

Oxidation of Coals in Liquid Phases. X. Mechanism of the Cleavage of Benzenecarboxylic Acids to Oxalic Acid and Carbon Dioxide by the Base-Catalyzed Oxygen-Oxidation

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A kinetic study of the oxidation of benzenecarboxylic acids has been performed in order to clarify the mechanism. The reaction products were oxalic acid and carbon dioxide, along with a trace of acetic acid. The oxidation rate of phthalic acid was proportional to the first order of the molality of phthalic acid, the molality of NaOH, and partial oxygen pressure, respectively; the apparent activation energy was 126 kJ mol⁻¹. These results show that the rate-determining step is a cleavage of the benzene ring proceeded by a base-catalyzed oxygen-oxidation mechanism in which a carbanion formed by hydrogen extraction from an aromatic ring is attacked by oxygen. In the cleavage of phthalic acid, NaOH increases the selectivity to form oxalic acid as well as the oxidation rate. In the oxidation of 1,2,3-benzenetricarboxylic acid the same mechanism was recognized, but not for benzenhexacarboxylic acid which has no hydrogen on the benzene ring.

The oxidation of coal in alkaline solutions at elevated temperatures is one of the important methods to produce coal chemicals.^{1,2} Parker³ et al. and Kamiya⁴ have studied the optimum conditions for producing aromatic carboxylic acids. In the presence of a great excess of free alkali, oxalic acid is produced selectively in high yield from coal;⁵ the optimum conditions⁶ and qualitative mechanism of the formation with model compounds⁷ have been investigated. During the course of oxidation the phenol group and ether groups in the coal structure are first oxidized to form aromatic carboxylic acids and acetic acid; the resulting carboxylic acids are then oxidized to oxalic acid. In these reactions it is known that the alkalis and oxygen promote the oxidation reaction, but essential mechanisms for individual carboxylic acid have not yet been disclosed, except for acetic acid.⁸ Especially, it is important to elucidate the mechanism of oxidative cleavage reactions of aromatic carboxylic acids so as to improve the yield of oxalic acid from coal, since they are major intermediates. However, quantitative studies on such reactions have not yet been performed at elevated temperatures. In the present study, the effects of the reaction conditions on the oxidation of aromatic carboxylic acids were investigated in order to clarify the reaction mechanism at elevated temperatures using phthalic acid and several benzenecarboxylic acids as model compounds.

Experimental

Reagents. All reagents used were of reagent grade. In the following text such expressions as Ni(0), Ni(Ni), and Ni(NiO) indicate following respective conditions without additive, with Ni powder, with NiO powder.

Apparatus. An SUS 316 stainless-steel autoclave of 1 dm³ with a magnet driving stirrer was used and parts contacting the solution were made of Ni.

Reaction Conditions. Oxidation was carried out under 0.02 mol kg⁻¹ of aromatic acid and 5.00 mol kg⁻¹ of a NaOH solution. The amount of metal or metal oxide powder added was 0.051 mol, equivalent to 3 g of Ni.

Direction. A Ni beaker containing benzenecarboxylic acid, NaOH, and water was placed in the autoclave and the air was replaced three times with 5 MPa N₂. The autoclave was then placed in an electric furnace and heated to the reaction temperature and the oxidation was initiated by the introduction of O₂. The partial oxygen pressure was added to the vapor pressure of the solution at the reaction temperature. An 8-cm³ portion was extracted with a small SUS 316 stainless-steel test tube for analyses of oxalic acid and unreacted benzenecarboxylic acid.

Analyses. The extracted solution was weighed, diluted to 50 cm³ and the corrosion product precipitated on standing overnight. The supernatant solution was taken out with a pipette and sodium ion was removed with a cation-exchange column. Organic acids in the eluate were determined by ion and liquid chromatographs.

H-D Exchange Reaction. Heavy water (40 g), NaOH (8 g, 5 mol kg⁻¹ D₂O), and phthalic acid (0.3 g, 0.043 mol kg⁻¹) were placed in 70 cm³ of an SUS 316 stainless-steel autoclave and N₂ exchange of air was repeated three times with 5 MPa N₂. It was then dipped in a silicone oil bath for 1 h at 523 K. The product in the solution was extracted by ethyl methyl ketone, dissolved in methanol-*d*₄ and analyzed by ¹³C NMR.

