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Carboxylations of alkali metal phenoxides with carbon dioxide

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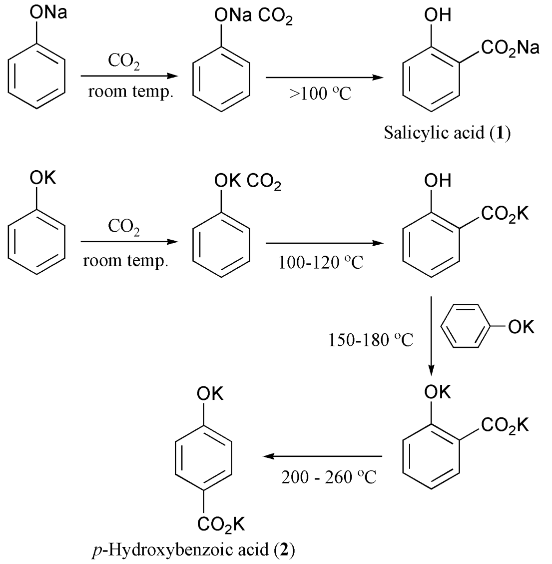
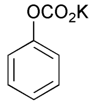
The reaction mechanism of the Kolbe–Schmitt reaction of phenol and 2-naphthol has been investigated. An alkali metal phenoxide–CO_2 complex is not an intermediate that can be easily transformed into a carboxylic acid, such as salicylic acid (SA) and *p*-hydroxybenzoic acid (*p*HBA). A direct carboxylation of phenoxide with CO_2 takes place even at room temperature, and is competitive with the formation of the CO_2 complex. The resulting complex decomposes thermally (above *ca.* 100 °C) to phenoxide, which then undergoes further competitive reactions. Experiments using a carbon-13 labeled complex support a mechanism of direct carboxylation, and not the mechanism *via* a CO_2 complex. The reactivity, C-13 NMR and MOPAC/PM3 calculations suggest a new carbonate-like structure for the CO_2 complex.

The Kolbe–Schmitt reaction[1] has been used for more than a century to produce industrially important aromatic hydroxy acids, such as salicylic acid (SA), *p*-hydroxybenzoic acid (*p*HBA), *p*-aminosalicylic acid (PAS), 3- and 6-hydroxy-2-naphthoic acids (3HNA and 6HNA, respectively). In spite of various investigations on the reaction, the mechanism of the carboxylation has not necessarily been clear.[2,3] Among several postulations, the most plausible reaction mechanism accepted today is the formation of an alkali metal phenoxide–CO_2 complex in the first stage of the reaction of phenoxide, followed by producing SA at elevated temperatures *ca.* 120 °C,[4,5] and *p*HBA is produced from dipotassium salicylate at much higher temperatures over 200 °C[6] (Scheme 1). The structure of the CO_2 complex has not been elucidated, probably because of its very hygroscopic nature and the inevitable contamination of inorganic carbonates such as potassium carbonate and hydrogen carbonates originating from potassium hydroxide used in the preparation of potassium phenoxide.

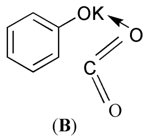


Scheme 1 Widely accepted mechanisms of the Kolbe–Schmitt reaction.

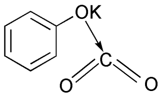
Phenyl carbonate (**A**) was originally proposed as an intermediate,[5] and later, structures **B**[7,8] and **C**[9] were suggested based on IR spectra. Meanwhile the amount of complex formed during reactions was estimated by titration, and the substituent effects on the amount of the complex formed were discussed.[10] In spite of all the available affirmative evidence this has not been used to suggest the possible structure, however Dewar[11] described an idea of a π-complex type structure (**D**).



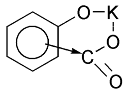
(**A**)



(**B**)



(**C**)



(**D**) π–Complex

The formation of a CO_2 complex at low temperatures has also been examined by thermal analyses (DTA, TGA)[10,12] and kinetic approaches.[13] In our recent studies,[14] it has been found that the carboxylation of alkali metal phenoxide with carbon dioxide takes place and produces not only SA but also *p*HBA even at room temperature.

These unexpected results have urged us to investigate the reaction mechanism and the nature of the CO_2 complex in more detail.

