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Photooxidation of 2-Hydroxy Acids by Copper(II) Species in Aqueous Solution

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Ultraviolet irradiation of aqueous lactic, glycolic, or 2-hydroxybutanoic acid in the presence of copper(II) leads to photoredox reaction to give corresponding α-keto acid, aldehyde with evolution of carbon dioxide, and the precipitate of copper(I). The mole ratio of the carbonyl products to the consumption of copper(II) is close to 0.5. Oxidative decarboxylation dominates at pH>1 while the formation of α-keto acids favors at lower pH. The formation of α-keto acids is selectively suppressed by the addition of free radical scavengers. Free radical oxidations of the acids with bromine atom or benzoyl radicals give exclusively α-keto acids. The reaction mechanism has been discussed.

Despite many publications and potential utility of the photoredox reactions of Cu(II)–organic substrate systems,[1] their mechanisms seem to have been less clarified, except for a few cases, *e.g.*, the Cu(II) complexes of malonate,[2] 2,9-dimethyl-1,10-phenanthroline,[3] and 2,2′-biquinoline derivatives.[4]

On the other hand, catalytic photoreactions of organic substrates with Cu(I)[5,6] and Cu(II)[7,8] species have received much attention in synthetic as well as in mechanistic photochemistry.

In several cases the apparent photocatalyses of Cu(II) species seem to be relevant to the reversible cycles leading to no final (apparent) reduction of Cu(II).

In this paper we deal with the photooxidation of 2-hydroxy acids by Cu(II) species whose results are comparable with those for the uranyl–lactic acid system.[9]

Experimental

Guaranteed grade reagents were used without further purification while water was used after deionization and distillation.

The acidity of solution was adjusted with dilute sodium hydroxide or perchloric acid solution using a pH meter (Toa Denpa). Each sample solution was deoxygenated by bubbling with oxygen-free nitrogen current for 30 min, after the upper surface of the solution had been covered with liquid paraffin to keep airtight in one of identical Pyrex test tubes. It was then irradiated with light from a 400 W high pressure mercury lamp by means of a merry-go-round irradiation apparatus thermostated at 20 °C.

The consumption of Cu(II) species during photolysis was followed either by measuring its 810 nm absorption, or by colorimetric determination of the Cu(I) precipitate formed. The carbonyl products (aldehydes and α-keto acids) were converted into the precipitate of 2,4-dinitrophenylhydrazone derivatives (2,4-DNP).

The 2,4-DNP derivatives were then separated from each other on PLC (silica gel–benzene) and were identified by comparing their IR and NMR spectra with those of authentic samples. The amounts of the aldehydes and the α-keto acids were determined by colorimetric measurements at 360 nm in chloroform and at 380 nm in aqueous 0.25 mol/dm^3 sodium carbonate solution respectively, after the mixture of the 2,4-DNP precipitates had been separated by extraction with chloroform/aqueous 0.25 mol/dm^3 sodium carbonate solution.[9] The formation of carbon dioxide was implied by white precipitate which was formed when the evolved gases from the photoreaction mixture were passed through an aqueous barium(II) solution. UV absorption was measured by means of a Hitachi 124-Type recording spectrophotometer.

Results

Photooxidation of Lactic Acid by Cu(II) Species. Aqueous acid solution containing 0.2—0.4 M† lactic acid and 0.1 M Cu(II) sulfate gave acetaldehyde with evolution of carbon dioxide, pyruvic acid, and Cu(I) precipitate, on irradiation with light of 313—366 nm at 20 °C. No carbonyl products were detected either by thermal reaction at 70—80 °C for 5 h or by photolysis in the absence of Cu(II) species. Aqueous pyruvic acid in the presence of Cu(II) species underwent no significant decomposition under the photolytic conditions.

