203. *The Constitution of Copper Peroxide and the Catalytic Decomposition of Hydrogen Peroxide.*

By Abraham Glasner.

On the evidence of photometric and gasometric measurements it is concluded that copper peroxide is formed by the simple addition of a HO_2 radical to cupric hydroxide and therefore should have the formula CuO,O_2H,aq. The measurements were made in the presence of sodium citrate which kept the intensely brown peroxide in solution. The formation of the copper peroxide is promoted by sodium hydroxide, but is retarded by an excess of citrate.

Copper peroxide is unstable; therefore its concentration in solutions in which it is prepared is a function of time, yielding bell-shaped curves (see Fig. 1). In solutions of otherwise similar composition, the maxima of the curves are proportional to the 1·5 power of the initial concentration of the hydrogen peroxide. These maxima may be regarded as corresponding to a steady state and can be represented by an equilibrium constant *K*, which was recorded for a few series of solutions at two temperatures, 10° and 20°.

The catalytic decomposition of hydrogen peroxide is shown to be proportional to the concentration of copper peroxide present at any moment in the solution. The rate of evolution of oxygen was found to correspond approximately to the order ½ with respect to the hydrogen peroxide, but this is explained by showing that it is a function of the equilibrium constants *K*.

It was suggested, in discussing the blue perchromates (Glasner, *J.*, 1950, 2795), that the HO_2 molecule is involved in their formation, and the suggestion afforded a feasible explanation of the properties of the perchromates and their function in the catalytic decomposition of hydrogen peroxide. It seemed probable, therefore, that some of the anomalies observed with the peroxides of the transitional elements might be explained on similar lines, and accordingly the brown copper peroxide has now been studied.

It is known that cupric salts in alkaline solution give with hydrogen peroxide a brown, very unstable precipitate which most investigators have tacitly assumed to have the composition CuO,H_2O_2, but analysis always gave a ratio $CuO : H_2O_2 > 1$, and this was ascribed to the unstable nature of this compound (Aldridge and Applebey, *J.*, 1922, **121**, 238; Teletov and Veleshinetz, *Ukrain. Chem. J.*, 1931, **6**, Sci., 53; *Chem. Abs.*, 1931, **25**, 3635; Mueller, *Bull. Soc. chim.*, 1936, **3**, 1913). Another red oxide, given the formula Cu_2O_3, was prepared by Buntin and Vlasov (*Acta Univ. Voronegiensis*, 1935, **8**, No. 4, 6; *Chem. Abs.*, 1938, **32**, 6598_8; Zhuze and Starchenko, *J. Exp. Theor. Phys. U.S.S.R.*, 1940, **10**, 331; *Chem. Abs.*, 1940, **34**, 7687). Wieland and Stein (*Z. anorg. Chem.*, 1938, **236**, 361), from a preparation at −79°, isolated and analysed a copper peroxide and gave it the formula $HO_2{\cdot}Cu{\cdot}O_2{\cdot}Cu{\cdot}O_2H$. (They gave a similar formula to a ferric peroxide which they prepared.) As they did not determine the molecular wieght of their copper peroxide, it might as well be written as the monomer $CuO{\cdot}O_2H$, formed by the addition of HO_2 to CuO, and the experimental results at 10° to 30° now described are believed to confirm this suggestion.

EXPERIMENTAL.

In presence of sodium citrate, the brown peroxide was not precipitated but formed an intensely coloured homogeneous solution which slowly decomposed evolving oxygen, thereby regaining its original pale blue colour. Such solutions of diverse composition were therefore studied. The measurements were made with a gasometer and a Hellige "panphotometer" to which a small thermostat enveloping the glass vessel had been attached, the same technique being used as described for the perchromates (Bobtelsky, Glasner, and Bobtelsky-Chaikin, *J. Amer. Chem. Soc.*, 1945, **67**, 966). The stock solutions were: (1) $CuSO_4,5H_2O$, Schering–Kahlbaum, "zur Analyse," 0·1038M. or 0·107M., determined by electrolysis. (2) Sodium citrate B.P., 0·108M., determined by conductometric titration with a cobalt salt of known concentration. (3) Sodium hydroxide, "for analysis," 0·1631M., free from carbonate. (4) Hydrogen peroxide, Merck's "perhydrol" diluted, and the concentration determined for each series of experiments by titration with standard permanganate solution.

