OH-Radical-induced oxidation of methanesulfinic acid. The reactions of the methanesulfonyl radical in the absence and presence of dioxygen

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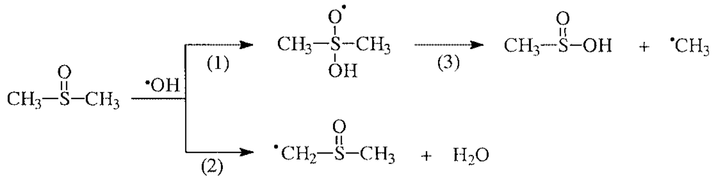
Hydroxyl radicals were generated radiolytically in N_2O-saturated solutions. As shown by pulse radiolysis, methanesulfinic acid reacts with $^{\bullet}OH$ ($k = 5.3 \times 10^9$ dm^3 mol^{-1} s^{-1}) and $N_3^{\bullet}$ giving rise to an intermediate which has an absorption maximum at 330 nm ($G\varepsilon \approx 5.2 \times 10^{-5}$ m^2 mol^{-1}). This is attributed to the methanesulfonyl radical, $CH_3S(O)O^{\bullet}$. Pulse radiolysis with conductometric detection indicates that $CH_3S(O)O^{\bullet}$ is formed in only ~80% yield. This is confirmed by scavenging experiments with $Fe(CN)_6^{4-}$, ascorbate and sulfite, which are oxidised by $CH_3S(O)O^{\bullet}$ with rate constants of ~2×10^9 dm^3 mol^{-1} s^{-1}. Steady-state radiolysis of methanesulfinic acid shows that methanesulfonic acid is the major product ($G = 2.1 \times 10^{-7}$ mol J^{-1}). Further products are sulfate (0.7×10^{-7} mol J^{-1}), methane (0.3×10^{-7} mol J^{-1}), ethane (0.08×10^{-7} mol J^{-1}) and dimethyl sulfone (not quantified). It is suggested that an OH-adduct is formed initially which mainly eliminates OH^-, but also decomposes yielding $^{\bullet}CH_3$ and bisulfite. The formation of methanesulfonic acid can be explained by a disproportionation of the methanesulfonyl radicals *via* recombination and subsequent hydrolysis. In the presence of dioxygen, a chain reaction occurs whereby 2 mol methanesulfonic acid are formed per 1 mol dioxygen consumed. *G*(methanesulfonic acid) ≈ 250×10^{-7} mol J^{-1} was found to be independent of dose rate (0.011–0.165 Gy s^{-1}), methanesulfinic acid concentration [(0.1–4) × 10^{-3} mol dm^{-3}] and dioxygen concentration. An efficient chain process was also observed upon electron beam irradiation [*G*(methanesulfonic acid) ≈ 200×10^{-7} mol J^{-1} at 0.8 Gy per pulse and 75×10^{-7} mol J^{-1} at 9 Gy per pulse (pulse duration 2 μs)]. It is proposed that the oxidation of the substrate by the methylsulfonylperoxyl radical, $CH_3S(O_2)OO^{\bullet}$, to give the strongly oxidising $CH_3S(O_2)O^{\bullet}$ radical, initiates the chain reaction, with the latter propagating the chain by reacting with a substrate molecule to give methanesulfonic acid and the methanesulfonyl radical. Branching and partial removal of the chain-carrying $CH_3S(O_2)O^{\bullet}$ radicals by H-abstraction from the substrate is suggested as the likely path leading to chain termination. Oxidation of methanesulfinate by ozone ($k = 2 \times 10^6$ dm^3 mol^{-1} s^{-1}) occurs only by O-atom transfer, and an electron transfer that would start a chain reaction was not observed.

The OH-radical-induced free-radical chemistry of sulfur-containing compounds is very different from that observed with their carbon analogues. For example, $^{\bullet}OH$ reacts with acetone only slowly by H-abstraction,[1] whereas its reaction with dimethyl sulfoxide is very fast, proceeding mainly by addition [reaction (1)]; only 7% H-abstraction [reaction (2)] occurs.[2] The adduct thus formed is very short-lived and rapidly decomposes by β-fragmentation into methanesulfinic acid and a methyl radical [reaction (3)]. In fact, this reaction sequence is the most convenient source of methyl radical in aqueous solution and has allowed us to study certain of its reactions in more detail (*cf.* refs. 3–7).

In the present study we have extended our investigation of $^{\bullet}OH$ radical reactions to the methanesulfinate ion whose carbon analogue, acetate, reacts by H-abstraction; electron transfer from the carboxylate group is negligible (2.5%).[8] Pulse radiolysis of methanesulfinic acid in the absence and presence of dioxygen has already attracted some attention,[9] and in various aspects we can build upon this interesting study.

