

Ozonolysis of Phenols

I. Ozonolysis of Phenol in Ethyl Acetate

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Phenol has been ozonised in ethyl acetate at 3–4°C. The ozonolysis fragments, carbon dioxide, formic and oxalic acids, and glyoxal, have been determined quantitatively. Possible reaction combinations are proposed to explain the experimental results. Classical formulae only are assumed in this connection.

The ozonolysis of phenols commands our interest for several reasons. There is for the present great interest in the mode of ozone attack on aromatic rings (and on olefinic double bonds). Aromatic systems and their reaction with ozone have been studied rather extensively, notably by Wibaut and collaborators. For references see Bailey¹. Kinetic studies by the Wibaut group have, among other qualitative relationships, established that anisole reacts much faster than benzene. Phenol itself has, however, neither been investigated in this connection, nor seems any rigorous product analysis of its ozonolysis to have been carried out.

Industrial sewage and waste liquors commonly contain phenolic constituents. Due to their toxicity these compounds create a serious problem in river pollution and if they reach drinking water reservoirs they are due to cause objectionable tastes and odours. The usual chlorine-treatment would here only aggravate the situation as chlorinated phenols are formed. Ozone-treatment of drinking water is a method of long standing in few places only (*e.g.* Paris), but in later years with the advent of more economical "tonnage ozone" the problem has received a careful reconsideration by the responsible authorities. The oxidation of phenols with ozone was shown by Roth² to result in compounds of little or no odour and Patrick³ demonstrated the nontoxicity of these oxidation products. Niegowski⁴ has presented additional information on the ozone oxidation of phenol, cresols and phenolic wastes from coke plants, chemical plants and refineries. A facile reaction is indicated and by appropriate adjustment of the initial pH of the solution an almost complete elimination of phenolic compounds can be achieved. All the mentioned ozonisation experiments were conducted in dilute aqueous solution and

Table 1. Rate of absorption of ozone by phenol dissolved in ethyl acetate.

Mins. from start	Total absorbed O ₃ (Mole O ₃ /mole phenol)	% absorbed O ₃ in preceding interval
2	0.22	97
6	0.68	88
10	1.12	85
14	1.55	84
18	1.98	82
22	2.40	80
26	2.77	73
30	3.12	68
34	3.40	51
38	3.57	33
42	3.70	24

in no case the products were isolated and identified or their relative amounts determined.

Phenol, dissolved in ethyl acetate, absorbed fairly readily ozone at 3–4°C. With our experimental set-up some ozone always passed unreacted through the reaction mixture. The amounts of this unreacted ozone increased as the reaction proceeded, as will be seen from Table 1. In this run 6.7 mmole of phenol was ozonised with 5.8 % (wt.) ozone at an oxygen flow of 30 lh⁻¹.

Somewhat more ozone than the three moles expected on the basis of a Kekulé structure is absorbed. On the other hand it is interesting to observe from Table 1 that when about three moles are absorbed the absorption curve dips rather steeply downwards. The ready consumption of ozone must be due to a facile reaction of the mono-ozonolysis products. This tendency is further shown by the determination of unreacted phenol when 1, 2 and 3 moles of ozone have been absorbed. The amounts of remaining phenol were, respectively, 60, 29, and 9 %. Consequently, when one mole of ozone had been absorbed only 0.4 mole of phenol had reacted corresponding to a consumption of 2.5 moles of ozone per mole of phenol. The immediate ozonolysis products seem therefore to react faster with ozone than phenol itself.

During the ozonolysis carbon dioxide was detected in the effluent gas. Since pure ethyl acetate only gives traces of carbon dioxide with ozone, it must result from the cleavage of phenol. The ozonised solution contained active oxygen and when left at room temperature it evolved carbon monoxide.

