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

INTRODUCTION

A recent study[1] has shown that hydrogen bonding occurs between small arms deterrents and unesterified hydroxyl groups in nitrocellulose (NC). Deterrents are materials that are diffused some distance into spherical nitrocellulose propellant grains in order to slow down their initial burning rate when the bed surface area is at maximum. The purpose of the current study was to determine if other compounds, which may be of use as deterrents, undergo hydrogen bonding with the unesterified hydroxyl groups of nitrocellulose. A previous study[2] has shown that the concentration profile of a conventional deterrent material (di-*n*-butyl phthalate) is level through a portion of the propellant grain with an abrupt drop off thereafter, and suggested that this could be caused by diffusion with interaction. Therefore, a new deterrent material, in addition to having the requisite thermal characteristics, would have to be capable of entering into a similar interaction. The specific compounds studied were a homologous series of benzoic acid esters. These compounds were selected because several of the phthalic acid esters are currently in use as deterrent materials.

Aside from obtaining information about deterrent materials, this study offered the possibility of observing the hydrogen-bonding characteristics of a homologous series of benzoic acid esters, the specific compounds used by Taft to establish his linear free-energy relationship.[3] A number of studies have established relationships between σ^* values and group frequency shifts in the infrared (IR). Several studies[4,5] have been concerned with measuring the $\Delta\nu$(OH) of a series of hydrogen-bonded complexes containing various substituents. It appears that the Taft σ^* value is a good measure of the inductive effects and therefore can be correlated with the $\Delta\nu$(OH) values obtained on bonding for each substituent. It was the purpose of this study to establish such a relationship for the hydrogen-bonding characteristic of benzoates present in cast films of NC.

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 P (10% NC by weight measured in a 10% ether–80% acetone solution). Methyl and ethyl benzoates were obtained from Aldrich Chemical Co., Inc.; propyl, butyl, and isobutyl were obtained from Eastman. The isopropyl benzoate was obtained from K & K Laboratories, Inc. A standard solution of NC was prepared by dissolving 1.12-g nitrocellulose in 100-ml reagent-grade ethyl acetate. Samples for IR study were made for each of the esters by adding between 1.96×10^{-4} to 2.53×10^{-4} moles of ester to 1 ml of NC solution. Films of each solution were cast on NaCl plates, air dried, and run on a Perkin-Elmer 621 IR Spectrophotometer with 5× abscissa expansion under dry-air purge conditions.

DISCUSSION

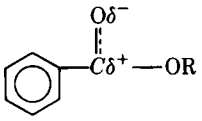
The hydrogen-bonding characteristics of cast films of a homologous series of benzoic acid esters to unesterified hydroxyl groups in nitrocellulose were studied by means of IR spectroscopy. A previous study[1] has shown that di-*n*-butyl phthalate hydrogen bonds through its carbonyl group with unesterified hydroxyl groups in NC. In the present study, the shift of the NC υ-OH was observed for each of the compounds shown in Table I. The specific nitrocellulose used in this study had a υ-OH at 3500 cm^{-1}. It has been shown[6] that the υ-OH observed for various nitrogen-content nitrocellulose varies and that this is caused in part by weak hydrogen bonds formed between hydroxyl groups within nitrocellulose. It is interesting that these interactions were weak enough to allow study of the hydrogen bonding of these esters. As can be seen in Table I from examination of the υ-OH, all of the esters hydrogen bonded to unesterified hydroxyl groups in NC. It was found that the shifted NC υ-OH for each of the esters studied followed the

TABLE I
Compounds Studied with Frequency Shifts and Taft σ^* Constants

Compound		σ^*	Shifted ν-OH, cm^{-1}	Δ_ν(OH), cm^{-1}
Methyl benzoate	1	0.00	3480	0
Ethyl benzoate	2	−0.10	3474	6
n-Propyl benzoate	3	−0.12	3472	8
n-Butyl benzoate	4	−0.13	3457	23
Isopropyl benzoate	5	−0.19	3454	26
Isobutyl benzoate	6	−0.21	3450	30

trends of the Taft constant values. It was possible to relate the shifted NC ν-OH to the Taft σ^* values and obtain an approximate linear relationship. Figure 1 shows a plot of Δ_ν(OH) (the difference in frequency between methyl benzoate and the given compound) versus the Taft constant. The fact that this linear relationship holds for the homologous series of benzoates indicates that steric factors do not play a significant role in determining the strength of the hydrogen bonds.

It seems reasonable that the Taft-σ^* (electron-donating effect) would increase the negative charge on the carbonyl oxygen as shown below:



More negative character would be imparted to the carbonyl oxygen as the magnitude of the Taft constant for the alkyl groups (electron donating) increases.

In the absence of steric factors, increased negative charge on the carbonyl oxygen would then result in a stronger hydrogen bond with the unesterified hydroxyl groups in nitrocellulose. Figure 1 shows this to be the case.

This study has shown that each benzoic acid ester studied hydrogen bonds to unesterified hydroxyl groups in NC and therefore is of potential interest as a deterrent for small arms propellants. The shift of the ν-OH has been correlated with the Taft σ^* values, and a linear relationship has been found indicating that the strength of the interaction is caused mainly by inductive effects. In the future, it may be possible to determine the strength of an interaction between unesterified hydroxyl groups in NC and a potential deterrent material from a consideration of Taft's σ^* value if steric factors are determined to be absent.

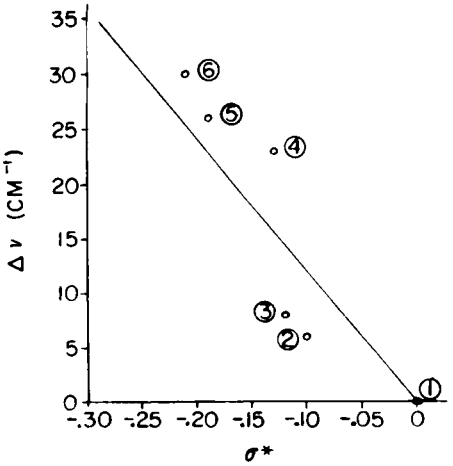


Fig. 1. Correlation of hydroxyl stretching frequency with Taft σ^* constants.

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