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Basic Copper(II)-Catalyzed Halogen Displacement Polymerization of 2,4,6-Trihalogenophenols

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The basic copper(II) complex-catalyzed halogen displacement polymerization of 2,4,6-trihalogenophenol was studied at the boiling point temperature of methanol under various reaction conditions. Using sodium methoxide as a base, the order of 2,4,6-trihalogenophenol reactivities is as follows: 2,4,6-triiodo- > 2,4,6-tribromo- > 2,4,6-trichlorophenol. This order is the same as the one obtained when potassium hydroxide is used as a base [Tsuruya, S., Okumoto, K., and Yoshimatsu, T., *J. Polym. Sci., Polym. Chem. Ed.* 16, 379 (1978)]. A small amount of H_2O was found to be effective in the present reaction though too much H_2O acts inversely. Of the copper(II) compounds studied, copper(II) halides were found to be more active than copper(II) nitrate, or copper(II) acetylacetonate. The reactions with basic copper(II) complexes isolated show that the copper(II) complex prepared at a mole ratio of copper(II) chloride/sodium methoxide = $\frac{1}{2}$ has maximum activity. The kinetics of the halogen displacement polymerization of 2,4,6-tribromophenol are first order in 2,4,6-tribromophenol and sodium methoxide concentrations, respectively. On the other hand, the rate of polymer formation is independent of copper(II) chloride concentration for the higher concentrations, and first order for lower copper(II) chloride concentrations. The rate law obtained empirically is consistent with a reaction scheme in which a copper(II)-phenoxo complex is formed as a reaction intermediate. The rate-determining step is between 2,4,6-tribromophenol and sodium methoxide for high concentrations of copper(II) chloride, and between 2,4,6-tribromophenolate and basic copper(II) complex for low concentrations of copper(II) chloride.

INTRODUCTION

Copper and its compounds are important as reagents or catalysts in organic reactions (*1*). It is well known that copper, or copper compounds catalyze substitution reactions of aryl halides with a nucleophile, i.e., $ArHal + X^- \rightarrow ArX + Hal^-$ (or HHal). In these reactions, alkali metal alkoxides, phenoxides, halides, cyanides, or other salts may provide the anion X^-, while amines and phenols are the main examples of nonionic nucleophiles, HX.

Due to an interest in the remarkably facile polymerization of trihalophenols reported many years ago by Hunter (*2*), a variety of oxidizing agents such as iodine, ferricyanide, lead dioxide, or stable phenoxy radical for the conversion of salt of halogenophenols to amorphous polymers have been discussed (*3*). In order to obtaining a polymer of more regular structure and higher molecular weight, Price and his group have investigated the polymerization of 4-halo-2,6-dimethylphenol with many oxidants (*4*).

In previous papers (*5*), we have reported the halogen displacement polymerization of halogenophenol catalyzed with heterogeneous basic copper complexes. The formation and the decomposition of the

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corresponding phenoxo–copper(II) complexes were suggested to be intermediate steps in this reaction. A series of bis(phenoxo)bis(pyridine) copper(II) complexes were prepared and characterized by Blachard *et al.* (*6*) using a variety of halogen-substituted phenols. Harrod (*7*) has also prepared a series of phenoxo complexes of copper(II) containing a variety of halophenoxo and amine ligands and studied the thermal stability of the complexes. We have prepared terakis(trichlorophenoxo)-μ-bis(hexamethylphosphoramide) dicopper(II) and studied the decomposition of this complex in the solid state (*8*). Harrod and Carr (*9*) have presented the results of a study on the solution decomposition of bis(2,4,6-trichlorophenoxo)bis(pyridine) copper(II). Such copper(II)-phenoxo complexes are of considerable chemical interest because of the important industrial and biological roles of copper (II) in the selective catalytic oxidation of phenols.

Although a great number of studies have been reported on the halogen displacement polymerization of halogenophenol, very little is known of the kinetics. In this paper we present the kinetic data on halogen displacement polymerization of halogenophenol under various reaction conditions. We also wish to report the effects of the catalyst composition, concentration of copper(II) chloride, and H_2O on reactivity.

EXPERIMENTAL

Ir spectra were obtained using KBr tablets and were recorded on a Hitachi Model 215. ESR spectra were recorded on a JEOL-3BS spectrometer system with 100-KHz field modulation. The magnetic field was calibrated with DPPH. The elementary analyses were conducted at Elemental Analysis Center of Kyoto University.

