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Ozonation of Organic Compounds. 2. Ozonation of Phenol in Water[1]

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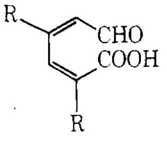
The rates and products of the ozonation of phenol were studied in water at 30 °C. In contrast to earlier works, it was found that the major product was formic acid with minor amounts of glyoxal, glyoxylic acid, oxalic acid, carbon dioxide, and hydrogen peroxide. Several other intermediates were also observed. The ozonation of several model compounds was also carried out. It was concluded that the anomalous ozonolysis of α,β-unsaturated carbonyl groups played an important role in the ozonation of phenol. The ratio of anomalous ozonolysis was measured in water for several olefins.

The ozonation of organic compounds, especially of olefins, has been studied extensively in organic solvents for many years.[2-4] As pointed out by Bailey,[5] however, ozonation in water has received less attention. Among the water-soluble organic compounds, phenol has been studied most extensively.[6] Recently, Gould and Weber[7] carried out careful analyses of the products and found hydroquinone, catechol, glyoxal, glyoxylic acid, and oxalic acid. Eisenhauer[8] also identified catechol, hydroquinone, and *o*-quinone as intermediates. Wako[9] observed, although only qualitatively, hydroquinone, *p*-quinone, muconic acid, maleic acid, and glyoxylic acid. On the other hand, Skarlatos et al.[10] reported acetic acid as one of the ozonation products from aqueous phenol. Bernatek and his collaborators[11,12] ozonized phenol in ethyl acetate and found that the products containing active oxygen gave formic acid, carbon dioxide, glyoxal, and oxalic acid by hydrolysis. They also found that the ozonation of catechol, resorcinol, and quinol gave the same products.[11,12] However, they did not find glyoxylic acid. Thus, the results hitherto reported are inconsistent, and neither the products nor the mechanism of the ozonation of phenol in water has been conclusively established.

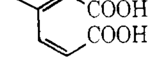
The objectives of our present study were to measure the rates and products of the ozonation of phenol and model compounds in water quantitatively as well as qualitatively and to elucidate the ozonation mechanism. It was found that the major products from phenol were formic acid and carbon dioxide and that the anomalous ozonolysis of the double bond conjugated with carbonyl groups played an important role.

Results

Ozonation of Phenol. Figure 1 shows the typical example of the ozonation of phenol in water; 0.618 mmol of phenol was oxidized with 0.12 mmol/min of ozone in 100 mL of water at 30 °C. It shows that phenol was oxidized quite readily with ozone without any noticeable induction period and that substantially all phenol disappeared in 90 min. The major product was formic acid with smaller amounts of muconaldehyde [*cis,cis*-6-oxo-2,4-hexadienoic acid (**2**)],[13] muconic acid [*cis,cis*-2,4-hexadienedioic acid (**3**)],[13] maleinaldehyde [*cis*-4-oxo-2-butenoic acid (**5**)],[13] glyoxylic acid, glyoxal, and oxalic acid. Besides the products shown in Figure 1, hydroquinone, catechol, carbon dioxide, and hydrogen peroxide were observed. In contrast to the results of Skarlatos,[10] acetic acid was not observed. As described later, catechol and hydroquinone are more reactive toward ozone than phenol, and hence these products are accumulated only at the initial stages of ozonation. These results are in agreement with those observed by Gould and Weber.[7] **2** and **3** are also readily oxidized, and their concentrations decreased after reaching a maximum at 45–60 min. Glyoxylic acid and oxalic acid concentrations increased with reaction time, whereas formic acid and **5** concentrations leveled off.



2



3

R = H or OH

Table I shows the final products after a 180-min ozonation. The total acid measured by titration was 1.34 mmol, which is in excellent agreement with 1.33 mmol observed by isotachophoretic analysis. The amount of double bond formed was approximately the same as that of **5**. Therefore, the amount of mucondialdehyde [*cis,cis*-1,6-dioxo-2,4-hexadiene (**1**)][13] and maleindialdehyde [*cis*-1,4-dioxo-2-butene (**4**)][13] should be small. The concentration of glyoxal was estimated from the total carbonyl groups, 0.90 mmol, and the amounts of glyoxylic acid and **5** observed, $(0.90 - 0.166 - 0.227)/2 = 0.253$ mmol. These organic products account for 69% of initial carbon. If it is assumed that the missing carbon is converted to carbon

