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Carboxylation of Phenol Derivatives. XXI. The Formation Reaction of the Complex from Alkali Phenoxide and Carbon Dioxide[1]

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The yield of the complex was examined using eleven potassium phenoxide or substituted phenoxides. The phenoxide with an electron-donating group gave a complex in a better yield than did that with an electron-attracting group. The infrared spectra of the four complexes were measured. From these results, it was concluded that, in the complex, the carbon atom of carbon dioxide binds to the oxygen atom or the π-electron of alkali phenoxide. The thermal analyses of the complex were also conducted by DTA and TGA in an atmosphere of carbon dioxide; a strong endothermic peak and a rapid weight loss were observed at the temperatures from 120 to 140 °C.

Hydroxybenzoic acids are mainly synthesized by the Kolbe-Schmidt reaction, and many methods have appeared for this reaction since Kolbe discovered it in 1860.[2] Some methods of preparing hydroxybenzoic acids are as follows:[2–4] (a) the reaction of alkali phenoxide with carbon dioxide in the absence of a solvent or in a nonpolar solvent; (b) the reaction of alkali phenoxide with carbon dioxide in an aprotic polar solvent such as dimethylformamide; (c) the reaction of phenol with carbon dioxide in the presence of an excess amount of potassium carbonate; (d) the reaction of alkali phenoxide with alkali alkyl carbonate, *etc.* Of these, a typical reaction is the (a) method, and the reaction mechanism has been investigated exclusively in reference to this method. The general procedure is divided into two steps. The first step is the absorption of carbon dioxide by alkali phenoxide at a low temperature (about 100 °C). The second step is the heating of the mixture obtained in the first step, the temperature being held at 150—160 °C for several hours.[2] In the first step, it is known that a certain product is formed when phenoxide comes into contact with carbon dioxide. Some investigations of

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[1] This paper was presented at the 27th (1972) Annual Meeting of the Chemical Society of Japan; Part XX of this series: T. Kito and I. Hirao, This Bulletin, **44**, 3123 (1971).

[2] A. S. Lindsey and H. Jeskey, *Chem. Rev.*, **57**, 583 (1957).

[3] I. Hirao, *Yuki Gosei Kagaku Kyokai Shi*, **24**, 1051 (1966).

[4] I. Hirao, T. Kondo, and T. Kito, *Kogyo Kagaku Zasshi*, **72**, 692 (1969); T. Kito and I. Hirao, This Bulletin, **44**, 3123 (1971).

this product have been done, but they have almost all been done in connection with the mechanism of the Kolbe-Schmidt reaction or in connection with the preparation of hydroxybenzoic acid.[5,6] However, in this paper the yields and analytical results of this product and its related compounds will be described.

Experimental

Complex Formation Reaction. In a 300 ml glass autoclave, we placed 100 ml of a light oil (as a medium of heat) and 0.02 mol of potassium phenoxide. After the air had been replaced by nitrogen, the autoclave was heated, vigorously stirred, and then kept at the prescribed temperature. The pressure was released and then a carbon dioxide pressure was exerted. The pressure was kept at a constant value during the reaction. Some adduct, which we will represent as "complex" or [I] for the sake of convenience, was formed from potassium phenoxide and carbon dioxide according to Eq. (1):

(1)

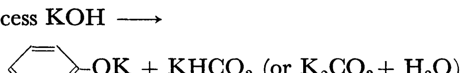
At the prescribed time, the carbon dioxide was replaced by nitrogen and the autoclave was allowed to cool to room temperature.

Determination of the Complex. It is difficult to separate the complex from unreacted potassium phenoxide because the complex is hardly soluble in either ordinary organic solvents or alkali phenoxides (we found that the adduct was also formed from DMF and alkali phenoxide when the latter was dissolved in DMF[7] and that alkali alkyl carbonate was formed when the complex was dissolved in alcohol;[8] therefore, they can not be used as solvents) and is thermally unstable.[5] For the above reasons, the determination of the complex was carried out according to the following procedure.

The lid of the autoclave was taken off, and the light oil was sucked out through a glass-filter by applying a vacuum. In this procedure, one must take care that the reaction mixture does not come in contact with the moisture or the carbon dioxide in the air.