Results and discussion

An introduction of carbon dioxide at room temperature into an autoclave to react with potassium (or sodium) phenoxide resulted in the formation of SA and *p*HBA. The total yield of the carboxylic acids was *ca.* 30% at 50 °C, and the rest of

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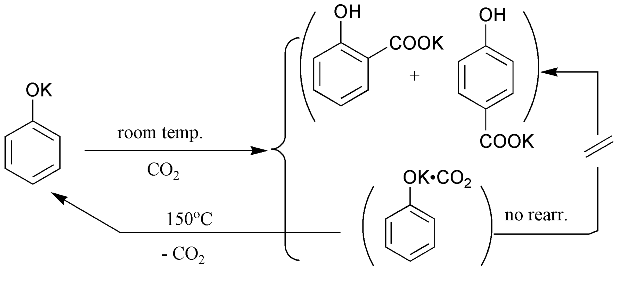
Table 1 Carboxylations of potassium phenoxide and 2-naphthoxide with carbon dioxide, and reactivities of potassium phenoxide–CO_2 complexes

			Carboxylation			Reaction mixture (%)[f]				
Run nos.	Phenoxides	CO_2 complex[a]	CO_2/MPa	Temp/°C	Time/min	Phenol	SA	*p*HBA	2-Naphthol	2H1NA
1	PhOK	—	5.0	20	5	80	12.5	7.0	—	—
2	PhOK	—	5.0	50	60	73	17.2	9.7	—	—
3	PhOK	—	5.0	30	60	80	13.2	7.4	—	—
4	PhOK	—	(5.0	30	60) × 2[c]	64	23.2	13.1	—	—
5	PhOK	—	(5.0	30	60) × 3[c]	53	30.4	16.6	—	—
6	—	PhOK–CO_2	5.0	50	60	100	0	0	—	—
7	—	PhOK–CO_2	(N_2 5.0)[d]	100	60	95	3.0	1.5	—	—
8	—	PhOK–CO_2	(evacuated)[e]	100	60	100	0	0	—	—
9	2-NaphOK	—	5.0	50	60	—	—	—	53	47
10	—	2-NaphOK–CO_2	5.0	50	60	—	—	—	100	0
11	2-NaphOK	PhOK–CO_2[b]	5.0	50	60	100	0	0	39	60
12	PhOK	2-NaphOK–CO_2[b]	5.0	50	60	87	8	4.5	41	58.5

[a] The CO_2 complexes were prepared by an introduction of low pressure CO_2 to potassium phenoxide (PhOK) or potassium 2-naphthoxide (2-NaphOK) at room temperature (*cf*. Experimental). [b] Blend mixtures of the complex and the phenoxide in a molar ratio of 1 : 1 were subjected to reactions in an autoclave. [c] Combination processes of a carboxylation with CO_2 at 3 °C and a decomposition under nitrogen at 150 °C were repeated twice or three times. [d] Nitrogen instead of carbon dioxide was applied. [e] Evolved carbon dioxide was removed by suction during the reaction. [f] Products (SA : salicylic acid, *p*HBA : *p*-hydroxybenzoic acid, and 2H1NA : 2-hydroxy-1-naphthoic acid) were determined by HPLC.

phenoxide changed into an alkali metal phenoxide–CO_2 complex. The carboxylation occurred in a few minutes at temperatures lower than 30 °C, but the yield did not change with a prolonged reaction time. These facts indicate that the carboxylation is very fast even at room temperature and is competing with the formation of the CO_2 complex. A gradual introduction of carbon dioxide of pressure less than 1.0 MPa onto potassium (or sodium) phenoxide produced preferentially the CO_2 complex at 30 °C. Thus 'pure CO_2 complex' free of the carboxylation products was prepared with carbon dioxide at the pressure of 0.1–1.0 MPa. The prepared complex was exposed to carbon dioxide at high pressure (5.0 MPa) for a longer time (60 min) at 50 °C, phenol was recovered in 100% yield after work-up. This fact means the complex is not an intermediate of the carboxylation reaction. Contrary to the mechanism widely accepted for a long time, once the CO_2 complex forms, the reaction does not proceed further to give carboxylic acids. The CO_2 complex starts decomposing to phenoxide at *ca*. 90 °C, and decomposes easily at 150 °C, while carboxylated products such as SA, *p*HBA are stable at higher temperature such as 180 °C, at least.

When the CO_2 complex was heated at *ca*. 100 °C in an autoclave filled with nitrogen instead of carbon dioxide, formations of SA and *p*HBA were in yields of only a few percent . This is ascribable to a reaction scheme where the CO_2 complex decomposes to phenoxide, and a part of the liberated carbon dioxide reacts with regenerated phenoxide to give carboxylic acids (Table 1 and Scheme 2).