Materials. 2,4,6-Trihalogenophenols were recrystallized from the mixed solvent of methanol and *n*-hexane. Copper(II) chloride dihydrate was of guaranteed reagent grade. Anhydrous copper(II) chloride was prepared by heating copper(II) chloride $\cdot 2H_2O$ at 110 to 130°C for 2 hr under vacuum. Methanol was dried by refluxing it over magnesium metal and distilled. Sodium methoxide was purchased commercially as a 28% methanolic solution. Other copper(II) salts, potassium hydroxide, and sodium hydroxide were guaranteed reagent grade and used without further purifications. Basic copper(II) complexes were prepared as follows: The desired copper(II) chloride was dissolved in a 40 ml of methanol. A 10-ml methanolic solution of sodium methoxide was added into the resultant homogeneous copper(II) chloride solution under stirring. The resultant precipitate was filtered, washed with methanol, and dried under vacuum overnight.

Method. The halogen displacement polymerization reaction was studied at 64.5°C (boiling point of methanol). The reactor was a 50-ml round-bottomed flask, fitted with condensor, mechanical stirrer, and gas inlet tube. The desired copper(II) chloride was dissolved in methanol, and a methanolic solution of sodium methoxide was added to the resultant homogeneous copper(II) solution. A methanolic solution of 2,4,6-trihalogenophenol was added into the catalytic system. The reaction mixture was stirred for the prescribed time under an oxygen atmosphere. The precipitate was filtered off, washed with methanol containing conc. HCl, and dried under vacuum overnight. The products obtained were identified as poly(dihalogenophenylene oxides) by means of their ir spectra and elementary analyses.

Anal. Calcd. for $C_6H_2Cl_2O$: C, 44.76; H, 1.25; Cl, 44.05. Found: C, 44.63; H, 1.36; Cl, 42.59.

Anal. Calcd. for $C_6H_2Br_2O$: C, 28.84; H, 0.81; Br, 63.96. Found: C, 28.95; H, 0.93; Br, 63.68.

Anal. Calcd. for $C_6H_2I_2O$: C, 20.95; H, 0.59; I, 73.81. Found: C, 20.67; H, 0.75; I, 74.97.

RESULTS

Halogen Displacement Polymerization of 2,4,6-Trihalogenophenol with Basic Copper(II) Catalyst

In a previous paper (*5*b), we reported the effect of KOH concentration on polymer yield, in which 2,4,6-triiodophenol was most active reagent. In this study, sodium methoxide was used as a base in place of KOH. Figure 1 demonstrates the effect of sodium methoxide added on polymer yield under a constant copper(II) chloride concentration. All the corresponding polymer yields increased with an increase of sodium methoxide in the range of the present reaction conditions. The reactivity order of 2,4,6-trihalogenophenols was iodo- > bromo- >chloro-substituted phenol. This order is consistent with the result obtained when KOH is used as a base (*5*b), though 2,4,6-tribromophenol has a larger activity than the corresponding iodophenol in the range of low concentration of sodium methoxide as shown in Fig. 1.

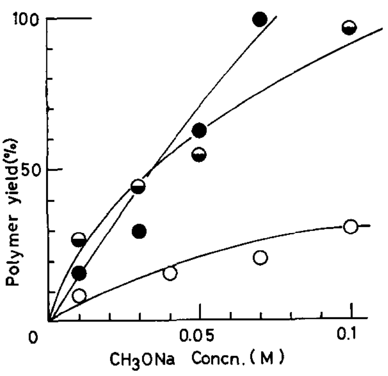


Fig. 1. Effect of sodium methoxide on polymer yield. Halogenophenol, 0.1 mole/liter; $CuCl_2 \cdot 2H_2O$, 0.1 mole/liter; reaction time, 30 min; reaction temperature, 64.5°C; solvent, 40 ml of methanol; O_2 atmosphere; ○, 2,4,6-trichlorophenol; ◒, 2,4,6-tribromophenol; ●, 2,4,6-triiodophenol.

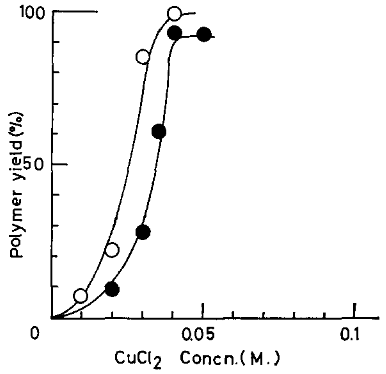


Fig. 2. Effect of copper(II) chloride concentration on polymer yield. 2,4,6-Tribromophenol, 0.1 mole/liter; CH_3ONa, 0.1 mole/liter; reaction time, 30 min; reaction temperature, 64.5°C; solvent, 40 ml of methanol; O_2 atmosphere; ○, $CuCl_2 \cdot 2H_2O$; ●, $CuCl_2$.