It will be shown that methanesulfinic acid behaves in many respects like dimethyl sulfoxide, *i.e.* the $^{\bullet}OH$ radical reacts preferentially by addition and subsequent fragmentation, giving rise to either methanesulfonyl or methyl radicals. In the



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presence of dioxygen, the former initiates a rapid chain reaction reminiscent of the OH-radical-induced autoxidation of the hydrogen sulfite ion.[10,11] In contrast, the acetate ion does not give rise to a chain reaction under otherwise identical conditions.[12]

Experimental

Pulse radiolysis of aqueous solutions of sodium methanesulfinate (97%, Lancaster; main impurity, ~3%, methanesulfonate as determined by HPIC) in Milli-Q-filtered (Millipore) water saturated either with N_2O or with N_2O–O_2 (4 : 1 v/v) was carried out with a 2.8 MeV Van de Graaff accelerator delivering electron pulses of 0.4 µs duration. For preparative pulse radiolysis 2 µs pulses were employed. Intermediates were monitored by optical and conductometric detection. The pulse radiolysis set-up has been described previously.[13] For dosimetry, N_2O-saturated 10^{-2} mol dm^{-3} thiocyanate solution was used for optical detection,[14,15] taking $G\varepsilon[(SCN)_2^{\bullet -}] = 5.28 \times 10^{-4}$ m^2 J^{-1} at 480 nm.[15] For conductometric detection, N_2O-saturated 10^{-2} mol dm^{-3} dimethyl sulfoxide solution[2] at pH 4 was used as dosimeter, taking $G(H^+) = G(CH_3SO_2^-) = 5.8 \times 10^{-7}$ mol J^{-1}.[16] At elevated methanesulfinate concentrations, the increased $^\bullet$OH-scavenging capacity[17] has been taken into account.

γ-Radiolyses were carried out in a panoramic ^{60}Co-source at dose rates varying between 0.011 and 0.165 Gy s^{-1}. Methanesulfinate and methanesulfonate, as well as sulfate anions, were separated by ion chromatography (Dionex DX-2010i, 3 × 250 mm AS4-14 column with a 3 × 50 mm AG-14 pre-column, ASRS-I suppressor). The eluent used was an 9×10^{-4} mol dm^{-3} Na_2CO_3–8.5×10^{-4} mol dm^{-3} $NaHCO_3$ solution at a flow rate of 1 cm^3 min^{-1}. Their retention times were 2.6, 3.6 and 23.5 min, respectively. Hydrogen peroxide cannot be determined using the sensitive molybdate-activated iodide method,[18] because iodide plus H_2O_2 induces the autoxidation of methanesulfinic acid, and so we had to rely on the less sensitive assay with titanium(IV) sulfate.[19] Methane and ethane in the irradiated samples were purged with argon and measured by GC on a 3.2 m Porapak-9 capillary column. Oxygen concentration in aqueous solution of sodium methanesulfinate was determined with an oxygen-sensitive Clark-electrode (TriOx EO 200, Wissenschaftlich-Technische Werkstätten, Weilheim). Product yields are considered to be accurate to within ±10%. Some of the irradiated samples were rotary evaporated, from which less volatile products were extracted with diethyl ether and analysed by GC-MS on a Hewlett-Packard 5971A Mass Selective Detector coupled with an HP 5890 Series II Gas Chromatograph. Dimethyl sulfone was thus identified by comparison of its mass spectrum with that of authentic material.

Ozone stock solutions were prepared by bubbling ozone from a dioxygen-fed ozonator (Philaqua Philoz 04, Gladbeck) for some minutes through water, and its ozone content was determined spectrophotometrically taking ε(260 nm)[20,21] = 3300 dm^3 mol^{-1} cm^{-1}. In all experiments, the methanesulfinic acid was in large excess over the added ozone concentration (methanesulfinic acid consumption <15%).

Results and discussion

The radical-generating system

Hydroxyl radicals are generated in the radiolysis of water [reaction (4)]. The radiation-chemical yields (G values) of the

$$H_2O \xrightarrow[\text{radiation}]{\text{ionizing}} e_{aq}^-,\ {}^\bullet OH,\ H^\bullet,\ H^+,\ H_2O_2,\ H_2 \qquad (4)$$

primary radicals are $G(^\bullet OH) \approx G(e_{aq}^-) = 2.9 \times 10^{-7}$ mol J^{-1}, $G(H^\bullet) = 0.6 \times 10^{-7}$ mol J^{-1}, and $G(H_2O_2) \approx 0.7 \times 10^{-7}$ mol J^{-1}. N_2O is used to convert the solvated electron into $^\bullet$OH [reaction (5)]. The $^\bullet$OH radical and the $H^\bullet$ atom will react with methanesulfinic acid. The rate constant of $^\bullet$OH has been determined[9] to be $(6 \pm 1) \times 10^9$ dm^3 mol^{-1} s^{-1} (our value: 5.3×10^9 dm^3 mol^{-1} s^{-1}, see below); that of $H^\bullet$ could not be measured, but it may be as low as those reported for dimethyl sulfoxide ($\leq 10^7$ dm^3 mol^{-1} s^{-1}).[22]

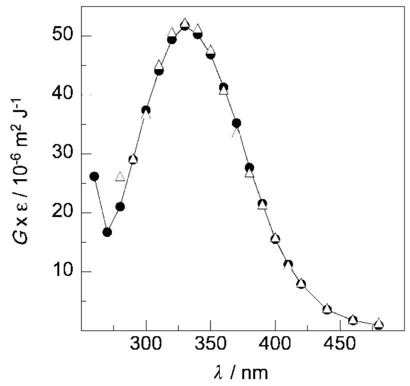


Fig. 1 Comparison of the spectra (5 µs after the pulse) of radicals produced in the pulse radiolysis (~5 Gy per pulse) of an N_2O-saturated solution of sodium methanesulfinate (10^{-3} mol dm^3) at pH 7.2 in the absence (●) and presence of sodium azide (10^{-2} mol dm^3) at pH 8.5 (△).

