[CONTRIBUTION FROM THE STARCH RESEARCH LABORATORY OF STEIN, HALL AND CO., INC.]

Nitration of Starches with Nitrogen Pentoxide in Presence of Sodium Fluoride

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A study of nitrogen pentoxide for the purpose of nitration was originally undertaken by this Laboratory with the object of forming undegraded nitric esters of starch. The literature covering the use of this reagent as a nitrating agent is meager, particularly in reference to starch. Gibson[1] in 1908 nitrated tartaric acid with nitrogen pentoxide and Dufay[2] claimed advantages for it in nitrating cellulose. Haines and Atkins[3] nitrated certain aromatic compounds with nitrogen pentoxide; Rogovin and Tikhonov[4] tested the effect of additions of nitrogen oxides, inclusive of the pentoxide, to nitric acid in nitrations of cellulose; Dalmon, Chédin and Brissaud[5] nitrated cellulose with nitrogen pentoxide in solution in carbon tetrachloride; Dalmon[6] passed this reagent through dried cotton; and Urbanski and Janiszewski[7] nitrated cellulose and starch with "gaseous" or "liquid" pentoxide. It seems possible that the rapid and very high degree of cellulose nitration reported by Berl[8] through the use of phosphoric acid fortified by phosphorus pentoxide, may have been due to partial dehydration of the nitric acid present. Dalmon, Chédin and Brissaud[5] reported nitrogen pentoxide in the Raman spectra of most nitrating mixtures.

The nitration investigations of this Laboratory with nitrogen pentoxide were principally confined to starch, although a number of nitrations also have been run on cellulose and a variety of other substances. In the initial experiments a form of starch was used in which the granular organization was disrupted. This material, dried to less than 1% moisture, was stirred into solutions of nitrogen pentoxide in chloroform or carbon tetrachloride and nitrated under varying conditions. This is the general procedure used by Dalmon, Chédin and Brissaud[5] on cellulose. The results were generally unsatisfactory and erratic. On occasion a rapid-burning starch nitrate was formed; more often the starch underwent a superficial solution or sliming which inhibited further nitration and made the product difficult, if not impracticable, to stabilize. It was observed that this sliming trouble was reduced when the ratio of volume of the nitrating solution to weight of starch increased. Accumulation of nitric acid was suspected, according to the reaction

$$ROH + N_2O_5 \longrightarrow RONO_2 + HONO_2$$

Formation of nitric acid was reported by Haines and Atkins[3] and by Dalmon.[6] It is also well known that nitric acid disperses or "dissolves" starch. The literature revealed no attempts to remove by-product nitric acid in spite of the obvious advantages of doing so.

In our first attempts to remove by-product nitric acid, phosphorus pentoxide was introduced into the nitration cycle in a porous container through which the solution of nitrogen pentoxide was continuously circulated. Greatly improved results were at once apparent. The starch retained its powdery character, and complete nitration (13.9–14% nitrogen) was consistently obtained over a considerable range of time, temperature and concentration. Use of phosphorus pentoxide, however, presented obvious difficulties. Accordingly, other means were sought. The problem is interesting. It was solved simply and with unique success through an application of hydrogen bonding. Nitric acid, $HO-NO_2$, is susceptible to hydrogen bonding; nitrogen pentoxide, N_2O_5, is not. Fluorine, the most electronegative atom, is known to form the strongest hydrogen bonds. It was postulated that a fluoride salt, insoluble in the pentoxide solvent, should act as a proton acceptor, *i. e.*, as a "base," and adsorb nitric acid effectively. Sodium fluoride was tried and found to be particularly efficient. One gram, for example, shaken at 10–15° in 10 ml. of a chloroform solution containing 5.06 g. of nitric acid per 100 ml., reduced the nitric acid concentration to 0.09 g. per 100 ml. The effect of sodium fluoride on the concentration of nitrogen pentoxide was negligible. A number of fluoride salts were tested but none, save possibly the rare rubidium fluoride, approached the effectiveness of sodium fluoride as an adsorbent of nitric acid. There was some evidence that radius ratio of ions and crystal type affect the proton acceptance.

