

Steric Effects in the Preparation and Saponification of Some Fibrous Cellulose Esters*

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Synopsis

Two reaction paths which can be followed when an acid chloride reacts with an alcohol are discussed. The role of pyridine as solvent and catalyst in this reaction is described. The importance of inductive and resonance effects and the size and arrangement of groups near the carbonyl are emphasized. The heterogeneous preparations of seven cellulose partial esters, the phenylacetate, benzoate, trimethylacetate, triphenylacetate, β,β,β -triphenylpropionate, α -(4-biphenyl)phenylacetate, and mesitoate are described. Pronounced interference with esterification is noted only in the preparation of the triphenylacetate. Steric hindrance and a poor ability to ionize are considered to be responsible for this result. Outstanding resistance to saponification, thought to be the result of steric hindrance and a reduced tendency to ionize, is reported for three of the cellulose esters, the triphenylacetate, the β,β,β -triphenylpropionate, and the mesitoate.

The goal of this work was to study the feasibility of preparing directly from cotton cellulose, sterically hindered, fibrous esters, as indicated by their response toward a standardized saponification test. However, at the same time advantage was taken of the opportunity to consider factors involved in the esterification reaction.

Since saponification requires the addition of a hydroxyl ion to the carbonyl carbon atom of an ester¹ and since most cellulose esters are readily saponified,² it follows that the alcoholic portion of these esters cannot provide enough steric protection to prevent attack. Hence, if alkali resistance is to be obtained, most of the protection must be brought in with the acyl group.

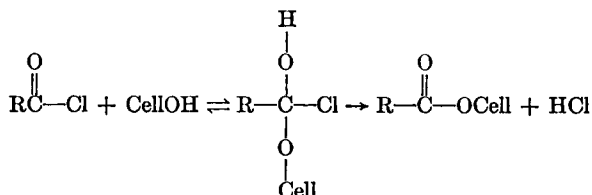
Although a number of methods³ have been used to prepare cellulose esters, the pyridine-acid chloride procedure seemed to be best suited for this work for at least two reasons. As Malm and Hiatt⁴ have stated, a variety of acid chlorides may be depended upon to react with cellulose in the presence of pyridine and therefore the method is rather general.

* Paper presented at the 142nd National Meeting of the American Chemical Society, Division of Cellulose, Wood, and Fiber Chemistry, Atlantic City, New Jersey, September 9-14, 1962.

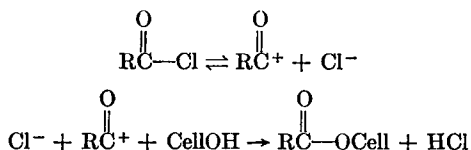
In addition, pyridine combines with the hydrogen chloride produced during esterification and thus prevents acid degradation of the cellulose.

Two paths can be followed in most reactions of acid chlorides⁵

Path A:



Path B:



With an alcohol, such as cellulose, path A involves carbonyl addition. Path B is applicable where ionization is involved.

Reactions occurring by path A are subject to steric hindrance since the reaction intermediate has four groups attached to what was formerly a carbonyl carbon with only three attached groups. Reactions by way of path B are not subject to steric hindrance, since not more than three groups are ever required at the carbonyl carbon.

Since pyridine exerts its catalytic effect on the reaction of an acid chloride by path A to form the reaction intermediate, the acylpyridinium ion,¹ one must question Royal's statement that the reaction of an acid chloride with an alcohol in pyridine is not subject to steric hindrance.⁶

Triphenylacetyl chloride and mesityl chloride were used in the present study because they were known to give highly sterically hindered esters of low molecular weight alcohols. For example, Schmidlin and Hodgson⁷ have reported that ethyl triphenylacetate is highly resistant to saponification, and Norris and Young⁸ have found that methyl mesitoate is extremely resistant to alkaline hydrolysis. However, the corresponding esters of cellulose apparently never have been studied.

Trimethylacetyl chloride, β,β,β -triphenylpropionyl chloride and α -(4-biphenyl)phenylacetyl chloride were used by the present authors to clarify some of the results obtained with the triphenylacetyl chloride.

Phenylacetyl chloride and benzoyl chloride were included as reference controls.

EXPERIMENTAL

Materials

Cellulose was in the form of 2-ply mercerized cotton yarns obtained from a commercial source. The pyridine was reagent grade. Commercial

benzoyl chloride was redistilled before using. Eastman* phenylacetyl chloride was used as received. Eastman trimethylacetic acid was converted to the acid chloride by means of thionyl chloride. The other acids were prepared in this laboratory by published procedures and then converted to the acid chlorides by the thionyl chloride procedure. The properties of these acid chlorides are given in Table I.