$$e_{aq}^- + N_2O + H_2O \longrightarrow {}^\bullet OH + OH^- + N_2 \qquad (5)$$

In the presence of O_2, *e.g.* in N_2O–O_2 (4 : 1)-saturated solutions, the solvated electron is still scavenged by N_2O. While $^\bullet$OH does not react with O_2, $H^\bullet$ is readily scavenged [reaction (6)]. In

$$H^\bullet + O_2 \longrightarrow HO_2^\bullet \qquad (6)$$

neutral solution, the $HO_2^\bullet$ radical is largely dissociated, and $O_2^{\bullet -}$ is the dominating species [pK_a($HO_2^\bullet$) = 4.8].[23]

Reactions in the absence of dioxygen

In the pulse radiolysis of an N_2O-saturated solution of methanesulfinate anion at pH 7, an intermediate is formed which is characterised by an absorption maximum at 330 nm (Fig. 1) and is assigned to the $CH_3S(O)O^\bullet$ radical (*cf.* also ref. 9). Assuming G(radicals) = 4.8×10^{-7} mol J^{-1} (85% of $^\bullet$OH, see below) an absorption coefficient of 1080 ± 100 dm^3 mol^{-1} cm^{-1} at 330 nm is calculated. These spectral characteristics agree well with those of the earlier study, where the absorption maximum was reported at 325 nm with $\varepsilon = 900 \pm 100$ dm^3 mol^{-1} cm^{-1}, assuming 100% of $^\bullet$OH.[9]

If its reaction with sulfoxides[2] [*cf.* reaction (1)] is a good guide, one must assume that also in the present system $^\bullet$OH mainly adds to methanesulfinate [reaction (7)] and that H-abstraction at the methyl group probably plays a minor role [reaction (8)]. The $^\bullet$OH-adduct may decompose by β-fragmentation in two directions; either it eliminates OH^- to give the $CH_3S(O)O^\bullet$ radical [reaction (9)], or it may split off a methyl radical, the other product being the bisulfite anion [reaction (10)]. Our data do not allow us to give rate constants for these very fast reactions. Evidence will be presented below to show that reaction (9) is in fact the major pathway, with a minor contribution of ~10–20% from reaction (10). The occurrence of latter pathway is supported by the formation of

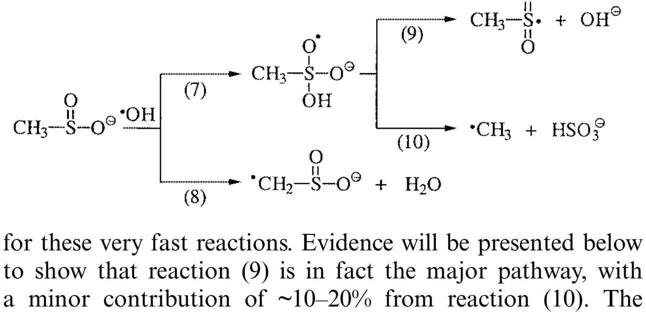
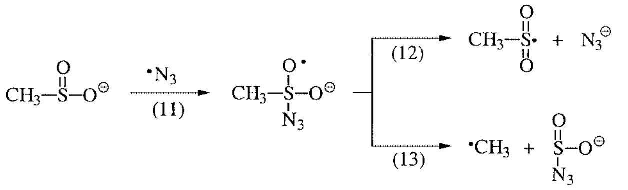


Table 1 Compilation of rate constants measured in the present study

Reaction	k/dm^3 mol^{-1} s^{-1}
$^{\bullet}OH + CH_3SO_2^- \longrightarrow$ products	5.3×10^9
$SO_4^{\bullet -} + CH_3SO_2^- \longrightarrow CH_3S(O)O^{\bullet} + SO_4^{2-}$	1.8×10^9
$CH_3S(O)O^{\bullet} + Fe(CN)_6^{4-} \longrightarrow CH_3SO_2^- + Fe(CN)_6^{3-}$	2.1×10^9
$CH_3S(O)O^{\bullet}$ + ascorbate $\longrightarrow CH_3SO_2^-$ + ascorbate radical	1.5×10^9
$CH_3S(O)O^{\bullet} + SO_3^{2-} \longrightarrow CH_3SO_2^- + {}^{\bullet}SO_3^-$	1.7×10^9
$2\ CH_3S(O)O^{\bullet} \longrightarrow$ products	1.8×10^9 ($2k$)

sulfate and methane/ethane (see below). The latter products have the methyl radical as precursor.

