ARTICLE

OBC
www.rsc.org/obc

Ozonolysis of vinyl compounds, CH_2=CH–X, in aqueous solution—the chemistries of the ensuing formyl compounds and hydroperoxides

Achim Leitzke,[a,b] **Roman Flyunt,**[a,b] **Jacob A. Theruvathu**[a] **and Clemens von Sonntag** *[a,b]
[a] *Max-Planck-Institut für Strahlenchemie, Stiftstr. 34-36, P.O. Box 101365, D-45470-Mülheim an der Ruhr, Germany. E-mail: Clemens@vonSonntag.de*
[b] *Institut für Oberflächenmodifizierung (IOM), Permoserstr. 15, D-04303 Leipzig, Germany*

Received 9th December 2002, Accepted 5th February 2003
First published as an Advance Article on the web 19th February 2003

Reactions of ozone with some vinyl compounds of the general structure CH_2=CH–X were studied in aqueous solution. Rate constants (in brackets, unit: $dm^3\ mol^{-1}\ s^{-1}$) were determined: acrylonitrile (670), vinyl acetate (1.6×10^5), vinylsulfonic acid (anion, 8.3×10^3), vinyl phenylsulfonate (*ca.* 200), vinyl diethylphosphonate (3.3×10^3), vinylphosphonic acid (acid, 1×10^4; mono-anion, 2.7×10^4; di-anion, 1×10^5), vinyl bromide (1×10^4). The main pathway leads to the formation of $HOOCH_2OH$ and HC(O)X. As measured by stopped flow with conductometric detection, the latter one may undergo rapid hydrolysis by water, *e.g.* HC(O)CN (3 s^{-1}). Other HC(O)X hydrolyse much slower, *e.g.* $HC(O)PO_3(Et)_2$ ($7 \times 10^{-3} s^{-1}$) and $HC(O)P(OH)O_2^-$ (too slow to be measured). The OH^--induced hydrolyses range from *ca.* 5 $dm^3\ mol^{-1}\ s^{-1}$ [$HC(O)PO_3^{2-}$] to 3.8×10^5 $dm^3\ mol^{-1}\ s^{-1}$ [HC(O)CN]. HC(O)Br mainly decomposes rapidly (too fast for the determination of the rate) into CO and Br^- plus H^+, and the competing hydrolysis is of minor importance (3.7%). The slow hydrolysis of $HC(O)PO_3^{2-}$ at pH 10.2, where $HOOCH_2OH$ is rapidly decomposed into CH_2O plus H_2O_2, allows an H_2O_2-induced decomposition (k = 260 $dm^3\ mol^{-1}\ s^{-1}$) to take place. Formate and phosphate are the final products.

Formyl chloride, the most simple acyl chloride, has the interesting property that it does not hydrolyse in water to a major extent [reaction (1)][1] but decomposes much more rapidly into CO plus HCl [reaction (2), $k = 1 \times 10^4\ s^{-1}$].[2] Hydrolysis only dominates at high pH [reaction (3), $k = 2.5 \times 10^4\ dm^3\ mol^{-1}\ s^{-1}$].[2]

$$HC(O)Cl + H_2O \longrightarrow HC(O)OH + HCl \qquad (1)$$

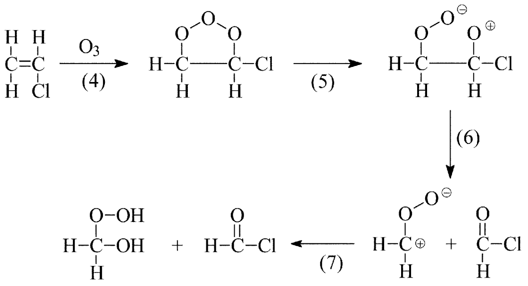
$$HC(O)Cl \longrightarrow CO + HCl \qquad (2)$$

$$HC(O)Cl + OH^- \longrightarrow HC(O)OH + Cl^- \qquad (3)$$

Obviously, for measuring a rate constant as high as $10^4\ s^{-1}$, formyl chloride has to be generated *in situ*, and this has been achieved with the help of the pulse radiolysis technique using changes in the conductance for detection.[2] In the gas phase, formyl chloride is stable, and under such conditions the activation energy for reaction (2) has been estimated by quantum-mechanical calculations at 184 kJ mol^{-1}.[3] This dramatic increase in rate upon going from the gas phase to aqueous solution has been suggested to be due to a change in mechanism. While in the gas phase the H and Cl atoms have to approach one another to an extent that H–Cl bond formation and CO release can occur, the concerted formation of H^+ and Cl^- is the likely process in aqueous solution. The high solvation energies,[4] especially that of H^+ (H^+: 1140 kJ mol^{-1}; Cl^-: 376 kJ mol^{-1}), may assist to reduce the activation barrier for reaction (2).

The fast rate of reaction (2) and the comparatively slow rate of reaction (3) prevented us from determining the rate constant of the latter by pulse radiolysis. Here, another approach to generate formyl chloride *in situ* has been followed. Ozonolysis of vinyl chloride in aqueous solution leads in its first step to the Criegee intermediate [reaction (4)] (*cf.* ref. 5). With unequal substituents, the Criegee intermediate can cleave heterolytically into two directions. However, one route is often strongly favoured.[6] In the case of formyl chloride, reactions (5)–(7) take place to an extent of >98%.[6]

DOI: 10.1039/b212194h



The *in situ* formation of formyl chloride by ozonolysis of vinyl chloride allowed us to study its hydrolysis by following CO and formate yield as a function of pH [*cf.* reactions (1)–(3)]. In the ozonolysis of vinyl chloride 6% of formate are formed, besides CO.[2,6] The overall rate of reactions (1) plus (2) is $1 \times 10^4\ s^{-1}$. Based on this value and the formate yield, the rate of reaction (1) must be $6 \times 10^2\ s^{-1}$. Similar values have been measured for the hydrolysis of other acyl chlorides.[7]

In the present paper, it will be shown that the ozonolysis of other adequately substituted vinyl compounds can be used to study the formation and decay of mixed anhydrides of formic acid whose rate of hydrolysis (or decomposition?) is as yet unknown. We will report the products and the kinetics of the ozonolysis of vinyl cyanide (acrylonitrile), vinyl acetate, vinyl phosphonic acid, diethyl vinylphosphonate, vinylsulfonic acid, vinyl phenylphosphonate and vinyl bromide. Data on the ozonolysis of 1,2-dibromoethene and vinylene carbonate will also be presented. The characterisation of short-lived intermediates will allow us to draw conclusions concerning some mechanistic details.

