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Charge Transfer Complexes of 1-Naphthylmethyl Cotton Cellulose

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ABSTRACT

A cotton cellulose derivative that forms charge-transfer complexes was prepared in yarn form. A charge-transfer complex is composed of two partners, one referred to as the donor and the other as an acceptor of electrical charge. In the present investigation, a donor was chemically bound to the cotton. It was shown that the modified donor cellulose adsorbs various acceptors from solution. Celluloses possessing donor or acceptor moieties are potentially useful as chromatographic agents and also in medicinal chemistry where a controlled release of a chemical agent is desired.

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INTRODUCTION

There has been considerable interest in the preparation and properties of polymers that form charge-transfer complexes [1-4]. The usual synthetic approach to these polymers has been homopolymerization of appropriate donor or acceptor monomers. Recently we have undertaken a study to explore the possibility of synthesizing charge-transfer (CT) complex-forming polymers from cellulose, a naturally occurring polymer. In a previous communication [5] we reported the preparation of 3,5-dinitrobenzoyl cotton cellulose (DNBC). This material was found to be a polymeric π-acceptor capable of forming polymer-donor CT complexes with a wide variety of donors. Consequently, when DNBC yarn was immersed in a solution of donor, the donor was adsorbed by the yarn. Occurring simultaneously with adsorption was the formation of characteristic yellow or orange colors on the surface of the yarn.

Since no previous example of a cellulose derivative which can function as a π-donor has been established, we wanted to provide at least one such example. While this study was in progress, Avny et al. [6] reported the results of a similar study employing cotton celluloses modified with several potential donors. These investigators found no complexation of π-acceptors by 1-naphthylmethyl cotton cellulose and similar derivatives. In contrast to these workers' results, we have found that 1-naphthylmethyl cotton cellulose (NMCC) does form π-complexes with known acceptors under the proper conditions of acceptor concentration, solvent polarity, and degree of cellulose substitution.

EXPERIMENTAL

The cellulose was loose twist 12/3 (tex-151) Pima kier boiled cotton yarn. The sym-trinitrobenzene, 2,4,7-trinitrofluorenone, p-benzoquinone, 1-chloromethylnaphthalene (Aldrich), and chloroform (Fisher) were commercial reagent grade chemicals used without further purification. NMCC was prepared by the method of Wade et al. [7]. The number of 1-naphthylmethyl groups introduced per anhydroglucose unit (DS) was calculated from the weight gain. The DS of the NMCC samples employed in this study ranged from 0.45 to 0.52.

Complexation of the various NMCC yarn samples of known weight (0.6 to 1.0 g) and DS was accomplished by immersing the yarn in 50 ml of chloroform solution containing a known amount of acceptor. Experiments were conducted at room temperature ($25 \pm 1^\circ$C). After equilibrating for 24 hr, the yarn was removed and dipped for 1 to 2 sec in chloroform to remove residual acceptor solution adhering to the surface of the yarn. The amount of bound acceptor was determined by

weight gain and by Kjeldahl nitrogen analyses when solutions of trinitrobenzene and trinitrofluorenone were employed. A correction in the weight of bound acceptor as determined from weight gains was necessary because the NMCC lost 1.2 to 1.3% of its weight upon immersion in chloroform. Control experiments in which samples of untreated cotton yarn were equilibrated with the highest concentrations of trinitrobenzene and trinitrofluorenone showed some adsorption of these compounds by the yarn.

RESULTS AND DISCUSSION

The percent weight gain undergone by NMCC yarn as a function of acceptor concentration (A) is shown in Table 1. The acceptor concentration is given as the residual concentration at equilibrium, that is, corrected for the amount of acceptor taken up by the NMCC. For each of the three acceptors studied, NMCC adsorbed significantly greater amounts of acceptor than unmodified cotton. In addition to the enhanced adsorption, we observed that the resulting NMCC-acceptor complexes were distinctly colored. The trinitrobenzene complex was yellow-gold and the trinitrofluorenone treated yarn was fluorescent orange. This suggests that the observed adsorption phenomenon is the result of acceptor immobilization on the cellulose via discrete CT complexes involving the bound naphthylmethyl groups.

