

Ozonolysis of Phenols

II. Catechol, Resorcinol and Quinol

ERLING BERNATEK, JAN MØSKELAND and KRISTIAN VALEN

Universitetets Kjemiske Institutt, Blindern - Oslo, Norway

Catechol, resorcinol and quinol have 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 paths are proposed to explain the experimental results. Classical formulae only are assumed in this connection.

In a previous communication¹ the ozonolysis of phenol in ethyl acetate was described. It was found that phenol readily absorbed three moles of ozone and was broken down to small fragments; mainly carbon dioxide and monoxide, formic acid, glyoxal and oxalic acid. Glyoxylic acid could not be detected among the reaction products. The course of reaction could fairly satisfactorily be described as a combination of anomalous ozonolysis (or rearrangement of a normal ozonide) and acid-rearrangement. We considered it of interest to extend the reaction to the simple dihydric phenols, as a preliminary to further research on the ozonolysis of phenolic compounds as well as for its own sake.

Catechol, resorcinol and quinol have been ozonised in aqueous solution by Otto² in 1898. The reaction products were intractable sticky solids and besides were found considerable amounts of unreacted phenols. Consequently no definite conclusions regarding the ozonolysis could be drawn on the basis of these experiments.

The present investigation concerns the ozonolysis of the mentioned dihydric phenols in ethyl acetate. Our interest is centered upon the ozone absorption and the (qualitative and quantitative) analysis of reaction products; further the possibility of explaining the course of reaction through simple steps involving classical formulae only, and whether in the case of catechol and quinol the material passes through a quinoid stage.

ANALYTICAL METHODS AND RESULTS

Ozone was determined in the usual way by absorption in aqueous potassium iodide and titration of the liberated iodine with standard thiosulphate.

Active oxygen in the ozonised solution was determined in accordance with standard practice by reaction with sodium iodide in glacial acetic acid and titration of the iodine. Hydrogen peroxide was found in the aqueous decomposition solution by the yellow coloration with titanium reagent.

Carbon monoxide was detected with palladium chloride reagent on filter paper strips.

Carbon dioxide was detected by reaction with aqueous barium hydroxide and determined quantitatively by absorption in soda asbestos.

Formic acid was identified through its S-benzylisothiuronium salt, and because acetic acid was present, determined by oxidation with potassium permanganate as described in the preceding communication ¹.

Oxalic acid was identified and determined quantitatively through its calcium salt.

Glyoxal was identified through its *p*-nitrophenylosazone and determined quantitatively through oxidation by hydrogen peroxide to formic acid.

Formaldehyde was identified and determined quantitatively by the colour reaction with chromotropic acid.

Unreacted amounts of the dihydric phenols were determined:

a) Catechol and quinol by oxidation with ferric chloride to the corresponding quinone and extraction of this with chloroform. The quinone was then determined iodometrically ⁴.

b) Resorcinol by precipitation under specified conditions with furfural and weighing of the precipitate ⁵.

Active oxygen after ozonolysis in moles/mole reactant:

Reacted with	Catechol	Resorcinol	Quinol
1 mole O ₃	0.5	0.6	0.4
2 » O ₃	0.9	0.9	0.8
3 » O ₃	1.6	1.2	1.1

Unreacted phenol after ozonolysis in per cent of starting material:

Reacted with	Catechol	Resorcinol	Quinol
1 mole O ₃	% 38	% 54	% 43
2 » O ₃	10	8	6

After the addition of 3 moles of ozone no unreacted material could be found.

Carbon dioxide was evolved during ozonolysis as well as under decomposition of the ozonised solution with water.

Total non-volatile products (oxalic acid, glyoxal and unidentified compounds) were isolated by evaporation of the ethyl acetate and aqueous phases and drying the residues *in vacuo*. Combustion analysis gave the content of carbon.

DISCUSSION

Ozone is very readily absorbed by the dihydric phenols, only towards the end of application of three moles small amounts of unreacted gas escape from the reaction vessel. This indicates a facile reaction with the aromatic nucleus.