The solutions for each experiment were made up to a total volume of 50 ml., and the reaction vessels were kept in thermostats at the temperatures indicated.

In the photometric measurements a 470 mμ. filter was found to be best, for with this the blue copper solution has a minimum, and the brown peroxide solution a maximum estinction. As controls, readings were taken also with a 500-mμ. filter (the ratio of the extinctions E_{470}/E_{500} was *ca.* 1·71). The depth of the solution in the photometer was always 5 mm., and for each measurement a new portion of the solution was taken.

Results.—Fig. 1, curve *a*, shows the change with time at 20° of the extinction of a solution having the composition (in millimols./l.): $CuSO_4$, 2·14; Na_3Cit, 4·32; NaOH, 8·328; H_2O_2, 30·2. There is an initial lag, then the extinction rises quickly to a maximum followed by a slower decrease. Curve *b* shows the evolution of oxygen from a similar solution. Here we have again a lag, and the curve is on the whole S-shaped. There is a complete agreement between all the phases of the two curves including a coincidence between the maximum extinction and the steepest part of the S-curve. Hence, there can be no doubt that the decomposition of the hydrogen peroxide and the formation of the copper peroxide are not two independent reactions, but represent two aspects of a series of consecutive reactions, the brown copper peroxide being an intermediate in the catalytic decomposition of the hydrogen peroxide.

When the concentration of any of the components in the solutions was changed, the results were rather complicated, since the relative amounts of copper, citrate, and hydroxide seemed to be all interrelated.

Variation of sodium hydroxide concentration. In Fig. 2 are given a series of curves showing the catalytic decomposition of hydrogen peroxide in solutions containing different amounts of sodium hydroxide but otherwise identical. The final concentrations of the reagents (in millimols./l.) were: $CuSO_4$, 2·076; Na_3Cit, 4·32; H_2O_2, 25·2; NaOH, 5·82—9·98. It is seen that an increase in the concentration of sodium hydroxide shortens the time lag and increases the velocity of decomposition up to about 5 mols. of sodium hydroxide to each mol. of copper sulphate. A further excess of sodium hydroxide reduces somewhat the velocity of decomposition and may result also in the formation of a brown precipitate.

At the lower limit, catalytic decomposition can take place only if the molar concentration of sodium hydroxide is greater than that of the citrate. With solutions containing a 1 : 1 molar ratio of copper to citrate, only slightly more than 1 mol. of sodium hydroxide is necessary for the decomposition of hydrogen peroxide to occur.

The copper citrate catalyst. Some light on the state of the copper in the solution before the formation of the peroxide is obtained from a consideration of the curves *c* and *d* (photometric) and *e* and *f* (gasometric) in Fig. 1. These pairs of curves were obtained from solutions having exactly the same composition, and only the order of the addition of the various reagents was altered: in all experiments hitherto discussed and also in *c* and *e* hydrogen peroxide was added last to the reaction mixture, but in *d* and *f* copper sulphate was the reagent added last. It is seen that in the photometric curve *d* the time lag is entirely absent, and in the gasometric curve *f* it is greatly shortened.

Again, on mixing the copper and citrate solutions and adding this mixture to a dilute alkaline hydrogen peroxide solution, the curves obtained are like *c* and *e* to which hydrogen peroxide was added last, showing a lag. Hence, it may be concluded that for the formation of the copper peroxide the pre-existence of a basic copper compound is necessary, and the rôle of the citrate is merely to keep the copper in solution, thus affording a homogeneous reaction. The effect of varying the concentration of the copper sulphate could not be studied independently of the concentration of the citrate and sodium hydroxide, as stated above, so the order of reaction with regard to copper sulphate could not be determined directly.

FIG. 1.

Formation and decomposition of copper peroxide. A comparison of photometric and gasometric measurements.