Sodium fluoride, therefore, was substituted for phosphorus pentoxide in nitration procedures with nitrogen pentoxide in chloroform.

Efficient laboratory production of nitrogen pentoxide constituted another problem which was considerably more difficult than anticipated from the classic method of Russ and Pokorny[9] and Daniels and Bright's[10] variation.

Experimental

Preparation of Nitrogen Pentoxide.—Nitrogen pentoxide was prepared by a modification of the methods used by Russ and Pokorny[9] and by Daniels and Bright.[10] The objective was to obtain as large a yield of nitrogen pentoxide as possible without great insistence on purity insofar as nitrogen tetroxide was concerned. It was found that

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(1) Gibson, *Proc. Roy. Soc. Edinburgh*, **28**, 705 (1908).

(2) Dufay, *Chem. News*, **106**, 211 (1912).

(3) Haines and Atkins, THIS JOURNAL, **47**, 1419 (1925).

(4) (a) Rogovin and Tikhonov, *Iskusstvennoe Volokno*, **5**, No. 7, 41 (1934); *cf. ibid.*, **5**, No. 5, 34 (1934); (b) *Cellulosechem.*, **16**, 11 (1935); (c) **15**, 102 (1934).

(5) Dalmon, Chédin and Brissaud, *Compt. rend.*, **201**, 664 (1935).

(6) Dalmon, *ibid.*, **201**, 1123 (1935).

(7) Urbanski and Janiszewski, *Roczniki Chem.*, **17**, 349 (1937).

(8) Berl, *Ind. Eng. Chem., Anal. Ed.*, **13**, 322 (1941).

(9) Russ and Pokorny, *Monatsh.*, **34**, 1051 (1913).

(10) Daniels and Bright, THIS JOURNAL, **42**, 1133 (1920).

use of oxygen instead of ozone did not substantially alter the yield or the quantity of nitrogen tetroxide produced. While the method used of raising the temperature of the reaction mass to the boiling point of water favored the formation of nitrogen tetroxide, it was also found that it substantially increased the yield of nitrogen pentoxide, probably owing to the increased mobility of the pasty phosphorus pentoxide–nitric acid mass.

The apparatus is shown in Fig. 1. Bottle A contains sulfuric acid to dry the oxygen, and serves as a bubble counter. Flask B contains the reaction mixture. Flask C is the condenser. It is held in a one-gallon thermos jug using alcohol and Dry Ice as the cooling medium. Tube D is a trap. Tube E contains water to absorb any fumes not condensed in Flask C and it also serves as a bubble counter.

Seventy to eighty ml. of nitric acid, sp. gr. 1.48–1.51, was placed in Flask B in a bath of Dry Ice and alcohol, and the oxygen stream turned on slowly. When the nitric acid was frozen, 100–125 g. of phosphorus pentoxide was added. The alcohol–ice bath was removed and replaced with a water-bath at room temperature. When the first rush of nitrogen pentoxide and tetroxide was substantially swept out of the reaction flask, as evidenced by the absence of red fumes of nitrogen tetroxide, the phosphorus pentoxide was briefly stirred into the nitric acid. When the second rush of nitrogen pentoxide was swept out of the reaction flask, a gentle flame was applied to the water-bath for three to four hours until the reaction was substantially completed and the nitrogen pentoxide cleared from the reaction flask. The bath was removed and oxygen was allowed to sweep through the apparatus for twenty to thirty minutes to promote oxidation of nitrogen tetroxide. The nitrogen pentoxide crystals, together with any nitrogen tetroxide present, were dissolved in chloroform or other solvent to be used for the nitration. By using two sets of apparatus 80–120 g. of nitrogen pentoxide along with 15–30 g. of nitrogen tetroxide were prepared daily as needed.

