

# NITRATION OF PENTAERYTHRITOL BY

## HNO<sub>3</sub> - H<sub>2</sub>SO<sub>4</sub> - H<sub>2</sub>O SYSTEM

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Nitration of primary alcohols or of primary alcoholic groups in polyhydric alcohols at 20°C takes place if nitric acid with concentrations between 100 and 60% is used, i. e., in the concentration range where free unionized nitric acid is detected spectroscopically [1, 2]. This coincidence suggests that the O-nitrating agent in the HNO<sub>3</sub> - H<sub>2</sub>O system is evidently not the nitronium ion, as suggested by Ingold and his co-workers [3-5], but the molecule of free unionized acid HONO<sub>2</sub>. It is natural to suppose that this nitrating agent must also exist under certain other O-nitration conditions, particularly in nitration by the HNO<sub>3</sub> - H<sub>2</sub>SO<sub>4</sub> - H<sub>2</sub>O system. The idea that nitric acid nitrates alcohols in the unionized form was put forward by Sapozhnikov [6]. The same conclusion was reached somewhat later in [7] and, in recent years, in [8-10]. Numerous authors, while investigating the formation of cellulose and starch nitrates [11, 12], have at one time made an enormous contribution to the theory and technology of both nitrates, which are extremely valuable chemical products.

Both of the investigated starting materials (cellulose and starch) are highly polymerized compounds which contain primary and secondary alcohol groups. They do not dissolve in the majority of nitrating mixtures, and therefore the formation of their nitrates takes place in other ways than by homogeneous O-nitration of the monomeric alcohols. Thus, for example, in the production of cellulose nitrates, the degree of O-nitration depends not only on the reactivity of the nitrating mixture and the hydroxyl group but is sometimes determined mainly by the ability of the nitrating mixture to penetrate into the cellulose fiber. This also applies to a considerable degree to the grains of starch. In spite of the detailed investigation of their O-nitration by nitrating mixtures and although they retain the general features of the process, the special characteristics of the structure of cellulose and starch do not allow a parallel to be drawn between them and other alcohols in reactions to form nitrates. These peculiarities do not allow full use to be made of the vast experimental material on the production of cellulose and starch nitrates in the desire to predict the behavior of the monomeric alcohol in the nitrating mixtures.

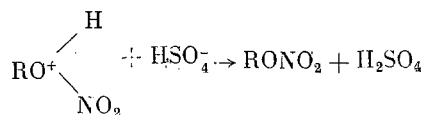
This is why the present work has been carried out to determine the nature of the nitrating agent in O-nitration of alcohols by nitrating mixtures and to investigate the formation of pentaerythritol tetranitrate over a wide range of compositions in the mixtures.

Pentaerythritol was chosen for investigation for three reasons: 1) high reactivity of all four sterically unhindered methyl groups; 2) the final product (the tetranitrate) is a crystalline substance, practically insoluble in the nitrating mixtures, which allows an extremely reliable gravimetric method to be used with confidence for determining the yield; 3) pentaerythritol tetranitrate can be purified exceptionally well by recrystallization. It should be expected that maximum nitrating ability will occur in mixtures with lower water contents if the nitrating agent is the nitronium cation. In this case, as proposed in [4, 5], O-nitration takes place irreversibly according to Eqs. (1) and (2):

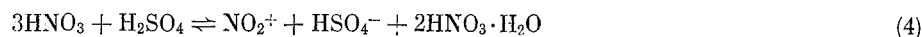
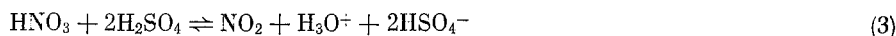


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and the nitronium cation forms in reactions (3) and (4), depending on the ratio between the nitric and sulfuric acids [13]:



If, on the other hand, the nitrating agent is the free unionized nitric acid molecule, maximum O-nitration will be shifted towards nitrating mixtures with a specific water content giving the largest amount of  $\text{HONO}_2$  in the system.