Figure 2 shows the effect of copper(II) chloride concentration under a constant sodium methoxide concentration on polymer yield, in which both dihydrated and anhydrous copper(II) chlorides are used. As evidenced from Fig. 2, dihydrated copper(II) chloride is more active than anhydrous copper(II) chloride. 2,4,6-Tribromophenol reacts almost quantitatively to produce the corresponding polymer at about 0.05 *M* dihydrated copper(II) chloride. The result obtained above indicates that a small amount of H_2O is

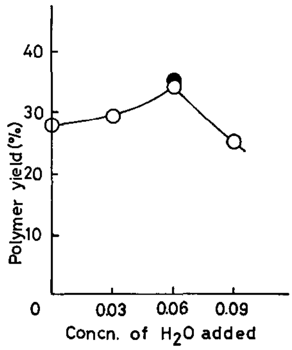


Fig. 3. Effect of H_2O addition on polymer yield. 2,4,6-Tribromophenol, 0.1 mole/liter; $CuCl_2$, 0.03 mole/liter; CH_3ONa, 0.03 mole/liter; reaction time, 30 min; reaction temperature, 64.5°C; solvent, 40 ml of methanol; O_2 atmosphere; ●, polymer yield with $CuCl_2 \cdot 2H_2O$ (0.03 mole/liter).

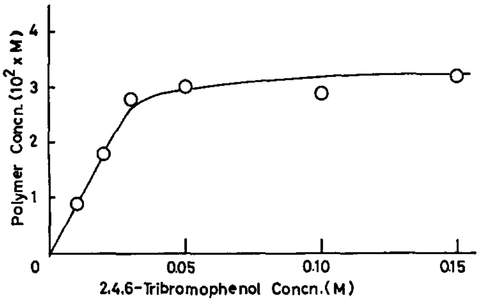


FIG. 4. Effect of 2,4,6-tribromophenol concentration on polymer yield. Reactant, 2,4,6-tribromophenol; $CuCl_2$, 0.03 mole/liter; CH_3ONa, 0.03 mole/liter; reaction time, 30 min; reaction temperature, 64.5°C; solvent, 40 ml of methanol; O_2 atmosphere.

necessary to promote the activity of halogen displacement polymerization of halogenophenol.

Because dihydrated copper(II) chloride is more active than anhydrous (as shown in Fig. 2), the effect of H_2O addition on polymer yield was studied as shown in Fig. 3. At first, the polymer yield increases gradually with the increase of H_2O, and maximum polymer yield is obtained at the H_2O concentration corresponded to dihydrated copper(II) chloride. However, further addition of H_2O causes the polymer yield to decrease appreciably.

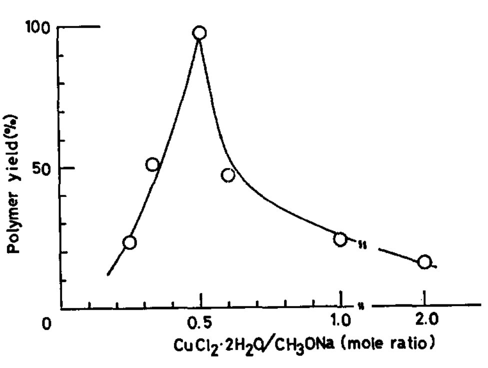


FIG. 5. Effect of $CuCl_2 \cdot 2H_2O/CH_3ONa$ mole ratio of isolated basic copper(II) complexes on polymer yield. 2,4,6-Tribromophenol, 0.1 mole/liter; basic copper(II) complex, 0.25 g; reaction time, 1 hr; reaction temperature, 64.5°C; solvent, 40 ml of methanol; O_2 atmosphere.

The effect of 2,4,6-tribromophenol concentration on polymer yield is shown in Fig. 4. The polymer yield increases with increasing concentration of 2,4,6-tribromophenol up to about 0.03 *M*, but at more than 0.03 *M* the polymer yield tended levels off under these reaction conditions.

Some basic copper(II) complexes were isolated in order to study the reactivity of halogen displacement polymerization of 2,4,6-tribromophenol. Figure 5 shows the polymer yield with some isolated basic copper(II) complexes. The yield increases with the increase of the mole ratio of copper(II) chloride$\cdot 2H_2O/CH_3ONa$ up to about 0.5. The maximum value of polymer yield is obtained with the catalyst corresponding to this ratio. Although the compositions of the catalysts isolated are ambiguous because we did not perform the elementary analyses, it is apparent that the mole ratio of copper(II) chloride/CH_3ONa is a very important factor in the catalytic activity.

