The Importance of Mesomerism in the Termination of α-Carboxymethyl Radicals from Aqueous Malonic and Acetic Acids

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Abstract: In the dioxygen-free aqueous malonic and acetic acid systems, α-carboxymethyl radicals are produced through hydrogen abstraction from the parent compound by radiolytically generated OH radicals. H abstraction from the CO_2^-/CO_2H group followed by decarboxylation is a process of small importance ($\leq 5\%$). The α-carboxymethyl radicals terminate by recombination. Two types of recombination product are observed which are characterised by the formation of a C–C linkage or a C–O linkage. α-Carboxymethyl radicals are mesomeric systems. Their mesomeric state depends on the state of protonation and determines the proportion of the C–C- versus C–O-linked dehydrodimers they produce.

Keywords: acetic acid · carboxylic acids · chemical oscillator · dimerization · malonic acid · radicals

Introduction

The oxidation of malonic acid to the dicarboxymethyl radical by the Ce^{IV} ion has been recognised as a major elementary step in the chemical oscillator known as the Belousov – Zhabotinsky reaction.[1–5] In general, dicarboxymethyl is produced from malonic acid by the action of free radicals; in systems which involve the reduction of a strong oxidant, for example, bromate, various free radicals that attack malonic acid, such as $Br^{\bullet}$ and $BrO_2^{\bullet}$, play a role and will contribute to the degradation of malonic acid.[2] These hydrogen-abstraction processes further complicate the reaction-mechanistic imaging of systems such as the Belousov – Zhabotinsky reaction. In addition, it has been recognised[4] that under conditions of oxygenation, peroxyl radical reactions[7] must be taken into account. Moreover, peroxyl radicals and molecular peroxidic species may effect redox cycling and Fenton-like reactions[9] in the case of transition metal-catalysed systems, though perhaps not with cerium.

In the larger context as to the fate of dicarboxymethyl in these malonic acid-containing systems, and also for the sake of systematic free-radical chemistry, it is of interest to explore the behaviour of the dicarboxymethyl radical, including its termination reactions over a wide pH range. Two recombination products, ethane-1,1,2,2-tetracarboxylic acid (2,3-dicarboxysuccinic acid) and monomalonyl malonate (malonic acid dicarboxymethyl monoester), have been observed upon oxidation of malonic acid with Ce^{IV} in aqueous solution.[10] From this it was inferred that *two distinct species* of malonic acid-derived free radicals, both of them undergoing recombination reactions, exist in these systems, namely, $^{\bullet}CH(COOH)_2$ and $HO_2CCH_2{-}C(O)O^{\bullet}$ in varying states of protonation depending on the pH, either generated independently[10] or *tautomerically* related.

The assumption that the lifetime of a carboxyl radical (here, $HO_2C{-}CH_2{-}C(O)O^{\bullet}$) is long enough for it to undergo recombination reactions is in contradiction with what is known of the behaviour of these radicals: the first-order decay lifetime of aliphatic carboxyl radicals [cf. reaction (7) later] has been estimated to be in the order of nanoseconds[11] (note that otherwise the Kolbe electrolysis, which generates these radicals at high local concentrations, could not be used as a synthetic method for the preparation of alkanes).

In this work, we demonstrate that the behaviour of dicarboxymethyl radicals can be much more plausibly described by a *single free-radical species* and by taking into account its *mesomeric* states.

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Experimental Section

Acetic acid (Merck, p.a.), malonic acid (Fluka), glycolic acid (EGA Chemie), acetoxyacetic acid (Aldrich), tricarballylic (3-carboxyglutaric) acid (Fluka), succinic acid (Merck), tartronic (hydroxymalonic) acid

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(Serva) and 1,1,2,2,-ethanetetracarboxylic acid tetraethyl ester (Aldrich) were commercially available. 1,1,2,2-Ethanetetracarboxylic acid was obtained by hydrolysis of the ester.[10] Monomalonyl malonate was synthesised from malonic acid and hydroxymalonic acid by condensation, with P_2O_5 as the dehydrating agent.[10] The crude product still contains malonic and hydroxymalonic acid. The purity was sufficient for assignment purposes.

