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Free-radical-induced oxidation of hydroxymethanesulfonate in aqueous solution

Part 2[†] A pulse and steady-state radiolysis study of oxygenated solutions

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At pH 4.0, the radical 'CH(OH)SO₃⁻ formed by reaction of 'OH with hydroxymethanesulfonate (HMS) reacts rapidly with oxygen to form the peroxyl radical, 'OOCH(OH)SO₃⁻, with $k_4 = (2.6 \pm 0.3) \times 10^9$ dm³ mol⁻¹ s⁻¹. This radical decays by a first-order process with $k = 2.4 \times 10^4$ s⁻¹ and $E_a = (29 \pm 1.2)$ kJ mol⁻¹. The decay is by a split pathway, reactions (6) and (7), with $k_6 = 1.7 \times 10^4$ s⁻¹ and $k_7 = 7.0 \times 10^3$ s⁻¹. Reaction (6) involves direct elimination of HO₂⁻. Reaction (7) initially forms the formylperoxyl radical, but this is hydrolysed, reaction (8), to formic acid and HO₂⁻ with $k_8 = 2.46 \times 10^3$ s⁻¹.

$$CH(OH)SO_{3}^{-} + O_{2} \rightarrow OOCH(OH)SO_{3}^{-}$$
(4)

$$^{\circ}OOCH(OH)SO_{3}^{-} \rightarrow HO_{2}^{\circ} + CHOSO_{3}^{-}$$
(6)

$$^{\circ}OOCH(OH)SO_{3}^{-} \rightarrow ^{\circ}OOCHO + HSO_{3}^{-}$$
(7)

$$OOCHO + H_2O \rightarrow OOCH(OH)_2 \rightarrow HCOOH + HO_2$$
(8)

The yield of formate is compatible with this mechanism if it is assumed that the product of reaction (6), *i.e.* $CHOSO_3^-$, can also yield formic acid. Yields of $SO_4^{2^-}$ have been determined and their origin is considered.

At pH 7.0, the radical 'CH(O⁻)SO₃⁻ reacts with oxygen to yield O₂⁻⁻ with $k_{11} = (1.6 \pm 0.1) \times 10^9$ dm³ mol⁻¹ s⁻¹.

(3)

$$CH(O^{-})SO_{3}^{-} + O_{2} \rightarrow CHOSO_{3}^{-} + O_{2}^{-}$$
(11)

Introduction

Hydroxymethanesulfonate (HMS), which is formed from the addition of sulfite/hydrogen sulfite to formaldehyde, reaction (1), has been detected in atmospheric droplets^{1,2} and it has been proposed that its formation enhances the wet deposition of formaldehyde and SO₂ from the atmosphere.³ It is also thought that its formation plays an important role in preventing the oxidation of S^{IV} by H₂O₂ in the aqueous phase of clouds.^{4,5} However, the oxidation of S^{IV} in clouds might also occur by a free-radical chain process initiated by 'OH radicals and involving the radicals SO₃⁻⁻, SO₄⁻⁻ and SO₅^{--, 6-10} Deister *et al.*¹¹ have concluded that, in the presence of oxygen, the reaction of 'OH with HMS results in the chain oxidation of HMS.

$$HCHO + HSO_3^{-} \rightleftharpoons CH_2(OH)SO_3^{-}$$
 (1)

where $K_1 = 3.6 \times 10^6 \text{ mol}^{-1} \text{ dm}^{3.12}$

In Part 1¹³ of this series we showed that 'OH reacts with HMS, reaction (2), to form 'CH(OH)SO₃⁻ and that this radical undergoes acid-base dissociation, reaction (3), with a pK_a of 6.35 \pm 0.1.

$$OH + CH_2(OH)SO_3^- \rightarrow CH(OH)SO_3^- + H_2O \qquad (2)$$

 $CH(OH)SO_3^{-} \rightleftharpoons CH(O^{-})SO_3^{-} + H^+$

where $k_2 = (3.0 \pm 0.3) \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

In this paper we present a study of the reactions of $'CH(OH)SO_3^-$ and $'CH(O^-)SO_3^-$ with oxygen and of the

mechanism of the overall oxidation. As outlined in Part 1,¹³ pulse radiolysis is a convenient means of studying the kinetics of the processes while the overall products of the oxidation are readily generated by steady-state radiolysis with a 60 Co γ -ray source.