Decomposition of the reaction mixture was effected by stirring with cold water until the active oxygen had disappeared, and the ethyl acetate was extracted with further amounts of water. Also during the decomposition evolution of carbon dioxide could be noticed. In the aqueous decomposition solution several ozonolysis fragments were identified: Formaldehyde through its reaction with chromotropic acid, formic acid through its S-benzylisothiuronium salt, oxalic acid analogously by conversion to S-benzylisothiuronium oxalate, glyoxal through the *p*-nitrophenylosazone.

These findings point towards a fairly complete degradation of phenol by ozonolysis, but a better picture of this can only be gained through knowledge of the relative amounts in which the products occur.

Formaldehyde was not determined quantitatively as it was evident from the qualitative tests that the amount was very small. Further, it is known that ethyl acetate alone can give traces of formaldehyde with ozone and it is difficult to say whether all of it in our case stems from the solvent or from the phenol as well.

Formic acid was determined by distilling *in vacuo* aliquots of the aqueous decomposition solution into aqueous sodium hydroxide. The alkaline solution was then concentrated to half its original volume and oxidised with potassium permanganate. After acidification with dilute sulphuric acid, excess permanganate and the formed manganese dioxide were reduced with ammonium iron sulphate and the excess of this titrated with standard potassium permanganate. This somewhat roundabout method was necessary because some acetic acid from ethyl acetate always occurred in the decomposition solution.

Oxalic acid was determined gravimetrically as calcium oxalate in accordance with the standard analytical procedure.

Glyoxal was precipitated as *p*-nitrophenylosazone, dried and weighed. The method is not of highest accuracy, but due to the very slight solubility of the osazone in aqueous solutions it was considered adequate for our purposes.

Carbon dioxide was absorbed by soda asbestos after the necessary precautions to exclude volatile substances had been taken.

The beforementioned unreacted phenol was precipitated as tribromophenol and weighed.

The quantitative determinations were performed after absorption of 3 moles of ozone per mole of phenol and the results are given in Table 2.

About 86 % of the carbon in the starting material can thus be accounted for.

The aqueous decomposition solution was titrated directly with 0.1 N sodium hydroxide and was found to contain *ca.* 3.4 equivalents of acid per mole of phenol ozonised. The sum of formic and oxalic acids, on the other hand, is *ca.* 3.2 equivalents. Probably, the difference is due to acetic acid from the ethyl acetate and to glyoxal, which in the presence of alkali can undergo a Cannizzaro reaction.

Active oxygen in the ozonised solution (3 moles of ozone absorbed) was determined iodometrically to *ca.* 1.5 moles per mole of phenol. After decomposition with water at most a very small part of the active oxygen was retained as hydrogen peroxide since the aqueous decomposition solution gave only a faint yellow colour with titanium reagent.

Table 2. Ozonolysis products from phenol.

Product	Moles/mole phenol	Moles/mole reacted phenol	Recovered carbon, %
Carbon dioxide from the ozonolysis	0.33	0.36	5.5
Carbon dioxide from the decomposition	0.72	0.79	12.0
Formic acid	3.15	3.46	52.7
Oxalic acid	0.04	0.04	1.4
Glyoxal	0.14	0.15	4.7
Phenol	0.09		9.4

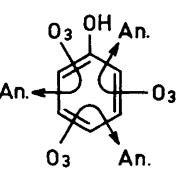
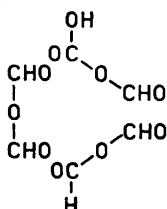
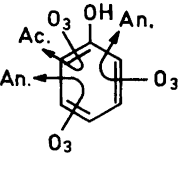
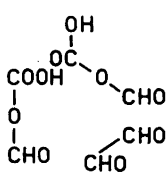
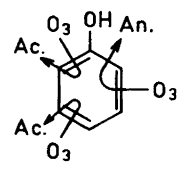
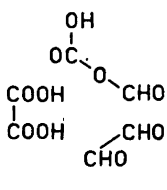
DISCUSSION

Even a brief examination of Table 2 gives some information regarding the ozonolysis of phenol: The degradation is of a certain complexity and more than one mode of reaction is indicated. The amount of formic acid seems somewhat low. The deficit in recovered carbon of 14.3 % is too large to be explained by analytical errors.

