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Oxidation of Coals in Liquid Phases. VII. Oxidation of Oxygen-containing Model Compounds of Coal by Oxygen in Concentrated Sodium Hydroxide Solutions

Hirohide Furuya, Ryoichi Uwabe, Nobuyuki Sutoh, Akitsugu Okuwaki,*
Akira Amano, and Taijiro Okabe
Department of Applied Chemistry, Faculty of Engineering, Tohoku University, Aramaki, Sendai 980

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Oxidation of 26 model compounds of low-ranked coal was performed to study the formation mechanisms of oxalic acid from coal. A mixture of 0.02 mol of the model compound, 4—60 g of NaOH, and 50 g of water was placed in a 300 cm^3 autoclave and oxidized at 523 K and P_{O_2}=5 MPa for 120 min. Acetic acid was produced from phenols within 15 min and oxidized selectively to oxalic acid. The yield ratio(yield of oxalic acid(%)/yield of CO_2 (%)) from most of the model compounds was higher than 1. These phenomena agreed well with those of low-ranked coal under the same oxidation conditions. The overall reaction rates, yields of oxalic acid, and yield ratios increased rapidly with an increasing concentration of NaOH as in the oxidation of coal. This behavior can be explained resonably well by an alkali-catalyzed oxidation mechanism regarding organic substances.

Oxalic acid is produced in high yields, 40—50%, on a carbon base during the oxidation of low-ranked coal by O_2 in concentrated NaOH solutions.[1] The mechanism of this reaction has been discussed.[2]

Oxidation of coal-model compounds by HNO_3[3] or by $KMnO_4$[3,4] has been carried out to elucidate the basic structure of coal, since it is very complicated. In this previous work, including $KMnO_4$ oxidation of lignite and peat,[5] the yield of oxalic acid was appreciably low. In the present study, 26 oxygen-containing model compounds were oxidized to investigate the formation mechanism of oxalic acid in high yield during the oxidation of coal by O_2 in concentrated NaOH solutions. The model compounds are classified as follows: (a) aliphatic carboxylic acids, (b) aromatic compounds such as phenols and carboxylic acids, and (c) alicyclic or heterocyclic compounds. Low-ranked coal contains these types of functional groups[2] and we may disclose what kinds of the functional groups in coal give oxalic acid in good yield during oxidation using these model compounds. The effect of the NaOH concentration on the oxidation of acetic acid, hydroxyacetic acid, 1,2-benzenediol, and 4-hydroxycinnamic acid is also examined, and the high selectivity in the formation of oxalic acid from acetic acid is explained in terms of the alkali-catalyzed oxidation mechanism.

Experimental

Reagents. Instead of free acid, the sodium salts of acetic acid, propionic acid, and butyric acid were used. The chemicals used were reagent grade except NaOH. Sodium hydroxide was the only guaranteed reagent and the amount of carbon contained in the NaOH as a carbonate was corrected in the calculation of the CO_2 yield for the model compounds.

Oxidation. A 240 cm^3 SUS 316 beaker was put in a 300-cm^3 autoclave fitted with a magnetic stirrer. A mixture 0.02-mol mixture of the model compound (0.03 mol only for acetic acid), 4-60 g of NaOH, and 50 g of water were placed in the beaker and heated to 523 K within 40—60 min after replacing the air with N_2. The O_2 partial pressure was kept at 5±0.2 MPa while stirring at 1200 min^{-1}. After a reaction time of 120 or 15 min, the autoclave was cooled and the reaction mixture was washed and diluted to 1 dm^3. Oxalate, carbonate, and the sodium salts of volatile acids contained in the solution were determined by a previously described methods.[2] In the present work, it was confirmed by a GC-MS analysis that the volatile acids were composed of acetic acid. For this reason, the yield of volatile acids was expressed as the yield of acetic acid.

Results and Discussion

Effect of Types of Model Compounds. The yields of oxalic acid, CO_2, and acetic acid and the yield ratios of oxalic acid to CO_2 are summarized in Table 1 for the oxidation of 26 model compounds for 120 min at 523 K. The numbers (from **1** to **9**) in the lefthand side of Table 1 correspond to each model compound in the following text.