Aqueous solutions of the substrates (concentrations typically 1×10^{-3} mol dm^{-3} for malonic acid and 3×10^{-3} mol dm^{-3} for acetic acid) were prepared in Milli-Q-filtered (Millipore) water and saturated with N_2O. The pH of the solutions was adjusted to the desired value with NaOH or $HClO_4$. γ-Radiolyses were carried out in a panoramic ^{60}Co-source at a dose rate of 0.16 Gy s^{-1} to total doses of up to 150 Gy (i.e., the conversion of the substrate remained below 10%), except for the determination of the secondary product 3-carboxyglutaric acid where the total dose was raised to 400 Gy (the dose of 1 Gy equals 1 *J* of radiation energy deposited in a substrate mass of 1 kg, here 1 dm^{-3} of solution).

Aliquot samples from the radiolysis of acetic acid were rotary evaporated and subsequently trimethylsilylated with (bis-*N*,*N*-trimethyl)silyltrifluoroacetamide (BSTFA) in pyridine. The trimethylsilylated samples were analysed by GC-MS (Hewlett-Packard 5971 A) on a 12 m HP-1 column (cross-linked methyl silicone gum). Glycolic, succinic, hydroxymalonic and 3-carboxyglutaric acids were identified by comparison of their mass spectra with those of authentic material. 1,1,2,2-Ethanetetracarboxylic acid and monomalonyl malonate were not derivatised adequately by this procedure and cannot be analyzed in this manner.

The quantitative determination of the products was carried out with ion chromatography (Dionex DX-2010i). Prior to injection, all samples were adjusted to pH 3.0, because it has been observed that the response of the acids can vary significantly depending on the pH of the injected solution.

Products from acetic acid: Succinic acid was analysed on an AS14 column [4×250 mm with 4×50 mm AG14 pre-column, ASRS-ULTRA suppressor, eluent: solution of Na_2CO_3 (9×10^{-4} mol dm^{-3}) and $NaHCO_3$ (8.5×10^{-4} mol dm^{-3}), flow rate: 1 mL min^{-1}, retention time: 22 min]. Under these conditions, glycolic acid has the same retention time as acetic acid (3.5 min). Therefore, the former was determined on an ICE-AS1 column (10×250 mm, without a pre-column and suppressor, flow rate: 1.0 mL min^{-1}, eluent: water), together with succinic acid, since both show practically the same retention times (4.7 versus 4.8 min) under these conditions. The yield of glycolic acid was then obtained from the difference between the results from the AS14 column and the ICE-AS1 column. 3-Carboxyglutaric acid was analysed on an AS16 column [2×250 mm, 2×50 mm AG16 pre-column, ASRS-ULTRA suppressor, eluent: NaOH (3.5×10^{-2} mol dm^{-3}), flow rate: 0.25 mL min^{-1}, retention time: 7.4 min].

Products from malonic acid: Monomalonyl malonate and ethane-1,1,2,2-tetracarboxylic acid were analysed under the same conditions that were used for 3-carboxyglutaric acid (AS16 column, retention times: 8.0 and 24 min). Under these conditions, an unidentified product was eluted (7.0 min) on the tail of malonic acid (4.5 min). Since the monomalonyl malonate reference material was not sufficiently pure for calibrational use, irradiated samples were hydrolysed to malonic acid and hydroxymalonic acid at 85 °C and pH 11 for 1 hour in order to quantify this compound. The hydroxymalonic acid thus produced was analysed on a 4×250 mm AS9 column with a 4×50 mm AG9 pre-column, eluent: solution of Na_2CO_3 (1.8×10^{-3} mol dm^{-3}) and $NaHCO_3$ (1.7×10^{-3} mol dm^{-3}), flow rate: 1 mL min^{-1}. Under these conditions the retention times of hydroxymalonic acid and malonic acid were 15 min and 12 min, respectively.

Methane and CO_2 were scrubbed from the irradiated samples with argon as the carrier gas[12] and measured by GC on a 3.2 m Porapak-9 capillary column.

