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On Nitration of Cellulose with Nitryl Chloride

by

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It was found by Steinkopf and Kühner [1], that so-called nitryl chloride (NO_2Cl) is an agent nitrating and chlorinating aromatic hydrocarbons. This was confirmed in a more recent work by Collis et al. [2].

On the other hand, Preis and Sears [3] found only the nitrating action on aromatic hydrocarbons of nitryl chloride.

The authors of the present paper examined the action of nitryl chloride upon cellulose. It was believed that nitryl chloride might yield cellulose nitrate of higher stability than that produced by the ordinary nitrating mixture composed of nitric and sulphuric acids. It is well known, that the presence of the latter in nitrating mixtures leads to the formation of mixed esters of nitric and sulphuric acids. These esters are not readily hydrolised during the usual process of stabilisation. It is also known that nitration with nitric acid alone cannot furnish a uniformly nitrated product, as, during nitration, swelling of cellulose fibres occurs.

It was also believed, that hydrogen chloride evolved during nitration of cellulose with nitryl chloride might produce a beneficial effect by hydrolysing unstable by-products.

Nitration of cellulose with nitryl chloride was carried out in the following ways:

(A) in gas-phase, by passing gaseous NO_2Cl through a layer of cellulose;

(B) with liquid NO_2Cl;

(C) with solution of NO_2Cl in solvents, such as carbon disulphide, chloroform, carbon tetrachloride.

All products were stabilised by boiling with water in a conventional way.

Only method (A) gave a satisfactory product. We found it necessary to draw gaseous NO_2Cl very slowly through cellulose, because quick action of a larger quantity of nitryl chloride produced swelling and even gelation of nitrocellulose formed in the course of reaction. However, we did not succeed in obtaining a nitrogen content higher than 12.2% N, even upon prolonged nitration. The product was compared with a standard nitrocellulose having the same nitrogen content, prepared in a conventional way with a mixture of nitric and sulphuric acids. The product prepared by method (A) was found to have a higher stability. The product does not contain any chlorine.

It was established that, at 132°, denitration of nitrocellulose prepared in a conventional way is faster than that of nitrocellulose prepared with NO_2Cl. Also the acidity of the latter, when warmed at 132°, is lower.

Method (B) yielded only a product of low nitrogen content and of very low stability. When method (C) was used, the nitrogen content was also found to be low (of the order of 9.5—10.0% N).

Experimental

Nitryl chloride. Nitryl chloride was prepared according to Dachlauer [4] by acting with chlorosulphonic acid on a mixture of nitric acid and 30% oleum at 0°. Nitryl chloride was purified by passing it through sulphuric acid, and collected in a container frozen with a mixture of solid carbon dioxide and acetone.

Nitration of cellulose in gas-phase. 10 g. of dried, finely divided cotton linters were placed in a glass tube, and a slow stream of NO_2Cl was passed through the cotton for 4 hours at 20°C. (temperature inside the tube).

The nitration product was immersed in a large volume of cold tap water, thoroughly mixed, filtered, and washed with cold water, until the washing water was no longer acid to Congo red.

After that, nitrocellulose was boiled in tap water four times. Each boiling lasted two hours and was followed by a change of water.

After the final washing, nitrocellulose was dried at 50°C. The yield was 16.8 g.

Analysis: 12.2% N (in nitrometer), no chlorine present. Heat test at 80°C.: no change of colour of potassium iodidestarch paper was observed during 60 min. The product was completely soluble in acetone.

We shall later refer to this nitrocellulose as NCn.

Nitration of cellulose in nitrating mixture. 10 g. of dried, finely divided cotton linters were gradually introduced into 1000 g. of mixture composed of 22.4% NHO_3, 60.8% H_2SO_4, 16.8% H_2O at 20°C. After 20 min. the product was filtered, washed with water, and stabilised as previously described for nitrocellulose prepared with gaseous NO_2Cl.

We shall later refer to this nitrocellulose as NCs.

Comparative examination of stability of NCn and NCs. Chemical stability of nitrocellulose warmed in Bergmann-Junk tubes at 132°C. was examined in the following two ways:

(1) by determining denitration of the product kept at this temperature for various lengths of time, up to 2 hours;

(2) by determining *pH* of the aqueous extracts from the samples warmed as in (1).

The results are tabulated in Table I.

TABLE 1

Time, in hours, of warming at 132°C.	Nitrogen content % N		*pH* of aqueous extract	
	NCn	NCs	NCn	NCs
0	12.20	12.20	—	—
½	12.15	12.00	4.12	3.94
1	12.09	11.92	3.88	3.73
1½	12.04	11.85	3.77	3.60
2	12.00	11.80	3.70	3.53

Nitration of cellulose with NO_2Cl dissolved in chloroform. 10 g. of cotton linters were suspended and stirred in 100 g. of chloroform. NO_2Cl was drawn through the suspension during 4 hours at a constant temperature of 20°C. Next, nitrocellulose was filtered and treated as previously described.

Analysis: 10.0% N (in nitrometer), no chlorine was present. Heat test at 80°C.: change of colour of potassium iodidestarch paper after 25 min.

Nitration of cellulose with NO_2Cl dissolved in carbon tetrachloride or carbon disulphide. Nitration was carried out in the same way as for chloroform.

The product in CCl_4 and in CS_2 contained 9.5% and 9.7% N, respectively.

Further experiments, including viscosity measurements, will be carried out later.

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