An Intermediate with a Copper–Carbon Bond Formed by the Reaction of Copper Ions with $\cdot CH_2CO_2H$ Radicals in Aqueous Solutions

By Mira Freiberg and Dan Meyerstein*

(*Chemistry Department, Nuclear Research Centre-Negev, P.O. Box 9001, Beer-Sheva* 84190, *and Ben-Gurion University of the Negev, Beer-Sheva, Israel*)

Summary The radical $\cdot CH_2CO_2^-$ reacts with Cu^{2+} (aq) forming an unstable intermediate with a specific rate of $(6{\cdot}4 \pm 1{\cdot}5) \times 10^8\ l\ mol^{-1}\ s^{-1}$; the intermediate, $Cu–CH_2CO_2^+$, decomposes *via* a first-order process with k $2{\cdot}8 \pm 0{\cdot}3\ s^{-1}$.

Copper ions are known to oxidize aliphatic free radicals[1,2]. Thus they have been used in the radical addition to double bonds,[3] oxidation of aliphatic compounds by Fenton's reagent,[2,4] and other oxidative radical processes.[1,5] It has been suggested[2] that for free radicals which are not strong reducing agents, *e.g.* $\cdot CH_2C(OH)Me_2$ and $\cdot CH_2CO_2^-$, the mechanism is as in reaction (1). Furthermore it was

$$Cu^{II} + \cdot CH_2R \rightarrow Cu^{III}–CH_2R \rightarrow Cu^{I} + HOCH_2R \qquad (1)$$

claimed that the expected lifetime of the $Cu^{III}–CH_2R$ intermediate is too short for it to be observed.[2] We have studied the reaction of $\cdot CH_2CO_2^-$ radicals with Cu^{2+} (aq) by the pulse radiolytic technique, with the hope of detecting the intermediate $Cu–CH_2CO_2^+$.

Nitrous oxide-saturated solutions containing acetate ($1{\cdot}0 \times 10^{-2}$ M) and $CuSO_4$ (2—10×10^{-5} M) at pH 6·0 were irradiated. Under these conditions all the e^- (aq) and OH radicals are transformed into $\cdot CH_2CO_2^-$ radicals during the pulse ($<1\ \mu s$).[6] The effect of Cu^{2+} (aq) on the kinetics of disappearance of the $\cdot CH_2CO_2^-$ radicals was studied.

Three reactions separated in time were observed. The absorption spectra immediately after the pulse and after the two first reactions are shown in the Figure. (No absorption remains after the third reaction.) The kinetics of the first reaction (2) obey a first-order rate law both in

$$\cdot CH_2CO_2^- + Cu^{2+}\ (aq) \xrightarrow{k_2} Cu–CH_2CO_2^+ \qquad (2)$$

Cu^{2+} and $\cdot CH_2CO_2^-$ with $k_2 = (7{\cdot}6 \pm 1{\cdot}5) \times 10^8$, $(4{\cdot}8 \pm 1{\cdot}5) \times 10^8$, and $(6{\cdot}6 \pm 1{\cdot}5) \times 10^8\ l\ mol^{-1}\ s^{-1}$ in solutions containing $MeCO_2Na$ (1×10^{-2} M), $MeCO_2Na$ (1×10^{-1} M)

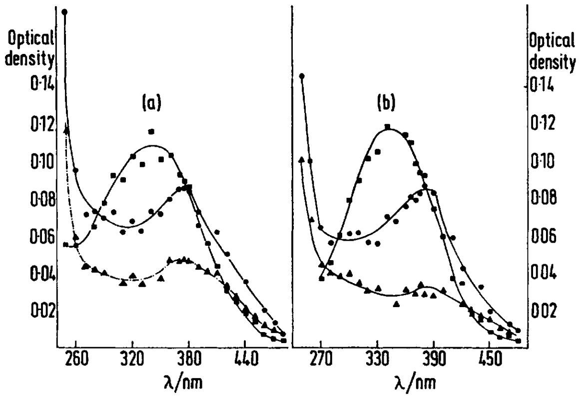

Figure. Absorption spectra of the intermediates observed. ■ Immediately after the pulse (attributed to $\cdot CH_2CO_2^-$ radicals); ● 200 μs after the pulse; ▲ 15 ms after the pulse. Solution composition: N_2O-saturated, 5×10^{-5}M $CuSO_4$, pH 6·0: (a) 0·01M $MeCO_2Na$; (b) 0·1M $MeCO_2Na$; pulse intensity 2500 rad.