Experimental

Chemicals

The chemicals used were as described in Part $1.^{13}$ In addition, oxygen (BOC) was taken directly from the cylinder.

Product analysis

Analysis of formate and sulfate was by ion chromatography. The system used consisted of a Dionex advanced gradient pump, a Dionex ionpac AS12A analytical column with an AG12A guard column, an AAMS-1 suppressor column, a conductivity detector and a chart recorder. The eluent used for the separation contained 0.3 mmol dm⁻³ NaHCO₃ and 2.7 mmol dm⁻³ Na₂CO₃. 10 ml of the solution was irradiated and a 20 μ l aliquot injected into the chromatograph by the complete-filling method. The HCOO⁻ peak elutes after 2.8 min and that of SO₄²⁻ after 19.0 min.

Steady-state irradiation

Steady-state irradiations were carried out using a 300 Ci 60 Co γ -ray source. Solutions were contained in a custom-made cell

[†] Part 1: ref. 13.

that allowed the solution to be bubbled in situ with an N_2O-O_2 mixture prior to irradiation. The gas mixture was produced by mixing separate flows of N_2O and O_2 , which were controlled by needle valves and monitored using flow meters. The resulting solutions contained 6.75×10^{-4} mol dm⁻³ O_2 and 1.25×10^{-2} mol dm⁻³ N_2O . The cell was positioned reproducibly relative to the γ -ray source and the volume of solution used was always 10 cm³. The mean dose rate throughout the sample was determined using the Fricke Dosimeter.¹⁴

Pulse radiolysis

The pulse radiolysis apparatus and procedures when using spectrophotometric detection have been described in detail elsewhere.¹⁵ Experiments with conductivity detection used the ac system described by Janata *et al.*¹⁶ The solution was contained in a rectangular Pyrex cell with internal dimensions of 5.0 mm \times 7.0 mm \times 10.0 mm and which had disc-shaped electrodes of platinum foil (3.0 mm diameter) mounted in parallel configuration (separation 5.0 mm) on tungsten wires, which were along the long axis of the cell. The cell was mounted so that the electron beam entered the cell perpendicular to the 7.0 mm \times 10.0 mm face. Side-arms in the vertical plane with B5 cones and sockets allowed the cell to be filled with solution. A similar cell mounted above the irradiated cell, but screened from the radiation, acted as a reference.

For the conductivity measurements, dosimetry was carried out using N₂O-saturated solutions containing 10^{-3} mol dm⁻³ dimethyl sulfoxide at pH 4.4, for which $\sum_{i} (G_i \lambda_i)$ was taken to be 2.02×10^{-8} S m² J⁻¹,¹⁷ where $G_i \lambda_i$ is the product of the radiolytic yield, G_i , of the ions contributing to the conductivity change in units of mol J⁻¹ and λ_i , their limiting ionic conductances in units of S m² mol⁻¹.

Solutions were saturated with argon, nitrous oxide or oxygen as required for a particular experiment and then stored in all-glass syringes in readiness for pulse radiolysis. To prepare solutions containing both N_2O and O_2 , syringes containing the separate saturated solutions were joined by a capillary tube and then an appropriate volume of one solution forced into the other. A glass disc in the receiving syringe allowed the solutions to be mixed by shaking.

Except where otherwise specified, all experiments were carried out at ambient temperature, 18-20 °C.