X-Ray Diffraction (XRD) and ESCA Spectra. XRD and ESCA spectra of nickel oxides were measured by Cu K α and Mg K α , respectively.

Mechanism of the Oxidation of Phthalic Acid

Effect of Reaction Conditions. The molalities of phthalic acid and NaOH, partial oxygen pressure and temperature: First-order plots of the molality of phthalic acid were linear under various conditions, including 0.01 and 0.04 mol kg⁻¹ of phthalic acid solution. The apparent rate constants from the slopes are shown in Table 1; these results show that the rate of oxidation of phthalic acid was proportional to the molality of phthalic acid, the molality of NaOH, and

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Table 1. Effect of Reaction Conditions on the Apparent Rate Constant (k/h^{-1}) of the First-Order Plots

(a) NaOH molality/mol kg ⁻¹	1.00	2.00	3.00	4.00
	5.00			
apparent rate constant	0.078	0.148	0.238	0.336
	0.403			
(b) p_{O_2} /MPa	1.0	2.0	3.0	4.0
	5.0			
apparent rate constant	0.109	0.226	0.296	0.358
	0.403			
(c) Temperature/K	503	513	523	
apparent rate constant	0.127	0.234	0.403	

Standard conditions: phthalic acid 0.02 mol kg⁻¹, NaOH 5.00 mol kg⁻¹, p_{O_2} 5.0 MPa, and 523 K.

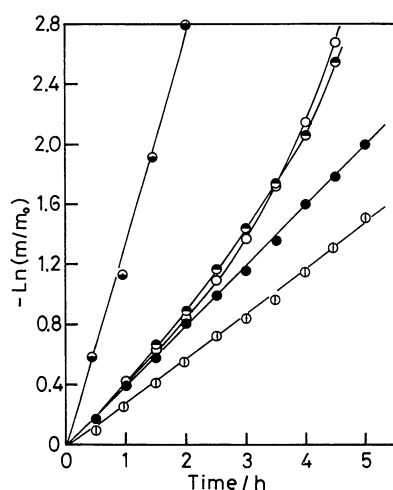


Fig. 1(a). Effect of metal powder on the rate of oxidation. ●: Ni(0), ●: Ni(Ni), ○: Ni(Ni, 5), ○: Ni(Fe), ○: Ni(Cu).

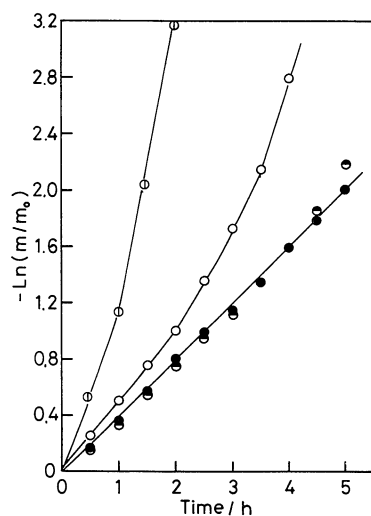
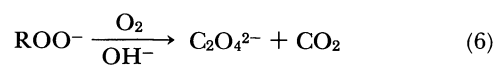
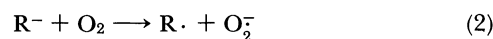
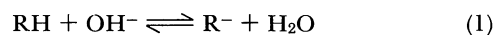


Fig. 1(b). Effect of metal oxide on the rate of oxidation. ●: Ni(0), ●: Ni(NiO), ●: Ni(NiSO₄), ○: Ni(Ni₂O₃), ○: Ni(CuO).

the partial oxygen pressure, respectively. The apparent activation energy was 126 kJ mol⁻¹.