An identical spectrum is observed when the methanesulfinate anion reacts with $N_3^{\bullet}$ (the latter is produced by the reaction of $^{\bullet}OH$ with N_3^-) (*cf.* Fig. 1). The $N_3^{\bullet}$ radical is known generally to undergo electron transfer reactions. Its reaction with the methanesulfinate anion is expected to yield quantitatively the $CH_3S(O)O^{\bullet}$ radical. However, in the γ-radiolysis of NaN_3 (2×10^{-2} mol dm^{-3}) and sodium methanesulfinate (1×10^{-3} mol dm^{-3}) in an N_2O-saturated solution, the yield of $CH_3S(O)O^{\bullet}$ is identical to that for the $^{\bullet}OH$-induced reaction, and there is reason to assume that in this case the reaction of the $N_3^{\bullet}$ radical might initially also proceed *via* addition to the methanesulfinate anion [reaction (11)]. This short-lived adduct subsequently undergoes either azide elimination to give the $CH_3S(O)O^{\bullet}$ radical as the main product [reaction (12)], or β-fragmentation to produce the methyl radical and $N_3SO_2^-$ [reaction (13)]. This is supported by the finding that methane ($G \sim 0.01 \times 10^{-7}$ mol J^{-1}) and ethane ($G \sim 0.06 \times 10^{-7}$ mol J^{-1}) are formed. The low yield of methane can be explained by the fact that the H atom is scavenged by the azide anion.[24]



The overall rate constant of $^{\bullet}OH$ with the methanesulfinate anion [reactions (7) and (8)] has been determined by competition kinetics with thiocyanate. From the slope of the linear competition plot the ratio $k_{7,8}/k(^{\bullet}OH + SCN^-) = 0.48$ was obtained. From the established rate constant of the reaction of $^{\bullet}OH$ with thiocyanate ($k = 1.1 \times 10^{10}$ dm^3 mol^{-1} s^{-1}),[22] $k_{7,8} = 5.3 \times 10^9$ dm^3 mol^{-1} s^{-1} is determined (for a compilation of rate constants see Table 1). This value is also in good agreement with the reported rate constant of 6.0×10^9 dm^3 mol^{-1} s^{-1} determined by build-up kinetics at 325 nm.[9]

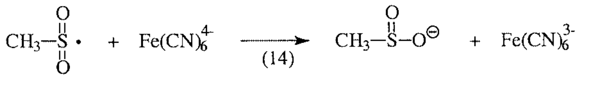
In the pulse radiolysis of slightly acidic N_2O-saturated solutions of methanesulfinate [pH 4.3–4.7; pK_a(methanesulfinic acid)[2] = 2.35] the conductance change observed 20 μs after the pulse is negative, corresponding to the consumption of $G(H^+ +$ anion$) = 4.0 \times 10^{-7}$ mol J^{-1}. This decrease of conductance can be explained by the release of OH^- in reaction (9) and the subsequent loss of H^+ upon neutralisation. At the same time the methanesulfinate anion is replaced by the neutral $CH_3S(O)O^{\bullet}$ radical. On the other hand, no change in conductance is associated with reactions (8) and (10), since the bisulfite anion (pK_a = 6.9) and the $^{\bullet}CH_2S(O)O^-$ radical have about the same equivalent conductance as the methanesulfinate anion. From the above G value of conductance decrease the decomposition of the intermediate OH-adduct radical appears to take place mainly *via* reaction (9) (70–80%) and to a lesser extent *via* reactions (8) and (10) (20–30%).

Table 2 Products and their G values of the γ-radiolysis of sodium methanesulfinate (10^{-3} mol dm^{-3}) in N_2O-saturated solutions at pH 6.8

Products	10^7 G values/mol J^{-1}
Methanesulfonate	2.1
Sulfate	0.7
Dimethyl sulfone	Detected, not quantified
Methane	0.3
Ethane	0.08

In basic solutions (pH 10–10.5), the conductance increase observed 20 μs after the pulse is equivalent to $G(OH^- -$ anion$) = 5.8 \times 10^{-7}$ mol J^{-1}. This indicates that the intermediate OH-adduct radical decays very largely *via* reaction (9), since reaction (10) does not release OH^- at this pH, but rather the formation of bisulfite anion actually leads to the consumption of OH^-. This relatively high $G(OH^-)$ to some extent conflicts with the observations made at acidic pH.

The $CH_3S(O)O^{\bullet}$ radical is strongly oxidising. Its reaction with $Fe(CN)_6^{4-}$ has been followed by absorption build-up of $Fe(CN)_6^{3-}$ in the pulse radiolysis of an N_2O-saturated solution of sodium methanesulfinate (10^{-2} mol dm^{-3}) and $Fe(CN)_6^{4-}$ (10^{-4} mol dm^{-3}) at 420 nm, where $Fe(CN)_6^{3-}$ has an absorption maximum (ε = 1020 dm^3 mol^{-1} cm^{-1}) [reaction (14)].