Experimental

Acrylonitrile (99.5%), vinyl acetate (99+%), vinyl phosphonic acid (97%), diethyl vinylphosphonate (97%), vinylsulfonic acid sodium salt (25% in water), phenyl vinylsulfonate (98%), vinyl

Table 1 Compilation of ozone rate constants (unit: $dm^3\ mol^{-1}\ s^{-1}$) determined in this study

Substrate	Rate constant	Method
Acrylonitrile	670 (830)[20]	Stopped flow
Vinyl acetate	1.6×10^5	Competition with NO_2^-
Vinyl sulfonate ion	8.3×10^3	Competition with NO_2^-
Phenyl vinylsulfonate	*ca.* 200	Competition with 1,2-dichloroethene
Diethyl vinylphosphonate	3.3×10^3	Competition with NO_2^-
Vinyl phosphonic acid	1×10^4	Stopped flow
Vinyl phosphonic acid (monoanion)	2.7×10^4	Stopped flow
Vinyl phosphonic acid (dianion)	1×10^5	Stopped flow
Vinyl bromide	1×10^4	Stopped flow
1,2-Dibromoethene	1.5×10^3	Stopped flow
Vinylene carbonate	2.6×10^4	Stopped flow

bromide (1 molar in THF), 1,2-dibromoethene (97%, *cis*/*trans* mixture) and vinylene carbonate (97%) were obtained from Aldrich and used as received.

Solutions were made up in Milli-Q-filtered (Millipore) water. A dioxygen-fed ozonator (Philaqua, Gladbeck) was used to produce the ozone stock solutions. Their ozone content was determined spectrophotometrically using $\varepsilon(260)^{8,9} = 3300\ dm^3\ mol^{-1}\ cm^{-1}$.

Stopped-flow experiments were carried out with the help of a Biologic (SF3) instrument equipped with a diode array system (Tidas–16, J&M, Aalen) for optical detection. The conductometric detection device was home-made and practically identical to that described before.[2,7] Slower rates of hydrolysis were followed with a conductometer (CDM3, Radiometer).

Formaldehyde yield was determined using the Hantzsch method,[10] and glyoxal as its osazone.[11] Organic hydroperoxides and H_2O_2 were quantified with molybdate-activated iodide.[12] In this assay, equal amounts of the two reagents and the solution to be analysed were mixed in a 1 : 1 : 1 ratio if not stated otherwise. Reagent A: 0.4 mol dm^{-3} KI, 3.6×10^{-2} mol dm^{-3} KOH, 1.6×10^{-4} mol dm^{-3} $(NH_4)_6Mo_7O_{24}$; reagent B: 0.1 mol dm^{-3} potassium hydrogen phthalate. The absorption of I_3^-, $\varepsilon(350\ nm) = 25000\ dm^3\ mol^{-1}\ cm^{-1}$, is read. By following the kinetics of this reaction, *e.g.* by stopped flow, the various hydroperoxides can be characterised.[6,13,14] For example, the hydroxymethylhydroperoxide, commonly formed in the reaction of ozone with vinyl compounds, reacts with this reagent at a rate of $3.4 \times 10^{-3}\ s^{-1}$, while H_2O_2 reacts at $0.27\ s^{-1}$.[6] Details of the determination of hydroperoxides by HPLC with post-column derivatisation are described elsewhere.[13,15] Formate, acetate, phosphonate and phosphate yields were determined by ion chromatography (Dionex DX100, column AS9HC) using 1×10^{-2} mol dm^{-3} $NaHCO_3$ as eluent. Bromide was determined on an AS14 column with 1.7×10^{-3} mol dm^{-3} $NaHCO_3$/ 1.8×10^{-3} mol dm^{-3} Na_2CO_3 as eluent. The quantitative determination of product yields is typically connected with an error of ±5% as deduced from a series of runs of the same experiment carried out at different days.

Kinetic simulations were carried out with the help of the Chemical Kinetics Simulator™ software, version 1.01 (from IBM, Almaden Research Center).

The formation of singlet dioxygen was checked for as described previously.[16]

Results and discussion

Ozone rate constants

The rate constants of ozone with the substrates were either determined directly by stopped flow (following the decay of the 260 nm absorption of ozone) or by competition.[17] Nitrite ($k = 3.7 \times 10^5\ dm^3\ mol^{-1}\ s^{-1}$, product: nitrate, 100%)[18,19] or *cis*-1,2-dichloroethene ($k = 540\ dm^3\ mol^{-1}\ s^{-1}$, product: chloride, 200%)[6] were used as competitors. The rate constants thus obtained are compiled in Table 1.

Ozone is an electrophilic agent,[21] and compared to their parent ethene ($k = 1.8 \times 10^5\ dm^3\ mol^{-1}\ s^{-1}$)[6] the substrates studied here react more slowly with ozone, *i.e.* the rate of reaction is reduced by the electron-withdrawing substituents (quantum-mechanical calculations[22] correlating ozone rate constants of olefins as a function of the substituents will be published elsewhere). In vinylphosphonic acid, the electron density in the in the C–C double bond increases upon dissociation and so does the rate of ozone reaction (Fig. 1).

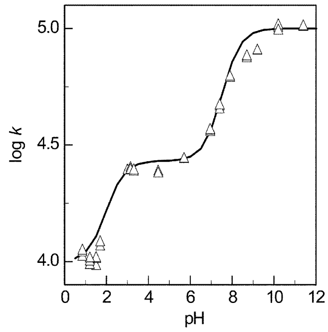


Fig. 1 The logarithm of the rate constant of the reaction of ozone with vinylphosphonic acid as a function of pH.

Vinylphosphonic acid has two pK_a values. For the first step, values of 1.7 and 2.2 and for the second one values of 7.1 and 7.23 have been reported for water and water–ethanol 93 : 7.[23,24] The solid line in Fig. 1 is the best fit through the data points requiring the above rate constants and pK_a values of 2.2 and 7.8 (the latter value is marginally higher than the literature value of 7.23). In the present system, the effect of the degree of protonation on the ozone rate constant is relatively small. With cinnamic acid, we find an increase in rate of about 8 upon deprotonation,[25] and with tertiary amines that have two nitrogens that can be protonated the rate increases by a factor of *ca.* 20 (EDTA) or even by three orders of magnitude (DABCO) upon deprotonation on going from the monoprotonated amine to the fully deprotonated one.[26]

As will be discussed below, the determination of the rate constant of phenylsulfonate by competition (*cf.* Fig. 7) results in a value that comes out too high due to the very fast reactions of the primary products with ozone. The value given in Table 1 accounts for this.

Ozonolysis of acrylonitrile—hydrolysis of formyl cyanide

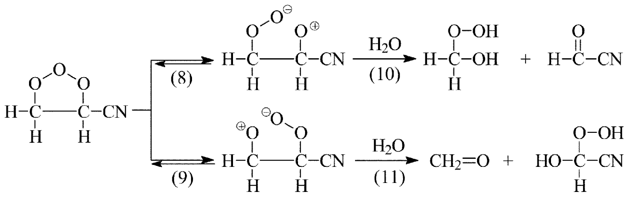
Upon ozonolysis of acrylonitrile in aqueous solution (1×10^{-3} mol dm^{-3}), the formaldehyde and formic acid yields increase linearly with increasing ozone concentrations (data not shown). They equal the amount of ozone consumed. The total hydroperoxide yield is also 100%. Based on a kinetic analysis of its reaction with molybdate-activated iodide, it is assigned to hydroxymethylhydroperoxide. According to this analysis, the yields of H_2O_2 and other fast-reacting hydroperoxides such as formic peracid are <5%.