Results and Discussion

The free radical-generating system: Hydroxyl radicals are generated by the radiolysis of water [reaction (1)]. The radiation-chemical yields (*G* values) of the primary radicals

$$H_2O \xrightarrow[\text{radiation}]{\text{ionising}} e^-_{aq},\ {}^{\bullet}OH,\ H^{\bullet},\ H^+,\ H_2O_2,\ H_2 \qquad (1)$$

are $G({}^{\bullet}OH) \approx G(e^-_{aq}) = 2.9 \times 10^{-7}$, $G(H^{\bullet}) = 0.6 \times 10^{-7}$ and $G(H_2O_2) \approx 0.7 \times 10^{-7}$ mol J^{-1}. N_2O was used to convert the solvated electron into ${}^{\bullet}OH$ [reaction (2)]. The rate constants

$$e^-_{aq} + N_2O + H_2O \longrightarrow {}^{\bullet}OH + OH^- + N_2 \qquad (2)$$

of the reaction of the hydroxyl radical with malonic acid ($pK_a = 2.8$ and 5.7) were re-determined by competition kinetics with KSCN and by build-up kinetics of the dicarboxylmethyl radical monitored optically at $\lambda = 340$ nm. We found $k_3 = 1.9 \times 10^7$ dm^3 mol^{-1} s^{-1} at pH 1.2 (free malonic acid) and $k_3 = 1.1 \times 10^8$ dm^3 mol^{-1} s^{-1} at pH 8.0 (malonic acid dianion). The value for the malonic acid monoanion, $k_3 = 4.2 \times 10^7$ dm^3 mol^{-1} s^{-1}, was determined by build-up kinetics at pH 4.1. There is good agreement between the value of k_3 for undissociated malonic acid and the value reported,[13] while the value of k_3 for the malonic acid *dianion* is lower than that reported.[13]

The OH radical reacts with malonic acid and acetic acid largely by abstracting a carbon-bound H atom [reactions (3) and (4)], and to a minor extent at the carboxyl group, either by H-atom abstraction when the carboxyl group is protonated, or by oxidation of the carboxylate [reactions (5) and (6)].

$$\cdot OH\ (H^{\bullet}) + CH_2(CO_2H)_2 \longrightarrow H_2O\ (H_2) + {}^{\bullet}CH(CO_2H)_2 \qquad (3)$$

$$^{\bullet}OH\ (H^{\bullet}) + CH_3CO_2H \longrightarrow H_2O\ (H_2) + {}^{\bullet}CH_2CO_2H \qquad (4)$$

$$\cdot OH + CH_3CO_2H \longrightarrow H_2O + CH_3C(O)O^{\bullet} \qquad (5)$$

$$\cdot OH + CH_3CO_2^- \longrightarrow OH^- + CH_3C(O)O^{\bullet} \qquad (6)$$

The methylcarboxyl radical and the corresponding carboxyl radical derived from malonic acid decompose rapidly [e.g., reaction (7), $k_7 \approx 1.3 \times 10^9$ s^{-1}][11] and, thus, cannot participate in the bimolecular termination reactions.

$$CH_3C(O)O^{\bullet} \longrightarrow {}^{\bullet}CH_3 + CO_2 \qquad (7)$$

It is apparent that in both the malonic and acetic acid systems the chemistry is largely determined by the formation and the termination reactions of the α-carboxymethyl radical, as indicated by the radiation-chemical yields of the products derived from the radical (sum of *G* in the close vicinity of 3×10^{-7} mol J^{-1}, cf. Figures 1 and 2). The low yields of CO_2

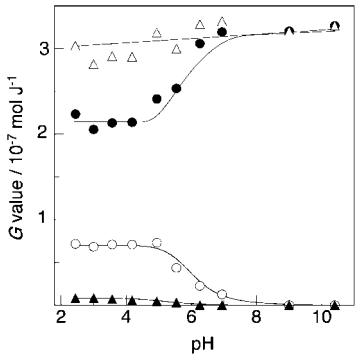

Figure 1. γ-Radiolysis of malonic acid in N_2O-saturated solution. Yields (*G* values) of ethane-1,1,2,2-tetracarboxylic acid (●), monomalonyl malonate (○), unknown product ▲, sum (△) of these three products.

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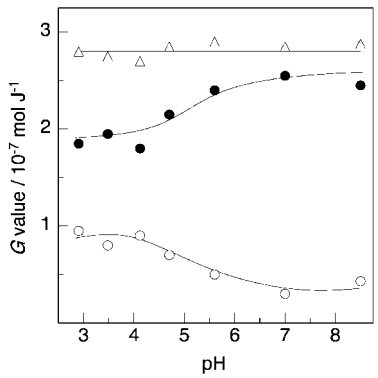


Figure 2. γ-Radiolysis of acetic acid in N_2O-saturated solution. Yields (G values) of succinic acid (●), glycolic acid (○), sum (△) of both products.