Aliphatic Carboxylic Acids: The oxidation of acetic acid gave a 75% yield of oxalic acid, and the yield ratio (yield of oxalic acid(%)/yield of CO_2(%)) was very high. The overall yields of oxalic acid at 120 min for acetic acid, propionic acid, and butyric acid were larger than those of the aromatic carboxylic acids as shown in Table 1B; however, there was not a great difference in the overall yield (93—98%) among these monocarboxylic acids. The yield ratio for propionic acid was the smallest among the monocarboxylic acids. Clearly, this indicates that propionic acid gives CO_2 and a certain C_2 compound. If the C_2 compound is acetic acid or hydroxyacetic acid, the yield ratio must be 1.0 or 1.7, respectively, since the yield ratios for acetic acid and hydroxyacetic acid were 3.4 and 18.9 at 120 min. The yield ratio for adipic acid was high but the reaction rate was slower than those of the three monocarboxylic acids. This tendency was also noted in $KMnO_4$ oxidation of dicarboxylic acids.[4] Both the reaction rate and the yield ratio for hydroxyacetic acid were extremely high.

Phenols and Aromatic Carboxylic Acids: Phenol was easily cleaved and gave oxalic acid in good yield and

Table 1. Oxidation of model compounds for 120 minutes at 523 K and 25 mol NaOH/kg water

Compd. No.	Model Compd.	Product yield/%			Yield ratio[b)]
		Oxalic acid	CO_2	Acetic acid	
	A. Aliphatic carboxylic acid				
	Acetic acid	75.4	22.2	1.4[c)]	3.4
	Propionic acid	54.6	41.7	0	1.3
	Butyric acid	61.6	29.9	1.5	2.1
	Adipic acid	32.8	13.3	19.4	2.5
	Hydroxyacetic acid	94.7	5.0	0	18.9
	Hydroxyacetic acid[a)]	96.7	3.2	0	30.2
	B. Phenols and aromatic carboxylic acids				
	Phenol	51.6	29.9	17.8	1.7
	1,2-Benzenediol	54.1	26.5	12.3	2.1
	1,3-Benzenediol	57.8	31.5	12.3	2.1
	1,4-Benzenediol	53.4	33.9	8.2	1.6
1	4-s-Butylphenol	49.2	42.6	2.6	1.2
2	*p*-Hydroxyacetophenone	49.3	48.7	0.5	1.0
3	4-Hydroxycinnamic acid	30.1	22.9	34.7	1.3
4	2-Hydroxy-1-naphthalene-carbaldehyde	20.8	18.9	5.8	1.1
	Benzoic acid	34.3	20.4	2.5	1.7
	1,2-Benzenedicarboxylic acid	29.9	17.5	0.8	1.7
	1,3-Benzenedicarboxylic acid	36.9	21.0	1.3	1.8
	1,4-Benzenedicarboxylic acid	4.3	3.2	0.2	1.4
	1-Naphthalenecarboxylic acid	17.5	14.2	0.8	1.2
	2-Naphthalenecarboxylic acid	13.2	11.3	0	1.2
5	9-Anthracenecarboxylic acid	17.6	15.9	0	1.1
6	3-Phenylpropionionic acid	35.7	22.0	3.0	1.6
7	4-Methoxycinnamic acid	24.0	24.1	33.9	1.0
	C. Alicyclic and heterocyclic compounds				
	Cyclohexanol	14.5	29.1	1.4	0.5
8	1,2-Cyclohexanedicarboxylic acid	57.9	36.6	1.1	1.6
9	3-Cyclohexylpropionic acid	44.7	35.1	14.2	1.3
	Furfural	40.1	48.6	3.1	0.8

a) Reaction time 1 h. b) Yield of oxalic acid(%)/yield of CO_2. c) Unreacted acetic acid.

yield ratio. There was not a great difference in the results among phenol and dihydric phenols as shown in Table 1B. Yield ratios among dihydric phenols were of the order of 1,2-$\simeq$1,3-$>$1,4-benzenediol.