Metal and Metal Oxide. In this experiment, the effect of nickel oxide, the corrosion product from the Ni reactor, on the rate of oxidation was inevitable to some extent, but smaller than that on the rate of oxidation of acetic acid.⁸⁾ Consequently, the effect of several metals and their oxides has been studied. First-order plots of the molality of phthalic acid in the presence of Ni, Cu, Fe and their oxides are shown in Fig. 1. In the cases of Ni(Ni) and Ni(Ni, 5), containing 3 g and 5 g of Ni powder, respectively, their oxidation rates were almost equal, but higher than that in the case of Ni(0). The similar rates in the cases of Ni(Ni) and Ni(Ni, 5) may have been caused by insufficient agitation. Their first-order plots gradually shifted upward with the reaction time. Nickel(II) oxide did not affect the oxidation rate, since it coincided for Ni(0), Ni(NiO), and Ni(NiSO₄), resulting in NiO being produced in the solution, as shown in Fig. 1(b). On the other hand, the oxidation rate for Ni(Ni₂O₃) was higher than that for Ni(0) and shifted largely upward from linearity. These results indicate that metallic Ni has no direct catalytic effect, and that the shift from linearity is caused by an accumulation of Ni(III) in the corrosion product. This can be recognized from the ESCA spectra of the corrosion products. In the case of Ni(Fe), the first-order plot was linear, and the apparent rate constant was 3/4 of that for Ni(0). Metallic Fe similarly controlled the oxidation of phthalic acid, as in the oxidation of acetic acid. This effect was brought about by controlling the formation of Ni(III) with Fe or the haematite formed.⁸⁾ Metallic Cu greatly promoted the oxidation rate but the first-order plot coincided well with that for CuO. Thus, the material accelerating the oxidation was not metallic Cu but CuO. Copper(II) oxide was identified in the materials in extracted solutions by XRD.

Mechanism of the Oxidation. Base-Catalyzed Oxygen-Oxidation. The general mechanism can be expressed by the following reactions:⁹⁾

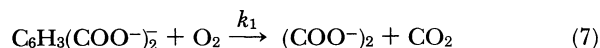


Here, RH is a carbonaceous substance and R⁻ is the carbanion formed by hydrogen extraction from RH.

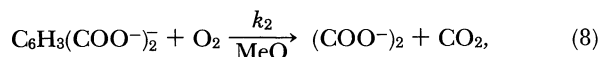
Concerning these steps, it is shown below that reaction (2) is rate-determining and, simultaneously, a

side reaction which has same effect due to corrosion of the Ni reactor.

In the oxidation of phthalic acid, reaction (2) and the side reaction can be expressed by Eqs. 7 and 8, respectively.



and



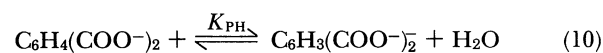
respectively.

In this case, the apparent oxidation rate of phthalic acid can be expressed by

$$-dm_{\text{PH}}/dt = k_1 m_{\text{P}^-} m_{\text{O}_2} + k_2 m_{\text{P}^-} m_{\text{MeO}}^{\S} m_{\text{O}_2}, \quad (9)$$

where PH is phthalate ion, P⁻ is the carbanion formed by hydrogen extraction from phthalate ion, MeO is metal oxide, m_i is the molality of each species, and k_i is the rate constant.

In the solution carbanion is formed by an acid-base equilibrium of phthalate ion, as shown in Eq. 10, and the molality of oxygen obeys Henry's law:



$$m_{\text{O}_2} = M p_{\text{O}_2} \quad (11)$$

where K_{PH} is the equilibrium constant, M is Henry's constant, and p_{O_2} is the partial oxygen pressure.

Consequently, Eq. 9 can be written as

$$-dm_{\text{PH}}/dt = k_1 K_{\text{PH}} M m_{\text{PH}} m_{\text{OH}^-} p_{\text{O}_2} + k_2 K_{\text{PH}} M m_{\text{MeO}} m_{\text{PH}} m_{\text{OH}^-} p_{\text{O}_2}, \quad (12)$$

where m_{OH^-} is the molality of the hydroxide ion.