and $\mathrm{MeCO_2Na}$ (1×10^{-2} M) + $\mathrm{NaClO_4}$ (9×10^{-2} M), respectively. The identification of the intermediate is based on the following arguments. It is clearly formed in a reaction between $\mathrm{Cu^{2+}}$ (aq) and $\mathrm{\cdot CH_2CO_2^-}$. It is not $\mathrm{Cu^+}$ (aq) as the latter does not absorb in the region studied.[7] It is not $\mathrm{Cu^{III}}$ (aq) as the kinetics of its decomposition differ considerably from those of $\mathrm{Cu^{III}}$ (aq).[8] The product analysis when $\mathrm{Cu^{2+}}$ (aq) is added to a Fenton system containing an organic solute such as $\mathrm{Bu^tOH}$ or $\mathrm{MeCO_2^-}$ indicates the formation of an intermediate with a copper–carbon bond.[2]

The two subsequent reactions obey first-order rate laws with specific rates of $90 \pm 5\ \mathrm{s^{-1}}$ and $2{\cdot}8 \pm 0{\cdot}3\ \mathrm{s^{-1}}$, respectively, which are independent of pH in the range 4·5–6·0, and of $[\mathrm{Cu^{+2}}]$ and $[\mathrm{MeCO_2^-}]$ (the value for the second of these two reactions increases slightly with $[\mathrm{MeCO_2^-}]$). However the portion of the absorption decrease during the faster reaction increases with increase in acetate concentration [compare Figures (a) and (b)]. The absorption spectrum of the intermediate is also slightly changed by the fast reaction, thus indicating that we observe the formation and decomposition of two similar intermediates. We suggest that these two reactions are the parallel decompositions of $\mathrm{MeCO_2Cu{-}CH_2CO_2}$ and $\mathrm{Cu{-}CH_2CO_2^+}$, the relative yield of the former increasing with acetate concentration [K_{diss} $(\mathrm{MeCO_2Cu^+}) =$ *ca.* 10^{-2} (ref. 9)]. The exact yield of the two forms depends also on the effect of complexation by acetate on k_2 (see above). It is suggested that the observed decompositions are reaction (3) since trivalent copper is known to cause fast decarboxylation of carboxylic ligands,[10] and reaction (4) in parallel to the mechanism suggested by Walling.[2,4]

$$\mathrm{MeCO_2Cu{-}CH_2CO_2} \xrightarrow{k_3\ 90\ \mathrm{s^{-1}}} \mathrm{CO_2} + \mathrm{Me\cdot} + \mathrm{Cu{-}CH_2CO_2^+} \rightarrow \text{products} \qquad (3)$$

$$\mathrm{Cu{-}CH_2CO_2^+} \xrightarrow[k_4\ 2{\cdot}8\ \mathrm{s^{-1}}]{\mathrm{H_2O}} \mathrm{Cu^+}\ (\mathrm{aq}) + \mathrm{HOCH_2CO_2^-} + \mathrm{H_3O^+} \qquad (4)$$

The kinetics observed upon repetitive pulsing or in argon-saturated solutions indicated that the $\mathrm{\cdot CH_2CO_2^-}$ radicals react also with the $\mathrm{Cu^+}$ (aq) formed under these conditions yielding another short-lived intermediate, the chemistry of which is under study. The maximum yield of products is thus $< 1 \times 10^{-5}$ M, so they cannot be identified.

Finally we report that preliminary results indicate the formation of similar intermediates in the reactions of $\mathrm{Me\dot{C}HCO_2^-}$ and $\mathrm{\cdot CHCl_2}$ or $\mathrm{\cdot CCl_3}$ with $\mathrm{Cu^{2+}}$ (aq). On the other hand no such intermediate is detected in the reactions of $\mathrm{R_2\dot{C}OH}$ and $\mathrm{\cdot CO_2^-}$ radicals with $\mathrm{Cu^{2+}}$ (aq) possibly as the reaction $\mathrm{Cu{-}COH(R)_2^{2+}} \rightarrow \mathrm{Cu^+} + \mathrm{R_2C{=}O} + \mathrm{H_3^+O}$ is very fast.

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