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HYDROGEN BONDING OF DETERRENTS TO
UNESTERIFIED HYDROXYL GROUPS IN
NITROCELLULOSE

Bruce W. Brodman, et al

Frankford Arsenal
Philadelphia, Pennsylvania

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The hydrogen bonding of four small arms propellant deterrents (di-n-butyl phthalate (I), Camphor (II), N, N'-dimethyl-N, N'-diphenylurea (IV) to unesterified hydroxyl groups in nitrocellulose was studied by means of infrared spectroscopy. The results indicate that the carbonyl groups of compounds I and II were involved in the hydrogen bonding with nitrocellulose while interactions were postulated for both the carbonyl group and the nitrogen atom of compounds III and IV. Bond lengths were determined for the carbonyl-hydroxyl hydrogen bonds.		

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Hydrogen Bonding of Deterrents to Unesterified Hydroxyl Groups in Nitrocellulose

INTRODUCTION

Deterrents are materials that are diffused into the surface of nitrocellulose-based small-arms propellant grains to decrease their initial burning rate. This is done to avoid overpressure early in the ballistic cycle, when the surface area of the propellant bed is at maximum. Elucidation of the type of chemical interaction which exists between the deterrent molecules and the nitrocellulose is important for manufacturing purposes as well as for long-term storage considerations.

The hydrogen bonding of four deterrent materials [di-*n*-butyl phthalate (I), camphor (II), *N,N'*-diethyl-*N,N'*-diphenylurea (III), and *N,N'*-dimethyl-*N,N'*-diphenylurea (IV)] to nitrocellulose was studied by means of infrared spectroscopy. Previous publications^{1,2} have indicated that hydrogen bonding occurs between the carbonyl groups of II and III and the unesterified hydroxyl groups of nitrocellulose. In the present study, we have attempted to clarify the type of bonding which occurs between III and nitrocellulose (NC), considered other deterrent materials, and calculated hydrogen bond lengths for each system.

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). Both the *N,N'*-diethyl-*N,N'*-diphenylurea and *N,N'*-dimethyl-*N,N'*-diphenylurea were obtained from Matheson Coleman and Bell, and were recrystallized from ethyl acetate. The purity of both compounds was verified by melting point determinations. The purified di-*n*-butyl phthalate was obtained from Fisher Scientific Co., and the reagent-grade thiourea was obtained from Matheson Coleman and Bell. Eastman Kodak was the source of the synthetic *d,l*-camphor used in this study. A standard solution of nitrocellulose was prepared by dissolving 1.11794 g nitrocellulose in 100 ml reagent-grade ethyl acetate. Similar standard ethyl acetate solutions were made for each of the deterrent materials. Samples for infrared study were prepared by pipetting the standard deterrent solution and standard nitrocellulose solution into a glass container (molarity for each series is reported in Table I). Films of each solution were cast on NaCl plates, air dried, and run on a Perkin-Elmer 621 infrared spectrophotometer.

RESULTS

Shifting of the OH stretching frequency in the infrared region for the unesterified hydroxyl groups in nitrocellulose was studied for each of the four deterrent-nitrocellulose systems. The specific nitrocellulose used in this study had a free OH stretching vibration at 3500 cm^{-1} when run as a cast film. This value is often taken as being the lower end of the free OH absorption range.³ A previous study¹ dealing with hydrogen bonding to nitrocellulose reported a free OH stretching frequency for nitrocellulose film of 3590 cm^{-1} ; however, no nitrogen content for the nitrocellulose was reported. Subsequent work² reported that the free OH stretching frequency in films of nitrocellulose (11.8% nitrogen corresponding to 0.7-0.8 free OH groups per repeat unit) appeared to occur near 3590 cm^{-1} and gave an indication that the free OH stretching frequency of cast films of NC varies with nitrogen content. The results obtained for each deterrent-NC system will be discussed.

Compound III and Nitrocellulose

Two previous studies^{1,2} considered the hydrogen bonding of III to NC. Josien et al.¹ observed a shift in the $\nu(\text{OH})$ frequency from 3590 cm^{-1} to both 3520 cm^{-1} and 3330 cm^{-1} . The 3330 cm^{-1} shift appeared to be the more intense absorption. As can be seen

TABLE I
Hydrogen Bonding Characteristics for Various Nitrocellulose-Deterrent Combinations

Deterrent	Deterrent concentration in film, (moles detergent/NC) $\times 10^4$	Free OH frequency, cm^{-1}	Shifted OH frequency OH—O bonding, cm^{-1}	Shifted OH frequency ^a OH—N bonding, cm^{-1}	OH—O bond length, Å
III ^b	2000	3500	3305	3405	2.80
IV ^c	2010	3490	3315	3455	2.81
I	1965	Absent	3480	—	2.90
II	2174	Absent	3450	—	2.87

^a OH—N Bonding has been hypothesized to explain these second shifted peaks occurring in the Centralite spectra.

^b At this concentration, the OH—O peak was the most intense, the OH—N peak secondary, and the free OH was present as a shoulder (see Fig. 1).