Table 1 lists the mole of Cu(II) species consumed, ΔCu(II), and the sum of the carbonyl products, A+P, formed during photolysis in various pH regions. In the pH region of 1.5—3.5 the mole ratio (A+P)/ΔCu(II) is close to 0.5 in consistent with the redox

TABLE 1. MOLE RATIO'S OF THE PHOTOCHEMICAL REDOX PRODUCTS OF AQUEOUS COPPER(II)-LACTIC ACID SOLUTION[a)]

pH	Atmosphere	ΔCu(II)[b)] / mM	(A+P)[c)] / mM	(A+P) / ΔCu(II)
0	air	0.0	0.98	
1.0	air	0.0	3.65	
1.5	air	12.6	6.40	0.51
1.5	N_2	9.6	7.63	0.80
2.0	air	11.3	8.23	0.73
2.5	air	16.2	8.50	0.53
2.5	N_2	15.6	10.9	0.70
3.0	air	16.5	8.50	0.52
3.0	N_2	22.6	12.5	0.55
3.5	air	19.8	9.88	0.50
3.5	N_2	23.5	11.5	0.49

a) Copper(II) sulfate: 0.1 M, lactic acid: 0.4 M, irradiation time: 5 h, temperature: 20 °C. b) Consumption of the copper(II) species. c) The sum of acetaldehyde and pyruvic acid concentrations.

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† 1 M=1 mol/dm^3.

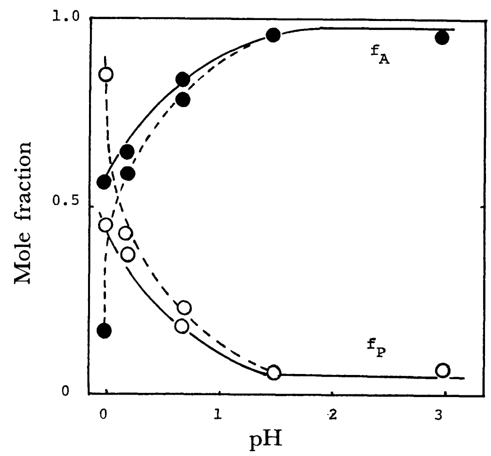


Fig. 1. Mole fractions of acetaldehyde (A) and pyruvic acid (P) formed in the photolysis of aqueous lactic acid–Cu(II) solution in Pyrex test tubes. (——): Deoxygenated, (----): not deoxygenated, before irradiation. Cu(II) sulfate: 0.1 M, lactic acid: 0.4 M, irradiation time: 5 h, f_A: A/(A+P), f_P: P/(A+P).

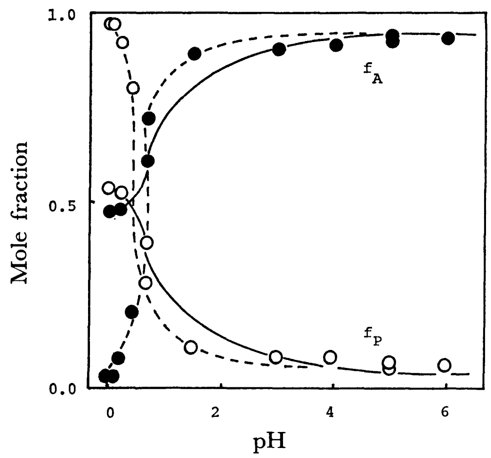


Fig. 2. Mole fractions of acetaldehyde (A) and pyruvic acid (P) formed in the photolysis of aqueous lactic acid–Cu(II) solution in glass ampuls. (——): Deoxygenated, (----): not deoxygenated, before irradiation. Other conditions and notations are the same as those in Fig. 1.

stoichiometry, both in the absence and presence of the dissolved oxygen. However, photolysis at $\mathrm{pH}\leqq 1$ in the presence of oxygen gives no final Cu(II)-reduction, implying reversible redox reaction of Cu(I) and Cu(II) species.