From Eq. 12 we can derive

$$-dm_{\text{PH}}/dt = k m_{\text{PH}} m_{\text{OH}^-} p_{\text{O}_2} \quad (13)$$

since the apparent rate constant, k , is expressed by

$$k = (k_1 + k_2 m_{\text{MeO}}) K_{\text{PH}} M \quad (14)$$

If k_1 is much larger than $k_2 m_{\text{MeO}}$, the apparent rate constant of oxidation of phthalate ion becomes

constant and the rate of oxidation can be expressed by a first-order rate equation, like Eq. 13.

The results shown in Table 1 satisfy the first-order rate equation for m_{PH} , m_{OH^-} , and p_{O_2} . Thus, the above mechanism is basically reasonable.

In order to emphasize the effect of the corrosion product on the rate of oxidation, the results of comparative experiments using several metals and their oxides are shown in Fig. 1. Table 2 shows the relationship among the various kinds of additives, the hypothesis regarding the second term in Eq. 9, $k_2 m_{\text{MeO}}$, and the properties of the resulting apparent rate constant. If the second term is assumed as in the second column, the apparent rate constant should have the property shown in the third column. These results can explain the effect of each metal and its oxide on the oxidation rate.

Consequently, it is concluded that base-catalyzed oxygen-oxidation takes place, essentially, during the oxidation of phthalic acid in alkaline solutions at elevated temperatures; the side reaction, however, is inevitable to some extent due to corrosion of the Ni reactor.

The side-reaction mechanism has not yet been recognized sufficiently. By analogy of the oxidation of acetic acid,⁸⁾ it is considered that Ni(III) in the corrosion product catalyzes the oxidation of the carbanion, as shown in Eq. 8, and that $m_{\text{Ni(III)}}$ seems to be proportional to m_{OH^-} .^{§§} The effect of Ni(III) is shown in Fig. 1(a). This tendency is also shown later in the oxidation of benzenhexacarboxylic acid (mellitic acid). In the presence of CuO the oxidation rate was great and oxalic acid was formed, even in a N₂ atmosphere. Thus, CuO is a very active catalyst and the second term in Eq. 9 represents the major process in the case of Ni(CuO). As for the species of phthalic acid, it is necessary to confirm further which is the reactant, the phthalate ion or its carbanion.

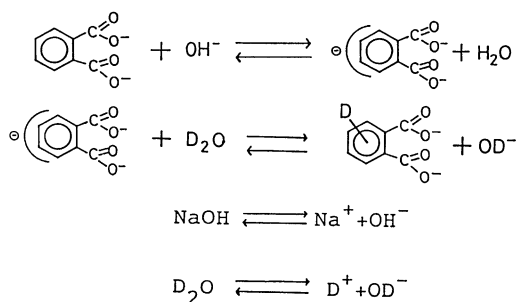
H-D Exchange of Hydrogen on Benzene Ring. If phthalic acid is related to the equilibrium shown in Eq. 10, an H-D exchange reaction is capable of occurring in phthalic acid-NaOH-D₂O through the equilibrium shown in Scheme 1. Figure 2 shows the ¹³C NMR spectra of phthalic acid: (1) Reagent, (2) treated with 5 mol kg⁻¹ NaOH-D₂O solution at 523 K, and (3) treated with D₂O at 523 K. In spectrum (2), the

Table 2. Relationships among Additive, Hypothesis, and Resulting Apparent Rate Constant

Additive	Hypothesis on $k_2 m_{\text{MeO}}$ term	Apparent rate constant
None, NiO, NiSO ₄	$k_2 m_{\text{Ni(III)}} < k_1$	Constant
Ni(Ni, 5), Ni ₂ O ₃	$k_2 m_{\text{Ni(III)}} < k_1$ and increase	Gradual increase
Fe	$k_2 m_{\text{Ni(III)}} \ll k_1$	Constant
Cu, CuO	$k_2 m_{\text{CuO}} \gg k_1$	Great

§ The m_{MeO} shows apparent molality of the metal oxides since the metal oxides are sparingly soluble.

§§ In this case, the rate of oxidation should be proportional to $m_{\text{OH}^-}^2$ as in the oxidation of acetic acid.



Scheme 1. H-D exchange mechanism of hydrogen on benzene ring.