(Table 1) indicate that the formation of alkylcarboxyl radicals, such as reaction (6), is not significant. In the acetic acid system, the formation of small amounts of methane, derived from the methyl radical produced in this decarboxylation, was also detected (pH 3.5, $G(CH_4) = 0.06 \times 10^{-7}$ mol J^{-1}; pH 7.2, $G(CH_4) = 0.01 \times 10^{-7}$ mol J^{-1}).

The malonic acid system: Three products are formed, ethane-1,1,2,2-tetracarboxylic acid, monomalonyl malonate and an unknown product. Their yields increase linearly with the dose (data not shown). G values were calculated from the slopes of the plot of the yield against the dose. The individual yields vary considerably with pH; however, their sum is essentially constant over the entire pH range studied (Figure 1). The value of G(sum) is $\approx 3 \times 10^{-7}$ mol J^{-1}, that is, a good material balance is obtained, based on the radiolytic yields of ·OH plus H·. Here, it has been assumed that the unknown species has the same response factor as monomalonyl malonate.

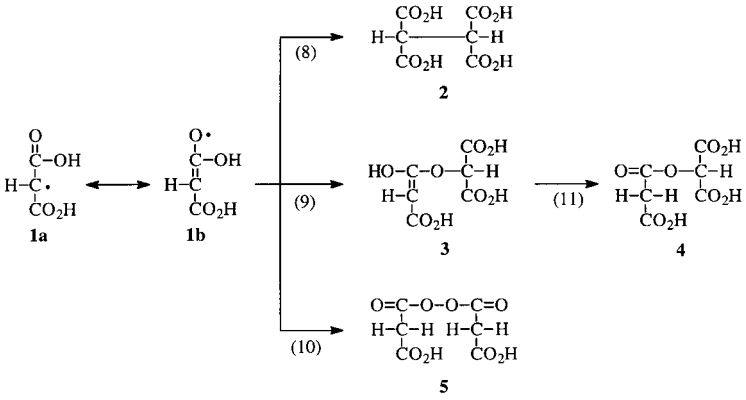
Table 1. Carbon dioxide production (G values [10^{-7} mol J^{-1}]) from malonic and acetic acids by ·OH in γ-radiolysis (N_2O-saturated solutions).

pH	3.0	3.5	7.2
malonic acid	0.2	–[a]	–[a]
acetic acid	–[a]	0.3	0.2

[a] – not determined.

As already stated above, the carboxyl radical promptly eliminates CO_2 [cf. reaction (7)]. The formation of monomalonyl malonate **4** must, therefore, find an explanation other than that offered previously.[10] This is provided by the recognition that the malonic acid radical is capable of mesomerism (radicals **1a** and **1b**), as shown in Scheme 1. Recombination may, in principle, lead to the compounds **2** [reaction (8)] and **4** [reactions (9) and (11)], as well as to the peroxide **5** [reaction (10)], as shown in Scheme 1, although the assignment of structure **5** to the unidentified product could not be established. It is observed that the proportion in which products **2** and **4** together with the unidentified compound (tentatively attributed to **5**) are formed depends on the pH of the solution (Figure 1). Because of the absence of α-hydrogen in these radicals, disproportionation reactions are not expected to play a role in these systems. This view is supported by the absence of hydroxymalonic acid from the products that might be formed if the disproportionation occurred by electron transfer.

Intermediate **3** could, in principle, undergo hydrolysis. This would afford hydroxymalonic acid, besides malonic acid. Since the former is not observed among the radiolysis products, the ketonisation of **3** [reaction (11), Scheme 1] must be favoured considerably over its hydrolysis. This situation



Scheme 1.

contrasts with the acetic acid system discussed below. The formation of an unidentified product in addition to **3** and **4** has already been reported in a UV-photolytic study of aqueous malonic acid.[14] It remains unclear whether this is identical with the unknown species (▲ in Figure 1), especially since the analytical procedures differ (HPIC here, HPLC in ref. [14].)

The straightforward pK-type curves (Figure 1, inflexion points at pH 5.8) shown by these three products imply that their formation is associated with a property of the malonic acid radical that is related to its second pK_a value of 5.7,[6] which appears to be the same as that of its parent compound, p$K_2 = 5.7$. This aspect will be discussed below.