One ml. of the chloroform solution of the nitrogen oxides was pipetted into about 25 ml. of water and titrated with 0.1 *N* sodium hydroxide followed by 0.1 *N* potassium permanganate. All the reducing matter was calculated as nitrogen tetroxide. The nitrogen pentoxide was obtained by deducting the nitrogen tetroxide equivalent from the total acidity.

Preparation of Starch Nitrate.—Fifteen hundred ml. of the solution of nitrogen pentoxide in chloroform was placed in a 2-liter beaker. For complete nitration the solution contained 10–20 g. of nitrogen pentoxide per 100 ml. of solution.

The beaker was placed in another vessel used as a bath and alcohol was added to the outer vessel to a depth of two to three inches. The beaker was fitted with a stirrer and thermometer.

The stirrer was started and 20 g. of sodium fluoride was added to the solution. A few lumps of Dry Ice were added to the bath, sufficient to bring the temperature to −10 to −20°. When the nitrating solution was approximately at 0°, 50 g. of powdered starch was added. The starch was previously dried at 105° for four to five hours. The nitration temperature was not allowed to rise above 16–18°. The temperature usually rose rapidly during the first three to five minutes, particularly in corn starch nitrations. Because of this initial temperature rise, it was found preferable to start the nitrating solutions at around 0° as indicated. The nitration of corn starch was usually allowed to proceed for twenty minutes, and from thirty minutes to one hour for potato starch, if complete nitration was desired.

The reaction mixture was filtered on a Buchner funnel into a clean dry suction flask and the filtrate was removed for subsequent recovery. The starch nitrate was rinsed with about 400 ml. of chloroform to remove nitrogen pentoxide. It was then made into a slurry with cold water and filtered. Hot water was poured through the filter cake until substantially all of the chloroform was evaporated. The filter cake was then put into about a liter of hot water and stabilized by boiling for three hours with an intermediate neutralization in very dilute ammonium hydroxide. The starch nitrate was stored in distilled water or 50% alcohol. Starch nitrate prepared and stabilized in this manner met standard specifications for stability.

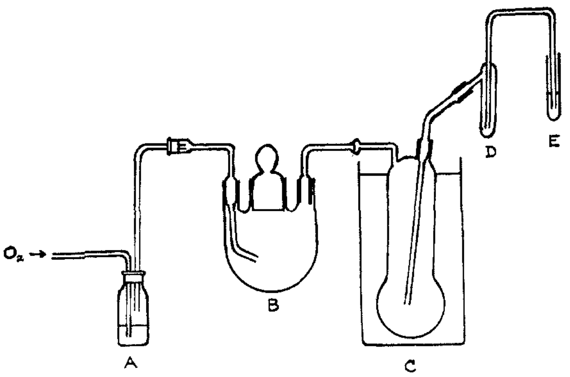

Fig. 1.—Apparatus for production of nitrogen pentoxide.

The spent nitrating solution was treated with sodium fluoride to remove any nitric acid and used again for nitration, if sufficiently concentrated; if not, it was fortified by the addition of more nitrogen pentoxide.

Nitrogen analyses were determined by du Pont nitrome-

TABLE I

NITRATION OF STARCHES

No.	G. N_2O_5/starch	G. N_2O_5/100 ml.	Time, min.	Temp., °C., av.	% N
Heavy-boiling Corn Starches[a]					
Complete Nitrations					
1	4.3	14.5	30	10	13.98
2	4.1	13.7	15	8	13.91
3	3.2	16.3	25	10	13.89
4[b]	3.9	12.7	15	10	13.92
5	4.2	13.8	20	12	13.91
6	4.0	13.2	20	11	13.90
7[c]	3.8	12.5	20	. .	13.90
8[d]	3.9	12.8	20	. .	13.93
9[e]	4.4	14.6	20	. .	13.92
10[f]	3.9	13.0	10	6	13.92
Incomplete Nitrations					
11	<1	3.0	30	6	1.8
12	*ca.* 1	3.4	20	11	2.7
13	*ca.* 1	3.4	30	8	3.9
14	*ca.* 1	3.4	30	8	4.9
15	*ca.* 1	3.4	30	12	5.5
16	>1	3.6	30	2	8.5
17	1.5	5.2	35	12	8.8
18	1.4	4.7	15	2	9.0
19	2.2	7.2	15	1	11.20
20	2.0	6.8	30	10	12.21
21	2.2	7.3	20	6	12.65
22	2.5	8.4	30	11	13.82
23	2.8	9.8	15	5	13.87
Heavy-boiling Potato Starches[a]					
24	4.6	15.2	60	2	11.33
25	3.9	13.0	64	16	13.92
26	4.4	14.7	60	12	13.89