Figure 1 illustrates the pH-dependence of the mole fractions of acetaldehyde f_A and pyruvic acid f_P; f_A decreases and f_P increases with the decrease in pH. The broken lines in Fig. 1 show the effects of the dissolved oxygen which are significant in a lower pH region. Figure 2 illustrates the results obtained by irradiation in glass ampoules in the absence (solid lines) and presence (broken lines) of the dissolved oxygen, somewhat differing from those by irradiation in Pyrex test tubes. The present experiments have been carried out by the latter method because of its better reproducibility and simplicity, without further clarification of the discrepancy between the two methods.

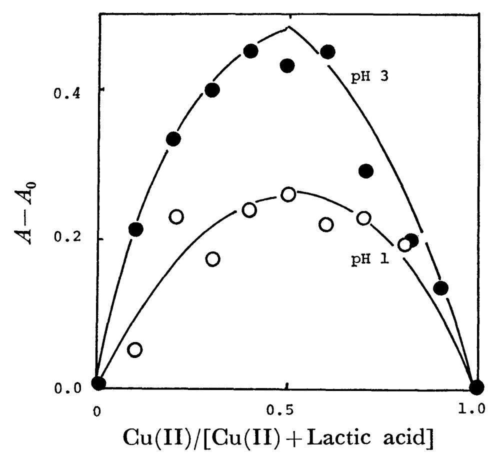


Fig. 3. Application of the continuous variation method to aqueous Cu(II)–lactic acid solution, as measured at 320 nm (pH 3) and at 290 nm (pH 1). Lactic acid+Cu(II)=0.20 M.

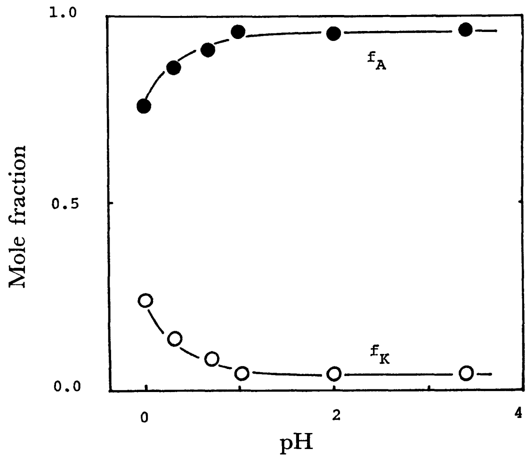


Fig. 4. Mole fractions of propanal (A) and 2-oxobutanoic acid (K) formed in the photolysis of deoxygenated aqueous 2-hydroxybutanoic acid–Cu(II) solution. Cu(II) sulfate: 0.1 M, 2-hydroxybutanoic acid: 0.2 M, f_F: A/(A+K), f_K: K/(A+K). Similar results were obtained for glycolic acid–Cu(II) solution.

The composition of aqueous Cu(II)–lactic acid solution in the ground state equilibrium was investigated, in relation to the pH-dependence of the photoproducts. Application of continuous variation method revealed the formation of a 1:1 Cu(II)–lactate complex in a higher pH region, while no such complex formation was observed at pH near zero (Fig. 3).

Photooxidation of Glycolic and 2-Hydroxybutanoic Acids by Cu(II) Species. On irradiation under conditions similar to those for the Cu(II)–lactic acid system, deoxygenated aqueous solution containing 0.2 M glycolic acid and 0.1 M Cu(II) sulfate gave glyoxylic acid, formaldehyde with evolution of carbon dioxide, and a small amount of unidentified carbonyl product, besides Cu(I) precipitate. Similar irradiation of 2-hydroxybutanoic acid–Cu(II) solution gave 2-oxobutanoic acid, propanal with evolution of carbon dioxide, and a small amount of unidentified carbonyl product, besides the Cu(I) precipitate. The pH-de-

TABLE 2. ADDITIVE EFFECTS OF SODIUM BROMIDE[a)]

[NaBr]/mM	[A]/mM	[P]/mM	f_A	f_P
0	34.7	3.68	0.90	0.10
2	35.0	1.74	0.95	0.05
20	34.7	0.70	0.98	0.02
200	17.0	0.03	1.00	0.00

a) Aerated aqueous solution containing 0.1 M copper(II) sulfate and 0.4 M lactic acid at pH 1.7, 20 °C, irradiation time: 5 h.