Table 1. Amounts of reaction products from ozonolysis of dihydric phenols with 3 moles of ozone. (The first figure gives the amount in moles/mole of starting material, while the second figure gives the percentage of recovered carbon).

Product	Catechol		Resorcinol		Quinol	
	moles/mole	%	moles/mole	%	moles/mole	%
Carbon dioxide (ozonolysis)	0.46	7.7	0.60	10.1	0.64	10.7
Carbon dioxide (hydrolysis)	1.02	17.1	1.00	16.7	1.00	16.5
Formic acid	1.95	32.5	2.12	35.4	2.25	37.5
Total non-volatile compounds		36.4		29.8		24.3
Oxalic acid	0.19	6.2	0.24	7.9	0.21	7.0
Glyoxal	0.13	4.2	0.12	4.0	0.14	4.8

The figures in Table 1 are calculated from the means of the analytical values in the experimental part.

A qualitative comparison with the ozone absorption by phenol reveals an even readier absorption in the present case, which, of course, is not unexpected. In the case of phenol there was after reaction with 3 moles of ozone still present about 9 % of unreacted material. The phenols now under consideration are completely removed when three moles of ozone are absorbed. Application of one or two moles of ozone per mole of dihydric phenol left relatively large amounts of unreacted material. This is, as in the case of phenol itself, due to a greater reactivity of ozone towards the primary ozonisation products than towards starting material.

Table 1 tells that the main part of the dihydric phenols is split up to rather small fragments, the greater part of the recovered carbon occurring as carbon dioxide and formic acid. Of the non-volatile reaction products only between one half and one third of the recovered carbon can be accounted for as oxalic acid and glyoxal. The remainder has, in spite of continued efforts, not yielded to our attempts at separation and identification. It can be said, however, that the unidentified substances mainly are of aldehydic and acidic nature, both functional groups presumably being present in the same molecule. The latter statement is partly based on our repeated experiments with chromatography of the reaction products on weakly basic anion exchangers.

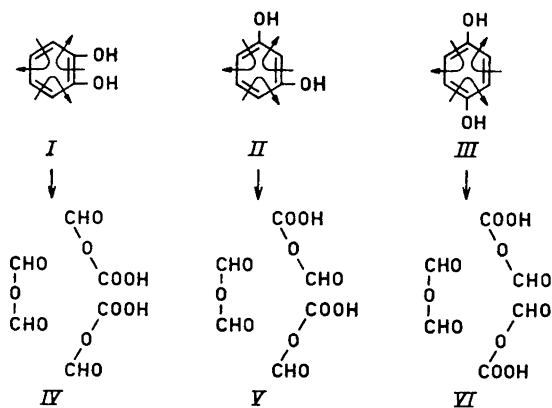
The total recovered carbon (whether in identified products or not) is 94 %, 92 % and 89 % for catechol, resorcinol and quinol, respectively. Since carbon dioxide, formic acid as well as carbon in the non-volatile products can be determined with a fair degree of accuracy it is reasonable to suppose that the deficiency in carbon is real, *i.e.*, that carbon has been lost in the form of a volatile compound. Formaldehyde has been detected among the reaction products, but has been estimated to occur in such minute amounts as to be without significance for the carbon balance. Further carbon monoxide has been found and albeit not determined quantitatively the amount seems to be great enough

to explain the missing carbon. If this is supposed, there is formed 0.36, 0.48 and 0.66 moles of carbon monoxide per mole of dihydric phenol from catechol, resorcinol and quinol, respectively. It is noteworthy that in no case the formation of maleic or glyoxylic acid could be demonstrated.

The analytical results show that the degradation obviously follows the same pattern in all the three phenols and it seems therefore unlikely that catechol and quinol should take a route through a quinone intermediate. In that case one would, for quinol at least, expect the occurrence of maleic and glyoxylic acids³ among the reaction products.