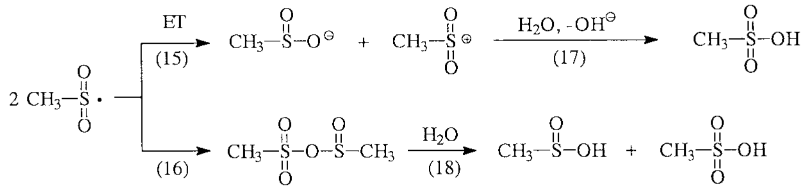


The rate of build-up at this wavelength was measured as a function of the $Fe(CN)_6^{4-}$ concentration, and from these data (not shown) the rate constant of 2.1×10^9 dm^3 mol^{-1} s^{-1} is obtained. Also, this system presents a further approach to determine $G[CH_3S(O)O^{\bullet}]$. From the absorbance build-up $G[Fe(CN)_6^{3-}]$ [corrected for the direct reaction of $^{\bullet}OH$ with $Fe(CN)_6^{4-}$] $G[CH_3S(O)O^{\bullet}] = 5.0 \times 10^{-7}$ mol J^{-1} is obtained, *i.e.* ~82% of $^{\bullet}OH$ reacting with methanesulfinate leads to the formation of the $CH_3S(O)O^{\bullet}$ radical. The same G value was obtained when the experiments were carried out under the low-dose-rate conditions of γ-radiolysis. Similarly, it was found that the $CH_3S(O)O^{\bullet}$ radical rapidly oxidises ascorbate. The rate constant $k = 1.5 \times 10^9$ dm^3 mol^{-1} s^{-1} was obtained by monitoring the build-up of the ascorbate radical (~86% of $^{\bullet}OH$ plus $H^{\bullet}$ at 360 nm) and sulfite [$k = 1.7 \times 10^9$ dm^3 mol^{-1} s^{-1}, obtained by monitoring the decay of the $CH_3S(O)O^{\bullet}$ radical at 360 nm].

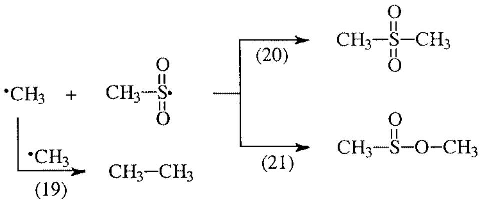
The final products and their G values of the γ-radiolysis of sodium methanesulfinate in N_2O-saturated solution are listed in Table 2.

The formation of the major product methanesulfonate indicates that the $CH_3S(O)O^{\bullet}$ radical decays mainly by bimolecular disproportionation or recombination and hydrolysis of the mixed anhydride [reactions (15)–(18)].

The formation of methane, ethane and dimethyl sulfone provides direct evidence for the formation of the methyl radical suggested in reaction (10). The small number of methyl radicals



can undergo either hydrogen abstraction with the starting material to give methane, or recombination to give ethane [reaction (19)], or cross-termination with $CH_3S(O)O^•$, the major radical in this system. The potential products are dimethyl sulfone [reaction (20), detected] and methyl methanesulfinate [reaction (21), not found].



$$^•CH_3 + ^•CH_3 \xrightarrow{(19)} CH_3{-}CH_3$$

$$^•CH_3 + CH_3{-}\overset{O}{\underset{O}{S}}{^•} \xrightarrow{(20)} CH_3{-}\overset{O}{\underset{O}{S}}{-}CH_3$$

$$^•CH_3 + CH_3{-}\overset{O}{\underset{O}{S}}{^•} \xrightarrow{(21)} CH_3{-}\overset{O}{S}{-}O{-}CH_3$$

The fact that sulfate (0.7×10^{-7} mol J^{-1}) instead of bisulfite or sulfite [reaction (10)] was observed as a final product can be explained by the rapid oxidation of sulfite by the $CH_3S(O)O^•$ radical [reactions (22) and (23), $k = 1.7 \times 10^9$ dm^3 mol^{-1} s^{-1}, see above].

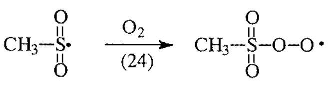
$$CH_3S(O)O^• + SO_3^{2-} \longrightarrow CH_3S(O)O^- + {}^•SO_3^- \quad (22)$$

$$CH_3S(O)O^• + {}^•SO_3^- + H_2O \longrightarrow CH_3S(O)O^- + SO_4^{2-} + 2\,H^+ \quad (23)$$

Altogether two $CH_3S(O)O^•$ radicals will be reduced by one sulfite. This will leave $G[CH_3S(O)O^•] = 4.2 \times 10^{-7}$ mol J^{-1} (*i.e.* 75%) for bimolecular self-termination. The yield found for methanesulfonate fits this material balance. Thus we can conclude from the above product analysis that ~88% of $^•OH$ reacting with methanesulfinate leads to the formation of the $CH_3S(O)O^•$ radical and ~12% to the methyl radical and bisulfite, leaving very little room for reaction (8).

Reactions in the presence of dioxygen

Pulse radiolysis observations. In the pulse radiolysis of an N_2O–O_2-saturated solution of sodium methanesulfinate, the absorption of the $CH_3S(O)O^•$ radical at 330 nm decays rapidly during the first 5–10 μs. This is then followed by a much slower decay ($t_{1/2}$ about 100 μs). As reported in the earlier study,[9] we likewise observe that, depending on the ratio of dioxygen to methanesulfinic acid, a residual absorption of the methanesulfonyl radical remains after the initial fast decay. The amount of initial absorbance decrease is only 10% at a methanesulfinate concentration of 1×10^{-3} mol dm^{-3} and a dioxygen concentration of 1.3×10^{-4} mol dm^{-3}. This amount increases to 80% at the lower methanesulfinate concentration of 4×10^{-4} mol dm^{-3} and higher dioxygen concentration of 6.5×10^{-4} mol dm^{-3}. From the kinetics of the initial fast decay, the rate constant of the addition of dioxygen to the methanesulfonyl radical [reaction (24)] is estimated to be ~ 8×10^8 dm^3 mol^{-1} s^{-1}, in fair agreement with the published value[9] of 1.2×10^9 dm^3 mol^{-1} s^{-1}.