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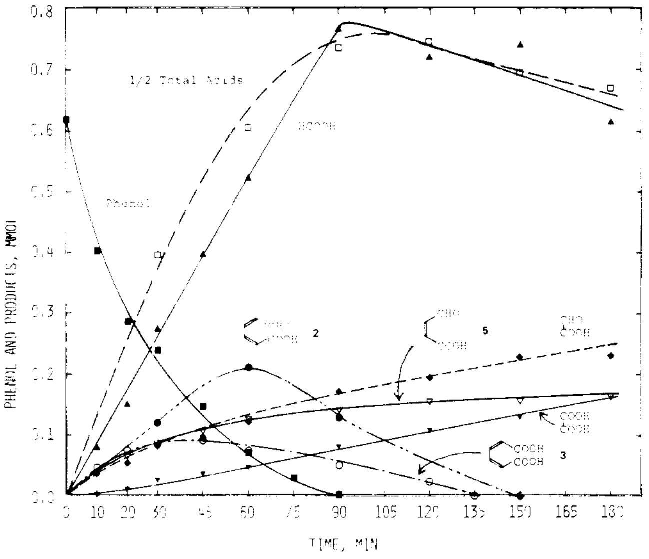
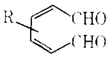
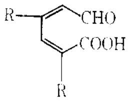
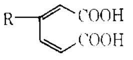
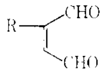
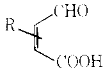
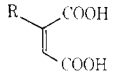


Figure 1. Ozonation of phenol in water at 30 °C.

Table I. Ozonation Products of Phenol (0.618 mmol) at 30 °C (180 min) [a]

product	amount	product	amount	product	amount
 1	~0	 2	0.0	 3	0.0
 4	~0	 5	0.166		0.0
$(CHO)_2$	0.253[b]	CHO-(COOH)	0.227	$(COOH)_2$	0.163
HCOOH	0.614	CO_2	1.14[c]	HOOH	0.23

[a] R = H or OH. Product amounts are in millimoles. [b] Calculated as described in the text. [c] Calculated from carbon balance (see text).

dioxide, 1.14 mmol of carbon dioxide is calculated to be formed.[14]

In order to elucidate the mechanism of the ozonation of phenol, the ozonations of catechol, hydroquinone, *trans, trans*-muconic acid, maleic acid, mesityl oxide, crotonic acid, crotonaldehyde, glyoxylic acid, and formic acid have been studied. The results are summarized in Figure 2 and Tables II and III.

As shown in Table I, hydrogen peroxide is an important ozonation product of phenol in water. It undergoes Baeyer–Villiger reaction[15] with other ozonation products such as glyoxal and glyoxylic acid. Table IV summarizes the results of the Baeyer–Villiger reaction of methylglyoxal and glyoxylic acid. Approximately equal amounts of formic and acetic acids were formed from methylglyoxal. Moreover, the amount of formic acid formed was the same as that of hydrogen peroxide reacted. In the case of glyoxylic acid, the amounts of hydrogen peroxide and glyoxylic acid consumed were approximately equal to the amount of formic acid produced. Glyoxylic acid reacted faster with hydrogen peroxide than methylglyoxal because hydrogen ion catalyzes the Baeyer–Villiger reaction.[15]

Table V summarizes the reactivities of phenol and several model compounds toward ozone. The rate constants k was calculated from eq 1, where D and t stand for the ozone dose rate expressed in mol of O_3/min/mol of substrate and time, respectively. When $k = 1$, the rate of mass transfer of ozone into solution is rate determining.

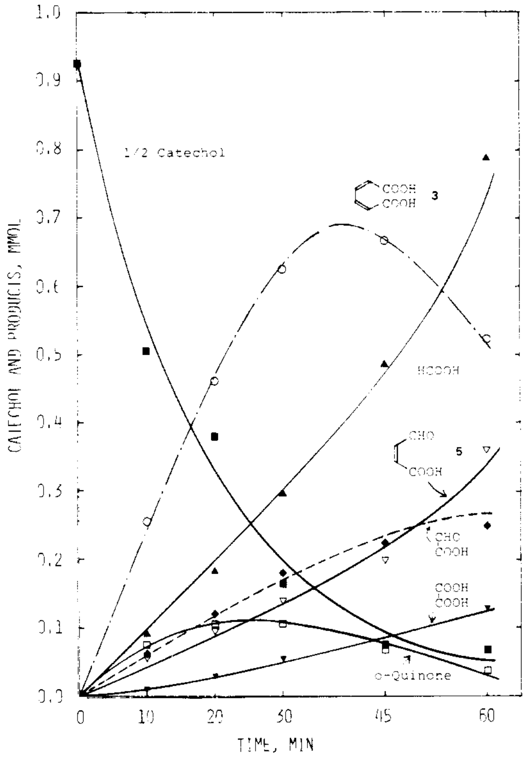


Figure 2. Ozonation of catechol in water at 30 °C.

