The reaction of the malonic acid derived radical with oxygen. A reinvestigation by pulse radiolysis

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The dicarboxymethyl radicals (derived from malonic acid) and their peroxyl radicals play an important role in the Belousov–Zhabotinsky reaction, and detailed knowledge of the rate constants are required for modelling this oscillating reaction. Dicarboxymethyl radicals were produced pulse radiolytically in aqueous solutions. They are characterized by absorption maxima at 310 nm at pH 0 (fully protonated, $\varepsilon = 1210\ \mathrm{dm^3\ mol^{-1}\ cm^{-1}}$) and at 340 nm at pH 8 (dianion, $\varepsilon = 1070\ \mathrm{dm^3\ mol^{-1}\ cm^{-1}}$). The radicals decay bimolecularly with rate constants of $4 \times 10^8\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$ at pH 0 and $1.4 \times 10^7\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$ at pH 8. In the presence of O_2, the dicarboxymethyl radicals add O_2, and their absorption decays with rate constants of $1.6 \times 10^9\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$ at pH 0 and $1.3 \times 10^9\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$ at pH 8. Whereas the second $\mathrm{p}K_a$ value of the radical is identical to that of the parent compound (5.7), the value of the corresponding peroxyl radical is as low as 3.

Recently, the oxidation of malonic acid by Ce(IV) in acid solution in the presence of oxygen has been investigated in order to elucidate how oxygen participates in the Belousov–Zhabotinsky reaction.[1] Using EPR spectroscopy for detection, it was observed that the dicarboxymethyl radicals which are formed as intermediates of the reaction of malonic acid and Ce(IV) [reaction (1)] rapidly add O_2 yielding dicarboxymethylperoxyl radicals [reaction (2)].

$$\mathrm{Ce(IV)} + \mathrm{CH_2(CO_2H)_2} \longrightarrow \mathrm{Ce(III)} + {}^{\bullet}\mathrm{CH(CO_2H)_2} + \mathrm{H^+} \quad (1)$$

$${}^{\bullet}\mathrm{CH(CO_2H)_2} + \mathrm{O_2} \longrightarrow {}^{\bullet}\mathrm{O_2CH(CO_2H)_2} \quad (2)$$

The dicarboxymethylperoxyl radicals react further to give products which differ from those formed under anaerobic conditions.[1] Moreover, the anaerobic and aerobic oxidation of malonic acid by Ce(IV) follow different stoichiometries.[2] For modelling, the kinetic behaviour of the dicarboxymethyl and the dicarboxymethylperoxyl radicals, the rate constants of *all* individual steps involved in the reaction are required.

In the above-mentioned stopped-flow ESR study (using Ce(IV) to generate the malonic acid radical in 1 molar sulfuric acid solution), the rate constant for reaction (2) had been assessed at $1.7 \times 10^7\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$.[1] However, this rate constant is two orders of magnitude lower than the typical rate constants for the reaction of carbon-centred radicals with O_2.[3,4] Hence, we decided to reinvestigate the system using another technique, namely pulse radiolysis.

Experimental

Pulse radiolysis of 0.02–0.4 mol dm^{-3} solutions of malonic acid (99%, Janssen) in Milli-Q-filtered (Millipore) water saturated with either N_2O or with N_2O–O_2 (adjusted to various O_2 concentrations through a gas-mixer) was carried out with a 2.8 MeV Van-de-Graaff generator delivering electron pulses of 0.4–2 μs duration and doses of 8–20 Gy pulse^{-1}. Dosimetry was performed with an N_2O-saturated 10^{-2} mol dm^{-3} solution of KSCN for which $G({}^{\bullet}\mathrm{OH}) = 6.2 \times 10^{-7}\ \mathrm{mol\ J^{-1}}$ and $\varepsilon((\mathrm{SCN})_2^{\bullet -}) = 7600\ \mathrm{dm^3\ mol^{-1}\ cm^{-1}}$ at 480 nm. Intermediates were monitored by optical detection. The pulse radiolysis set-up was described previously.[5]