Table 2 Compilation of hydrolysis rate constants determined in this study and in ref. 2

Reaction	Rate constant
$HC(O)Cl + H_2O \longrightarrow HC(O)OH + HCl$	$6 \times 10^2\ s^{-1}$ (ref. 2)
$HC(O)CN + H_2O \longrightarrow HC(O)OH + HCN$	$3\ s^{-1}$
$HC(O)OC(O)CH_3 + H_2O \longrightarrow HC(O)OH + CH_3C(O)OH$	$0.25\ s^{-1}$
$HC(O)S(O)_2O^- + H_2O \longrightarrow HC(O)OH + HSO_3^-$	$3\ s^{-1}$
$HC(O)S(O)_2OPh + H_2O \longrightarrow HC(O)OH + SO_2 + PhOH$	*ca.* $5\ s^{-1}$
$HOOCH(OH)OC(O)OC(O)H \longrightarrow HC(O)OH + CO_2 + HC(O)OOH$	$0.33\ s^{-1}$
$HC(O)P(O)(OEt)_2 + H_2O \longrightarrow HC(O)OH + HOP(OEt)_2$	$7 \times 10^{-3}\ s^{-1}$
$HC(O)Cl + OH^- \longrightarrow HC(O)OH + Cl^-$	$2.5 \times 10^4\ dm^3\ mol^{-1}\ s^{-1}$ (ref. 2)
$HC(O)CN + OH^- \longrightarrow HC(O)OH + CN^-$	$3.8 \times 10^5\ dm^3\ mol^{-1}\ s^{-1}$
$HC(O)S(O)_2O^- + OH^- \longrightarrow HC(O)OH + SO_3^{2-}$	$2 \times 10^4\ dm^3\ mol^{-1}\ s^{-1}$
$HC(O)P(O)(OEt)_2 + OH^- \longrightarrow HC(O)OH + {}^-OP(OEt)_2$	$3.2 \times 10^4\ dm^3\ mol^{-1}\ s^{-1}$
$HC(O)PO_3^{2-} + OH^- \longrightarrow HC(O)OH + PO_3^{3-}$	*ca.* $5\ dm^3\ mol^{-1}\ s^{-1}$
Vinylene carbonate + $OH^- \longrightarrow$ Products	*ca.* $10\ dm^3\ mol^{-1}\ s^{-1}$
$CH_2{=}CHOC(O)CH_3 + OH^- \longrightarrow CH_3C(O)H + CH_3C(O)O^-$	*ca.* $2\ dm^3\ mol^{-1}\ s^{-1}$

The identification of the organic hydroperoxide as hydroxymethylhydroperoxide is not in contradiction with the above statement that the formaldehyde yield is 100%, because under the conditions of the Hantzsch reaction which has been used for the determination of formaldehyde hydroxymethylhydroperoxide is quantitatively converted into formaldehyde [and H_2O_2, *cf.* reaction (25), for the equilibrium constant see ref. 27].

In principle, the hydrolysis of the Criegee intermediate, formed in the first step (see above) may take two routes [reactions (8) and (9)], but the electron-withdrawing cyano substituent disfavours the carbocation formed as an intermediate in reaction (11), and hence reaction (10) becomes practically the only process (*cf.* the similar situation in the case of vinyl chloride).[6]



In this reaction, formyl cyanide is one of the products. It is not stable under these conditions, and the full yield of H^+ and formate ion is present right after mixing ozone and acrylonitrile solutions, as shown by conventional conductometry. For the determination of the kinetics of reactions (12) and (13), stopped-flow with conductometric detection was used.

$$HC(O)CN + H_2O \longrightarrow HC(O)O^- + H^+ + HCN \quad (12)$$

$$HC(O)CN + OH^- \longrightarrow HC(O)O^- + CN^- + H^+ \quad (13)$$

The acrylonitrile concentration was chosen sufficiently high to ensure that the rate of the reaction of ozone with acrylonitrile is not the rate-determining step. Also, the ozone concentration was kept low in order not to disturb the kinetics of H^+ plus $HC(O)O^-$ formation by buffering effects [pK_a(HCO_2H) = 3.75]. The rate constant of formyl cyanide hydrolysis at pH ~7 [reaction (12)] is 3 s^{-1} as determined from the data presented in Fig. 2 (for a compilation of hydrolysis rate constants see Table 2).

In neutral solution, the hydrolysis of formyl cyanide leads to an increase in conductance due to the formation of H^+ and $HC(O)O^-$ [dissociation of HCN can be neglected under these conditions; pK_a(HCN) = 9.3]. In basic solutions, the rate of hydrolysis increases due to a contribution from reaction (13). The conductance signal is now negative (inset in Fig. 2), because OH^- consumed in this reaction has a higher equivalent conductance than the formate and cyanide ions.

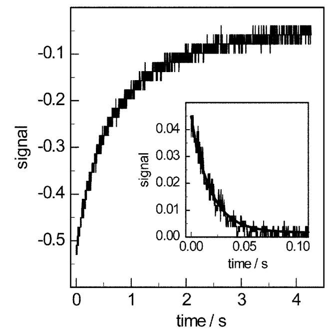


Fig. 2 Ozonolysis of acrylonitrile in aqueous solution (0.5 mol dm^{-3}) at pH 7. Kinetics of the hydrolysis of formyl cyanide as followed by the build-up of conductance in a stopped-flow experiment. Inset: kinetics of the formyl cyanide hydrolysis at $[OH^-] = 1.25 \times 10^{-4}$ mol dm^{-3}.

A plot of k_{obs} *vs.* the OH^- concentration yields a straight line (Fig. 3, main graph), from where the rate constant of reaction (13) was calculated. The intercept is due to a contribution from reaction (12).

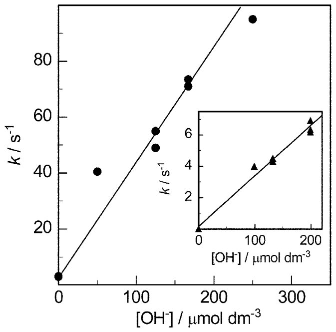
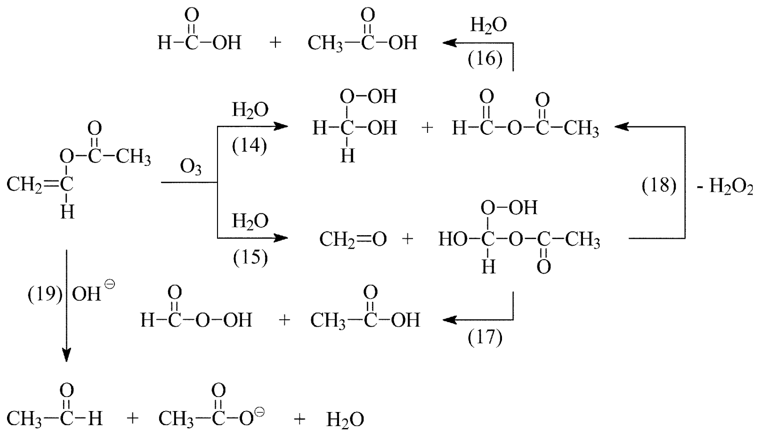


Fig. 3 Ozonolysis of acrylonitrile in aqueous solution. Rate of the hydrolysis of formyl cyanide as a function of the OH^- concentration. Inset: ozonolysis of diethyl vinylphosphonate. Rate of the hydrolysis of diethyl formylphosphonate as a function of the OH^- concentration.