Table II. Ozonation of Model Compounds in Water at 30 °C [a]

	run no.		
	1	2	3
substrate (RH)	catechol	hydroquinone	b
initial RH, mmol	5.10	5.32	0.197
ΔRH, mmol	2.54	1.90	0.120
time, min	30	30	10
Products, mmol			
HCOOH	0.227	0.332	0.049
CHO(COOH)	0.199	0.132	0.121
$(COOH)_2$	0.041	0.021	0.0
5	0.158	0.184	0.053[c]
2	0.725	0.633	
3	0.713	0.258	

[a] R = H or OH. [b] *trans,trans*-Muconic acid. [c] *trans*-4-Oxo-2-butenoic acid.

$$\ln [\text{substrate}]_0/[\text{substrate}] = kDt \qquad (1)$$

Discussion

The results given above show that phenol is readily ozonized in water at 30 °C by several competing reactions. The initial attack of ozone on the aromatic ring brings about either hydroxylation or cleavage of the aromatic ring. Ozone behaves as an electrophilic reagent,[5,16] and the hydroxylation of phenol gives predominantly catechol and hydroquinone,[7] both of which, however, are so reactive toward ozone that they are only transient intermediates and not accumulated to any appreciable extent.

The ozonation of catechol exhibited a similar pattern to that of phenol as shown in Figure 2. Major products were **2** and **3**; the addition of ozone to the 1,2 position gives **3**, while that to the 2,3 and 1,6 positions gives **2**.

Table III. Ozonation of Model Compounds in Water at 30 °C

	run no.										
	4	5	6	7	8	9	10	11	12	13	14
substrate (RH)	*f*	*f*	*f*	*g*	*g*	*g*	*a*	*b*	*b*	*c*	HCOOH
initial RH, mmol	2.05	2.05	1.71	3.00	3.47	5.61	5.18	11	11	1.07	1.27
ΔRH, mmol	0.113	0.455	0.764				3.59			0.496	1.20
time, min	10	30	60	10	20	25	40	25	30	120	200
				Products, mmol							
hydrogen peroxide	0	0	0	0.71	1.35	1.78	1.74	1.24	1.34	0	
peroxides	0	0	0	0	0	0	0	trace	trace	0	
formic acid	0.107	0.273	0.562	0.32	0.47	0.69	1.67	0.834	1.102	0	
acetic acid				0.32	0.47	0.69	0	trace	trace		
glyoxylic acid	0.168	0.614	0.905				1.57	0	0		
acetaldehyde							>2.05	>0.79	*d*		
acetone				*d*	*d*	*d*					
methylglyoxal				*d*	*d*	*d*					
crotonic acid								0.026	0.032		
oxalic acid	0	0	0				0	0	0	0.465	
carbon dioxide											>0.73
normal ozonolysis	0.031	0.171	0.172	0.71	1.35	1.78	1.74	1.24	1.34		
anomalous ozonolysis	0.107	0.273	0.562	0.32	0.47	0.69	1.67	0.417	0.051		
α[e]	0.78	0.62	0.77	0.31	0.26	0.28	0.49	0.25	0.29		

[a] Crotonic acid. [b] Crotonaldehyde. [c] Glyoxylic acid. [d] Found. [e] α = anomalous ozonlysis/total ozonolysis (see text). [f] Maleic acid. [g] Mesityl oxide.

Table IV. Baeyer–Villiger Oxidation of Methylglyoxal and Glyoxylic Acid by Hydrogen Peroxide in Water at 30 °C

	run no.		
	15	16	17
CH_3COCHO[a]	5.21	8.68	
$CHO(COOH)$[a]			2.22
H_2O_2[a]	5.45	1.83	2.84
initial acids[a]	0.331	0.554	2.72
time, min	300	270	160
$-\Delta H_2O_2$[a]		0.879	1.39
$-\Delta CHO(COOH)$[a]			1.55
	Products		
$HCOOH$[a]	0.878	0.875	1.40
CH_3COOH[a]	0.889	0.856	
$(COOH)_2$[a]	0.0	0.0	0

[a] In millimoles in 100-mL solution.

