

Ozonization of Organic Compounds. V. Aromatic Compounds

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The ozonization of several aromatic compounds has been carried out at 30 °C in carbon tetrachloride. It was found that three processes proceeded simultaneously; that is, normal and anomalous ozonolyses to give respectively α,β -dicarbonyl and carboxylic compounds and polymerization. Carboxylic acids were the major products. Benzene and hexamethylbenzene gave formic acid and acetic acid respectively, while toluene and 1,3,5-trimethylbenzene gave mixtures of these acids. As the ozonization proceeded, white gummy polymers precipitated, the molecular weight ranged from several hundreds to a few thousands. They contained high concentrations of oxygen which was incorporated into polymer as carbonyl, carboxylic acid, peroxide and/or ether. The polymers were thermally stable below 150 °C.

The interactions of ozone with organic compounds, especially olefins, have been studied quite extensively¹⁾ and this reaction has been applied in preparation and identification of organic compounds. Recently the ozone chemistry has received much attention in the fields of atmospheric oxidation and purification of water. We have previously reported²⁾ that polypropylene underwent cleavage by ozonization to give lower molecular weight carboxylic acids but that the ozonization of polystyrene brought about crosslinking as well as chain scission, giving rise to broadening of molecular weight distribution.

The ozonization of aromatic ring has also been studied for long time. In 1904, Harries and Weiss³⁾ found that the ozonization of neat benzene and subsequent hydrolysis gave about 2 equivalents of glyoxal and no hydrogen peroxide. They surmised that the third mole of equivalent of glyoxal reacted with hydrogen peroxide during homolysis to give carbon dioxide and water. Later, in addition to α,β -dicarbonyls, peroxides, and carboxylic acids have been observed as ozonization products from aromatic compounds.⁴⁾ Keaveney *et al.*⁵⁾ attempted to produce glyoxal from benzene in high yield and they obtained glyoxal in 73 and 52% yields based on ozone absorbed and benzene reacted, respectively. No by-products such as glyoxylic acid, oxalic acid, formic acid, and carbon monoxide were observed. The ozonization of aromatic compounds is not fully understood and much of the data so far obtained are only qualitative.

We have undertaken the study of the ozonization of several aromatic compounds and found that three major processes proceeded simultaneously, that is, normal ozonolysis, anomalous ozonolysis, and polymer formation.

Experimental

Materials. Most of the organic compounds used in this study were those of the highest grade available commercially. They were either used as received or purified when necessary. 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.

Procedures. Ozonization was carried out in 100 ml vessel equipped with a condenser. It was started after thermal equilibrium at 30 °C had been reached by bubbling O_3-O_2 gas through the reaction mixture which was stirred with a magnetic stirrer. The gas was introduced at a speed of 100–120 ml/min, the rate of ozone supply being 0.12–0.20

mmol/min.

The amounts of substrate reacted and products formed were measured by gas liquid chromatography and high pressure liquid chromatography. Total amount of peroxides was determined by iodometric titration. Acids were measured by titration and identified by isotachophoretic analysis and liquid chromatography as described previously.²⁾ Carbon dioxide was also analyzed as previously.⁶⁾

Total yield of carbonyl groups was measured by treating the product solution with a 2 N aqueous hydrochloric acid and by following the consumption of hydrazine spectrometrically, $\lambda_{max}=322$ nm and $\epsilon=1.10 \times 10^4$ M⁻¹ cm⁻¹.

Polymeric material precipitated from the solution was dissolved into methanol or acetone, dried under vacuum and analyzed. Elemental analysis was carried out at Shonan Analytical Center. Total carbonyl content in the polymer was determined as described above. Double bonds were determined by the Hanus' method.⁷⁾ The molecular weight distribution was measured at 40 °C by gel permeation chromatography,⁸⁾ Shimadzu-DuPont Model 830. Infrared, ¹H NMR, and ¹³C NMR spectra were recorded on JASCO spectrometer Model IR-G, Varian EM 360A, and Hitachi NMR Model R-40 respectively.

Thermal decomposition of polymer was performed by dissolving 30 mg dried polymer into 2 ml acetic acid and heating at 150 °C for 2 h in a sealed ampoule under vacuum. The evolved gas was collected by Toepler pump and analyzed by gas chromatography. The solution was analyzed by gas liquid chromatography and gel permeation chromatography.