[a] Commercial powdered starches. [b] In CCl_4. [c] Average of 2 runs. [d] Average of 5 runs. [e] Average of 14 runs. [f] P_2O_5 in place of NaF.

ter in the laboratories of the Massachusetts Institute of Technology. A number of analyses were cross-checked by industrial laboratories.

TABLE II

NITRATION OF STARCH FRACTIONS

	G. N_2O_5/ starch	G. N_2O_5/ 100 ml.	Time, min.	Temp., °C. av.	% N
Corn amylose[a]	3.9	10.8	20	5	13.96
Potato amylose[b]	5.7	14.3	20	10	13.2
Corn amylopectin[c]	4.6	15.4	20	10	13.98
Potato amylopectin[b]	4.7	14.3	20	9	12.8

[a] From Northern Regional Research Lab., Dept. of Agriculture. [b] From Eastern Regional Research Lab., Dept. of Agriculture. [c] Waxy maize from American Maize Products Co.

TABLE III

NITRATION OF THIN-BOILING CORN STARCHES[a] AND CORN DEXTRINS[a]

No.	G. N_2O_5/ dextrin	G. N_2O_5/ 100 ml.	Time, min.	Temp., °C. av.	% N
		Thin-boiling Starches			
1	3.5	11.9	20	10	13.95
2	4.2	14.2	19	8	13.96
3	4.8	15.9	20	8	13.97
4	3.4	11.4	20	6	14.03
		Dextrins			
5	4.6	15.3	20	12	14.01
6	4.0	12.8	20	9	13.87
7	5.6	18.1	20	11	13.90
8[b]	4.3	14.4	20	12	13.95

[a] Commercial products. [b] Tapioca envelope dextrin.

Experimental Results and Discussion

Tables I–III summarize starch and dextrin nitrations by this Laboratory after the discovery of an efficient method of removal of by-product nitric acid. With two exceptions, all nitrations were with nitrogen pentoxide in chloroform, with sodium fluoride as the nitric acid adsorbent. Concentrations of nitrogen tetroxide are not listed. They ranged from a minimum of 10.7% of the combined nitrogen oxides present (Expt. 1, Table I) to a maximum of 43% (Expt. 5, Table I), but the amount had no appreciable effect on the time or degree of nitration. It was experimentally demonstrated that nitrogen tetroxide alone, under our usual conditions of nitration, brought about no appreciable degree of esterification.

From Table I it is seen that complete nitration of corn starch by nitrogen pentoxide may be very rapid, ten minutes sufficing at an average temperature as low as 6° (Expt. 10, Table I). The nitrogen values obtained are unusually high.[11] Allowing for the non-carbohydrates present in corn starch, complete nitration to the trinitrate is readily obtained. The degree of nitration may be varied at will. It appears to be dependent primarily upon the ratio of nitrogen pentoxide to starch. At a ratio of about 2.5 or higher, complete nitration is obtained under wide variations of time and temperature.

Complete nitration of potato starch is more difficult. The effect of temperature is pronounced (Expts. 24–26, Table I), and the usual nitration time range for corn starch, ten to thirty minutes, is insufficient for the complete nitration of potato starch.

