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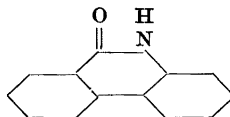
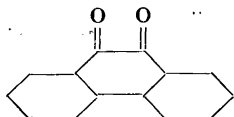
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The Stoichiometry of the Reaction between Hydrazoic Acid and Phenanthrenequinone

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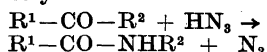
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Caronna¹ states that phenanthrenequinone and retenequinone dissolved in concentrated sulphuric acid reacts with hydrazoic acid to give phenanthridone and 1-methyl-7-*iso*-propyl-phenanthridone respectively.



The initial stage of this reaction is possibly the same as in the Schmidt reaction in which compounds containing a carbonyl group react with hydrazoic acid in the presence of strong Lewis acids to give amides. (For a review of the Schmidt reaction see H. Wolff².) The sequence of reactions following the initial stage of the reaction considered here must, however, be different from that of the Schmidt reaction as the overall reaction in the former case is the substitution of a NH group for a CO group, whereas in the latter an amide is formed by interposing a NH group between the CO group and a group attached to it. Accordingly the stoichiometry of the two reactions appears to be entirely different.

The Schmidt reaction has the following stoichiometry



as side reactions are probably responsible for the small production of ammonia

observed. In the reaction studied by us we observed formation of ammonia to a considerably greater extent, and we interpret this as a property in the stoichiometry.

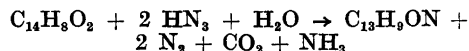
The stoichiometrical proportions were determined in the following way: The reaction was carried out with dilute solutions (0.1 M) of phenanthrenequinone and hydrazoic acid in concentrated sulphuric acid. After some hours the reaction mixture was diluted with water, the residual hydrazoic acid distilled off in a Kjeldahl-apparatus and titrated with 0.1 N ceric sulphate³. The liquid was made alkaline and the ammonia was distilled off and titrated in the usual way.

The molar ratio between converted hydrazoic acid and the ammonia formed is calculated, and, when hydrazoic acid is present in excess, the molar ratio between converted hydrazoic acid and converted phenanthrenequinone can be calculated as well.

We found	Mean value	Standard deviation
Hydrazoic acid : Ammonia	1.95	0.06
Hydrazoic acid : Phenanthrenequinone	2.18	0.17

These ratios are independent of the ratio between the initial concentrations of hydrazoic acid and phenanthrenequinone within the range examined (0.5–6.0 for $\text{HN}_3 : \text{NH}_3$; 2.0–6.0 for $\text{HN}_3 : \text{C}_{14}\text{H}_8\text{O}_2$).

The gas evolved from the sulphuric acid solution was analysed and found to be pure nitrogen. Only after the addition of water an evolution of carbon dioxide took place. This suggests the following stoichiometry for the overall reaction:



When ice is added together with water to dilute the reaction mixture a black tarry intermediate product is often observed, which within a certain time decomposes, forming the white phenanthridone. The same stoichiometry is found when the reaction is carried out with retenequinone instead of phenanthrenequinone. We have prepared 1-methyl-7-*iso*-propylphenanthridone as follows:

20 g of retenequinone is dissolved in 200 ml of concentrated sulphuric acid. To the dark green solution is added 15 g of sodium azide in small portions over a period of 10 minutes during which the temperature rises to 70–80°. The reaction mixture is diluted with 800 ml of water, and the solution is kept at 60–70° for one hour. The phenanthridone is filtered off by suction and is dried at 100°. The product formed has a m.p. of 200–205°, and the yield is almost quantitative. After one recrystallisation with charcoal from 500 ml of benzene a product melting at 220° (corrected) is obtained in a yield of about 60 %.

The investigation of the reaction is being continued.

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Liquefaction of Endolymph from Sharks by Hyaluronidase

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On account of the great similarity between vitreous humor from the eye and the endolymph of the inner ear

we have investigated whether the latter like the former might contain hyaluronic acid. We have made the following experiments on the endolymph from about twenty sharks (*Ascanthias vulgaris*).

One ml of the endolymph was incubated with a trace of testicular hyaluronidase (Schering) at room temperature for 72 hours. After some hours the jelly began to liquify. After 72 hours the viscosity of the fluid which prior to the addition of enzyme was very high, was close to that of water. This experiment was repeated with the same result. In a further trial endolymph liquified within 4 hours. A sample without enzyme did not change its consistence within the same time.

As the enzyme is known to be highly specific^{1,2,3} this result proves that the endolymph contains hyaluronic acid or at least a substance closely related to that acid.

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