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SOME REMARKS ON THE THEORY OF NITRATION

T. URBAŃSKI and J. HACKEL
Department of Organic Technology, Institute of Technology, Warsaw, Poland

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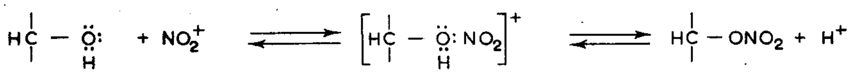
Abstract—Experiments on formation of nitric esters of starch ("O-nitration" of starch) led to the conclusion, that nitration occurs not necessarily by means of NO_2^+ ions, but NO_3^- ions and/or undissociated nitric acid are nitrating agents.

Nitrating mixtures rich in nitric acid may yield products of higher nitrogen content owing to the fact that the reaction occurs in one phase system.

THE excellent review by Gillespie and Millen[1] which was partly based on the extensive work of Ingold and his school published later[2] gave a first summary of the present state of our knowledge on the nature of nitration agents and particularly on the role of nitronium ion in aromatic nitration

So far not very much attention had been paid to the role of nitronium ion in the nitration of hydroxyl compounds, i.e. in the formation of O-nitro compounds. The only note is by Israelashvili[3] and in it he suggested that the formation of the nitrates is due to an attack of the nitronium ion on a lone electron pair of the hydroxyl oxygen followed by elimination of a proton from the transient intermediate product:



$$\mathrm{HC{-}}\underset{\mathrm{H}}{\ddot{\mathrm{O}}}{:} + \mathrm{NO_2^+} \rightleftharpoons \left[\mathrm{HC{-}}\underset{\mathrm{H}}{\ddot{\mathrm{O}}}{:}\mathrm{NO_2}\right]^+ \rightleftharpoons \mathrm{HC{-}ONO_2} + \mathrm{H^+}$$

However, according to Miles[4] it is not necessary to assume that NO_2^+ ion plays any part in the esterification of cellulose and there are two very strong reasons to believe that in the greater part of the cellulose "nitration field" it cannot have any effect.

According to Miles one of the proofs is the fact that nitration can take place in the vapour of nitric acid at very low pressure when no liquid can be present and the formation of NO_2^+ or any other ion is most improbable.

Another one is the possible nitration of cellulose by means of dilute nitration mixtures which do not contain spectroscopically detectable NO_2^+.[5]

Again according to Miles the modern work elaborates and confirms an old idea of Sapozhnikov[6] that the nitrating action of mixtures of nitric acid, sulphuric acid and water upon cellulose is related to the partial vapour-pressure of HNO_3 in the mixtures.

This theory was based on the similarity of the curves of constant nitrogen content of nitrocellulose and of constant vapour-pressure of HNO_3.

Sapozhnikov's work on the nitration of cellulose and on vapour-pressure was later repeated and confirmed by a number of authors.[7,8,9],

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[1] R. J. Gillespie and D. J. Millen *Quart. Rev. Chem. Soc. Lond.* **2,** 277 (1948).

[2] C. K. Ingold *et al. J. Chem. Soc.* 2400–2678 (1950).

[3] Sh. Israelashvili *Nature, Lond.* **165,** 686 (1950).

[4] F. D. Miles *Cellulose Nitrate* p. 87. Oliver and Boyd, London–Edinburgh (1955).

[5] J. Chédin *Mém. Serv. Chim. de l'État* **31,** 113 (1944).

[6] A. Sapozhnikov *Z. phys. Chem.* **49,** 697 (1904); *Ibid.* **51,** 609 (1905); *Ibid.* **53,** 225 (1905); *Z. Ges. Schiess–U. Sprengstoffw.* **1,** 453 (1906); *Ibid.* **4,** 441 (1909).

[7] E. Berl and E. Berkenfeldt *Angew. Chem.* **41,** 130 (1928).

[8] F. G. Miles and M. Milbourn *J. Phys. Chem.* **34,** 2598 (1930).

[9] R. Vandoni *Mém. Serv. Chim. de l'État* **31,** 87 (1944).

O-NITRATION OF STARCH*

The authors of the present paper carried out a number of experiments on O-nitration of starch and partly published their results between 1932 and 1939.[10]

The action of over 100 nitration mixtures of nitric acid, sulphuric acid and water was examined. The compositions varied within the ranges:

15–100 per cent HNO_3
0–75 per cent H_2SO_4
0–75 per cent H_2O

and the weight to weight ratio of starch to nitration mixture was 50. The temperature during the reaction was 10–12°C and the time 1 hr.

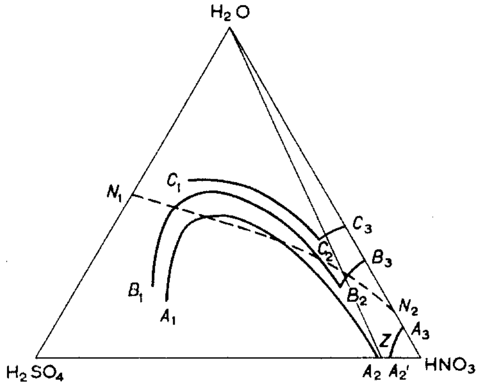

Fig. 1

The degree of O-nitration produced in our experiments is represented on the triangular diagram (Fig. 1), where the composition of the mixtures is expressed in molar percentages. The curves are formed by joining points corresponding to the composition of nitration mixtures yielding products of the same degree of nitration (constant nitrogen lines).