A test tube, in which 50 ml of aqueous KOH solution (about 1 M) had been placed, was inserted into the autoclave, and then the lid was put on tightly. Then, making the aqueous KOH solution run over from the test tube by inclining the autoclave, the complex was caused to decompose into potassium phenoxide and carbon dioxide, the latter being absorbed by the aqueous KOH solution to change into potassium carbonate or potassium bicarbonate. The number of complex molecules formed should be equal to the total number of the molecules of potassium carbonate and potassium bicarbonate if the reaction proceeds according to Eqs. (1) and (2):

$$[\mathrm{I}] + \text{excess KOH} \longrightarrow$$



(2)

The reaction mixture was diluted with water to 500 ml; from this solution a 5 ml portion was pipetted and titrated with 0.1 M HCl. In most cases there are two clear inflexion points, that is, P_1 and P_2, which generally appear at the pH values of 7.9 and 4.6 respectively. At P_1, the potassium carbonate is completely converted to potassium bicarbonate. In the range from P_1 to P_2 only potassium bicarbonate, whose amount should be equal to the amount of the complex, is present. Therefore, the number of complex molecule formed in this reaction is obtained by multiplying the difference between P_1 and P_2 by 100.

When the solution contains some hydroxy acid which is formed in the carboxylation of potassium phenoxide by carbon dioxide, P_2 is generally indistinct. In such a case, the following procedure could be used. To 5 ml of the aqueous solution, hydrochloric acid was added until P_1 was attained. At this point, the aqueous solution contains only potassium bicarbonate and mono potassium salt of hydroxy acid as potassium salts in amounts represented here as A mol and B mol respectively. When a sufficient amount of M mol of hydrochloric acid is further added, $M-(A+B)$ mol of hydrochloric acid and B mol of hydroxy acid remain as acid components. This solution was again titrated with 0.1 M aqueous sodium bicarbonate. There is also a clear inflexion point, P_3, which generally appears at the pH of 4.5. When N mol of sodium bicarbonate is added until P_3 (at P_3 both hydrochloric acid and hydroxy acid are neutralized by sodium bicarbonate) is attained, the following equation must be valid:

$$M-(A+B)+B=N \qquad \therefore\ A=M-N$$

The yield of the complex can be calculated according to Eq. (3), where: L represents the number of molecules of

$$\text{Complex yield } (\%) = \frac{M-N}{L} \times \frac{500}{5} \times 100 \qquad (3)$$

potassium phenoxide used as the starting material.

Infrared Absorption Spectra of the Complex. The spectra were measured with a Japan Spectroscopic spectrometer (IRA-2).

The complex was prepared at room temperature by the method described above, but light oil was replaced by *n*-hexane because the latter has no absorption in the carbonyl absorption region. The complex containing *n*-hexane was placed on filter paper, which blots *n*-hexane, and was then suspended in Nujol on a mortar.

Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA). The complex was prepared as follows. Potassium phenoxide was set in the apparatus and heated at 150 °C in a vacuum. After 1 hr, it was allowed to cool to room temperature, applying a vacuum, and then the atmosphere was replaced by carbon dioxide.

After 30 min, the temperature was again raised at a rate of about 3 °C/min in an atmosphere of carbon dioxide. Apparatus: Cho Keiryoki, $\mathrm{TRDA_1}$-L.

Results and Discussion

Effect of the Reaction Temperature and the Reaction Time. The yields of the complex and of the hydroxybenzoic acids were examined under various conditions. Potassium phenoxide was heated under a carbon dioxide pressure of 5 kg/cm^2 for 30 min at various temperatures. The results are shown in Table 1.

The complex was formed in a 76—80% yield at temperatures lower than 70 °C and then decreased above that temperature. On the contrary, such

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[5] J. L. Hales, J. I. Jones, and A. S. Lindsey, *J. Chem. Soc.*, **1954**, 3145.

[6] R. Ueno, K. Muramoto, and I. Hirao, *Kogyo Kagaku Zasshi*, **64**, 1213 (1961); I. Hirao, K. Ota, S. Sueta, and Y. Hara, *Yuki Gosei Kagaku Kyokai Shi*, **24**, 1047 (1966).

[7] Unpublished.

[8] The 28th (1973) Annual Meeting of the Chemical Society of Japan, Tokyo.