The latter point can be rationalised by carbon loss through the mentioned evolution of carbon monoxide. Probably this occurs already during the ozonisation and at the expense of formic acid, thereby explaining also the second of the above points.

Assuming thus that 14.3 % of the carbon is contained in the evolved carbon monoxide, we find that 0.94 mole of this compound is formed per mole of reacted phenol. On this basis the formation of the reaction products as well

Table 3. Reaction combinations in the ozonolysis of phenol. In the first column An. means anomalous ozonolysis, and Ac. means acid rearrangement.

Reaction combination	Moles of phenol reacted	Primary products	Secondary products	Moles of secondary products
	0.85		CO ₂ 5 [HCOOH or CO]	0.85 4.25
	0.11		2 CO ₂ 2 [HCOOH or CO] CHO CHO	0.22 0.22 0.11
	0.04		CO ₂ [HCOOH or CO] CHO CHO COOH COOH	0.04 0.04 0.04 0.04

as their relative amounts can reasonably well be explained by a scheme comprising three reaction combinations. In all of these only two types of reaction are assumed: Anomalous ozonolysis (partly, in view of the content of active oxygen after ozonolysis, also ozonide formation with subsequent rearrangement) and acid rearrangement which is frequent in aldozonides.

In Table 3 the reaction combinations are given schematically. The primary reaction products consist largely of anhydrides of formic and carbonic acids. Such anhydrides are very unstable and break down rapidly to carbon monoxide and dioxide. In view of this, probably most of the formic acid found after hydrolysis is formed through a rearranged ozonide. It should, perhaps, be remarked that the immediate products from anomalous ozonolysis and ozonide rearrangement generally are identical.

Addition of the amounts of secondary products required by Table 3 gives: Carbon dioxide 1.11 mole (found 1.15 mole); oxalic acid 0.04 mole (found 0.04 mole); glyoxal 0.15 mole (found 0.15 mole); formic acid and carbon monoxide 4.51 mole (if assumed 0.94 mole carbon monoxide, found 4.40 mole).

Regarding the initial ozone attack on phenol and the sequence of bond cleavage the experimental evidence warrants no definite statement. One point might, however, be brought to attention. If in a Kekulé structure the double bond adjacent to the hydroxyl group is severed first, the two remaining double bonds, now in an aliphatic structure, will react rapidly and quantitatively with ozone. Assuming an initial attack on the 3,4 or 5,6 double bond, the resulting structure would be an aliphatic enol which most probably rapidly would be transformed to the keto form, thereby withdrawing one double bond from reaction with ozone contrary to experimental fact.

As will have been noted classical formulae alone are sufficient to explain the qualitative and quantitative course of the ozonolysis. A curious fact, however, is the absence of glyoxylic acid, a substance one would have expected to be formed in ample amounts.

EXPERIMENTAL

Ozonisation technique. The phenol (redistilled pure commercial product) was dissolved in pure ethyl acetate and the solution cooled in an ice-bath during the reaction. Ethyl acetate was chosen as a solvent preferably to chloroform because of the much higher distribution coefficient with respect to phenol of the system ethyl acetate-water than chloroform-water. It was thus possible to keep practically all the unreacted phenol in the organic phase during the decomposition with water. Ozone was produced by silent electrical discharge through dry oxygen and at an oxygen flow of 30 l h^{-1} there was formed ca. $2.5 \text{ g O}_3/\text{h}$. The ozone production was checked iodometrically before and after each run. As reaction vessel served a gas washing bottle with a sintered glass bottom which ensured a good distribution of the gaseous reactant. Connected to the reaction vessel was another gas washing bottle containing neutral aqueous potassium iodide where unreacted ozone would liberate iodine and be determined quantitatively by subsequent titration with sodium thiosulphate.