TABLE 3. ADDITIVE EFFECTS OF ACRYLONITRILE(AN) AT VARIOUS pH'S[a)]

pH	[AN]/mM	[A]/mM	[P]/mM	f_A	f_P
0	0	1.8	1.4	0.56	0.44
0	40	0.63	0.04	0.94	0.06
0.7	0	4.8	1.0	0.83	0.17
0.7	40	1.0	0.08	0.92	0.08
1.6	0	8.4	0.45	0.95	0.05
1.6	40	1.4	0.08	0.95	0.05
2.9	0	8.6	0.58	0.94	0.06
2.9	40	3.0	0.09	0.96	0.06

a) Copper(II) sulfate: 0.1 M, lactic acid: 0.4 M, irradiation time: 5 h, temperature: 20 °C.

TABLE 4. EFFECTS OF ACRYLONITRILE(AN) AT pH≒0[a)]

[AN]/mM	Irrd. time/h	[A]/mM	[P]/mM	f_A	f_P
0	5	1.60	1.43	0.53	0.47
1	5	1.05	0.80	0.57	0.43
2	5	0.95	0.45	0.68	0.32
3	5	0.73	0.01	0.88	0.12
4	5	0.83	0.06	0.94	0.06
0	8	0.70	1.20	0.37	0.63
8	8	1.15	0.03	0.91	0.03
16	8	0.95	0.03	0.97	0.03
24	8	0.95	0.02	0.97	0.03
32	8	1.00	0.05	0.96	0.04
40	8	1.05	0.03	0.98	0.02

a) Copper(II) sulfate: 0.1 M, lactic acid: 0.4 M, perchloric acid: 1.0 M.

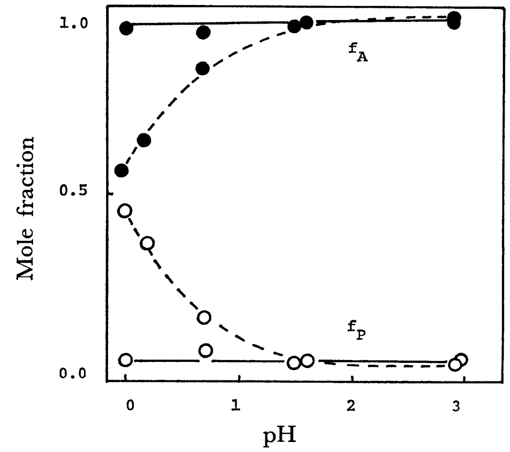


Fig. 5. Additive effects of acrylonitrile in the photolysis of deoxygenated aqueous lactic acid–Cu(II) solution. (——): In the presence of 40 mM acrylonitrile, (----): in the absence of acrylonitrile. Cu(II) sulfate: 0.1 M, lactic acid: 0.4 M.

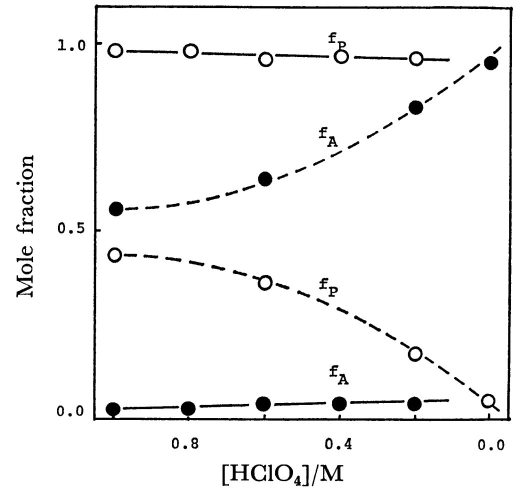


Fig. 6. Additive effects of maleic acid in the photolysis of deoxygenated aqueous lactic acid–Cu(II) solution, in the absence (----) and presence (——) of 0.1 M maleic acid. Cu(II) sulfate: 0.1 M, lactic acid: 0.4 M.

pendences of the mole fractions of the carbonyl products are shown in Fig. 4, which is comparable with those in Fig. 1.