The malonate-derived radical can be readily produced pulse radiolytically [reactions (3)–(5)].[6] Hydroxyl radicals are generated in the radiolysis of water [reaction (3)]. The radiation-chemical yields (G values) of the primary radicals are $G({}^{\bullet}\mathrm{OH}) \approx G(\mathrm{e_{aq}}^-) = 2.9 \times 10^{-7}\ \mathrm{mol\ J^{-1}}$ and $G(\mathrm{H}^{\bullet}) = 0.6 \times 10^{-7}\ \mathrm{mol\ J^{-1}}$. N_2O is used to convert the solvated electrons into ${}^{\bullet}$OH [reaction (4)]. The OH radical then abstracts an H atom from the methylene carbon of malonic acid (pK_a 2.8 and 5.7) [reaction (5); pH ≈ 1: $k \approx 2 \times 10^7\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$; pH ≈ 7: $k \approx 3 \times 10^8\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$].[7]

$$\mathrm{H_2O} \xrightarrow[\text{radiation}]{\text{ionizing}} \mathrm{e_{aq}}^-,\ {}^{\bullet}\mathrm{OH},\ \mathrm{H}^{\bullet},\ \mathrm{H^+},\ \mathrm{H_2O_2},\ \mathrm{H_2} \quad (3)$$

$$\mathrm{e_{aq}}^- + \mathrm{N_2O} + \mathrm{H_2O} \longrightarrow {}^{\bullet}\mathrm{OH} + \mathrm{OH^-} + \mathrm{N_2} \quad (4)$$

$${}^{\bullet}\mathrm{OH} + \mathrm{CH_2(CO_2H)_2} \longrightarrow \mathrm{H_2O} + {}^{\bullet}\mathrm{CH(CO_2H)_2} \quad (5)$$

Results and discussion

Pulse-radiolytic studies

For aliphatic acids, *e.g.* acetic acid, the pK_a values of the radicals are typically very similar to those of their corresponding parent compounds.[8] This also holds for malonic acid. In alkaline solution, the dicarboxymethyl radical derived from malonate has been reported[6] to have a broad spectrum with λ_{max} at 340 nm (confirmed in this study, $\varepsilon = 1070\ \mathrm{dm^3\ mol^{-1}\ cm^{-1}}$, data not shown). In the acidic region, however, the dicarboxymethyl radical absorbs less strongly at this wavelength. From a plot of the absorbance *vs.* pH the second pK_a value of the dicarboxymethyl radical was determined as 5.7 (*cf.* inset of Fig. 1), in complete agreement with the reported value.[6] By contrast, the first pK_a value of the dicarboxymethyl radical cannot be detected using a similar experimental protocol,[6] since the absorption coefficients of the radicals are not sufficiently different in the pH interval 0–4 (*cf.* Fig. 1 inset).

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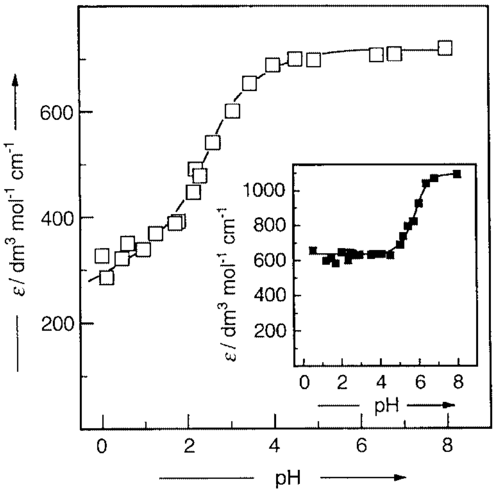

Fig. 1 Absorption coefficient (at 340 nm) *vs.* pH curves of the transients produced upon pulse radiolysis of malonic acid (0.02 mol dm^{-3}) in N_2O–O_2 (4 : 1 v/v)-saturated solution (main figure) and in N_2O-saturated solution (inset).