Results and Discussion

Reaction of 'CH(OH)SO₃ - with oxygen

Absorption spectrum of 'OOCH(OH)SO₃⁻. The reaction of 'CH(OH)SO₃⁻ with oxygen was investigated by pulse radiolysis with 500 ns, 15 Gy pulses of solutions at pH 4.0 containing 0.1 mol dm⁻³ HMS and with $[N_2O] = 1.25 \times 10^{-2}$ mol dm⁻³ and $[O_2] = 6.75 \times 10^{-4}$ mol dm⁻³. The ratio of N₂O/O₂ in the solutions is such that 90% of the e_{aq}⁻ generated by radiolysis reacts with N₂O to yield 'OH.

At the concentrations of HMS used here reaction (2) is effectively complete during the pulse, and the end-of-pulse absorption is that of 'CH(OH)SO₃⁻¹³ (see Fig. 1, A). After the pulse, a further growth of absorption occurred over about 2.5 μ s and the absorption then decayed over $\approx 100 \ \mu$ s and then decayed back to the baseline over 2–20 ms. This variability was attributed to the influence of trace metal ions on the decay of HO₂'/O₂⁻ (see below). Spectra obtained at 2.5 μ s and 140 μ s after the pulse are also shown in Fig. 1(B and C). The spectrum observed at 2.5 μ s (B) is assigned to the peroxy radical formed by addition of O₂ to 'CH(OH)SO₃⁻, reaction (4).

$$O_2 + CH(OH)SO_3^- \rightarrow OOCH(OH)SO_3^-$$
 (4)



Fig. 1 Absorption spectra obtained by pulse radiolysis of 0.1 mol dm⁻³ HMS solutions at pH 4.0. A, spectrum of 'CH(OH)SO₃⁻ obtained in N₂O-saturated solution; B, spectrum at 2.5 μ s; and C, 143 μ s after the pulse for solutions with [O₂] = 6.75 × 10⁻⁴ mol dm⁻³.

Rate constant for the reaction. The kinetics of the reaction were investigated by monitoring the growth of absorption at 245 nm on pulse radiolysis of solutions with [HMS] = 0.1 mol dm⁻³ for which the oxygen concentrations varied from 192 to 675 µmol dm⁻³. The growth of absorption obeyed first-order kinetics and the rate constants obtained, k_{obs} , were proportional to the oxygen concentration with slope, $k_4 = (2.6 \pm 0.3) \times 10^9$ dm³ mol⁻¹ s⁻¹, which is of the order expected for the addition of oxygen to a carbon-centred radical.

Decay of 'OOCH(OH)SO₃⁻. The decay of 'OOCH(OH)SO₃⁻ was monitored at 300 nm for solutions at pH 4.0 and was found to be first-order and independent of $[O_2]$ with a rate constant of $(2.4 \pm 0.1) \times 10^4$ s⁻¹. The temperature dependence of this rate constant was investigated for temperatures between 5 and 40 °C. A plot of ln k vs. 1/T was linear and gave $E_a = (29 \pm 1.2)$ kJ mol⁻¹ and ln(A/ s⁻¹) = 22.3 \pm 0.5.

The spectrum of the product of the decay of 'OOCH(OH)SO₃⁻ is shown in Fig. 1, C. α -Hydroxyperoxyl radicals are known to dissociate by elimination of HO₂',¹⁸ so the possibility that this is the case for 'OOCH(OH)SO₃⁻ was tested by comparing the spectrum at 143 µs, after allowance for the yield of HO₂' formed from the small yield of H-atom formed on the radiolysis of water [G(H) = 6 × 10⁻⁸ mol J⁻¹], with that expected for HO₂'/O₂⁻ at pH 4.0 (see Fig. 2). The molar absorption coefficients for the experimental spectrum were calculated assuming that, at the concentration of HMS employed, G['OOCH(OH)SO₃⁻] = G('OH) = 6.0 × 10⁻⁷ mol J⁻¹. The spectrum of HO₂' /O₂⁻⁻ was calculated from the known spectra of HO₂' and O₂'⁻⁻¹⁹ and K_a for equilibrium (5).²⁰

$$\mathrm{HO}_{2} :\rightleftharpoons \mathrm{H}^{+} + \mathrm{O}_{2} :^{-} \tag{5}$$