The acetic acid system: The proportion of the major product succinic acid (**7**) to glycolic acid (**10**), increases again at high pH (Figure 2). A reasonable material balance is obtained over the entire pH range studied (cf. ● in Figure 2). The inflexion point is at pH ≈ 5, not far from the pK_a value of the acetic acid radical for which values of ≈ 4.5 (pulse radiolysis, optical detection)[13] and ≈ 4.2 (pulse radiolysis, conductometric detection)[15] are reported.

The formation of succinic acid (**7**) is the result of recombination of the acetic acid radical via its mesomeric form **6a** [reaction (12), Scheme 2]. The formation of glycolic acid (**10**) is suggested to proceed via **8**, the combination product of **6a** plus **6b** [reaction (13)], followed by hydrolysis [reaction (14), Scheme 2].

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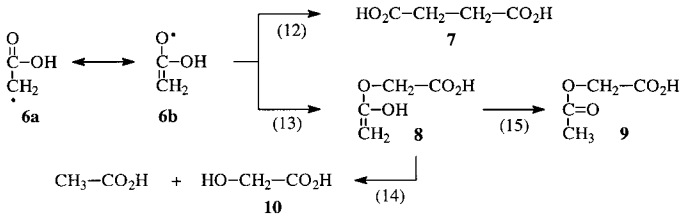


Scheme 2.

Interestingly, acetoxyacetic acid (**9**), the compound that one expects to be produced provided that the ketonisation reaction (15) (Scheme 2) proceeds at an appreciable rate in competition with hydrolysis [reaction (14), Scheme 2], is not formed under the present conditions, in contrast to the ketonisation product **4** in the case of malonic acid [reaction (11), Scheme 1]. The reference material, acetoxyacetic acid, itself is only hydrolysed slowly under these conditions. The reasons for the differing behavior of the enol esters produced initially (**8** undergoing hydrolysis to glycolic acid **10**, versus **3** undergoing ketonisation to **4**) are not evident. However, the main difference appears to lie in the fact that **3** has an internal C=C bond, while this bond is in a terminal position in **8**. In fact, enol *ethers* with the corresponding structural characteristics show a drastic difference with respect to the rate of hydrolysis.[16, 17] If, in the case of a terminal C=C bond, hydrolysis occurred by protonation at carbon, as one expects for the ketonisation of the enol esters, the enol *ether* case would present an interesting analogy.

The formation of small amounts of a secondary product, 3-carboxyglutaric acid (**12**), which has been identified by its mass spectrum (trimethylsilylation, GC-MS) and by comparison with the reference material, has been observed in the acetic acid system (Figure 3). It is proposed that the precursor

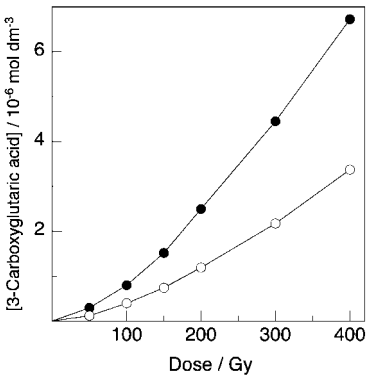
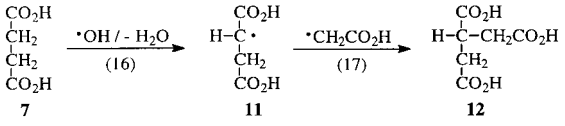


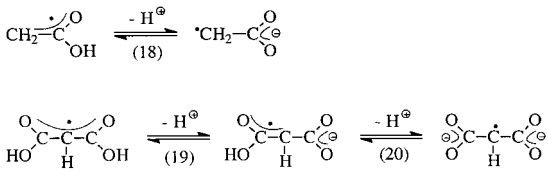
Figure 3. Formation of 3-carboxyglutaric acid as a secondary product in the radiolysis of N_2O-saturated acetic acid (3×10^{-3} mol dm^{-3}) solutions (●, pH 3.4; ○, pH 7.0). For comparison: at a dose of 50 Gy, the concentration of the primary product succinic acid has reached values of $\approx 10^{-5}$ mol dm^{-3} (cf. Figure 2).

of this compound is the primary product **7** whose rate constant for the reaction with ·OH [reaction (16), Scheme 3] is about an order of magnitude larger than that of acetic acid.[18] The recombination of the succinic acid radical (**11**) with the acetic acid radical then gives rise to **12** [reaction (17), Scheme 3].



Scheme 3.