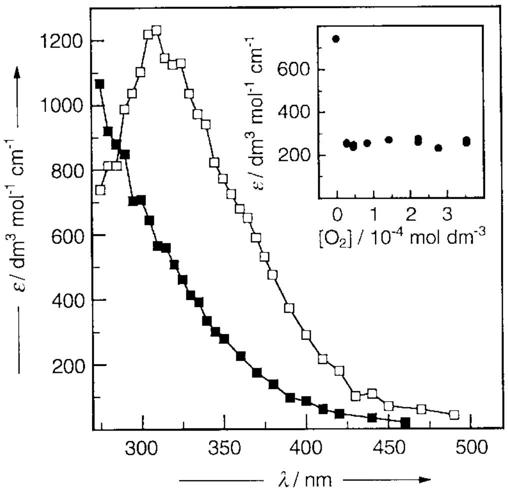

Fig. 2 Absorption spectra of the transient species produced by pulse radiolysis (8 Gy pulse^{-1}) of malonic acid (0.4 mol dm^{-3}) at pH 0 in N_2O (2 μs after the pulse, □) and in N_2O–O_2 (4 : 1 v/v)-saturated aqueous solution (14 μs after the pulse, ■). Inset: Oxygen concentration dependence of the absorbance at 350 nm in N_2O–O_2-saturated solution of malonic acid at pH 0.

The high concentration of protons in a 1 molar solution of perchloric acid converts the solvated electrons quantitatively into hydrogen atoms [reaction (6), $k_6 = 2.3 \times 10^{10}$ dm^3 mol^{-1}

$$e_{aq}^- + H^+ \longrightarrow H^\bullet \qquad (6)$$

s^{-1}][7] which, in turn, react very slowly with malonic acid ($k_H = 4.0 \times 10^5$ dm^3 mol^{-1} s^{-1}).[7] In Fig. 2, the transient absorption spectrum recorded 2 μs after the pulse (□) represents the dicarboxymethyl radical produced in reaction (5) with $G = 2.9 \times 10^{-7}$ mol J^{-1} (with the high concentration of malonic acid used, this spectrum includes some contribution from the reaction of H atoms with malonic acid). The absorption maximum is located at 310 nm ($\varepsilon = 1210$ dm^3 mol^{-1} cm^{-1}), *i.e.* it is blue-shifted by 30 nm with respect to that of the dianion. In the presence of O_2, this absorption decays giving rise to the spectrum of the resulting peroxyl radical produced in reaction (2) (Fig. 2). All hydrogen atoms are scavenged by O_2 to yield hydroperoxyl radicals [reaction (7)]; the latter have negligible

$$H^\bullet + O_2 \longrightarrow HO_2^\bullet \qquad (7)$$

absorption $\lambda > 280$ nm,[9] and, hence, do not interfere in the spectrum presented in Fig. 2 (■).

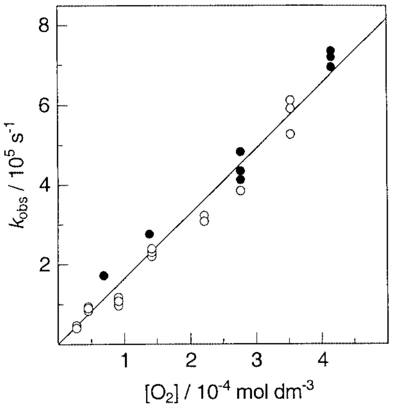

Fig. 3 Oxygen concentration dependence of the decay rate constant monitored at 350 nm in the pulse radiolysis of malonic acid (0.2 mol dm^{-3}) at pH 1 (●) and at pH 0 (○).

In the following investigations, we monitor the kinetics at $\lambda = 350$ nm. Although located on the flanks of the spectra of the dicarboxymethyl and the dicarboxymethylperoxyl radicals, this wavelength is associated with the largest relative difference between the absorption coefficients of the two radicals (Fig. 2). The observed rate constants of the absorption decay at 350 nm of the fully protonated dicarboxymethyl radical are plotted as a function of the O_2 concentration (for two data sets in the relevant pH range see Fig. 3). We obtain a linear relationship whose slope yields the rate constant of oxygen addition [reaction (2)] as $k = 1.6 \times 10^9$ dm^3 mol^{-1} s^{-1} (for a compilation of rate constants see Table 1). A similar rate constant, $k = 1.3 \times 10^9$ dm^3 mol^{-1} s^{-1}, is determined for the oxygen addition to the twice deprotonated dicarboxymethyl radical at pH 9.6 (data not shown). The values we found for these rate constants are typical for the addition of oxygen to carbon-centred radicals.[4]