In order to make a quantitative evaluation of the position we used data in [8, 13-15], where  $\text{HNO}_3 - \text{H}_2\text{SO}_4 - \text{H}_2\text{O}$  systems were represented in the form of a phase diagram (Fig. 1). On this diagram the line ALC represents the geometrical positions of points for compositions where the frequency of the nitronium cation ( $\Delta\nu = 1400 \text{ cm}^{-1}$ ) completely disappears with further addition of water and the  $\alpha\lambda\gamma$  line corresponds to mixtures where the nitric acid is in the form of 100%  $\text{HNO}_3$ . The area bounded by the line EDC and the coordinate axes represents nitrating mixtures in which all the nitric acid is ionized to nitronium cation. Thus, in O-nitration by the nitronium cation, it should be expected that compositions possessing nitrating ability will lie to the left of the line ALC. With nitrating mixtures containing, for example, 10% nitric acid, maximum nitrating ability should occur at a water content of ~0-2%, and the nitrating ability should be at a minimum or completely absent when the water content is increased to more than 14.6%.

Practically the opposite effect should be observed in O-nitration of the alcohol by molecules of free unionized nitric acid in the same mixtures containing 10% nitric acid; the nitrate should not form when the mixtures contain ~0-2% water, and the yield of tetranitrate should be at a maximum when the water content reaches ~15%.

The second assumption was verified experimentally. In O-nitration of pentaerythritol by nitrating mixtures containing a constant amount of nitric acid (10%), it was found that the tetranitrate was absent from nonaqueous mixtures and that maximum yield was obtained with water contents between 17 and 25% (Fig. 2). A similar type of dependence of pentaerythritol tetranitrate yield on the water content, and consequently on the nitronium cation content, was also found with other concentrations of nitric acid (Fig. 3).

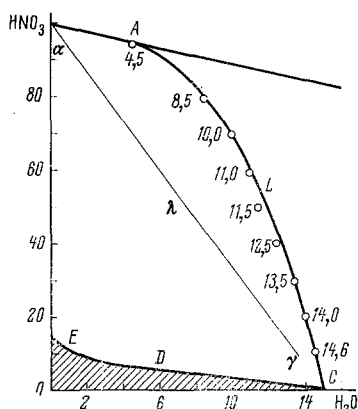


Fig. 1

Fig. 1. Areas of  $\text{HNO}_3 - \text{H}_2\text{SO}_4 - \text{H}_2\text{O}$  nitrating system with full (EDC region) and partial (to the left of ALC) ionization of the nitric acid to nitronium cation according to data from [8, 14].

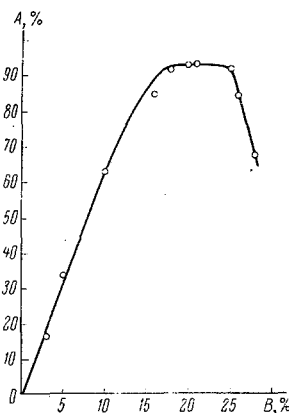


Fig. 2

Fig. 2. Tetranitrate yield during O-nitration of pentaerythritol by nitrating mixtures containing 10% nitric acid. A) Yield of tetranitrate; B) water content in original nitrating mixture.

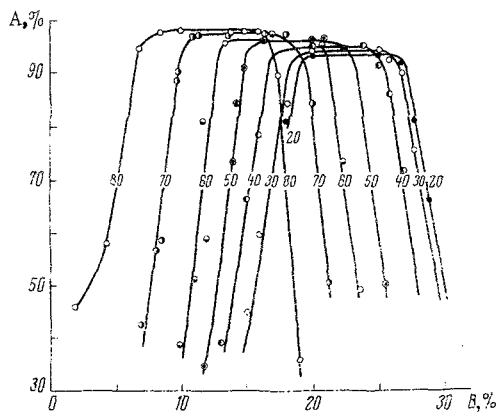


Fig. 3

Fig. 3. Tetranitrate yield during O-nitration of pentaerythritol by nitrating mixtures containing 20-80% nitric acid. The amount of nitric acid is indicated by the figures on the curves. A) Yield of tetranitrate; B) water content in original nitrating mixture.

