

Oxidation of glyoxal initiated by $\cdot\text{OH}$ in oxygenated aqueous solution

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The kinetics and mechanism of the oxidation of glyoxal, which is a constituent of cloud water, initiated by $\cdot\text{OH}$ in oxygenated solution have been investigated using pulse radiolysis with optical and conductivity detection of the transient species, and steady-state radiolysis with spectrophotometric and ion chromatographic analysis of the permanent products. The data obtained are consistent with glyoxal being present in the form of the dihydrate $[\text{CH}(\text{OH})_2]_2$ which is oxidised to glyoxylic acid ($\text{pK}_a = 3.4$) and hydrogen peroxide via a peroxy radical $\cdot\text{O}_2\text{C}(\text{OH})_2\text{CH}(\text{OH})_2$ that splits off $\text{HO}_2\cdot$ in a non-rate determining step. The following rate constants have been determined: $k\{\cdot\text{OH} + [\text{CH}(\text{OH})_2]_2\} = (1.10 \pm 0.04) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k[\cdot\text{C}(\text{OH})_2\text{CH}(\text{OH})_2 + \text{O}_2] = (1.38 \pm 0.11) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. It is concluded that oxidation of glyoxal by $\cdot\text{OH}$ in cloud water can proceed by a chain reaction involving H_2O_2 .

Hydrocarbons have been identified in the atmosphere and are known to be emitted from human and biological activity.¹ Glyoxal, an α -dicarbonyl compound, has been identified² in cloud water with a mean concentration of $2 \mu\text{mol dm}^{-3}$.³ It is a product of the oxidation of aromatic compounds, which are abundant in motor-vehicle emissions and in the combustion products of biomass; it is also a product of the oxidation of terpenes, in particular isoprene, which is the predominant hydrocarbon emitted from forests.⁴ The hydroxyl radical has been suggested as an important intermediate in the aqueous-phase chemistry of the atmosphere which contributes to the generation of acid precipitation.⁵ It is ubiquitous in the gas phase of the atmosphere from which it can enter cloud droplets, and it may be generated within cloud droplets in several different photochemical and thermal reactions of compounds that are present there.⁶

In this paper we report on a study of the oxidation of glyoxal by $\cdot\text{OH}$ in the presence of oxygen, using the techniques of pulse and steady-state radiolysis. From the evidence available in the literature^{7,8} we conclude that glyoxal exists primarily in a monomeric form as the dihydrate, $[\text{CH}(\text{OH})_2]_2$, at the concentrations found in cloud water droplets and used in the present experiments.

Experimental

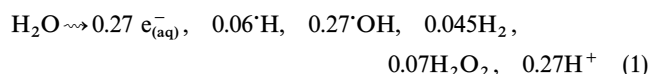
The pulse radiolysis apparatus and procedures used here have been described in detail elsewhere.⁹ For optical measurements, dosimetry was carried out using an O_2 -saturated solution of $10^{-2} \text{ mol dm}^{-3}$ KSCN with $G\varepsilon[(\text{SCN})_2]^-$ at 475 nm taken to be¹⁰ $2.59 \times 10^{-4} \text{ m}^2 \text{ J}^{-1}$ where G is the radiation chemical yield (mol J^{-1}) and ε is the molar absorption coefficient ($\text{m}^2 \text{ mol}^{-1}$). For conductivity measurements, the dosimeter was an N_2O -saturated solution containing $10^{-3} \text{ mol dm}^{-3}$ dimethyl sulfoxide at pH 4.4 for which $GA = 2.02 \times 10^{-8} \text{ S m}^2 \text{ J}^{-1}$.¹¹ Steady-state radiolysis was carried out using a ^{60}Co γ -ray source at a dose rate of 15.7 Gy min^{-1} as measured by Fricke dosimetry.¹² All experiments were carried out at ambient temperature ($18\text{--}20^\circ\text{C}$) unless otherwise stated.

Glyoxal was $>98\%$ pure (Fluka) and was used as received. All other reagents (BDH or Hopkin and Williams) were AnalaR grade or better. Solutions were made up with distilled water which had been further purified by Millipore filtration (MilliQ). The pH of the solutions was adjusted with perchloric acid or phosphate buffer. Oxygen and nitrous oxide (BOC) were of the highest purity available and were taken straight from the cylinder.