Thus, all nitrating agents with compositions lying on the curves A_1A_2 and $A_2'A_3$ give starch nitrates (which we shall call "nitrostarch") containing 12·75 per cent N. All mixtures lying between curve A_1A_2 and the baseline and between curve A'_2A_3 and the baseline give products with more than 12·75 per cent N.

The curves $B_1B_2B_3$ and $C_1C_2C_3$ correspond to nitration to 11·11 per cent and 9·15 per cent respectively. Mixtures with compositions between the curves A_1A_2–$A_2'A_3$ and $B_1B_2B_3$ give starch nitrates of nitrogen content between 12·75 and 11·11 per cent. Mixtures with compositions between $B_1B_2B_3$ and $C_1C_2C_3$ yield products with between 11·11 and 9·15 per cent N.

DISCUSSION

The curves A_1A_2, B_1B_2 and C_1C_2 are remarkably similar in shape to those given by Sapozhnikov[6] and others[7,8] for the nitration of cellulose.

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* The authors suggest using the term "O-nitration" to denote the formation of nitric esters, by analogy with "N-nitration" and "C-nitration" to form nitramines and nitro-compounds respectively.

[10] J. Hackel and T. Urbański *Roczn. Chem.* **12,** 276 (1932); *Z. ges. Schiess-u. Sprengstoffw.* **28,** 306 (1933); *VIe Congrès Intern. des Industries Agricoles* p. 766. Budapest (1939).

As with cellulose the region of mixtures which can O-nitrate starch evidently extends beyond that containing detectable concentrations of NO_2^+ ions which is bounded by the curve N_1N_2 according to Chédin[5] and Gillespie and Millen.

Thus nitronium ion cannot be considered as the only nitrating agent yielding O-nitro derivatives of starch—a statement analogous to that on cellulose nitration made by Miles.[4] It must be admitted therefore that nitric acid itself, probably in the undissociated form NO_2OH, and possibly also the nitrate ion NO_3^- are both O-nitrating agents for starch. Nevertheless it is mixtures rich in NO_2^+ ion which give nitrostarch of the highest degree of nitration and nitronium ions should still be considered as a most efficient nitrating agent.

In addition the rule of Sapozhnikov[6] on the importance of the vapour-pressure of HNO_3 seems to be confirmed by the general trend of the curves A_1A_2, B_1B_2 and C_1C_2.

However, the curve $A_2'A_3$ and the branches B_2B_3 and C_2C_3 show a definite deviation from the rule as established for the nitration of cellulose. The curves mentioned above lie between the H_2O–HNO_3 axis and the line H_2O—Z which represents mixtures with the HNO_3/H_2SO_4 ratio running from about 90/10 to 100/0.

It is evident that these mixtures have a relatively stronger nitrating action upon starch than upon cellulose.

An important property of all these nitrating mixtures is their ability to dissolve starch partly or totally. The higher the HNO_3/H_2SO_4 ratio in this region, the more completely soluble is the starch. This would account for the trend of the curves $A_2'A_3$, B_2B_3 and C_2C_3. The nitrogen content of the products also increases with increasing HNO_3/H_2SO_4 ratio.

The nitration of starch proceeds in this region in a system which is either completely single phase or partly so in contrast with cellulose, which swells only in mixtures rich in nitric acid and low in sulphuric acid. Swelling of cellulose hinders the uniformity of the process and makes the nitration even more difficult. Once more the importance of the effect of the factor of diffusion of nitrating mixture into the cellulose fibres upon the rate and degree of nitration can be pointed out. According to Sakurada[11,12] the kinetics of nitration of cellulose can be characterised by means of an equation:

$$x = k \cdot z^m$$

where: x is the weight of the product,
z is the time required for the reaction,
k and m are constants depending on the rate of diffusion of the acid into the fibres.

It is true that cellulose can also be dissolved in mixtures very rich in nitric acid but this requires a longer time and leads to marked degradation of the cellulose.

On the contrary starch is quickly dissolved in nitric acid or in the nitrating mixtures rich in nitric acid and can be isolated by pouring the solution into water.

SUMMARY

O-Nitration of starch was examined by means of nitrating mixtures composed of nitric acid, sulphuric acid and water and curves relating constant nitrogen content in the product to mixture composition were plotted on a triangular diagram.

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[11] I. Sakurada *J. Soc. Chem. Ind., Japan* **35**, 123, 282 (1932); *Ibid.* **36**, 28, 299 (1933).

[12] I. Sakurada, T. Nakashima and H. Nakahara *J. Soc. Chem. Ind., Japan* **39**, 51 (1936).

The following conclusions can be drawn from the experiments:

(1) Starch, like cellulose, can be nitrated by relatively dilute nitrating mixtures which do not contain nitronium ions. This indicates that undissociated nitric acid (NO_2OH) and/or nitrate ion (NO_3^-) are also O-nitrating agents.

(2) The constant nitrogen curves all have two branches. The main branches follow remarkably well the trend of the Sapozhnikov curves established for the nitration of cellulose and for the partial vapour-pressure of HNO_3.

The shorter branches correspond to mixtures rich in nitric acid. Their nitrating action upon starch does not follow the rule of Sapozhnikov. This deviation is probably due to the ability of these mixtures to readily dissolve starch.

(3) The higher the HNO_3/H_2SO_4 ratio in the nitrating mixtures in the region from 90/10 to 100/0, the greater is the solvent power for starch and at any given HNO_3/H_2O ratio the higher is the nitrogen content of the product.

(4) Comparison of the action of mixtures rich in nitric acid upon cellulose and starch leads once more to the establishment of the importance in nitration of the factor of diffusion of the acids into the cellulose fibres.