Tetrahedron, 1965, Vol. 21, pp. 2791 to 2797. Pergamon Press Ltd. Printed in Northern Ireland

KINETICS OF THE AMINE–CUPROUS CHLORIDE-CATALYSED AUTOXIDATION OF *o*-CRESOL[1]

Y. OGATA and T. MORIMOTO
Department of Applied Chemistry, Faculty of Engineering, Nagoya University
Chikusa-ku, Nagoya, Japan

(*Received* 1 *March* 1965; *in revised form* 29 *April* 1965)

Abstract—The autoxidation of *o*-cresol catalysed by amine–cuprous chloride complex in benzene or chlorobenzene has been studied kinetically by estimating the consumption of oxygen. According to the IR spectrum the product is a kind of polyether. One mole of oxygen is absorbed by 2 moles of *o*-cresol on completion of the reaction. The rate is expressed as: $-(\mathrm{d}p/\mathrm{d}t) = k_2[o\text{-cresol}]p^{1/2}$ at the oxygen pressure (p) below 400 mm, while $-(\mathrm{d}p/\mathrm{d}t) = k_3[o\text{-cresol}]$ at the oxygen pressure over 400 mm. A probable mechanism is suggested, which involves a rate-determining attack of the autoxidized amine–cuprous chloride complex.

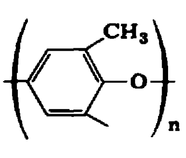
IT IS well-known that the amine–cuprous salt complex is an excellent catalyst for the autoxidation of anilines[2] and phenols.[3,4] Thus far, very little is known on a similar autoxidation of *o*-cresol and in this communication, the kinetics and mechanism of the amine–cuprous ion-catalysed autoxidation of *o*-cresol has been investigated.

The reaction product is an amorphous solid of molecular weight 1300–1600, has a characteristic IR peak of an ether linkage, and is probably polyethers (I) and (II) as in the case of 2,6-dimethylphenol.

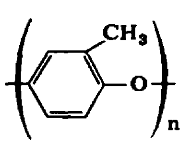
In the kinetic experiments, various initial oxygen pressures, catalyst concentrations and solvents were used in order to obtain information on the mechanism of the autoxidation.

RESULTS AND DISCUSSION

Reaction products criterion. When oxygen gas was introduced into a benzene solution of *o*-cresol in the presence of pyridine and cuprous chloride, a brown solid (70–76% of the initial wt. of *o*-cresol) was obtained, which was soluble in benzene, toluene, carbon disulphide and chloroform and difficultly soluble in water, alcohols and carbon tetrachloride. The IR spectrum of the carbon disulphide solution showed peaks of an ether linkage (1190 and 1230 cm^{-1}). The mol. wt. calculated from the cryoscopic method with a benzene solution was 1300–1600. Therefore, one of the main



I or $(C_6H_2CH_3.O)_n$



II or $(C_6H_3CH_3.O)_n$

---

[1] Contribution No. 74.

[2] K. Kinoshita, *Bull. Chem. Soc. Japan* **32**, 776, 780 (1959).

[3] A. S. Hay, H. S. Blanchard, G. F. Endres and J. W. Eustance, *J. Amer. Chem. Soc.* **81**, 6335 (1959); A. S. Hay, *J. Polymer Sci.* **58**, 581 (1962).

[4] E. Ochiai, *Tetrahedron* **20**, 1831 (1964).

components of the product is probably a polyether (I). As the elemental analysis did not agree with the theoretical, less oxygenated polyethers e.g., (II) may be present as also indicated by presence of three neighbouring hydrogen atoms (IR peak at 770 cm^{-1}) and two neighbouring hydrogen atoms (815 cm^{-1}).

Absorption of oxygen by the catalyst alone. The catalyst, amine–cuprous complex, itself absorbs oxygen, but the rate is so fast that it becomes unappreciable after ca. 4 min and was measured at 1 hr from the start.

The amount of absorbed oxygen increases with increasing concentration of pyridine at the constant [CuCl] until [pyridine] reaches to 0·052 M. The amount of absorbed oxygen also increases with increasing [CuCl] at constant [pyridine] (Fig. 1). The slopes of lines in Fig. 1 give the value of 1·66 for [pyridine]/[O_2 absorbed] and 3·44 for [CuCl]/[O_2 absorbed] and thence [CuCl]/[pyridine] = 2·07. This value shows that the main catalysing complex should have the composition of [CuCl]: [pyridine] = 2:1.

