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CHEMISTRY

On the Preparation of Hydroxylamine Sulphate from 1,2-Dinitroethane

by

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It is well known that primary nitroparaffins can isomerise to hydroxamic acids [1]—[5] and the latter can be subjected to further hydrolysis to hydroxylamine [5].

1,2-dinitroethane can be used as a primary nitroparaffin, readily available by preparation from ethylene and nitrogen dioxide [6]—[9]. Thus, Levy, Scaife and Wilder Smith [9] suggested hydrolysing small portions (0.30 g.) of 1,2-dinitroethane with hydrochloric acid at 150°C. for 13 minutes in a sealed tube. The yield was 90.8 per cent.

The authors of the present paper have, however, found that hydrolysis of slightly larger quantities of 1,2-dinitroethane (e. g., 2 g.) by this method is difficult; hydrolysis under pressure is often accompanied by decomposition, which can take a violent course.

It has now been found that hydrolysis of 1,2-dinitroethane with conc. sulphuric acid (molar ratio 1:2) is safer, since it does not require a temperature higher than 100° and can be carried out in an open vessel. The hydrolysis occurred almost immediately after portions of 1,2-dinitroethane were added to sulphuric acid warmed to 100° and stirred.

After the reaction mixture was cooled below room temperature, hydroxylamine sulphate in pure form was precipitated by adding ethyl alcohol.

A lower concentration of sulphuric acid reduced the yield of hydroxylamine and required a higher temperature (e. g., 120°) and a longer reaction-time.

The method seems to be more economic than the classical method of preparing hydroxylamine salts from sodium nitrite and sodium hydrogen sulphite. The cost of raw materials in the new method is c. 85 per cent of the costs in the classic method.

An application for the patent has been filed at the Polish Patent Office [10].

Experimental

2 g. of 1,2-dinitroethane (DNE) were added by small portions to 3.5 g. of conc. sulphuric acid (98 per cent) previously heated to 100°C. and stirred. The reaction was very vigorous with gas evolution produced by decomposition of oxalic acid formed during the reaction.

The reaction mixture was cooled below room temperature (5—10°C.) and 8—10 ml. of ethyl alcohol were added. A precipitate of hydroxylamine sulphate was filtered off, washed with alcohol and ether. The yield was 2.13 g. (79 per cent of theoretical).

A lower yield was obtained, when concentration of sulphuric acid was below 98 per cent. The rate of hydrolysis was also much lower, and it was necessary to raise the temperature of the reaction.

The comparative figures are shown in the Table.

TABLE

Concentration of sulphuric acid (% H_2SO_4)	98	85	85
Temperature (°C.)	100	100	120
Time (minutes)	2—3	180	15
Yield g. (from 2 g. DNE)	2.13	2.0	2.0
(per cent)	79	75	75

When 75% sulphuric acid was used, the yield dropped to 67%, at 65% — to 63% and at 55% — to 59%. Lower concentrations of sulphuric acid (e. g., 45%) did not allow hydroxylamine sulphate to be isolated by adding alcohol to the reaction mixture.

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REFERENCES

[1] E. Bamberger, E. Brüst, Chem. Ber., **35** (1902), 45.
[2] C. D. Nenitzescu, D. A. Isacescu Bull. Soc. Chim. Roumanie, **14** (1932), 53.
[3] T. Urbański, J. Chem. Soc. (1949), 3374.
[4] T. Urbański, W. Gurzyńska, Rocz. Chem., **25** (1951), 213.
[5] S. B. Lippincott, H. B. Hass, Ind. Eng. Chem., **31** (1939), 118.
[6] Semenoff, Z. Chem. Pharm., **7** (1864), 129; Jahresber. (1864), 480.
[7] N. Y. Demianov, Thesis (in Russian), Moscow, 1899.
[8] N. Y. Demianov, K. Sidorenko, J. Russ. Chem. Soc., **41** (1909), 832 (in Russian).
[9] N. Levy, Ch. W. Scaife, A. E. Wilder Smith, J. Chem. Soc. (1946), 1096.
[10] T. Urbański, T. Dobosz, Polish Patent application, No. P 83,479 (1956).