Results

Table 1 shows the results of ozonization of several aromatic compounds in carbon tetrachloride, a non-participating solvent that does not interreact with carbonyl oxide intermediate. The results in Table 1 show that the reactivities increase in the order of benzene < toluene < 1,3,5-trimethylbenzene < hexamethylbenzene in agreement with the previous reports,^{4,8–11)} suggesting that the attack of ozone to aromatic ring is electrophilic in nature. Since, as shown later, the oxidation of benzylic hydrogens is not important, these reactivities can be taken as those of aromatic ring toward ozone. Runs 4 and 5 show that the rate of ozonization is determined not by concentration of substrate but by ozone dosage. As observed previously,⁶⁾ phenols were quite reactive toward ozone and gave similar products as aromatic hydrocarbons.

Runs 1, 2, and 3 show that the ozonization of benzene in carbon tetrachloride gave formic acid as a

TABLE 1. OZONIZATION OF AROMATIC COMPOUNDS IN 50 ml CARBON TETRACHLORIDE AT 30 °C

Run No.	1	2	3	4	5	6	7	8	9	10
Substrate, R	Benzene	Benzene	Benzene	Toluene	Toluene	TMB ^{f)}	HMB ^{g)}	HMB ^{g)}	Phenol	BP ^{h)}
R ₀ , mmol	11.2	112	225	9.4	94	7.2	9.9	10.0	10.6	5.43
O ₃ fed, mmol	2.6	15	37	15	15	15	15	24	15	13
Time/min	21.5	120	307	120	120	120	120	120	120	65
ΔR, mmol				2.4		3.4	4.6	8.9	5.7	4.4
ΔR/O ₃ fed, (mol/mol)				0.16		0.23	0.31	0.37	0.38	0.34
Products in mmol										
Peroxide	0.08	0.11	0.17	0.34	0.34	0.67	2.3	4.6	0.19	0.73
Carbonyl ^{a)}			0.17			0.70	3.7	9.3		1.1
Carbonyl ^{b)}	0.20						3.9	9.8		
2,3-Butanedione ^{c)}							0.5	1.6		
Acids ^{d)}	1.2	4.4	15.3	3.9	5.1	5.1	2.4	5.5	2	1.7
Formic acid ^{e)}	1.1	3.6	16.0	4.1	3.9	2.3	0.3	0.5	1.0	0.5
Acetic acid ^{e)}				1.4	1.6	4.3	2.3	5.4		
Other acid ^{e)}			0.6 ^{j)}	0.4 ^{j)}	0.5 ^{j)}	0.5 ^{j)}			0.1 ^{j)}	0.4 ^{k)}
CO ₂							1.1			
Polymer, mg		95	333	found	found	found	1004	found	found	found
C, %		34.26	39.94		44.07					
H, %		4.05	4.53		5.00					
O, %		61.69	55.53		50.93					

a) From disappearance of 2,4-dinitrophenylhydrazine determined by UV analysis at 322 nm. b) From weight of 2,4-dinitrophenylhydrazine assuming glyoxal and 2,3-butanedione are formed from benzene and hexamethylbenzene respectively. c) By gas liquid chromatography. d) By titration. e) By isotachophoretic analysis. f) 1,3,5-Trimethylbenzene. g) Hexamethylbenzene. h) *p*-Benzylphenol. i) Glyoxylic acid. j) Not identified. k) Malonic acid.

major product with minor amounts of peroxide and glyoxal. The peroxide must be mostly ozonide, 1,2,4-trioxolane. Glyoxal is further oxidized to glyoxylic acid, but no oxalic acid was found under the present reaction conditions. One of the interesting features of this reaction is the formation of polymeric products. As the ozonization proceeded, white gummy material precipitated from the reaction mixture. The polymer will be discussed in some more detail later in this text.