TABLE 1. EFFECT OF THE REACTION TEMPERATURE AND TIME ON THE YIELDS OF COMPLEX AND HYDROXYBENZOIC ACIDS

Temp (°C)	Time (hr)	Yield (%) Complex	Yield (%) Acids
20	0.5	77.6	0
29.5	0.5	78.8	0
50	0.5	75.6	0
70	0.5	79.4	0
100	0.5	67.4	4.1
130	0.5	20.6	32.9[a]
150	0.5	10.4	60.6[b]
150	3.0	3.2	64.2[c]
180	0.5	4.4	72.3[d]

a) SA (Salicylic acid), 22.7%; POB (*p*-Hydroxybenzoic acid), 9.8%; 4-OIP (4-Hydroxyisophthalic acid), 0.4%.
b) SA, 39.1%; POB, 20.2%; 4-OIP, 1.3%.
c) SA, 43.8%; POB, 20.0%; 4-OIP, 0.4%.
d) SA, 43.6%; POB, 24.7%; 4-OIP, 4.0%.

hydroxybenzoic acids as salicylic acid and *p*-hydroxybenzoic acid were formed at 100 °C in only a 4.1% yield. The effect of the reaction time on the yields of complex and hydroxybenzoic acids was examined at 150 °C (see Table 1). On the basis of these results, it can be said that the complex yield decreases at temperatures higher than 70 °C not because it changes into hydroxybenzoic acids, but because it is thermally unstable.

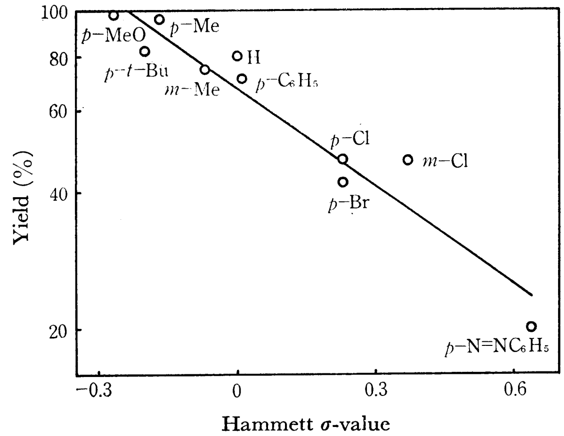
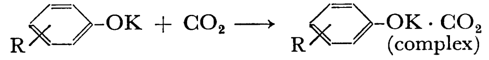


Fig. 1. Effect of the substituent on the yield of complex.
CO_2: 5 kg/cm^2, temp: 70 °C, time: 30 min

Reaction:



Ordinate: a logarithmic graduation
p-SO_3K: $\sigma = +0.64$, Yield 5.8%. This point is omitted in this figure because it deviates largely from the straight line.

Effect of the Substituent. Potassium salts of phenols were heated at 70 °C under a carbon dioxide pressure of 5 kg/cm^2 for 30 min. In Fig. 1 the complex yields are plotted against the Hammett σ-values. We observed a linear relationship between the yield and the σ-value, and it was concluded that a phenoxide with an electron-donating group, that is, a lower σ-value, gave the complex in a better yield than that with an electron-attracting group.

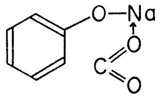
Some discussions have been made of the alkali phenoxide–carbon dioxide complex because the complex has been regarded by some investigators to an important intermediate in the carboxylation of alkali phenoxide, the Kolbe-Schmidt reaction. For example, Schmidt[2] considered that the intermediate, which we will here describe as the complex, is an alkali phenyl carbonate. He proposed the following reaction processes, Eqs. (4) and (5). The second step, Eq. (5),

$$C_6H_5ONa + CO_2 \longrightarrow C_6H_5OCOONa \quad (4)$$

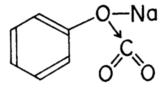
$$C_6H_5OCOONa \longrightarrow HOC_6H_4COONa \quad (5)$$

is a rearrangement of sodium phenyl carbonate to salicylic acid.

