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Aromatic Polynitro Ether Derivatives of Cellulose

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SUMMARY

The nucleophilic reaction of sodium cellulosate in the form of membrane or cotton fabric with 2,4-dinitrohalobenzenes, 2,4,6-trinitrochlorobenzene, 2,4,6-trinitrobenzyl bromide, and 2,4,6-trinitrostyrene was investigated. The degree of substitution attained with the dinitroaryl derivatives was much higher than that with the trinitroaryl derivatives. The reaction proceeded through Meisenheimer complexes, which in the case of the trinitro derivatives could be isolated. The ability of the polynitro phenyl ether derivatives of the cellulose to form n - and π -complexes was investigated using naphthalene and *p*-toluidine. No π -complex was formed with the former, and the latter gave complexes only with the 2,4,6-trinitrobenzyl or -phenethyl cellulose derivatives but not with the trinitrophenyl. The results were explained as due to steric hindrance from the polymeric cellulosic backbone.

INTRODUCTION

It is well known that polynitro aromatic compounds such as 2,4-dinitrobenzene and 2,4,6-trinitrobenzene form n - and π -complexes with a wide range of aromatic compounds [1]. It was interesting to attach such compounds to cellulose and investigate the influence of the polymeric backbone on their complexing ability.

The dinitrophenyl ether of cellulose was reported by Rogovin [2]. It was prepared by nitration of cellulose phenyl ether, and degree of substitution (D.S.) values up to 0.75 were obtained. The reaction was, however, accompanied by nitration of the hydroxyl groups of the cellulose. We investigated the direct formation of the polynitrophenyl ethers of cellulose by reaction between sodium cellulose and 2,4-dinitro- and 2,4,6-trinitrohalo derivatives of benzene. The reaction is a nucleophilic aromatic substitution in which Meisenheimer complex intermediates are formed [3]. It was interesting to investigate the influence of the polymeric backbone on complex formation and on the reaction course.

It is known that while in the reaction of 2,4-dinitrohalobenzene with nucleophiles the complex formed is only a transient intermediate, with the 2,4,6-trinitrobenzene derivatives, stable Meisenheimer complexes were reported [4], such as the complex formed between 2,4,6-trinitroanisole and sodium ethoxide [5].

Cellulose 2,4,6-benzyl and 2,4,6-phenethyl ethers were also prepared by reaction of sodium cellulose with 2,4,6-trinitrobenzyl bromide and 2,4,6-trinitrostyrene. In the latter case no anionic polymerization of the monomer was expected [6].

EXPERIMENTAL

Materials

Cellulose membrane (A. H. Thomas Co.), dialyzer tubing No. 4465-A2, and scoured and bleached cotton fabrics were used. DMSO (Fluka) was dried by azeotropic distillation with benzene. Tetrahydrofuran (Fluka) was dried as previously described [7]. 2,4-Dinitrofluorobenzene, 2,4-dinitrochlorobenzene, and 2,4,6-trinitrochlorobenzene (Fluka) were used. 2,4,6-Trinitrobenzyl bromide [8] and 2,4,6-trinitrostyrene [6] were prepared according to the literature.

Preparation of Sodium Cellulosate

The reaction was carried out in a closed glass cylinder. Cellulose membrane (0.52 g) was swelled in DMSO (40 ml) for 6 hr and was solvent exchanged with dry methanol. Sodium methoxide solution (40 ml) of a desired concentration was added. Reaction mixture was shaken mechanically for 15 min, and the methoxide solution was decanted. Unreacted sodium methoxide was removed from the membrane by extraction with DMSO. Sodium cellulosate D.S. was determined by a known procedure [9]. When cotton fabric was used it was first cleaned by a known procedure [10]. Prior to reaction the cotton fabric (1.52 g) was swelled in 17% sodium hydroxide solution (40 ml) for 20 min. The fabric was washed with water, neutralized with 2% acetic acid, and rinsed with water until neutral. Water in the fabric was solvent exchanged with dry methanol, and sodium cellulosate was prepared as described above.