Similar results were observed with toluene, 1,3,5-trimethylbenzene, hexamethylbenzene, and phenols. Carboxylic acids were obtained as major products, formic and acetic acids from both toluene and 1,3,5-trimethylbenzene, and acetic acid from hexamethylbenzene. Run 4 shows that 34 and 58% of aromatic carbons of toluene yielded formic and acetic acids respectively. Selectivities for formic and acetic acids from 1,3,5-trimethylbenzene based on reacted aromatic carbons are 23 and 42% respectively, and no 2,4,6-trimethylphenol was observed. The higher yields of acetic acid than formic acid from toluene and 1,3,5-trimethylbenzene may partly because of higher reactivity of formic acid toward ozone than acetic acid.⁶⁾ Hexamethylbenzene gave carboxylic acid in lower yield than benzene, toluene, and 1,3,5-trimethylbenzene. Interestingly, malonic acid was formed from *p*-benzylphenol roughly as much as formic acid.

The carbonyl compounds formed by the normal ozonolysis are glyoxal, methylglyoxal, and 2,3-butanedione from benzene, 1,3,5-trimethylbenzene, and hexamethylbenzene respectively. 2,3-Butanedione analyzed by gas liquid chromatography was smaller than that estimated from the disappearance of 2,4-dinitro-

phenylhydrazine (Runs 7 and 8 in Table 1). It is not clear at present if this discrepancy is due to experimental uncertainty or due to the formation of other carbonyl products. It may be noteworthy, however, that the amounts of 2,3-butanedione estimated from 2,4-dinitrophenylhydrazine formed were in good agreement with those analyzed from the disappearance of 2,4-dinitrophenylhydrazine.

Peroxides are one of the important products but their structure is not clear. Most of peroxides could be reduced by triphenylphosphine and dimethyl sulfide.

Quite a small amount of benzaldehyde was observed in the ozonization of toluene. However, little benzyl alcohol was observed even after the treatment with triphenylphosphine, suggesting that little benzyl hydroperoxide was present. Therefore, it may be concluded that oxidation of benzylic hydrogens is not important under the present reaction conditions. Furthermore, hexamethylbenzene was once oxidized in the presence of 2,6-di-*t*-butyl-4-methylphenol, a typical radical scavenger, and no decrease in rate of ozonization of hexamethylbenzene was observed. This suggests that oxidations by free radicals do not play an important role in this ozonization.¹²⁾

It has been reported^{10,11,13)} that ozonization intermediates oxidize carboxylic acids to corresponding peroxy acids, but no direct evidence for the formation of peroxy acids could be found.

One of the interesting features of the ozonization of aromatic compounds in carbon tetrachloride is the formation of polymeric materials. As mentioned above, white gummy material precipitated as the ozonization proceeded. The ozonization of hexamethyl-

TABLE 2. POLYMER FORMED IN THE OZONIZATION OF BENZENE IN CARBON TETRACHLORIDE (RUN 3)

Molecular weight	200—4000
Elemental analysis	C 39.94, H 4.53, O 55.53%— $C_3H_4O_3$
Oxygen	17% Carboxylic acid 28% Carbonyl <1% Peroxide (IPA-KI) $\approx$ 54% Dialkyl peroxide, ether
Double bond	none
IR	3250 cm^{-1} (H-bonded OH) 1725 cm^{-1} (carbonyl) 950—110 cm^{-1} (peroxide or ether)
Aromatic hydrogen	none
Thermal decomposition at 150 °C, 2 h:	small

benzene did not give a precipitate, but the presence of polymeric materials was found by gel permeation chromatography. The precipitated polymer was insoluble in carbon tetrachloride and benzene, but partly soluble in chloroform and very soluble in methanol, acetone, tetrahydrofuran, and acetic acid.

The example of gel permeation chromatogram is shown in Fig. 1. The molecular weight of the precipitated polymer ranges from 200 to 4000, while the product solution contained compounds with a molecular weight of a few hundreds. Some data on the polymers are also included in Table 1. The polymer was pale-yellowish white and very deliquescent. In Runs 2 and 3, 95 and 333 mg of polymers precipitated respectively. The ratio of polymer to formic acid on carbon base in these experiments is 1/1.35 and 1/1.44 respectively, suggesting that the polymers are one of the important major products. The analyses of the polymer obtained in Run 3 are summarized in Table 2. It shows that it contains quite a high ratio of oxygen and that 17 and 28% of oxygen incorporated were found as carboxylic and carbonyl oxygen. The hydroperoxidic oxygen was very small. The remaining 55% of oxygen must be peroxidic and/or ether oxygen. No double bond was observed. The 1H NMR analysis showed the absence of aromatic and methyl hydrogens. The infrared spectrum also showed the absence of aromatic hydrogen but it showed strong absorption at 3250 and 1750 cm^{-1} , which are ascribed to hydrogen-bonded hydroxyl and carbonyl groups respectively. A broad absorption was also observed between 950 and 1100 cm^{-1} , which must be ascribed to peroxide and/or ether linkage in the polymer. ^{13}C NMR analysis also showed the presence of ether, ester, and carboxylic acid.