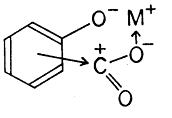
By infrared study Hales and his co-workers[5] determined the structure of the adduct obtained from sodium phenoxide and carbon dioxide as II. (Many authors have described the molecule of carbon dioxide in the complex as a bending form, as is shown in the figure, without explanation, although carbon dioxide is usually considered to have a straight-lined form; however, Kwan and his co-workers[9] presumed the structure of carbon dioxide in the complex to be a bending form on the basis of the infrared study.) They proposed the structure of II on the basis of the fact that it has an IR absorption due to the carbonyl band at 1684 cm^{-1}. They considered that if the product is a sodium phenyl carbonate, it must have a carbonyl absorption at about 1630 cm^{-1} because sodium methyl carbonate has an absorption due to carbonyl at 1630 cm^{-1}. In addition, dimethyl carbonate and methyl phenyl carbonate possess carbonyl absorptions at 1748 and 1754 cm^{-1} respectively, indicating that the phenyl group has little effect on the position of the carbonyl absorption. However, we consider that although they rejected the sodium phenyl carbonate structure on the basis of a reasonable method, no clear structure can be given because whether carbon dioxide binds to sodium metal or to the residue can not be determined by only their IR investigations. Shilov and his co-workers[10] proposed that the structure of the complex can be denoted as III, not II, because II must be very weak; however, this assumption was not based on experimental data.



[II]



[III]



M=K, Na [IV]

The results presented in Fig. 1 also give some interesting information. If the oxygen atom of carbon dioxide binds to the alkali atom, as is shown in II, the poorer the electron density on the alkali atom, the stronger the binding force between the alkali atom and carbon dioxide. Therefore, the yield of a complex must increase as the substituent on the phenyl nucleus attracts an electron from the nucleus or the oxygen

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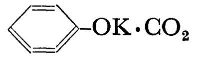
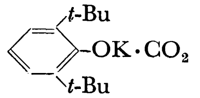
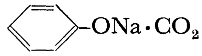
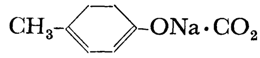
9) T. Kwan, H. Yamamoto, H. Mori, and H. Samejima, *Kagaku Kogyo*, **74**, 1618 (1972).

10) E. A. Shilov, I. V. Smirov-Zamkov, and K. I. Matkovskiĭ, *Ukrain. Khim. Zhur.*, **21**, 484 (1955).

atom. However, this idea is contrary to the results shown in Fig. 1. The results in Fig. 1 suggest that the (III) structure is more reasonable than the (II) structure because it is expected that the yield increases as the electron density on the oxygen atom of phenoxide increases. On the other hand, another structure, a π-complex structure shown as IV, which we have described here ionically, is possible; a similar structure has been proposed by Hales and his co-workers[5] as one state in the carboxylation of sodium phenoxide. In IV, of course, carbon dioxide should bind to the alkali atom more loosely than to the π-electron on the phenyl nucleus. However, we have no reliable data for a discussion as to which structure, (III) or (IV), is more reasonable.

Infrared Absorption Spectra. The IR absorptions due to the carbonyl groups of four complexes were measured; the results are listed in Table 2.

TABLE 2. INFRARED SPECTRA OF THE COMPLEX

Complex	$\nu_{C=O}$(cm^{-1})
 -OK·CO$_2$	1645
 t-Bu -OK·CO$_2$ t-Bu	1650 1628
 -ONa·CO$_2$	1685
 CH$_3$- -ONa·CO$_2$	1668

a) Lit,[5] 1684 cm^{-1}.

First, the validity of the (II) structure is considered in the following. The O$^-$K$^+$ bond in potassium phenoxide is more polarized than the O$^-$Na$^+$ bond in sodium phenoxide. Therefore, the K atom in potassium phenoxide is more positive than the Na atom in sodium phenoxide, but the electron density on the former may be higher than that on the latter because the ionic radius of K$^+$ is greater than that of Na$^+$. Yamamoto explained,[11] on this basis, a greater tendency toward the solubility of Na salts compared with K salts and other differences between sodium and potassium compounds. If this assumption is true, $C_6H_5OK \leftarrow O_2C$[12] can be expected to give a carbonyl absorption at a higher frequency than does $C_6H_5ONa \leftarrow O_2C$ since the oxygen atom of carbon dioxide binds to the K atom more loosely than to the Na atom.

On the other hand, it is obvious that the electron density on the Na atom in sodium p-cresoxide is higher than that on the Na atom in sodium phenoxide. Therefore, p-$CH_3C_6H_4ONa \leftarrow O_2C$ is also expected to give a carbonyl absorption at a higher frequency than does $C_6H_5ONa \leftarrow O_2C$. However, the results listed in Table 2 were not in accord with this expectation.