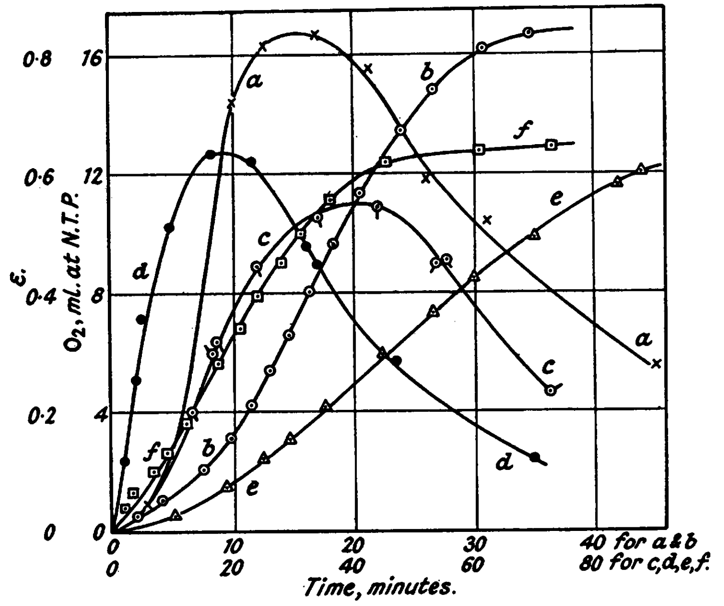
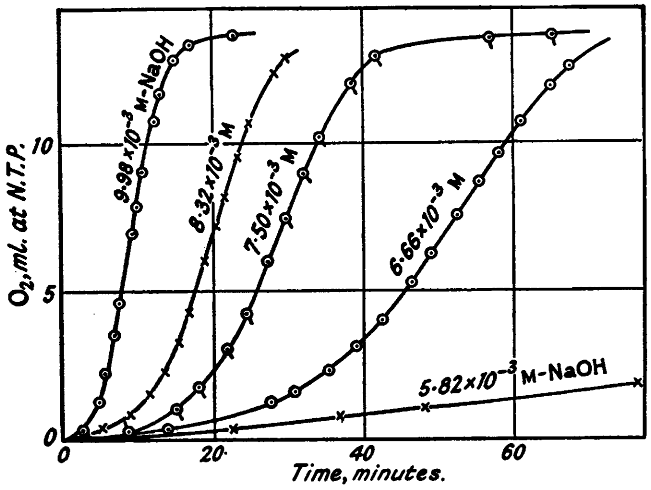


FIG. 2.

Catalytic decomposition of H_2O_2 *by copper citrate :* NaOH *varied.*



Variation of hydrogen peroxide concentration. (a) Photometric measurements. Fig. 3 shows the variation with time at 20° of the extinction of a series of solutions having the general composition (in millimols./l.) = $CuSO_4$, 1·038; Na_3Cit, 2·16; NaOH, 8·328; with various concentrations of hydrogen peroxide in a total volume of 50 ml. On increasing the concentration of hydrogen peroxide a maximum extinction $E_{470} = 0{\cdot}540$ is obtained, *i.e.*, at this or higher concentrations of hydrogen peroxide, all the copper in the solution is converted into the peroxide, and so the molecular extinction of the brown copper peroxide can be calculated. Each individual curve in Fig. 3 attains a maximum extinction ($E_{max.}$) at a definite moment. At these maximum points the velocities of formation and decomposition of the peroxide are equal; *i.e.*, $E_{max.}$ is a point of " pseudo equilibrium " or steady state and we may write

FIG. 3.

Extinction–time curves of copper peroxide : H_2O_2 *varied.*

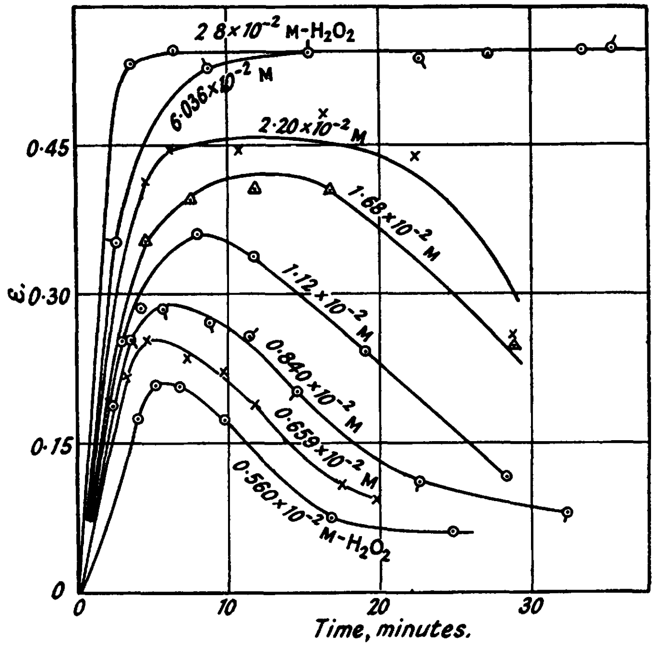


TABLE I.