Because of the high ionic strength of the solutions (0.1 mol dm⁻³), [H⁺] and $[O_2^{\cdot-}]$ were evaluated using K_c for equilibrium (5) rather than K_a . K_c was estimated from K_a as indicated in ref. 21. Also, account was taken of the influence of the high ionic strength on the glass electrode of the pH meter. This was done by comparing pH readings for solutions with $[H^+] = 10^{-4}$ mol dm⁻³ in the absence and presence of 0.1 mol dm⁻³ NaClO₄. The effect of 0.1 mol dm⁻³ NaClO₄ was to shift the pH reading by +0.18.

It is apparent from Fig. 2 that the experimental spectrum differs from the predicted one for HO_2'/O_2^- and that 'OOCH(OH)SO₃⁻ does not dissociate simply to yield HO₂' as in reaction (6).



Fig. 2 Comparison of the spectrum obtained at 143 μ s after the pulse in solutions at pH 4.0 and $[O_2] = 6.75 \times 10^{-4} \text{ mol dm}^{-3}$, (\blacksquare), with the spectrum of HO₂'/O₂⁻ at pH 4.0, (\bigcirc) (see text)

$$:OOCH(OH)SO_{3}^{-} \rightarrow HO_{2}^{-} + |_{SO_{3}^{-}}$$
(6)

A possible alternative mode of decay of 'OOCH(OH)SO₃⁻ is that SO_3^{2-} acts as a leaving group to yield HSO_3^{-} and 'OOCHO, reaction (7).

$$OOCH(OH)SO_3^- \rightarrow OOCHO + HSO_3^-$$
 (7)

To explore further the decay of 'OOCH(OH)SO₃, it was deemed appropriate to study the release of H⁺ using conductivity detection. As conductivity measurements can not readily be made at high salt concentrations, the concentration of HMS in these experiments was reduced to 12.5 mmol dm^{-3} . Increases in conductivity were observed on two timescales, see Fig. 3(a) and (b). Fig. 3(a) indicates a biphasic growth of conductivity, the fast initial rise of which corresponds approximately with the rate of decay of OOCH(OH)SO3 determined optically. The extent and kinetics of the conductivity changes shown in Fig. 3(a) are compatible with the decay of 'OOCH(OH)SO₃⁻ proceeding by a split path involving reactions (6) and (7) if it is also assumed that the product of reaction (6), *i.e.* 'OOCHO, can react to release further H⁺. We propose that the process involved is the hydrolysis of 'OOCHO to yield the hydrated peroxyformyl radical, which is known to decompose in $<1 \,\mu s$ to formic acid and HO₂, reaction (8).²² This reaction also provides one route to the formation of the formate, which is observed as a product (see below).

$$OOCHO + H_2O \rightarrow OOCH(OH)_2 \rightarrow$$

$$HCOOH + HO_2$$
. (8)

The line superimposed on the trace in Fig. 3(a) results from fitting the experimental trace using the FACSIMILE kinetics



Fig. 3 (a) Conductivity signal developing over 1 ms in oxygenated solution at pH 4.0. The superimposed line is calculated using FAC-SIMILE (see text). (b) Conductivity signal developing over 10 s in oxygenated solution at pH 4.0.