Hydrogen peroxide was analysed by the Ghormley method¹³ and glyoxylic acid was determined using ion chromatography (Dionex 2000i).¹⁴

Results and Discussion

The radiolysis of water is summarised by reaction (1)



where the numbers are the yields ($\mu\text{mol J}^{-1}$) of the radiolysis products.

Pulse radiolysis experiments

Rate of reaction of $\cdot\text{OH}$ with glyoxal. The rate of this reaction was measured in N_2O -saturated solution over the pH range 2.0–6.0 by competition kinetics using $\text{Fe}(\text{CN})_6^{4-}$ as the competitor and measuring the yield of $\text{Fe}(\text{CN})_6^{3-}$ by observing the optical absorbance at a wavelength of 420 nm. Under these conditions $e_{(\text{aq})}^-$ is converted to $\cdot\text{OH}$ during the pulse ($0.6 \mu\text{s}$), so that at $\text{pH} > 3$, $G(\cdot\text{OH}) = 0.55 \mu\text{mol J}^{-1}$,¹⁵ and $\cdot\text{H}$ is unreactive on this timescale. In more acidic solutions some $e_{(\text{aq})}^-$ react with H^+ to form more $\cdot\text{H}$, but this does not affect the determination of k_2 .



Values of k_3 at the relevant pH were taken from ref. 16. The data gave $k_2 = (1.10 \pm 0.04) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 20°C , independent of pH over the range 2.0–6.0. At $\text{pH} \geq 4.0$, k_2 was also measured by direct observation of the formation of the glyoxal radical and the same value was obtained as by the competition method. An activation energy for reaction (2) of $12.6 \pm 0.9 \text{ kJ mol}^{-1}$ was obtained from direct measurements of k_2 at pH 4.0 over the temperature range $6\text{--}46^\circ\text{C}$. At $\text{pH} < 4$, values of k_2 could only be obtained by the competition method because further absorbance changes occurred after the glyoxal radical had been formed.

The spectrum of the product radical, assumed to be $\cdot\text{C}(\text{OH})_2\text{CH}(\text{OH})_2$, measured in N_2 -saturated solution containing $1 \times 10^{-3} \text{ mol dm}^{-3}$ glyoxal is shown in Fig. 1. The spectrum was measured $3 \mu\text{s}$ after the pulse, *i.e.* the time when reaction (2) was complete, and was found to be independent of pH. As noted above, further changes in absorbance occurred after the formation of the glyoxal radical below pH 4.0; these changes are thought to be due to the acid-catalysed dehydration of the radical but they are not relevant to the present study.

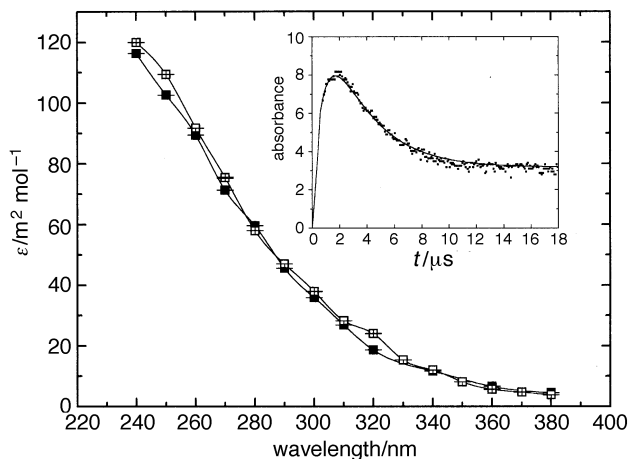


Fig. 1 Spectrum of the product from reaction (2) in N_2O -saturated solutions containing $1 \times 10^{-3} \text{ mol dm}^{-3}$ glyoxal at pH 2.5 (■) and pH 4.0 (□). The spectra were taken 3 μs after the pulse. Inset: FACSIMILE fit (—) for the absorbance change (●) due to reactions (2) and (5) at pH 3.0.