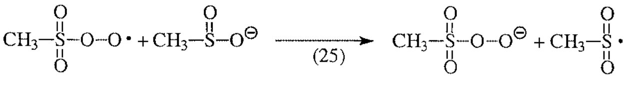
$$CH_3{-}\overset{O}{\underset{O}{S}}{^•} \xrightarrow[(24)]{O_2} CH_3{-}\overset{O}{\underset{O}{S}}{-}O{-}O^•$$

Following the initial fast decay of the absorbance of the $CH_3S(O)O^•$ radical, which can be attributed to reaction (24), the subsequent evolution of the remaining absorbance at 330 nm suggests the existence of an "equilibrium" concentration of the $CH_3S(O)O^•$ radical. The assumption of a reversibility of the dioxygen addition reaction (24), which has been observed in the case of certain thiyl radicals,[25,26] cannot, however, explain the above observations that the "equilibrium" concentration of the $CH_3S(O)O^•$ radical does not only depend on the dioxygen concentration, but also on the methanesulfinic acid concentration. It was suggested by Sehested and Holcman[9] that the methylsulfonylperoxyl radical $[CH_3S(O)_2OO^•]$ initiates a chain reaction by rapidly oxidising the substrate to re-form the $CH_3S(O)O^•$ radical [reaction (25), $k_{25} = 6.2 \times 10^8$ dm^3 mol^{-1} s^{-1}]. Indeed, the sulfonylperoxyl radical has been considered as one of the most reactive peroxyl radicals.[27] The propagating radicals would thus be $CH_3S(O)O^•$ and $CH_3S(O)_2OO^•$. The intermediate product, the methaneperoxymonosulfonic acid formed in reaction (25), was suggested to subsequently react with methanesulfinic acid to give two molecules of the final product, methanesulfonic acid [reaction (26), $k_{26} \approx 5 \times 10^3$ dm^3 mol^{-1} s^{-1}].[9]

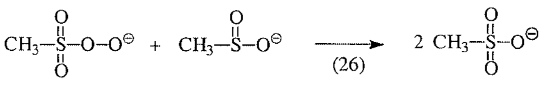
Table 3 Products and their G values in the γ-radiolysis (dose rate 0.011 Gy s^{-1}) and pulse radiolysis (6 Gy per pulse)[a] of sodium methanesulfinate (10^{-3} mol dm^{-3}) in N_2O–O_2 (4 : 1 v/v)-saturated solution at pH 6.8

	10^7 G values/mol J^{-1}	
Products	γ-Radiolysis	Pulse radiolysis[a]
Methanesulfinate consumption	270	
Methanesulfonate	250	83
Oxygen consumption	125	
Hydrogen peroxide[b]	2	
Sulfate	2.2	1.2
Formaldehyde	2.2	

[a] For data on other conditions see text. [b] Includes 0.75×10^{-7} mol J^{-1} formed in the radiolysis of water.



$$CH_3{-}\overset{O}{\underset{O}{S}}{-}O{-}O^• + CH_3{-}\overset{O}{S}{-}O^\ominus \xrightarrow[(25)]{} CH_3{-}\overset{O}{\underset{O}{S}}{-}O{-}O^\ominus + CH_3{-}\overset{O}{\underset{O}{S}}{^•}$$



$$CH_3{-}\overset{O}{\underset{O}{S}}{-}O{-}O^\ominus + CH_3{-}\overset{O}{S}{-}O^\ominus \xrightarrow[(26)]{} 2\,CH_3{-}\overset{O}{\underset{O}{S}}{-}O^\ominus$$

Methaneperoxymonosulfonic acid is analogous to peroxymonosulfuric acid (Caro's acid). We have in the present context looked at the reaction of Caro's acid (2×10^{-5} mol dm^{-3}) with methanesulfinic acid (1×10^{-4} mol dm^{-3}) and found that the reaction is completed in less than 2 min (not taking into account the time required for chromatography). This gives support to the above value of the rate constant suggested for reaction (26).[9]

Products of the chain reaction. In the present study, the products of the chain oxidation of methanesulfinic acid and their yields have been determined under the low dose rate of γ-radiolysis and the high dose rate of pulsed electrons (*cf.* Table 3).

In N_2O–O_2 (4 : 1)-saturated solutions, the dioxygen concentration is 2.6×10^{-4} mol dm^{-3}. As long as the chain reaction proceeds, dioxygen is consumed with a G value of 125×10^{-7} mol J^{-1} (Fig. 2) and methanesulfonic acid is formed with $G = 250 \times 10^{-7}$ mol J^{-1} (*cf.* inset in Fig. 2). A noticeable break in the further formation of methanesulfonic acid is observed after the depletion of dioxygen. As can be seen from Fig. 2, the overall stoichiometry for the formation of the major product, methanesulfonate, can be described by reaction (27).

$$2\,CH_3S(O)OH + O_2 \longrightarrow 2\,CH_3S(O)_2OH \quad (27)$$

This chain reaction is characterised by the fact that the chain length is independent of the concentration of the two major components, methanesulfinic acid (varied from 1×10^{-4} to 4×10^{-3} mol dm^{-3}) and dioxygen (varied from 2.6×10^{-4} to