TABLE I
Physical Properties of the Acid Chlorides

Acid chloride	Molecular weight	M.p., °C.		B.p., °C.	
		Found	Literature	Found	Literature
Trimethylacetyl	120.5	—	—	103–105	103–104 ^a
Triphenylacetyl	306.5	127	127–128 ^b	—	—
β,β,β -triphenylpropionyl	320.5	130	132 ^c	—	—
α -(4-Biphenyl)phenylacetyl	306.5	96	99–101 ^d	—	—
Mesityl	182.6	—	—	110/9 mm.	124/26 mm. ^e
Phenylacetyl	154.6	—	—	—	94–95/12 mm.
Benzoyl	140.6	—	—	—	197

^a Data of Brown.⁹

^b Data of Greene et al.¹⁰

^c Data of Hellerman.¹¹

^d Data of Blicke and Grier.¹²

^e Data of Cohen and Schneider.¹³

Pretreatment of Yarns

One-gram skeins of the air-dried mercerized cotton yarns were reactivated by treatment with 17.5% sodium hydroxide, washed with water, 5% acetic acid, and water, and solvent-exchanged to pyridine.

The skein to be used in the reaction with the triphenylacetyl chloride was further dried¹⁴ by storing it in pyridine over bone-dry cotton.

Preparation of the Cellulose Esters

The acid chloride, in the ratio of 2.5 or 5.0 moles per mole of anhydroglucose was dissolved in 17.1 ml. of pyridine contained in a small round bottom flask. A 1-g. skein of pyridine-exchanged yarn was then centrifuged or pressed between filter paper and added to the solution. The flask containing the mixture was then shaken in an oil bath at 100°C. for 1.5 hr. At the end of this time the reacted yarn was washed three times with pyridine, once with approximately 50:50 pyridine and methanol, three

* Trade names have been used to identify materials used in the work, but such use does not imply endorsement or recommendation by the U. S. Department of Agriculture over the products not mentioned.

times with methanol, once with approximately 50:50 methanol and water, and then with running water. The sample was centrifuged between washes. The treated yarn was then oven-dried at 115°C. In every case the fibrous structure and acceptable textile strength of the original cellulose were maintained.

First attempts to prepare cellulose triphenylacetate by heating cellulose with triphenylacetyl chloride in pyridine were unsuccessful. Even when the pyridine-exchanged yarns were specially dried only slight add-ons were obtained.

Low ratios of acyl chloride to anhydroglucose were necessitated in the cases of α -(4-biphenyl)phenylacetate and benzoate because of the tendency for the yarn to disperse when more concentrated reaction mixtures were used.

Since chlorine and nitrogen are sometimes introduced in side reactions¹⁵ during the acid chloride-pyridine esterification of cellulose, qualitative tests were performed on the base-resistant esters, i.e., the triphenylacetate, the β,β,β -triphenylpropionate, and the mesitoate. The tests showed only traces of chlorine and no nitrogen.

Saponification of the Cellulose Esters

The alcoholic alkali method for the determination of acyl values, as given by Genung and Mallatt,⁹ was used to test the cellulose esters for resistance to saponification. Samples (0.5 g.) of the treated yarns were suspended in 40 ml. of 0.25*N* alcoholic (95% ethanol-5% water) sodium hydroxide and allowed to stand overnight. A slight excess of 0.5*N* hydrochloric acid was then added, and the yarns were left in the acid solution for 4 hr. After this time, the samples were back-titrated with 0.25*N* aqueous sodium hydroxide to a phenolphthalein endpoint.

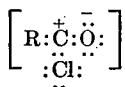
Small portions of the esters were also saponified for definite time intervals. The samples differed somewhat from the others in size and degree of substitution but otherwise the conditions were maintained comparable.

RESULTS AND DISCUSSION

Esterification

The results of esterification reactions are presented in Table II. The arrangement is such that reactions by path A above (i.e., polarity, reaction intermediate) would be favored at the top of the table and those by path B (ionization) at the bottom. However, no hard and fast commitment of the exact order is intended.

The reactivity of an acid chloride is dependent upon inductive, resonance and steric effects. In path A reactions of acid chlorides, development of the positive charge at the carbonyl carbon in the structure



favors reactivity with the nucleophilic oxygen of the cellulose. Substituents, R, which attract electrons increase this positive character and those which provide electrons tend to decrease it. Where substituents increase the electron density near the chlorine atom, the tendency to ionize and react by way of path B also increases.