Table V. Reactivities of Phenol and Model Compounds toward Ozone in Water at 30 °C

substrate	concn, × 10^2 M	k[a]
crotyl alcohol	10.9	1.0
3-butenoic acid	10.2	1.0
mesityl oxide	5.61	1.0
crotonic acid	5.18	1.0
catechol	5.10	1.0
hydroquinone	5.32	~1.0
crotonaldehyde	11	0.600
trans,trans-muconic acid	0.197	0.152
phenol	0.618	0.152
phenol	4.38	0.393
propanal	5.56	0.331
maleic acid	2.05	0.141
formic acid	1.27	0.129
hydrogen peroxide	10.7	0.068
glyoxylic acid	3.98	0.051
glyoxylic acid	1.07	0.042
acetic acid	1.1	0.0
oxalic acid	0.69	0.0

[a] In mol substrate/mol ozone, which shows the amount of substrate reacting when 1 mol of ozone is introduced.

The major product in the ozonation of hydroquinone was **2**. Interestingly, some **3** was also observed. Since the oxidation of aldehyde to carboxylic acid is much slower than ozonolysis of a double bond (as discussed later), **3** must have arisen from 1,2,4-trihydroxybenzene, formed by the hydroxylation of hydroquinone. This implies that the hydroxylation may be faster than the cleavage of aromatic ring.

It is also claimed[17,18] that the ring opening proceeds through phenoxy radicals formed by hydrogen atom abstraction from phenol. However, the formation of **3** and formic acid in high yields suggests that this is not an important reaction pathway.

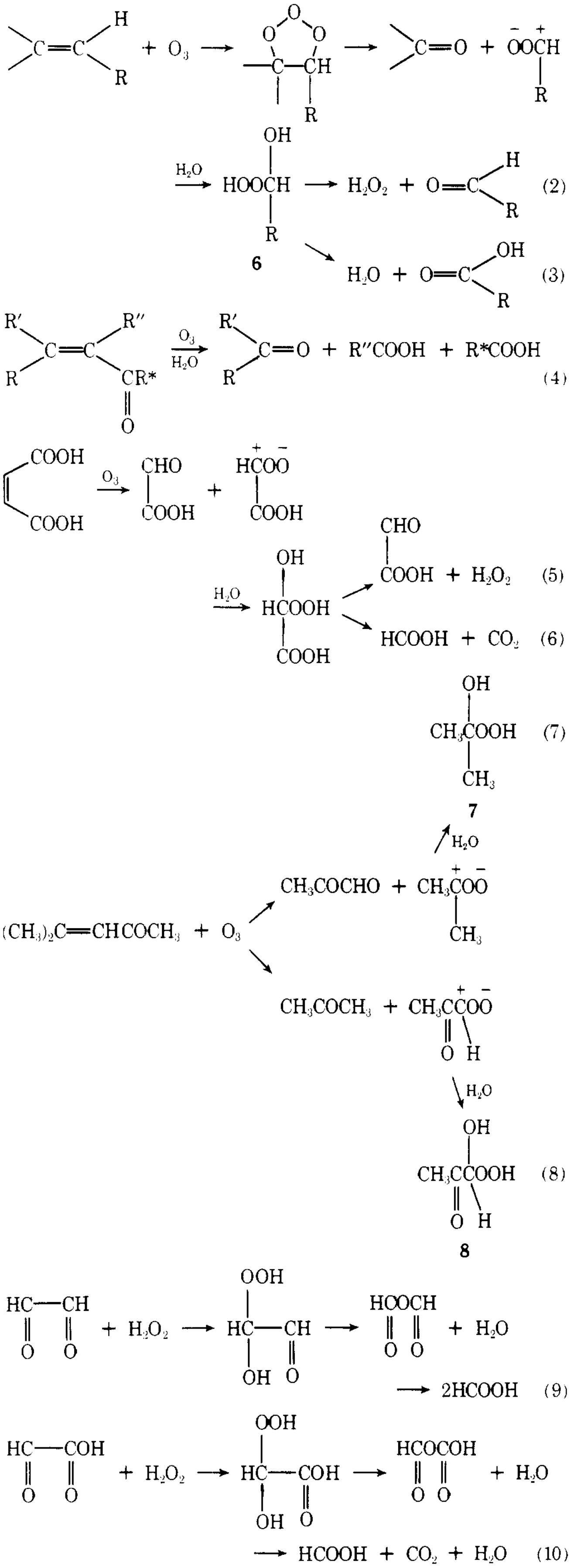
Catechol and hydroquinone are cleaved to give **2** and **3** or oxidized to the corresponding quinones, the latter being only a minor reaction because the amount of *o*-quinone formed was several times less than that of **3** as shown in Figure 2. Quinones are also reactive toward ozone and readily cleave (Figure 2). Thus, the solution was colored at the initial stages, but it disappeared as the reaction proceeded.