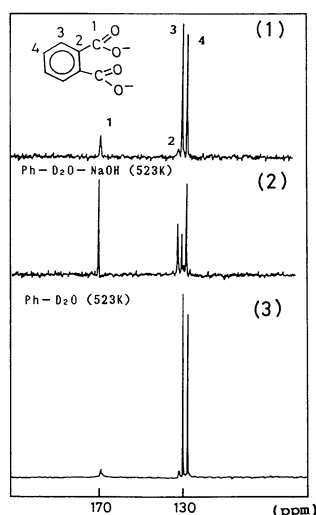


Fig. 2. ^{13}C NMR spectra of phthalic acid treated at 523 K. (1) Reagent, (2) Treated with 5 mol NaOH kg^{-1} D_2O , (3) Treated with D_2O .

height of peaks 3 and 4 are lower, compared to these of peaks 1 and 2. This shows that an H-D exchange takes place. Additionally, the height of peak 3 is lower than that of peak 4. This indicates that the hydrogen on carbon 3 is extracted more easily than on carbon 4 due to the effect of the electrophilic carboxylic group. An H-D exchange ratio of 64% was obtained by a calculation of the ratio of the integrated peak area of phenyl protons to that of the methyl protons in the ^1H NMR spectrum of the dimethyl ester of deuterated phthalic acid. In a treatment in D_2O , no H-D exchange was observed, as shown in the spectrum (3). Consequently, the carbanion can be formed in an alkaline solution at 523 K.

Identification of Ni(III) in the Corrosion Products with ESCA. Figure 3 shows the ESCA spectra of $\text{Ni}2p_{3/2}$ of corrosion products precipitated in extracted solutions for analyses of organic acids in the case of Ni(0). Only NiO was identified in the corrosion products by XRD. Generally, peaks of Ni(II) and Ni(III) in ESCA spectra appear in the energy range 854.0⁽¹⁰⁾–854.8⁽¹¹⁾ eV and 855.6⁽¹²⁾–856.8⁽¹³⁾ eV, respec-

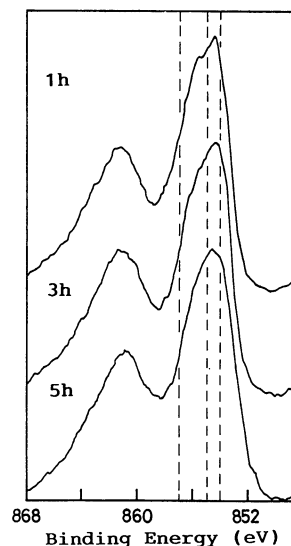


Fig. 3. ESCA spectra of $\text{Ni}2p_{3/2}$ of the nickel oxide formed by corrosion of Ni.

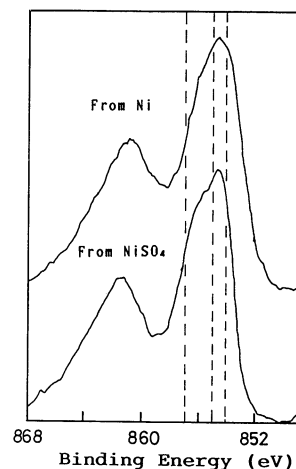


Fig. 4. ESCA spectra of $\text{Ni}2p_{3/2}$ of the nickel oxide formed from NiSO_4 .

tively. Thus, the 1-hour sample contains much NiO, since the peak around 854 eV is sharp. In the 3-hour spectrum, a range of 855–857 eV swells and becomes round. This tendency is remarkable and the peak shifts slightly to the high-energy side, around 855 eV in the 3-hour spectrum. These changes in the ESCA spectra show that the Ni(III) content gradually increases with the reaction time.

Figure 4 is the ESCA spectra of precipitates in the case of $\text{Ni}(\text{NiSO}_4)$. Nickel(II) sulfate was converted to $\text{Ni}(\text{OH})_2$ upon heating, and pale-green NiO was formed after 1 hour. This color shows that it is stoichiometric NiO. The Ni(III) content in NiO seems to be low, as shown in Fig. 4, indicating that Ni(III) is produced only slightly by the oxidation of suspended NiO in the solutions but, rather by a heterogeneous oxidation of metallic Ni.