Equilibrium constants, from photometric measurements.

(*a*) At 20°.

$1{\cdot}038 \times 10^{-3}$M-$CuSO_4$; $8{\cdot}328 \times 10^{-3}$M-NaOH; $E_{100\%} = 0{\cdot}540$.

$H_2O_2 \times 10^2$.	E_{470}.	$K \times 10^3$.
0·560	0·213	0·643
0·659	0·255	0·598
0·840	0·294	0·644
1·120	0·360	0·593
1·680	0·420	0·622
2·196	0·456	0·599
		Mean 0·618

$2{\cdot}14 \times 10^{-3}$M-$CuSO_4$; $8{\cdot}328 \times 10^{-3}$M-NaOH; $E_{100\%} = 1{\cdot}113$.

$H_2O_2 \times 10^2$.	E_{470}.	$K \times 10^3$.
3·04	0·840	1·72

(*b*) At 10°.

$2{\cdot}076 \times 10^{-3}$M-$CuSO_4$; $8{\cdot}328 \times 10^{-3}$M-NaOH; $E_{100\%} = 1{\cdot}080$.

$H_2O_2 \times 10^2$.	E_{470}.	$K \times 10^3$.
0·750	0·305	1·65
0·844	0·365	1·52
1·000	0·435	1·47
1·250	0·510	1·65
2·110	0·740	1·42
		Mean 1·54

$1{\cdot}038 \times 10^{-3}$M-$CuSO_4$; $8{\cdot}328 \times 10^{-3}$M-NaOH; $E_{100\%} = 0{\cdot}540$.

$H_2O_2 \times 10^2$.	E_{470}.	$K \times 10^3$.
0·540	0·225	0·539
0·810	0·314	0·504
1·080	0·372	0·481
1·350	0·415	0·472
		Mean 0·499

$$[Cu^{++}]^m[H_2O_2]^n/[Per]^p = (b - E_{max.})^m a^n/E^p_{max.} = K$$

where a is the initial concentration of hydrogen peroxide and b that of the copper salt expressed in the same units as $E_{max.}$. The experimental values of $E_{max.}$ being used, the indices in this equation were found by trial; on taking $m = p = 1$ and $n = 1{\cdot}5$ fairly constant values for K were obtained as shown in Table I(*a*).

In Table I(*b*) are summarized the results of two other series of experiments at 10°. The ratio of citrate to copper sulphate in all the solutions was slightly more than 2 : 1, and it should be remembered that only solutions containing similar amounts of the three reagents, copper, citrate, and hydroxide, should be compared. With these considerations, and account being taken of the single solution with a concentration of 2·14 × 10^{-3}M-$CuSO_4$ at 20°, the temperature coefficients of K are 1·24 and 1·12. The maximum extinctions obtained are slightly higher at 10°, but the time taken for the attainment of these maxima was far shorter at 20°.

FIG. 4.

Catalytic decomposition of H_2O_2 : H_2O_2 *varied.*

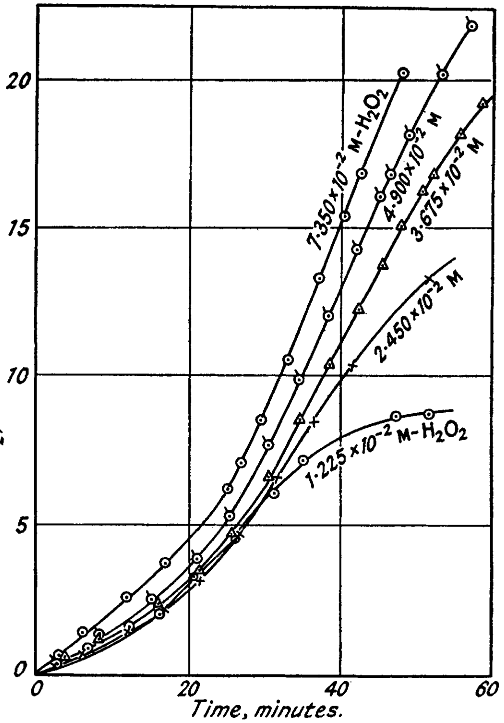
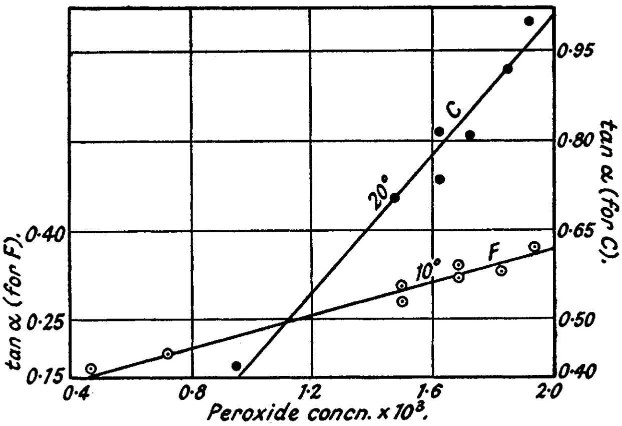