Preparation of Aromatic Polynitro Ether Derivatives of Cellulose

The reaction was carried out in a closed glass cylinder. Sodium cellulosate of cellulose membrane (0.52 g) or cotton fabric (1.50 g) was reacted with the corresponding polynitrohalo derivative of benzene in DMSO (40 ml) for 12 hr under constant mechanical shaking. The reaction mixture was decanted, the membrane was extracted four times with DMSO (40 ml), neutralized with 2% acetic acid solution, and washed with water followed by methanol. Cellulose ether was dried in vacuum at 65° over P_2O_5 .

Complexation by the Aromatic Polynitro Cellulose Ethers

Cellulose ether (0.100 g) was kept in 0.001 M anhydrous solution (50-100 ml) of p-toluidine or naphthalene for 48 hr. Extent of complexation was determined from the decrease of the complexant concentration in solution which was determined from its UV absorption.

RESULTS

Cellulose in the form of cellophane membranes or of cotton fabric was swelled and converted to the sodium cellulosate derivative by exchange reaction with sodium methoxide in methanol [9, 11]. The D.S. of the sodium cellulosate was determined by acid-base titration. The dependence of D.S. on the sodium methoxide concentration is shown in Fig. 1. Under similar reaction conditions the D.S. values obtained with cellulose membrane were higher than those obtained with cotton.

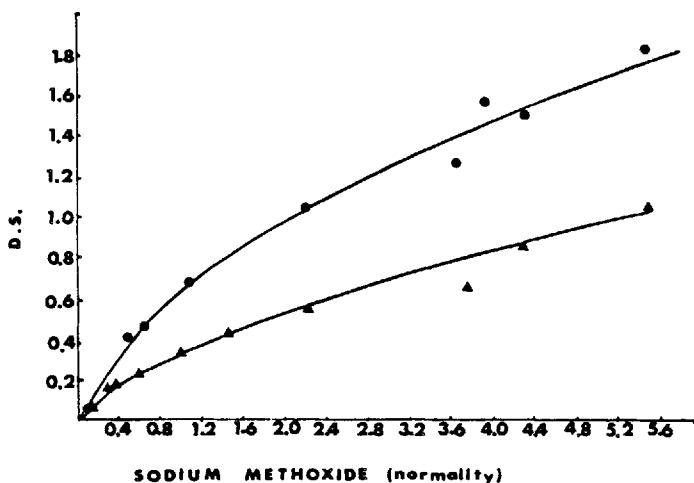


FIG. 1. Dependence of sodium cellulosate D.S. on sodium methoxide concentration. (▲) Sodium hydroxide preswollen cotton fabric. (●) Cellulose membrane.

Reaction with 2,4-Dinitrohalobenzene

The reaction of sodium cellulosate in the form of membrane or fabric with 2,4-dinitrofluorobenzene (excess) was carried out in DMSO (Table 1). The D.S. of the 2,4-dinitrophenyl ether formed

TABLE 1. Reaction of 2,4-Dinitrohalobenzene with Sodium Cellulosate^a

Sodium cellulosate (D.S.)	Weight gain (%)	N (%)	2,4-Dinitrophenyl ether ^b (D.S.)
<u>Series A</u>			
0.20	20.8	2.50	0.20 (0.17)
0.55	62.0	-	0.60
0.55	57.0	-	0.55
0.73	80.9	-	0.78
1.03	112.9	8.33	1.09 (0.95)
1.24	90.8	7.92	0.88 (0.87)
0.44 ^c	43.9	-	0.43
0.75 ^c	62.7	-	0.61
1.16 ^c	92.8	6.98	0.91 (1.02)
<u>Series B</u>			
0.13	13.4	-	0.13
0.21	20.5	2.82	0.20 (0.20)
0.33	34.0	3.73	0.33 (0.28)
0.53	48.8	5.31	0.47 (0.45)
0.66	40.9	-	0.40
0.74	37.1	-	0.36

^aSodium cellulosate of cellulose membrane (0.52 g) (Series A) and cotton fabric (1.50 g) (Series B) were reacted with 2,4-dinitrofluorobenzene (2 ml, 15.6 mmole) in DMSO (40 ml) at room temperature for 24 hr.