The normal ozonolysis of the aliphatic double bond in water must proceed by the reaction pathways shown in Scheme I.[5] The zwitterion reacts with water to give the α-hydroxyalkyl hydroperoxide **6**, which is unstable and decomposes to hydrogen peroxide and aldehyde (or ketone) or to water and carboxylic acid. Reaction 2 resembles the oxidation of alcohol by molecular oxygen,[19] although it is not conclusively established whether hydrogen peroxide arises from α-hydroxy alkyl hydroperoxide or from the hydroperoxy radical formed from the α-hydroxyalkyl peroxy radical.[20]

The results in Table III suggest that reaction 3 is not important under the present reaction conditions; the ozonation of maleic acid gave no oxalic acid (runs 4–6), and furthermore neither acetic acid nor oxalic acid was observed in the ozonation of crotonic acid (run 10). The absence or near absence of glyoxylic acid or acetic acid in the ozonolysis of crotonaldehyde (runs 11 and 12) also suggests that reaction 2 is more important than reaction 3.

Scheme I shows how *trans*-4-oxo-2-butenoic acid and glyoxylic acid could be formed from *trans,trans*-muconic acid. However, the products shown in Tables I–III cannot be accounted for by the normal ozonolysis alone; instead, they

Scheme I. Normal Ozonolysis of Double Bonds in Water



strongly indicate the contribution of anomalous ozonolysis,[2,21,22] which leads to cleavage not of the olefinic bond but of the adjacent carbon–carbon single bond to give products with fewer than the expected number of carbon atoms (eq 4).

α,β-Unsaturated carbonyl compounds are one of the olefins which undergo the anomalous ozonolysis.[2,21] For example, in the ozonolysis of maleic acid in water, Gilbert[23] observed not only glyoxylic acid but also formic acid and carbon dioxide as anomalous products. Storesund and Bernatek[24] also reported anomalous ozonolysis products from methylmaleic acid in water. We obtained similar results to those of Gilbert, and Table III shows that the carbon balance is satisfactory. The ratio α of anomalous ozonolysis to the total ozonolysis was calculated from the amount of anomalous ozonolysis products divided by that of the total ozonolysis products. The results in Table III show that on the average, 72% of ozonolysis of maleic acid was anomalous; in run 4, for example, the normal ozonolysis product is given by (0.168 − 0.107)/2 = 0.031 mmol and the anomalous product is given by the amount of formic acid. The anomalous ozonolysis products have been considered to be formed from carbonyl group substituted hydroxyalkyl hydroperoxides as shown in eq 6.[2]

In the ozonolysis of mesityl oxide in water, two kinds of hydroperoxides (7 and 8) are formed (eq 7 and 8). Hydroperoxide 7 must not undergo anomalous ozonolysis, but it should give hydrogen peroxide and acetone. It may be noted that no organic peroxide was observed as shown in Table III. Hydroperoxide 8 gives either methylglyoxal and hydrogen peroxide by the normal pathway or formic acid and acetic acid by the anomalous pathway.[2] Runs 7–9 in Table III show that formic and acetic acids were formed in equal amounts as expected. The ratio of anomalous ozonolysis to total ozonolysis is calculated as 0.28 from formic acid/(formic acid + hydrogen peroxide).

The normal ozonolysis of crotonic acid gives acetaldehyde, glyoxylic acid, and hydrogen peroxide, while the anomalous ozonolysis gives acetaldehyde, formic acid, and carbon dioxide. Run 10 in Table III shows that the amounts of hydrogen peroxide and glyoxylic acid are approximately equal and that the hydrogen peroxide and formic acid observed account for 95% of the crotonic acid ozonized. The ratio of anomalous/total ozonolysis is 1.67/(1.74 + 1.67) = 0.49.

Table III shows that the ozonation of glyoxylic acid gave oxalic acid almost quantitatively. It was also found that the oxidation of propanal with ozone gave propionic acid exclusively with small amounts of acetic acid, acetaldehyde, and ethanol. No formic acid was found from either glyoxylic acid or propanal.

