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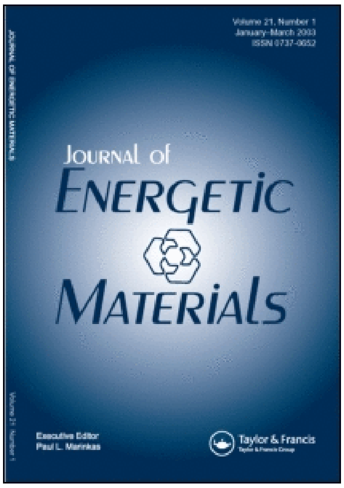

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THE REACTION OF CELLULOSE NITRATE WITH SEVERAL NUCLEOPHILES

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ABSTRACT

Replacement of the nitrate groups in cellulose nitrate (CN) to varying degrees by azide, bromide, iodide, thiocyanate, or nitro groups was accomplished by heating with the corresponding alkali-metal salt in organic solvents. Extensive chain degradation also occurred, increasing with the nitrogen content of the CN used, and with the alkalinity of the reagent; this was the sole reaction with sodium cyanide. A simplified procedure for preparing CN containing less than 10% nitrogen is described.

INTRODUCTION

As part of a program on polymers containing both azide and nitrate groups[1], it was decided to attempt the preparation of azidodeoxycellulose nitrate (ACN), a material heretofore unknown.

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Two approaches were considered for making ACN. The first method involves preparation of the known azidodeoxycellulose, followed by nitration; we have successfully used this approach, and will report later on the results obtained. The second method comprises possible reaction of nitrocellulose with sodium azide. This is the general type of procedure which we used recently to prepare poly(vinyl azidonitrate) from poly(vinyl nitrate)[1]. The reaction is:

$$RNO_3 + NaN_3 \longrightarrow RN_3 + NaNO_3$$

Other aliphatic azides have been prepared in this way[2,3,4,5,]. The success achieved by Murray and Purves[6] in reacting CN with sodium iodide, with the introduction of up to 33% iodine, also suggested that the corresponding azide might be similarly obtained from sodium azide. The results of this study are reported herein, together with the findings from a brief examination of the reaction of CN with five other nucleophilic reagents, using the procedure developed with azide.

MATERIALS AND PROCEDURE

Caution! Some of the materials described herein can explode when subjected to heat or impact. Although no difficulty was experienced in the present study, these materials should be handled with appropriate care.

The CN used varied in nitrogen content from 4.9 to 13.5%; available military grade material covered the range 12.2 to 13.5%. The CN containing less nitrogen has been made in the past by treating cellulose with mixed acid[6] or with 99% nitric acid in an organic solvent[7]. We have found that it can be conveniently prepared using the latter procedure, but with substitution of 90% nitric acid, which is commercially available, for the 99% acid which is not. Details are as follows:

Cellulose (Buckeye linters, ground in a Waring Blender and in a Wylie Attrition Mill, then dried in vacuo to constant weight) is added at room temperature to a magnetically stirred solution of commercial 90% nitric acid in dichloromethane placed in a stoppered Erlenmeyer flask. After stirring for one hour, the suspension is filtered on a fritted glass filter, and the precipitate is washed with dichloromethane and then with water. The solid is twice boiled with water, filtered, and dried to constant weight in vacuo. The data are summarized in Table 1.

TABLE 1

Preparation of CN with 90% Nitric Acid*

Run	Cellulose Used (gm)	Acid (ml)/ Cellulose (gm)	Yield (gm)	N (%)
1	1.0	4	1.2	5.9
2	5.0	4	5.9	6.0
3	1.0	6	1.3	8.2
4	10.0	6	13.0	8.5
5	1.0	12	1.3	10.0
6	1.0	24	1.4	9.6

*Using 50 ml. dichloromethane/gm cellulose in all cases.

The general procedure for reacting the CN with nucleophiles involved stirring it with the finely ground sodium (or potassium) salt in an organic (or aqueous) solvent at a temperature ranging from 15 to 120° for 2.5 to 120 hours. The reaction mixture was then poured into water for precipitation of the product; if necessary, this could be facilitated by adding a small quantity of 10% hydrochloric acid. The solid was filtered, boiled briefly twice with water to remove solubles, filtered, and dried to constant weight.