In general, the addition of O_2 to carbon-centred radicals is practically irreversible at room temperature, and only strongly conjugated radicals such as the hydroxycyclohexadienyl radical show reversibility under such conditions (for a review see ref. 4). In the present case, O_2 addition must be irreversible for two reasons: first, the k_{obs} *vs.* O_2 concentration plot intersects the origin (*cf.* Fig. 3), and, secondly, the absorbance of the dicarboxymethylperoxyl radical at 350 nm is independent of the oxygen concentration in the solution (*cf.* inset in Fig. 2). This eliminates the possibility that the earlier determination of the rate constant by EPR (1.7×10^7 dm^3 mol^{-1} s^{-1},[1] *i.e.* a value lower by two orders of magnitude compared to the one determined now) was caused by neglecting a substantial reverse reaction.

By monitoring the absorbance of the peroxyl radical of malonic acid at 340 nm in the pH range 0–8 (Fig. 1), an inflection point near pH 3 is observed which is attributed to the second pK_a of the dicarboxymethylperoxyl radical. This value is lower by more than 2 pH units than that of the parent dicarboxymethyl radical. This remarkable drop of the pK_a value upon converting the parent radical into the corresponding peroxyl radical is caused by the strong electron-withdrawing properties of the peroxyl radical function.[8] The absorbance at 340 nm shows further changes in the pH range 0–2 (Fig. 1), indicating that the first pK_a of the peroxyl radical might be found in this pH interval.

The potential decay reactions of the two radicals under consideration, *i.e.* the dicarboxymethyl and the dicarboxymethylperoxyl radicals, were also reinvestigated. The bimolecular decay [reactions (8)/(8a)] rate constant of the dicarboxymethyl

$$2\,{}^\bullet CH(CO_2^-)_2 \longrightarrow (CH(CO_2^-)_2)_2 \qquad (8)$$

$$2\,{}^\bullet CH(CO_2H)_2 \longrightarrow (CH(CO_2H)_2)_2 \qquad (8a)$$

radical increases with increasing acidity of the solution ($2k_8 = 1.4 \times 10^7$ dm^3 mol^{-1} s^{-1} at pH 8, and $2k_{8a} \approx 4 \times 10^8$ dm^3

Table 1 Compilation of rate constants (in units of $dm^3\ mol^{-1}\ s^{-1}$)

No	Reaction	Rate constant	Reference
(1)	$Ce^{4+} + CH_2(CO_2H)_2 \longrightarrow Ce^{3+} + {}^\bullet CH(CO_2H)_2 + H^+$	0.3	Ref. 10
(2)	$O_2 + {}^\bullet CH(CO_2H)_2 \longrightarrow {}^\bullet O_2CH(CO_2H)_2$	1.6×10^9	This work
		1.7×10^7	Ref. 1
	$O_2 + {}^\bullet CH(CO_2^-)_2 \longrightarrow {}^\bullet O_2CH(CO_2^-)_2$	1.3×10^9	This work
(8)	$2\ {}^\bullet CH(CO_2^-)_2 \longrightarrow$ Dimer	1.4×10^7	This work
(8a)	$2\ {}^\bullet CH(CO_2H)_2 \longrightarrow$ Dimer	4×10^8	This work
		4.2×10^8	Ref. 10
(9)	$2\ {}^\bullet O_2CH(CO_2^-)_2 \longrightarrow$ Products	3.2×10^7	This work
(9a,b)	$2\ {}^\bullet O_2CH(CO_2H)_2/{}^\bullet O_2CH(CO_2H)_2 + HO_2^\bullet \longrightarrow$ Products	5×10^8	This work

$mol^{-1}\ s^{-1}$ at pH 0.5–4; in good agreement with the literature;[10] *cf.* Table 1).