In order to examine the stability of the polymer, especially of the peroxidic bond possibly involved, thermal decomposition of the polymer was carried out at 150 °C in 2 h in acetic acid under vacuum. Carbon monoxide and carbon dioxide were found by gas analysis and two unknown volatile products were found by gas chromatography, but their formation was small. Little change was observed in the gel permeation chromatogram after thermal treatment, implying that this polymer is thermally stable. Therefore, this polymer is not a dimeric peroxide of the

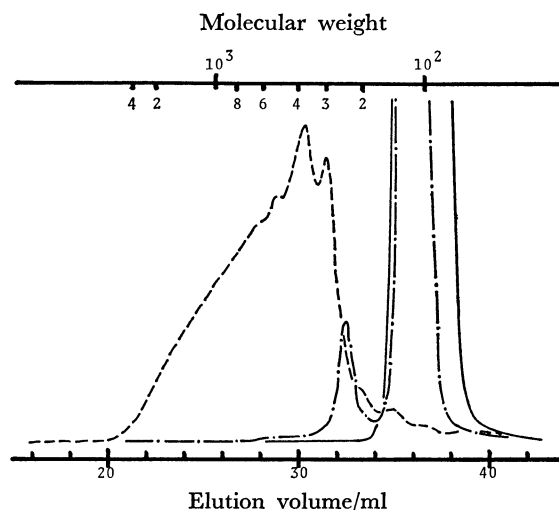


Fig. 1. Gel permeation chromatogram of ozonization products from benzene at 30 °C.

—: Initial solution, ---: product solution, ----: precipitate.

carbonyl oxides.

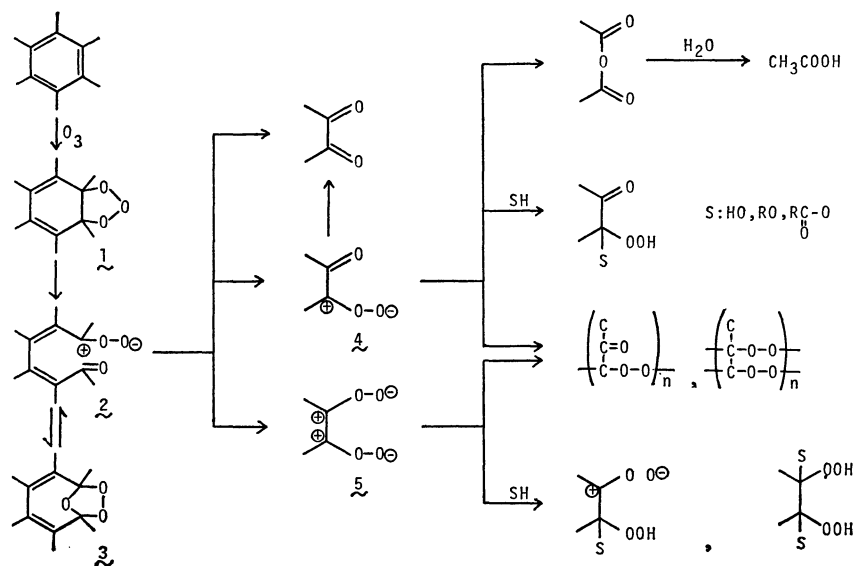
It should be noted on the safe handling of the polymeric material. We usually dissolved the precipitate in methanol or acetone and then the solvent was removed and dried under vacuum to obtain a stable polymeric solid. However, once the precipitate was taken out of the reaction mixture and dried directly at room temperature under vacuum, which brought about an explosion. At any time, this polymeric material should be handled with all precautions.