Table 1 shows the effect of the copper(II) compounds on polymer yield. Copper(II) bromide is the most active of the copper(II) salts investigated here. Copper(II) chelate complexes such as copper(II) acetylacetonate are considered to be rather inactive in the present reaction. It may be considered that halide anions are necessary,

TABLE 1

Effect of Copper(II) Compounds on Polymer Yields[a]

Copper(II) compound	Polymer yield (%)
$CuCl_2 \cdot 2H_2O$	54
$CuBr_2$	65
$Cu(NO_3)_2 \cdot 3H_2O$	8
$Cu(CH_3COCHCOCH_3)_2$	7

[a] 2,4,6-Tribromophenol, 0.1 mole/liter; copper(II) compound, 0.05 mole/liter; sodium methoxide, 0.05 mole/liter; reaction time, 30 min; reaction temperature, 64.5°C; solvent, 40 ml of methanol; O_2 atmosphere.

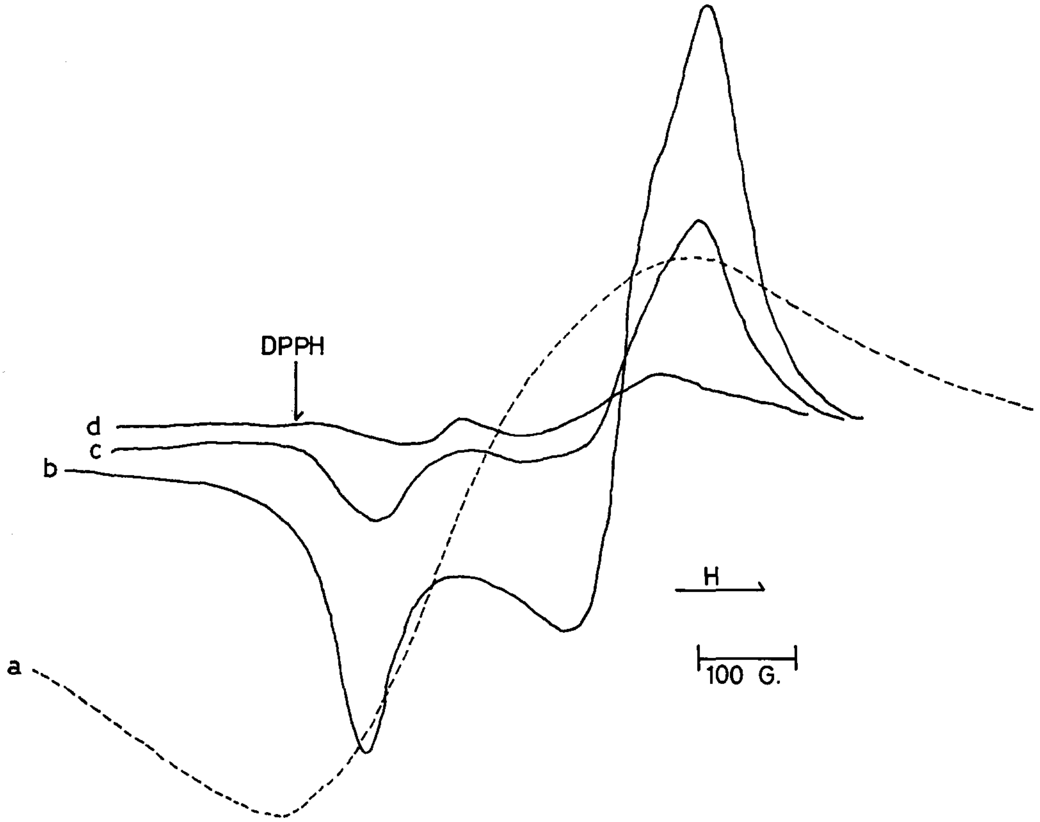


FIG. 6. ESR spectra of basic copper(II) complexes isolated. a, $CuCl_2$; $CuCl_2 \cdot 2H_2O/CH_3ONa$ at mole ratios of: b, 2/1; c, 1/1; d, 3/4.

though the reason is not certain at this stage.

