

# A Common Carbanion Intermediate in the Recombination and Proton-Catalysed Disproportionation of the Carboxyl Radical Anion, $\text{CO}_2^{\cdot-}$ , in Aqueous Solution

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**Abstract:** The carboxyl radical anion,  $\text{CO}_2^{\cdot-}$ , was produced by the reactions of OH radicals with either CO or formic acid in aqueous solution. The  $\text{p}K_{\text{a}}(\text{CO}_2\text{H})$  was determined by pulse radiolysis with conductometric detection at  $\text{pH} \approx 2.3$ . The bimolecular decay rate constant of  $\text{CO}_2^{\cdot-}$  ( $2k \approx 1.4 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) was found to be independent of pH in the range 3–8 at

constant ionic strength. The yields of the products of the bimolecular decay of the carboxyl radicals,  $\text{CO}_2$  and the oxalate anion were found to depend strongly on the pH of the solution with an inflection

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point at pH 3.8. This pH dependence is explained by assuming a head-to-tail recombination of the  $\text{CO}_2^{\cdot-}$  radicals followed by either rearrangement to oxalate or a protonation of the adduct, which subsequently leads to the formation of  $\text{CO}_2$  and formate. The recombination of  $\text{CO}_2^{\cdot-}$  to give oxalate directly is estimated to have a contribution of <25%.

## Introduction

The carboxyl radical,  $\text{CO}_2^{\cdot-}$ , is one of the most widely used species in free-radical studies because of its excellent reducing properties [ $E(\text{CO}_2^{\cdot-}/\text{CO}_2) = -1.9 \text{ V}$ ]<sup>[1]</sup> and its facile generation in aqueous solutions by ionising radiation.<sup>[2]</sup> For example, this radical may be produced by the reactions of hydroxyl radicals and H atoms with formic acid/formate ion, of hydroxyl radicals with carbon monoxide or of solvated electrons with carbon dioxide.<sup>[3, 4]</sup> In neutral to basic solutions, oxalate was found to be the main product of the bimolecular decay of  $\text{CO}_2^{\cdot-}$ .<sup>[4, 5]</sup> However, in acidic solutions  $\text{CO}_2$  is formed instead.<sup>[6, 7]</sup> In the present work we have reinvestigated the reactions of  $\text{CO}_2^{\cdot-}$  by means of pulse radiolysis and product analysis with the aim of finding an explanation for the surprising pH dependence of product formation upon its bimolecular decay.

## Experimental Section

Aqueous solutions of the substrates (concentrations typically  $1 \times 10^{-3} \text{ mol dm}^{-3}$  for sodium formate) were prepared in Milli-Q-filtered (Millipore) water and saturated with  $\text{N}_2\text{O}$ . The pH of the solutions was adjusted to the desired value with NaOH or  $\text{HClO}_4$ .  $\gamma$ -Radiolyses were carried out in a panoramic  $^{60}\text{Co}$  source at a dose rate of  $0.16 \text{ Gy s}^{-1}$  to total doses of up to 150 Gy (i.e., the conversion of the substrate remained below 10%; the dose of 1 Gy equals 1 J of radiation energy deposited in a substrate mass of 1 kg, here  $1 \text{ dm}^{-3}$  of solution).

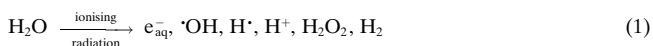
Oxalic acid was analysed by ion chromatography (Dionex DX-2010i) on an AS14 column ( $4 \times 250 \text{ mm}$  with a  $4 \times 50 \text{ mm}$  AG14 pre-column, ASRS-ULTRA suppressor). The eluent was an aqueous solution of  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  ( $1.8 \times 10^{-3} \text{ mol dm}^{-3}$  and  $1.7 \times 10^{-3} \text{ mol dm}^{-3}$ , respectively) at a flow rate of  $1 \text{ mL min}^{-1}$ . The retention time was 13.6 min.

$\text{CO}_2$  was scrubbed from irradiated samples with argon as the carrier gas and measured by GC on a 3.2 m Porapak-9 capillary column.

Pulse radiolysis was carried out with a 2.8 MeV Van-de-Graaff accelerator delivering electron pulses of  $0.4 \mu\text{s}$  duration. Intermediates were monitored by optical detection. The pulse radiolysis set-up has been described previously.<sup>[8]</sup> For dosimetry, a  $\text{N}_2\text{O}$ -saturated  $10^{-2} \text{ mol dm}^{-3}$  thiocyanate solution was used for optical detection, with  $G \times \epsilon((\text{SCN})_2^{\cdot-}) = 4.8 \times 10^{-4} \text{ m}^2 \text{ J}^{-1}$  at  $480 \text{ nm}$ <sup>[9]</sup> (although more recently a 10% higher value for  $G \times \epsilon$  has been redetermined,<sup>[10]</sup> for consistency with our previous measurements the lower value was used).