Reaction of the glyoxal radical with oxygen. The reaction of $\text{C}(\text{OH})_2\text{CH}(\text{OH})_2$ with oxygen was measured in solutions containing $1 \times 10^{-3} \text{ mol dm}^{-3}$ glyoxal, $6.85 \times 10^{-4} \text{ mol dm}^{-3} \text{ O}_2$ and $1.14 \times 10^{-2} \text{ mol dm}^{-3} \text{ N}_2\text{O}$. Under these con-

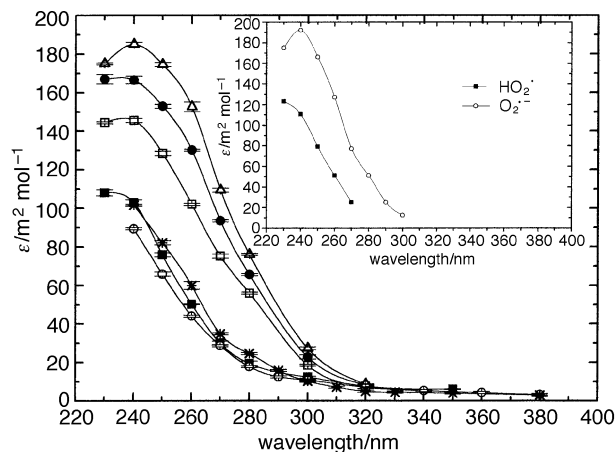


Fig. 2 Spectrum of the observed product of reaction (5) measured in solutions containing $10^{-3} \text{ mol dm}^{-3}$ glyoxal, $6.85 \times 10^{-4} \text{ mol dm}^{-3} \text{ O}_2$ at pH 2.0 (■), pH 3.0 (○), pH 4.0 (*), pH 5.3 (□), pH 5.7 (●) and pH 6.9 (△). Spectra of HO_2^* and $\text{O}_2^{*\cdot-}$ are shown in the inset.

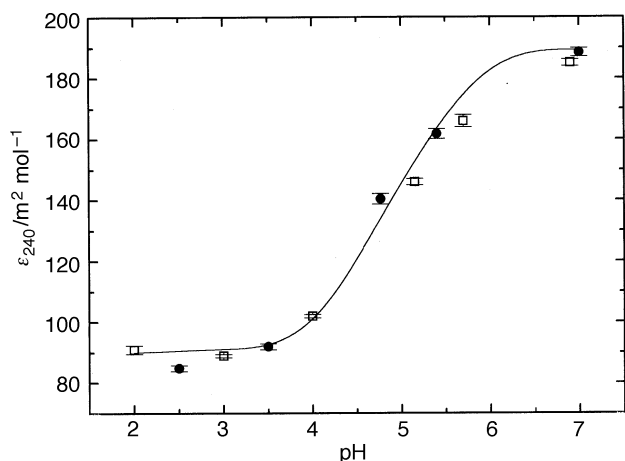


Fig. 3 Dependence of the molar absorption coefficient of the observed product of reaction (5) (□) at a wavelength of 240 nm on pH. The expected dependence calculated for $\text{HO}_2^*/\text{O}_2^{*\cdot-}$ is shown (—). The formate/formic acid data (●) are shown for comparison.

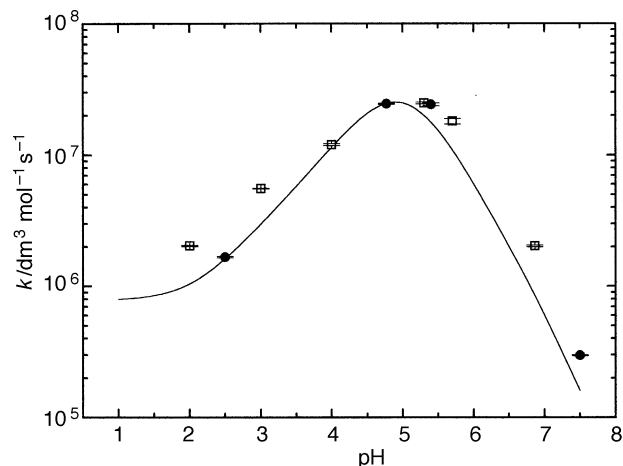
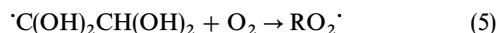
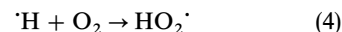


