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The Solvent Effect on the Rates of Autoxidation of *o*-Cresol[1]

By Yoshiro OGATA and Takashi MORIMOTO

Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya

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The effects of alcohols, carbonyl compounds and dimethyl sulfoxide on the pyridine-cuprous chloride-catalyzed autoxidation of *o*-cresol in benzene have been studied kinetically by estimating the consumption of oxygen. The rate is first-order in the concentration of *o*-cresol and one-half order in the partial pressure of oxygen at constant concentrations of pyridine and cuprous chloride in a solvent of methanol-benzene (20 : 80 in vol.). The reaction in a benzene solution is retarded by the addition of below 0.1 vol.% methanol or ethanol; having passed through a minimum at ca. 0.1 vol.%, it is accelerated by the addition of alcohol more than 0.1 vol.%. The reaction in a benzene solution is retarded by the addition of carbonyl compounds. A probable mechanism which explains these solvent effects is discussed.

In our previous report[2] it has been suggested that the pathway for the pyridine - cuprous chloride-catalyzed autoxidation of *o*-cresol in a benzene solution involves the reaction of *o*-cresol anion and an autoxidized pyridine - copper complex. The similar autoxidation of 2, 6 - dimethylphenol catalyzed by the pyridine - cuprous salt complex is sometimes carried out in a mixed solvent, e. g., benzene - isopropanol or toluene - isopropanol.[3] However, the autoxidation of aniline by the same catalyst is retarded on addition of methanol.[4]

The present study was undertaken to clarify the kinetic solvent effect on the pyridine-cuprous chloride-catalyzed autoxidation of *o*-cresol.

Results and Discussion

The rates were measured in the presence of anhydrous magnesium sulfate to eliminate the water which is formed as a product and which inhibits the reaction.

The rate of absorption of oxygen at constant concentrations of pyridine and cuprous chloride in methanol-benzene (20 : 80 in vol.) is expressed as:

$$-\frac{dp}{dt} = k[\mathrm{CrlH}]\,p^{1/2} \qquad (1)$$

Here, [CrlH] is the concentration of *o*-cresol and p is the partial pressure of oxygen. This rate law agrees with that in pure benzene as previously reported; therefore, the oxidation in benzene containing 20 vol.% methanol may also involve the same mechanism.

TABLE I. THE 1.5TH- AND SECOND-ORDER RATE CONSTANTS FOR THE AUTOXIDATION OF *o*-CRESOL AT CONSTANT CONCENTRATION OF CATALYST, PYRIDINE (0.2467 M) AND CUPROUS CHLORIDE (5.05×10^{-3} M), IN METHANOL-BENZENE (20 : 80) AT 35°C

o-Cresol M	O_2 press. p, mmHg	1.5th-order const $\mathrm{mmHg}^{1/2}\,\mathrm{M}^{-1}\,\mathrm{min}^{-1}$	Second-order const. $\mathrm{M}^{-1}\,\mathrm{min}^{-1}$
0.1889	100	4.63	5.50
0.1889	200	4.57	3.45
0.1889	400	4.58	2.29
0.0994	200	5.15	3.50

$$o\text{-}CH_3C_6H_4OH + C_5H_5N \xrightleftharpoons{\text{fast}} o\text{-}CH_3C_6H_4O^- + C_5H_5\overset{+}{N}H \qquad (2)$$

$$m\,C_5H_5N + n\,Cu^+ \xrightleftharpoons{\text{fast}} (C_5H_5N)_m(Cu^+)_n \qquad (3)$$

$$2(C_5H_5N)_m(Cu^+)_n + O_2 \xrightleftharpoons{\text{fast}} [(C_5H_5N)_m(Cu^+)_n]_2O_2 \qquad (4)$$

$$[(C_5H_5N)_m(Cu^+)_n]_2O_2 \xrightleftharpoons{\text{fast}} 2(C_5H_5N)_m(Cu^+)_nO\cdot \qquad (5)$$

$$(C_5H_5N)_m(Cu^+)_nO\cdot + o\text{-}CH_3C_6H_4O^- \xrightarrow{\text{slow}} o\text{-}CH_3C_6H_4O\cdot + \text{etc.} \qquad (6)$$

Figure 1 illustrates the effect of the addition of alcohols, carbonyl compounds and dimethyl sulfoxide on the pyridine-cuprous chloride-catalyzed autoxidation of *o*-cresol in benzene. As shown in the figure, the rate constant decreased on addition of below 0.1 vol.% methanol, but with above 0.1 vol.% methanol the constant increased with increasing concentration of methanol, approaching a constant value at more than 20 vol.% methanol. The ratio of the rate constant in 20 vol.% methanol

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[1] Contribution No. 87.

[2] Y. Ogata and T. Morimoto, *Tetrahedron*, **21**, 2791 (1965).

[3] *Chem. Eng. News*, **42**, Dec. 7, 1964, p. 57.

[4] K. Kinoshita, This Bulletin, **32**, 777 (1959).

