Hydrogen Bonding of Phthalic Acid Esters to Unesterified Hydroxyl Groups in Nitrocellulose

INTRODUCTION

A recent study[1] has shown that all the members of a homologous series of benzoic acid esters hydrogen bond to unesterified hydroxyl groups in nitrocellulose (NC). Further, this study indicated that the Taft σ^* constant for each alkyl group could be correlated with the strength of the resulting hydrogen bond formed with the nitrocellulose hydroxyl group. The alkyl benzoates as well as the alkyl phthalates are of interest as both plasticizers and deterrents for small arms propellants. Deterrents are compounds which are diffused some distance into spherical nitrocellulose based small arms propellant grains in order to slow down their initial burning rate when the bed surface area is at maximum. Previous studies have shown that the type of diffusion gradient obtained for small arms deterrents in ball propellants results from a case of diffusion with interaction. The interaction involved is hydrogen bonding between the unesterified hydroxyl groups in nitrocellulose and the deterrent carbonyl group. Therefore, a consideration of the hydrogen bonding characteristics of phthalic acid esters to unesterified hydroxyl groups in nitrocellulose is important for determining their utility as deterrents. Only one phthalic acid ester, di-*n*-butyl phthalate, has been reported[2] as hydrogen bonding to unesterified hydroxyl groups in nitrocellulose.

EXPERIMENTAL

The nitrocellulose used was obtained from Hercules Inc. and had a nitrogen content of 12.63% (this corresponds to 0.54 free OH groups per repeat unit) and a viscosity of 83.6 poises (10% NC by weight measured in 10% ether–80% acetone solution). The dimethyl, diethyl, and di-*n*-butyl phthalates were obtained from the Aldrich Chemical Co. The di-*n*-propyl, diisopropyl, di-*n*-pentyl, di-*n*-octyl, and di-*n*-nonyl phthalates were obtained from the Eastman Kodak Co. The di-*n*-heptyl, diisobutyl, and di-*n*-decyl phthalates were obtained from ICN-K&K laboratories. A standard solution of nitrocellulose was prepared by dissolving 1.12 g nitrocellulose in 100 ml reagent-grade ethyl acetate. Samples for IR study were prepared by pipetting .035–.045 ml of the ester and 1 ml of the standard nitrocellulose solution into a glass container. Films of each were cast on NaCl plates, air dried, and run on a Perkin-Elmer 621 infrared spectrophotometer utilizing a 5× abscissa expansion and dry air purge conditions.

DISCUSSION

The hydrogen bonding characteristics of a homologous series of phthalic acid esters to unesterified hydroxyl groups in nitrocellulose were studied by means of infrared spectroscopy. A similar study involving benzoic acid esters indicated that the inductive effects of the alkyl group could be related via their Taft σ^* constants to the strength of the resulting hydrogen bond. In the present study, no such relationship could be found. As can be seen from the shifted ν-OH values in Table I, all of the esters studied formed hydrogen bonds with unesterified hydroxyl groups in NC. In the case of the methyl and ethyl esters, no single major interaction could be identified. There appeared to be a range of interactions from 3470 to 3490 cm^{-1}. With the exception of di-*n*-pentyl phthalate, the NC ν-OH appeared to be shifted to higher wave numbers with increasing size of the alkyl group. This would tend to indicate that as the size of the alkyl group increased, weaker hydrogen bonds were formed until a constant value was obtained (3490–3496 cm^{-1}) for the last four members of the series. The fact that the last four members of the series resulted in a constant NC ν-OH value may indicate that some sterically limiting factor has been reached.

TABLE I
Shifted Nitrocellulose ν-OH Resulting from Hydrogen Bonding to Phthalic Acid Esters

Phthalic acid ester	Shifted ν-OH, cm^{-1}[a,b]
Dimethyl	3470–3490[c]
Diethyl	3470–3490[c]
Di-*n*-propyl	3472–3476
Diisopropyl	3474–3476
Di-*n*-butyl	3480–3482
Diisobutyl	3482–3484
Di-*n*-pentyl	3474–3478
Di-*n*-heptyl	3492–3496
Di-*n*-octyl	3490–3492
Di-*n*-nonyl	3492–3494
Di-*n*-decyl	3492–3494

[a] All spectra were run with a dry air purge and a 5× expansion of the abscissa. The range of values indicates the variation obtained from a minimum of five runs for each sample.

[b] The free NC ν-OH was measured at 3500 cm^{-1}.

[c] The large range of values for dimethyl and diethyl phthalates indicates the range of interactions observed for these two esters.

References

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