Inductive effects can operate through a saturated carbon atom next to the carbonyl, but resonance effects cannot. Resonance interaction with the carbonyl requires the presence of an unsaturated carbon atom next to the carbonyl. Of the acid chlorides used in this study only the aroyl compounds have such an unsaturated carbon. The possible interaction is illustrated below:

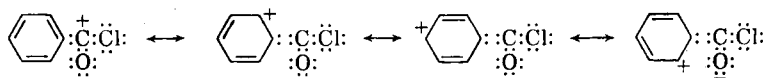


TABLE II
Data on Cellulose Esters

Ester	Acid chloride to anhydro- glucose mole ratio	Substitution based on add-on, DS	Acyl based on add-on, %	Acyl based on saponification, %
Triphenylacetate	5:1	0.02	3.8 ^a	0.3
α -(4-Biphenyl)- phenylacetate	2.5:1	0.65	52.1	47.6
Phenylacetate	5:1	0.26	16.0	17.8
β,β -Triphenyl- propionate	5:1	1.01	64.2	5.7
Trimethylacetate	5:1	1.16	38.0	37.3
Benzoate	2.5:1	1.00	39.5	42.6
Mesitoate	5:1	0.95	46.5	1.8

^a The original add-on was 4.3%. Two treatments with 50 ml. of methanol plus 2 ml. of concentrated HCl to remove trityl groups, which might have added in a side reaction, lowered this value to 3.9%. This procedure for the removal of trityl groups from cellulose was reported previously by Hearon et al.¹⁶

In considering whether steric effects play a part in heterogeneous esterification reactions the accessibility of the reagents to the cellulose itself needs to be kept in mind. Accessibility may be influenced by structural factors such as swelling, hornification, crystallinity, crystallite size, orientation and substituent volume, all of which to a greater or lesser extent influence the rate of diffusion. In the present study the diffusion factors, with the exception of substituent bulk, were maintained constant by use of a constant source of cellulose, brought to a high state of accessibility by alkali treatment, followed by solvent exchange to pyridine. As to substituent bulk a casual examination of the molecular weights of the chlorides (Table I) shows that there is no evident relationship between this and degree

of substitution reached. It is the arrangement of the bulky groups in the chlorides which determines the steric effect.

A tendency toward gradual improvement of esterification is noted with descent from the top of the table. In considering the results it should be kept in mind that both the α -(biphenyl)phenylacetate and the benzoate resulted from half the mole concentrations of the chlorides as did the other esters, and doubtless both would have given somewhat higher substitutions had equal concentrations been used. Therefore, it may be that the benzoyl chloride would have maintained the improvement had an equal concentration been possible.

As stated earlier, it was extremely difficult to obtain the cellulose triphenylacetate from the corresponding chloride. Steric hindrance and a poor ability to ionize are considered to be responsible for this result.

When crowding at the carbonyl groups was reduced, either by rearranging the phenyl groups on the α -carbon, as in α -(4-biphenyl) phenylacetyl chloride, or by introducing a methylene group between the trityl and carbonyl, as in β,β,β -triphenylpropionyl chloride, high add-ons were obtained. Similarly, a high add-on was obtained when the phenyl groups of the triphenylacetyl chloride were replaced with the smaller methyl groups.

The ready formation of cellulose mesitoate undoubtedly depends primarily upon the ability of the sterically hindered mesitoyl chloride to ionize before reacting with the cellulose. This ionization mechanism has been used to explain the rapid reaction between mesitoyl chloride and methanol.⁵

The reason for the low substitution with phenylacetyl chloride is not presently clear. A somewhat similar observation was made by Mench.¹⁷

Saponification

As we have noted, both ionization and addition reactions are possible in esterification. On the other hand only the addition-type reaction is available in saponification. Furthermore, in the case of acyl chlorides the tendency to form addition intermediates with cellulose should decrease as we proceed from top to bottom of the tables, except for steric effects. This same order should also hold for ease of saponification, again barring steric effects, since acyl groups still retain their same order of electronegativity which they have carried over into the ester. Therefore, the tendency to form an addition intermediate with the OH^- ion should decrease from top to bottom of Table II or III.

The results of saponification studies are shown in Tables II and III, the latter representing a repetition of the measurements at a number of preselected time intervals. In Table II results are expressed in absolute quantity of acyl present, in Table III on the basis of the total acyl cleaved. Barring steric effects the rate of saponification would be expected to decrease as we proceed from the top to the bottom of the table.