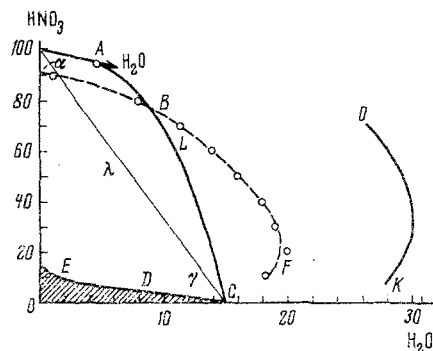


Fig. 4

Fig. 4. Nitration region for pentaerythritol in  $\text{HNO}_3 - \text{H}_2\text{SO}_4 - \text{H}_2\text{O}$  system (between curves BF and OK).

We will examine O-nitration by nitrating mixtures containing 60%  $\text{HNO}_3$ , for example, in rather more detail. As seen from Fig. 3, such nitrating mixtures secure the maximum equilibrium yield of tetranitrate at certain water contents (between 13 and 21%). When the amount of water in the nitrating mixture is decreased the yield drops sharply and is accompanied by oxidative processes with abundant evolution of nitrogen oxide. The tetranitrate yield also decreases and oxidation is also observed if the water content of the original mixture is greater than 21%, although to a considerably lesser degree than on the left hand branch of the curve. The beginning of the inflection on the right hand branch is determined not by the composition of the original nitrating mixture but by the composition of the spent acid and therefore depends on the original ratio between nitric acid and pentaerythritol. (In our experiments this ratio was six for all the nitrating systems.) The position of the left inflection is determined by the composition of the original mixture and by the nature of the alcohol. With nitration by mixtures lying on the horizontal part of the curve very pure O-nitration, completely free from oxidative side processes, is observed. The maximum equilibrium yield of tetranitrate stays constant for each series of nitrating mixtures with identical nitric acid contents, but its value depends appreciably on the amount of nitric acid in the system (Fig. 3).

For the sake of clarity, on the Chedin diagram (Fig. 4) we give points which define the region of acid mixtures corresponding to maximum equilibrium yield from O-nitration. The curve BF embraces compositions of original nitrating mixtures corresponding to the left-hand inflections on the curves in Fig. 3, while the curve OK represents the corresponding compositions of the spent acid. It is seen from this comparison that the region of acid mixtures BFOK which interests us lies considerably to the right of the line ALC and, moreover, the line EDC (the region corresponding to complete ionization of nitric acid to nitronium ion). In other words, the experimental results confirm fairly clearly the supposition that the nitrating agent in acid mixtures containing  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{H}_2\text{O}$  is evidently the free unionized nitric acid molecule.

At the end of the nitration process, apart from other equilibria which also take place to a greater or lesser degree, equilibrium is established in the system between the O-nitrating agent and the alcohol. As known, the equilibrium state does not depend on the nitrate formation mechanism but is determined by the composition of the spent acid. Therefore, in the general case, three main reactions take place simultaneously at the equilibrium point:

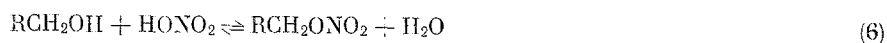
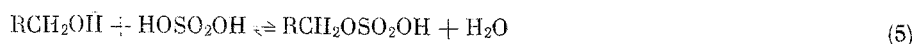


TABLE 1. Dependence of Equilibrium Tetranitrate Yield on Content of Nitric and Sulfuric Acids in Spent Acid

Composition of spent acid, %			Yield of pentaerythritol tetranitrate, % of theoretical
HNO <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>	H <sub>2</sub> O	
58,0	13,0	29,0	97,5
40,0	30,9	29,1	96,5
23,0	48,0	29,0	94,5
6,2	66,7	28,1	91,5

