# *Hydrogen Bonding of HMX and RDX to Unesterified Hydroxyl Groups in Nitrocellulose*

## INTRODUCTION

Both octahydro-1,3,5,7-tetranitro-*s*-tetrazine (HMX) and hexahydro-1,3,5-trinitro-*s*-triazine (RDX) are promising new candidates for small-arms propellant formulations. These formulations generally include one of the aforementioned energetic nitramines in combination with nitrocellulose (NC). A knowledge of the interaction between the nitramines and nitrocellulose would be a valuable aid in propellant formulation and potentially useful in alteration of the combustion characteristics of composite propellants. No report could be found in the literature of an interaction study involving either of the two nitramines with nitrocellulose. However, various investigators have reported complex formation between the nitramines and other materials.[1-8] Selig[8] suggests that these complexes may be due to the formation of a sandwich-type adduct in which the guest molecule has to meet certain spatial requirements. Further, it was suggested that hydrogen bonding might be of secondary importance in adduct formation.

## EXPERIMENTAL

Two well-characterized nitrocellulose samples of 12.6% N and 12.1% N were obtained from Picatinny Arsenal and have been described in a previous publication.[9] Both the HMX and RDX were obtained from Picatinny Arsenal and were representative of the purity found under production conditions. Standard solutions of the nitramines and the nitrocellulose samples were prepared by dissolving the appropriate quantities in MC&B reagent-grade ethyl acetate (EA). In order to obtain cast films of the various combinations, appropriate quantities of the standard nitrocellulose and nitramine solutions were mixed, and the resultant solutions were evaporated on a salt plate. Table I shows the weights and composition of the various mixtures used. The resulting cast films were placed in a vacuum desiccator and subjected to roughing pump vacuum for a minimum of 140 hr. Infrared data for each dried cast film were obtained under dry air purge conditions on a Perkin-Elmer Model 621 infrared spectrophotometer, utilizing a 5× abscissa expansion and a 3–5× ordinate expansion.

## DISCUSSION

Cast films of two different nitrogen content nitrocellulose samples (12.6% and 12.1% N) were prepared containing either HMX or RDX. The $\nu$-OH of these cast films were examined by means of infrared spectroscopy. Table II contains the $\nu$-OH of the pure nitrocellulose samples as well as those obtained for each sample when RDX or HMX was present. It can be seen that the $\nu$-OH in the pure nitrocellulose cast films were observed at 3516 $cm^{-1}$ for the 12.6% N sample and at 3506 $cm^{-1}$ for the 12.1% N sample. Both RDX and HMX when present in the cast films caused a shift in $\nu$-OH. In both cases, the RDX caused a greater shift than the HMX, indicating stronger hydrogen bond formation. This may be due in part to the smaller molecular dimensions of the RDX. Further, both HMX and RDX caused a greater shift in the nitrocellulose $\nu$-OH with the lower nitrogen-content nitrocellulose sample. This may be due to the greater number and less sterically hindered hydroxyl groups in the 12.1% N nitrocellulose sample.

By examining the Nakamoto[10] relationship between hydrogen bond distance and hydrogenic stretching frequency, and considering the elements present in the molecules capable of participating in hydrogen bonding, it was decided that the only possibility would be an OH. . . .O interaction having bond length from 2.85 to 2.90 Å. Further, the theory that HMX forms a sandwich-type adduct is unlikely in this case, since the nitrocellulose samples used in this study contained on the average one OH group per glucose unit.

In summary, it has been shown that both HMX and RDX form hydrogen bonds of the OH. . .O type with unesterified hydroxyl groups in nitrocellulose and an oxygen atom of the respective nitramine, and that RDX forms the stronger bonds.

TABLE I
Nitrocellulose and Nitramine Solutions

| NC and nitramine soln. | Soln. vol. used, ml/ml | Ratio wts, g/g |
|---|---|---|
| NC (12.6%)[a]–HMX[c] | 1:3 | 1:0.67 |
| NC (12.6%)–RDX[d] | 1:1.5 | 1:1.34 |
| NC (12.1%)[b]–HMX | 1:6 | 1:1.18 |
| NC (12.1%)–RDX | 1:3 | 1:2.36 |

[a] NC (12.6%) solution = 1.12 g NC/100 ml EA.
[b] NC (12.1%) solution = 1.27 g NC/100 ml EA.
[c] HMX solution = 0.25 g HMX/100 ml EA.
[d] RDX solution = 1.0 g RDX/100 ml EA.

TABLE II
$\nu$-OH Values and Bond Lengths

| Sample | $\nu$-OH, $cm^{-1}$ | $\Delta\nu$[a] $cm^{-1}$ | No. of runs | Bond length,[b] Å |
|---|---|---|---|---|
| NC (12.6%) | 3516 | — | 4 | — |
| NC (12.6%)–HMX | 3490 | 26 | 3 | 2.90 |
| NC (12.6%)–RDX | 3452 | 64 | 3 | 2.87 |
| NC (12.1%) | 3506 | — | 4 | — |
| NC (12.1%)–HMX | 3444 | 62 | 3 | 2.86 |
| NC (12.1%)–RDX | 3422 | 84 | 3 | 2.85 |

[a] $\Delta\nu = [\nu\text{-OH(NC)} - \nu\text{-OH(sample)}]$.
[b] These values were obtained from the Nakamoto graphic correlation.

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