## Results and Discussion

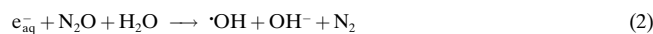
**The radical-generating system:** Hydroxyl radicals are generated during the radiolysis of water [reaction (1)]. The



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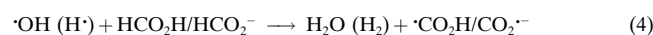
radiation-chemical yields ( $G$  values) of the primary radicals are  $G(\cdot\text{OH}) \approx G(e_{\text{aq}}^-) = 2.8 \times 10^{-7}$ ,  $G(\text{H}\cdot) = 0.6 \times 10^{-7}$  and  $G(\text{H}_2\text{O}_2) \approx 0.7 \times 10^{-7} \text{ mol J}^{-1}$ .  $\text{N}_2\text{O}$  is used to convert the solvated electron into  $\cdot\text{OH}$  [reaction (2)]. In acidic solutions,



protons also compete with  $\text{N}_2\text{O}$  for the solvated electron [reaction (3)]. The  $\text{OH}$  radical and the  $\text{H}$  atom will react with



formic acetic/formate anion [ $\text{p}K_{\text{a}}(\text{HCO}_2\text{H}) = 3.75$ ] to yield the carboxyl radical or its anion,  $\cdot\text{CO}_2\text{H}/\text{CO}_2^{\cdot-}$  [reaction (4)].



Alternatively, the reaction of  $\cdot\text{OH}$  with carbon monoxide can be used to generate  $\cdot\text{CO}_2\text{H}/\text{CO}_2^{\cdot-}$  [reaction (5)].<sup>[11]</sup> At a formate concentration of  $1 \times 10^{-3} \text{ mol dm}^{-3}$ , the radiation-chemical yield,  $G$  value, is  $G(\text{CO}_2^{\cdot-}) \approx 6.2 \times 10^{-7} \text{ mol J}^{-1}$ , and a material balance can be based on this value.



The  $\cdot\text{CO}_2\text{H}$  radical is an acid [equilibrium reaction (6)]. There is considerable uncertainty as to its  $\text{p}K_{\text{a}}$  value. Fojtik et al.<sup>[11]</sup> have produced this intermediate by the reaction of  $\cdot\text{OH}$  with  $\text{CO}$  [reaction (5)], and from pulse radiolysis with conductometric detection they concluded that the  $\text{p}K_{\text{a}}$  value is  $\approx 3.9$ . By following the optical absorption change of the  $\text{CO}_2^{\cdot-}/\cdot\text{CO}_2\text{H}$  radical at  $\lambda = 250 \text{ nm}$  in a pulsed irradiated solution of formic acid/formate ion as a function of pH, Buxton and Sellers<sup>[12]</sup> obtained a  $\text{p}K_{\text{a}}$  value of 1.4. An even lower value of  $-0.2$  has been determined by Jeevarajan et al.<sup>[13]</sup> by measuring the change in the  $^{13}\text{C}$  hyperfine constant as a function of pH.

We have repeated the experiments by Fojtik et al.<sup>[11]</sup> and arrived at a value of  $\text{p}K_{\text{a}} \approx 2.3$  (Figure 1), which is significantly lower than that given by Fojtik et al., but still considerably higher than those of the other studies.

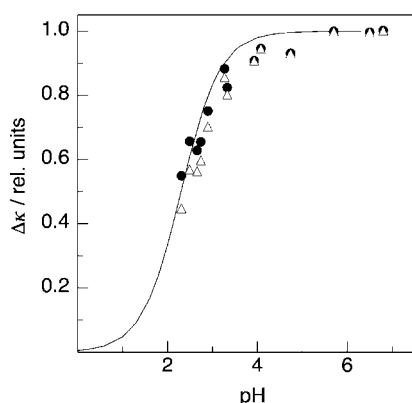


Figure 1. Pulse radiolysis of  $\text{N}_2\text{O}/\text{CO}$  (4:1 v/v)-saturated aqueous solutions. Conductivity changes as a function of pH ( $\Delta$ : original experimental data;  $\bullet$ : experimental data corrected for the loss of  $\text{OH}$  radicals by competition of protons with  $\text{N}_2\text{O}$  for the solvated electrons; —:  $\text{p}K_{\text{a}}$  curve based on  $\text{p}K_{\text{a}} = 2.3$ ).