Discussion

As shown above, three processes proceeded competitively in the ozonization of aromatic compounds; they are normal and anomalous ozonolyses and polymer formation. The normal ozonolysis gives α,β -dicarbonyls, whereas the anomalous ozonolysis gives carboxylic acids. The plausible mechanisms are briefly discussed below.

Scheme 1 summarizes the possible major steps in the ozonization of hexamethylbenzene. The primary step is an electrophilic attack of ozone to aromatic ring to yield primary ozonide **1**. Thus the reactivities of polymethylbenzenes increase as observed with increasing number of methyl groups. The primary ozonide **1** is unstable and readily decomposes to give carbonyl group and carbonyl oxide **2**.

The aliphatic double bonds are more reactive than aromatic ring toward ozone and hence **2** must react with ozone to give eventually 2,3-butanedione and carbonyl oxides **4** and **5**. In non-participating solvents, the carbonyl oxide intermediate undergoes either ozonide formation, rearrangement or dimerization and/or polymerization. The latter reactions must become more important with increasing methyl substitution of the aromatic ring due to the decreased 1,3-dipolarophilic and electrophilic character of a ketone carbonyl in comparison to that of an aldehyde carbonyl.¹⁾ For example, Fliszar and coworkers¹⁴⁾ found in the ozonolysis of tetraphenylethylene that no ozonide was



Scheme 1. Major reaction pathways in the ozonization of hexamethylbenzene.

formed but 57% of diphenylcarbonyl oxide dimerized and 43% formed an peroxidic oligomer. The carbonyl oxide may react with itself, aldehyde, ketone, and also primary ozonide.¹⁵⁾

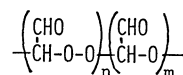
The participating solvents such as water, alcohol, and carboxylic acid react with carbonyl oxide rapidly and convert it into hydroxy, alkoxy, or acyloxy alkyl hydroperoxides.¹⁾

The carboxylic acids are anomalous ozonolysis products and formed by the rearrangement of carbonyl oxide or ozonide.^{1,16)} The detailed mechanism is not discussed here, but this anomalous ozonolysis is known to occur with special ease when there are carbonyl groups attached to the double bond as in **4** and when the temperature is relatively high.^{16,17)}

Thus benzene and hexamethylbenzene give formic and acetic acids respectively, while toluene and 1,3,5-trimethylbenzene give mixtures of formic and acetic acids.

As mentioned already, the polymer formation is one of the characteristic points in the present study. The formation of polymer or oligomers in the ozonization of olefins has been observed in several instances from quite a long time ago^{1,18)} and several mechanisms have been proposed.^{1,15)} However, there are only a few cases which describe the polymers from aromatic compounds. Several structures have been proposed for polymeric substances¹⁾ such as open chain polymers of carbonyl oxide with some ether linkages,^{14,19,20)} polyozonide,²¹⁾ and cyclic peroxide.²²⁾ Greenwood and Rubinstein¹⁵⁾ concluded that the alkene ozonization polymer does not have any specific structure and that both the dipolar ion fragment and the aldehyde fragment are incorporated into the polymer in varying ratios.

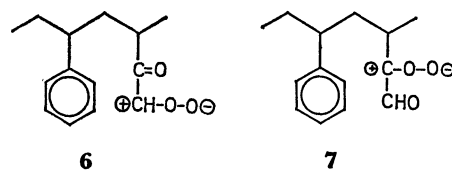
Our data also show that the polymer contained a high ratio of oxygen as carboxylic, carbonyl, peroxidic, and ether oxygen. Although it is not clearly elucidated, the data in Table 2 imply that the most plausible structure of the polymer from benzene may be written as follows.



Some of the aldehyde group must be oxidized to carboxylic acid.

Keaveney *et al.*²²⁾ surmised that glyoxal initially formed in the ozonization of benzene underwent condensation to give polymers, especially since such condensations are acid catalyzed.²³⁾ It is difficult to estimate the importance of this process relative to that involving carbonyl oxide.

Finally, in connection with the ozonization of polystyrene,²⁾ the above results and discussion show that the aromatic ring of polystyrene is cleaved to give carbonyl oxide such as **6** and **7**, which react with other carbonyl oxide or carbonyl group to yield eventually crosslinked polymer.



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