Scheme 2 Carboxylation of potassium phenoxide with carbon dioxide.

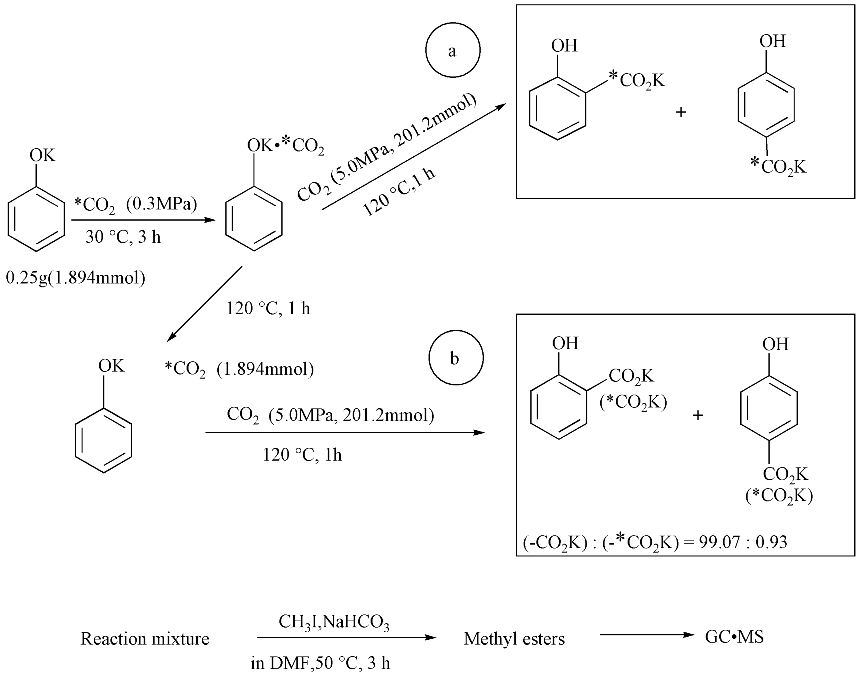
A similar reaction was repeated and the evolved gas was evacuated continually by a low-power pump (*ca*. 100 mmHg). None of carboxylic acids were obtained after 1 h heating. Upon heating at 150 °C under a nitrogen atmosphere, the complex decomposed to phenoxide, and a subsequent introduction of carbon dioxide at high pressure to the cooled mixture led to competitive reactions between carboxylations and a reformation of the complex. After the second carboxylation at 30 °C, the total yield of the carboxylic acids was double the amount (36.3%), and was 47.0%, almost equivalent to the expected value (50%) with another repetition of a combination process of decomposition–carboxylation (Table 1). Since the amount of alkali metal ion for restoring phenoxide decreased with the accumulation of both inorganic carbonates and dipotassium (or disodium) carboxylates, the repetitive reactions at room temperature did not give yields higher than *ca*. 70%. It is known that a CO_2 molecule is involved in a complex composed of transition metals or heavy metals which coordinate to an antibonding π-orbital of CO_2.[15,16] Among various possible structures, MOPAC/PM3 calculations have suggested **E** as the most appropriate structure for potassium phenoxide CO_2 complex. This is energetically much more stable than a π-complex, **D** (+209 kJ mol^{-1}), and more stable by 60.9 kJ mol^{-1} than the transition states or the intermediates which control products[17] (+3.9 and +2.9 kJ mol^{-1} for *ortho* and *para* carboxylates, respectively). Therefore, the formation of the complex is predominant (four times more) over the direct reaction of CO_2 on the benzene ring.

A carboxylation of potassium 2-naphthoxide gave 2-hydroxy-1-naphthoic acid (2H1NA) of rather high yields (*ca*. 50%) at 50 °C. The CO_2 complex of potassium 2-naphthoxide was prepared in a similar manner to that of the phenoxide, and was allowed to react with carbon dioxide of high pressure (5 MPa). Essentially, any carboxylations did not take place. This result proves again that the CO_2 complex is inert to carbon dioxide. In order to scrutinize the reactivity of the complex further, carboxylations of phenoxide or 2-naphthoxide were carried out in the presence of the complex. These two kinds of powder were blended in a dry-box using a mortar prior to the reaction with 5 MPa CO_2 at 50 °C for 60 min. The CO_2 complex of potassium phenoxide blended with potassium 2-naphthoxide did not produce SA or *p*HBA as expected, but 2H1NA was obtained in a yield exceeding 50%. On the other hand, a reaction of the CO_2 complex of potassium 2-naphthoxide in the presence of potassium phenoxide suppressed formations of SA and *p*HBA, but unexpected 2H1NA was produced in a yield of 58%. These results suggest that the carbon dioxide molecule in the CO_2 complex presumably binds to potassium phenoxide more strongly than potassium 2-naphthoxide, and therefore, the CO_2 molecule in the 2-naphthoxide complex shifts to the phenoxide in a structure like **F**. Successive shifts of CO_2 from inactive 2-naphthoxide complex resulted in production of higher yields of 2H1NA. When the 2-naphthoxide complex and phenoxide were placed separately using aluminium foil in an autoclave,