The comparative difficulty of nitrating potato starch is further revealed in Table II, summarizing nitration of the unbranched and branched fractions of starch.[12] Unbranched corn starch (amylose) and branched corn starch (amylopectin) are easily and completely nitrated in twenty minutes; but under equally favorable conditions potato amylose attains 13.2% nitrogen and potato amylopectin only 12.8% nitrogen.

The nitration of thin-boiling corn starches and corn dextrins (Table III) is as rapid and complete as of heavy-boiling corn starch. Nitrogen values for thin-boiling starches may be expected to average slightly higher than for heavy-boiling starches owing to chain scission and the relatively increased effect of tetranitrate chain ends. There is some suggestion of this in the nitrogen values of nos. 1–4 which represent nitrations of a series of thin-boiling starches decreasing in viscosity from nos. 1–4. Experiments 5–8 (Table III) were run on commercial corn dextrins, no. 5 being a medium soluble "white" type converted with relatively high content of aqueous mineral acid and moderate heat. Nos. 6–8 inclusive are high-soluble "canary" types converted with moderate content of mineral acid and high heat, the "pyro" type dextrins investigated by Brimhall.[13]

Nitration by nitrogen pentoxide, according to the method described, is so nearly anhydrous, and the conditions of nitrations are relatively so mild, that the nitric esters thus produced should reflect to the utmost possible extent the original degree of polymerization of the substances nitrated. The method therefore seems particularly applicable to structural studies of polysaccharide polymers.

Number average molecular weights and intrinsic viscosities of the starch and dextrin nitrates produced in these experiments are being determined and will be the subject of a further contribution by this Laboratory on the structure of these starch and modified starch nitric esters.

Acknowledgments.—The authors wish to express their appreciation to Dr. Tenney L. Davis[14] for his consultation and interest in the development of the nitration process[15]; to Dr. Alberto F. Thompson[16] and Mr. Leslie M. Redman[16] for

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[11] Reported nitrogen values in excess of about 13.5% for unfractionated starches are usually regarded with suspicion by experts in high explosives. The values reported by the authors were repeatedly cross-checked and proven correct.

[12] (a) Schoch, *Cereal Chem.*, **18**, 121 (1941); (b) Schoch, THIS JOURNAL, **64**, 2957 (1942); (c) Wilson, Schoch and Hudson, *ibid.*, **65**, 1380 (1943).

[13] Brimhall, *Ind. Eng. Chem.*, **36**, 72 (1944).

[14] Norwell, Mass.

[15] Patents pending.

[16] Organic Research Lab., M. I. T.

their nitrogen determinations and stability tests; to Capt. M. L. Cushing[17] formerly of this Laboratory and initially connected with this development; and to Dr. N. Gruenhut for her able assistance.

Summary

Complete nitration of starches and modified starches by means of nitrogen pentoxide in solution in a suitable non-aqueous solvent, such as chloroform, is described, together with an effective laboratory method of producing crude nitrogen pentoxide. A simple and effective means of removal of nitric acid, the by-product of pentoxide nitrations, is accomplished by use of sodium fluoride, a hydrogen-bonded complex, NaF. . .$HONO_2$, being probably formed, by which the efficiency of the nitration reaction is greatly increased. Trinitrates of corn starch, potato starch, thin-boiling corn starches, and corn dextrins are readily obtained and stabilization of the nitric esters is relatively simple and rapid. Owing to the completely anhydrous character of the nitration and the relatively low temperatures involved, the nitric esters produced are considered to reflect the degree of polymerization of the original materials. It is believed that nitrogen pentoxide nitration offers a new and important means of investigation of the structure of starch and modified starch, and, possibly, of other polysaccharides.