software package²³ to a scheme involving reactions (6), (7) and (8) and the dissociation of HO₂⁻ and formic acid in equilibria (5) and (9). The fitting procedure assumed that $k_6 + k_7 = 2.4 \times 10^4 \text{ s}^{-1}$, *i.e.* the value obtained from the optical measurements for the decay of 'OOCH(OH)SO₃⁻. The additional parameters used in the curve-fitting are listed in Tables 1 and 2 and the process yielded $k_6 = 1.7 \times 10^4 \text{ s}^{-1}$, $k_7 = 7.0 \times 10^3 \text{ s}^{-1}$ and $k_8 = 2.5 \times 10^3 \text{ s}^{-1}$. The ratio of k_6 to k_7 obtained is somewhat dependent on the value of $\lambda_{O_2^-}$ used. For example, reducing $\lambda_{O_3^-}$ by 10% resulted in k_6 increasing by about 2.5%.

$$HCOOH \rightleftharpoons H^+ + HCOO^-$$
(9)

The low value of E_a and negative entropy of activation $[\Delta S^{\ddagger}_{\ddagger} = -(68.2 \pm 4.2) \text{ J K}^{-1} \text{ mol}^{-1}]$ obtained from the temperature dependence of the decay of O_2 CH(OH)SO₃⁻ is in keeping with the heterolytic nature of reactions (6) and (7).

The slow growth of conductivity over a period of seconds illustrated in Fig. 3(b) was not studied in detail, but corresponds with the release of H⁺ with $G(H^+) \approx 6.7 \times 10^{-7}$ mol J⁻¹, probably by several concurrent processes (see below).

Table 1 Reactions and rate constants used in the FACSIMILE programme for fitting the 'fast' changes in conductivity

reaction	k	reference
$\label{eq:constraint} \begin{array}{c} \begin{tabular}{lllllllllllllllllllllllllllllllllll$	$\begin{array}{c} 2.6\times10^9\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}\\ 1.7\times10^4\ \mathrm{s^{-1}}\\ 7.0\times10^3\ \mathrm{s^{-1}}\\ 2.5\times10^3\ \mathrm{s^{-1}}\\ 1.0\times10^6\ \mathrm{s^{-1}},\ 3.6\times10^{10}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}\\ 9.0\times10^6\ \mathrm{s^{-1}},\ 3.6\times10^{10}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}\\ \end{array}$	this work this work ^a this work ^a this work ^a 20, corrected for high ionic strength K_{diss} corrected for high ionic strength

^a Result of FACSIMILE fit.

Table 2 Other parameters used in the FACSIMILE programme for fitting the 'fast' changes in conductivity

parameter	value	reference
$\begin{array}{c} G(\text{'OOCH(OH)SO}_{3}^{-}) \\ G(H') \\ \lambda_{H^{+}} \\ \lambda_{O_{2}^{-}} \\ \lambda_{HCOO^{-}} \\ \lambda_{HSO_{3}^{-}} \end{array}$	$\begin{array}{c} 5.6 \times 10^{-7} \mbox{ mol } J^{-1} \\ 6.0 \times 10^{-8} \mbox{ mol } J^{-1} \\ 0.0335 \mbox{ S } m^2 \mbox{ mol}^{-1} \\ 0.0065 \mbox{ S } m^2 \mbox{ mol}^{-1} \\ 0.00545 \mbox{ S } m^2 \mbox{ mol}^{-1} \\ 0.0040 \mbox{ S } m^2 \mbox{ mol}^{-1} \end{array}$	see text 24 estimated 24 24 ^a

^{*a*} Assumed the same as HCO_3^{-} and corrected to 20 °C.