An explanation for the pH effect: With regard to the pH-dependence of product formation, the inflexion point in the acetic acid system is at pH $\approx$ 5 and at pH = 5.8 in the malonic acid system. These values mirror the pK_a values of the corresponding radical, in the case of malonic acid that of its second pK_a value [equilibrium reactions (18) and (20), Scheme 4]. The first pK_a of the malonic acid radical [equilibrium reaction (19)] is either considerably below two, or its



Scheme 4.

determination by pulse radiolysis has failed because of the spectral similarities of the monoprotonated and fully protonated radicals.[6] The fact that the pK_a values of the parent and of their corresponding radicals are found to be very close in those cases for which the latter are observable, suggests that the first pK_a value of the malonic acid radical should also not be far from that of the parent, namely pH 2.8. The absence of any feature in this pH region (Figure 1) leads to the suggestion that the reactivity pattern of the malonic acid radical does not change at pK_1, in contrast to the situation near pK_2, at which the mesomeric state of the malonic acid radical changes in such a way that in the dicarboxylate form the expression of the radical function in one of the carboxyl groups is essentially suppressed as the carbonyl moiety of the latter loses its identity in the dissociated state. As the *second* carboxyl group becomes deprotonated, the free-radical function in the malonic acid radical is frozen onto the methine carbon atom. By analogy, in the acetate system the radical is highly delocalised when protonated, but much less so in the anionic state.

Implications of the postulate of transient enol forms: The C–O-linked termination product (of the α-alkylcarboxy acid-type) is more stable in the malonic acid than in the acetic acid system. In the former case, an alkaline pH and an elevated temperature are required to hydrolyse this product into the indicator product to be analysed, namely, hydroxymalonic acid. In the acetic acid system, on the other hand, glycolic acid is observed directly at ambient temperature upon analysis of the irradiated solution. This last observation, in conjunction with the fact that the relevant reference material, acetoxyacetic acid, under these conditions undergoes hydrolysis relatively slowly (i.e., on a timescale of many hours), suggests that the C–O-linked termination product is generated in the enol form **8**, which presumably hydrolyses more rapidly, as the reaction scheme indeed demands (Scheme 2). The malonic-

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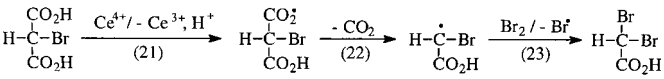
acid-derived compound would not suffer the same fate if, in its case, carbonyl – enol tautomerisation is sufficiently fast and if the equilibrium strongly favours the carbonyl **4** over the enol **3** form.

The initial, though transient, presence of the C–O-linked recombination product in the *enol* form may give rise to secondary products (the appearance of such enols may in fact be of some relevance to minor behavioral details of malonic acid/bromate-type chemical oscillators). This process would be initiated by the addition of the α-carboxyalkyl radical to the C=C bond and subsequent disproportionation or recombination of this adduct radical. This may lead, for instance, to a structure with a hemiacetalic function that is expected to hydrolyse. In principle, a variety of products could be formed in this manner. The more highly carboxylated such a compound is, the longer is its ion-chromatographic retention time, and therefore the greater the difficulty of detecting it at small concentrations.

This leads back to the question of the nature of the unknown product (▲ in Figure 1). Its ion-chromatographic behaviour suggests that it might actually carry three carboxyl groups rather than two, since its retention time (7.0 min) under the present analytical conditions exceeds that of another tricarboxylic reference compound, citric acid (6.0 min), preceding (the also tricarboxylic) monomalonyl malonate (8.0 min) by a similarly narrow margin. In any case, the fact that its pH dependence parallels that of the C–O-linked recombination product monomalonyl malonate, indicates that it owes its existence to either a C–O or an O–O linkage.

Importance of fragmentation reactions in the context of malonic acid/bromate chemical oscillators: It has been seen above that in the oxidation of malonic acid by the OH radical, decarboxylation, that is, fragmentation of the carboxymethyl-carboxyl radical, is practically absent. The data shown in the Table 1 of ref. [19] implies that Ce^{IV} does not oxidise *malonic acid* at the carboxyl group, but that the CO_2 evolution is the result of the decarboxylation of certain oxidation products of malonic acid that are more reactive towards Ce^{IV} in this respect. Attack at carboxyl group apparently occurs more readily with methylmalonic acid for which the formation of the decarboxylation product pyruvic acid has already been observed.[5] Of course, for ketomalonic and oxalic acids,[20] this pathway is the only one possible. The formation of dibromoacetic acid, which is an important (secondary) product in addition to bromomalonic acid (primary product) in the Ce^{IV}-catalyzed malonic acid/bromate system,[1] may also involve this type of process [reactions (21) and (22) in Scheme 5], which appears to be more facile in bromomalonic than in malonic acid.[19]



Scheme 5.