Effects of Additives. In order to test the possible involvement of free radical intermediates, the effects of some free radical scavengers have been investigated for the photoredox reaction of the Cu(II)–lactic acid system. Table 2 lists the results with bromide ion, showing selective suppression toward the formation of pyruvic acid. Tables 3 and 4 are the effects of acrylonitrile in different pH regions and in different acrylonitrile concentrations at pH 0 respectively, which again reveal selective suppression toward the formation of pyruvic acid. For example, the yield of pyruvic acid is decreased to 1/25 (from 1.43 to 0.056 mM) while that of acetaldehyde to 1/2 (from 1.60 to 0.83 mM), by the addition of 4 mM acrylonitrile. Figure 5 is a plot of f_A and f_P as a function of pH in the presence and absence of acrylonitrile. The addition of *t*-butyl alcohol (20 v/v%) as a scavenger of hydroxyl radical[10)] suppressed the formation of pyruvic acid almost completely without affecting the yield of acetaldehyde, in the photooxidation of lactic acid with Cu(II) chloride at pH 0, 1, and 1.5.

Figure 6 illustrates the effects of maleic acid, showing selective suppression toward acetaldehyde formation. Though maleic acid suppresses the formation of both acetaldehyde and pyruvic acid considerablly, the effect is much more pronounced toward the former.

Neither acetaldehyde nor pyruvic acid formation was suppressed by the addition of 1 mM sodium azide, an effective scavenger of singlet molecular oxygen, in the photolysis of the Cu(II)–lactic acid system at pH 0, 1, and 1.5.

Free Radical Oxidations of 2-Hydroxy Acids. Since the formation of α-keto acids has been assumed

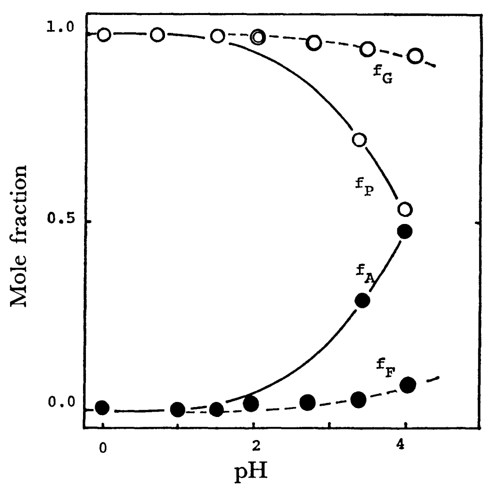


Fig. 7. Mole fractions of aldehydes (●) and α-keto acids (○) formed in the photolyses of aqueous lactic acid (——) and glycolic acid (----), in the presence of 0.5 M bromine. The results with 2-hydroxybutanoic acid were similar to those with lactic acid.

to involve free radical processes, it appeared of interest to investigate free radical oxidations for comparison with the Cu(II)-photooxidation. Reaction of 2-hydroxybutanoic acid with benzoyl peroxide at 80—90 °C in benzene for 20 min led, indeed, to the formation of 2-oxobutanoic acid without propanal formation. Photooxidation of lactic, glycolic, and 2-hydroxybutanoic acids by bromine water (without deoxygenation) gave corresponding α-keto acids with minor amounts of aldehydes. The pH-depencences of the two sets of the carbonyl products are shown in Fig. 7. The pH-dependences appear to be in sharp contrast to those of the Cu(II)-photooxidation.