Table 2 Mass spectral data of esters of products

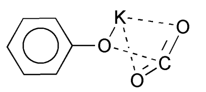
Esters ($C_8H_8O_3$)	*m*/*z* 152	*m*/*z* 153
Methyl salicylate	89.86 (%)	10.14 (%)
Methyl *p*-hydroxybenzoate	91.11	8.89
Observed (average)	90.49	9.51
If path a (Intramolecular migration)	0	100
If path b (Decompositon of the complex followed by carboxylation)	90.28	9.72[a]

[a] This figure is based on the following calculations: $^{13}CO_2$ = 0.93 (%) and unlabeled CO_2 = 99.07 (%) were used. The latter included ^{13}C of natural abundance (= 1.10%). Theoretical amounts of ^{13}C in the carboxyl carbon would be 0.93(%) + 99.07(%) × 0.0110 = 2.02 (%) and ^{13}C in the other 7 carbons : 1.10(%) × 7 = 7.70 (%). Therefore, the total amount of ^{13}C in the esters should be: 2.02 + 7.70 = 9.72 (%)

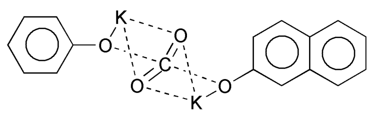


Scheme 3 Incorporation of carbon-13 in the reaction of potassium phenoxide–carbon dioxide complex

and warmed at 50 °C for 60 min, followed by an introduction of carbon dioxide of 5 MPa, 2H1NA was not produced at all, and SA and *p*HBA were obtained in 28% yield, as much as normal. Calculations by MOPAC/PM3 method support a coordination structure **E**, and prove 2-NaphOK–CO_2 (−48.3 kJ mol^{-1}) is less stable than PhOK–CO_2 (−57.5 kJ mol^{-1}). These energy differences may be enough for the CO_2 in the complex to shift from 2-NaphOK to PhOK in a sandwich form like structure **F** during the blending process under nitrogen atmosphere at room temperature.



(**E**) Carbonate like complex



(**F**)

Experiments of CO_2 complex labeled with carbon-13

The CO_2 complex was prepared using $^{13}CO_2$. The PhOK–$^{13}CO_2$ complex was heated in the presence of a large excess of normal CO_2 at 120 °C for 1 h. The produced carboxylic acids were subjected to esterification with methyl iodide in DMF, followed by GC/MS analyses. If an internal migration of the CO_2 in PhOK–$^{13}CO_2$ would be involved in the reaction (path a), the relative intensity of the molecular peak of *m*/*z* 153 should be 100%. However, a found value, 9.51% relative to *m*/*z* 152 (90.49%) agrees with the calculated figures based on the assumption of a thorough mixing of $^{13}CO_2$ with CO_2, which is containing $^{13}CO_2$ by natural abundance (1.1%) (Scheme 3 and Table 2). These labeled experiments have furnished unambiguous support for the direct reaction between carbon dioxide and benzene ring, but not for the mechanism of carboxylations *via* a CO_2 complex. It is rather natural for chemists in a laboratory to be reluctant to open the lid of an autoclave where very hygroscopic materials are kept dry. Any consideration to the competitive formation of carboxylic acids with the formation of a CO_2 complex even at the initial stage of the reaction has not been given in the past experimental work elaborated on the mechanism using kinetics,[8,13] reactivity,[6,12] and thermal analysis.[10,12]