^bDetermined from weight gain. Values in brackets calculated from per cent N.

^c2,4-Dinitrochlorobenzene (3.35 g, 15.6 mmole) was used instead of 2,4-dinitrofluorobenzene.

was determined from weight gain and nitrogen analysis. Essentially the same results were obtained by both methods. Any deviations found should be attributed to inhomogeneity of the samples. Quantitative reactions were obtained with the cellulose membrane up to cellulose D.S. values of 1. With the cotton fabric the maximum D.S. of the ether derivative obtained was only 0.5, even on increasing the cellulose D.S.

Similar results were obtained in the reaction with 2,4-dinitrochlorobenzene (Table 1).

TABLE 2. Reaction of 2,4,6-Trinitrochlorobenzene with Sodium Cellulosate^a

Sodium cellulose (D.S.)	Weight gain (%)	2,4,6-Trinitrophenyl ether ^b (D.S.)
<u>Series A</u>		
0.92	8.8	0.069 ^c
0.97	9.3	0.071
0.98	7.5	0.060
1.26	25.1	0.190 ^d
<u>Series B</u>		
0.50	2.1	0.02
0.50	4.4	0.04
0.66	5.0	0.04

^aReaction was carried between sodium cellulosate of cellulose membrane (0.52 g) (Series A) or cotton fabric (1.50 g) (Series B) and 2,4,6-trinitrochlorobenzene (1.0 g, 4 mmole) in benzene at room temperature for 24 hr.

^bDetermined from weight gain.

^c2.45% N, corresponding to a D.S. of 0.11

^d3.38% N, corresponding to a D.S. of 0.16.

Reaction with 2,4,6-Trinitrochlorobenzene

The reaction with 2,4,6-trinitrochlorobenzene (picryl chloride) proceeded with more difficulty than that with the 2,4-dinitrohalobenzenes. Although molar excess of the reagent was used as well as high sodium cellulosate D.S., only low D.S. of etherification were observed both in the case of cellulose membrane and fabric (Table 2). Most of the alcoholate groups did not react. During reaction the cellulosic material became deep red in color. The color disappeared only on neutralization with acetic acid. The course of reaction was also followed from the decrease in the concentration of the free picryl chloride, determined by titration according to a known procedure [12]. It was interesting to find out that although the D.S. obtained was low, about 50% of the picryl chloride (3.82 mmole/g cellulose) was reacted after 10 hr (Fig. 2).

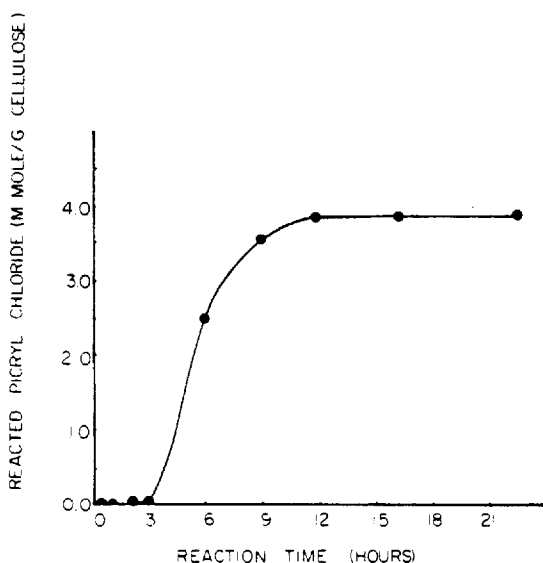


FIG. 2. Reaction of 2,4,6-trinitrochlorobenzene with sodium cellulosate. Reaction was carried between sodium cellulosate (0.52 g) of cellulose membrane and 2,4,6-trinitrochlorobenzene (1.00 g) in benzene (36 ml) at room temperature.