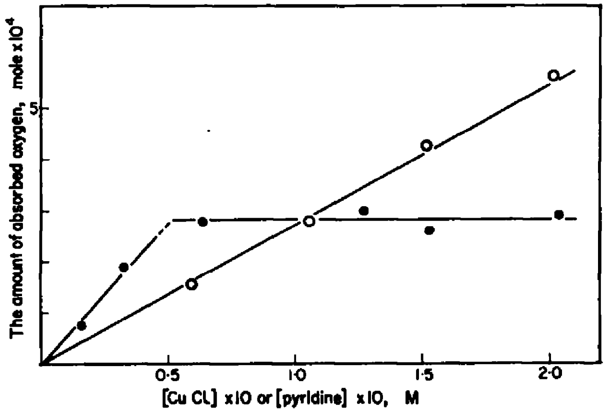


Fig. 1. Dependency of the total consumption of oxygen on the concentration of CuCl or pyridine.
●: constant [CuCl], ○: constant [C_5H_5N]

The absorption of oxygen by the catalyst, however, is so small that it may be neglected in comparison with that of *o*-cresol, e.g., the 1–15 × 10^{-5} mole CuCl complex absorbs only 0·271 – 4·35 × 10^{-5} mole of oxygen, while *o*-cresol absorbs 0·5 – 2 × 10^{-3} mole of oxygen. Further, the absorption by catalyst is unappreciable at early stages, hence it can be eliminated in kinetic runs.

Reaction rates. The ratio of the amount of reacted cresol and reacted oxygen was 1·90 in average on completion of the reaction (ca. 23 hr), i.e., 2 moles of cresol reacted with 1 mole of oxygen as observed in the case of 2,6-dimethylphenol.[5] Since the change of the partial pressure of oxygen does not affect the ratio (Table 1), the reaction is not reversible.

$$2n\, o\text{-}CH_3C_6H_4OH + nO_2 \rightarrow 2[o\text{-}CH_3C_6H_3(O)^-]_n + 2n\, H_2O \text{ etc.} \qquad (1)$$

The rates were measured in the presence of anhydrous magnesium sulphate to eliminate the water formed, which inhibits the reaction.

---

[5] G. F. Endres, A. S. Hay and J. W. Eustance, *J. Org. Chem.* **28**, 1300 (1963).

TABLE 1. RELATIONSHIP BETWEEN THE REACTED AMOUNTS OF OXYGEN AND *o*-CRESOL AT 35° IN BENZENE IN THE PRESENCE OF PYRIDINE (0·2542 M) AND CuCl (5·05 × 10^{-3} M)

o-$CH_3C_6H_4OH$ reacted (x), 10^3 × mole	O_2 absorbed (y), 10^3 × mole	x/y	Initial pressure O_2, mm Hg
1·852	0·924	2·00	202
1·852	0·938	1·97	300
1·852	1·026	1·81	400
1·852	1·003	1·85	501
0·926	0·505	1·84	202
1·482	0·758	1·95	200
	Av.	1·90	

TABLE 2. 1·5th-ORDER RATE CONSTANTS FOR THE AUTOXIDATION OF *o*-CRESOL AT THE CONSTANT CONCENTRATION OF CATALYST COMPLEX, [PYRIDINE] = 0·2542 M AND [CuCl] = 5·05 × 10^{-3} M

[*o*-$CH_3C_6H_4OH$] M	O_2 pressure mm Hg	k mm $Hg^{1/2}$ M^{-1} min^{-1}
0·1602	200	3·45
0·1852	202	3·35
0·2778	210	3·67
0·3704	202	3·84
0·1852	300	3·97
0·1852	100	3·65
		Av. 3·66
		mm Hg M^{-1} min^{-1}
0·1852	400	9·03[a]
0·1852	500	9·03[a]
0·1852	600	9·03[a]

[a] The same absorption curve.