^c At this concentration, the OH—O peak was the most intense, the OH—N peak secondary, and the free OH peak least intense (see Fig. 1).

in Table I, a peak was obtained at 3305 cm^{-1} in this study. However, no peak was observed near 3520 cm^{-1} . A second less intense $\nu(\text{OH})$ was observed at 3450 cm^{-1} , in addition to a shoulder near 3500 cm^{-1} which indicated some free $\nu(\text{OH})$. Examination of the published spectra of Josien shows an indication of a peak at about 3440 cm^{-1} although none was reported.

A second study² of hydrogen bonding of III to NC reported a single shifted $\nu(\text{OH})$ at 3350 cm^{-1} . This $\nu(\text{OH})$ does not agree with the previously published data of Josien, or with those obtained in this study. An infrared study was made of thiourea in an NC film in order to establish if the hydrogen bonding with the OH of NC was due to the carbonyl group or the nitrogen of III. This was necessary because the shift of the carbonyl stretching frequency could not be observed due to overlapping of the NC- ONO_2 valence vibration. Since thiourea has no carbonyl group, and the sulfur did not appear to be involved in hydrogen bonding because no shift in the $\nu(\text{C}=\text{S})$ (near 1408 cm^{-1}) was observed, only the nitrogen could participate. Thiourea gave a single $\nu(\text{OH})$ at 3495 cm^{-1} . On this basis, it is suggested that the shifted $\nu(\text{OH})$ observed at 3450 cm^{-1} may be due to hydrogen bonding involving the nitrogen in III, and the shifted $\nu(\text{OH})$ at 3305 cm^{-1} due to bonding involving the carbonyl group of III.

Compound IV and Nitrocellulose

No published data could be found regarding the hydrogen bonding of IV with nitrocellulose. As expected, the results obtained were very similar to those for NC and III. The free $\nu(\text{OH})$ was shifted to two different frequencies, 3315 cm^{-1} and 3455 cm^{-1} , with a low-intensity peak still present near 3500 cm^{-1} . Again by comparison with the data for cast films of NC and thiourea, it is suggested that the 3455 cm^{-1} peak is due to hydrogen bonding between the unesterified hydroxyl groups of NC and the nitrogen of IV. Similarly, it is suggested that the 3315 cm^{-1} peak is due to bonding of the carbonyl group of IV with unesterified OH groups present in NC.

II and NC

Both previous studies^{1,2} have included the hydrogen bonding of camphor with the OH in nitrocellulose. Josien reported a shift of the $\nu(\text{OH})$ to 3450 cm^{-1} , while Chefubin reported the shifted $\nu(\text{OH})$ at 3400 cm^{-1} . The results of this study (Table I) agree with those obtained by Josien. However, Josien reported that the $\nu(\text{OH})$ shifts with increas-

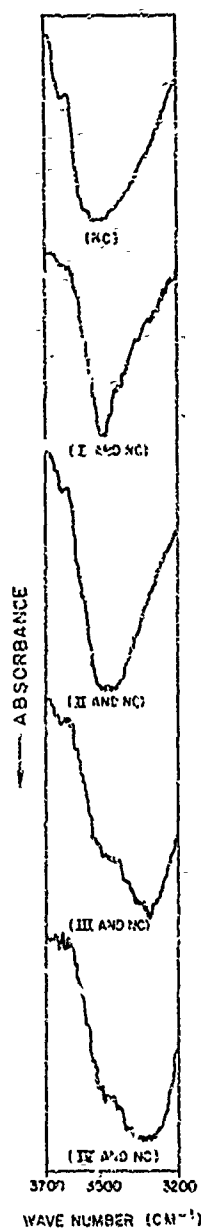


Fig. 1. Infrared spectra of hydroxyl stretch region for various nitrocellulose-detergent combinations.

ing camphor concentration. Although various concentrations of II and NC were run in this study, no concentration-related shift was observed. At the concentration recorded in the table, no residual free $\nu(\text{OH})$ was noted. Further, none was reported in the two previous studies. A further indication of hydrogen bonding involving the carbonyl group of II was a shift of 10 cm^{-1} for the $\nu(\text{C}=\text{O})$ frequency.

I and NC

No previous study of hydrogen bonding between I and NC was found in the literature. At the concentration reported in the table, a single shifted $\nu(\text{OH})$ was observed at 3480 cm^{-1} . No residual free $\nu(\text{OH})$ was observed.

Evidence for hydrogen bonding involving the carbonyl group of I was obtained from a shift of $\nu(\text{C}=\text{O})$ from 1720 cm^{-1} for I to 1710 cm^{-1} for I and NC. Lengths of the hydrogen bonds resulting from the interaction of the hydroxyl groups of the nitrocellulose and the carbonyl groups for each system are listed in Table I (these bond lengths were determined from a relationship established by Nakamoto et al.⁴). These values indicate that the strongest bond results with compounds IV and III, the next strongest with II, and the weakest with I. Figure 1 shows the spectral region containing the OH stretching frequency for pure NC and for NC in combination with each of the four detergents.

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B. W. BRODMAN
M. P. DEVINE
M. T. GURBARG

Munitions Development and Engineering Directorate
Frankford Arsenal
Philadelphia, Pennsylvania 19137

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