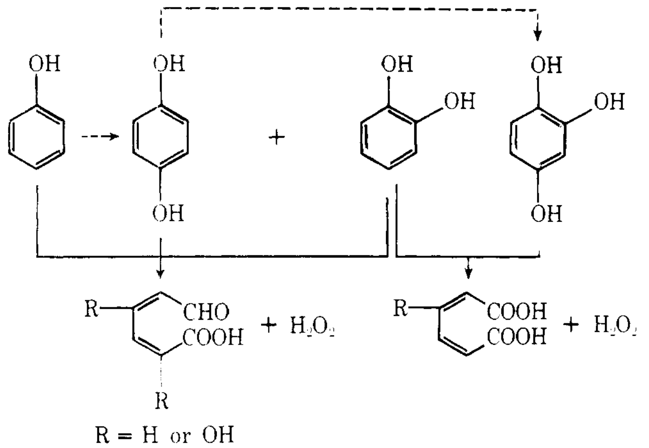
On the contrary, glyoxal and glyoxylic acid gave formic acid by Baeyer–Villiger reaction as shown in eq 9 and 10. These results suggest conclusively that the aldehyde group is ozonized to the corresponding carboxylic acid as observed before[25] and that in the ozonation of phenol in water formic acid is formed primarily by the anomalous ozonolysis of α,β-unsaturated carbonyl compounds and by the Baeyer–Villiger reactions of glyoxal and glyoxylic acid.

Table V shows that the reactivities toward ozone decrease in order of dihydroxybenzenes, olefins > phenol > aldehydes > hydrogen peroxide > carboxylic acids. The reactivity of the double bond decreases with decreasing electron density at the double bond.[2] Ozonolysis of the double bond proceeded faster than oxidation of the aldehyde group in the ozonation of crotonaldehyde, with a ratio of (1.24 + 0.417)/0.026 = 64 in run 11 or (1.34 + 0.551)/0.032 = 59 in run 12 (Table III). Although the carboxylic acids are generally stable toward ozone, formic acid is ozonized at a steady rate to carbon dioxide (Tables III and V). This is apparently due to the reactive acyl carbon–hydrogen bond.

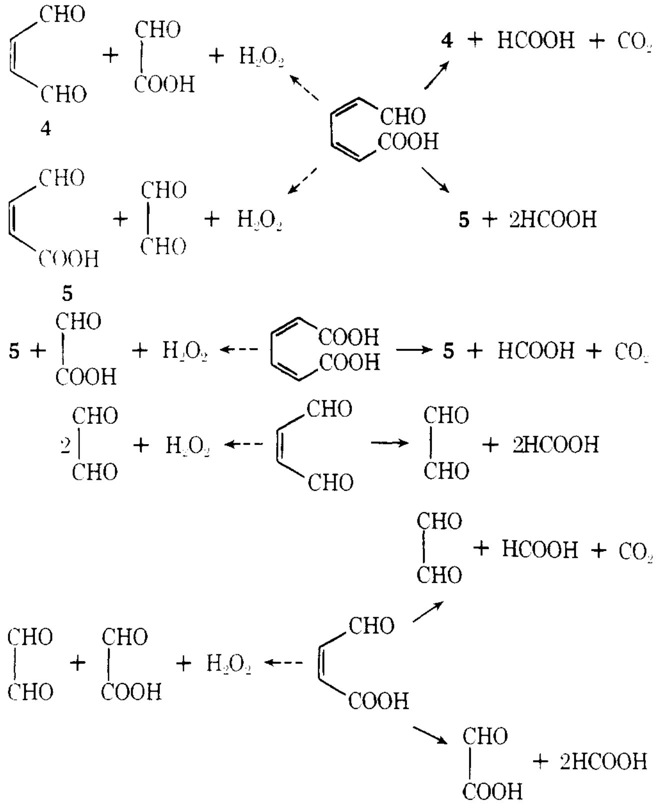
The results and discussion given above show that phenol is oxidized by ozone ultimately to oxalic acid and carbon dioxide as illustrated in Scheme II. The ratio of oxalic acid to

Scheme II. Proposed Major Reaction Pathways in the Ozonation of Phenol in Water

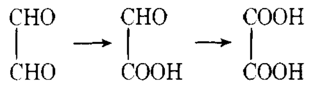
A. Hydroxylation (- - -) and Cleavage (—) of Aromatic Ring



B. Normal (- - -) and Anomalous (—) Ozonolysis of α,β-Unsaturated Aldehyde and Acid

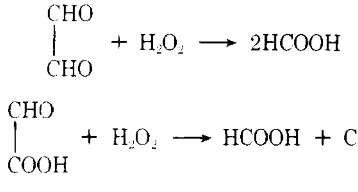


C. Oxidation of Aldehyde and Decarboxylation of Formic Acid by Ozone



$$HCOOH \longrightarrow CO_2 + H_2O$$

D. Baeyer-Villiger Oxidation of Glyoxal and Glyoxylic Acid by Hydrogen Peroxide



$$(CHO)_2 + H_2O_2 \longrightarrow 2HCOOH$$

$$CHO\text{-}COOH + H_2O_2 \longrightarrow HCOOH + CO_2$$

carbon dioxide is determined by the relative importance of normal and anomalous ozonolyses and Baeyer–Villiger reactions of glyoxal and glyoxylic acid.