On the other hand, dibromoacetic acid is also formed by decarboxylation of dibromomalonic acid; in acidic solutions this is a relatively slow process ($t_{1/2} \approx 1$ h in 1 molar H_2SO_4)[21] which might, in principle, be capable of being differentiated from a free-radical process by following the kinetics of its accumulation.

[1] R. J. Field, in *Oscillations and Traveling Waves in Chemical Systems* (Eds.: R. J. Field, M. Burger), Wiley-Interscience, New York, **1985**, pp. 55 – 92.
[2] L. Györgyi, T. Turanyi, R. J. Field, *J. Phys. Chem.* **1990**, *94*, 7162 – 7170.
[3] Y. Gao, H.-D. Försterling, Z. Noszticzius, B. Meyer, *J. Phys. Chem.* **1994**, *98*, 8377 – 8380.
[4] B. Neumann, S. C. Müller, M. J. B. Hauser, O. Steinbock, R. H. Simoyi, N. S. Dalal, *J. Am. Chem. Soc.* **1995**, *117*, 6372 – 6373.
[5] P. O. Kvernberg, E. W. Hansen, B. Pedersen, A. Rasmussen, P. Ruoff, *J. Phys. Chem.* **1997**, *101*, 2327 – 2331.
[6] M. N. Schuchmann, R. Rao, M. Hauser, S. C. Müller, C. von Sonntag, *J. Chem. Soc. Perkin Trans. 2* **2000**, 941 – 943.
[7] C. von Sonntag, H.-P. Schuchmann, *Angew. Chem.* **1991**, *103*, 1255 – 1279; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1229 – 1253.
[8] C. von Sonntag, H.-P. Schuchmann, in *Peroxyl Radicals* (Eds.: Z. B. Alfassi), Wiley, Chichester, **1997**, pp. 173 – 234.
[9] I. L. Yurkova, H.-P. Schuchmann, C. von Sonntag, *J. Chem. Soc. Perkin Trans. 2* **1999**, 2049 – 2052.
[10] A. Sirimungkala, H.-D. Försterling, Z. Noszticzius, *J. Phys. Chem.* **1996**, *100*, 3051 – 3055.
[11] J. W. Hilborn, J. A. Pincock, *J. Am. Chem. Soc.* **1991**, *113*, 2683 – 2686.
[12] F. Weeke, E. Bastian, G. Schomburg, *Chromatographia* **1974**, *7*, 163 – 170.
[13] M. Simic, P. Neta, E. Hayon, *J. Phys. Chem.* **1969**, *73*, 4214 – 4219.
[14] I. Szalai, H.-D. Försterling, Z. Noszticzius, *J. Phys. Chem. A* **1998**, *102*, 3118 – 3120.
[15] M. N. Schuchmann, H.-P. Schuchmann, C. von Sonntag, *J. Phys. Chem.* **1989**, *93*, 5320 – 5323.
[16] E. Staude, F. Patat, in *The Chemistry of the Ether Linkage* (Eds.: S. Patai), Interscience Publishers, London, **1967**, pp. 21 – 80.
[17] I. Janik, P. Ulanski, J. M. Rosiak, C. von Sonntag, *J. Chem. Soc. Perkin Trans. 2* **2000**, 2034 – 2040.
[18] G. V. Buxton, C. L. Greenstock, W. P. Helman, A. B. Ross, *J. Phys. Chem. Ref. Data* **1988**, *17*, 513 – 886.
[19] S. Nagygyöry, M. Wittmann, S. Pintér, A. Visegrády, A. Danscó, N. B. Thuy, Z. Noszticzius, L. Hegedüs, H.-D. Försterling, *J. Phys. Chem. A* **1999**, *103* – 4885.
[20] J.-J. Jwo, R. M. Noyes, *J. Am. Chem. Soc.* **1975**, *97*, 5422 – 5431.
[21] J. Oslonovitch, H.-D. Försterling, M. Wittmann, Z. Noszticzius, *J. Phys. Chem. A* **1998**, *102*, 922 – 927.

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