309. *Oxidations of Organic Compounds by Cupric Salts. Part II.*[1] *The Oxidation of Benzoin.*

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The kinetics of the oxidation of benzoin by alkaline cupric citrate resembles that for the oxidation of acetoin: the oxidation step is slower than the base-catalysed enolisation of benzoin. These results substantiate the reaction mechanisms suggested in Part I.

IN Part I[1] it was shown that the oxidations of acetoin by two alkaline cupric salts were preceded by an induction period and thereafter were of zero order with respect to [Cu^{2+}] but of first order with respect to both [acetoin] and [OH^-]. It was suggested that the acetoin was oxidised in the form of its enol anion, *E*, the rate-determining stage being, not the slow forward step of the enolisation (1), but a still slower bimolecular reaction (4) which produced a cuprous chelate complex, *C*, which was then attacked by cupric ions. Parentheses, *e.g.*, (Cu^+), (Cu^{2+}), were used in this scheme to indicate that the copper ions involved in these reactions are linked to co-ordinating groups, *e.g.*, citrate or malate: consequently reaction (4) represents the displacement of one chelating group by another.

By concluding that (*C*) and not (*E*) was attacked by cupric ions it was possible to explain the occurrence of an induction period in which cuprous ions are very slowly being formed by way of the radical structure (*R*) which, as equilibrium (8) shows, can have some cupric character.

If the enolisation (1) were the rate-determining reaction then the oxidation would promptly set in at its full velocity and the measured oxidation rate would be equal to, and not less than, the enolisation rate. We now present further evidence in support of our reaction mechanism.

The stoicheiometric oxidation of benzoin to benzil by cupric citrate in the presence of an excess of sodium carbonate has been examined in 40% aqueous dioxan and has all the kinetic features reported in Part I for the oxidation of acetoin. The oxidation has an induction period, which (compare Figs. 3 and 4 of Part I) can in part be eliminated by

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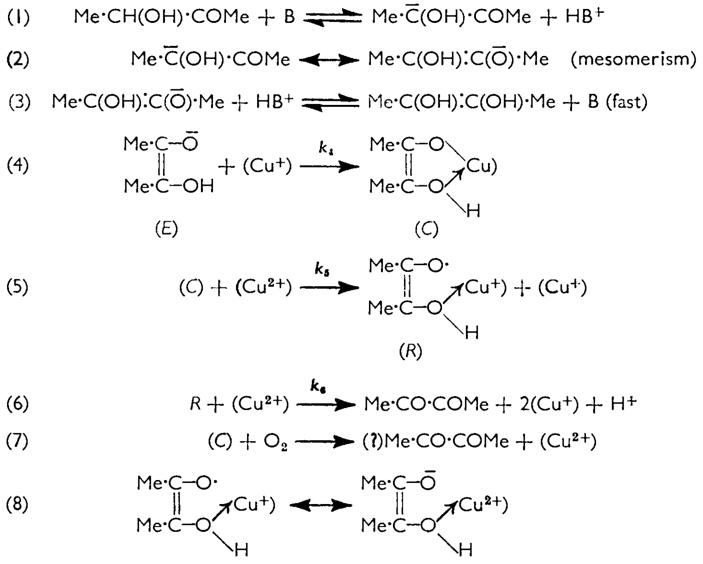
[1] Part I, Marshall and Waters, *J.*, 1960, 2392.

operating under nitrogen and thus preventing any regeneration of cupric ions by autoxidations, such as (7), of the ene-diol complex *C*. Following the induction period, the oxidation is of zero order with respect to [Cu^{2+}].



(mesomerism of the radical *R*)

Table 1 shows that the oxidation is of first order with respect to [Benzoin]; Table 2 shows that the oxidation is of first order with respect to [CO_3^{2-}] at low carbonate concentrations, but departs from this at high carbonate concentrations; and Table 3 shows that for carbonate–bicarbonate mixtures the reaction velocity depends on [OH^-] and not on [CO_3^{2-}]. These observations are in accord with those of Weissberger, Schwarze, and Mainz,[2] who oxidised benzoin in aqueous alcohol with Fehling's solution. Whereas we have regularly taken [Benzoin] in large excess over [Cu^{2+}], these workers took [Cu^{2+}] in excess and then, naturally, found that the reaction was of first order with respect to [Cu^{2+}], though independent of the initial concentration of the copper salt, for under their

TABLE 1. *Oxidation of benzoin with* Cu^{2+} *at* 30°.

[Each solution contained 0·005M-copper sulphate, 0·03M-sodium citrate, and 0·15M-potassium carbonate in 40% (v/v) dioxan–water.]