Experimental Section

Materials. Commercial phenol was purified by distillation under reduced pressure, 78 °C (13 torr). Model compounds were those of the highest grade available commercially. Water was purified by passing through an ion exchange resin. Ozone was produced in a standard ozone generator, Nippon Ozone Co., Ltd., Model O-3-2, by charging pure oxygen dried beforehand by silica gel.

Ozonation Procedures. A 100-mL aqueous solution of phenol was put into a reaction vessel equipped with a dry ice condenser. The solution was stirred vigorously with a magnetic stirrer. The ozonation was started by bubbling ozone–oxygen gas into the vessel after thermal equilibrium at 30 °C had been reached. Ozone was usually introduced at a speed of 0.12 mmol/min. The ozonations of model compounds have been performed similarly. The concentration of ozone in the gas was determined by absorption in neutral 2% potassium iodine, followed by acidification with hydrochloric acid and titration with sodium thiosulfate solution.

Analytical Methods. The rates of disappearance of phenol and formation of products except acids were followed by a gas–liquid chromatograph equipped with FID using a Porapak Q column. Peroxides were determined by iodometric titration. The amount of organic peroxides was found to be very small. Therefore, decomposition of peroxides on GLC to yield nonperoxidic products is not important. Hydrogen peroxide was determined separately from the difference between the titers before and after treatment with catalase. It was ascertained that hydrogen peroxide could be decomposed selectively and quantitatively by catalase over the pH range 2.8 to 8.0. If the reaction solution contained more than 0.001 M acid, it was neutralized by sodium hydroxide. Acids were measured by titration and also by isotachophoretic analysis using a Shimadzu isotachophoretic analyzer, Model IP-1B. An aqueous solution of 0.01 M glutamic acid was used as a terminal electrolyte, and an aqueous solution containing 0.01 M L-histidine and 0.01 M L-histidine hydrochloride was used as a leading electrolyte. Under these conditions, oxalic acid, formic acid, 3 (and/or maleic acid), acetic acid, glyoxylic acid, and 5 could be determined qualitatively and quantitatively when their concentration was higher than 10^{-4} M. An aqueous solution of 0.005 M caprylic acid was used as a terminal electrolyte for the analysis of 2.

The total yield of carbonyl groups produced was measured by treating the product solution with a 1 N aqueous hydrochloric acid solution of 2,4-dinitrophenylhydrazine and following the consumption of hydrazine spectrometrically, λ_{max} 323 nm (ϵ 1.10 × 10^4 M^{-1} cm^{-1}). Double bonds were determined by the Hanus' method.[26] In some cases, the exhaust gas was introduced into aqueous sodium hydroxide solution in order to measure carbon dioxide. After the neutralization, carbon dioxide was collected from the solution by a Toepler pump and analyzed by gas chromatography with an active charcoal column. Total organic carbon content was measured by a Shimadzu T.O.C. analyzer, Model TOC-100B.

The relative reactivities of various compounds toward ozone shown in Table V were measured by following the rate of disappearance of the substrates by either GLC, isotachophoretic analysis, or iodometry. The plots of substrate concentration as a function of time gave satisfactory straight lines.

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Registry No.—1 (R = H), 64330-65-0; 2 (R = H), 69815-28-7; 3 (R = H), 1119-72-8; 4 (R = H), 3675-13-6; 5 (R = H), 1575-59-3; glyoxal, 107-22-2; glyoxylic acid, 298-12-4; oxalic acid, 144-62-7; formic acid, 64-18-6; carbon dioxide, 124-38-9; hydrogen peroxide, 7722-84-1; maleic acid, 110-16-7; catechol, 120-80-9; hydroquinone, 123-31-9; *trans,trans*-muconic acid, 3588-17-8; acetic acid, 64-19-7; acetaldehyde, 75-07-0; acetone, 67-64-1; methylglyoxal, 78-98-8; crotonic acid, 3724-65-0; mesityl oxide, 141-79-7; crotonaldehyde, 4170-30-3; crotyl alcohol, 6117-91-5; 3-butenoic acid, 625-38-7; phenol, 108-95-2; propanal, 123-38-6; *trans*-4-oxo-2-butenoic acid, 4437-06-3.