The products were evaluated by IR spectrum, elemental analysis, melting behavior and (in some cases) by molecular weight determination. All of them had the same general IR spectrum as the starting CN (peaks at 3500 (broad, OH), 2900 (CH), 1625 (ONO_2), 1260 (ONO_2), 1000-1050 (broad, CHOH), 820 (ONO_2)cm^{-1}, with additional peaks for the entering nucleophile, except as noted below. The samples containing azide groups usually blackened at about 200° without noticeable gas evolution; some of them flashed when small amounts were heated on a spatula over a low Bunsen flame. The iodinated compounds blackened at about 245° with the evolution of iodine.

Molecular weight data were obtained by gel permeation chromatography. (The requisite solubility of these samples in tetrahydrofuran was attained by nitration (dichloromethane solvent, 100% nitric acid, 25°, 0.5 hr.); this procedure has been found not to degrade cellulose, and it is assumed that this also applies to the ACN samples.) A Waters "GPC-2" chromatograph was used, flow rate: 1 ml/min. at 40° using three Ultrastyrogel columns with porosites of 10^3, 10^4, and 10^5 angstroms, and a 254 nm UV detector.

RESULTS

Tests with Sodium Azide

Reaction with CN Containing 10% N and Higher

Blank runs were first made without the addition of azide. The CN (13.5% N), dissolved in dimethyl sulfoxide (DMSO), was recovered quantitatively and unchanged after stirring for 90 hours at 25°. A similar result was obtained with CN (12.6% N) suspended in water for 30 hours at 100°.

Quite different results were noted in the presence of sodium azide. At 25°, a DMSO solution soon turned reddish-brown, and workup after 67 hours gave no solid product, indicating that the CN had been completely degraded to water-soluble fragments. Use of a milder CN solvent (ethylene glycol monomethyl ether), at 85° for 95 hours, likewise gave no solid product. Even when using water, no solid was obtained after only 5 hours at 100° if a surface-active agent was added. It was concluded that the CN undergoes degradation as a result of the alkalinity of the azide; it was noted that a 1-molar solution of sodium azide has a pH of about 9. The alkaline degradation of CN (with basic materials other than sodium azide) has been shown[8] to be extensive and complex, yielding a mixture of water-soluble monomeric and polymeric materials.

Efforts were then made to obtain the desired introduction of azide by modifying the reaction conditons. Although complete destruction of the CN occurred in aqueous medium when a surface-active agent was added, without it a 60% recovery of solid was obtained at 100° in 30 hours. Infrared spectral analysis, however, indicated the absence of azide, showing that degradation occurs under these conditions more easily than the desired reaction. Somewhat more promising results were obtained with DMSO as reaction solvent. Three runs at 25° gave the following: 2.5 hours, 85% weight yield, weak azide IR peak at 2100 cm^{-1}; 25 hours, 60% yield, stronger peak; 40 hours, 40% yield, even stronger peak. It was concluded that the desired reaction does occur, but with substantial degradation.

The third run cited above, made from CN with 12.6% N, gave a product with 15.5% N, which corresponds to replacement of about 1 nitrate group out of 10. When a series of additional trials, using other solvents and conditions, gave no further increase in azide content, it was concluded that this degree of conversion was too low to justify further study of this approach.

A modified procedure was then tried, based on a report[9] that an organic halide was converted in good yield to the corresponding azide with sodium azide in refluxing acetic acid, a medium which should eliminate the alkaline degradation of CN. No introduction of azide was achieved, with CN, however.

From the above trials, it was concluded that CN with a high nitrogen content does not appear promising for conversion to the corresponding azide, a conclusion also reached by Murray and Purves[6] in their study of the reaction of CN with sodium iodide. The use of CN with low N content is therefore considered below.

Reaction with CN Containing Less than 10% N

Unlike the CN considered in the previous section, low nitrogen CN is insoluble in organic solvents, and the reaction is therefore heterogeneous. The DMSO was chosen as the preferred solvent, since it gave products with a higher azide content than dimethylformamide, tetramethylene sulfone, 1-methyl-2-pyrrolidinone, or hexamethylphosphoramide. The ketonic solvents used successfully by Murray and Purves, and in the present study (cf. below) for reacting CN with sodium iodide, proved unsatisfactory with sodium azide. Sodium azide is soluble in DMSO to the extent of about 5 g/100 ml at 70°.

