

The powder pattern of Zr_4Al_3 was obtained from a sample annealed at 850°C for several days. It was possible to index it with the following hexagonal unit cell dimensions:

$$a = 5.430 \text{ \AA}, \quad c = 5.389 \text{ \AA}.$$

The observed density, 5.32 g cm^{-3} , is in good agreement with the value, 5.37 g cm^{-3} , calculated for a cell content of one formula unit Zr_4Al_3 . The intensity data suggest that the structure contains chains of zirconium atoms ($Zr-Zr = \frac{1}{2}c$) similar to those present in the Zr_3Al_2 phase.

Further studies on these structures are in progress.

In connection with the investigations on the zirconium-aluminium system, the aluminium-rich region of the hafnium-aluminium system has also been studied. Thus, three compounds, viz. Hf_3Al_2 , $HfAl_2$ and $HfAl_3$, have been prepared so far. The X-ray powder patterns demonstrate clearly that they are all isomorphous with the corresponding phases in the zirconium-aluminium system.

$HfAl_3$ has a hexagonal C14 type of structure with the unit cell axes:

$$a = 5.288 \text{ \AA}, \quad c = 8.739 \text{ \AA}$$

$HfAl_2$ has a tetragonal $D0_{23}$ type of structure with the unit cell axes:

$$a = 4.010 \text{ \AA}, \quad c = 17.310 \text{ \AA}$$

For valuable discussions and a continuous interest in this research work, the authors are much indebted to Dr. Arne Magnéli.

1. Mc. Pherson, D. J. and Hansen, M. *Trans. Am. Soc. Metals* **46** (1954) 354.
2. Keeler, J. H. and Mallery, J. H. *J. Metals* **7** (1955) 394.
3. Wilson, C. G., Sams, D. and Renouf, T. J. *Acta Cryst.* **12** (1959) 947.
4. Wilson, C. G. *Acta Cryst.* **12** (1959) 660.
5. Brauer, G. *Z. anorg. Chem.* **1** (1939) 242.
6. Westman, S. and Magnéli, A. *Acta Chem. Scand.* **11** (1957) 1587.
7. Aronsson, B. *Acta Chem. Scand.* **9** (1955) 1107.
8. Nowotny, H. and Parthé, E. *Planseeber. Pulvermet.* **2** (1954) 34.
9. Nowotny, H., Parthé, E., Kieffer, R. and Benesovsky, F. *Monatsh.* **85** (1954) 255.
10. Brewer, L. and Krikorian, O. *UCRL 2544, University of California 1954.*

Received January 15, 1960.

Ozonolysis of *p*-Benzoquinone. III. Counter-current Ozonisation

ERLING BERNATEK and KRISTIAN VALEN

*Universitetets Kjemiske Institutt, Blindern-
Oslo, Norway*

On two previous occasions^{1,2} we have reported on the ozonolysis of *p*-benzoquinone and discussed some of the possible reaction paths. Anomalous ozonolysis and/or rearrangement of normal ozonides occurred to a large extent. This was to be expected since in quinone two carbonyl groups are conjugated with the double bonds attacked by ozone.

The experimental procedure employed — being a batch procedure — had the drawback that the primary reaction products were in contact with ozone for a comparably long time. Consequently some of the isolated products could have been formed by further oxidation. In order to avoid this and especially to investigate closer the formation of a monoazonide and its decomposition products, we adopted a counter-current procedure similar to that of Pummerer and Richtzenhain³ which allowed a brief contact between the quinone solution and ozone, rapidly followed by hydrolysis.

Previous experiments with the batch procedure has shown that even if quinone was present in excess to the amount of ozone required for mono-ozonolysis only minor amounts of reaction products originating from cleavage of one double bond were found. It thus seems that secondary reactions proceed about as fast as the initial ozonolysis.

In Table I is summarised some of the relationships between the amount of applied ozone per mole of quinone, % reacted quinone and consumed ozone as found by the counter-current method. Finally the theoretically possible amount of monoazonide (or products from mono-ozonolysis) in moles per mole of quinone is calculated.

When about one mole of ozone is applied per mole of quinone 65 % of the latter is attacked. A substantial part of the quinone must therefore have consumed two molecules of ozone. From the last column it is clear that mono-ozonolysis occurs in increasing amounts with decreasing ozone-quinone ratio.