In the light of the present  $\text{p}K_{\text{a}}$  value of  $\approx 2.3$ , its previous determinations deserve a comment. The data reported by Buxton and Sellers<sup>[12]</sup> have been remeasured, and the inflection point near pH 1.4 was found to have been an artefact (G. V. Buxton, private communication). Jeevarajan et al.<sup>[13]</sup> stated that their data could be also consistent with a higher  $\text{p}K_{\text{a}}$  value if their measured changes of the  $^{13}\text{C}$  hyperfine constants were the result of the protonation of  $\cdot\text{CO}_2\text{H}$ , and the  $^{13}\text{C}$  hyperfine constants of  $\text{CO}_2^{\cdot-}$  and  $\cdot\text{CO}_2\text{H}$  were identical. Our  $\text{p}K_{\text{a}}$  value of 2.3 is supported by the (empirical) Pauling rule of  $\text{p}K_{\text{a}}$  values of oxoacids of the general form  $\text{XO}_p(\text{OH})_q$ .<sup>[14]</sup> This rule indicates that the  $\text{p}K_{\text{a}}$  value of an oxoacid is largely determined by the number of oxygen atoms at the central atom and that the latter has only moderate influence ( $\text{p}K_{\text{a}} = 8 - 5p$ ). Thus all mono-oxo acids should have  $\text{p}K_{\text{a}}$  values of  $\approx 3.0$ . Within a certain range, this is indeed the case:  $\text{CO}(\text{OH})_2$  (3.6),  $\text{HC}(\text{O})\text{OH}$  (3.75),  $\text{OClOH}$  (2.0),  $\text{ONOH}$  (3.15)  $\text{OP}(\text{OH})_3$  (2.2)  $\text{OAs}(\text{OH})_3$  (2.25),  $\text{OSe}(\text{OH})_2$  (2.46) and  $\text{OTe}(\text{OH})_2$  (2.48). As to the discrepancies of our data with those reported by Fojtik et al.<sup>[11]</sup>, there is no obvious explanation, since both are based on the same system and obtained with the same technique.

We have redetermined the rate of the bimolecular decay of  $\text{CO}_2^{\cdot-}$  by monitoring the absorption decay at  $\lambda = 250 \text{ nm}$  at a constant ionic strength of  $0.5 \text{ mol dm}^{-3}$ , and found that this rate constant practically does not vary over the pH range 3–9 (Figure 2,  $2k \approx 1.4 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ). This agrees fairly well with the reported values of  $1.5 \times 10^9$ ,<sup>[4]</sup>  $9.0 \times 10^8$ ,<sup>[11]</sup>  $1.0 \times 10^9$ <sup>[3]</sup> and  $7.6 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .<sup>[12]</sup> The latter two values were obtained at zero ionic strength. These authors also found no change in the bimolecular decay rate constant of  $\text{CO}_2^{\cdot-}$  within a pH range of 3–7.

It is generally believed that  $\text{CO}_2^{\cdot-}$  only reacts by a recombination at carbon to give oxalate [reaction (7)].<sup>[4, 5, 7]</sup>



Indeed, when product studies were carried out in neutral and alkaline aqueous solutions, oxalate was practically the

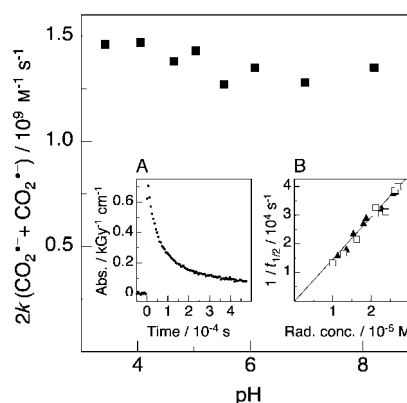


Figure 2. Pulse radiolysis of  $\text{N}_2\text{O}$ -saturated aqueous solutions of formic acid ( $10^{-3} \text{ mol dm}^{-3}$ ) in the presence of  $0.5 \text{ mol dm}^{-3} \text{ NaClO}_4$ . Rate constant of the bimolecular decay as a function of pH. Inset A: Decay of the absorption at  $\lambda = 270 \text{ nm}$  as a function of time, pH 4.6, 26 Gy per pulse. Inset B: The inverse of the first half-life of absorption decay of  $\text{CO}_2^{\cdot-}$  at  $\lambda = 270 \text{ nm}$  as a function of the  $\text{CO}_2^{\cdot-}$  concentration at pH 4 ( $\square$ ) and pH 5 ( $\blacktriangle$ ).