Ozonolysis of vinyl acetate—hydrolysis of formyl acetate

The yields of formaldehyde and formate ion are both 100%. Acetate cannot be measured, because vinyl acetate itself hydrolyses too quickly (see below). The hydroperoxide yield is also unity, and a kinetic analysis of its reaction with molybdate-activated iodide shows that it has to be assigned to hydroxymethylhydroperoxide. The absence of significant amounts of formic peracid and H_2O_2 indicates that reaction (15), and thus also the subsequent reactions (17) and (18), do not take place.

In reaction (14), one of the products is formyl acetate, the mixed anhydride of formic and acetic acid. The pK_a value of



acetic acid is 4.8, and for this reason the ozone concentration in these experiments was kept ≤ 6 × 10^{-5} mol dm^{-3} in order to avoid a major distortion of the conductivity build-up due to buffering effects of acetic acid at the later stages of the reaction. From these data (not shown), the rate of hydrolysis of formyl acetate has been calculated (see Table 2).

Hydrolysis of vinyl acetate [reaction (19)] was followed by conventional conductometry ($[OH^-] = 2.5 \times 10^{-3}$ mol dm^{-3}, [vinyl acetate] = 1 × 10^{-3} mol dm^{-3}). From the data (not shown), $k(OH^- + \text{vinyl acetate}) \approx 2$ dm^3 mol^{-1} s^{-1} is obtained. This rate is evidently too fast for studying the OH^--induced hydrolysis of formyl acetate under our experimental conditions.

Ozonolysis of diethyl vinylphosphonate

Formaldehyde and formic acid yields are 100%, as is the total hydroperoxide yield. The latter one does not change with time, although right after ozonolysis practically only an organic hydroperoxide is present that slowly converts into H_2O_2 (Fig. 4).

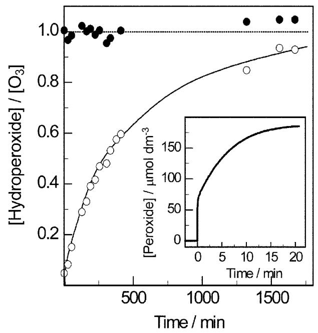
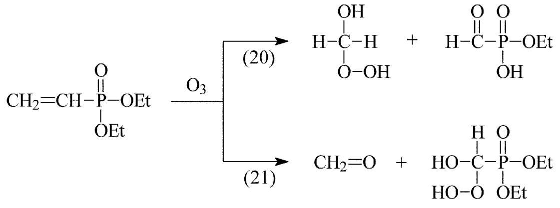
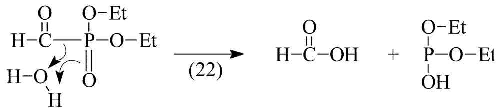


Fig. 4 Ozonolysis of diethyl vinylphosphonate (1 × 10^{-3} mol dm^{-3}) in aqueous solution at pH ~7.2. Yield of hydroperoxides per mol ozone ($[O_3]$ = 185 µmol dm^{-3}) as a function of time; ● total hydroperoxides, ○ hydrogen peroxide. Inset: kinetics of the reaction of the hydroperoxides with molybdate-activated iodide 190 min after ozonolysis. The fast component is due to the reaction of H_2O_2.

The organic hydroperoxide is characterised by a slow reaction with molybdate-activated iodide, within the experimental error of ±10% identical to that of authentic hydroxymethylhydroperoxide formed in the reaction of 1,1-dichloroethene plus ozone. Unless catalysed by base or buffer, hydroxymethylhydroperoxide is long-lived.[27] Under the conditions shown in Fig. 4, where the pH was ~7.2, the hydroperoxide is also long-lived and releases H_2O_2 only slowly, albeit somewhat faster ($k = 3.8 \times 10^{-5}$ s^{-1}) than at pH 5.7 ($k = 1.5 \times 10^{-6}$ s^{-1}).[27] The formation of H_2O_2 in this reaction has been characterised by its fast reaction with molybdate-activated iodide (*cf.* inset in Fig. 4). In agreement with its assignment to H_2O_2, this fast step is eliminated upon the addition of catalase without affecting the slower process. These data show that in the primary process mainly hydroxymethylhydroperoxide and diethyl formylphosphonate are formed [reaction (20)], and the other potential route leading to formaldehyde and diethyl hydroperoxyhydroxymethylphosphonate [reaction (21)] must be minor in comparison.



The subsequent hydrolysis of diethyl formylphosphonate gives rise to formic acid and diethyl phosphonate. This reaction is slow at around pH 7, where its hydrolysis [reaction (22)] was followed by conventional conductometry.



The OH^--induced hydrolysis was studied by stopped-flow with conductometric detection (inset in Fig. 3). Rate constants are given in Table 2. A further hydrolysis of diethyl phosphonate is not observed under these conditions. It may be worth mentioning that the eluent for the determination of formic acid reported above is slightly basic, and this must have caused the release of formic acid during analysis.

Ozonolysis of vinylphosphonic acid

At pH 7, the formaldehyde yield is unity, and also the total hydroperoxide yield measured immediately after ozonolysis is very close to this value (96%; *cf.* inset in Fig. 5). It consists

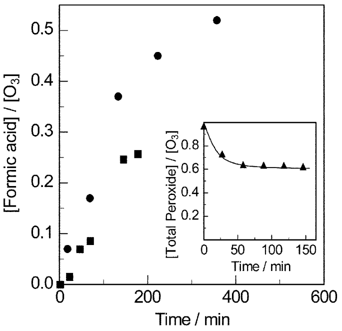


Fig. 5 Ozonolysis of vinylphosphonic acid at pH ~7. Release of formic acid as a function of time (two sets of data, ● and ■). Inset: decay of the H_2O_2 component of the total hydroperoxide yield as a function of time.

largely (71%) of a hydroperoxide that reacts with molybdate-activated iodide at a rate compatible with its assignment to hydroxymethylhydroperoxide, but there is also a contribution of 25% whose rate of reaction with molybdate-activated iodide agrees with that of H_2O_2. This fraction is largely wiped out by the addition of catalase, and in the absence of catalase it decays with time (inset in Fig. 5); only hydroxymethylhydroperoxide remains after *ca.* 1 h.