Fig. 4 Comparison of the pH dependence of the second-order rate constant for the decay of the observed product of reaction (5) (□) with that for $\text{HO}_2^*/\text{O}_2^{*\cdot-}$ (—) from ref. 19 and in this work from the formate/formic acid system (●)

ditions the expected reactions are (2), (4) and (5), with $G(\text{HO}_2^*) = 0.06 \mu\text{mol J}^{-1}$ and $G(\text{RO}_2^*) = 0.55 \mu\text{mol J}^{-1}$ so that RO_2^* comprises *ca.* 90% of the initial products.



The rate constant for reaction (5) was obtained from the rate of decay of the absorbance of $\text{C}(\text{OH})_2\text{CH}(\text{OH})_2$ at a wavelength of 280 nm. Because the growth of absorbance due to reaction (2) overlapped the beginning of this decay, k_5 was calculated using FACSIMILE curve-fitting software¹⁷ as illustrated in the inset to Fig. 1. Measurements made at pH 3 and 4 gave $k_5 = (1.38 \pm 0.11) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$; at higher pH, there was little change in absorbance with time so that k_5 could not be determined under those conditions.

Fig. 2 shows the sum of the absorption spectra of the products of reactions (4) and (5) at different pH. The shapes and pH dependence of these spectra are very similar to those of HO_2^* and $\text{O}_2^{*\cdot-}$ (see Fig. 2 inset) suggesting that RO_2^* rapidly dissociates to form $\text{HO}_2^*/\text{O}_2^{*\cdot-}$ and glyoxylic acid as in reac-

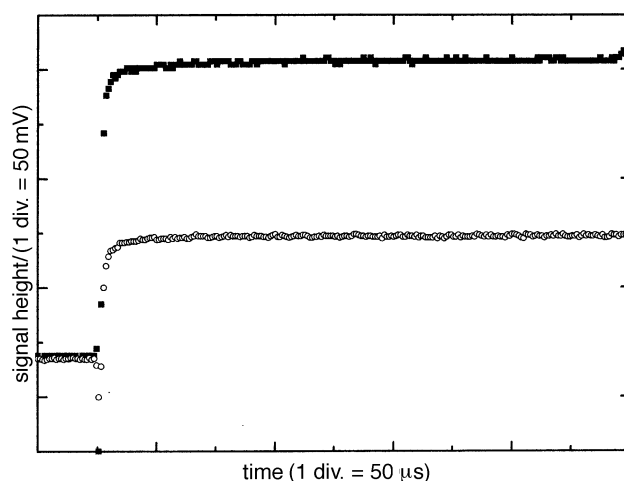
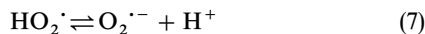


Fig. 5 Oscilloscope traces associated with conductivity changes due to reactions (4) and (5) measured at pH 3.0 (○) and pH 4.0 (■) in solutions containing $1 \times 10^{-3} \text{ mol dm}^{-3}$ glyoxal, $6.85 \times 10^{-4} \text{ mol dm}^{-3} \text{ O}_2$ and $1.14 \times 10^{-2} \text{ mol dm}^{-3} \text{ N}_2\text{O}$

Table 1 Measured and calculated conductivity changes at pH 3.0 and 4.0

pH	$\sum G_i \lambda_{i, \text{meas.}} / \text{S m}^2 \text{ J}^{-1}$	$\sum G_i \lambda_{i, \text{calc.}} / \text{S m}^2 \text{ J}^{-1}$
3.0	5.32×10^{-9}	5.61×10^{-9}
4.0	1.62×10^{-8}	1.60×10^{-8}

tions (6) and (7),

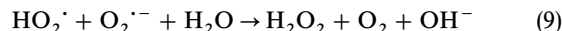
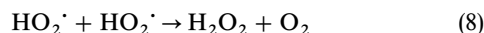