If one of the hydrogens on a benzene ring of phenol was substituted by a saturated aliphatic side chain such as **1** and **2**, the yield ratios were lowered from 1.7 to 1.0—1.2. These values are close to the yield ratios for low-ranked coal.[1)] This may be caused by an increasing formation of CO_2 by the oxidation of the side chain. Compound **3** was easily oxidized and yielded a large amount of acetic acid but both yields of oxalic acid and CO_2 were small. The yield ratio for **4** was 1.1, however, the reaction rate was small. The benzenecarboxylic acids were more stable than the phenols during the oxidation as shown in Table 1C. 1,4-Benzenedicarboxylic acid was especially stable. This is due to the extremely slow reaction rate, as it hardly dissolves into concentrated NaOH solutions.[6)] Although the reaction rates for **4**, **5**, 1-naphthalenecarboxylic acid, and 2-naphthalenecarboxylic acid were very small, the yield ratios for these naphthalene- and anthracenecarboxylic acids were as high as 1.2. The yield ratios for phenol and benzenediols (1.6—2.1) were a little larger than those for benzoic acid and benzenedicarboxylic acids (1.4—1.8). This may be caused by the difference in the yield of acetic acid since acetic acid afforded 75% oxalic acid. The phenols yielded 8.2—17.2% acetic acid whereas the benzenecarboxylic acids yielded only 0.2—2.5% as shown in Table 1B and 1C. The fact that the yield ratios for the above four phenols and benzenecarboxylic acids were as high as 1.4—2.1 indicates that the aliphatic carboxylic acids of even carbon numbers are predominantly formed during the cleavage of both aromatic rings. Such aliphatic carboxylic acids produced oxalic acid more than the aliphatic carboxylic acids of odd carbon numbers. Acetic and butyric acids afforded 75.4 and 61.6% oxalic acid respectively, whereas, propionic acid 54.6%. Work is in progress to clarify the cleavage products.

Model compounds **3** and **7** yielded 30% of oxalic acid: close to that for 1,2- and 1,3-benzenedicarboxylic acids. The important characteristics of these compounds are that a large amount of acetic acid was produced and the reaction rates were also large.

Alicyclic and Heterocyclic Compounds Containing Oxygen: The reaction rate for cyclohexanol was slow

Table 2. Formation of acetic acid at 15 minutes oxidation

Model	Product yield/%			Yield
Compound	Oxalic acid	CO_2	Acetic acid	ratio[b)]
Propionic acid	5.2	5.2	87.3[a)]	1.0
1,2-Benzenediol	28.8	12.7	28.9	2.3
1	16.6	9.3	29.5	1.8
2	4.0	5.9	13.9	0.7
3	8.1	3.8	29.1	2.2
7	8.5	2.8	4.6	1.8

a) Unreacted propionic acid. b) Yield of oxalic acid(%)/yield of CO_2(%).

and the yield ratio was the smallest. Model compounds **8** and **9** were oxidized more easily than the corresponding aromatic compounds, 1,2-benzenedicarboxylic acid and **6**, respectively. A furan ring was cleaved as easily as phenol, however, the yield ratio was small, 0.8.

Formation of Acetic Acid in the Initial Stage of Oxidation. The results of oxidation for 15 min are shown in Table 2 for propionic acid, 1,2-benzenediol, **1**, **2**, **3**, and **7**. The yield of acetic acid for **7** was the smallest after 15 min of oxidation. This shows the effect of substituents on the reactivity of aromatic rings. Model compound **3** with a phenolic hydroxyl group was easily oxidized to afford a large amount of acetic acid compared to **7** with a methoxyl group as shown in Table 2.

The model compounds, except **7**, yielded acetic acid in large amounts. This behavior agreed well with that of low-ranked coal which also afforded 20—25% of acetic acid at 15 min of oxidation.[1)] 1,2-Benzenediol yielded 29% of acetic acid and 41% of oxalic acid and CO_2, respectively. Clearly, the aromatic rings activated by the substitution of the hydroxyl group were easily cleaved and yielded large amounts of oxalic acid. 1,2-Benzenediol was cleaved to afford muconic acid derivatives.[7)] The mechanism in which three hydrogen atoms combine with one carbon atom to produce a methyl group in acetic acid under such strong oxidative conditions may be a disproportionation of the double bonds in these intermediates.

In spite of the fact that the sum of the yield of oxalic acid and the yields of CO_2 for **1** and **3** were 26 and 12%, respectively, the corresponding yields of acetic acid were about 30%. Consequently, not only the cleavage of the aromatic rings but also the cleavage of side chains *via* peroxide anions[8)] contribute to the formation of acetic acid. An identification of the cleavage products is necessary for a detailed determination of the mechanism.