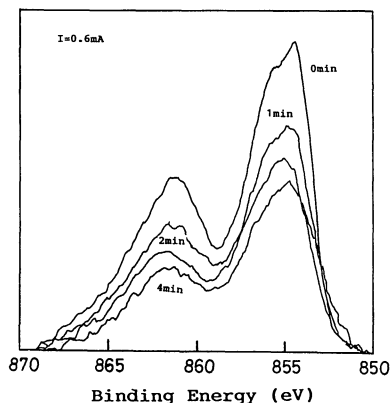


Fig. 5. ESCA spectra of $\text{Ni}2p_{3/2}$ of the nickel oxide containing unreacted Ni on Ar etching.

In the 1-hour sample of Ni(Ni), unreacted Ni could still be identified by XRD. The valence of Ni in it was measured with Ar etching on ESCA. The ESCA spectra are shown in Fig. 5. The peak of the $\text{Ni}2p_{3/2}$ orbital shifted to the high-energy side with an increase in the depth but with 4-minute etching it shifted contrarily to the low-energy side, by the peak of metallic Ni at 852.3 eV. This shows that Ni(III) is formed by the oxidation of the surface of Ni.

These tendencies were also observed from the ESCA spectra of the $\text{O}1s$ orbital of the oxides, in which the slope of the peak at 530 eV by $\text{O}1s$ clearly swelled at 532 eV due to the oxygen combined Ni(III).

Oxidative Cleavage Reaction of Benzene Ring. Steps (1) and (2) have been clarified by kinetic studies. Generally, the formation of the peroxyanion by steps (3) to (5) is accepted,⁹ though there is no information concerning the oxidative cleavage of the peroxyanion of benzenecarboxylic acid.

Chemical and biochemical oxidative cleavages of

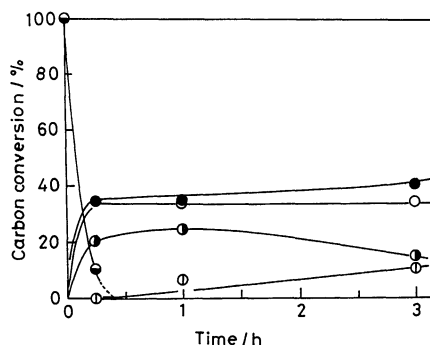


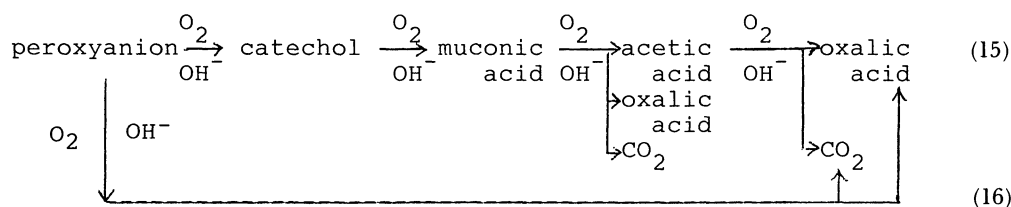
Fig. 6. Oxidation curve of maleic acid in 25 mol kg^{-1} NaOH solution at p_{O_2} 5 MPa and 498 K. ●: malic acid, ●: oxalic acid, ○: acetic acid, ●: succinic acid, ○: CO_2 .

phenols and catechols have been reviewed^{9,14} and the formation of aliphatic dicarboxylic acids, such as muconic acid, has been indicated.

If phenols and catechols are formed as intermediates in the cleavage of the benzene ring, both acetic and oxalic acids should be produced in high yield in alkaline solutions.⁷ Actually, acetic acid was found only in trace amounts in these runs.

Maleic acid, which is supposed to behave similarly to muconic acid, was oxidized under 498 K, NaOH 25 mol kg^{-1} , and p_{O_2} 5 MPa. Maleic acid was hydrated at once to malic acid during heating. It was almost oxidized within 30 min; succinic, oxalic and acetic acids were produced, as shown in Fig. 6.^{§§§}

These two experimental results do not suggest that the oxidative cleavage of phthalic acid proceeds slowly by a stepwise mechanism, as shown in Eq. 15, in which a derivative of catechol is formed, and then cleaves to produce an aliphatic dicarboxylic acid, such as derivatives of muconic acid.



