# Kinetics of $\beta$ -Hydroxyl Elimination from $[(H_2O)_mCu^{II}CH_2C(CH_3)_2OH]^+$ in Aqueous Solution

A Pulse-radiolysis Study

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The reaction of  ${}^{C}H_{2}C(CH_{3})_{2}OH$  with  $Cu_{aq}^{+}$  yields the short-lived transient complex  $[Cu^{II}CH_{2}C(CH_{3})_{2}OH]_{aq}^{+}$ . The spectrum of the latter complex is reported.  $[Cu^{II}CH_{2}C(CH_{3})_{2}OH]_{aq}^{+}$  decomposes into  $Cu_{aq}^{+}+CH_{2}=C(CH_{3})_{2}+OH^{-}$ . The specific rate of this reaction is  $5.0 \times 10^{4} + 8.6 \times 10^{7}[H_{3}O^{+}] s^{-1}$ . The kinetics are discussed in comparison with those of analogous reactions reported earlier.

Copper ions are known to affect the nature of products in aliphatic free radical, R, reactions.<sup>1,2</sup> It has been suggested that short-lived intermediates with copper-carbon bonds are formed in these systems *via* 

$$Cu_{aq}^{2+} + R \rightarrow Cu^{III} R_{aq}^{2+}$$
(1)

and/or via

$$Cu_{aa}^{+} + R \rightarrow Cu^{II}R_{aa}^{+}.$$
 (2)

Recent pulse-radiolysis studies have pointed out that indeed reactions (1) and (2) occur and that the chemical properties of the short-lived intermediates can be studied by this technique. It was found that reaction (2) is generally considerably faster than reaction (1).<sup>3-9</sup>

Several mechanisms for the decomposition of  $Cu^{II}R_{aq}^{+}$  transients were observed. These include

$$Cu^{II}R_{ao}^{+} + H_2O \rightarrow Cu_{ao}^{2+} + RH + OH^{-}$$
(3)

(e.g. for  $R = CH_3$  at  $pH < 1.0^7$ )

$$Cu^{II}R_{aq}^{+} \rightleftharpoons Cu_{aq}^{+} + R$$
(4)

(e.g. for  $R = CR^1R^2OH^4$  and  $CHCH_2OCH_2CH_2O$ ).<sup>9</sup>

$$2Cu^{11}CH_{3aq}^{+} \rightarrow 2Cu_{aq}^{+} + C_{2}H_{6}^{-7}$$
(5)

$$Cu^{11}CH_2CHR^1OH \rightarrow Cu^{2+}_{aq} + CH_2 = CHR^1 + OH^- \text{ where } R^1 = H, CH_3.^4$$
(6)

Reaction (6) is of importance as it might be a key step in radiobiological damage sensitized by copper ions and in synthesis as it is the opposite reaction to the Wacker process. However, reaction (6) was observed only as a side reaction and could therefore not be studied in detail.<sup>4</sup> The results obtained suggested that the  $\beta$ -hydroxyl eliminations from Cu<sup>II</sup>CR<sup>1</sup>R<sup>2</sup>CR<sup>3</sup>R<sup>4</sup>OH<sub>aq</sub> are faster than all analogous reactions studied.<sup>10</sup> It seemed therefore of importance to study reaction (6) in detail in a system where it will be the only process occurring.

We chose to study the kinetics of decomposition of  $[(H_2O)_mCu^{II}CH_2C(CH_3)_2OH]^+$  as this intermediate is expected to be the only intermediate observed in N<sub>2</sub>O-saturated

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solutions containing Cu<sub>aq</sub><sup>+</sup>, Cu<sub>aq</sub><sup>2+</sup> and C(CH<sub>3</sub>)<sub>3</sub>OH, vide infra, and as the mechanism of decomposition of the analogous complexes  $[(H_2O)_5Cr^{111}CH_2C(CH_3)_2OH]_{aq}^{2+11}$  and  $[(tspc)Co^{111}CH_2C(CH_3)_2OH]^{4-12}$  (where tspc = tetrasulphophthalocyanine) were studied in detail.