These results seem to provide some evidence for the intermediacy of free radical processes in the formation of α-keto acids as will be discussed in the following section.

Reaction of lactic acid with Fenton's reagent, which generates hydroxyl and hydroperoxyl radicals,[11] gave no carbonyl products. Nor was formed 2-oxobutanoic acid by reaction of 2-hydroxybutanoic acid with singlet molecular oxygen generated by reaction of sodium hypochlorite with hydrogen peroxide.[12]

Discussion

The pH-dependences of the photooxidation of 2-hydroxy acids by Cu(II) species are apparently similar to those of the photolysis of the uranyl–lactic acid system under similar conditions.[9]

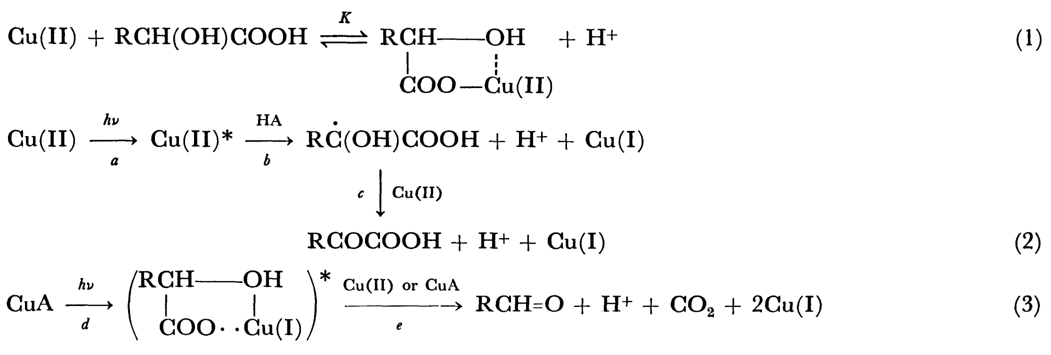
Because of the similarity it seems reasonable to refer to the outline of the latter photoreactions. It has been shown that pyruvic acid is formed at pH≦1 *via* electron or α-hydrogen atom abstraction by excited state uranyl ion on bimolecular collisions with lactic acid while the formation of acetaldehyde and carbon dioxide dominates in a higher pH region *via* unimolecular photodecomposition of uranyl–lactate complex, for the photolysis of aqueous uranyl–lactic acid solution. Later, ESR detection of free radical intermediates, such as $\dot{\mathrm{R}}\mathrm{C(OH)R'}$,[13] and kinetic isotope effects[14] have strongly supported the assumed mechanisms for the photooxidation of alcohols and acids by uranyl ion.

Similar mechanism seems to be applicable to the photooxidation of 2-hydroxy acids by Cu(II) species with a minor modification.

Equation 1 represents the ground state equilibrium between Cu(II), 2-hydroxy acid (HA), and a 1:1 chelate complex (CuX). Here, Cu(II) represents aquo complex ion which may be present far apart from or in the close proximity of HA without formation of chelate complex. Equations 2 and 3 represent the processes for the formation of α-keto acids and aldehydes, respectively.

The pH-dependence of the two carbonyl products may be interpreted as a reflection of the ground state equilibrium. Equations 1—3 may explain the fact that the formation of α-keto acids is favored by the decrease in pH while oxidative decarboxylation is favored by the increase in pH. UV excitation of CuA would lead to unimolecular redox, *i.e.*, electron transfer from the carboxyl group to the metal center (*d*), followed by oxidative decarboxylation to give aldehyde (*e*). On the other hand, Cu(II) is excited to its LMCT excited state, Cu(II)*, which then undergoes redox reaction with HA on bimolecular collision to produce radical intermediate, $\mathrm{R\dot{C}(OH)COOH}$. This radical would be rapidly oxidized by Cu(II)[15] to give α-keto acid.