ESR Spectra of the Basic Copper(II) Catalysts Isolated

Some ESR spectra of the basic copper(II) catalysts isolated were measured in order to shed light on the state of the copper ion and the environment around the copper ion. Figure 6 shows the ESR spectra of copper(II) chloride/sodium methoxide at mole ratios of 2/1, 1/1, and 3/4, in addition to copper(II) chloride·$2H_2O$ itself. The ESR spectrum of $CuCl_2 \cdot 2H_2O$ is a broad symmetrical absorption. However, the ESR spectra of the basic copper(II) complexes isolated are typical axially symmetric absorption spectra as shown in Fig. 6. Increasing the sodium methoxide amount results in a decrease in the ESR absorption intensity based on Cu(II) ion.

Kinetics

A number of factors affecting the rate of halogen displacement of halogenophenol were studied using 2,4,6-tribromophenol as the halogenophenol. The time dependences of polymer yields were measured under a variety of reaction conditions. Figure 7a shows the plots of polymer yield vs reaction time for varying 2,4,6-tribromophenol concentrations at constant copper (II) chloride and sodium methoxide concentrations. The dependence of polymer yield on time for varying sodium methoxide concentrations is shown in Fig. 7b. Similar plots were obtained for the variation of copper(II) chloride concentrations. From these re-

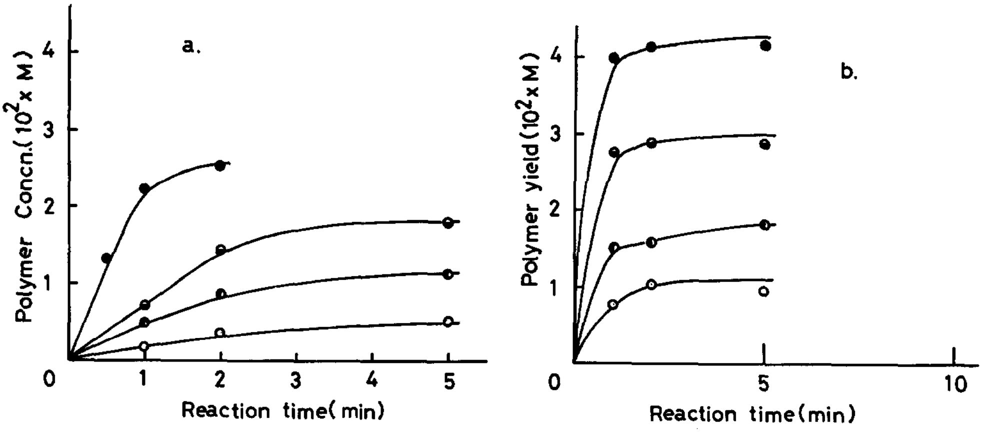


FIG. 7. Plots of polymer yield vs reaction time. (a) $CuCl_2$, 0.03 mole/liter; CH_3ONa, 0.03 mole/liter; solvent, 40 ml of methanol; reaction temperature, 64.5°C; concentration of 2,4,6-tribromophenol: ○, 0.01, ◐, 0.02; , ◒0.03; and ●, 0.05 mole/liter. (b) 2,4,6-Tribromophenol, 0.1 mole/liter; $CuCl_2$, 0.03 mole/liter; solvent, 40 ml of methanol; reaction temperature, 64.5°C; concentration of CH_3ONa: ○, 0.01; ◐, 0.02; ◒, 0.03; and ●, 0.04 mole/liter.

sults, it is evident that the polymer yields level off at a relatively early reaction stage. The log–log plots of initial rates vs 2,4,6-tribromophenol and sodium methoxide concentrations are shown in Figs. 8a and b, respectively. Both plots show linear relationships with slopes of 1. These results mean the initial rate is first-order dependent on both the concentration of 2,4,6-tribromophenol and sodium methoxide. The initial rate vs copper(II) chloride concentration is shown in Fig. 8c. As evidenced from Fig. 8c, the plots show a folded straight line, in which at low-level copper(II) chloride concentrations the slope of this straight line is 1 and at high levels of copper(II) chloride the slope is zero. From the results obtained above, the rate equations of polymer formation are represented as follows:

$$r = k\cdot[\text{2,4,6-tribromophenol}]^1 \times [CH_3ONa]^1[CuCl_2]^0,$$

$$CuCl_2 > 0.02 \text{ mole/liter}$$

$$r = k'\cdot[\text{2,4,6-tribromophenol}]^1 \times [CH_3ONa]^1[CuCl_2]^1,$$

$$CuCl_2 < 0.02 \text{ mole/liter.}$$

DISCUSSION

It was confirmed that the order of reactivity of 2,4,6-trihalogenophenol is iodo >bromo > chloro, which is consistent with that of the displacement reaction of aryl halides with cuprous salt, ArI > ArBr >ArCl (*1*). A similar trend of reactivity is also obtained when potassium hydroxide is used in the place of sodium methoxide (*5*b).