On the contrary, the following expectations can be drawn from the (III) structure. The electron densities on the oxygen atoms in potassium phenoxide and sodium p-cresoxide may be higher than that on the oxygen atom in sodium phenoxide. Therefore, both $C_6H_5O(K) \rightarrow CO_2$ and p-$CH_3C_6H_4O(Na) \rightarrow CO_2$[13] can be expected to give carbonyl absorptions at lower frequencies than does $C_6H_5O(Na) \rightarrow CO_2$ because the carbon atom of carbon dioxide may be neutralized by the oxygen atom in potassium phenoxide or sodium p-cresoxide to a greater extent than by that in sodium phenoxide. A similar reasoning can be also drawn from the (IV) structure. The results listed in Table 2 are in good agreement with the above expectations.

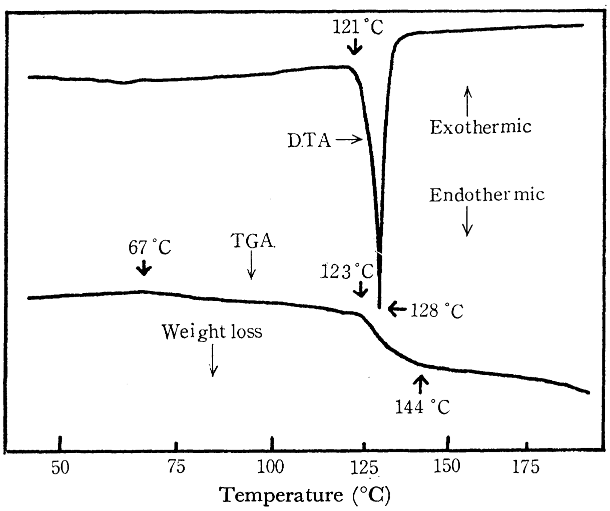
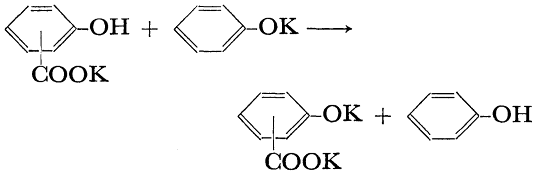


Fig. 2. DTA and TGA curves of the complex.

DTA and TGA. The complex obtained from potassium phenoxide and carbon dioxide was analyzed by DTA and TGA in an atmosphere of carbon dioxide. The results are shown in Fig. 2. In this experiment, the following reactions may occur: (a) the decomposition of the complex, (b) the formation of monopotassium salicylate and monopotassium p-hydroxybenzoate by the carboxylation of potassium phenoxide, (c) the conversion of the monopotassium salts into the dipotassium salts, and (d) the rearrangement of dipotassium salicylate to dipotassium salt of p-hydroxybenzoic acid. The weight loss in the range of the temperatures from 67 to 123 °C in Fig. 2 may correspond to the (a) process; this is in good agreement with the results listed in Table 1.

On the other hand, the weight loss did not occur below 200 °C when monopotassium salicylate or monopotassium p-hydroxybenzoate was heated in an atmosphere of carbon dioxide, while it began at 165 °C when a mixture of monopotassium p-hydroxybenzoate, monopotassium salicylate, and potassium phenoxide (weight ratio of 1: 2: 7) was heated in an atmosphere of nitrogen. In the latter case, the weight loss must be caused by the evaporation of the phenol formed in Eq. (6). In



(6)

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[11] T. Yamamoto, *Kagaku to Kogyo*, **23**, 1004 (1970).

[12] The $C_6H_5OM \leftarrow CO_2$ formula represents a complex with the structure of II.

[13] The $C_6H_5O(M) \rightarrow CO_2$ formula represents a complex with the structure of III.

addition, we often observed the following phenomenon. A complex was prepared from potassium phenoxide and carbon dioxide in light oil at room temperature, and then the temperature was gradually raised (about 2 °C/min). When the temperature reached about 130 °C, the solid coagulated in a mass, but it was soon dispersed into the light oil.

On the basis of these data, the strong endothermic peak and the rapid weight loss in the range of temperatures from 120 to 140 °C in Fig. 2 can be explained as follows: the monopotassium salt of hydroxybenzoic acid converts into the dipotassium salt by taking a potassium atom from the complex. At that time, the complex decomposes and liberates carbon dioxide, which results in a strong endothermic peak and a great decrease in weight. The coagulation observed must be one step in this process.

Thanks are due to Mr. Hiroshi Yamaguchi and Mr. Kazumi Hirakawa for their assistance in the experimental work.