When the pH is raised to 10.2 with borate buffer, hydroxymethylhydroperoxide rapidly decomposes into formaldehyde and H_2O_2 [*cf.* reaction (25)]. Although H_2O_2 is stable at this pH, it decays quite rapidly under our conditions (Fig. 6). As can be seen from the inset in Fig. 6, the decay follows second-order kinetics ($k = 260$ dm^3 mol^{-1} s^{-1}).

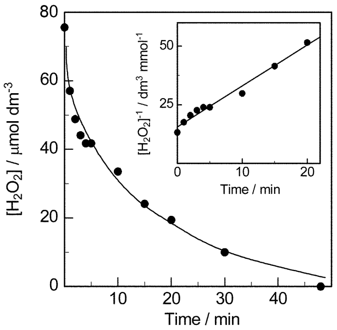


Fig. 6 Ozonolysis of vinylphosphonic acid. After ozonolysis, the pH has been raised to 10.2 with borate buffer. Decay of H_2O_2 as a function of time. Inset: second-order kinetic plot of the data up to 20 min.

In neutral solution, formic acid is formed only slowly (Fig. 5). Its final value of *ca.* 100% is reached at *ca.* 4000 min. When the pH is raised to 10.1 with NaOH, the formate release is speeded up dramatically, and the full yield is practically reached at *ca.* 150 min. These data are not shown, since a detailed kinetic study was not possible. In the determination of formate by ion chromatography, each run takes too much time for obtaining a series of reliable data at short times (consecutive injections lead to considerable scatter). In these experiments, a buffer could not be used, and upon formic acid release the pH dropped. Most likely, the rate of formic acid release would have been even faster if the system had been buffered. Upon the addition of a large excess of H_2O_2 at pH 10.2, the full formate yield is formed practically immediately. The formate yield is matched by an equal amount of phosphate.

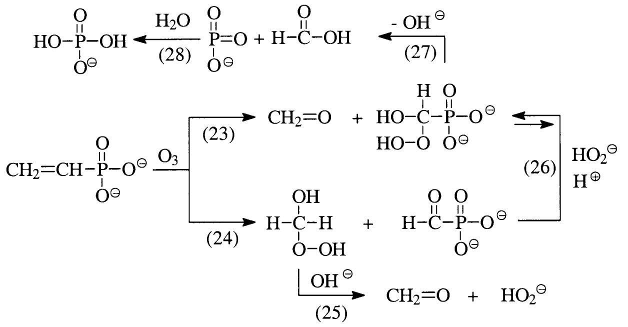
When after ozonolysis the pH was raised to 10.2 and catalase was added to destroy H_2O_2, the rate of formate formation was substantially delayed ($k \approx 5$ dm^3 mol^{-1} s^{-1} based on the prevailing "average" OH^- concentration; the value was hence only very approximate), and the major corresponding product then was phosphonate, while the phosphate yield fell below 30%. We attribute the above rate constant to the OH^--induced hydrolysis of $HC(O)PO_3^{2-}$ into formate and phosphonate.

Our formate data (unbuffered conditions) are not good enough to decide whether the decay of H_2O_2 and the release of formate coincide or whether there is a delay in formate release. There was no further organic hydroperoxide reacting with molybdate-activated iodide at a measurable rate detected upon the decay of H_2O_2, and we thus concluded that the hydroperoxide formed as an intermediate must have either reacted quite slowly with molybdate-activated iodide (there are examples)[13] or it had only a short lifetime, *i.e.* the kinetics of the decay of H_2O_2 and the formation of formate practically coincided. The latter possibility is more likely, and the seemingly slower release of formic acid, as compared to the decay of H_2O_2, must be largely due to a drop in pH in the unbuffered system required for the determination of formic acid.

From the above, we now conclude that the slow hydrolysis of $HC(O)P(OH)O_2^-$ at pH ≤7 by water (*cf.* Fig. 5) and of $HC(O)PO_3^{2-}$ at pH ~10.2 by OH^- allows another reaction to compete successfully: the H_2O_2-induced decomposition into formate and phosphate.

It is recalled that in water many aldehydes are present as hydrates. The neighbouring group of the HC(O)– function determines to what extent the aldehyde is hydrated. For example, formaldehyde is practically fully hydrated, glyoxylic acid[25] to 98.2% and acetaldehyde[28] to 55%. The formation of α-hydroxyhydroperoxides seems to be favoured over the formation of hydrates, and even very low H_2O_2 concentrations result in the formation of α-hydroxyhydroperoxides at quite high rates. Their presence can be readily deduced if these α-hydroxyhydroperoxides undergo rapid fragmentation. A case in point is the reaction of H_2O_2 with glyoxylic acid.[25]

We suggest that the Criegee intermediate of vinylphosphonic acid decomposes to *ca.* 75% according to reaction (24) and *ca.* 25% take route (23).



The α-hydroxyhydroperoxide formed in reaction (23) is not very stable and eliminates H_2O_2 [equilibrium (26)], but it also decomposes [reaction (27)]. The situation is somewhat more complex than shown in this scheme. Similarly to the educt vinyl phosphonate (*cf.* Fig. 1), hydroperoxyhydroxymethylphosphonate should be mono-protonated at pH ≤7 and fully dissociated at pH 10.2. The state of protonation must affect the rates of decomposition and H_2O_2-elimination [*cf.* reactions (27) and (−26)]. This could be the reason why we observe mainly an H_2O_2-elimination at pH 7 and rapid decomposition at pH 10.2. Reaction (27) is analogous to the well-established decay of the α-hydroxyhydroperoxide derived from glyoxylic acid (*cf.* ref. 25). Phosphoric acid, the other final product in the formic acid releasing process, is subsequently formed in reaction (28).

At the conditions of the experiment shown in Fig. 6, the H_2O_2 required for the above reactions to proceed had to come from the slow hydrolysis of the hydroxymethylhydroperoxide. Addition of alkali to the ozonated solution speeds up the hydrolysis of hydroxymethylhydroperoxide [reaction (25)]. Alkaline conditions and the presence of H_2O_2 now enhance the rate of formic acid release substantially. Moreover, the addition of H_2O_2 in excess dramatically increases the rate of formate and phosphate formation. In a separate experiment, it has been shown that phosphonate is not oxidised to phosphate by H_2O_2, neither at low nor at high pH. This supports the above mechanistic proposal.

From the foregoing, we conclude that the difference in mechanism of the ozonolysis of diethyl vinylphosphonate and vinyl phosphonate is largely due to the fast hydrolysis of $HC(O)PO_3(Et)_2$ as compared to the several orders of magnitude slower hydrolysis of $HC(O)P(OH)O_2^-/HC(O)PO_3^{2-}$. As a consequence, an H_2O_2-induced decomposition of the latter compounds competes successfully with their hydrolysis.