It is interesting to note that dihydrated copper(II) chloride is more active than the corresponding anhydride as is shown in Fig. 2. It is well known (*10*) that a small amount of H_2O formed as a reaction product acts as an inhibitor for the oxidative coupling polymerization of 2,6-dimethylphenol. However, in the present reaction H_2O addition to the extent of two H_2O molecules per Cu(II) gives a maximum polymer yield as shown in Fig. 3. Although it is difficult to clarify the function of H_2O at the present stage, a small amount of H_2O may act as a reservoir for hydrogen halide formed during reaction. In this case, it may be possible to prevent the basic copper(II) catalyst from being decomposed by the

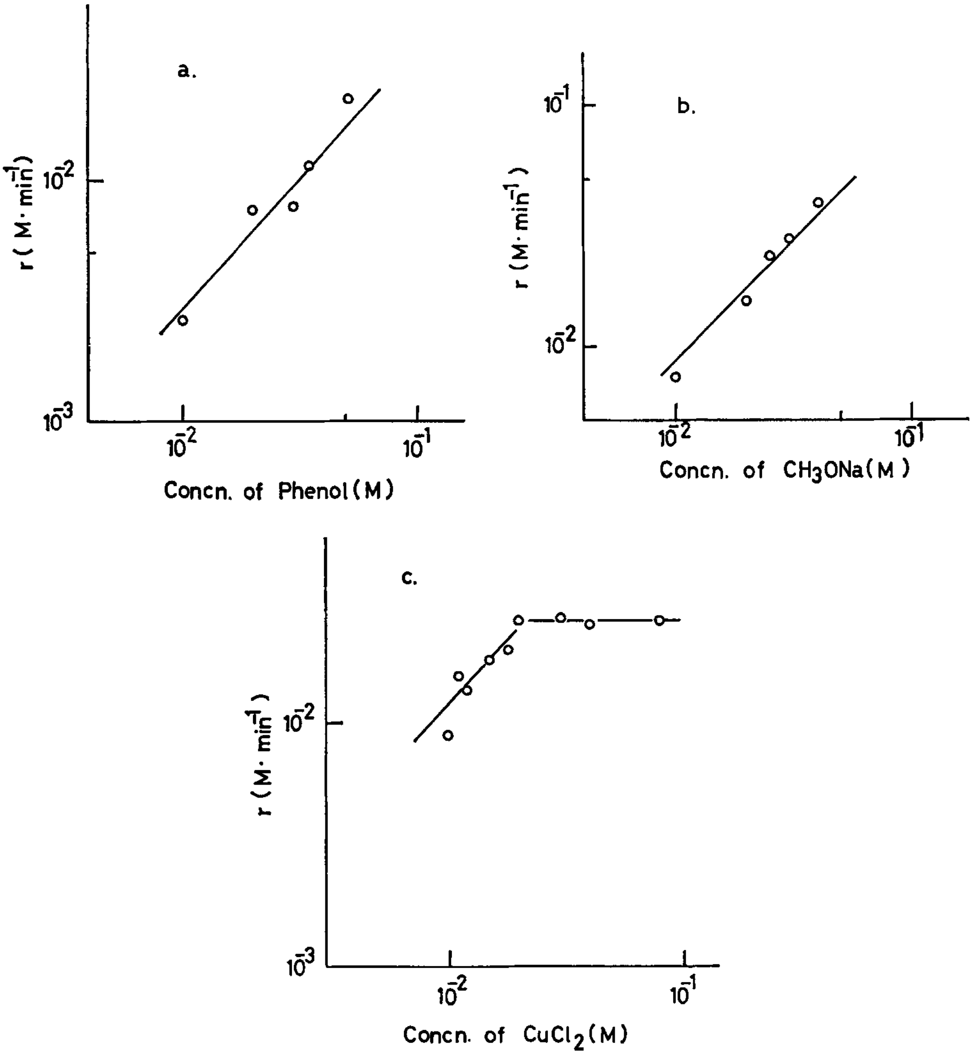
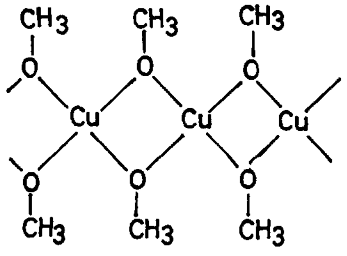


FIG. 8. The log–log plots of the initial rate vs the concentrations of 2,4,6-tribromophenol, sodium methoxide, and copper(II) chloride. (a) $CuCl_2$, 0.03 mole/liter; CH_3ONa, 0.03 mole/liter. (b) 2,4,6-Tribromophenol, 0.1 mole/liter; $CuCl_2$, 0.03 mole/liter. (c) 2,4,6,-Tribromophenol 0.1 mole/liter; CH_3ONa, 0.03 mole/liter.

hydrogen halide formed. But additional water may weaken the catalytic activity of basic copper(II) catalyst by the direct interaction of water with basic copper(II) complex.