At constant concentrations of pyridine and CuCl and at the oxygen pressure of 100–400 mm, the rate was expressed as:

$$-\frac{dp}{dt} = k_2[\mathrm{CrlH}]p^{1/2} \tag{2}$$

Here, [CrlH] is the concentration of *o*-cresol and p is the partial pressure of oxygen. On the other hand, at the oxygen pressure over 400 mm, the rate was independent on the oxygen pressure.

$$-\frac{dp}{dt} = k_3[\mathrm{CrlH}] \tag{3}$$

As shown in Table 2, the constant k_2 does not depend on the variation of the initial concentration of cresol or the initial pressure of oxygen, while the constant k_3 does not vary with varying [O_2].

Fig. 2 shows the variation of the constant k_2 with changing concentration of CuCl; the obtained straight line passing origin in the Fig. gives the rate equation.

$$-\frac{dp}{dt} = k_4[\mathrm{CrlH}]p^{1/2}[\mathrm{CuCl}] \tag{4}$$

Fig. 3 illustrates the effects of the variation of concentration of pyridine on the rate constant with constant [CuCl], [*o*-cresol] and *p*. As shown in the Fig. the rate constant increases linearly until the ratio of [pyridine]/[CuCl] reaches 10 and then the increase is slowed down and the constant decreases gradually at the ratio over 50.

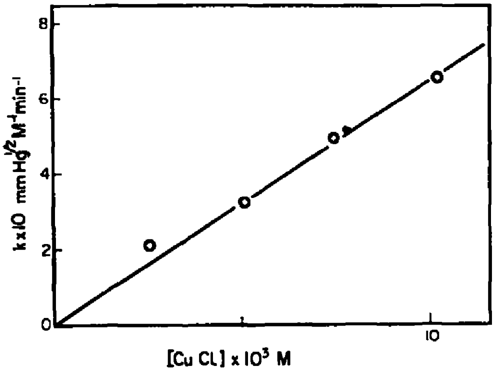


FIG. 2. Variation of rate constant k_2 in benzene at 35° with concentration of CuCl at constant concentrations of [pyridine] = 0·5102 M and [*o*-cresol] = 0·1835 M and constant oxygen pressure (p = 200 mm).

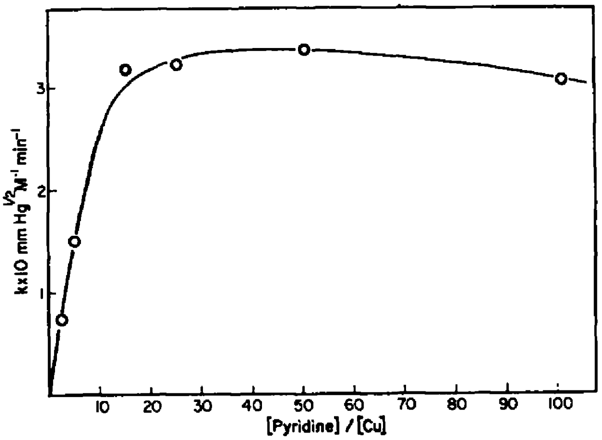


FIG. 3. Variation of rate constant k_2 in benzene at 35° with concentration of pyridine at constant concentrations of [CuCl] = 5·05 10^{-3} M and [*o*-cresol] = 0·1835 M and constant oxygen pressure (p = 200 mm).

The same tendency has been observed with 2,6-dimethylphenol oxidation.[5] These phenomena are explicable (i) by the increase in the concentration of more reactive *o*-cresol anion (in Eqn. 5) with increasing concentration of pyridine, or (ii) the increased activity of CuCl by complexing with pyridine.

Since the amount of pyridine is small compared with solvent, the increase is not the result of an increase in dielectric constant. The use of chlorobenzene (dielectric constant, 5·62 at 25°)[6] instead of benzene (2·4 at 20°)[6] results in only a 1·81 fold increase in the rate constant.

---

[6] J. A. Riddick and E. E. Toops, Jr., *Organic Solvent*, in *Technique of Organic Chemistry* (Edited by A. Weissberger) Vol. III. Interscience, New York, N.Y. (1955).