Thus, the oxidative cleavage takes place all at once to produce oxalic acid and CO_2 , as shown in Eq. 6. However, the reaction mechanism shown in Eq. 16 is not clear.

The formation of succinic acid during the oxidation of maleic acid is interesting and indicates that the oxidation of aliphatic dicarboxylic acid with a double bond may accompany the formation of radicals and its recombination.

Effect of Reaction Conditions on the Selective Formation of Oxalic Acid. Figures 7(a)—(b) show a

decrease in the yield ratio of oxalic acid to carbon dioxide with the reaction time under various conditions. The consecutive oxidation of oxalic acid decreases the yield ratio with the reaction time. Thus, the effect of the reaction conditions on the yield ratio of the oxidation of phthalic acid, itself, can be discussed in terms of the value obtained by extrapolation to $t=0$, since no consecutive oxidation of oxalic

§§§ Batch runs have been performed with a 300 cm^3 autoclave.

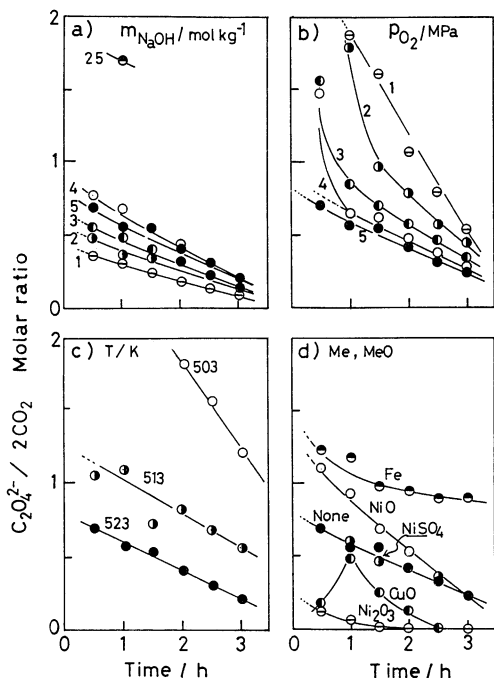


Fig. 7. Effect of reaction conditions on the selective formation of oxalic acid in the oxidation of phthalic acid. (a) m_{NaOH} , (b) p_{O_2} , (c) temperature, (d) metal, metal oxide.

acid takes place at $t=0$.

The selectivity was higher at higher NaOH molality and the yield ratio was as high as 1.7, even after 1 hour in a 25 mol kg⁻¹ NaOH solution,⁷⁾ as shown in Fig. 7(a). These results show that a high NaOH molality not only accelerates the rate of oxidation but also increases the selectivity. Since the mechanism of oxidative cleavage of the peroxyanion, itself, is not clear, there is no clue to discuss the mechanism in which NaOH enhances the selectivity. Practically, this result coincides with the fact that high NaOH molalities in the oxidation of coal are quite effective, both on the oxidation rate and on the selective formation of oxalic acid due to the oxidative cleavage of a large number of aromatic compounds formed as intermediates.⁸⁾

A low partial oxygen pressure and temperature increased the selectivity, as shown in Figs. 7(b) and 7(c), but decreased the oxidation rate, as shown in Tables 1(b) and 1(c).