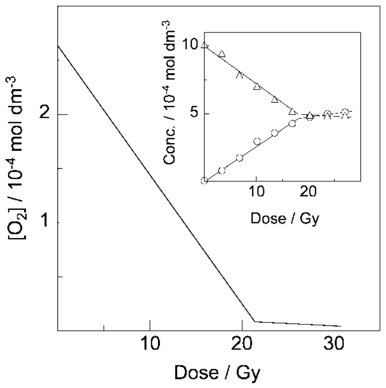


Fig. 2 γ-Radiolysis of N_2O–O_2-saturated aqueous solutions of methanesulfinic acid (1×10^{-3} mol dm^{-3}). Consumption of O_2 as a function of dose. Inset: Consumption of methanesulfinic acid (△) and formation of methanesulfonic acid (○) as functions of dose.

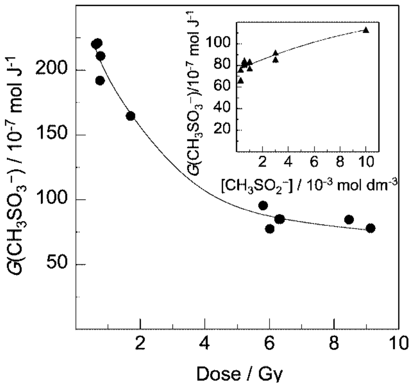


Fig. 3 Pulse radiolysis of neutral N_2O–O_2 (4 : 1)-saturated aqueous solutions of methanesulfinate (1×10^{-3} mol dm^{-3}). *G*(methanesulfonic acid) as a function of dose rate (Gy per pulse). Inset: *G*(methanesulfonic acid) as a function of the methanesulfinate concentration, 6 Gy per pulse.

1.3×10^{-3} mol dm^{-3}). The chain length is also independent of the dose rate in the range of 0.011 to 0.165 Gy s^{-1} (γ-radiolysis). Only at very much higher dose rates of pulse radiolysis do the chain lengths become noticeably shorter (Fig. 3), although at a dose of 0.8 Gy per μs pulse the yield of methanesulfonic acid still is not much lower than the value obtained under the low dose rate of γ-radiolysis (Table 3).

Owing to the fact that the methanesulfinic acid used in our experiments contains ~3% methanesulfonic acid, and that these two compounds elute close together in our ion chromatography analyses, it was difficult to evaluate the formation of methanesulfonic acid in the presence of very high methanesulfinic acid concentrations. However, sulfate has a sufficiently long retention time, and a study of its formation as a function of a larger variation of the substrate concentration could be made. As can be seen from Fig. 4, its yield increases noticeably at higher methanesulfinic acid concentrations.

The nature of the chain reaction. From their pulse radiolysis data, Sehested and Holcman[9] convincingly concluded that the steady-state concentration of the methanesulfonyl radicals depends on the [dioxygen] : [methanesulfinic acid] ratio. Under our experimental conditions the steady-state concentration of the methanesulfonyl radicals is rather high. Accordingly, reaction (25), combined with the rapid addition of dioxygen ($k_{24} = 1.2 \times 10^9$ dm^3 mol^{-1} s^{-1}), is expected to lead to a very fast chain reaction. Indeed, our results show that even under the very high dose rate of the pulse radiolysis experiments the methanesulfonic acid yields are still very high (Fig. 3). In fact, such a chain reaction would proceed so fast that the bimolecular termination of the methanesulfonyl radical, although its rate is close to diffusion controlled (see Table 1), cannot compete effectively with its propagation. Thus the chain would continue to run until one of the components, dioxygen or methanesulfinic acid, is exhausted. The branching [reactions (9) and (10)] occurs at the initiation stage and does not impact the reaction chain postulated[9] [reactions (24) and (25)]. Moreover, taking into account the rates of bimolecular termination of all the radicals involved, assumed to be diffusion controlled, it can be readily shown by a computer simulation that these do not alter the situation substantially. Thus, the simple mechanism suggested by Sehested and Holcman[9] cannot explain the limited extent of the chain reaction determined by our product studies.

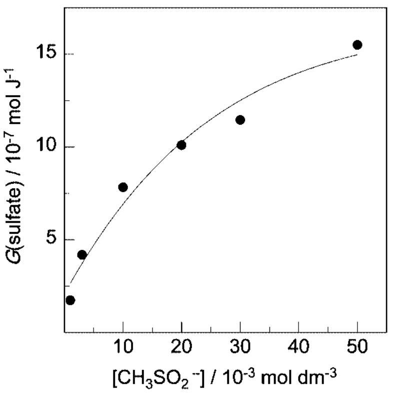
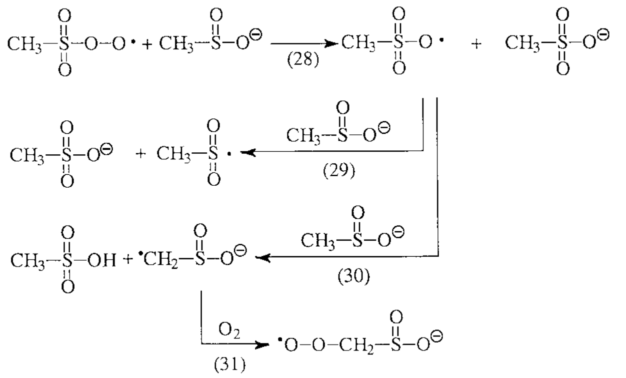
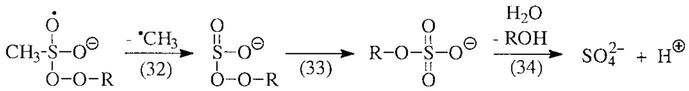


Fig. 4 γ-Radiolysis of neutral N_2O–O_2 (4 : 1)-saturated aqueous solution of methanesulfinate at 0.011 Gy s^{-1}. *G*(sulfate) as a function of the substrate concentration.