Ozonolysis of vinyl phenylsulfonate—hydrolysis of formyl phenylsulfonate

The rate of the reaction of ozone with vinyl phenylsulfonate has been determined in competition with *cis*-1,2-dichloroethene. It has been mentioned above that the data shown in the inset of

Fig. 7 would be compatible with a rate constant of 850 dm^3 mol^{-1} s^{-1}, but since the products react much faster with ozone than vinyl phenylsulfonate itself (see below), the apparent rate constant of 850 dm^3 mol^{-1} s^{-1} comes out much too high. A rate constant of only *ca.* 200 dm^3 mol^{-1} s^{-1} is required to accommodate all data, the competition data and the data that are reported next.

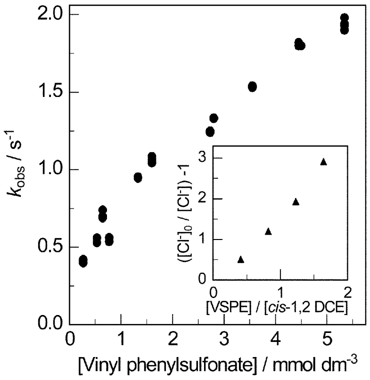
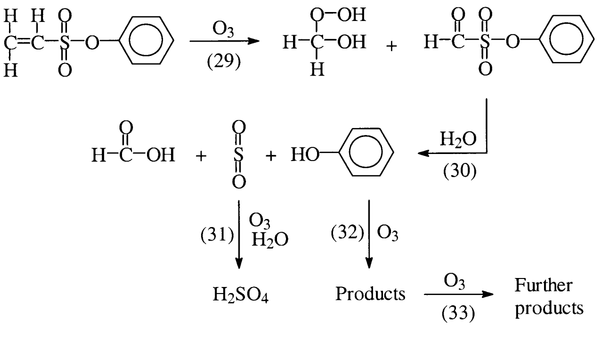


Fig. 7 Rate of conductance build up in the ozonolysis of vinyl phenylsulfonate as a function of the vinyl phenylsulfonate concentration. Inset: competition plot of *cis*-1,2-dichloroethene and vinyl phenylsulfonate.

The final products that were measured are formaldehyde (21%), formate (32%), sulfate (28%/21%), phenol (12%/7%/6%) and total peroxide (30%/23%). Upon HPLC, further products were detected, but their yields and stability were too low to collect major quantities for their identification. There is an unusual scatter of data from run to run pointing to a complex mechanism that is sensitive to minor variations in the reaction conditions. Yet, it seems fair to say that the yields of the key products formaldehyde, formate and sulfate centre around 27 ± 5%.

Using the stopped-flow technique with conductometric detection, the rapid formation of protons was observed. As is seen from Fig. 7, the rate of formation of conductance increases with increasing vinyl phenylsulfonate concentration.

Yet, this increase is not a linear function of the vinyl phenylsulfonate concentration as would be expected if the rate-limiting step were the reaction of ozone with vinyl phenylsulfonate. An analysis of the data shows that a primary product of the ozonolysis decays giving rise to conductance and that the rate of this reaction must be in the same order as the reaction of ozone with vinyl phenylsulfonate. Furthermore, the low yields of formaldehyde, formate and the formation of sulfate point to a rapid reaction of products with ozone. A low phenol yield and further UV-absorbing products detected by HPLC is an additional hint as to the mechanism shown in reactions (29)–(33).



The major products formed in the ozonolysis of vinyl phenylsulfonate are hydroxymethylhydroperoxide and formyl phenylsulfonate [reaction (29)]. The latter hydrolyses into formic acid, SO_2 and phenol [reaction (30)]. Modelling of the data in Fig. 8 indicates that the rate of hydrolysis must be *ca.* 5 s^{-1}. This value and the value for the ozone rate constant are fraught with a considerable uncertainty, since the modelling procedure that is based on the competition data, the rate of conductance as a function of the vinyl phenylsulfonate concentration and product yields requires two adjustable parameters: the rate of reaction and the decomposition of formyl phenylsulfonate.

The reactions of ozone with S(IV) compounds are fast ($k \approx 2 \times 10^6$ dm^3 mol^{-1} s^{-1}),[29] *i.e.* as soon as SO_2 is formed it is converted into sulfuric acid [reaction (31)]. Phenol also reacts with ozone faster [reaction (32), $k = 1.3 \times 10^3$ dm^3 mol^{-1} s^{-1}][29] than vinyl phenylsulfonate. The phenolate ion reacts even faster ($k = 1.4 \times 10^9$ dm^3 mol^{-1} s^{-1}),[29] and at pH 7 k_{obs} will be *ca.* 10^6 dm^3 mol^{-1} s^{-1}. This value will drop considerably, when the pH drops as reactions (30) and (31) proceed. The ozonolysis of phenol has been studied in some detail recently,[30] and the major products react also fast, some even faster, with ozone (hydroquinone, $k = 2.3 \times 10^6$ dm^3 mol^{-1} s^{-1}; catechol, $k = 5.2 \times 10^5$ dm^3 mol^{-1} s^{-1}; 1.4-benzoquinone, $k = 2.5 \times 10^3$ dm^3 mol^{-1} s^{-1}; *cis-,cis*-muconic acid, $k = 4 \times 10^4$ dm^3 mol^{-1} s^{-1})[30] and thus contribute to ozone consumption [reaction (33)]. This is certainly one of the reasons why further products were detected but do not build up to marked concentrations.

It is intriguing that we failed to detect the formation of singlet dioxygen in the present system. This short-lived intermediate is formed in 100% yield in the reaction of ozone with sulfides,[16] disulfides[16] and methanesulfinic acid.[16,31] Only when the ozone-to-substrate adduct has a sufficient lifetime to allow the release triplet (ground-state) dioxygen, the yield of singlet dioxygen may be considerably lowered.[14] A case in point are the halide ions Br^- and I^-. Here, the heavy-atom effect assists the singlet⟶triplet conversion. Although such an effect has not been observed with sulfur compounds as yet, attention is drawn to the observation that some sulfur compounds seem to undergo ozone reactions beyond simple O-transfer. For example, the oxidation of H_2S/HS^- by ozone to sulfate requires only 2.4 mol ozone.[32,33] One also may consider that the primary ozone adduct to SO_2 which has some zwitterionic character will react with water giving rise to a hydrotrioxide [reactions (34) and (35)].

$$SO_2 + O_3 \longrightarrow {}^-OOOS(O)_2{}^+ \qquad (34)$$

$${}^-OOOS(O)_2{}^+ + H_2O \longrightarrow HOOOS(O)_2OH \qquad (35)$$

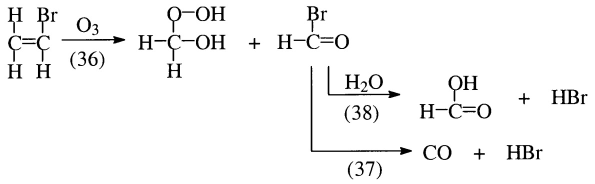
The formation of hydrotrioxides in the ozonolysis of aliphatic compounds, notably alcohols, is well documented.[34–39] In the case of 2-propanol, $HOOOC(CH_3)_2OH$ is formed. In water, this hydrotrioxide decays without giving rise to singlet dioxygen.[16] Details are not fully understood, but its analogy to the hydrotrioxide that we are concerned with here is obvious.