Determination of phenol. Unreacted phenol was determined after absorption of 1,2 and 3 moles of ozone. Phenol (629 mg, 6.7 mmoles) was dissolved in ethyl acetate and ozonised. To the reaction mixture was added water (50 ml) and the ethyl acetate evaporated off the heterogeneous mixture at room temperature. A 20 % solution of bromine in glacial acetic acid was added dropwise to the resulting aqueous solution until a light yellow colour persisted. The precipitate was washed and dried in a desiccator over phosphorus pentoxide until constant weight. Found after absorption of 1,2 and 3 moles of

ozone, respectively, (mean of three determinations): 1 320, 650, and 348 mg of the tribromo derivative.

Determination of carbon dioxide during ozonisation. Before entering the ozone generator the oxygen was led through a soda asbestos tube to remove traces of carbon dioxide. From the reaction vessel containing phenol (629 mg) in ethyl acetate (50 ml), the effluent gas was led through neutral potassium iodide to remove unreacted ozone which otherwise would have interfered with the determination. Thereafter the gas was led through a dry ice trap and concentrated sulphuric acid and finally into the soda asbestos tube. After the ozonisation a few ml dilute acetic acid was added to the potassium iodide solution and oxygen led through the apparatus for some minutes. Found in five determinations: 111, 99, 90, 95, and 91 mg. Mean 97 mg.

Decomposition of the ozonised solution. The ozonised solution was mixed with water (50 ml) and stirred in a closed vessel (magnetic stirrer) for 6 h. The ethyl acetate was then extracted four times with 30 ml portions of water and the aqueous extracts combined and made up to 250 ml. After evaporation of the ethyl acetate the residue weighed only ca. 4 mg. This is less than the amount of unreacted phenol which must, at least partly, have evaporated under the experimental conditions.

Determination of carbon dioxide during decomposition. The ozonised solution was transferred to a closed vessel fitted with gas inlet and outlet and a dropping funnel containing water. Through the vessel was led purified nitrogen and the water in the funnel (50 ml) added to the organic solution with continuous stirring with a magnetic stirrer. The effluent gas was led through a dry ice trap and through concentrated sulphuric acid before it entered a soda asbestos tube. Found in five determinations: 198, 216, 177, 236, 236 mg. Mean 213 mg.

Determination of formic acid. 25 ml aliquots of the decomposition solution were distilled to dryness *in vacuo* at a temperature of 28–30°C. The receiver contained aqueous sodium hydroxide (ca. 50 ml, 2 N). After the distillation the alkaline solution was evaporated to half its original volume and mixed with a solution of potassium permanganate (0.1 N). The mixture was heated on a water-bath for one hour, acidified with dilute sulphuric acid and excess aqueous iron ammonium sulphate added. When all the manganese dioxide had dissolved, excess ferrous iron was titrated with standard potassium permanganate. Found in three ozonolyses: 933, 969, and 1 012 mg. Mean 971 mg.

Determination of oxalic acid. To 50 ml aliquots of the decomposition solution was added aqueous calcium chloride and the mixture heated to ca. 75°C. Dilute aqueous ammonia was then added until a yellow colour was formed with methyl red. The precipitate was filtered after 2 h, washed and dried. Found from three ozonolyses: 38.5, 37.0 and 35.0 mg. Mean 36.8 mg.

Determination of glyoxal. To the decomposition solution was added *p*-nitrophenylhydrazine dissolved in glacial acetic acid. A precipitate soon formed and was filtered off, washed and dried to constant weight. 288 mg. This is probably a maximum value for glyoxal *p*-nitrophenylosazone. The precipitate was recrystallised from glacial acetic acid and nitrobenzene and decomposed then at 298–300°C. Its infra-red spectrum was identical with that of authentic glyoxal *p*-nitrophenylosazone.

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