stopcock on the outlet tube was closed and thereafter the stopcock on the inlet tube. In this way, a slight hydrogen over-pressure was built up in the reactor tube. In the case of low-boiling liquids, 4—6 μl were injected at this stage through the serum cap into the platinum bowl. A voltage of 5 V was then applied to the platinum wire, causing it to glow.

As mentioned above, the time of pyrolysis had to be adjusted to the aggregation state of the sample as well as to the element which was to be determined. For the determination of halogen and sulphur in liquid organic compounds, a pyrolysis time of 10—15 sec was enough while for solid substances 20—30 sec were necessary. To determine nitrogen in liquids, a pyrolysis time of 50—60 sec was required and in solids 100—110 sec. This means that, whenever a full analysis is wanted, the long pyrolysis times have to be applied. After the completion of the pyrolysis, a test tube with 0.5 ml 10 % sodium hydroxide was connected to the outlet tube of the reactor and the pyrolysis products swept through the alkaline solution by a stream of hydrogen. The solution was analyzed for sodium halides, sodium sulphide and sodium cyanide using mainly the procedure described by Widmark [3].

When analyzing for H, 10—15 mg of sulphur was placed in the platinum bowl and, in the case of solid samples or not too fugitive liquids, mixed with about 5 mg of the substance. Low-boiling liquids (about 5 μl) were injected into the bowl after flushing the reactor with nitrogen. A pyrolysis time of 20—30 sec was found to be adequate and the pyrolysis products were absorbed, as before, in a 10 % solution of sodium hydroxide and the solution analyzed for sodium sulphide.

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Ozonolysis of Naphthoquinones

III. 1,2-Naphthoquinone

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In our previous papers in this series [1,2] we have confined ourselves to the discussion of the ozonolysis of some 1,4-naphthoquinones. We wish now to report on certain aspects of the behaviour of 1,2-naphthoquinone under ozonolytic cleavage.

The quinone, in chloroform, absorbed ozone readily though not quantitatively and the ozonisation was terminated when 3 moles of the gas had been applied. At this point the dark colour of the solution had changed to a light yellowish green. If the initial quinone solution was saturated or if carbon tetrachloride was added, a faintly yellow substance separated during ozonisation. It contained active oxygen but decomposed explosively in a few seconds if isolated and dried. This product may be a true ozonide, but a closer examination of it was difficult due to its labile character. Immediately after the ozonisation the solution contained about 1.2 g atoms of active oxygen per mole of starting material.

Table 1 gives the identified reaction products together with the results from the quantitative determinations.

Table 1.

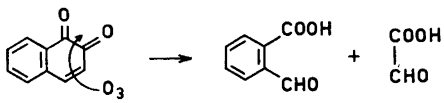
Product	% recovered carbon	moles/mole reacted quinone
Carbon monoxide	0.80	0.08
Carbon dioxide	11.50	1.14
Formaldehyde	0.75	0.075
Formic acid	7.30	0.73
Phthaladehydic acid	61.50	0.77
Phthalic anhydride	15.50	0.19

The carbon oxides were evolved during ozonolysis as well as during hydrolysis of the reaction mixture, the phthalic anhydride was then usually recovered as phthalic acid. It will be noticed that more than 97 %

of the initial carbon is recovered in the products and that the aromatic balance (*i.e.* recovery of benzene nucleus) is about 96 % indicating an almost exclusive attack on the quinone ring.

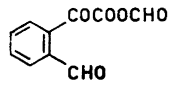
A conspicuous feature of the results is that both aromatic products have lost two carbon atoms, but on the other hand no C_2-fragments could be found. This is not wholly unexpected, however, since the application of as much as three moles of ozone was needed to degrade the quinone quantitatively.

Formation of phthalaldehydic acid can simply be explained as an abnormal ozonolysis as indicated in (I) (or, in view of the content of active oxygen in the reaction mixture, as a rearrangement of an ozonide in the same direction) with the simultaneous formation of glyoxylic acid.



I

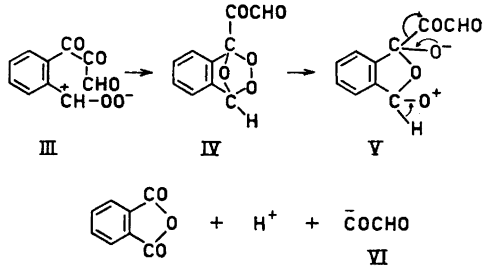
Glyoxylic acid is then probably oxidised by the prolonged action of ozone to carbon dioxide and formic acid. An abnormal ozonolysis with the expulsion of only a C_1-fragment followed by oxidation of the side-chain in the aromatic product is also theoretically possible. This reaction, however, produces the intermediate (II), which is a mixed anhydride of formic acid and will split off carbon monoxide. If this reaction path was dominant, far larger amounts than those found of this oxide would have been formed.



II

The really interesting result of this investigation is the formation of phthalic anhydride. It is fairly certain that the anhydride is a primary product and not the result of an anhydridisation of phthalic acid. If the free acid was formed initially it should have separated from the chloroform solution, where it is very slightly soluble. Further, some anhydride could be isolated in the chloroform phase even after addition of water to the reaction mixture.

Mechanistically the reaction can be explained in more than one way but the simplest one is to assume the initial formation of the zwitterion (III), which undergoes a ring-closure to the sterically more probable of three possible ozonides (IV).



