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Nitramines as Nitrating Agents

by

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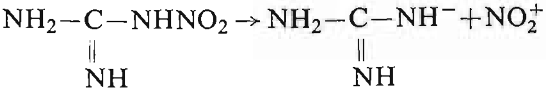
Davis and Abrams [1] have reported that some aromatic compounds readily undergoing nitration (phenol, acetanilide, etc.) can be nitrated by a freshly prepared solution of nitroguanidine in sulphuric acid. According to these authors nitroguanidine decomposes in the presence of sulphuric acid to give nitramine which is hydrolyzed, in the presence of substances convertible to nitro-compounds, to ammonia and nitric acid.

One of the authors (T.U.) of the present paper has advanced the hypothesis [2]—[4] that nitronium ion is liberated from nitroguanidine under the influence of sulphuric acid, and hence the solution possesses nitrating properties:



$$NH_2-\underset{\underset{NH}{\|}}{C}-NHNO_2 \rightarrow NH_2-\underset{\underset{NH}{\|}}{C}-NH^- + NO_2^+$$

The decomposition of cyclonite in sulphuric acid seems also to follow the same pattern. Šimeček [5] has suggested the formation of the nitronium ion in addition to N_2O:

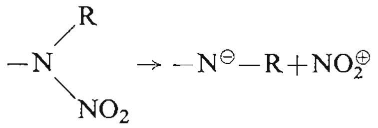
$$C_3H_3O_6N_6 + 2nH^{\oplus} \rightarrow 3CH_2O + (3\text{-}n)\,N_2O + nNO_2^+ + NH_4^+$$

This is in contradiction with the earlier equation of Vernazza [6] who suggested only the formation of H_2O.

The present paper reports the results of experiments which confirm the hypothesis of NO_2^+ formation when nitramines are dissolved in concentrated sulphuric acid.

Anthraquinone dissolved in concentrated sulphuric acid ($d = 1.84$) was treated with an excess of nitroguanidine, nitrourea or dimethyldinitrooxamide and the solution was kept at room temperature or heated to 110—120°. Under these experimental conditions anthraquinone could not be sulphonated and yielded 1,5-dinitroanthraquinone in a yield up to 77 per cent. Cyclonite gave the same product, but the yield was lower (~34%).

It seems that the reaction is of a general character and occurs with both primary and secondary nitramines and nitramides, presumably according to the diagram:



$$-N\begin{matrix}\diagup R\\ \\ \diagdown NO_2\end{matrix} \rightarrow -N^{\ominus}-R+NO_2^{\oplus}$$

where R = H or alkyl or a part of a heterocyclic ring.

When the solution of anthraquinone in sulphuric acid is heated with an excess of nitramine to a higher temperature (150—200°) until it turns red and is then poured into cold water, a magenta-coloured product precipitates. This is due to the known transformation of 1,5-dinitroanthraquinone into blue-coloured substances on heating with concentrated sulphuric acid [7], [8].

This colour reaction can be used for qualitative detection of nitramines or NO_2^+ ions and in general of substances which under the action of sulphuric acid can split off the nitronium ion.

Experimental

Nitration of anthraquinone with nitrourea

Anthraquinone (4.15 g.; 0.02 mole) was dissolved in 20 ml. concentrated sulphuric acid (*d* = 1.84; 36.8 g.) and nitrourea (4.2 g., 0.04 mole) was added portionwise at room temperature. Nitrogen dioxide fumes evolved and a small quantity of yellow precipitate appeared.

The reaction mixture was processed in two ways: (A) and (B).

(A) The solution was left for 24 hrs. at room temperature. The yellow precipitate of 1,5-dinitroanthraquinone was collected (yield 3.6 g., 60% of theoretical), washed with concentrated sulphuric acid and methanol, crystallized from nitromethane and found to be identical with a standard sample prepared according to the literature [9].

Analysis: Calc. for $C_{14}H_6O_6N_2$: N, 9.4. Found: N, 9.1%.

The filtrate was poured into water and a magenta-coloured precipitate was collected. It was extracted with hot methanol. The insoluble residue (0.2 g.) was unconverted anthraquinone.

(B) The solution was heated for 1 hr at 110—120°C. After cooling, the yellow product (1,5-dinitroanthraquinone) was collected and washed with concentrated sulphuric acid and methanol. Yield 4.0 g. (67%).

The filtrate was poured into water. Traces of anthraquinone were precipitated.

Nitration of anthraquinone with nitroguanidine

Anthraquinone was dissolved in sulphuric acid as before and nitroguanidine (4.2 g., 0.04 mole) was added portionwise at room temperature. Fumes of nitrogen dioxide evolved but no precipitate was formed at this stage of the reaction.

The solution was processed in two ways: (A) and (B).

(A) The solution was left for 24 hrs. and 1,5-dinitroanthraquinone was collected and washed as before. Yield: 2.4 g. (40%). Unchanged anthraquinone (1.2 g., 30%) was isolated from the filtrate (as above).

(B) The solution was heated at 110—120° for 1 hr. and after cooling 1,5-dinitroanthraquinone was collected and washed as above. Yield: 4.0 g. (67%). The filtrate contained only traces of anthraquinone.

Nitration of anthraquinone with dimethyldinitrooxamide

To a solution of anthraquinone (as above), dimethyldinitrooxamide (4.1 g., 0.02 mole) was added. Fumes of nitrogen dioxide evolved. The reaction mixture was left for 24 hrs at room temperature and 1,5-dinitroanthraquinone was collected and washed as above. Yield: 4.6 g. (77%).

Nitration of anthraquinone with cyclonite

To a solution of anthraquinone (as above), cyclonite (6.0 g., 0.027 mole) was added portionwise, Fumes of nitrogen dioxide evolved. The reaction is strongly exothermic and efficient cooling is necessary to maintain room temperature.

The solution was processed in two ways: (A) and (B).

(A) The precipitated 1,5-dinitroanthraquinone was collected after keeping the solution 24 hrs at room temperature. It was washed as above. The yield was 2.05 g. (36%). The unconverted anthraquinone was isolated from the filtrate (1.4 g., 34%).

If the quantity of cyclonite used for the reaction was smaller (3.0 g., 0.0135 mole), the yield of 1,5-dinitroanthraquinone was much lower, 0.7 g. (12%), and the quantity of unconverted anthraquinone was 2.8 g. (68%).

(B) The solution was warmed at 100° for 1 hr. A strong evolution of formaldehyde was noted, and only traces of 1,5-dinitroanthraquinone were obtained. Unconverted anthraquinone was collected, 2.3 g. (55%).

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