Carbon-13 NMR spectra

Phenyl carbonate ($PhOCO_2M$, where M was K or Na) was originally proposed for the complex,[5] but the IR absorption spectra[7] showed a band at 1684 cm^{-1} which was not in agreement with those of structurally similar carbonates such as methyl phenyl carbonate (1754 cm^{-1}) and dimethyl carbonate (1748 cm^{-1}). Therefore a structure **D** was proposed based on a plausible interaction between the π-electrons and CO_2.[7,11] But the IR spectrum itself is not sufficient for providing persuasive evidence, because the adulteration of inorganic carbonates in the sample is more or less inevitable in the preparation of phenoxides.[18] Their strong absorption bands (*e.g.* both potassium carbonate and potassium hydrogen carbonate show very broad and strong absorptions at *ca.* 1650 cm^{-1}) mar the characteristic absorption around 1600–1700 cm^{-1}. This contamination also makes X-ray analysis of the structure difficult. The complex was slightly soluble in dimethylformamide (DMF), but most

Table 3 Carbon-13 chemical shifts of CO_2 of an alkali metal phenoxide–CO_2 complex and related compounds

Compounds	δ_C/ppm	Notes
CO_2 in C_6H_5OK–CO_2	154	[a]
COOK of potassium salicylate	169	[b]
K_2CO_3 in D_2O–acetone-d_6	168	[c]
$KHCO_3$ in D_2O–acetone-d_6	162	[c]
$(NH_4)_2\,CO_3$ in D_2O–acetone-d_6	160	[c]
CO_2 in DMF	124	[d]

[a] The complex was prepared with potassium phenoxide and carbon-13 enriched carbon dioxide of 0.1 MPa at room temperature. A CP-MAS was applied. [b] The carbon-13 enriched complex prepared as in footnote a was heated with $^{13}CO_2$ at 130 °C. A CP-MAS was applied. [c] A mixture of deuterium oxide and acetone-d_6 in a ratio of 3 : 1 was used. [d] Carbon dioxide was saturated in DMF at room temperature.

decomposed to phenol or phenoxide, disturbing measurements of proton NMR spectra of the complex. A CP-MAS NMR spectrum of the CO_2 complex of potassium phenoxide enriched with carbon-13 showed a peak at 154 ppm (Fig. 1). Chemical shifts of several kinds of carbonates were 168–160 ppm, and potassium salicylate showed a peak at 169 ppm for the carboxyl carbon of less electron density (Table 3). These data indicate that the complex is not a carbonate, but a more polarized molecule than carbon dioxide (124 ppm). A broad IR absorption band at *ca.* 1650 cm^{-1} of the complex indicates a bent CO_2 molecule (most stable at 130–140°), and is different from an absorption at 2349 cm^{-1} of carbon dioxide in a linear sp configuration. Unlike alkali alkyl carbonate,[19] *O*-alkylation which would give phenyl carbonate such as $PhOCO_2K$, did not occur under conditions employed for the present carboxylations.

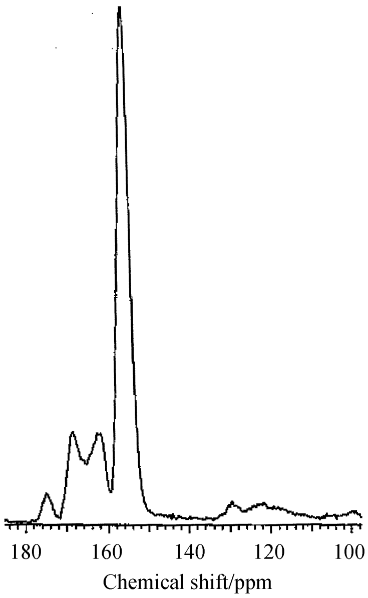


Fig. 1 A CP-MAS (6 K) carbon-13 NMR spectrum of the potassium phenoxide–$^{13}CO_2$ complex in a sealed ampoule.

In the NMR spectra, the chemical shifts of *o*-, *m*- and *p*-carbons of the potassium complex were 121.4, 130.4 and 115.0 ppm, respectively. Differences of chemical shifts ($\Delta\delta_C$) from those of potassium phenoxide were 0, -2.4 and $+1.0$ ppm, respectively. Such small changes in the carbon-13 NMR spectrum would not be expected for the formation of a π-complex on the benzene ring.[20] On the other hand, the *ipso*- carbon shifted significantly upfield (-6.5 ppm), which was similar to the chemical shift of undissociated phenol, but not of phenoxy species.

Experimental

All chemical reagents of extra pure grade were purchased from Tokyo Kasei Chemical Co.Ltd. Carbon dioxide of purity more than 99.95% was supplied by Sanin Sanso Co.Ltd. Carbon-13 more than 99% enriched CO_2 was supplied by ISOTEC INC (Miamisburg, Ohio).