Table 1.

Run	Moles O ₃ quinone	% Reacted quinone	% Reacted O ₃	Moles monozone quinone
1	2.17	95.4	86.8	0.06
2	1.74	83.8	88.2	0.17
3	1.43	79.4	97.7	0.24
4	1.05	67.2	~ 100	0.44
5	1.01	65.0	100	0.45
6	0.98	60.3	100	0.37
7	0.82	56.9	100	0.56
8	0.80	57.5	100	0.61

Oxidation of the aqueous decomposition solution with hydrogen peroxide and analysis for maleic acid constituted another method to determine the degree of mono-ozonolysis. For run 7 and 8 it was found *ca.* 0.20 moles of maleic acid per mole of reacted quinone, the calculated amount of mono-ozonolysis products being *ca.* 0.6 mole. This large difference must have significance and is most likely due to the inability of some mono-ozonolysis products to form maleic acid on oxidation with hydrogen peroxide. It must be remarked, however, that maleic acid is not entirely stable towards hydrogen peroxide under the prevailing conditions and the obtained results are therefore probably rather low.

In the later runs we always kept the ratio between ozone and quinone close to 0.80. The aqueous decomposition solution had an acidic reaction, gave a precipitate with 2,4-dinitrophenylhydrazine and reduced Tollens reagent. Oxalic and maleic acids could not be detected. Formic acid was produced in an amount of 0.78 moles per mole of reacted quinone. Some fractionation of the carbonyl compounds could be achieved by means of a weakly basic ion-exchange column. Neutral components were eluted with water and acidic components with 5% aqueous formic acid.

The neutral eluate contained glyoxal as identified through its *p*-nitrophenylhydrazone. Mesoxalic dialdehyde was not present in detectable amounts.

From the acidic eluate was precipitated a complex mixture of dinitrophenylhydrazones. This could be separated into three fractions: Glyoxylic acid dinitrophenylhydrazone (from one run only), some red crystals (DNP I) and yellowish crystals (DNP II). The infra-red solid-state spectra of DNP I and II were very similar differing mainly in the relative intensities of some bands. Absorptions at 1 720 cm⁻¹ and 1 425

cm⁻¹ probably represent a free carboxyl group while the presence of an unreacted carbonyl group seems less probable but cannot be entirely excluded. In composition, however, the two derivatives differ somewhat and none of them corresponds very closely to a rational formula. Closest comes DNP II to the formula C₁₇H₁₃N₂O₁₀ which could represent a bis-dinitrophenylhydrazone of a conceivable mono-ozonolysis product CHO—CH=CH—CO—COOH. Our only possible conclusion for the present is therefore that in the acidic eluate there are carbonyl compounds resulting from mono-ozonolysis and of a rather complicated nature.

Experimental. Ozonisation procedure. The ozonisation apparatus was essentially that of Pummerer and Richtzenhain³ with only minor modifications. The reaction column proper was 60 by 2 cm and filled with Fenske helices. Surrounding this was a cooling mantle, during the runs filled with ice. *p*-Benzoquinone in chloroform was trickled down the reactor while ozone was let in at the bottom. After ozonisation the reaction mixture passed into a flask containing continuously agitated water. A liquid seal prevented ozone from entering the decomposition vessel. After completion of the ozonisation the apparatus was rinsed briefly with chloroform.

Ozone in the oxygen from the ozone generator and in the effluent gases from the counter-current reactor was determined by absorption in neutral potassium iodide and titration with standard thiosulphate after acidification.

In all the experiments the rate of flow of ozonised oxygen was kept constant at 20 l/h which gave 1.68 g O₃/h. Variations in experimental procedure was therefore effected through varying the concentration of *p*-benzoquinone in chloroform and the flow of this solution.

After ozonisation and decomposition the liquid layers were separated and the chloroform phase exhaustively extracted with water. Some unreacted *p*-benzoquinone went into the water and the combined aqueous extracts were therefore extracted with a small amount fresh chloroform. The unreacted quinone was determined iodometrically in the combined chloroform solutions.

Maleic acid. The aqueous decomposition solution was evaporated to a small volume and barium chloride added. In none of the runs thus investigated any barium maleinate separated. Due to a slight solubility of this salt a minor amount of maleic acid may have escaped detection.