Nitrous-oxide-saturated solutions containing  $(5-20) \times 10^{-4} \text{ mol dm}^{-3} \text{ CuSO}_4$ ,  $(5-30) \times 10^{-5} \text{ mol dm}^{-3} \text{ Cu}_{aq}^+$ ,  $(5-30) \times 10^{-5} \text{ mol dm}^{-3} \text{ Cr}_{aq}^{111}^{111}$  and  $(0.1-1.0) \text{ mol dm}^{-3}$ C(CH<sub>3</sub>)<sub>3</sub>OH, in the pH range 2.7–4.5 were irradiated with  $0.3-1.5 \,\mu$ s pulses of 200 mA, 5 MeV electrons. The experimental apparatus was identical with that described earlier in detail.<sup>3</sup> The pulse intensity was 6-30 Gy. Under these conditions the following reactions have to be considered:

$$H_2O \xrightarrow{e} e_{a_0}, OH, H, H_2, H_2O_2, H_3O_{a_0}^{+14}$$
(7)

$$e_{ao}^{-} + N_2 O \rightarrow OH + OH_{ao}^{-} + N_2$$
  $k = 8.7 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1.15}$  (8)

$$e_{a0}^{-} + H_3 O^+ \rightarrow H \quad k = 2.0 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1.15}$$
 (9)

$$e_{ao}^{-} + Cu_{ao}^{2+} \to Cu_{ao}^{+}$$
  $k = 3.1 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1.15}$  (10)

$$H + Cu_{aq}^{+} \rightarrow CuH_{aq}^{+} \quad 5 \times 10^{9} < k/dm^{3} \text{ mol}^{-1} \text{ s}^{-1} < 2 \times 10^{10}$$
 (11)

$$\operatorname{Cu} H_{aq}^{+} \xrightarrow{\operatorname{H}_{2}O} \operatorname{Cu}_{aq}^{2+} + \operatorname{H}_{2}^{16}$$
(12)

$$COH/H + C(CH_3)_3OH \rightarrow CH_2C(CH_3)_2OH + H_2O/H_2$$
(13)

$$k_{\rm OH} = 4.2 \times 10^8 \,\rm dm^3 \, mol^{-1} \, s^{-1.17}$$

$$\kappa_{\rm H} = 8 \times 10^{6} \text{ um mor s}$$

$$CH_2C(CH_3)_2OH + Cu_{\rm aq}^{2+} \rightarrow [Cu^{\rm III}CH_2C(CH_3)_2OH]_{\rm aq}^{2+} \qquad (14)$$

$$k = 5 \times 10^{6} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1.3} \text{ t}$$

$$[Cu^{III}CH_{2}C(CH_{3})_{2}OH]^{2+}_{aq} \rightarrow Cu^{+}_{aq} + HOCH_{2}C(CH_{3})_{2}OH$$
  
$$k = 4.5 \times 10^{2} \text{ dm}^{3} \text{ mol}^{-1} \text{ s}^{-1.3}$$

$${}^{\bullet}CH_{2}C(CH_{3})_{2}OH + Cu_{aq}^{+} \rightarrow [Cu^{II}CH_{2}C(CH_{3})_{2}OH]_{aq}^{+}.$$

$$(15)$$

 $(k_{15} = 2.6 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  was estimated<sup>5</sup> from a pulse-radiolytic study in which  $Cu_{ao}^+$  was formed in situ by the pulse:

$$2CH_2C(CH_3)_2OH \rightarrow (CH_2C(CH_3)_2OH)_2$$
  $2k = 1.4 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1.19}$  (16)

Thus reactions (7)–(13) convert all the primary free radicals formed by the radiation into  $CH_2C(CH_3)_2OH$  free radicals during the pulse.