Mechanism of the Oxidation. *Concentration Effects Regarding NaOH*: Figures 1—4 show the effects of the NaOH concentration on the yields of oxalic acid, CO_2, and acetic acid during the oxidation (120 min) of acetic acid, hydroxyacetic acid, 1,2-benzenediol, and **3**. The important phenomena regarding the oxidation are shown in Fig. 1 for acetic acid and can be summarized as follows:

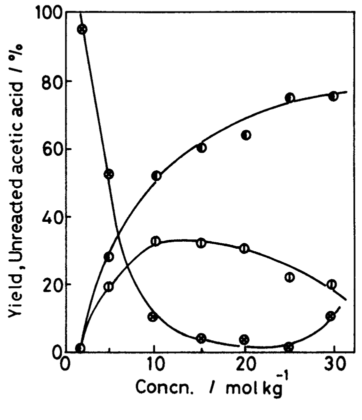


Fig. 1. Effect of NaOH concentration on the yields of oxalic acid, CO_2, and unreacted acetic acid in the oxidation of acetic acid: (◐) oxalic acid, (⌽) CO_2 (⊗) unreacted acetic acid.

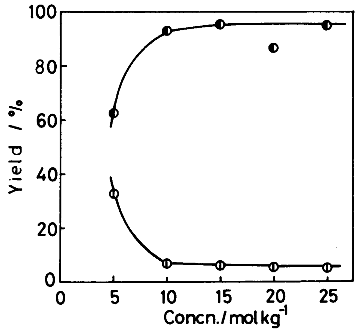


Fig. 2. Effect of NaOH concentration on the yields of oxalic acid and CO_2 in the oxidation of hydroxyacetic acid: (◐) oxalic acid, (⌽) CO_2.

I. Acetic acid was hardly oxidized at 2 mol kg^{-1}.

II. The reaction rate, yield of oxalic acid, and yield ratio increased rapidly upon increasing the NaOH concentration at 5—20 mol kg^{-1}.

III. The yield of CO_2 was held almost constant at 10—20 mol kg^{-1}.

IV. The reaction rate decreased at 20—30 mol kg^{-1} and the previously produced acetic acid remained.

The yield ratios for 1,2-benzenediol and **3** (Figs. 3 and 4) were lowered at concentrations of 20 mol kg^{-1} or higher; however, these yield ratios should

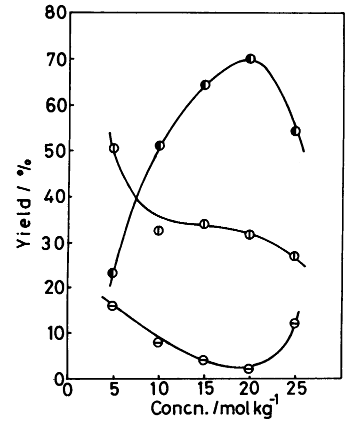


Fig. 3. Effect of NaOH concentration on the yields of oxalic acid, CO_2, and acetic acid in the oxidation of 1,2-benzenediol: (◐) oxalic acid, (⦶) CO_2, (⊖) acetic acid.

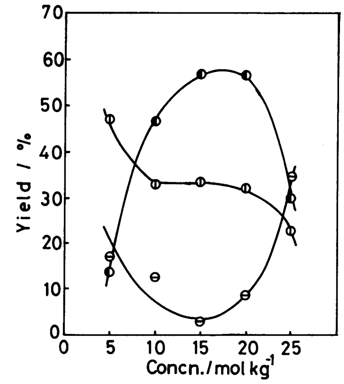
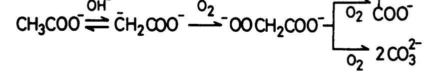


Fig. 4. Effect of NaOH concentration on the yields of oxalic acid, CO_2, and acetic acid in the oxidation of 4-hydroxycinnamic acid: (◐) oxalic acid, (⦶) CO_2, (⊖) acetic acid.

increase with longer reaction times (>120 min). The reason is that the large amount of acetic acid produced within 120 min produces selectively oxalic acid which increases the yield ratios with longer reaction times. The oxidation rates of oxalic acid are very small under such conditions.[2]

Mechanism: Scheme 1 shows a mechanism for the formation of oxalic acid and CO_2 from acetic acid. A carbanion is formed by the abstraction of a proton from the acetate ion with OH^- and yields an intermediate peroxide anion by the reaction with O_2. An oxalate ion may be produced by further abstraction of a proton and successive oxidation of the intermediate from which CO_2 may be formed competitively by the monomolecular cleavage of the C–C bond by a mechanism such as the epoxide mechanism or the Baeyer-Villiger mechanism.[9]



Scheme 1.