TABLE 3. Comparison of Calculated Minimum Modulus M with Practical Modulus

Composition of nitrating mixture, %			Value of minimum modulus	
HNO <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>	H <sub>2</sub> O	practical	calculated from equation (8)
80,0	4,0	16,0	7,6	7,4
70,0	12,0	18,0	8,7	8,5
60,0	20,0	20,0	10,0	10,0
50,0	28,0	22,0	12,0	12,2
40,0	36,0	24,0	15,0	15,5
30,0	44,5	25,5	20,0	19,2
20,0	52,8	27,2	30,0	26,5

Note: The appreciable difference in the values of the modulus in original mixtures poor in nitric acid is explained by the fact that an approximate equation for the material balance of the reaction, which does not take account of the drop in the equilibrium tetranitrate yield, was used for the calculation.

molar ratio of water to nitric acid is 1.36, which is a characteristic value for this alcohol and determines the technological limit of O-nitration for the system.

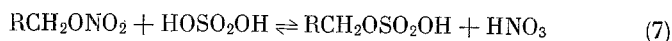
Starting from the ideas in [15] on the distribution of water in the acid mixtures, we will determine the molar ratio between water and sulfuric acid at which oxidative processes begin to appear and where further addition of reaction water no longer increases the amount of water in the hydrate 1.36 H<sub>2</sub>O·HNO<sub>3</sub> but is completely held by the sulfuric acid in the form of the hydrate xH<sub>2</sub>O·H<sub>2</sub>SO<sub>4</sub>. From the equality of the energetic possibilities for occurrence of hydration reactions in both acids it is clear that the desired state starts with a single and sufficient condition (equality in the differential heats of both processes) and the solution of the problem then reduces to determination of the sulfuric acid concentration at which the differential heat effect of dilution with water is the same as with 72% nitric acid.

We solved the problem graphically by means of the relationship for the integral heat of dilution of acids with water (L<sub>C</sub>) using data from [16]. In essence the method is extremely simple. On the L<sub>C</sub> = f(C) curves for nitric and sulfuric acids (plotted in the same coordinate system with heat effect against acid concentration) two parallel tangents are drawn with one of them touching the L<sub>C</sub> = f(C) HNO<sub>3</sub> curve at a point corresponding to 72% nitric acid concentration. The solution to the problem is given by the contact point of the second tangent to the L<sub>C</sub> = f(C) H<sub>2</sub>SO<sub>4</sub> curve, since it determines the desired sulfuric acid concentration, which in our special case corresponds to the composition of the hydrate 2.46 H<sub>2</sub>O·H<sub>2</sub>SO<sub>4</sub>. The distribution of water found between nitric and sulfuric acids in the spent acid now makes it possible to determine

TABLE 2. Equilibrium Tetranitrate Yield and Amount of Combined Sulfuric Acid (in form of sulfate esters) in O-Nitration of Pentaerythritol by Nitrating Mixture

Composition of original nitrating mixture, %			Content of combined sulfuric acid at end of process (τ = 30 min), % of theoretical *	Yield of pentaerythritol tetranitrate, % of theoretical
HNO <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>	H <sub>2</sub> O		
10,0	90,0	0,0	86,4	0,0
10,0	87,0	3,0	71,7	17,2
10,0	80,0	10,0	17,7	63,2
10,0	72,0	18,0	3,5	91,0

\* Calculated on pentaerythritoltetrasulfonic acid C(CH<sub>2</sub>OSO<sub>2</sub>OH)<sub>4</sub>.



As mentioned earlier, the equilibrium yield of tetranitrate depends on the nitric acid content (with constant water content) of the spent acid. As the sulfuric acid increases its competing effect also increases and reactions (5) and (7) become appreciable, due to which the tetranitrate yield decreases (Table 1). Complete dissociation of HONO<sub>2</sub> to nitronium cation leads to predominance of Eq. (5) in the system, and with addition of water to the original nitrating mixture a larger amount of free unionized nitric acid appears and the equilibrium is displaced towards nitrate formation in accordance with Eq. (6). Such a state is clearly illustrated by the data in Table 2.