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(13) The ozonolysis of phenol should give *cis,cis*-6-oxo-2,4-hexadienoic acid, while the ozonolyses of 1,4-dihydroxybenzene and 1,2,4-trihydroxybenzene should give, respectively, *cis,cis*-4-hydroxy-6-oxo-2,4-hexadienoic acid and *cis,cis*-3-hydroxy-2,4-hexadienedioic acid as the major primary products. However, these are represented simply as muconaldehyde (**2**) and muconic acid (**3**) in the text for convenience. Hydroxy groups substituted on maleinaldehyde (**5**), mucondialdehyde (**1**), and maleindialdehyde (**4**) are also neglected, and they are expressed simply as shown in the text.

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Catalytic Conversion of Alcohols. 8. Gallium Oxide as a Dehydration Catalyst.

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Gallia is a very selective dehydration catalyst for several primary, secondary, and tertiary acyclic alcohols. The alkene distribution from 2-ols with about 50% *cis*-2-, 30% 1-, and 20% *trans*-2-alkene resembles those obtained with alumina. For 2-methylcyclohexanols, the cis isomer is converted more rapidly than the trans isomer and a cis–trans isomerization of the alcohol does not occur. The alkenes from the cis and the trans isomers suggest that an anti elimination is a major reaction pathway in the conversion of 2-methylcyclohexanol. In general, gallia closely resembles alumina as an alcohol conversion catalyst.

Alumina is a widely studied alcohol dehydration catalyst and much of the work has been covered in recent reviews.[1-3] It is generally accepted that the elimination of water follows an anti mechanism; however, the elimination from 2-methylcyclohexanol may be more complicated.[4] A puzzling aspect of the reaction is the high cis/trans ratio for the alkene product from the dehydration of acyclic alcohols; a protonated alkene intermediate has been postulated to account for this.[1] Indium oxide, a member of the same family as aluminum oxide, is diametrically opposed to aluminum oxide in catalytic selectivity since it was much more selective for dehydrogenation and for the formation of 1-alkenes from 2-ols.[5]

Recently two studies have been concerned with the conversion of 2-propanol over various phase modifications of gallia. Bremer and Bogatzki[6] found that 50–80% of the conversion was dehydrogenation for most of the gallia catalysts they tested. Shilyaeva et al.[7] found the β modification about equally active for dehydration and dehydrogenation, the α phase showed an increased proportion of dehydration, and the δ phase only catalyzed dehydration.

The present results, in addition to adding more definition to the catalytic character of gallia, provide data to show how the catalytic selectivity and activity changes within a family in the periodic table.

Results

Gallia was a very selective dehydration catalyst. For the six acyclic secondary 2-ols listed in Table I, 3-pentanol and 4-octanol, and for cyclohexanol and the 2-methylcyclohexanols in Table II, >98% of the total conversion was dehydration to alkenes. Ether was not a significant product from the conversion of secondary alcohols. The dehydration selectivity did not change for the duration of a run or over the temperature range from 160 to 225 °C used with the above alcohols. The catalytic activity was also stable during the run and, except for 3-pentanol, the conversion declined by only 2–4% during the course of a run. The activity declined rapidly with the 3-pentanol reactant; it has not been determined whether this is due to a low concentration of impurity in the alcohol or to a reaction product peculiar to 3-pentanol. The activity of gallia was comparable to the activity of the transitional aluminas under similar reaction conditions and may be slightly higher if the conversion is expressed on the basis of unit surface area.[8]

To determine the amount of isomerization of the alkene products, we have previously used the technique of adding an alkene that is similar to the dehydration product.[8,9] In the present study, by adding 1- or 2-heptene to the 2-octanol charge, we ascertained that the octene dehydration products did not undergo isomerization after desorbing to the gas phase. Likewise, the conversion of a mixture of 1-octene and *trans*-2-methylcyclohexanol took place without isomerization of the added 1-octene. Consequently, the alkene dehydration products that we obtained are the primary gas-phase products.

The alkene distributions in Table I for the conversion of several 2-ols are for later times-on-stream and are representative of the entire run. The percentage yields of the products in the runs of Table I were constant to within ±2% during the runs. As with alumina, about 50% of the alkene fraction was the cis-2 isomer. The 1 isomer was present in a larger amount than the trans-2 isomer. An exception to this may be the products from 4,4-dimethyl-2-pentanol, where the trans-2 isomer was the major product; however there is some uncer-

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