Ozonolysis of vinylsulfonic acid—hydrolysis of formyl sulfonate

Vinyl sulfonate was only available as 25% aqueous solution. We have the impression that the material is not stable (confirmed by ion chromatography), and remeasuring some product yields a few months later resulted in much lower values [formaldehyde (26%, but a lower value of 10% was also measured), hydroxymethylhydroperoxide (*ca.* 25–31%), formate (75%), sulfate (70%) and some glyoxal (3.7%)]. We, therefore, hesitate to base on these data a detailed reaction mechanism. The obvious complexities that we observed with vinyl phenylsulfonate (see above) is an additional warning that a quantification may not be possible. Yet, it is reasonable to assume that the formylsulfonate anion is a major product and that the kinetic data that were obtained by conventional conductometry for the hydrolysis by water and by stopped flow for the OH^--induced reaction (see Table 2) are reliable.

Ozonolysis of vinyl bromide and 1,2-dibromoethene—decomposition and hydrolysis of formyl bromide

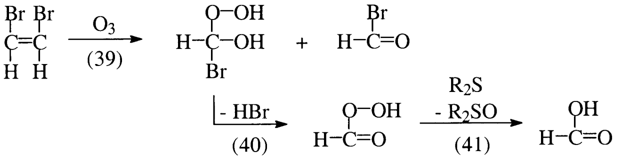
The chemistry of vinyl bromide [reactions (36)–(38)] is very similar to that of vinyl chloride discussed in the Introduction.



The bromide yield is practically quantitative (*ca.* 92%) and that of formate is 3.6%; CO was detected in large amounts but not quantified. The formate yield is less than in the case of vinyl chloride (6%).[2] Without knowing the rate of the decomposition plus hydrolysis of formyl bromide, it cannot be decided whether this lower formate yield is due to a faster decomposition into CO and Br^- plus H^+ [reaction (37)] or a slower hydrolysis [reaction (38)]. It is also possible that with formyl bromide both processes are faster than with formyl chloride. Then, substitution of chloride by bromide would speed-up the rate of decomposition more strongly than that of hydrolysis. We favour this possibility, since the stronger electron-withdrawing property of bromide should speed-up also hydrolysis.

In its reaction with ozone, the *cis*/*trans* mixture of 1,2-dibromoethene yields Br^- (200%) and formic peracid (95%, kinetic analysis; *cf.*[6,13]). The formate yield after reduction with $S(CH_2CH_2OH)_2$ [reaction (41), k = 220 dm^3 mol^{-1} s^{-1}][14] has been determined in two different runs at 97% and 110%.

The Criegee ozonide must decompose into BrCH(OH)OOH and formyl bromide [reaction (39)]. The former is a geminal bromohydrine. This type of compound must loose HBr within a few μs[40,41] thereby forming formic peracid [reaction (40)].



In the presence of formic peracid, formate yields cannot be determined with accuracy, since some of the formic peracid decomposes under the conditions of ion chromatography. However, the yields measured after reduction of formic peracid with the sulfide clearly indicate that not much formic acid is formed upon hydrolysis of formyl bromide, the other product formed in reaction (39). This agrees with the conclusion drawn above, *i.e.* that the decomposition of formyl bromide into Br^- and H^+ is much faster than its hydrolysis.

Ozonolysis of vinylene carbonate—hydrolysis of formyl bicarbonate

The total hydroperoxide yield is 97%. As indicated by kinetic analysis of the iodide reaction and by the sulfide assay which eliminates formic peracid but not H_2O_2 and HPLC with post-column derivatisation, it mainly (93%) consists of formic peracid. The minor hydroperoxide (4%) is H_2O_2. Cleavage of the Criegee intermediate (not shown) could give rise to a short-lived hydroperoxide [reaction (42)] that may decompose into the anhydride of formic acid and hydrocarbonic acid and formic peracid [reaction (43)]. Upon the decay of the anhydride of formic acid and hydrocarbonic acid, CO_2 plus formic acid are formed [reaction (46)]. These products could also be formed in the concerted reaction (44). The formation of the formic peracid as a major product has been ascertained (see above). Determination of formic acid yields by ion chromatography was not reliable due to the presence of considerable amounts of formate in the blank. However, as is indicated by conductometry (Fig. 8), the formic acid yield is *ca.* 90% right after ozonolysis. Formic peracid (pK_a = 7.1) does not contribute to conductance significantly under these conditions.

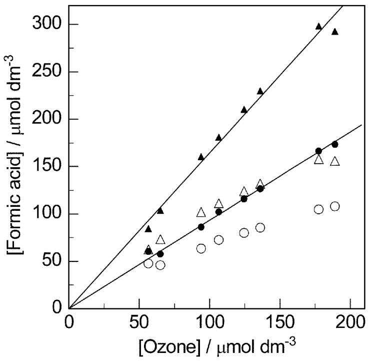
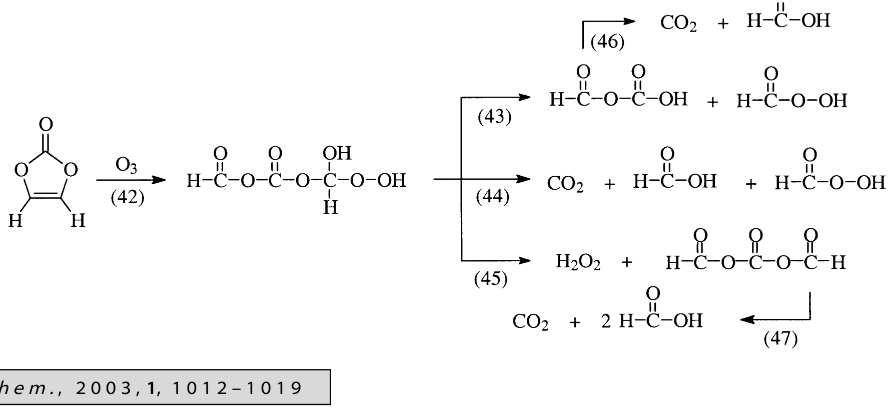


Fig. 8 Ozonolysis of vinylene carbonate in aqueous solution. Formation of proton plus anion as determined by conductometry without (○, ●) and with (△ ▲) the addition of sulfide. Open symbols are experimental values. The closed symbols are corrected values based on the incomplete dissociation of formic acid (pK_a = 3.75) at elevated formic acid concentrations.

After reduction of formic peracid with sulfide [*cf.* reaction (41)], this value rises to *ca.* 170% (Fig. 8). We consider this as a reasonable material balance, since the conductometric determination of product yields is fraught with a noticeably larger error than the ±5% stated in the experimental section for the other assays. Despite the larger error margin, the first step is significantly higher (90%) than the second step measured after the addition of sulfide (80%). This difference fades away when we consider that *ca.* 4% H_2O_2 are formed. This is connected with the formation of two mol of formic acid [reactions (45) and (47)].