The validity of this determination of the nature of the O-nitrating agent is also confirmed fairly reliably on the basis of thermodynamic considerations. The O-nitration process begins to stop when the concentration of free unionized nitric acid becomes immeasurably small (unless the alcohol is previously oxidized) or, while approaching this limit, reaches some measurable value, but oxidation of the alcohol (as a competing reaction) takes place so quickly that it completely suppresses the O-nitration reaction. During O-nitration by the HNO<sub>3</sub> - H<sub>2</sub>O system (at 30°C) pentaerythritol begins to be oxidized by 72% nitric acid. In this case the

a very important quantity for practical work, namely the minimal modulus  $M = k/p$  for an original mixture of composition  $s\%$   $H_2SO_4$ ,  $a\%$   $HNO_3$ ,  $w\%$   $H_2O$ , if use is made of the approximate equation for the material balance:

$$\frac{1.36}{63} \left( \frac{ak}{100} - \frac{252p}{136} \right) + \frac{2.46}{98} \cdot \frac{sk}{100} = \frac{1}{18} \left( \frac{wk}{100} + \frac{72p}{136} \right),$$

where  $k$  is the amount of the original nitrating mixture,  $g$ ;  $p$  is the amount of pentaerythritol,  $g$ .

By solving the equation with respect to  $k/p = M$ , we obtain

$$M = \frac{89.89}{a + 1.048s - 72} \quad (8)$$

The data in Table 3 demonstrate, for O-nitration of pentaerythritol, good agreement between the calculated and experimental values of the modulus, which in turn confirms and verifies experimentally the accuracy of the nature found for the O-nitrating agent.

## EXPERIMENTAL

The pentaerythritol used in the work melted at 257–258°C and consisted of crystals which passed through sieve No. 14 but were retained on sieve No. 27. It had the following characteristics and impurity contents: 0.09% moisture, 0.03% ash, 0.00% acidity, 0.10% sugar compounds.

For preparation of the nitrating mixture 94% sulfuric acid, 98% nitric acid, and 114% oleum were used, and all these acids were cp. The original acids and also acids of various dilution with water prepared from them were analyzed by the usual methods [17–19] and formed the set from which the nitrating mixtures were prepared. The mixtures were prepared 20–30 min before the work was commenced.

Nitration was only carried out with mixtures where the difference between the calculated overall acidity and that obtained by experimental means did not exceed  $\pm 0.2\%$  (converted to sulfuric acid).

Procedure for O-Nitration of Pentaerythritol. The amount of acid mixture taken for O-nitration of pentaerythritol was chosen so that the weight ratio of  $HNO_3$  to pentaerythritol was 6. The calculated amount of the mixture was weighed in the reaction vessel with an accuracy up to 0.01 g and was heated to 30°C with the stirrer running. As soon as the temperature reached this limit the heating was stopped, and 5.00 g pentaerythritol was added. The temperature of the reaction mixture was kept at  $30 \pm 0.5^\circ C$  by cooling the reaction vessel with cold water. The time taken for addition of the pentaerythritol in the experiments varied between 1 and 3 min. At the end of the addition the reaction mixture was kept at 30°C for 0.5 h (with the stirrer in operation) and then cooled to 20°C. The cooled mixture was weighed, after which it was diluted with water so that the diluted spent acid had a total acidity of  $\sim 20$ –30%, converted to  $H_2SO_4$ .

The pentaerythritol tetranitrate which separated on dilution, together with the solid products from the side reactions, was separated from the spent acid on a glass vacuum filter funnel, where it was washed with cold water, twice with hot water (70–80°C), with hot 2% soda solution, and once more with hot water. Each washing operation took a 20-ml portion of the washing liquid.