As evidenced from Table 1, the copper(II) acetylacetonate complex is not a good catalyst for the present reaction. In copper(II) chelate complexes like copper(II) acetylacetonate the ligands are considered to be too difficult to displace. This may be one of the reasons that the copper(II) acetylacetonate complex does not have catalytic activity. On the other hand, copper(II) nitrate also has a low activity. It is well known that the nitrate anions in copper(II) nitrate are labile. Although we have no idea why copper(II) nitrate has only low catalytic activity for the halogen displacement polymerization, the nitrate anions may act as inhibitors.

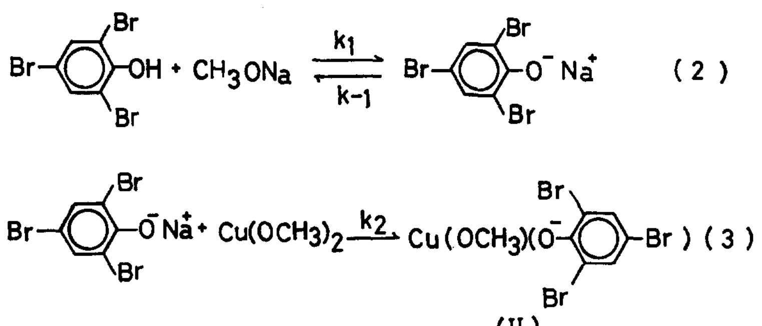
Information about the active catalytic system can be obtained from the results presented in Fig. 5. Figure 5 shows that the polymer yields are remarkably dependent on the mole ratio of copper(II) chloride to sodium methoxide. The maximum polymer yield was obtained at a mole ratio of about one-half this mole ratio. Although we have no knowledge about the quantitative composition of these basic copper(II) catalysts at the present stage, active catalytic systems may have the composition of polymeric $Cu(OCH_3)_2$ as in scheme I, in which methoxide ligands may be replaced by phenoxo group in the process of halogen displacement polymerization to form the copper(II)-phenoxo complex reaction intermediate (*5*b).


(I)

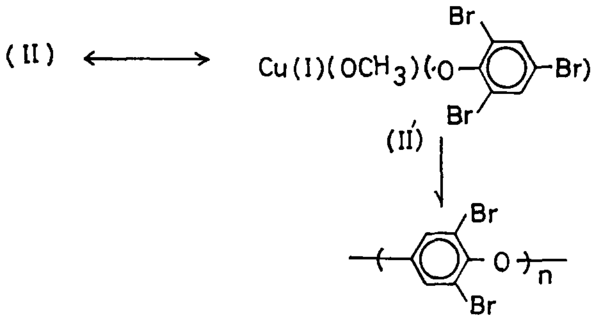
The ESR spectra of basic copper(II) complexes are shown in Fig. 6, in addition copper(II) chloride. The ESR spectrum of copper(II) chloride is a almost symmetrical broad absorption peak. However, the ESR spectra of basic copper(II) complexes show axially symmetric absorption peaks. From the difference of these ESR spectra, it may be proposed that the environment of copper(II) ion of the basic copper(II) complex, which has catalytic activity, is a distorted square plane and of copper(II) chloride, which has no catalytic activity, is tetrahedral or distorted tetrahedral. Thus considering the difference in the ESR spectra, we may assume that ligand displacement is easier in the basic copper(II) complex than in copper(II) chloride. This ligand displacement step is considered to be an important step, as discussed subsequently.

From the kinetic data for the halogen displacement reaction of 2,4,6-tribromophenol, it was determined that the rate of polymer formation is first order in 2,4,6-tribromophenol and sodium methoxide. On the other hand, the rate is first order in copper(II) chloride concentration for the lower concentrations and zero order for the higher concentrations. This rate equation is consistent with the following mechanism for the steady-state condition. The mechanism, although speculative, will serve as a starting point for further work.

$$CuCl_2 + CH_3ONa \longrightarrow Cu(OCH_3)_2 \qquad (1)$$



(II)