Products of γ-radiolysis at pH 4.0

45 40

[product] / 10⁻⁴ mol dm⁻³ 0 25 25 10 10 10

The yields of formate and sulfate formed on γ -irradiation of solutions with [HMS] = 0.01 mol dm⁻³, [N₂O] = 0.0125 mol dm⁻³ and $[O_2] = 6.75 \times 10^{-4}$ mol dm⁻³ were studied for doses up to 1500 Gy. Experiments were carried out at two dose rates, namely, 16.3 and 2.3 Gy min⁻¹. The yields of formate were proportional to the absorbed dose and were independent of dose rate, see Fig. 4. The gradient of the graph indicates that $G(\text{formate}) = (7.1 \pm 0.2) \times 10^{-7} \text{ mol J}^{-1}$, which is somewhat higher than G(OH) at this concentration of HMS (5.7 × 10^{-7} mol J⁻¹). This yield of formate also implies that $CHOSO_3^{-}$, the product of reaction (6), must also lead ultimately to the formation of formic acid. Hydrolysis of CHOSO₃⁻ to HCOOH and HSO₃⁻, reaction (10), is a plausible pathway for this and this process is a possible contributor to the release of H^+ illustrated in Fig. 3(b).

$$\begin{array}{c} \text{CHO} & \text{CH}(\text{OH})_2 \\ | & \text{H}_2\text{O} \rightarrow | \\ \text{SO}_3^- & \text{SO}_3^- \end{array} \rightarrow \text{HSO}_3^- + \text{HCOOH} \quad (10) \end{array}$$

Unlike the formate, the yields of sulfate depend on dose rate and there is some indication of departures from linearity at the upper extremity of the dose range studied (see Fig. 4). The slopes of the yield vs. dose plots give $G(SO_4^{2-}) = 2.0 \times 10^{-6}$ mol J⁻¹ at a dose rate of 16.3 Gy min⁻¹, and 2.7×10^{-6} mol J^{-1} at a dose rate of 2.3 Gy min⁻¹. Both yields are considerably in excess of G(OH), but as discussed above there is no evidence to suggest that SO_4^{2-} is generated by the decomposition of 'OOCH(OH)SO₃⁻. Plausible mechanisms for the formation of SO_4^{2-} are: (i) reaction of the hydrogen peroxide formed by the radiolysis of water and the disproportionation



sulfate ions formed on y-radiolysis of oxygenated HMS solutions at pH 4.0. Yields of formate ion and sulfate at dose rates of 2.3 Gy min⁻¹, (\blacksquare) and (\square), and at 16 Gy min⁻¹, (\bullet) and (\blacktriangle), respectively; [O₂] = 6.75 × 10⁻⁴ mol dm⁻³.

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of HO₂[•] with the HSO₃⁻, which is in equilibrium with HMS, and (ii) the 'OH radical-initiated chain oxidation of $HSO_3^{-.11}$ The first of these is unable to account for the full yield of SO_4^{2-} since, on the mechanism given above for the decay of $OOCH(OH)SO_3^{-}$, the yield of sulfate would be given by

$$G(SO_4^{2^-}) = G(H_2O_2)$$

= $\frac{1}{2}G(HO_2^{-}) + G_{H_2O_2}$
= $\frac{1}{2}[G(\cdot OH) + G_H + G_{H_2O_2}]$
 $\approx 4.0 \times 10^{-7} \text{ mol } \text{J}^{-1}$

where $G_{\rm H}$ and $G_{\rm H_2O_2}$ are the primary yields of H and $\rm H_2O_2$ from the radiolysis of water. The yield of SO₄²⁻ by (ii) is difficult to predict, but it appears, on the basis of the small fraction of 'OH that reacts with HSO₃⁻, that initial chain lengths are approximately 50 and 70, respectively, at the two dose rates. The non-linear formation of SO_4^{2-} is probably due to the formate product interfering with the chain reaction as a result of it scavenging radicals involved in the chain propagation, e.g. SO_4 .