Typical data are given in Table 2. In most cases, the conditions used were: ACN:azide:solvent volume ratio of 1:1:50 at 75° for 48-70 hours. These conditions were not optimized, but it is noteworthy that two 24-hour runs using a third of the usual volume of solvent gave similar results. The yields were quite variable and never exceeded 70% by weight; the lower yields (30-40%) usually coincided with the higher degrees of nitrate group replacement.

The analytical data in Table 2 agree fairly well with partial replacement of the nitrate groups by azide. As noted by Murray and Purves[6], this also occurs in the iodination of CN and nitrated glucosides. Removal of secondary nitrate groups by side reactions is also sometimes noted in iodination, but this does not appear to be a factor in azide replacement under our conditions.

Molecular weight data on three samples of ACN prepared from CN containing 8 to 9.4% N are given in Table 3, together with a typical range of data on production grade CN for comparison. It is evident that very extensive degradation has occurred during the reaction with azide.

TABLE 3

Molecular Weight Data on ACN*

Sample	Mw	Mn	Mw/Mn
1	11,100	2,548	4.37
2	11,100	2,253	4.90
3	15,100	2,245	6.74
CN**	414,000-513,000	55,000-78,000	6.6-8.6

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* Further nitrated for solubility (see text).

**Typical range for production grade CN (12.6-13.5% N).

Tests with Other Nucleophiles

Pattison and Brown[10] have shown that iodides, bromides, thiocyanates and nitriles can be made in fair yields from primary aliphatic nitrates by reaction with the corresponding alkali metal salt, and Bachman and Connon[11] report that sodium nitrite behaves similarly, forming the corresponding nitro compounds. Even prior to the paper by Pattison and Brown, Murray and Purves[6] had noted that low-nitrogen CN reacts smoothly with sodium iodide with the introduction of iodine. Accordingly, we report below the results from exploratory attempts to react CN with six nucleophiles. Five of the salts tested (sodium and potassium iodide, potassium thiocyanate, sodium bromide, and sodium nitrite) all gave a pH in the range 5.6 to 6.5 for a 1 molar aqueous solution. This suggested that yield loss resulting from alkaline degradation might be less with these materials than with sodium azide or sodium cyanide (pH 8.9 and 11.1, respectively).

Iodide

Murray and Purves[6] obtained nearly quantitative weight percent yields of products containing 20-33% iodine with as low as 0.7% nitrogen using ketonic solvents and sodium iodide at 115-120° for 12 hours, starting with CN containing 5 to 9% nitrogen. They also noted extensive degradation with CN containing above 10% nitrogen, and state that secondary nitrate groups "might be removed but were not replaced."

These observations were all confirmed in the present study using their conditions (cf. Table 4), except that we obtained products containing 33% iodine in less time. We also noted that products containing only 15-23% iodine were obtained under the same conditions from potassium iodide - not tested by Murray and Purves, and that use of DMSO under these conditions gave more degradation and a product with only 12.9% iodine. Milder conditions using DMSO gave a much lower iodine content (cf. Table 4). It was therefore concluded that DMSO is inferior to the ketonic solvents for the introduction of iodine.

None of the iodinated products gave IR peaks for - CH_2I at 550 or at 1200 cm^{-1}. The brominated derivatives behaved similarly, as noted below.

Bromide

Pattison and Brown[10] have shown that benzyl nitrate gives 64% of benzyl bromide upon refluxing in acetone with sodium bromide.

Products with 9-15% bromine were obtained from CN using DMSO (cf Table 4). On the other hand, the Murray-Purves procedure, using the same conditions as for sodium iodide (acetonylacetone or 2-butanone at 115-20° for 7 hours), gave nearly quantitative weight percent yields of products containing only 1-3% bromine and about 7% residual nitrogen. This suggests that the use of more drastic conditions with the latter procedures might give good yields of more highly brominated products.

Like the iodides, as noted above, the bromide derivatives of CN did not have IR peaks characteristic of the $-CH_2Br$ group at 550 or 1200 cm^{-1}.

Thiocyanate

Pattison and Brown[10] prepared several thiocyanates in 33-86% yields by refluxing the corresponding aliphatic nitrates with potassium thiocyanate in ethanol.

Using DMSO under fairly drastic conditions (Table 4), we obtained an estimated 50% replacement by the SCN group, although the analytical data in this case are in poor agreement. The Murray-Purves procedure (2-butanol, 115°, 7 hours) gave an 80%

yield of a product with 7.3% S, which suggests that further study using this approach under more drastic conditions may be warranted. These products have IR peaks for the thiocyanate group at about 2100 cm^{-1}, in agreement with Klein and Snowden[12], who prepared a thiocyanodeoxycellulose derivative via the mesylate.