To determine the yield of pure tetranitrate a sample ( $\sim 3$  g) was taken from the washed and dried product and was carefully treated with 30 ml 85%  $HNO_3$ . All the impurities dissolved, and the pure tetranitrate was washed as before, dried, and weighed. A quantity of 0.224 g was added to the weight obtained to allow for the amount of tetranitrate which passed into solution during the 0.5-h washing with 85%  $HNO_3$ , and the yield was determined.

Analysis of Spent Acid. The total acidity, sulfuric acid content, and nitrogen oxide content were determined. The analysis was only performed in cases where the competing action of sulfuric acid could arise and this could give acid sulfates of pentaerythritol. The main purpose of the analysis was therefore to determine the amount of free sulfuric acid, from which it would be possible to judge whether reesterification had taken place. Our method for determination of sulfuric acid differed somewhat from the method generally used in analytical chemistry. We reduced the period for maturation of the barium sulfate precipitate to 20 min and did not heat the solution above 25°C, which almost completely prevented hydrolysis of the acid sulfates of pentaerythritol. All the other operations in the analysis were the same as described in [19]. In

order to take account of the effect of nitric acid sorbed in the form of nitrate ion on the barium sulfate precipitate on the results from the analysis, we obtained an empirical coefficient (0.953) to allow for this effect in mixtures containing between 5 and 80% nitric acid.

The content of nitrogen oxides was determined by oxidation with a standard solution of potassium permanganate.

### CONCLUSIONS

It was shown experimentally that the nitrating agent in the O-nitration of pentaerythritol by  $\text{HNO}_3$  -  $\text{H}_2\text{SO}_4$  -  $\text{H}_2\text{O}$  nitrating mixtures is not the nitronium cation but evidently the free unionized nitric acid molecule.

### LITERATURE CITED

1. L. T. Eremenko, L. V. Kustova, and É. I. Moiseeva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1344 (1966).
2. L. T. Eremenko and A. M. Korolev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1436 (1966).
3. E. L. Blackall and E. D. Hughes, *Nature*, **170**, 972 (1952).
4. E. L. Blackall, E. D. Hughes, S. C. K. Ingold, and R. B. Pearson, *J. Chem. Soc.*, 4366 (1958).
5. C. K. Ingold, E. L. Blackall, E. D. Hughes, and R. B. Pearson, *Reports, Papers, and Reports from Foreign Scientists at Eighth Mendeleev Congress on General and Applied Chemistry*, *Izd. Akad. Nauk SSSR* (1959), p. 9.
6. A. V. Sapozhnikov, *Zh. Russk. Khim. Obshch.*, **41**, 1712 (1909).
7. R. C. Farmer, *J. Soc. Chem. Ind.*, **50**, 75T (1931).
9. F. G. Miles, *Cellulose Nitrate*, Oliver and Boyd, London - Edinburgh (1955).
10. T. Urbanski and J. Hackel, *Tetrahedron*, **2**, 300 (1958).
11. J. Hackel and T. Urbanski, *Roczn. Chem.*, **12**, 276 (1932).
12. J. Hackel and T. Urbanski, *Z. Schiess-Sprengstoffw.*, **28**, 306 (1933).
13. J. Chedin and S. Fénéant, *Compt. Rend.*, **243**, 41 (1956).
14. J. Chedin, *Chimie et Industrie*, **56**, 7 (1946).
15. J. Chedin, S. Fénéant, and R. Leclerc, *Compt. Rend.*, **224**, 1058 (1947).
16. *Selected Values of Chem. Thermodynamic Properties*, Circular of the National Bureau of Standards, **1**, 500 (1952).
17. A. G. Amelin, *Sulfuric Acid Production* [in Russian], Goskhimizdat (1956).
18. I. D. Fotinich, *Production of Concentrated Nitric Acid* [in Russian], Goskhimizdat, Moscow - Leningrad (1952).
19. E. V. Alekseevskii, R. K. Gol'ts, and A. P. Musakin, *Quantitative Analysis* [in Russian], Gosnauchtekhizdat, Moscow - Leningrad (1953).