The bimolecular decay rate constant of the fully deprotonated dicarboxymethylperoxyl radical [reaction (9)] was found to

$$2\ {}^\bullet O_2CH(CO_2^-)_2 \longrightarrow \text{products} \qquad (9)$$

$$2\ {}^\bullet O_2CH(CO_2H)_2 \longrightarrow \text{products} \qquad (9a)$$

$${}^\bullet O_2CH(CO_2H)_2 + HO_2^\bullet \longrightarrow \text{products} \qquad (9b)$$

be $3.2 \times 10^7\ dm^3\ mol^{-1}\ s^{-1}$ at pH 8. Under acidic conditions the $HO_2^\bullet$ radicals contribute 55% of the total primary radical yield. They also interact with the dicarboxymethylperoxyl radicals [*cf.* reaction (9b)] so that the obtained rate constant ($5.0 \times 10^8\ dm^3\ mol^{-1}\ s^{-1}$ at pH 1) only describes the overall decay rate of the dicarboxymethylperoxyl radicals [reactions (9a) and (9b)] under such conditions.

The much lower value at the higher pH reflects electrostatic repulsion caused by the four negative charges of the two dianions which must encounter in order to react. Hence the repulsive forces retard the reaction considerably below diffusion-controlled (*cf.* ref. 11).

Relevance for the Belousov–Zhabotinsky reaction

In the previous study,[1] the kinetics of the dicarboxymethyl and the dicarboxymethylperoxyl radicals formed transiently in the aerobic reaction of malonic acid with Ce(IV) were investigated by a stopped-flow technique using EPR for detection, and rate constants were arrived at by fitting the data to a simple mechanistic model consisting of reactions (1), (2), (8a), (9a) as well as reactions (10)–(12).[1]

$${}^\bullet O_2CH(CO_2H)_2 + CH_2(CO_2H)_2 \longrightarrow HO_2CH(CO_2H)_2 + {}^\bullet CH(CO_2H)_2 \qquad (10)$$

$$Ce^{4+} + HO_2CH(CO_2H)_2 \longrightarrow Ce^{3+} + {}^\bullet O_2CH(CO_2H)_2 + H^+ \qquad (11)$$

$$HO_2CH(CO_2H)_2 \longrightarrow \text{products} \qquad (12)$$

Based on the more direct data obtained in the present study, the (low)[1] value obtained for reaction (2) has to be revised. Their fitting procedure also required a rate constant of $300\ dm^3\ mol^{-1}\ s^{-1}$ value for reaction (10).[1] In the meantime, the rate of reaction of peroxyl radicals with very good H-donors such as thiols has been investigated in more detail. For example, the reaction of the peroxyl radicals derived from poly(acrylic acid) could no longer be monitored by kinetic EPR spectroscopy because it is too slow ($k < 200\ dm^3\ mol^{-1}\ s^{-1}$).[12] Such a low rate is, furthermore, in good agreement with the low rate of reaction of the HO_2 radical with 1,4-dithiothreitol ($120\ dm^3\ mol^{-1}\ s^{-1}$).[13] One now has to realize that malonic acid is an extremely poor H-donor compared to thiols; for example, the rate of reaction of the very reactive OH radical with malonic acid is three orders of magnitude slower than its reaction with thiols.[7] Therefore, we conclude that the rate of reaction (10) must be much lower than $1\ dm^3\ mol^{-1}\ s^{-1}$. Hence, this reaction will only play a minor role, if any, in the context of the Belousov–Zhabotinsky reaction.

We have attempted to model the observed[1] EPR stopped-flow kinetics using the set of revised data (k_1, k_2, k_{8a}, k_{9a}, see Table 1; k_{10}, see above). Calculations with these rate constants were able to reproduce the main features of the kinetic EPR measurements qualitatively, but it was not possible to achieve quantitative agreement between simulation and experiment. This may suggest that the mechanism of the aerobic reaction is more complex than the minimal model consisting of reactions (1), (2), and (8)–(12). Thus, further studies are required to elucidate the entire mechanism of the reaction of malonic acid with cerium(IV) in the presence of oxygen. The first steps in this direction have already been undertaken.[14] One of the oxidation products of malonic acid with Ce(IV) in the presence of oxygen is hydroxymalonic (tartronic) acid.[14] The latter is much more readily oxidized than malonic acid and may undergo secondary oxidation. The complex peroxyl radical chemistry of hydroxymalonic acid has been reported.[15] Besides hydroxymalonic acid, the other major expected[4] product of the bimolecular decay of the malonic-acid-derived peroxyl radicals is ketomalonic acid whose reaction with the superoxide radical leads to the formation of oxalic peracid in a chain reaction.[16,17]

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