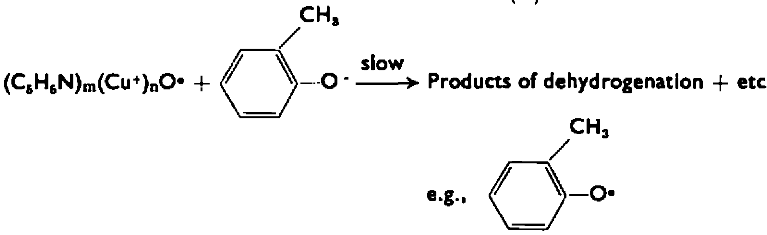
Reaction mechanism. The above results suggest a mechanism involving one-electron abstraction by the autoxidized amine–cuprous complex.

$$o\text{-}CH_3C_6H_4OH + C_5H_5N \rightleftharpoons o\text{-}CH_3C_6H_4O^- + C_5H_5NH^+ \qquad (5)$$

$$mC_5H_5N + nCu^+ \overset{\text{fast}}{\rightleftharpoons} \underset{\text{(III)}}{(C_5H_5N)_m(Cu^+)_n} \qquad (6)$$

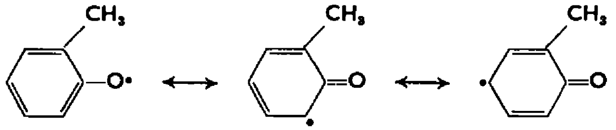
$$2(C_5H_5N)_m(Cu^+)_n + O_2 \overset{\text{fast}}{\rightleftharpoons} \underset{\text{(IV)}}{[(C_5H_5N)_m(Cu^+)_n]_2O_2} \qquad (7)$$

$$[(C_5H_5N)_m(Cu)_n{}^+]_2O_2 \overset{\text{fast}}{\rightleftharpoons} \underset{\text{(V)}}{2(C_5H_5N)_m(Cu^+)_nO\bullet} \qquad (8)$$



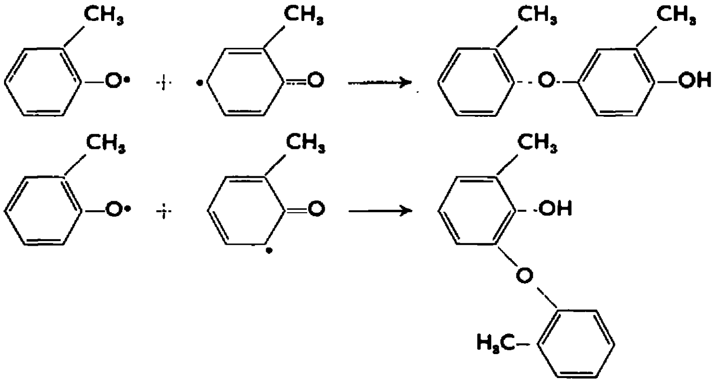
(9)

The formed *o*-methylphenoxy radical may have canonical forms:



(10)

and they may further react each other in the following scheme.



(11)

Equilibria 6, 7 and 8 give the following Eqs, where *K*'s are equilibrium constants of subscripted steps.

$$[\mathrm{III}] = K_6[C_5H_5N]^m[Cu^+]^n \qquad (12)$$

$$[\mathrm{IV}] = K_6{}^2K_7[O_2][C_5H_5N]^{2m}[Cu^+]^{2n} \qquad (13)$$

$$[\mathrm{V}] = K_6K_7^{1/2}K_8^{1/2}[O_2]^{1/2}[C_5H_5N]^m[Cu^+]^n \qquad (14)$$

The stoichiometric concentration of cuprous chloride is expressed as:

$$[Cu^+]_s = [Cu^+] + n[\mathrm{III}] + 2n[\mathrm{IV}] + n[\mathrm{V}] \qquad (15)$$

When $[Cu^+]$ and [IV] is negligible

$$[Cu^+]_s = n([III] + [V]) = nK_6[C_5H_5N]^m[Cu^+]^n(1 + K_7^{1/2}K_8^{1/2}[O_2]^{1/2}) \quad (16)$$

Therefore,

$$[V] = \frac{1}{n} K_7^{1/2}K_8^{1/2} \frac{[Cu^+]_s[O_2]^{1/2}}{1 + K_7^{1/2}K_8^{1/2}[O_2]^{1/2}} \quad (17)$$

$$-\frac{d[CrlH]}{dt} = -\frac{1}{2}\frac{dp}{dt} = \frac{1}{n} k_9K_7^{1/2}K_8^{1/2} \frac{[Cu^+]_s[O_2]^{1/2}[Crl^-]}{1 + K_7^{1/2}K_8^{1/2}[O_2]^{1/2}} \quad (18)$$