III IV V

VI

A heterolysis of the O—O bond takes us to the transitory entity (V), which by the indicated electronic shifts eliminates a proton and the carbanion (VI) thereby forming phthalic anhydride. The proton and (VI) combine, perhaps synchronously with the elimination, to glyoxal. Also this C_2-fragment is then oxidised by excess ozone to formic acid and carbon dioxide.

Formaldehyde, which is found in very small amounts only, is probably formed by hydrolytic cleavage of a carbonyl intermediate in a way similar to that discussed in connection with the ozonolysis of *p*-benzoquinone [3].

Experimental. Ozonolysis. The ozonisation technique and the decomposition with water were performed as decribed for 1,4-naphthoquinone [1,2].

Ozone absorption was measured by leading the effluent gases into aqueous potassium iodide, which was changed at intervals and the liberated iodine titrated. Active oxygen was also determined iodometrically by running aliquots of the reaction mixture into sodium iodide in glacial acetic acid.

Determination of products. Carbon monoxide and formic acid were determined as previously described [1,2]. Carbon dioxide was determined as accounted for in the ozonolysis of phenol [4]. Formaldehyde was identified through its dimedone derivative (m.p. and mixed m.p. 187°C) and determined spectroscopically through its colour reaction with chromotropic acid.

Phthalaldehydic acid was found in the aqueous decomposition solution as well as in the chloroform phase. It was identified through its 2,4-dinitrophenylhydrazone, m.p. 250.5°C. (Found: C 51.2; H 3.3; N 16.5. Calc. for

$C_{14}H_{10}N_4O_6$: C 50.9; H 3.3; N 17.0) and through its *p*-nitrophenylhydrazone, m.p. 206.5°C. (Found: C 58.5; H 3.9; N 15.1. Calc. for $C_{14}H_{11}N_3O_4$: C 58.9; H 3.9; N 14.8). For the quantitative determination the precipitation with dinitrophenylhydrazine was utilised after a small correction for the solubility of the derivative had been applied.

Phthalic anhydride was found as such in the chloroform phase, especially if the hydrolysis had been of short duration. By thermal decomposition of the ozonisation solution or by reduction with sodium iodide the formed phthalic anhydride can be isolated almost quantitatively while the content of phthalic acid is practically nil. M.p. and mixed m.p. 130°C (Found: C 64.3; H 2.9. Calc. for $C_8H_4O_3$: C 64,7; H 2.7). Quantitatively the anhydride was determined by two methods:

(*a*) After the hydrolysis the chloroform is evaporated from the heterogeneous mixture whereby the anhydride dissolves in the water as phthalic acid. The water is removed at room temperature and the residue (A) is extracted repeatedly with chloroform leaving almost pure phthalic acid which is then weighed. This method gives probably somewhat low results.

(*b*) The residue (A) is dissolved in water again and titrated with standard sodium hydroxide (indicator: phenolphthalein). From the titration values is then deducted the amount due to phthalaldehydic acid.

In all quantitative work the ozonisation batches consisted of 1.00 g of 1,2-naphthoquinone in 100 ml of chloroform.

Results:

Carbon monoxide during ozonisation 8.1, 8.6, 9.6 mg. Mean 8.8 mg. During hydrolysis 6.2, 6.8, 5.6 mg. Mean 6.2 mg.

Carbon dioxide during ozonisation 102, 86, 78, 94 mg. Mean 90 mg. During hydrolysis 302, 276, 307, 283 mg. Mean 290 mg.

Formaldehyde 14.2, 14.6 mg. Mean 14.4 mg.

Formic acid 182, 224, 215, 232 mg. Mean 213 mg.

Phthalaldehydic acid 733, 745, 711 mg. Mean 730 mg.

Phthalic anhydride. Method (*a*) 173, 161, 182 mg. Mean 172 mg.

Method (*b*) 191, 194, 200 mg. Mean 195 mg. Mean for both methods 183 mg.

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Partition Chromatography on Ion Exchange Resins.

Separation of Sugars

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In earlier papers it has been demonstrated that strongly polar non-electrolytes such as sugars can be taken up effectively from ethanol-water mixtures by means of ion exchange resins. Only a few chromatographic separations have been carried out based upon this sorption mechanism [1,2]. In separations of monosaccharides overlapping curves are obtained in many systems. A systematic study of the factors which govern this sorption has shown that the ethanol concentration, and the rate of diffusion inside the resin particles are critical factors [3,4]. For this reason it is necessary to use an appropriate ethanol concentration, a small resin particle size, and a low flow rate in order to achieve satisfactory separations. In the present work some results are given demonstrating applications of this method to sugar separations.

Experimental. The resin (Dowex 1 X-8) was classified hydraulically to obtain the fraction 45 – 75 μ and transformed into its sulfate form. The column was prepared and operated in the normal way, and precautions were taken to avoid gas bubbles in the column [5]. The dimensions of the resin bed were 10 × 840 mm. The sample solutions which had a volume of 5 ml contained 75 % ethanol (by weight). The eluant was fed on to the column with a pump at a constant flow rate (0.8 ml $cm^{-2}min^{-1}$). The temperature was kept constant at 28°C.

The eluate was collected in a fraction collector and analyzed using the Technicon Auto-Analyzer [6].