate the $\text{O}_2^{\cdot-}$ yield because of a consumption of NF^- by ozone. Raising the substrate concentration to account for this may not be always possible due to solubility limitations. To minimize the reaction of ozone with $\text{O}_2^{\cdot-}$, TNM should be present at a ~ 10 -fold concentration with respect to ozone. At a TNM concentration of 1 mM (close to the solubility limit), the ozone concentration should be kept below 10^{-4} M .

Often, it does not matter, whether TNM reacts with $\text{O}_2^{\cdot-}$ or a reducing radical that is formed in the course of an ozone reaction. A case in point is the triethylamine system,⁶ where NF^- may be formed directly by the reaction of TNM with reducing carbon-centered radical (cf. reactions 56, 61, and 63) or at the later stage, when dioxygen is converted by reducing carbon-centered radical into $\text{O}_2^{\cdot-}$ which further reacts with TNM (reactions 64 and 9).^{91,92}



There is, however, also the possibility that $\text{O}_2^{\cdot-}$ is a primary product in an ozone reaction (reaction 65),⁹³ and this reaction is not related to an electron-transfer reaction.



There has never been an example for this type of reaction. Adenine and its derivatives react very slowly with ozone ($k(\text{Ado} + \text{O}_3) = 12 \text{ M}^{-1} \text{ s}^{-1}$)⁴⁹ and is known^{94,95} to produce $\cdot\text{OH}$ in remarkable yields⁴⁹ despite its high reduction potential (Table 2). It is thus a potential candidate for undergoing reaction 65. The $\cdot\text{OH}$ that were detected would then have $\text{O}_2^{\cdot-}$ as the precursor.

We have now set up an experiment where the concentration of adenosine was ~ 10 times higher than that of TNM in order to protect TNM from being attacked by ozone. The TNM concentration was chosen as high as possible, and the ozone concentration was kept as low as possible in order to prevent $\text{O}_2^{\cdot-}$ from reacting with ozone to a major extent. Moreover, tertiary butanol was added at a ~ 100 -fold excess over adenosine to ensure that $\cdot\text{OH}$ would react with tertiary butanol. Experimental details and the data for the key products nitrate and nitroform anion (for $\text{O}_2^{\cdot-}$) and formaldehyde (for $\cdot\text{OH}$) are given in Table 3. The 2-hydroxy-2-methylpropanal yield was also determined.

The nitrate, nitroform anion, and formaldehyde yields in this system have been modeled on the basis of a series of equations

TABLE 3: Product Yields (%) in the Reactions of Adenosine in the Presence of Tertiary Butanol and TNM of Ozone Consumed ([adenosine] = 10 mM, [tertiary butanol] = 0.95 M, and [TNM] = 1.1 mM; for Calculations, See Text)

products	exptl	calcd (43% •OH)	calcd (43% O ₂ ^{•-})
nitrate	43	45	56
nitroform anion	1	0.2	6.8
formaldehyde	5.3	7.6	0.2
2-hydroxy-2-methylpropionaldehyde	16	—	—

using the rate constants determined above. From the experiments in the absence of TNM, it was concluded that in this system •OH are generated in ~43% yield (Table 2). As mentioned above, these could have been formed directly by electron transfer and subsequent decay of O₃^{•-} or via O₂^{•-} and its reaction with ozone (which gives O₃^{•-}; see above) that may be produced in the not yet established reaction 65. As is seen from Table 3, the simulations based on •OH (O₃^{•-}) as the primary product are in very reasonable agreement with the experimental data in contrast to O₂^{•-} as the primary species. This rules out a significant contribution of reaction 65 to the •OH yield in this system. We thus conclude that ozone reacts with adenosine by electron transfer despite the fact that the reaction is endothermic. The very low rate constant of this reaction; i.e. the absence of other very efficient competing reactions allows this reaction to proceed nevertheless. We have, therefore, not yet an example for reaction 65.

In Table 3, the yield of 2-hydroxy-2-methylpropanal is also given. It is seen that the ratio of the 2-hydroxy-2-methylpropanal to formaldehyde yields is above the value of ~1.5 typical for the pure tertiary butanol system. This is an indication that the adenosine-derived radicals also interact with the tertiary-butanol-derived ones, as already suggested above. As a result, the formaldehyde yield is lower than expected, and, in principle, the •OH yield might be even somewhat higher than the value given in Table 2.

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