Clearly, Ni(III) promotes the oxidation of oxalic acid and reduces the selectivity of the formation of oxalic acid. This can be confirmed by the result that Ni₂O₃ reduces the yield ratio to a great extent and rapidly to zero with the reaction time shown in Fig. 7(d). This result also indicates that the decrease in the yield ratio is caused by a consecutive oxidation of oxalic acid by Ni(III) in the nickel oxide formed by the corrosion of metallic Ni. Since Fe controls remarkably the formation of Ni(III),⁸⁾ the yield ratio in the case of

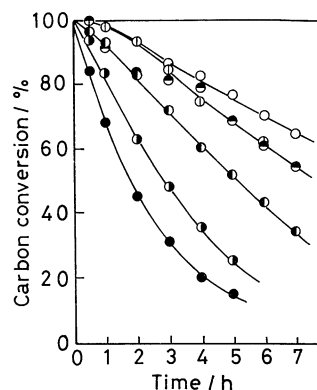


Fig. 8. Oxidation curves of benzenecarboxylic acids. ●: 1,2-benzenedicarboxylic acid, ○: 1,2,3-benzenetricarboxylic acid, ⊙: 1,3,5-benzenetricarboxylic acid, ⊕: 1,2,4-benzenetricarboxylic acid, ⊖: benzenepentacarboxylic acid, ⊗: benzenhexacarboxylic acid.

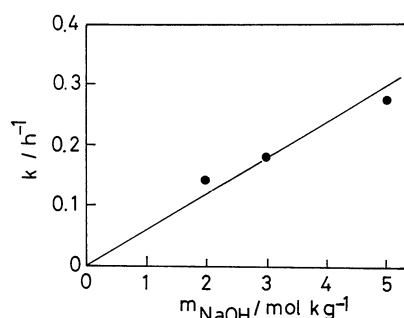


Fig. 9. Effect of NaOH molality on the oxidation of hemimellitic acid.

Ni(Fe) was high and decreased gradually. On the other hand, CuO promotes the oxidation of oxalic acid as well as phthalic acid. Thus, further study is necessary to clarify the effect of metal oxides on the selectivity of the formation of oxalic acid as well as the mechanism in the oxidative cleavage of phthalic acid.

Oxidation of the Other Benzenecarboxylic Acids

Effect of the Structure of Substrates. Figure 8 shows the oxidation curves of various benzenecarboxylic acids under standard conditions. Benzenecarboxylic acids seem to be oxidized faster as the number of carboxyl group decreases. The effect of the position of the carboxyl group is not yet clear.

Oxidation of Hemimellitic Acid and Mellitic Acid.

The effect of the NaOH molality on the rate of oxidation of hemimellitic acid is shown in Fig. 9. The apparent rate constant was also proportional to the NaOH molality. Consequently, hemimellitic acid is oxidized by the same mechanism as phthalic acid is oxidized. This result supports a hypothesis that an aromatic carboxylic acid having hydrogens on its ring are oxidized by a base-catalyzed oxygen-oxidation mechanism in alkaline solutions at elevated temper-

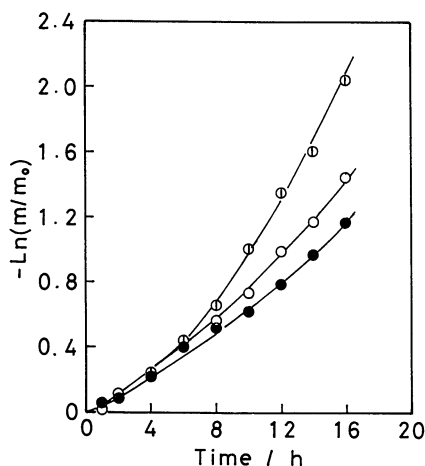


Fig. 10. Effect of NaOH molality on the oxidation of mellitic acid. NaOH molality. mol kg⁻¹ ●: 2, ○: 3, ⊙: 5.

atures.

The effect of the NaOH molality on the first-order plots for the oxidation of mellitic acid is shown in Fig. 10. The first-order plots shifted upward from a straight line with an increase in the reaction time and the NaOH molality. These results indicate that the amount of Ni(III) formed by the corrosion of Ni increases with increasing the reaction time and the NaOH molality. The progress of corrosion could easily be recognized by the amount of corrosion products in extracted solutions. Also, the NaOH molality did not affect the initial rate of the oxi-

dation, which should be proportional to the NaOH molality in the base-catalyzed oxygen-oxidation mechanism, as shown in Table 1 and Fig. 9. These results indicate that this mechanism does not work on the oxidation of mellitic acid which has no hydrogen on the benzene ring.

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