In this system, the formation of acid is too fast to resolve its kinetics by conventional conductometry, and the rate constant given in Table 2 had to be determined by stopped flow (data not shown). The rate of the OH^--induced reaction could not be measured, since vinylene carbonate itself hydrolyses too fast ($k \approx 10$ dm^3 mol^{-1} s^{-1}, determined by conventional conductom-



etry). In the scheme, two conceivable routes to formic acid were envisaged: two consecutive reactions [reactions (43) and (46)] and a concerted decay after deprotonation of the tertiary OH group by water [reaction (44)]. We tentatively attribute the measured rate to this reaction.

Conclusions

There is a wide spread (five orders of magnitude) of the hydrolysis rates in water of the mixed anhydrides of formic acid with some other acids ranging from 600 s^{-1} (formyl chloride[2,6] and possibly even higher in the case of formyl bromide) to 7×10^{-3} s^{-1} (formyl diethylphosphonate). The rate of the reaction of formyl phosphonate mono-anion was too slow to be measured. The rate constant for the OH^--induced hydrolysis ranges in the order of 10^4 to 10^5 dm^3 mol^{-1} s^{-1} for formyl cyanide, sulfonate and diethylphosphonate. However the rate of the OH^--induced hydrolysis of formyl phosphonate di-anion is only in the order of 5 dm^3 mol^{-1} s^{-1}. As a consequence of this slow rate of hydrolysis, the H_2O_2-induced decomposition of the formyl phosphonate dianion becomes the major pathway in the ozonolysis vinyl phosphonate.

Acknowledgements

J. A. T. would like to thank the World Laboratory for a stipend. The continuing support by Prof. Dr. R. Mehnert, enabling us to finalise the work at the IOM, is highly appreciated.

References

1 K. B. Krauskopf and G. K. Rollefson, *J. Am. Chem. Soc.*, 1934, **56**, 2542.

2 P. Dowideit, R. Mertens and C. von Sonntag, *J. Am. Chem. Soc.*, 1996, **118**, 11288.

3 R. M. Tyrell, *Photochem. Photobiol.*, 1979, **29**, 963.

4 B. E. Conway, *Ionic Hydration in Chemistry and Biophysics*, Elsevier, New York, 1981.

5 R. Criegee, *Angew. Chem.*, 1975, **87**, 765.

6 P. Dowideit and C. von Sonntag, *Environ. Sci. Technol.*, 1998, **32**, 1112.

7 L. Prager, P. Dowideit, H. Langguth, H.-P. Schuchmann and C. von Sonntag, *J. Chem. Soc., Perkin Trans. 2*, 2001, 1641.

8 E. J. Hart, K. Sehested and J. Holcman, *Anal. Chem.*, 1983, **55**, 46.

9 L. Forni, D. Bahnemann and E. J. Hart, *J. Phys. Chem.*, 1982, **86**, 255.

10 T. Nash, *Biochem. J.*, 1953, **55**, 416.

11 M. Ahmad, M. H. Awan and D. Mohammad, *J. Chem. Soc. B*, 1968, 945.

12 A. O. Allen, C. J. Hochanadel, J. A. Ghormley and T. W. Davis, *J. Phys. Chem.*, 1952, **56**, 575.

13 R. Flyunt, A. Leitzke and C. von Sonntag, *Radiat. Phys. Chem.*, 2003, in the press.

14 R. Flyunt, A. Leitzke, G. Mark, E. Mvula, E. Reisz, J. A. Theruvathu and C. von Sonntag, *J. Phys. Chem.*, 2003 in the press.

15 R. Flyunt, J. A. Theruvathu, A. Leitzke and C. von Sonntag, *J. Chem. Soc., Perkin Trans. 2*, 2002, 1572.

16 F. Muñoz, E. Mvula, S. E. Braslavsky and C. von Sonntag, *J. Chem. Soc., Perkin Trans. 2*, 2001, 1109.

17 F. Muñoz and C. von Sonntag, *J. Chem. Soc., Perkin Trans. 2*, 2000, 661.

18 J. Hoigné, H. Bader, W. R. Haag and J. Staehelin, *Wat. Res.*, 1985, **19**, 993.

19 J. A. Theruvathu, R. Flyunt, C. T. Aravindakumar and C. von Sonntag, *J. Chem. Soc., Perkin Trans. 2*, 2001, 269.

20 W. A. Pryor, D. Giamalva and D. F. Church, *J. Am. Chem. Soc.*, 1983, **105**, 6858.

21 J. Hoigné and H. Bader, *Wat. Res.*, 1983, **17**, 173.

22 S. Naumov, A. Leitzke and C. von Sonntag, to be published.

23 F. Rochlitz and H. Vilcsek, *Angew. Chem.*, 1962, **74**, 970.

24 M. I. Kabachnik, *J. Gen. Chem. USSR*, 1963, **33**, 375.

25 A. Leitzke, E. Reisz, R. Flyunt and C. von Sonntag, *J. Chem. Soc., Perkin Trans. 2*, 2001, 793.

26 F. Muñoz and C. von Sonntag, *J. Chem. Soc., Perkin Trans. 2*, 2000, 2029.

27 E. Bothe and D. Schulte-Frohlinde, *Z. Naturforsch.*, 1980, **35b**, 1035.

28 J. L. Kurz, *J. Am. Chem. Soc.*, 1967, **89**, 3524.

29 P. Neta, R. E. Huie and A. B. Ross, *J. Phys. Chem. Ref. Data*, 1988, **17**, 1027.

30 E. Mvula and C. von Sonntag, submitted.

31 R. Flyunt, O. Makogon, M. N. Schuchmann, K.-D. Asmus and C. von Sonntag, *J. Chem. Soc., Perkin Trans. 2*, 2001, 787.

32 P. K. Overbeck and P. K. Overbeck, *Proc. -Annu. Conf.*, Am. Water Works Assoc., 1995, p. 241.

33 G. Mark, E. Mvula and C. von Sonntag, unpublished results.

34 F. Kovac and B. Plesnicar, *J. Am. Chem. Soc.*, 1979, **101**, 2677.

35 M. N. Schuchmann and C. von Sonntag, *J. Water Supply: Res. Technol.—Aqua*, 1989, **38**, 311.

36 B. Plesnicar, in *The Chemistry of Functional Groups. Peroxides*, ed. S. Patai, Wiley, London, 1983, p. 483.

37 J. Koller and B. Plesnicar, *J. Am. Chem. Soc.*, 1996, **118**, 2470.

38 B. Plesnicar, J. Cerkovnik, T. Tekavec and J. Koller, *J. Am. Chem. Soc.*, 1998, **120**, 8005.

39 B. Plesnicar, J. Cerkovnik, T. Tekavec and J. Koller, *Chem. Eur. J.*, 2000, **6**, 809.

40 R. Köster and K.-D. Asmus, *Z. Naturforsch.*, 1971, **26b**, 1108.

41 R. Mertens, C. von Sonntag, J. Lind and G. Merényi, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1259.