When regarding the mode of reaction between the phenols and ozone one must take into consideration the three main reaction types, *viz.* anomalous ozonolysis, normal ozonide formation followed by hydrolysis, and acid-rearrangement. There is a great number of possible combinations of these reactions, especially in the case of catechol where two different Kekulé-structures can be written. We need here, however, consider only the combinations which give no glyoxylic acid.

Since carbon dioxide and formic acid are the main products it seems very likely that most of the material undergoes a complete anomalous ozonolysis. This can be depicted in the diagrams I, II and III (only one Kekulé-structure is taken into account for catechol). The primary products will be the anhydri-

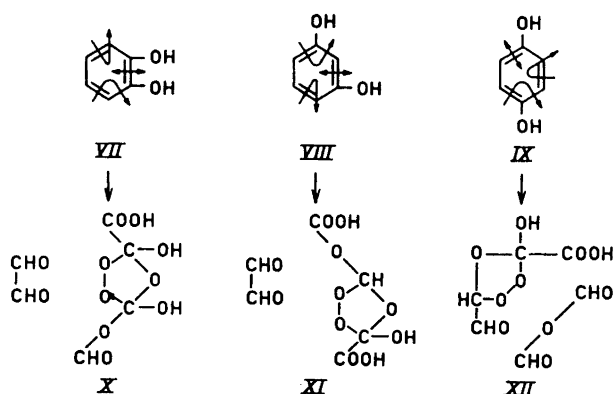


des in IV, V and VI. Such anhydrides are generally very unstable and will break down rapidly to carbon monoxide and dioxide under anhydrous conditions. With water present also formic acid will be formed. Probably most of the formic acid actually found is formed through rearrangement of an ozonide (the ozonised solution contains an appreciable amount of peroxidic material) since the anhydrides must be supposed to break down before the hydrolysis can be performed. Rearrangement of the ozonides of course leads to the same structures (IV, V and VI) as the direct anomalous ozonolysis. Total anomalous ozonolysis gives for all three phenols two moles of carbon dioxide and four moles of formic acid and/or carbon monoxide per mole of phenol. The found mole ratios are:

	Catechol	Resorcinol	Quinol
$\frac{\text{CO}_2}{\text{HCOOH} + \text{CO}}$	$\frac{1.48}{2.31}$	$\frac{1.60}{2.60}$	$\frac{1.64}{2.91}$

The amounts of formic acid-carbon monoxide fall somewhat short of what is required by the above reaction modes. Exact agreement with any particular reaction scheme is hardly to be expected in view of the relatively large amounts of unidentified products.

Glyoxal and oxalic acid can be formed through several reaction paths. Since some hydrogen peroxide was found in the aqueous decomposition solution it seems reasonable to suppose that the reactions at some stage involve the hydrolysis of ozonides. Schematically the reactions can be visualised in the following way:



In VII, VIII and IX the arrows mean:



The anhydridic and peroxidic structures in X, XI and XII will on hydrolysis all give the same products and in the same amounts, *viz.* one molecule each of glyoxal, oxalic acid, carbon dioxide, formic acid and hydrogen peroxide. Table 1 gives the molecular ratio of oxalic acid to glyoxal closer to two than to one, but in view of the difficulties in exact determination of glyoxal this cannot be regarded as a serious argument against the operation of schemes VII, VIII and IX or something akin to it.

EXPERIMENTAL

Ozonolysis. The ozonisation technique and the decomposition with water were the same as described in the previous communication ¹.

Determination of dihydric phenols: Unreacted phenols were determined after absorption of 1 and 2 moles of ozone.

(a) Resorcinol. 1.000 g of resorcinol was ozonised and hydrolysed. An aliquot of the aqueous decomposition solution (25 ml) was made up to 100 ml with hydrochloric acid and water thereby adjusting the content of mineral acid to 12 %. To this was added freshly distilled furfural (50 mg), the mixture shaken and left for 24 h. The blue-black precipitate was collected, washed and dried in a hydrogen atmosphere. The ethyl acetate phase from the decomposition was evaporated to dryness and the residue taken up in hydrochloric acid (100 ml, 12 %). Furfural (1 100 mg) was added and the mixture treated as above.