The above phenomena can essentially be explained by the following mechanism.

I. Equations 1 and 2 are the dissociation equilibrium in a $NaOH-CH_3COONa$ solution at elevated temperatures.

$$CH_3COONa \longrightarrow CH_3COO^- + Na^+ \qquad (1)$$

$$NaOH \rightleftharpoons OH^- + Na^+ \qquad (2)$$

At 523 K, NaOH behaves as a weak electrolyte, as the pK_b is estimated to be 1.5.[10] Consequently, the concentration of OH^- is much smaller than the formal concentration of NaOH. In addition, the dissociation of NaOH is depressed by a common-ion effect of the Na^+ liberated from a complete dissociation of CH_3COONa (0.6 mol kg^{-1}). Thus, the reaction rate is very small because the equilibrium concentration of the carbanion is extremely low.

II. The formation of carbanion is promoted upon increasing the concentration of OH^- through the equilibrium. Thus, oxidation is accelerated. The yield of oxalic acid and the yield ratio increase with an increasing OH^- concentration. This is due to the effect of the abstraction of a proton by OH^- from the peroxide anion. This enhances the selective formation of oxalic acid in competitive reactions. On the other hand, the monomolecular cleavage of the C–C bond is not affected by the OH^- concentration.

III. The solubility of CH_3COONa decreases with an increasing concentration of NaOH. Such a tendency is observed in a great number of NaOH–sodium salt systems.[6] In contrast, the formation of the carbanion and the peroxide anion is promoted with an increasing NaOH concentration. In 10—20 mol kg^{-1} concentrations, these opposite effects compensate each other and the concentration of peroxide anions is kept almost constant. Thus, the yield of CO_2 *via* peroxide anions is held constant.

IV. In 20—30 mol kg^{-1} concentrations, the solubillity of CH_3COONa drops further and the concentration of the peroxide anion begins to fall. The rate-of-formation of oxalic acid drops, but the selectivity to form oxalic acid is relatively promoted. Thus, the yield ratio continues to increase, whereas, the overall reaction rate drops.

Based on this mechanism, the difference in the reactivities among several compounds can be explained in connection with the pK_a for the separation of hydrogen from the model compounds. The peroxide anions for acetic acid and hydroxyacetic acid may be $(^-OO)H_2CCOO^-$ and $OH(OO^-)HCCOO^-$, respectively. The value of pK_a for methylene hydrogen tends to be larger than that for methine hydrogen.[11] Thus, the reaction rate and yield ratio for hydroxyacetic acid are much larger than those for acetic acid. In the case of aliphatic monocarboxylic acids, the reactivities for acetic acid, propionic acid, and butyric acid were approximately equal. This may indicate that the reaction takes place by the abstraction of hydrogen on the opposite carbon to the carboxyl carbon. Consequently, the reason for the low reactivity of adipic acid is that the opposite carbon is stabilized as a carboxyl carbon and no hydrogen is abstracted. The difference in the reactivities between 1,2-cyclohexanedicarboxylic acid and 1,2-benzenedicarboxylic acid or between **7** and **9** can be similarly explained.

Relationships between the Behavior of Model Compounds and That of Coal. The behavior of many model compounds and low-ranked coal such as Tempoku peat (C 54.7% daf), Yallourn coal (C 62.3% daf), and Nakayama coal (C 67.9% daf) agreed well with the formation of acetic acid and the high yield ratio of 1 or more.[1] This is because low-ranked coal contains a large amount of oxygen such as phenolic hydroxyl and carboxyl groups,[2] and the development of condensation of aromatic rings is inadequate. In contrast, a low yield ratio of 0.8 for high-ranked coal such as Goonyella coal (C 90.2% daf) and Miike coal (C 86.9% daf) was not obtained except with cyclohexanol and furfural. This is because most of the model compounds used were oxidized in an aqueous phase, and gas-phase oxidation of insoluble compounds did not take place as was observed in the oxidation of the high-ranked coal.[1] However, the reaction rate for the model compounds with fused aromatic rings such as **4**, 1-naphthalenecarboxylic acid, 2-naphthalenecarboxylic acid, and **9** were smaller than those for the model compounds with a benzene ring such as phenol, 1,2-benzenediol, benzoic acid, **6**, **7**, *etc.* Thus, regarding reaction rates, the behavior of model compounds with fused aromatic rings agreed with that of high-ranked coal.

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