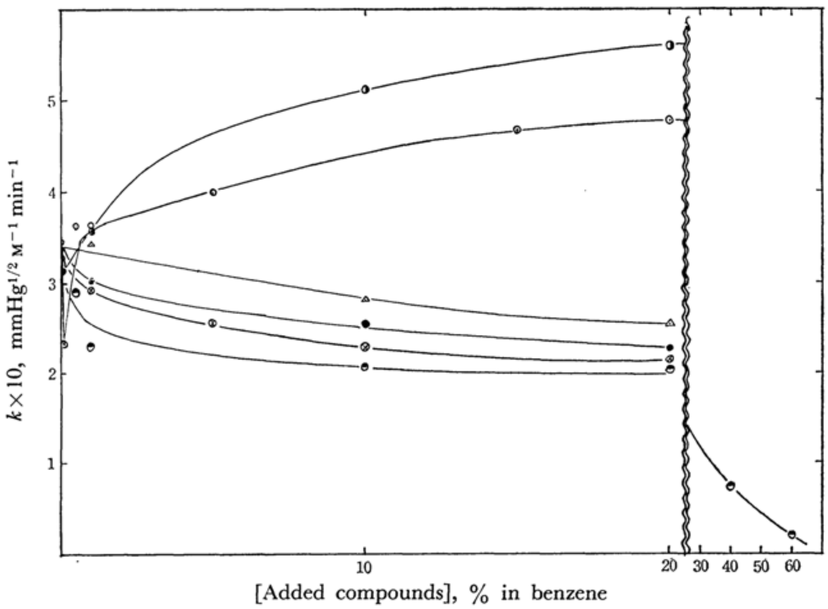

Fig. 1. The solvent effect on the rate constant for the autoxidation of *o*-cresol in benzene at 35°C or at constant oxygen pressure ($p=200$ mmHg) and at constant concentration of catalyst: [CuCl] $=5.05\times10^{-5}$ M and [pyridine] $=0.2469$ M. Initial concn. of *o*-cresol: 0.1918 M. ⊙, Methanol; ◑, Ethanol; △, Methyl ethyl ketone; ●, Dimethylformamide; ⊗, Ethyl acetate; ◓, Dimethyl sulfoxide.

to that in pure benzene was about 1.3. These phenomena are not due to the formation of formaldehyde from methanol, since no absorption of oxygen was observed in the absence of *o*-cresol and no formaldehyde was detected in the effluent gas.

In contrast, the rate constant gradually decreased with increasing concentration of carbonyl compounds or dimethyl sulfoxide. For example, in 60 vol.% dimethyl sulfoxide in benzene, the rate was too low to measure.

This retardation with carbonyl or sulfoxide compounds may be due to the deactivation of the catalyst, (i) by the substitution of a carbonyl or sulfoxide compound for pyridine molecule:

$$\mathrm{Py}_m\mathrm{Cu}^+{}_n + (\rangle\mathrm{C{=}O}) \rightleftarrows \mathrm{Py}_{m-1}(\rangle\mathrm{C{=}O})\mathrm{Cu}^+{}_n + \mathrm{Py} \qquad (7)$$

or (ii) by the steric inhibition of the approach of molecular oxygen to the active site of catalyst by a coordinated carbonyl or sulfoxide compound:

$$\mathrm{Py}_m\mathrm{Cu}^+{}_n + (\rangle\mathrm{C{=}O}) \rightleftarrows \mathrm{Py}_m\mathrm{Cu}^+{}_n(\rangle\mathrm{C{=}O}) \qquad (8)$$

Although the rate increased with an increase in the dielectric constant[2,5] by the addition of chlorobenzene ($\varepsilon=5.62$[6]), the reaction was retarded by the addition of dimethylformamide ($\varepsilon=37.6$[7]) or dimethyl sulfoxide ($\varepsilon=46$[8]) to the solvent. These results suggest that the catalyst is deactivated by the coordination of the oxygen atom in these compounds.

On the other hand, methanol may act as an acid, as shown in the following equilibrium:

$$\mathrm{C_5H_5N + CH_3OH \rightleftarrows C_5H_5\overset{+}{N}H + CH_3O^-} \qquad (9)$$
$$\text{or } \mathrm{C_5H_5N^+\cdots H\cdots \overset{-}{O}CH_3}$$

It is expected that methoxide anion, like carbonyl compounds, will coordinate with the catalyst to retard or inhibit the reaction. In fact, the pyridine solution containing *o*-cresol and cuprous chloride absorbs oxygen (1.38×10^{-4} mole after 180 min. at 13.9 mmHg), but no absorption was observed on addition of 10 vol.% methanol to the solvent. At a lower concentration of pyridine (below 1 M) in a benzene solution, the reaction may be retarded by a small amount of methanol, probably because the methoxide ion formed acts much like carbonyl compounds, while the reaction is accelerated by the addition of more than 0.1 vol.% methanol, as is obvious in Fig. 1. It is difficult to explain this acceleration at present, but it is probable that an increase in the dielectric constant and solvation power by the addition of methanol results in an increase in the concentration of the more

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

6) J. A. Riddick and E. E. Toops, Jr., "Organic Solvents," in "Technique of Organic Chemistry," Vol. VII, Ed. by A. Weissberger, Interscience, New York (1955), p. 190.