1 O₃: Found resorcinol in water 145, 164 and 172 mg. From ethyl acetate 364, 345 and 431 mg.

2 O₃: In water 1 mg. From ethyl acetate 79 mg.

(b) Quinol: 1.000 g of quinol was ozonised and hydrolysed. An aliquot of the aqueous decomposition solution was mixed with aqueous ferric chloride (15 ml, 10 %). The mixture was extracted with three portions (30 ml) of chloroform and to the combined extracts was added acidified potassium iodide solution (15 ml, 10 % + H₂SO₄, 10 ml, 10 %). The heterogeneous mixture was shaken vigorously for 2 min and the liberated iodine titrated with standard thiosulphate. The ethyl acetate phase from the decomposition was evaporated to dryness and the residue taken up in water and analysed as above.

1 O₃: Found quinol in water 139, 134 and 136 mg. From ethyl acetate 269, 280 and 338 mg.

2 O₃: In water 8 mg. From ethyl acetate 50 mg.

(c) Catechol. The analysis was performed essentially in the same way as for quinol with the modification that less aqueous ferric chloride was used (5 ml) and the extraction with chloroform was repeated a fourth time.

1 O₃: Found catechol in water 64 and 53 mg. From ethyl acetate 328 and 314 mg.

2 O₃: In water 4 mg. From ethyl acetate 96 mg.

Determination of products after the absorption of 3 moles of ozone. The determinations of carbon dioxide during ozonisation and decomposition, formic and oxalic acids and glyoxal were performed as in the previous communication¹.

(a) Resorcinol. Carbon dioxide during ozonisation 284, 243 and 246 mg. During hydrolysis 409, 405 and 356, 445 and 380 mg CO₂. Formic acid 1 019, 737, 735, 971 and 866 mg. Oxalic acid 190, 200 and 190 mg. Glyoxal 61 and 65 mg.

(b) Quinol. Carbon dioxide during ozonisation 251 and 276 mg. During hydrolysis 417, 397 and 383 mg, CO₂. Formic acid 822, 1 019 and 978 mg. Oxalic acid 180, 162 and 172 mg. Glyoxal 79 and 72 mg.

(c) Catechol. Carbon dioxide during ozonisation 200, 198 and 210 mg. During hydrolysis 390, 416 and 427 mg CO₂. Formic acid 866, 722, 998 and 676 mg. Oxalic acid 165, 140 and 153 mg. Glyoxal 63, 72 and 65 mg.

(d) Non-volatile matter. The ozonised solutions were hydrolysed and extracted exhaustively with water. The combined extracts were evaporated and the residue dried to constant weight above phosphorus pentoxide and potassium hydroxide (Table 2).

Table 2.

Phenol	Weight of non-volatile matter	Per cent carbon
	mg	
Catechol	733	31.3 , 31.2
	694	35.7 , 35.6
Resorcinol	620	31.8 , 30.8
	622	31.5 , 31.4
Quinol	456	31.0 , 31.2
	530	34.5 , 34.1
	505	29.5 , 30.4

All the above determinations refers to the ozonolysis of 1.000 g of dihydric phenol. The different figures under (a), (b), (c) and (d) are independent results from separate ozonolysis runs.

REFERENCES

1. Bernatek, E. and Frøngen, C. *Acta Chem. Scand.* **15** (1961) 471.
2. Otto, M. *Ann. chim. (Paris)* [7] **13** (1898) 137.
3. Bernatek, E. and Straumsgård, K. A. *Acta Chem. Scand.* **13** (1959) 178.
4. Böck, F. and Lock, G. *Monatsh.* **54** (1929) 888.
5. Votocek, E. and Potmesil, R. *Ber.* **49** (1916) 1185.

Received March 10, 1961.