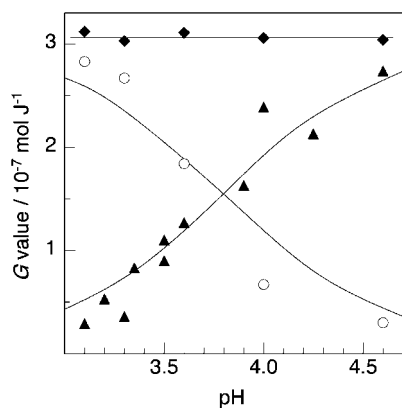
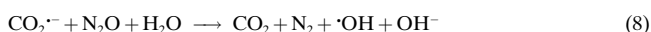


Figure 3.  $\gamma$ -Radiolysis of formate ( $1 \times 10^{-3} \text{ mol dm}^{-3}$ ) in argon-saturated solution.  $G$  values of oxalate ( $\blacktriangle$ ) and  $\text{CO}_2$  ( $\circ$ ) as a function of pH. The sum ( $\blacklozenge$ ) of these two products is also plotted as function of pH. Some oxalate measurements were also carried out in  $\text{N}_2\text{O}$ -saturated solutions.

only product with  $G(\text{oxalate}) = 3.5 \times 10^{-7} \text{ mol J}^{-1}$  [ $0.5 G(\cdot\text{OH} + \text{H}\cdot)$ ].<sup>[4]</sup> We observed that  $G(\text{oxalate}) = 2.7 \times 10^{-7} \text{ mol J}^{-1}$  at pH 4.6, and the oxalate yield drops as the pH is decreased (Figure 3). At pH 3 its yield is negligible (Figure 3). In this system, one has to recall that when  $\text{N}_2\text{O}$  is used to convert  $e_{\text{aq}}^-$  into  $\cdot\text{OH}$  [reaction (2)] a chain reaction takes place to yield  $\text{CO}_2$  as a chain product [reaction (8)].<sup>[15]</sup> Hence, for most of the experiments, the system was saturated with argon, and  $e_{\text{aq}}^-$  was converted into  $\text{H}\cdot$  according to reaction (3)



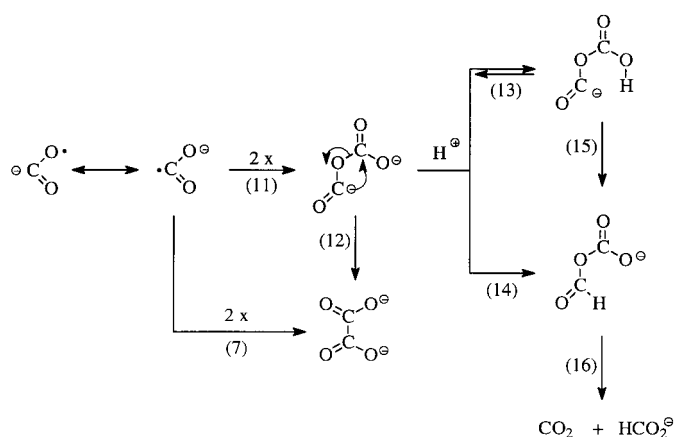
We also found that the yield of  $\text{CO}_2$ , in contrast to that of oxalic acid, increased with increasing proton concentration (Figure 3), in excellent agreement with a previous report.<sup>[7]</sup> As shown in Figure 3, these two yield curves cross at the inflection point of pH 3.8.

Disproportionation between two  $\text{HCOO}\cdot$  radicals [reaction (9)] is generally assumed to be responsible for the formation of  $\text{CO}_2$  in acidic solutions of formic acid (for a review see ref. [16]). Similarly, the cross-termination between  $\cdot\text{CO}_2\text{H}$  and  $\text{CO}_2^{\cdot-}$  could give the same products [reaction (10)]



However, our results show that the above simple mechanism [reactions (7), (9) and (10)] as generally proposed, is inadequate to explain the observations in the pH range of Figure 3. In order for the displacement of the pH for the cross-over in yields of  $\text{CO}_2$  and oxalate from the radical  $\text{p}K_a$  of 2.3 (cf. Figure 1) to 3.8 (Figure 3) to be explained, the rate constants of reactions (9) and (10) would have to be about 18 times higher than  $2k_7$ . The bimolecular rate constant of  $\text{CO}_2^{\cdot-}$ ,  $2k_7 \approx 1.4 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  (Figure 2, the slight variation over the pH range shown is within experimental error), is already close to diffusion controlled. Moreover, a value of  $2k_9 = 1.7 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  determined at pH 0 has been reported.<sup>[12]</sup>

To account for our results we propose the mechanism represented by reactions (11)–(16) in Scheme 1. The major



Scheme 1.

aspect of this mechanism is that the  $\text{CO}_2^{\cdot-}$  radicals react mainly (> 90%) by a head-to-tail recombination, and that the rearrangement reaction (12) competes with the  $\text{H}^+$ -assisted disproportionation reactions (13)–(16) (Scheme 1).

