Anomalous Ozonolysis in 2,3-Disubstituted Naphthoquinones

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In continuation of the studies on the ozonolysis of naphthoquinones [1-3] and to test the hypothesis regarding substituent influence on the direction of anomalous ozonolysis, we have ozonised the following disubstituted naphthoquinones:

I 2-Chloro-3-methyl-1,4-naphthoquinone
II 2-Hydroxy-3-methyl-1,4-naphthoquinone
III 2-Amino-3-chloro-1,4-naphthoquinone

Anomalous ozonolysis of quinone I was found to give the expected reaction products, methylphenylglyoxal-*o*-carboxylic acid and phthalonic acid, in 65 and 33 % yield, respectively. Quinone II gave the same reaction products in 67 and 32 % yields. Finally quinone III yielded 95 % phthalonic acid semiamide. These results correspond to the formation of zwitterion:

In I 33 % at carbon atom 3, 65 % at carbon atom 2
In II 32 % at carbon atom 3, 67 % at carbon atom 2
In III at least 95 % at carbon atom 3

To evaluate the probable Δ_i-values for the three quinones, in order to employ the Hammett type relationship

$$\log (x_i/x_0) = \varrho\Delta_i$$

it is necessary to consider the steric conditions of the molecules. By the aid of the Courtaulds molecular models, different conformations of the quinones have been regarded. The ones which have been chosen for our calculations are those which seem to be sterically most favourable and which give the best fit to the experimental values. This leads to structures where the quinone ring no longer is coplanar.

Quinone I: The best conformation has the carbonyl oxygen farthest from the chlorine atom out of plane. Using the σ values from our previous work [1] we obtain $\Delta_2 = 0.170$, and by taking $\varrho = 0.693$, this corresponds to the formation of zwitterion at carbon atom 3 in amount of 65 % (experimental: 65 %).

Quinone II: A hydrogen bonding exists between the hydroxyl and the neighbouring carbonyl group. A favourable conformation occurs when the molecule is twisted somewhat and in such a way that the chelate ring as well as the opposite carbonyl oxygen and the methyl group are out of plane. In this case the value $\Delta_2 = 0.190$ is obtained, from which is calculated 68 % formation of zwitterion at carbon atom 3 (experimental 67 %).

Quinone III: In this quinone there are some difficulties in deciding which conformation is the most favourable. A slightly twisted molecule analogous to II seems to be a good choice. In that case we have $\Delta_3 = 0.534$ corresponding to an exclusive formation of zwitterion at carbon atom 3 (experimental 95 % or more).

As a conclusion it may be said that the ozonisation of 2,3-disubstituted naphthoquinones seems to support the validity of using "net substituent constants" (Δ_i) and inserting these in a Hammett type equation.

Experimental. Materials. 2-Chloro-3-methyl-1,4-naphthoquinone was prepared according to Willstaedt [4] from 2-methylnaphthoquinone by epoxidation and treatment with hydrogen chloride. A modification of the method where the dry epoxide was dissolved in glacial acetic acid and treated with hydrogen chloride raised the yield from 20 to 40 %. Recryst. from ethanol, m.p. 144°.

2-Hydroxy-3-methyl-1, 4-naphtoquinone was prepared according to Fieser [5] by hydrolysing the abovementioned epoxide with dilute sulphuric acid. Recryst. from methanol, m.p. 173.5°.

2-Amino-3-chloro-1,4-naphthoquinone was prepared according to Ullmann [6] by treating 2,3-dichloronaphthoquinone with dry ammonia in boiling nitrobenzene. Recryst. from glacial acetic acid, m.p. 193°.

Ozonisation procedure. As solvent was employed dry, alcohol-free chloroform. The ozone generator yielded ca. 2 g O_3/h at an oxygen flow of 30 l/h. Usually 2 g of substance was dissolved in 25 ml of the solvent and ozonised at 0° with one molecule of ozone. At that point the yellow colour of the quinone had disappeared. The absorption of ozone was nearly quantitative. The reaction mixture was stirred with a large excess of water (250 ml) until the

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active oxygen had disappeared. Isolation of products as well as quantitative determinations were carried out separately for the two phases.

2-Chloro-3-methyl-1,4-naphthoquinone. From the chloroform phase was isolated methylphenylglyoxal-*o*-carboxylic acid, m.p. 65°C (benzene-petrol ether). Quinoxaline derivative with *o*-phenylenediamine, m.p. 182.5° alone and mixed with an authentic sample. Equiv. wt. 279, calc. 282. From the aqueous phase was isolated phthalonic acid, m.p. 146°C (ether), undepressed in mixture with an authentic sample. Equiv. wt. 96, calc. 97. Further was identified acetic acid (S-benzylisothiuronium acetate, m.p. and mixed m.p. 139°C) and chloride ions.

Quantitative determinations. Methylphenylglyoxal-*o*-carboxylic acid occurred almost quantitatively in the chloroform phase, accompanied by 0.5 % or less phthalonic acid. The chloroform was evaporated and the residue dissolved in water. Aliquots were titrated with 0.05 N NaOH (phenolphthalein). Found, as a mean of four ozonolyses, 64.5 % of theoretical. The aqueous phase was distilled with additions of several portions of water until no more volatile acid passed over. Aliquots of the residue, containing phthalonic acid only, were titrated with 0.05 N NaOH (phenolphthalein). Found, as a mean of three ozonolyses, 32.7 % of theoretical.

Total acid in the distillate (acetic and hydrochloric) was titrated with 0.05 N NaOH. Hydrochloric acid was determined separately as AgCl. Found acetic acid, as a mean of three ozonolyses, 34.5 % of theoretical.

The ratio of phthalonic to acetic acid is thus 0.95, and close to the theoretical ratio of 1.00. Recovered carbon is 98 %.

2-Hydroxy-3-methyl-1,4-naphthoquinone. From the chloroform phase was isolated and determined methylphenylglyoxal-*o*-carboxylic acid as above. Found, as a mean of three ozonolyses, 67.1 % of theoretical. The aqueous phase was also treated and analysed as above. Found phthalonic acid, as a mean of three ozonolyses, 32 % of theoretical. Found acetic acid, as a mean of three ozonolyses, 34.2 % of theoretical.

The ratio of phthalonic to acetic acid is 0.93. Recovered carbon is 98 %.

2-Amino-3-chloro-1,4-naphthoquinone. The chloroform phase contained only very small amounts of organic matter. The aqueous phase was concentrated to a small volume and a white substance separated. Recrystallised at low temperature from strong hydrochloric acid, m.p. 134–36°C (decomp.) undepressed in mixture with an authentic sample of phthalonic acid semiamide. Infra-red spectra of the product and authentic compound coincided completely. The semiamide could be titrated as a monobasic acid in the residue of the aqueous phase after removing the volatile acids. Found, as a mean of three ozonolyses, 95.0 % of theoretical.

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Note on the Crystal Structure of NH_4CuSO_3

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The crystal structure of ammonium copper(I) sulphite has been determined from three-dimensional X-ray data obtained with Cu$K\alpha$ radiation for a single-crystal selected from a sample prepared according to Ramberg.[1] The structure was derived from Patterson and Fourier syntheses. The parameters of the nonhydrogen atoms were refined using least squares techniques with isotropic temperature factors.

The following data were obtained for the trigonal structure:

Unit cell dimensions (from a Guinier powder photograph taken with Cu$K\alpha_1$ radiation): $a = 5.4287 \pm 0.0004$ Å, $c = 23.166 \pm 0.004$ Å.