This value corresponds to D.S. = 0.21. However, after neutralization of the membrane, the D.S., as determined from weight gain, was only 0.07. To find the cause for this, an experiment was carried out using sodium cellulosate (membrane) having D.S. = 0.92. At the end of the reaction no neutralization of the reaction mixture was carried out. The membrane was isolated and its weight gain, nitrogen, and chlorine contents were determined. The D.S. values calculated from these results were 0.34, 0.24, and 0.32 respectively. After neutralization with dilute acetic acid, the D.S., as determined from weight gain, was 0.07 and from nitrogen content 0.11. This clearly shows that only a portion of the picryl chloride which initially reacted with the sodium cellulosate remained attached to the cellulose after neutralization.

Reaction of 2,4,6-Trinitrobenzyl bromide and 2,4,6-Trinitrostyrene with Sodium Cellulosate

Since in the reaction with picryl chloride only low D.S. values of 2,4,6-trinitrophenyl ether groups were obtained, we investigated the reaction of sodium cellulosate with 2,4,6-trinitrobenzyl bromide and 2,4,6-trinitrostyrene in order to achieve higher D.S. values of ether derivatives containing the 2,4,6-trinitrobenzene group. Sodium cellulosate membrane was reacted with 2,4,6-trinitrobenzyl bromide (Table 3). Only low D.S. values were obtained. With 2,4,6-trinitrostyrene, even on using high cellulosate D.S., the 2,4,6-trinitrophenethyl ether derivative obtained had a very low D.S. (Table 3).

Complexation by the Aromatic Polynitro Ether Derivatives of Cellulose (Table 4)

The ability of the aromatic polynitro ether derivatives of cellulose to form n - and π -complexes was investigated. This was studied on the one hand using an aromatic amine *p*-toluidine, and on the other a polycyclic aromatic hydrocarbon, naphthalene. *p*-Toluidine in THF was brought in contact with the polynitro ether derivatives of cellulose. Complexation was determined from the disappearance of *p*-toluidine from solution. It was found that unmodified cellulose membrane absorbed 0.277 mmole of *p*-toluidine/g cellulose and absorption by the modified cellulose was corrected accordingly. The di- and

TABLE 3. Reaction of 2,4,6-Trinitrobenzyl Bromide and 2,4,6-Trinitrostyrene with Sodium Cellulosate (Cellulose Membrane)^a

	Sodium cellulosate (D.S.)	Weight gain (%)	Ether (D.S.)
2,4,6-Trinitrobenzyl bromide	1.22	16.5	0.12
2,4,6-Trinitrobenzyl bromide	1.21	19.9	0.15
2,4,6-Trinitrostyrene	1.21	15.7	0.24
2,4,6-Trinitrostyrene	1.28	14.5	0.21

^aReaction was between sodium cellulosate of cellulose membrane (0.52 g) and molar excess of 2,4,6-trinitrobenzyl bromide (1.0 g, 3.3 mmole) and 2,4,6-trinitrostyrene (1.0 g, 4.1 mmole) in DMSO (40 ml) at room temperature for 24 hr.

TABLE 4. Complexation of p-Toluidine by Aromatic Polynitro Derivatives of Cellulose^a

Ether derivative	Cellulose-ether		Complexed p-toluidine ^b (mmole/g)	Complexed aromatic polynitro groups ^c (%)
	(D.S.)	(g)		
2,4-Dinitrophenyl cellulose	0.17	0.06	0.00	0.0
	0.33	0.03	0.00	0.0
2,4,6-Trinitrophenyl cellulose	0.11	0.06	0.00	0.0
2,4,6-Trinitrobenzyl cellulose	0.15	0.04	0.57	73.3
2,4,6-Trinitrophenethyl cellulose	0.24	0.08	0.24	50.0
Cellulose	-	0.06	0.28	-

^aComplexation was carried out in 0.001 M p-toluidine solution in THF (50 ml) at room temperature.

^bDetermined from the decrease in p-toluidine concentration, corrected for absorption by the cellulose.