Nitrite

Bachman and Connon[11] have shown that primary aliphatic nitrates can be converted to the corresponding nitro compounds with sodium nitrite in DMSO in about 20% yield; addition of ethyl malonate as a nitrite ester scavenger increased the yield to 40%. Secondary nitrates gave very poor yields. Our attempts to react CN (8 to 9% N) with sodium nitrite in DMSO or in 2-butanone gave either complete degradation or no reaction, as indicated by the absence of IR peaks for the nitro group at 1350 and 1530 cm^{-1}. The addition of ethyl malonate gave some inhibition of degradation, and a 25% yield was so obtained with weak peaks, indicating that the desired reaction had occurred in low yield. Since low-nitrogen CN may have about equal amounts of primary and secondary nitrate groups[6], a low yield is not surprising in the light of the results of Bachman and Connon noted above.

Cyanide

Pattison and Brown[10] obtained fair yields (45-77%) of several nitriles from primary aliphatic nitrates and sodium cyanide.

With CN (6-8% N), we found that degradation to water-soluble products was complete using sodium cyanide in DMSO, except under very mild conditions. This is consistent with the high alkalinity of sodium cyanide as noted above. Under conditions yielding a product (1 hour at 75°, or 7 hours at 25° with DMSO; 7 hours at 115° with 2-butanone), none of the desired reaction occurred, as indicated by the absence of an IR peak for the nitrile group in the product at 2250 cm^{-1}. It should be noted that Klein and Snowden[12] report preparation of a cyanodeoxycellulose from the mesylate, but no data are given.

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TABLE 2

Reaction of Sodium Azide with Low Nitrogen CN in DMSO

	NC Used		Reaction Data			Elemental Analysis[2]						Product Composition[3]		
						C		H		N				
Run No.	N (%)	Nitrate Groups[1]	Hrs	Temp (°C)	Yield Wt. %	Cal.	Fd.	Cal.	Fd.	Cal.	Fd.	Nitrate	Azide	Replacement (%)[4]
1	4.9	0.66	66	85	50	38.8	38.8	5.1	5.5	10.1	10.4	0.33	0.33	50
2	6.0	0.83	48	75	70	38.0	37.2	4.8	5.3	13.5	13.5	0.33	0.50	60
3	8.4	1.33	66	55	70	33.4	33.6	4.0	4.1	13.0	13.6	1.00	0.33	25
4	8.4	1.33	48	75	36	34.5	34.8	4.2	4.5	17.9	18.9	0.66	0.66	50
5	8.5	1.33	48	75	40	35.6	35.8	4.3	4.4	23.1	22.5	0.33	1.00	75

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[1] Nitrate Groups per anhydroglucose (AHG) unit.

[2] The calculated values are for the compositions given in the Product Composition column.

[3] Approximate number of groups per AHG unit.

[4] Of nitrate by azide.

TABLE 4

Reaction of Several Nucleophiles with CN[1]

	Reaction Data			Elemental Analysis[2]								Product Composition[3]		
				C		H		N		Other				Recent
Reagent	Hrs	Temp (°C)	Yield Wt. %	Cal.	Fd.	Cal.	Fd.	Cal.	Fd.	Cal.	Fd.	Nitrate	Other	Replacement[4]
NaI	96	75	80	31.4	30.2	3.8	3.9	7.5	6.4	6.2(I)	6.5	1.22	0.11	8
NaI[5]	7	120	100	29.6	28.3	3.8	4.0	1.0	0.7	34.9(I)	33.1	0.17[6]	0.67	50
NaBr	96	75	95	31.2	30.7	3.8	3.7	5.1	5.0	17.3(Br)	15.5	0.83	0.50	38
KSCN	96	90	60	36.5	30.7	4.0	3.3	8.5	10.7	9.7(S)	10.6	0.66	0.66	50

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[1] CN (8.5% N) used in all cases; it has 1.33 nitrate groups per AHG unit. All runs made with DMSO, except as indicated.

[2] As in Note 2, Table 2.

[3] As in Note 3, Table 2, except as noted.

[4] Of nitrate by the nucleophilic group.

[5] This run made with 2-butanone.

[6] It is assumed that 0.49 nitrate group per AHG is replaced by hydrogen.