Decomposition solutions from runs 7 and 8 were mixed with 3 ml 30 % hydrogen peroxide and evaporated to dryness on a water-bath. The residues consisted of white, somewhat sticky crystals which were identified as maleic acid. In the runs 0.935 g and 1.153 g *p*-benzoquinone reacted with ozone and gave 199 mg and 228 mg maleic acid, respectively. Controls by precipitating the dissolved residues with barium chloride were satisfactory.

Formic acid. Aliquots of the decomposition solutions were distilled *in vacuo* to dryness. The distillate was taken up in standard sodium hydroxide and backtitrated with hydrochloric acid. The capillary was connected to a sodium hydroxide-asbestos tube to prevent the entrance of carbon dioxide. Substituting the air in the distilling apparatus with nitrogen did not alter the titration values significantly.

Ion-exchange chromatography. The decomposition solution was passed through a column of De-acidite G and washed with water. The neutral washings which reduced ammoniacal silver solution were combined and precipitated with *p*-nitrophenylhydrazine. This precipitate was extracted with glacial acetic acid and recrystallised from nitrobenzene m. p. ca. 270° (decomp.). Through its infra-red spectrum it was identified as glyoxal *p*-nitrophenylosazone. Further elution was performed with 5 % formic acid when more aldehydic material appeared. The acidic eluate was precipitated with 2,4-dinitrophenylhydrazine and the material extracted with boiling water. In one case there separated yellow needles from the aqueous extracts, m. p. 190°, identified as glyoxylic acid dinitrophenylhydrazone. The residue from the extraction was partially soluble in hot glacial acetic acid. From the acetic acid separated red crystals, m. p. 226° (decomp.). (Found: C 43.9; H 3.2; N 20.6.) The insoluble part was recrystallised from nitrobenzene. Yellowish crystals, m. p. 255° (decomp.). (Found: C 41.6; H 2.7; N 22.4. Calc. for C₁₇H₁₂N₈O₁₀: C 41.8; H 2.5; N 22.9.)

1. Bernatek, E. *Acta Chem. Scand.* **8** (1954) 1943.
2. Bernatek, E. and Straumsgård, K. A. *Acta Chem. Scand.* **13** (1959) 178.
3. Pummerer, R. and Richtzenhain, H. *Ann.* **529** (1937) 50.

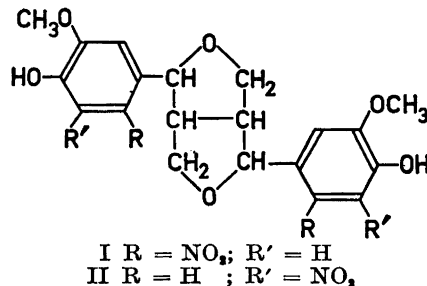
Received December 12, 1959.

The Structure of Dinitropinoresinol

JARL GRIPENBERG and INGEGERD PETRELL

Department of Chemistry, Finland Institute of Technology, Helsingfors, Finland

Some years ago the preparation of dinitropinoresinol was reported¹. Its structure was not determined, but it was assumed to be I in analogy with dinitropinoresinol dimethylether. Dinitropinoresinol gives, however, upon treatment with nitric acid 4,6-dinitroguaiacol, m. p. 122°, and must therefore have structure II



The aim of the earlier work¹ was the degradation of the aromatic rings of pinoresinol to carboxylic groups. We have now attempted to achieve this by ozonolysis (*cf.* Ref.²), but the desired acid could not be obtained. The only products that could be identified were oxalic acid and in some experiments where the reaction time was kept very short, maleic acid.

In connection with this work we had to prepare relatively large amounts of pinoresinol and we found that when the crude pinoresinol from the potassium salt³ was treated with dioxan it immediately crystallised. The crystals contain 1 molecule of dioxan, which can readily be removed by heating under vacuum on a boiling water bath. This method of purification is more convenient than the customary one *via* the acetate³.

1. Gripenberg, J. and Lindahl, B. *Acta Chem. Scand.* **6** (1952) 1147.
2. Carnmalm, B. *Acta Chem. Scand.* **10** (1956) 477.
3. Erdtman, H. *Svensk Kem. Tidskr.* **46** (1934) 229.

Received January 18, 1960.

Acta Chem. Scand. **14** (1960) No. 1