FIG. 5.

Relation between decomposition rate and copper peroxide concentration.



(*b*) Gasometric measurements. Curves in Fig. 4 represent the evolution of oxygen at 20° from a series of solutions having the general composition (millimols./l.): $CuSO_4$, 2·14; Na_3Cit, 4·32; NaOH, 7·495. The concentration of hydrogen peroxide was varied; total volume 50 ml. Hydrogen peroxide was the reactant added last. The general form of the curves has been discussed (p. 905). The increase in the concentration of hydrogen peroxide has a regular accelerating effect on the velocity of decomposition (unless the hydrogen peroxide is added in a very large excess), which is best demonstrated by the tangents of the inflection points on the S-curves : the middle parts of the curves are very nearly straight for a considerable period, and therefore the tangents of the angles these lines make with the abscissa (tan α) are most convenient for a quantitative comparison.

Table II (*a*) shows that tan α divided by the square root of the hydrogen peroxide concentration (C) is

TABLE II.

Rate of evolution of oxygen.

NaOH, M × 10^3.	2·14 × 10^{-3}M-$CuSO_4$. H_2O_2, M × 10^2 = C × 10^2.	tan α.	tan $\alpha/C^{0.5}$.
	(*a*) At 20°.		
6·246 (Series A)	1·525	0·197	1·59
	1·525	0·189	1·53
	2·768	0·250	1·50
	3·050	0·306	1·75
	3·050	0·280	1·60
	4·152	0·327	1·60
	5·536	0·408	1·74
	6·920	0·437	1·66
7·495 (Series B)	1·225	0·280	2·54
	2·450	0·375	2·40
	3·675	0·495	2·58
	4·900	0·580	2·62
	7·350	0·640	2·36
8·328 (Series C)	1·231	0·435	3·92
	2·462	0·703	4·48
	3·04	0·815	4·68
	3·04	0·735	4·21
	3·693	0·810	4·22
	4·924	0·920	4·16
	6·08	0·950	3·85

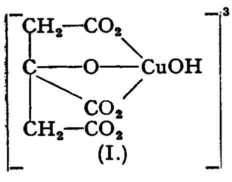
NaOH, M × 10^3.	2·076 × 10^{-3}M-$CuSO_4$. H_2O_2, M × 10^2 = C × 10^2.	tan α.	tan $\alpha/C^{0.5}$.
	(*b*) At 30°.		
7·50 (Series D)	1·362	0·560	4·78
	2·724	1·210	7·33
	4·086	1·320	6·47
	5·448	1·480	6·36
	6·810	1·730	6·63
	(*c*) At 10°.		
7·50 (Series E)	4·42	0·272	1·32
	6·63	0·286	1·11
	8·84	0·338	1·14
	8·84	0·338	1·14
	13·26	0·316	0·87
8·328 (Series F)	0·584	0·165	2·16
	0·876	0·190	2·03
	2·52	0·280	1·76
	2·52	0·306	1·93
	3·78	0·320	1·65
	3·78	0·340	1·75
	5·04	0·330	1·47
	7·56	0·370	1·35

a constant (k), not only for the solutions represented in Fig. 4, but also for two other series of solutions having a different concentration of alkali; *i.e.*, the velocity of hydrogen peroxide decomposition is proportional to the square root of this reagent in most of the solutions studied.

Some experiments were repeated at 30° and at 10°. The results are summarized in Table II, (*b*) and (*c*). The temperature coefficient calculated from the average of the rate constants k (wherever this seems to hold) is about 2·5.