[Benzoin] (10^{-2}M)	0·75	1·00	1·25	1·50	1·75	2·00
$10^4 \times -d[Cu^{2+}]/dt$ (mole l.$^{-1}$ min.$^{-1}$)	0·84	1·08	1·60	1·86	2·16	2·35
$10^2 \times$ Rate/[Benzoin]	1·11	1·08	1·28	1·24	1·23	1·17

TABLE 2. *Dependence of oxidation rate on potassium carbonate concentration.*

(Each solution contained 0·005M-copper sulphate, 0·03M-sodium citrate, and 0·02M-benzoin.)

K_2CO_3 (10^{-2}M)	$10^4 \times -d[Cu^{2+}]/dt$ (mole l.$^{-1}$ min.$^{-1}$)	$10^3 \times$ Rate/[K_2CO_3] (min.$^{-1}$)	K_2CO_3 (10^{-2}M)	$10^4 \times -d[Cu^{2+}]/dt$ (mole l.$^{-1}$ min.$^{-1}$)	$10^3 \times$ Rate/[K_2CO_3] (min.$^{-1}$)
2·50	0·51	2·04	10·00	1·80	1·80
3·75	0·69	1·84	11·25	2·04	1·81
5·00	0·99	1·98	12·50	2·10	1·68
6·25	1·24	1·98	13·75	2·21	1·61
7·50	1·47	1·96	15·00	2·35	1·57
8·75	1·66	1·90	17·50	2·55	1·46

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[2] Weissberger, Schwarze, and Mainz, *Annalen*, 1930, **481**, 68.

conditions, since $\Delta[\text{Benzoin}] = 2\Delta[\text{Cu}^{2+}]$, $-d[\text{Benzoin}]/dt = 2\,d[\text{Cu}^{2+}]/dt$, though, as we have shown $-d[\text{Cu}^{2+}]/dt = 2k_4[E][\text{Cu}^{+}]$.

Since it has been shown by Bartlett[3] and by Bell and Longuet-Higgins[4] that the rates of bromination of ketones and of acyloins by alkaline hypobromite measure the rates of their base-catalysed enolisations, this reaction has been used to find the rate of enolisation of benzoin. It has been necessary to work with very dilute aqueous solutions of benzoin since no suitable mixed solvent inert to alkaline hypobromite could be found, but fortunately the optical density of hypobromite at 331·5 mμ is sufficiently high to allow of spectrophotometric measurements being made in 10^{-3}—10^{-4}M-solution. It was found that each equivalent of benzoin reacted with two equivalents of hypobromite to give

TABLE 3. *Effect of hydroxide-ion concentration on the rate of oxidation at constant carbonate concentration.*

(Each solution contained 0·005M-copper sulphate, 0·03M-sodium citrate, 0·15M-potassium carbonate, and 0·02M-benzoin.)

Added $NaHCO_3$ (M)	pH *	$10^3[OH^-]$	$10^4 \times -d[Cu^{2+}]/dt$ (mole l.$^{-1}$ min.$^{-1}$)	$10^2 \times \dfrac{[\text{Rate} - 0{\cdot}51\dagger \times 10^{-4}]}{[OH^-]}$
0·00	11·91	8·13	2·35	2·26
0·01	11·66	4·57	1·23	1·58
0·02	11·45	2·82	1·05	1·91
0·03	11·30	2·00	0·89	1·90
0·04	11·19	1·55	0·80	1·87
0·05	11·13	1·35	0·79	2·07

* pH measurements were made with a Doran glass electrode and pH meter. † By extrapolation.

$$\text{Ph·CH(OH)·COPh} + 2\text{HOBr} = 2\text{Ph·CO}_2\text{H} + 2\text{HBr}$$

benzoic acid (see Table 4), though the rate was, as expected, independent of the concentration of the hypobromite, and, with $[OBr^-]$ in large excess, a pseudo-first-order reaction (see Table 5) dependent on the alkalinity of the solution (Table 6).

TABLE 4. *Stoicheiometry of the bromination of benzoin.*

(The benzoin concentration was $2{\cdot}82 \times 10^{-4}$M.)

$[OBr^-] \times 10^4$: Initial	15·30	15·35	15·23	16·48	15·10
$[OBr^-] \times 10^4$: Final	9·7	9·95	9·89	10·96	9·40
$[\text{Benzoin}]/[OBr^-]$ reacted	1·99	1·91	1·89	1·96	2·02

TABLE 5. *Bromination of benzoin by alkaline hypobromite at* 30°.

(Initial [Benzoin], $2{\cdot}82 \times 10^{-4}$M; initial $[OH^-]$, $4{\cdot}6 \times 10^{-2}$N; initial $[OBr^-]$, $1{\cdot}52 \times 10^{-3}$M by titration.)