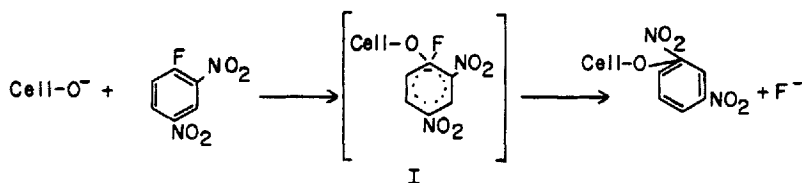
^cPercent of the total aromatic polynitro ether groups.

trinitrophenyl ether derivatives of the cellulose did not form any n -complexes with *p*-toluidine, but the ethers having the trinitrophenyl groups further away, namely the 2,4,6-trinitrobenzyl and -phenethyl ether derivatives gave complexes. Thus up to 77% of the trinitrophenyl groups in the case of the benzyl ether derivative were complexed in THF solution, 50% in aqueous solution and 60% in methanol.

Complex formation with naphthalene was studied using 0.001 M naphthalene solution in THF. No absorption of naphthalene by cellulose itself was observed, and none of the aromatic polynitro ether derivatives formed π -complexes with naphthalene.

DISCUSSION

The nucleophilic substitution reactions in which the polynitrophenyl ether derivatives of cellulose were formed proceed via a Meisenheimer complex intermediate, which in the case of 2,4-dinitrofluorobenzene may be formulated as follows:



The intense red color which developed on the cellulose membrane or fabric during the reaction and which disappeared later should be attributed to the formation of such a complex (I). In the reaction of 2,4,6-trinitrochlorobenzene, it was shown that the extent of substitution found prior to neutralization was much higher than that obtained after it. The cellulose membrane isolated before neutralization contained chlorine and in an amount which was in agreement with the nitrogen content and the weight gain of the membrane, indicating clearly that a polymeric stable Meisenheimer complex was formed of the type of I and the reaction stopped, at least partly, at this stage. On neutralization the complexes formed either decompose to reactants in a reversible reaction or yield the polynitrophenyl ether derivative.

From the low D.S. values obtained after neutralization, it is seen that about 2/3 of the Meisenheimer complexes decompose back to the reactants.

The much higher D.S. values obtained in the reaction with the dinitrohalobenzenes, as compared with 2,4,6-trinitrochlorobenzene, although the latter is more reactive in nucleophilic substitution, should be attributed to steric hindrance from the glucopyranoside rings. This steric hindrance, which is present also in the Meisenheimer complex, may also help in reversing the reaction, thus lowering the D.S. The reaction of 2,4,6-trinitrobenzyl bromide and 2,4,6-trinitrostyrene with sodium cellulose, which gave low D.S. values, may also be attributed to steric factors. Although the reaction center is removed from the benzene ring by one or two carbon atoms, steric hindrance still prevails.

Higher D.S. values were obtained with the cellulose membrane as compared with cotton fabric. This may be attributed to the less crystalline nature of the cellophane which permits more permeability of the reagents and lends itself to greater swelling and also to its lower molecular weight.

The complex formation studies have shown that with naphthalene no π -complex could be isolated with all the aromatic polynitro ether derivatives of cellulose investigated. With *p*-toluidine complexes were formed only with the benzyl and phenethyl ethers but not with the phenyl ether derivatives. These results are in contrast with what is known concerning the ease of formation of complexes of *p*-toluidine and naphthalene with simple 2,4-dinitrobenzene and 2,4,6-trinitrobenzene derivatives [13].

Steric factors, connected with the polymeric cellulosic backbone, may be the cause for this behavior. According to the Mulliken concept of complex formation [14], interactions of aromatic donors and acceptors should be most favored if the rings are parallel and are oriented in the same way with their centers directly over each other. It seems that the polymeric cellulosic backbone interferes with such an arrangement and therefore with complex formation. The complex formed between *p*-toluidine and the 2,4,6-trinitrophenyl group in 2,4,6-trinitrobenzyl and 2,4,6-trinitrophenethyl cellulose should be an *n*-complex in which the amino group rather than the π -electron system of the ring attached to the nitrogen is the coordination center of the donor. Therefore, by removal of the trinitrobenzene ring by one carbon atom steric hindrance is decreased, and that is why complex formation became possible and more than 50% of the trinitrobenzyl groups of the cellulosic ether participated in complex formation.

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