Under these conditions the formation of a short-lived transient is observed, the spectrum of which is plotted in fig. 1. This spectrum is similar to that of all  $Cu^{II}R_{aq}^+$ complexes, though the absolute absorption coefficient ( $\varepsilon_{400}$  1400 mol cm<sup>-1</sup>) is somewhat smaller than that observed for R = CH<sub>3</sub>,<sup>7</sup> CH<sub>2</sub>OH,<sup>4</sup> CO<sub>2</sub><sup>-6</sup> and CHCH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>O,<sup>9</sup> The spectrum differs significantly from that of [Cu<sup>111</sup>CH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>OH]<sup>2+.3</sup><sub>ao</sub>.<sup>3</sup>

The rate of formation of this transient obeys a pseudo-first-order rate law, the rate depending linearly on the concentration of  $Cu_{aq}^+$  and being independent of pH,  $[Cu_{aq}^{2+}]$ , [C(CH<sub>3</sub>)<sub>3</sub>OH] and pulse intensity. We identify therefore the short-lived transient as

<sup>&</sup>lt;sup>†</sup> The  $Cu_{aq}^{+}$ -containing solutions were prepared by mixing solutions containing  $Cu_{aq}^{2+}$  and  $Cr_{aq}^{2+}$  using the syringe technique. Under these conditions the reaction  $Cu_{aq}^{2+} + Cr_{aq}^{2+} \rightarrow Cu_{aq}^{+} + Cr_{aq}^{1+}$  occurs.<sup>13</sup>  $Cr_{aq}^{11}$  is known to be relatively unreactive towards free radicals and was found not to compete with  $Cu_{aq}^{+}$  in such reactions.<sup>7</sup>

<sup>&</sup>lt;sup>‡</sup> The formation of other oxidized organic products cannot be ruled out, as no analysis of the final organic products was carried out in the previous study.<sup>3</sup>



Fig. 1. U.v.-visible-absorption spectrum of  $[Cu^{II}CH_2C(CH_3)_2OH]_{aq}^+$ . Solution composition  $2 \times 10^{-4} \text{ mol } dm^{-3} Cu_{aq}^+$ ,  $2 \times 10^{-4} \text{ mol } dm^{-3} Cr_{aq}^{III}$ ,  $7 \times 10^{-4} \text{ mol } dm^{-3} Cu_{aq}^{2+}$ , 0.09 mol  $dm^{-3} C(CH_3)_3OH$ ; pH 3.8; N<sub>2</sub>O saturation; pulse intensity 10 Gy per pulse.

**Table 1.** Effect of methyl substituents on the specific rates of  $\beta$ -hydroxyl elimination from  $[(H_2O)_5Cr^{III}CH_2CH_2OH]^{2+}$  and  $[Cu^{II}CH_2CH_2OH]^{4}_{aq}$  complexes

complex	$k/s^{-1}$	ref.
[Cu <sup>II</sup> CH <sub>2</sub> CH <sub>2</sub> OH] <sup>+</sup>	$3.2 \times 10^3 + 3.8 \times 10^7 [H_3O^+]$	4
Cu <sup>11</sup> CH <sup>2</sup> CH <sup>(CH<sup>2</sup>)</sup> OH] <sup>+</sup>	$1.5 \times 10^4 + 1.5 \times 10^8 [H_{3}O^+]$	4
Cu <sup>11</sup> CH <sup>1</sup> <sub>2</sub> C(CH <sub>2</sub> ),OH <sup>+</sup> <sub>2</sub>	$5.0 \times 10^4 + 8.6 \times 10^7 [H_{3}O^+]$	this work
(H <sub>3</sub> O) Cr <sup>III</sup> CH CH CH OH P <sup>2+</sup>	$2.0 + 1.4 \times 10^{4} [H_{3}O^{+}]$	20
[(H <sub>2</sub> O) <sub>5</sub> Cr <sup>III</sup> CH(CH <sub>2</sub> )CH <sub>2</sub> OH] <sup>2+</sup>	$10 + 1.1 \times 10^{5} [H_{3}O^{+}]$	20
(H <sub>2</sub> O), Cr <sup>111</sup> CH(CH <sub>2</sub> )CH(CH <sub>2</sub> )OH] <sup>2+</sup>	$230 + 9.8 \times 10^{4} [H_{3}O^{+}]$	20
$[(H_2O)_5Cr^{III}CH_2C(CH_3)_2OH]_{aq}^{2+}$	$100 + 1.1 \times 10^{3} [H_{3}O^{+}]$	11