If the free radical $\mathrm{P\dot{C}(OH)COOH}$ is actually the precursor of α-keto acids in the photooxidation by Cu(II) species, as suggested in Eq. 2, then α-hydrogen atom abstraction by other oxidants should also give α-keto acids. In fact, oxidation by free radicals generated in thermolysis of benzoyl peroxide or in photo-



$$\mathrm{Cu(II)} + \mathrm{RCH(OH)COOH} \overset{K}{\rightleftharpoons} \begin{array}{l}\mathrm{RCH{-}{-}OH} \\ \;\,| \qquad \vdots \\ \mathrm{COO{-}Cu(II)}\end{array} + \mathrm{H^+} \qquad (1)$$

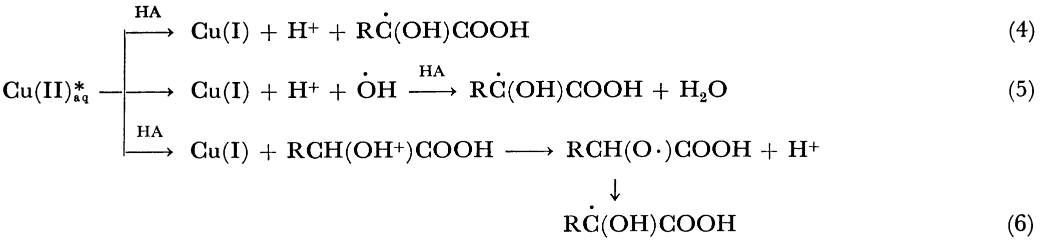
$$\mathrm{Cu(II)} \xrightarrow[a]{h\nu} \mathrm{Cu(II)^*} \xrightarrow[b]{\mathrm{HA}} \mathrm{R\dot{C}(OH)COOH} + \mathrm{H^+} + \mathrm{Cu(I)}$$

$$\Big\downarrow c \;\; \mathrm{Cu(II)}$$

$$\mathrm{RCOCOOH} + \mathrm{H^+} + \mathrm{Cu(I)} \qquad (2)$$

$$\mathrm{CuA} \xrightarrow[d]{h\nu} \left(\begin{array}{l}\mathrm{RCH{-}{-}OH} \\ \;\,| \qquad\; | \\ \mathrm{COO\cdot \cdot Cu(I)}\end{array}\right)^* \xrightarrow[e]{\mathrm{Cu(II)\ or\ CuA}} \mathrm{RCH{=}O} + \mathrm{H^+} + \mathrm{CO_2} + 2\mathrm{Cu(I)} \qquad (3)$$

Scheme 1.



$$\mathrm{Cu(II)^*_{aq}} \xrightarrow{\mathrm{HA}} \mathrm{Cu(I) + H^+ + R\dot{C}(OH)COOH} \qquad (4)$$

$$\mathrm{Cu(II)^*_{aq}} \longrightarrow \mathrm{Cu(I) + H^+ + \dot{O}H} \xrightarrow{\mathrm{HA}} \mathrm{R\dot{C}(OH)COOH + H_2O} \qquad (5)$$

$$\mathrm{Cu(II)^*_{aq}} \xrightarrow{\mathrm{HA}} \mathrm{Cu(I) + RCH(OH^+)COOH} \longrightarrow \mathrm{RCH(O\cdot)COOH + H^+} \longrightarrow \mathrm{R\dot{C}(OH)COOH} \qquad (6)$$

Scheme 2.

lysis with bromine water (where bromine atoms are formed as active species)[16] gave α-keto acids as the main carbonyl products, in consistent with our assumption.