Reaction of 'CH(O⁻)SO₃⁻ with oxygen

Absorption spectrum of the product. The reaction of CH(O⁻)SO₃⁻ with oxygen was investigated at pH 7.0 using solutions containing 0.1 mol dm⁻³ HMS that were buffered with 0.1 mol dm⁻³ phosphate buffer, thus causing equilibrium (3) to be established in 120 ns.¹³ Following the pulse, an absorption grew over 6 µs for wavelengths between 240 and 300 nm and then decayed, only slowly, over millisecond timescales. The spectrum measured after completion of the growth is shown in Fig. 5. This spectrum is not due to 'OOCH(OH)SO₃⁻ (cf. Fig. 1, B), but corresponds very closely with that of $O_2^{\cdot-}$, ¹⁹ which is shown in the figure for comparison. This spectrum is calculated assuming a yield given by

$$G(O_2^{-}) = G[CH(O)SO_3^{-}] + G(HO_2^{-})$$
$$= G(OH) + G(H^{-})$$

where $G(OH) = 6.0 \times 10^{-7} \text{ mol } \text{J}^{-1}$ at the concentration of HMS and $G(H) = 6.0 \times 10^{-8}$ mol J⁻¹. This suggests that $CH(O^{-})SO_{3}^{-}$ reacts directly with O_{2} to yield O_{2}^{-} [reaction (11)] and that if a peroxy radical is formed as an intermediate its lifetime is very short.

$$CH(O^{-})SO_{3}^{-} + O_{2} \rightarrow O_{2}^{-} + CHOSO_{3}^{-}$$
 (11)

Further evidence that the long-lived product is O_2 .⁻ was sought by studying the decay kinetics of the product. Since the



Fig. 5 Comparison of the spectrum obtained on pulse radiolysis of oxygenated solutions at pH 7.0 (\triangle) with that of O₂⁻⁻ (the solid line is calculated as described in the text); [O₂] = 6.75 × 10⁻⁴ mol dm⁻³

decay of O_2 . is known to be sensitive to the presence of transition metal ions, the decay of absorption was monitored at 250 nm in the presence of 100 μ mol dm⁻³ EDTA to complex any metal ions. The decay was second-order with 2k/ $\varepsilon = 9.7 \times 10^{2} \text{ cm s}^{-1}$ which, taking $\varepsilon_{250}(O_2^{-1}) = 1890 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$,¹⁹ yields $2k = 1.8 \times 10^{6} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. This value is close to, but slightly higher than, the literature value²⁰ of 1.4×10^6 dm³ mol⁻¹ s⁻¹ for the disproportionation of O_2 . This reaction involves reactions (12) and (13) with $k_{13} \approx 33k_{12}$, and the slightly higher value of the rate constant observed here is probably due to the influence of the secondary salt effect on K_{diss} (HO₂[•]) owing to the high ionic strength of the solutions.

$$HO_2' + HO_2' \xrightarrow{H_1} H_2O_2 + O_2$$
(12)

$$HO_2' + O_2' \xrightarrow{-} \longrightarrow H_2O_2 + O_2$$
(13)

Rate of reaction (11). The rate of reaction (11) was studied by pulse radiolysis with 15 Gy, 200 ns pulses of solutions containing 0.1 mol dm⁻³ HMS, 0.1 mol dm⁻³ phosphate buffer, oxygen in the range $(2-11) \times 10^{-4}$ mol dm⁻³ and nitrous oxide in the range (4.6–20) mmol dm^{-3} . The formation of O2.-, monitored at 250 nm, obeyed first-order kinetics and the observed rate constant, k_{obs} , was proportional to [O₂] with slope $k_{11} = (1.6 \pm 0.1) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

Conclusions

At pH 4.0, 'OOCH(OH)SO₃⁻ dissociates by a split pathway, reactions (6) and (7), but the final products are in each case formic acid and HO₂', which in turn disproportionates to H_2O_2 and O_2 , but we have found no evidence for a chain production of formate as suggested by Deister and Warneck.⁸ The hydrogen peroxide is expected to form sulfuric acid by its reaction with the HSO3⁻, which is in equilibrium with the HMS. Sulfate is also generated by an additional path, which is most likely the free-radical chain oxidation of HSO₃⁻.

At pH 7, the 'CH(O⁻)SO₃⁻ radical reduces O₂ directly to O_2^{-} with no evidence for the intermediate formation of an RO_2 radical.

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