Potassium (or sodium) phenoxide and 2-naphthoxide were prepared with potassium (or sodium) hydroxide and the corresponding phenols. Phenoxide–CO_2 complexes were prepared by introducing carbon dioxide of 0.1 MPa onto fine powdered phenoxide for 24 h. The potassium 2-naphthoxide–CO_2 complex was prepared in a similar manner to the phenoxide complex, but CO_2 of 1.0 MPa was used in an autoclave for 1.5 h. Phenoxides or these complexes of *ca.* 0.5 g were placed in an autoclave (SUS-316) with a volume of 200 ml (Taiatsu Techno Co. Osaka). An autoclave was flashed with nitrogen and warmed to the reaction temperature prior to the introduction of carbon dioxide. Carbon dioxide was released after the reaction, and the reaction mixture was washed out with H_2O–CH_3OH, and was analyzed by HPLC (Shimadzu LC-10AD) using a silica gel column of 10 cm with an eluent of aqueous phosphate buffer solution–CH_3OH (70:30 v/v%) at a flow rate of 1.0 ml min^{-1}. Carbon-13 enriched CO_2 complex was heated in an autoclave at 120 °C for 1 h. An aqueous solution of the reaction mixture was neutralized and was extracted with diethyl ether to remove phenol. Diluted hydrochloric acid was added to the aqueous layer, adjusting the pH value to 2–3 before extraction of the carboxylic acids with diethyl ether. The products were esterified with methyl iodide and sodium hydrogen carbonate in dimethylformamide at 50 °C for 3 h.[21] These methyl esters were obtained with conversions of 100%. A Shimadzu GC17A/QP5000 MS spectrometer was used for isotopic analyses. Semiempirical calculations using a program of MOPAC6 with Hamiltonian PM3 were carried out for unimolecular models. While distances of PhO-K and CO_2-K were fixed to be 3.0 Å and 3.2 Å, respectively, the distance (R) between the phenoxide and CO_2 was variable to minimize the energy. A CP-MAS sample, potassium phenoxide–$^{13}CO_2$, was prepared using C-13 enriched carbon dioxide. The sample was sealed in a glass tube of $5 \times 5^{\Phi}$ mm, and was set in a NMR rotor. Spectra were obtained on a Varian XL-400 spectrometer (^1H: 400 MHz, ^{13}C: 100 MHz). CP-MAS conditions applied were as follows: MAS rate: 6 KHz, CP contact time: 3 ms, relaxation delay: 5 sec, 90 degree pulse width: 6.5 μsec, number of repetition: 384, spectrum width: 40 000 Hz.

Conclusion

The Kolbe–Schmitt reaction is the reaction of alkali metal phenoxide with carbon dioxide, and has been a useful method over more than a century to obtain aromatic hydroxy carboxylic acids. An alkali metal phenoxide–CO_2 complex had been widely accepted for a long time as an intermediate of the reaction, but it has been proved, in this paper, that the CO_2 complex is not an intermediate to give carboxylic acids, such as salicylic acid (SA) and *p*-hydroxybenzoic acid (*p*HBA). A direct carboxylation of phenoxide with CO_2 takes place even at room temperature, and is competitive with formation of the CO_2 complex. The resulting complex decomposes thermally (above *ca.* 90 °C) to phenoxide, which then undergoes further competitive reactions. Thus the increment of yields of the carboxylic acids is directly dependent on the repetition number of carboxylations at room temperature in combination with decompositions at 150 °C under nitrogen atmosphere. The new mechanism is also supported by labeling experiments: the CO_2 complex prepared with carbon dioxide enriched with carbon-13 does not give carboxylic acids with labeled by carbon-13, but completely scrambled with normal carbon dioxide.

A carbonate-like structure has been proposed for the CO_2 complex suitable for the data of the reactivity, C-13 NMR and MOPAC/PM3 calculations. Spectral and thermoanalytical data in past studies may have been required to consider the instant and competitive formation of carboxylic acids, though relatively small amounts, at any stage of the reaction.

Acknowledgements

The endowment of carbon-13 enriched CO_2 by Professor Takeshi Kobayashi (Department of Bio-Engineering, Nagoya Univ.) is very much appreciated. Preliminary measurements of CP-MAS NMR of very hygroscopic samples were conducted by Dr Hisayuki Tsuno (JEOL Ltd.). Financial support by San-In Kensetsu Kougyou Co., Ltd. is acknowledged.

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