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[17] Chemical Warfare Service, U. S. A.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF EMORY UNIVERSITY]

Studies in *p*-Cymene. I. The Saponification Rate of Isomeric Benzoates Derived from *p*-Cymene[1]

BY CHARLES T. LESTER AND CARROLL F. BAILEY[2]

In connection with studies on *p*-cymene, we had prepared the two well-known isomeric acids, 2-methyl-5-isopropylbenzoic acid and 3-methyl-6-isopropylbenzoic acid.[3] It seemed to us of interest to determine what difference in the rate of saponification the esters of these two acids would show. Accordingly, we converted these into their known methyl and ethyl esters[3] and determined the rate of saponification of each of the four esters at three temperatures.

Experimental Preparations

Isomeric Acids.—2-Methyl-5-isopropylbenzoic acid was prepared by a series of steps starting with *p*-cymene, which we found more satisfactory than the procedure of Bogert and Tuttle[3] starting with crude 2-bromo-*p*-cymene, since our method avoids the tedious separation of the isomeric acids by fractional crystallization. *p*-Cymene was first converted into 2-aceto-*p*-cymene by a previously reported method[4]; then by its reaction with sodium hypochlorite, following also a previously described procedure for preparing β-naphthoic acid,[5] we obtained the desired acid in a 61% yield, b. p. 171° at 20 mm., m. p. 71°. These values checked with those reported[3] for the compound.

3-Methyl-6-isopropylbenzoic acid was prepared by a series of reactions starting with thymol. 3-Bromo-*p*-cymene, obtained in 71% yield by the reaction of thymol with phosphorus pentabromide, as described by Fileti and Crosa,[6] was treated with magnesium in dry ether to give the Grignard reagent. Dry Ice was then added to the ether solution over a period of one hour until the solution became very viscous. Additional Dry Ice was added as needed for a period of eight hours. On working up in the usual manner, 3-methyl-6-isopropylbenzoic acid, m. p. 84°, was obtained in 56% yield, based on the bromo compound. This series of reactions was almost identical with that reported by Bogert and Tuttle.[3] They reported the same melting point and a 55% yield for the acid. We found the use of Dry Ice an easier method of carbonation than the use of carbon dioxide under pressure, as reported by them.

Isomeric Esters.—The chlorides of the above acids were prepared by the procedure described by Bogert and Tuttle.[3] Our yields and boiling points agreed with their values. To a solution of 5 cc. of absolute ethanol in 50 cc. of dry pyridine was added slowly 20 g. of 2-methyl-5-isopropylbenzoyl chloride. The mixture warmed spontaneously and pyridine hydrochloride crystallized from the mixture. When all the acid chloride had been added, the solution was heated until the pyridine hydrochloride re-dissolved. It was then refluxed for ten minutes, cooled and 100 cc. of dilute hydrochloric acid added. The ester was then extracted with ether. The ether extract was washed repeatedly with dilute acid until free of pyridine, then with water, three times with 5% sodium bicarbonate solution, water again, and then dried over anhydrous sodium sulfate. The ether was removed on a water-bath, the ester fractionally distilled through a Penn State column,[7] and finally fractionally distilled through a Smith semi-micro column. The sample used was the middle cut of the final distillation. There was no range of temperature in this fraction.

The other esters were prepared and purified in the same manner. Their yields and physical properties are given in Table I. Bogert and Tuttle[3] reported the boiling points of the esters at a variety of pressures. They did not report yields or refractive indices.

Rate of Saponification

The method of Evans, Gordon and Watson was followed in detail.[8] Duplicate samples were used in each run. The duplicate values showed an average deviation of 2.6%. The reaction rate

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[1] Presented before the Meeting-in-Miniature of the Georgia Section of the American Chemical Society, Atlanta, Ga., September 28, 1945.

[2] Community Trust Fellow, 1944–1945.

[3] Bogert and Tuttle, THIS JOURNAL, **38**, 1349 (1916).

[4] "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 3.

[5] Ref. 4, p. 428.

[6] Fileti and Crosa, *Gazz. chim. ital.*, **16**, 292 (1886).

[7] Whitmore and Lux, THIS JOURNAL, **54**, 3451 (1932).

[8] Evans, Gordon and Watson, *J. Chem. Soc.*, 1430 (1937).