The selective suppression toward the formation of α-keto acid by free radical scavengers (Tables 2—4) may be interpreted as follows. Because of its bareness the intermediate $\mathrm{R\dot{C}(OH)COOH}$ would be sensitive to the radical scavengers and be effectively scavenged, whereas the intermediate precursor for aldehyde is assumed to be less sensitive to the additives due to complexation or less bareness (Eq. 3). Studies on the flash photolysis of Cu(II)–malonate complex have demonstrated that the oxidized ligand remains bound to the reduced metal center until it undergoes further redox reaction.[2] The suppression of both acetaldehyde and pyruvic acid formation by maleic acid may be ascribable to the dual effects of maleic acid acting as both a masking agent toward complex formation and a radical scavenger.

No satisfactory explanation is available as yet for the effects of the dissolved oxygen. Singlet molecular oxygen is ruled out since its reaction with 2-hydroxybutanoic acid did not give 2-oxobutanoic acid and since sodium azide did not affect the yields of the carbonyl products in the Cu(II)-photooxidation of lactic acid. Nor is the role of the hydroperoxyl radical relevant since pyruvic acid was not produced by reaction of lactic acid with Fenton's reagent. Reoxidation of the Cu(I) species by the dissolved oxygen to Cu(II) species is considered to be relevant to the oxygen effects, at least partly. In aerated solution at pH near 0 no practical (final) reduction is observed, while in a higher pH region the ratio $(A+P)/\Delta\mathrm{Cu(II)}$ is close to the value expected from Scheme 1. This in turn implies that cyclic (or catalytic) photooxidation by Cu(II) species can only be effective in a highly acidic (pH$\leqq$0) solution in the presence of the dissolved oxygen.

As to the primary interactions of Cu(II)* with HA to give $\mathrm{R\dot{C}(OH)COOH}$, following processes may be considered; 1) direct H-atom abstraction, 2) oxidation of water by LMCT interaction to give $\mathrm{\dot{O}H}$ radical, followed by H-atom abstraction by $\mathrm{\dot{O}H}$ from HA, 3) electron transfer from HA to Cu(II)* giving radical cation, followed by deprotonation and radical rearrangement to the more stable radical (Scheme 2). The $\mathrm{\dot{O}H}$ radical mechanism (Eq. 5) might be supported by the selective suppression by *t*-butyl alcohol toward pyruvic acid formation. In fact, photoredox reaction of the labile Cu(II) complex of 2,9-dimethyl-1,10-phenanthroline has been shown to involve the $\mathrm{\dot{O}H}$ radical process.[3] However, the failure to observe pyruvic acid formation by reaction of lactic acid with Fenton's reagent excludes this possibility. The direct H-atom abstraction (Eq. 4) is a likely process, and many thermal and photochemical oxidations of organic substrates by transition metal ions seem to involve this process. However, it seems more likely that electron transfer (Eq. 6) occurs as the primary act than the direct H-atom abstraction, because of the LMCT character of Cu(II)* and larger affinity of Cu(II) for the hydroxyl group than for the α-hydrogen atom of HA.

The primary bimolecular interactions between Cu(II)* and HA would only be effective in a short range. This is because Cu(II)* is assumed to be too short-lived to permit a long range bimolecular reaction, whereas the long lifetime of the excited state uranyl ion, 10^{-5}—10^{-4} s,[17] may permit it.

It may be notable that the pH-dependences of the carbonyl products in the Cu(II)-photooxidation appear to be contrast to those in thermal permanganate oxidation: permanganate oxidation of 2-hydroxy acids gives α-keto acids in basic solution but undergoes oxidative decarboxylation to give aldehydes in acidic solution.[18] Permanganate oxidation of 2-hydroxy acids may be assumed to occur by a similar process to that proposed for the permanganate oxidation of alcohols, *i.e.*, α-hydrogen abstraction as hydrogen atom or hydride ion.[19] The decarboxylation in the acid permanganate oxidation may be ascribable to the vigorousness of the oxidation conditions, whereas in the case of the Cu(II)-photooxidation the decarboxylation is relevant to the unimolecular LMCT interactions of the CuA complex.

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