7) J. Parker, *Quart. Revs.*, **16**, 163 (1962).

8) T. J. Wallace, H. Pobiner, F. A. Baron and A. Schriesheim, *J. Org. Chem.*, **30**, 3147 (1965).

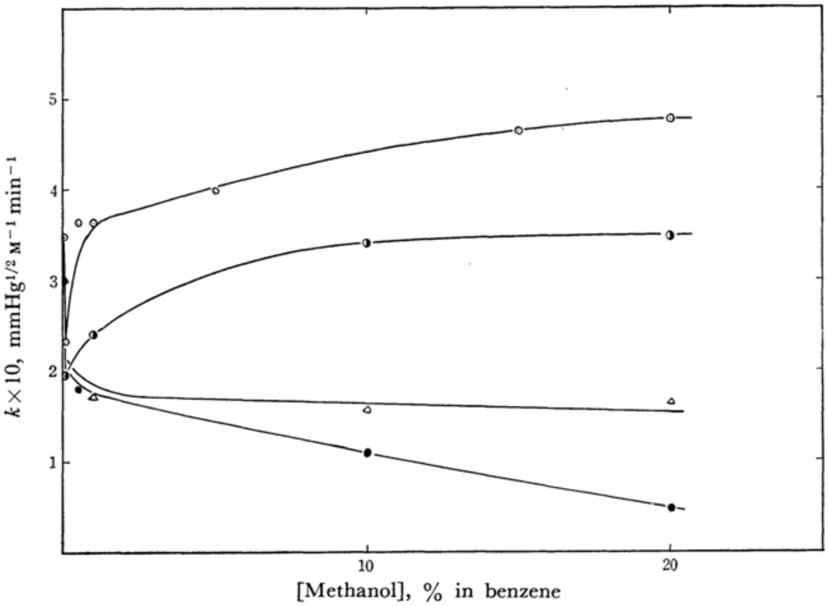

Fig. 2. The effects of concentrations of methanol and pyridene on the rate constant for the autoxidation of *o*-cresol in benzene at 35°C at constant concentration of CuCl (5.05×10^{-5} M) and *o*-cresol (0.1918 M) and constant oxygen pressure (200 mmHg).
⊙, [pyridene]=0.247 M; ◑, 0.99 M; △, 2.48 M; ●, 4.99 M.

reactive *o*-cresol anion and that this effect surpasses the deactivation of the catalyst by methanol.

At higher concentrations of pyridine (over 2 M), the oxidation was always inhibited or retarded by the addition of methanol in any concentration. The effect of the methanol concentration on the rate constant at various pyridine concentrations is illustrated in Fig. 2. Apparently, at higher concentrations of pyridine (e. g., over 2 M), the rate constant decreases with increasing concentration of methanol. On the other hand, at lower concentrations of pyridine (below 1 M), the rate constant sharply decreases and then increases with increasing concentration of methanol. These facts seem to support the above assumption that the deactivation with methanol is not caused by methanol itself, but by methoxide ions, which can only be produced by the presence of pyridine.

A similar effect is expected for the autoxidation of 2, 6-dimethylphenol by the same catalyst. In fact, the acceleration was appreciable by the addition of 20 vol% ethanol or isopropanol to a benzene solution at 0—35°C at initial concentrations of 0.1979 M 2, 6-dimethylphenol, 0.2461 M pyridine, and 5.05×10^{-3} M cuprous chloride. However, the reaction in both pure benzene and the mixed solvent was too rapid for the rate constants to be compared (80% conversion after 20 min. at 35°C in pure benzene).

Experimental

Materials.—*o*-Cresol, cuprous chloride, pyridine, and benzene were purified as reported previously.2) Methanol (b. p. 64.1—64.5°C), ethanol (b. p. 78.1—78.2°C), methyl ethyl ketone (b. p. 78.8—79.1°C) and ethyl acetate (b. p. 77.0—77.2°C) were purified by rectification. Dimethylformamide (b. p. 56.5—56.7°C/27 mmHg) and dimethyl sulfoxide (b. p. 85—87°C/25 mmHg) were distilled in a vacuum after having been dried over anhydrous potassium carbonate. 2, 6-Dimethylphenol was recrystallized from *n*-hexane (m. p. 44.0—44.5°C).

Rate Measurements.—The same apparatus and procedure2) were used for the rate measurements.

The Detection of Formaldehyde.—Oxygen gas, after having been passed through the reaction solution, was bubbled into an aqueous solution of sodium sulfate containing thymolphthalein as an indicator. No color was observed. This proved the absence of formaldehyde.

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