An efficient chain breaking process is required to limit the chain length, *e.g.* to G ~250×10^{-7} mol J^{-1}, *i.e.* a turnover of ~50, as under our experimental conditions. We propose that, as in the peroxyl-radical-induced oxidation of organic sulfides,[28–30] the $CH_3S(O)_2OO^•$ peroxyl radical reacts with the methanesulfinate ion by an overall two-electron oxidation [equivalent to an oxygen-atom transfer, reaction (28), but possibly proceeding *via* an adduct intermediate] to yield the $CH_3S(O)_2O^•$ oxyl-type radical. This is then proposed to be followed by an electron transfer from the methanesulfinate ion to the strongly oxidising $CH_3S(O)_2O^•$ [reaction (29)], whereby the $CH_3S(O)O^•$ radical is regenerated. The difference between our extended mechanism and that proposed by Sehested and Holcman[6] is that the propagating radicals in our case include the $CH_3S(O)_2O^•$, besides the $CH_3S(O)O^•$ and $CH_3S(O)_2OO^•$ radicals.



The $CH_3S(O)_2O^•$ radical can be viewed as possessing a reactivity intermediate between $^•OH$ (good H-abstractor) and $SO_4^{•-}$ (good electron abstractor). Hence, parallel to the chain-propagating step [reaction (29)], a branching reaction, in the form of H-abstraction by the $CH_3S(O)_2O^•$ radical to give the carbon-centred radical and methanesulfonic acid [reaction (30)], can take place. The alkylperoxyl radical originating from the carbon-centered radical in its reaction with dioxygen



[reaction (31)] has a much lower oxidising power than the chain-carrying S-centered peroxyl and oxyl radicals in this system (for a study on the reduction potentials of peroxyl radicals see ref. 31). The relatively inert $^{\bullet}OOCH_2S(O)O^-$ radical may thus undergo termination reactions rather than propagating the chain. The chain length of about 50 suggests a branching ratio k_{29}/k_{30} in the order of 10^2.

A more detailed description of this complex chain reaction would also require an explanation for the increase in sulfate yields with increasing substrate concentration (see Fig. 4). Here, one might tentatively suggest that the $^{\bullet}OOCH_2S(O)O^-$ radical [*cf.* reaction (31)], which normally decays by bimolecular termination, may, at sufficiently high substrate concentration, also play a role as a chain carrier by oxidising the substrate. The *bona fide* hydroperoxide resulting from this mechanism would readily decompose into formaldehyde and SO_3 (→sulfate). The decomposition of similar hydroperoxides is well documented.[32–34] Another hypothesis postulates loss of $^{\bullet}CH_3$ radicals from an $RO_2^{\bullet}$–methanesulfinic acid adduct [$RO_2^{\bullet}$ being a peroxyl radical of relatively low reactivity, *e.g.*, $CH_3OO^{\bullet}$ and $^{\bullet}OOCH_2S(O)O^-$], rearrangement and hydrolysis of the sulfate monoester [reactions (32)–(34)]. Evidence for the existence of similar adducts of $RO_2^{\bullet}$ to sulfides has been reported.[29]

Oxidation of methanesulfinic acid by ozone

With reducing compounds, ozone can undergo both O-atom transfer as well as electron transfer. One such system involves tertiary amines, which give rise mainly to aminoxides but to a small extent (~10%) may also undergo electron transfer.[35] Using buten-3-ol ($k = 7.9 \times 10^4$ dm^3 mol^{-1} s^{-1})[36] as a competitor,[37] we determined the rate constant of methanesulfinate ion with ozone to be 2×10^6 dm^3 mol^{-1} s^{-1}. This value is comparable to the rate constants reported for bisulfite, which range between 3.7×10^5 and 2×10^6 dm^3 mol^{-1} s^{-1}.[38] We observed that 1 mol methanesulfonic acid is formed per mol of ozone, *i.e.* the reaction proceeds presumably only by O-atom transfer. If electron transfer had occurred, even at a very small percentage, the high rate of the chain reaction discussed above would have resulted in a much higher methanesulfonic acid yield. In the O-atom transfer reactions of ozone the dioxygen is formed in its singlet excited state [$O_2(^1\Delta_g)$], and also in the reaction of ozone with methanesulfinic acid $O_2(^1\Delta_g)$ is formed in 100% yield.[39] If the reduction potential of bisulfite[40] can be used as a reference for methanesulfinate, $O_2(^1\Delta_g)$ is also not capable of one-electron oxidation of methanesulfinate to induce the chain reaction, as indeed confirmed by our results.

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