The  $\text{CO}_2^{\cdot-}$  radical can be represented by two mesomeric forms, one with the spin at carbon and one with the spin at oxygen. We now suggest that the  $\text{CO}_2^{\cdot-}$  radicals react with one another by a head-to-tail recombination [reaction (11), Scheme 1]. The resulting carbanion may rearrange into oxalate [reaction (12)]. When protonated [reactions (13) and (14), followed by reaction (15)], however, the mixed anhydride decomposes into carbon dioxide and formic acid [reaction (16)]. Although the latter product cannot be determined under our experimental conditions (formic acid was used as the source for  $\text{CO}_2^{\cdot-}$ ), it is inferred that two  $\text{CO}_2^{\cdot-}$  radicals give rise to either one molecule of oxalate or one molecule of  $\text{CO}_2$  plus one molecule of formic acid. The sum of  $G(\text{oxalate}) + G(\text{CO}_2)$  should be constant over the whole pH range and equal to  $3.1 \times 10^{-7} \text{ mol J}^{-1}$  [ $0.5 G(\cdot\text{OH} + \text{H}\cdot)$ ]. This material balance is indeed obtained (Figure 3).

Protonation at a heteroatom is fast (between  $5 \times 10^9$  and  $5 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ); however, protonation at carbon is typically slower.<sup>[17]</sup> Thus, reaction (13) should be faster than reaction (14) (Scheme 1), but once protonated at oxygen [reaction (13)] subsequent intramolecular protonation at carbon [reaction (15)], possibly assisted by a molecule of water, may speed-up the protonation at carbon. If the rate constant for the relevant protonation reaction is taken as  $1 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and the inflection point at pH 3.8 ( $[\text{H}^+] = 1.6 \times 10^{-4} \text{ mol dm}^{-3}$ ), then the competing reaction (12) must have a rate constant of  $\approx 1.6 \times 10^6 \text{ s}^{-1}$ . A slower rate of protonation would require a longer lifetime of the postulated carbanion [reaction (11)].

This mechanistic scheme depicted by reactions (11)–(16) (Scheme 1) requires that the oxalate yield vanishes in a sigmoidal fashion at low pH. The solid lines in Figure 3 were calculated on the basis of the competition between reaction (12) versus reaction (13)/(14) with an inflection point at pH 3.8. Taking our  $\text{p}K_a$  value of 2.3 (cf. Figure 1), the  $\cdot\text{CO}_2\text{H}$  radical concentration at  $\text{pH} \approx 3.3$  is  $\approx 10\%$  of the total  $\text{CO}_2^{\cdot-}/\cdot\text{CO}_2\text{H}$  radical concentration. In this pH range, the potential contribution of  $\cdot\text{CO}_2\text{H}$  to product formation [cf. reactions (9)

and (10)] will be of the same magnitude. This would explain the fact that the experimental oxalate data are somewhat lower than the calculated curve at  $\text{pH} < 3.5$ .

One expects that reaction (7) occurs in competition with reaction (11) (Scheme 1). However, if there were a substantial contribution from reaction (7) (>25%) then the oxalate yield at low pH should be noticeably higher than the calculated curve.

In water, unusual disproportionation reactions are not uncommon. For example at pH 12, the hydroxymethyl radical, which at these conditions is fully deprotonated ( $\text{p}K_{\text{a}} = 10.7$ ) and is present as  $\cdot\text{CH}_2\text{O}^-$ , only disproportionates into formaldehyde and methanol, despite the fact that no  $\beta$ -hydrogen is available for a straightforward disproportionation reaction.<sup>[18]</sup> Furthermore, the radicals derived from acetic acid ( $\cdot\text{CH}_2\text{CO}_2\text{H} \leftrightarrow \text{CH}_2=\text{C}(\text{O}\cdot)\text{OH}$ ), which show structural similarities to the  $\text{CO}_2\cdot^-$  radicals (spin density at oxygen), undergo disproportionation, despite the absence of  $\beta$ -hydrogens, in addition to the expected recombination at carbon (formation of succinic acid). It was concluded that a labile head-to-tail dimer must be the intermediate on the route to disproportionation.<sup>[19]</sup> Similarly, head-to-tail dimers play a major role in the free-radical chemistry of malonic acid.<sup>[19]</sup>

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