Examination of the data collected in Table 1 showed that the binding of the three acceptors employed in this study could be described by the following relationship [8]:

$$\frac{1}{r} = \frac{1}{n} + \frac{1}{nKA} \tag{1}$$

where r is the number of moles of bound acceptor per mole of NMCC anhydroglucose units at a given concentration of acceptor (A), n is the number of accessible binding sites per mole of NMCC anhydroglucose units, and K is the equilibrium constant for the adsorption of acceptor by NMCC:

$$NMCC_{solid} + A_{solution} \rightleftharpoons (NMCC \cdot A_n)_{solid} \tag{2}$$

The ratio f of (bound acceptor molecules)/(naphthylmethyl groups in NMCC) is given by f = r/DS and can thus be readily calculated from the tabulated values of r.

The calculated values of the slope and intercept derived from a linear regression treatment of the data found in Table 1, in accordance with Eq. (1), permitted us to solve for the values of K that are

TABLE 1. Adsorption of Acceptors by 1-Naphthylmethyl Cotton Cellulose Yarn[a]

Yarn DS	(A) Residual conc	% wt gain	Theoretical % N[b]	% N Found	(r) moles bound of acceptor[b] per mole of NMCC anhydroglucose units (10^{-1})
			Trinitrobenzene		
0.463	2.90 (10^{-1} M)	15.4	2.65	2.66	1.64
	1.92	11.3	2.02	2.05	1.20
	1.35	9.31	1.70	1.74	0.99
	0.95	6.41	1.20	1.40	0.68
	0.72	5.03	0.95	1.08	0.53
	2.90[c]	1.40			
			Trinitrofluorenone		
0.446	4.60 (10^{-2} M)	7.15	0.90	0.93	0.51
	2.83	5.42	0.69	0.62	0.39
	1.94	3.69	0.48	0.45	0.27
	1.37	2.93	0.38	0.34	0.21
	0.99	2.33	0.30	0.25	0.17
	4.60[c]	1.10			
			p-Benzoquinone		
0.518	8.32 (10^{-1} M)	3.61			0.97
	6.00	2.83			0.76
	4.00	2.45			0.66
	2.96	1.61			0.45
	8.32[c]	0.00			

[a]Solvent is $CHCl_3$.
[b]Based on weight gain.
[c]Control using unmodified cotton yarn.

TABLE 2. Formation Constants for 1-Naphthylmethyl Cotton Cellulose-Acceptor Complexes

Acceptor	$K(\underline{M}^{-1})$	$K_{naphthalene}(M^{-1})$	Refs.	n	DS	Correlation coeff
2,4,7-Trinitrofluorenone	18	0.7	12	0.11	0.45	0.995
sym-Trinitrobenzene	1.4	1.8	11	0.59	0.46	0.997
p-Benzoquinone	0.8	0.3[a]	13	0.26	0.52	0.972

[a]The solvent was CCl_4.

presented in Table 2. For the purpose of comparison, literature values of the formation constants for the corresponding naphthalene complexes in solution have also been collected in this table. It is of interest to note that the K values for complexes of NMCC with trinitrobenzene and p-benzoquinone are about the same as solution formation constants for the corresponding naphthalene complexes, while the K value for the NMCC-trinitrofluorenone complex is about 25 times the literature K value for the naphthalene-trinitrofluorenone complex. In contrast to the conclusions of Avny et al. [6], our results indicate that steric hindrance by the cellulose backbone is not prohibitive to complexation. The failure to detect complexation of π-acceptors by NMCC in the study by Avny et al. [6] can probably be attributed to the low concentrations of acceptor employed, and to competition effects of the tetrahydrofuran solvent which has known donor properties [9].

Previous applications of CT complexes in organic chemistry have been discussed by Foster [10]. Since complexation is a reversible process, donor or acceptor celluloses could prove to be useful chromatographic agents. Moreover, in medicinal chemistry, it is often desirable to have a slow or controlled release of a chemical agent. Such a situation might be achieved using polymer acceptor or donor molecular complexes.

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SUMMARY

1-Naphthylmethyl cotton cellulose (NMCC), a polymeric donor, was prepared, and its interaction with three known π-acceptors in chloroform solution studied. For the three acceptors investigated, polymer-acceptor charge-transfer complexes were observed.

From a study of the concentration dependence of the amount of acceptor adsorbed by NMCC, it was found that the cellulose-bound naphthylmethyl groups participating in binding have approximately the same affinity for sym-trinitrobenzene and p-benzoquinone as does naphthalene in solution for these same acceptors. The affinity of the immobilized naphthylmethyl group for 2,4,7-trinitrofluorenone was, however, about an order of magnitude greater than expected.

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