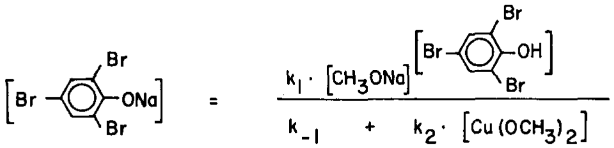


(4)

Reaction scheme

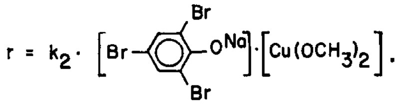
At first, we assume that basic copper(II) complexes are formed from the reaction of copper(II) chloride and sodium methoxide and that only these complexes have catalytic activity for the present reaction. This assumption is reasonable because no polymer was yielded when the halophenol was reacted with copper(II) chloride without sodium methoxide, or with sodium methoxide without copper(II) chloride. Equation (2) shows the equilibrium between 2,4,6-tribromophenol and the corresponding phenolate. It is reasonable that the resulting phenolate anions react with the basic copper(II) catalyst to form the copper(II)-phenoxo complex which is considered as a model compound for the reaction intermediate (*5*b). Furthermore, it is assumed that the decomposition step of this copper(II)-phenoxo complex is a relatively fast one.

If the intermediate sodium 2,4,6-tribromophenolate never accumulate to an appreciable extent during the reaction and $[\mathrm{CH_3ONa}]_{\mathrm{Total}} > [\mathrm{Cu(OCH_3)_2}]$,



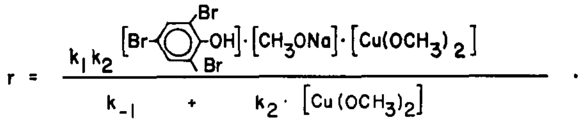
(5)

Since the decomposition step of copper(II)-phenoxo complex, which produce polymer is assumed to be fast, the rate of formation of polymer (r) is



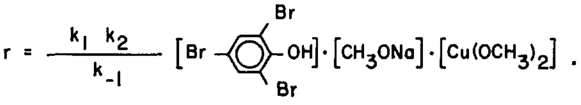
(6)

Substituting from Eq. (5),



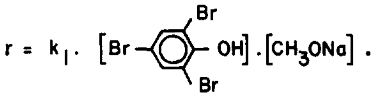
(7)

If $k_{-1} > k_2[\mathrm{Cu(OCH_3)_2}]$,



(8)

This is the case in which the second step is rate-limiting. If $k_2[Cu(OCH_3)_2] > k_{-1}$,



$$r = k_1 \cdot [\mathrm{Br}\text{-}C_6H_2Br_2\text{-}OH] \cdot [CH_3ONa] \qquad (9)$$

This is the case in which the first step is rate-limiting. Thus rate equations obtained experimentally are consistent with the reaction scheme proposed above in which copper(II)-phenoxo complexes are reaction intermediates. The schemes specifically account for the observed dependence of the rate on copper(II) chloride concentration; that is, first order on copper(II) chloride concentration for the lower range, and zero order for the higher range. The rate-limiting step is considered to change with the concentration of copper(II) chloride.

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REFERENCES

1. Bacon, R. G. R., and Hill, H. A. O., *Quart. Rev.* **14**, 95 (1965).
2. Torrey, H. A., and Hunter, W. H., *J. Amer. Chem. Soc.* **33**, 194 (1911); Hunter, W. E., and Dahlen, M. A., *J. Amer. Chem. Soc.* **54**, 2456 (1932).
3. Hay, A. S., *Advan. Polym. Sci.* **4**, 496 (1967); Hall, J. R., *J. Polym. Sci. Part B* **4**, 463 (1966).
4. Price, C. C., *J. Paint Technol.* **38**, 704 (1966) and papers cited therein.
5. (a) Tsuruya, S., Kawamura, T., and Yonezawa, T., *J. Polym. Sci. Part B* **8**, 275 (1970); (b) Tsuruya, S., Okumoto, K., and Yoshimatsu, T., *J. Polym. Sci. Polym. Chem. Ed.* **16**, 379 (1978).
6. Blanchard, H. S., Finkbeiner, H. L., and Russel, G. A., *J. Polym. Sci.* **58**, 469 (1962).
7. Harrod, J. F., *Canad. J. Chem.* **47**, 637 (1969).
8. Tsuruya, S., Kawamura, T., and Yonezawa, T., *J. Polym. Sci. Part A* **9**, 1659 (1971).
9. Carr, B., and Harrod, J. F., *J. Amer. Chem. Soc.* **95**, 5707 (1973).
10. Endres, G. F., Hay, A. S., and Eustance, J. W., *J. Org. Chem.* **28**, 1300 (1963).