Here $[Crl^-]$ is the concentration of *o*-cresol anion.
If p is small, $K_7^{1/2}K_8^{1/2}[O_2]^{1/2} \ll 1$, hence

$$-\frac{1}{2}\frac{dp}{dt} = \frac{1}{n} k_9K_7^{1/2}K_8^{1/2}[Cu^+]_s[O_2]^{1/2}[Crl^-] \quad (19)$$

If p is large, $K_7^{1/2}K_8^{1/2}[O_2]^{1/2} \gg 1$, hence

$$-\frac{1}{2}\frac{dp}{dt} = \frac{1}{n} k_9[Cu^+]_s[Crl^-] \quad (20)$$

These Eqs. 19 and 20 agree with the observed Eqs. 2 and 3, respectively.

EXPERIMENTAL

Materials. *o*-Cresol (b.p. 186·5–188°), pyridine (b.p. 133–133·5°) and benzene (b.p. 80·0–80·2) was purified by rectification. Cuprous chloride was prepared by the reaction of cupric sulphate and sodium sulphite[7]; the precipitate was filtered through a sintered glass funnel, washed with water, acetic acid and ether successively, and then dried *in vacuo*.

Reaction product. A benzene solution (50 ml) of pyridine (5 ml) and CuCl (1·0 g) was stirred at room temp for 30 min, added to *o*-cresol (5·03 g) and stirred for another 28 hr. The reaction mixture was added to a 10% HCl methanolic solution. The *brown precipitate* was filtered off, washed with a small amount of MeOH and dried *in vacuo* at 60°. The yield was 3·59 g (71·6%), m.p. 150–210°. The dissolution of the product in $CHCl_3$ followed by reprecipitation with MeOH was repeated several times but the purified product showed the same m.p. 150–210°. (Found: C, 78·25; H, 5·39. $(C_7H_5O)n$ requires: C, 79·99; H, 4·79 and $(C_7H_6O)n$ requires: C, 79·22; H, 5·70%.)

The product was dissolved in $CHCl_3$ or CS_2 and its IR spectrum recorded by Shimadzu IR-27B spectrophotometer using a NaCl cell. The spectrum shows characteristic peaks for an ether linkage (1190, 1230 cm^{-1}) but no peak for OH (3200–3600 cm^{-1}).

Rate measurements. The apparatus was the same as that used for the autoxidation of phenylhydroxylamine.[8] Cuprous chloride, magnesium sulphate, a benzene solution of *o*-cresol (10 ml) and pyridine were placed in one flask of the apparatus and 10 ml of the same solution in the other. After evacuation of the apparatus, N_2 was introduced and the same procedure was repeated several times. The apparatus was brought to temp equilibrium in a thermostat and then pure O_2 was introduced to start the reaction with magnetic stirring.

The absorption of oxygen is almost complete after 6 hr, but the reaction was continued for 23 hr and then the amount of reacted oxygen estimated.

The rate, $-dp/dt$, was determined from the tangent of the plots of O_2 press vs. time and the consumed concentrations of *o*-cresol were estimated by the following equation.

$$\Delta[o\text{-cresol}] = (1000/10)2\Delta n = \left(\frac{200V}{RT}\right)\Delta p$$

---

[7] C. S. Marvel and S. M. McElvain, *Organic Synthesis* Coll. Vol. I; p. 170, J. Wiley, New York, N.Y. (1948).

[8] Y. Ogata, Y. Sawaki, J. Mibae and T. Morimoto, *J. Amer. Chem. Soc.* **86**, 3854 (1964).

Here Δ[ ] is the consumed concentration of *o*-cresol, Δn is the number of moles of consumed O_2, V is the whole volume of gas in the reaction vessel, R is the gas constant and T is the absolute temp.

The measured rate constants in a typical run, for example, were:

time in min.	30	60	120	240
$k \times 10$ mm $Hg^{1/2}$ M^{-1} min^{-1}	3·28	3·41	3·24	3·47

Acknowledgment—The authors wish to thank Mr. Kazuo Matsuyama for his helpful assistance in performing experiments.