Further evidence that the observed absorbing product is $\text{HO}_2\cdot/\text{O}_2^{\cdot-}$ rather than $\text{RO}_2\cdot$ is provided by the data in Fig. 3 where the dependence of the molar absorption coefficient of the product at a wavelength of 240 nm on pH is compared with that of $\text{HO}_2\cdot/\text{O}_2^{\cdot-}$. Also shown in Fig. 3 are data for solutions where glyoxal was replaced by formate/formic acid, which is known to produce $\text{HO}_2\cdot/\text{O}_2^{\cdot-}$.^{16,18} Supporting evidence is also provided by the data in Fig. 4 where the pH-dependent second-order rate constants for the decay of the observed product compare well with those for self reaction of $\text{HO}_2\cdot/\text{O}_2^{\cdot-}$.¹⁹

Conductivity changes associated with reactions (4) and (5) are illustrated in Fig. 5. The magnitude of the change in conductivity with pH is consistent with dissociation of a proton from a species with a $\text{p}K_a$ less than 4.0. Taking the $\text{p}K_a$ of glyoxylic acid to be 3.4 at an ionic strength of $10^{-3} \text{ mol dm}^{-3}$, based on the value²⁰ of 3.18 at an ionic strength of 0.1 mol dm^{-3} , and the $\text{p}K_a$ of $\text{HO}_2\cdot = 4.8$,²¹ one can calculate the expected change in conductivity, taking $\lambda_{\text{H}^+} = 3.15 \times 10^{-2} \text{ S m}^2 \text{ mol}^{-1}$, and $\lambda_i = 4.1 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1}$ for glyoxylate (the value for acetate ion²²) and $\text{O}_2^{\cdot-}$. The calculated values are compared with the measured values in Table 1; the agreement is good at each pH. The rate of growth of the conductivity signal was limited by the response time of the measuring device (*ca.* 5 μs), indicating that changes resulting from reactions (6) and (7) occurred on a shorter timescale.

Steady-state radiolysis experiments

These were carried out to identify the permanent products of the oxidation of glyoxal by $\cdot\text{OH}$ in the presence of oxygen. Analysis of the irradiated solution for hydrogen peroxide showed that $G(\text{H}_2\text{O}_2) = (3.57 \pm 0.01) \times 10^{-7} \text{ mol J}^{-1}$. This is very close to the expected result of $[G(\cdot\text{OH}) + G(\cdot\text{H})]/2 + 0.07 \text{ mol J}^{-1}$ [see reaction (1)] if $\text{HO}_2\cdot$ is produced in reaction (6), which will be followed by reactions (8) and (9),

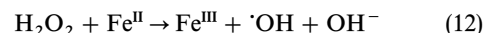


When catalase was added to the irradiated solution immediately before analysis no oxidising product was detected by the Gormley method. This result is also consistent with H_2O_2 being one of the final oxidation products. The other expected product, glyoxylic acid, was detected by ion chromatography with a yield of $(4.7 \pm 0.1) \times 10^{-7} \text{ mol J}^{-1}$, which is 15% lower than expected. Nevertheless, this result provides further support for the proposed mechanism.

Conclusions

All of the data presented above are consistent with the product of reaction (5) rapidly dissociating to glyoxylic acid and $\text{HO}_2\cdot$. This is characteristic of α -hydroxy-peroxy radicals²³ and consistent with glyoxal being in the form of the

dihydrate since only one type of radical was detected as the product of reaction (2) (see Fig. 1). Thus free radical oxidation of glyoxal in cloud water will be a source of $\text{HO}_2\cdot$ and hence hydrogen peroxide. Both of these species are in turn sources of $\cdot\text{OH}$ via reactions (7), (10), (11) and (12),



with the result that oxidation of glyoxal in cloud water initiated by $\cdot\text{OH}$ generates glyoxylic acid ($\text{p}K_a = 3.4$) in a chain reaction without any diminution in the oxidising capacity of the atmosphere. Further oxidation of glyoxylic acid to oxalic acid ($\text{p}K_{a1} = 1.23$) is expected to occur by the same mechanism. The concentrations of glyoxylic and oxalic acids in atmospheric water droplets are typically in the range $0.1\text{--}20 \mu\text{mol dm}^{-3}$,²⁴ of the same order of magnitude as dissolved iron. Moreover, it has been shown under these conditions²⁴ that the photolysis of iron(III) oxalato complexes could be a major source of H_2O_2 in cloud, fog and rain water.

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