Time (min.)	O.D.*	$10^3[OBr^-]$ (M)	k_1 (min.$^{-1}$) (calc. from $t' = 1{\cdot}50$)
0	—	(1·52)	—
1·50	0·363	1·35	—
2·25	0·355	1·31	0·15
3·00	0·344	1·27	0·16
3·75	0·330	1·22	0·22
4·50	0·325	1·20	0·17
5·25	0·317	1·17	0·20
6·00	0·310	1·15	0·17
7·75	0·295	1·11	0·17
8·50	0·300	1·11	0·15
10·00	0·292	1·08	0·16
12·00	0·289	1·07	0·14
15·00	0·285	1·05	0·12
Infin.	0·267	0·98	—

Mean k_1 (graphical) = 0·177 min.$^{-1}$; $k_1/[OH^-]$ = 3·85 l. mole^{-1} min.$^{-1}$.

* O.D. = Optical density.

From our measurements the velocity constant k for the oxidation of benzoin by alkaline cupric citrate at 30° has values ranging from 1·0 to 1·3 l. mole^{-1} min.$^{-1}$ in the pH range 11—12, whilst that for the bromination in aqueous alkali at the same temperature is about

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[3] Bartlett, *J. Amer. Chem. Soc.*, 1934, **56**, 967.

[4] Bell and Longuet-Higgins, *J.*, 1946, 636.

3·8 l. mole^{-1} min.$^{-1}$. Both reactions obey the kinetic laws $-d[\text{Benzoin}]/dt = k[\text{Benzoin}] \times [OH^-]$ and thus the enolisation is the faster reaction by a factor of about 3.

The two reactions have perforce been measured in different solvents, but general theories of reaction kinetics in solution [5] and the directly relevant studies by Weissberger [6,7] of the rate of autoxidation of benzoin in mixed solvents indicate that the enolisation of benzoin would probably occur even more rapidly in a solvent less polar than water. Our measurements thus give very strong support for the view that in the reactions of acyloins with cupric salts oxidation occurs much less rapidly than does enolisation.

TABLE 6. *Rates of bromination of benzoin at different alkalinities.*

$10^2[OH^-]$ (N)	7·6	6·6	5·6	4·6	3·6
k_1 (min.$^{-1}$)	0·292	0·265	0·187	0·177	0·136
$k_1/[OH^-]$ (l. mole^{-1} min.$^{-1}$)	3·8	4·0	3·4	3·8	3·7

EXPERIMENTAL

Benzoin was repeatedly crystallised from 50% acetic acid and obtained in needles, m. p. 134—135°. Dioxan, purified as described by Vogel,[8] was stored under nitrogen. Before use it was run through activated alumina to remove any traces of peroxides. A 40% (v/v) mixture with distilled water was used in kinetic experiments, a solution of benzoin in 50% dioxan being mixed with an equal volume of alkaline cupric citrate in 30% dioxan after each had been brought separately to the temperature of the thermostat. The oxidation was followed as described in Part I.[1]

Bromination of Benzoin.—Sodium hydroxide solution (approx. N), prepared from washed pellets and air-free distilled water, was standardised against potassium hydrogen phthalate. " AnalaR " bromine (0·04 ml.) was added to 20 ml. portions of this alkali and the mixtures were diluted to 100 ml. The hypobromite concentrations of these solutions were determined iodometrically, and the free hydroxide concentrations were computed by using the equation $Br_2 + 2OH^- = Br^- + OBr^- + H_2O$. Benzoin (18·7 mg.) was dissolved by shaking it in water (200 ml.), and the clear solution was diluted to 250 ml. Freshly prepared benzoin and hypobromite solutions were rapidly mixed at 30° and transferred to a 1 cm. silica cell that fitted an Adkins thermostatic cell-holder, set to 30°, inserted into a Unicam S.P. 500 spectrometer. The change in absorption of the $[OBr^-]$ ion was followed at 330 mμ wavelength by using a 0·165 mm. spectrometer slit. Under these conditions $\varepsilon_{\text{max.}}$ for $[OBr^-]$ was found to be 270. The optical density of reacting solutions decreased rapidly with time (see Table 5 for an example) but reached an almost constant value after 30—60 min. The stoicheiometry of the reaction (Table 4) was determined from the overall change of optical density. A spectroscopic test showed that the final solution contained benzoic acid and neither benzil nor benzilic acid.

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[5] Frost and Pearson, " Kinetics and Mechanism," Chap. 7, Wiley & Sons, New York, 1953.

[6] Weissberger, Mainz, and Strasser, *Ber.*, 1929, **62**, 112.

[7] Weissberger and Bach, *J.*, 1935, 226.

[8] Vogel " Text Book of Practical Organic Chemistry," Longmans, Green & Co., London, 3rd edn. 1956, p. 177.