Both tables show essentially the same results. Three of the esters studied, the triphenylacetate, the α -(4-biphenyl)phenylacetate, and the

TABLE III
Proportion of Cellulose Ester Saponified After Different Periods

Cellulose ester	Acyl based on add-on, %	Cellulose saponified after various times, %			
		2 hr.	4 hr.	8 hr.	16 hr.
Triphenylacetate	3.8	—	—	—	8
α -(4-Biphenyl)phenyl- acetate	51.0	—	79	100	100
Phenylacetate	11.8	93	98	99	100
β,β,β -Triphenylpropi- onate	64.2	0.3	0.6	1.2	2.5
Trimethylacetate	28.6	54	60	68	78
Benzoate	45.2	57	79	91	100
Mesitoate	46.5	0	0	0	0

phenylacetate are derivatives of α -phenyl-substituted acetic acids. The ease with which the last two saponified is attributed to the presence of at least one α -hydrogen, which, without any β -substituents to reinforce it, is too small to be much of a shield for the carbonyl group. The reluctance with which the triphenylacetate saponified is attributed to effective carbonyl shielding by the three α -phenyl groups. Gyr,¹⁸ working with the methyl esters of phenylacetic, diphenylacetic, and triphenylacetic acids, found that the rate of saponification fell progressively as the number of α -hydrogen atoms decreased and that the methyl triphenylacetate did not saponify.

High resistance to saponification of cellulose β,β,β -triphenylpropionate is best explained by an examination of a molecular model of this compound. Such an examination shows that even with two α -hydrogen atoms present there is still a considerable amount of shielding of the carbonyl group due to the presence of the three large phenyl groups in β -positions.

That size of the group used is important in bringing about steric hindrance is demonstrated by the fact that replacement of the three phenyl groups on the α -carbon with the three methyl groups produce an ester, cellulose trimethylacetate, which is less resistant to saponification than cellulose triphenylacetate.

Cellulose mesitoate, as expected, showed high resistance to saponification. Most of the hindrance to hydroxyl attack undoubtedly arises from the two *ortho* methyl groups flanking the carbonyl part of the ester. Cellulose benzoate, in which there are no flanking methyl groups, saponified readily.

CONCLUSIONS

Steric effects in the reaction of an acid chloride with cellulose are not as clear cut as those involved in the saponification of the cellulose ester derived from it. Hindrance which would seriously interfere with carbonyl addition

in the acid chloride could be reduced to a minimum if the acylium ion should form before reaction with the cellulose.

Once the cellulose ester has formed, however, the tendency to ionize is reduced since the carbon to oxygen bond is more stable than the carbon to chlorine bond. Here, addition to the carbonyl of the nonionized ester is the usual reaction, and the effects of steric factors are more predictable.

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Résumé

La réaction d'un chlorure d'acide avec un alcool peut suivre deux voies différentes qui sont soumises à discussion. On décrit le rôle de la pyridine comme solvant et catalyseur de cette réaction. On insiste sur l'importance des effets inductifs et de résonance de même que de la grandeur et de la disposition des groupes voisins du carbonyle. On décrit la préparation en système hétérogène de 7 celluloses partiellement estérifiées: phénylacétate, benzoate, pivalate, triphénylacétate, β,β -triphénylpropionate, α -(4, biphenyl)phénylacétate et mésitoate. Une interférence prononcée avec l'estérification est uniquement notée dans le cas du triphénylacétate. L'empêchement stérique et un faible pouvoir d'ionisation sont tenus comme responsables de ce résultat. Une résistance excellente à la saponification, attribuée à la fois à l'encombrement stérique et à la faible tendance à ioniser, est mentionnée pour trois esters cellulosiques, le triphénylacétate, la β,β -triphénylpropionate et le mésitoate.

Zusammenfassung

Zwei mögliche Reaktionswege bei der Reaktion eines Säurechlorids mit einem Alkohol werden diskutiert. Die Rolle von Pyridin als Lösungsmittel und Katalysator bei dieser Reaktion wird beschrieben. Die Bedeutung induktiver und Resonanzeffekte sowie der Grösse und Anordnung der dem Carbonyl benachbarten Gruppen wird betont. Die heterogene Darstellung von sieben partiellen Celluloseestern, nämlich von Phenyl-

acetate, Benzoat, Trimethylacetat, Triphenylacetat, β,β -Triphenylpropionat, α -(4-Biphenylyl)-phenylacetat und Mesitoat wird beschrieben. Schwierigkeiten bei der Veresterung treten nur bei der Darstellung des Triphenylacetates auf. Es wird angenommen, dass sterische Hinderung und eine geringe Ionisierungstendenz dafür verantwortlich sind. Eine ungewöhnliche Beständigkeit gegen Verseifung, die wahrscheinlich auf sterische Hinderung und reduzierte Ionisierungstendenz zurückzuführen ist, wird bei drei von den Celluloseestern, dem Triphenylacetat, dem β,β -Triphenylpropionat und dem Mesitoat festgestellt.

Received December 4, 1962