DISCUSSION.

We have seen that the decomposition of hydrogen peroxide is catalysed by the copper citrate complex only in solutions containing more than 1 mol. of sodium hydroxide for each mol. of copper sulphate. Bobtelsky and Jordan (*J. Amer. Chem. Soc.*, 1945, **67**, 1831) assigned to the complex produced under similar conditions the formula (I), containing one hydroxyl group directly attached to the copper atom. Hence it may be assumed that the peroxide studied in this paper is similarly constituted, and undergoes the same reactions as the copper peroxide produced in the absence of the citrate. In the following we shall abbreviate (I) to (Cit CuOH)$^{3-}$. From the equilibrium constants K (Table I) we may conclude that the brown peroxide (II) ([Per] for short) is formed from one molecule of the basic copper complex and 1·5 molecules of hydrogen peroxide, and also that the decomposition of the per-compound is of the first order. This suggests the following series of reactions :



(I.)

$$(1)\quad [\mathrm{Cit\ CuOH}]^{3-} + HO_2 \longrightarrow \underset{\text{(II.)}}{[\mathrm{Cit\ CuO_2}]^{3-}} + H_2O$$

$$(2)\quad \text{(II)} \longrightarrow \underset{\text{(III.)}}{[\mathrm{Cit\ Cu}]^{3-}} + O_2$$

$$(3)\quad \text{(III)} + H_2O_2 \longrightarrow \underset{\text{(I.)}}{[\mathrm{Cit\ CuOH}]^{3-}} + OH \text{ (rapid)}$$

For reaction (1) it is assumed (Glasner, *J.*, 1950, 2798) that in all hydrogen peroxide solutions the following equilibria exist :

$$H_2O_2 \rightleftharpoons 2OH \text{ and } HO + H_2O_2 \rightleftharpoons HO_2 + H_2O$$

and therefore

$$[HO_2] = K_{HO_2}[H_2O_2]^{1\cdot5}$$

Thus the odd-electron ion O_2^- in the peroxy-compound (II) may be made responsible for the intense colour of this per-compound and its labile nature.

In analogy with the perchromates, it is further considered that the odd electron from the O_2^- is transferred to the copper, which is thus reduced to the univalent state. This could be tested by examining the magnetic susceptibility of (II).

According to reaction (2), the evolution of oxygen in the gasometric measurements should be proportional to the concentration of the per-compound present at any moment in the solution. Fig. 1 shows this to be the case. Furthermore, the *K* values from Table I may be used to calculate the concentration of the per-compound at the steady state, for the series of solutions C (at 20°) and F (at 10°) by the equation

$$[Per] = b[H_2O_2]^{1\cdot5}/(K + [H_2O_2]^{1\cdot5})$$

where all the symbols have the meanings previously assigned to them. When [Per] is plotted against tan α, straight lines are obtained as shown in Fig. 5. This not only proves the unimolecular decomposition of (II), but also confirms the correctness of the equilibrium equation at the steady state.

It should be added that the proportionality found between tan α and the square root of the initial concentration of the hydrogen peroxide should hold only for a limited range. This will be seen on considering the two extreme cases :

$$(A) \quad K \gg [H_2O_2]^{1\cdot5} \quad [Per] = b[H_2O_2]^{1\cdot5}/K$$

and

$$(B) \quad K \ll [H_2O_2]^{1\cdot5} \quad [Per] = b$$

showing that the order of the reaction with respect to the initial concentration of the hydrogen peroxide ought to vary from 1·5 to zero. As has been noted (p. 909), a large excess of hydrogen peroxide does not increase tan α after this has attained a maximum value (zero order).

In order to close the catalytic cycle it is plausible to assume the rapid reaction (3) in which the copper is reoxidized to the bivalent state. It was observed during the experiments that the brown colour in the solutions persisted for some time after all the hydrogen peroxide was decomposed (see Fig. 3). This brown colour may be due to the univalent copper which is slowly oxidized in the air. The hydroxyl radical produced by reaction (3) possibly oxidizes another univalent copper complex ion, or two of them reunite to reform hydrogen peroxide. In any case, it would be worth while to try the use of the copper citrate complex in the polymerization of slightly alkaline solutions in place of Fenton's reagent.

DEPARTMENT OF INORGANIC AND ANALYTICAL CHEMISTRY,
HEBREW UNIVERSITY, JERUSALEM, ISRAEL.

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