 $[Cu^{II}CH_2C(CH_3)_2OH]_{aq}^+$  formed in reaction (15). From the results we obtain  $k_{15} = (4.5 \pm 1.10) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . This specific rate is in accord with the rates reported for the analogous reactions of other aliphatic free radicals with  $Cu_{aq}^+$ .<sup>4, 7, 9</sup> As  $k_{15}$  is three orders of magnitude higher than  $k_{12}$ , clearly the latter reaction does not contribute to the observed processes under our experimental conditions.

The decomposition of  $[Cu^{II}CH_2C(CH_3)_2OH]_{aq}^+$  obeys a first-order rate law. The rate depends on  $[H_3O^+]$  and is independent of  $[Cu_{aq}^+]$ ,  $[Cu_{aq}^{2+}]$ ,  $[C(CH_3)_3OH]$  and pulse intensity. From the pH dependence is obtained  $k_d = (5.0 \pm 1.7) \times 10^4 + (8.6 \pm 3.0) \times 10^7$   $[H_3O^+] s^{-1}$ . The kinetics cannot be studied at  $[H_3O^+] > 2 \times 10^{-3}$  mol dm<sup>-3</sup> as, at this pH,  $k_d = 2.2 \times 10^5 s^{-1}$  and the rate of formation of  $[Cu^{II}CH_2C(CH_3)_2OH]_{aq}^+$  is  $\leq 1.3 \times 10^6 s^{-1}$ . The final products were analysed by g.c. and  $CH_2=C(CH_3)_2$  was found to be formed in a yield equal to that of  $CH_2C(CH_3)_2OH$ . It must therefore be concluded that the reaction observed is

$$[Cu^{II}CH_{2}C(CH_{3})_{2}OH]_{aq}^{+} \rightarrow Cu_{aq}^{2+} + CH_{2} = C(CH_{3})_{2} + OH^{-}$$
(17)  
$$k = (5.0 \pm 1.7) \times 10^{4} + (8.6 \pm 3.0) \times 10^{7} [H_{3}O^{+}] s^{-1}.$$

as expected.

The results thus corroborate the earlier suggestion<sup>12</sup> that the specific rate of  $\beta$ -hydroxyl elimination from [Cu<sup>II</sup>CR<sup>1</sup>R<sup>2</sup>CR<sup>3</sup>R<sup>4</sup>OH]<sup>+</sup><sub>aq</sub> complexes is considerably higher than those observed for the analogous complexes of (H<sub>2</sub>O)<sub>5</sub>Cr<sup>III</sup>R, <sup>11, 12</sup> (tspc) Co<sup>III</sup>R<sup>12</sup>

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and PPFe<sup>II</sup>R<sup>10</sup> (PP = protoporphyrin). It is of interest to analyse the effect of methyl substituents on the  $\beta$ -carbon on the rate of the  $\beta$ -elimination. The results in table 1 suggest that methyl substituents on the  $\beta$ -carbon enhance the specific rate of the [H<sub>3</sub>O<sup>+</sup>]-independent path for both the chromium(III) and copper(II) complexes. However, no such effect was observed for the analogous (tspc) Co<sup>III</sup> complexes.<sup>12</sup> The effect of methyl substituents on the acid-catalysed reaction is even more confusing. Thus the result seems to suggest that methyl substituents on the  $\beta$ -carbon slightly enhance the rate of  $\beta$ -elimination for the Cu<sup>II</sup>R complexes whereas they slow down the reaction for the Cr<sup>III</sup>R complexes. [This point could not be studied for the (tspc)Co<sup>III</sup>R complexes.]<sup>12</sup> The effect of methyl substituents on the rate of  $\beta$ -elimination is therefore complicated, *i.e.* different effects are observed for the acid-dependent and acid-independent processes, and for different central cations. Further studies on other substituents are required before an attempt to explain the effects can be made.

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