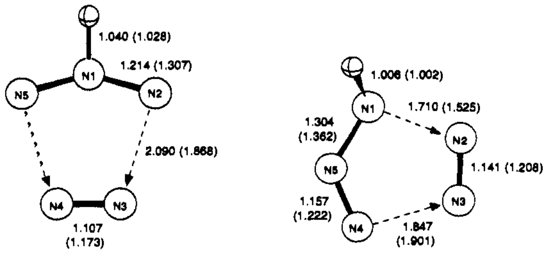

Figure 2. SCF transition-state structures for symmetric and nonsymmetric decomposition pathways of hydrogen pentazole. MBPT(2) structures are given in parentheses. Bond lengths are given in angstroms.

Å.[13] Experimental structural determination of the 4-(dimethylamino)phenyl derivative has found that the N–N bond distances are 1.30–135 Å. The N–N bond lengths for the pentazole anion are 1.298 Å at SCF, 1.350 Å at the MBPT(2) level, and 1.333 Å for CCSD.

Vibrational analyses performed at the SCF and MBPT(2) levels demonstrate that HN_5 is a minimum on its energy surface. It would be expected that the out-of-plane modes (b_2) would be particularly sensitive to electron correlation as these interactions involve the nitrogen lone pairs. Accordingly, the infrared intensities of the normal modes change, and the b_2 modes are reordered at the MBPT(2) level (Table I). Such qualitative changes with correlation were previously observed for the N_3H_3 isomer, and they differ from the agreement usually expected between scaled SCF frequencies and MBPT(2) predictions.

The stability of these molecules, and whether they can be successfully synthesized, depends on the activation energy for decomposition, among other factors.[14] To investigate possible unimolecular decomposition pathways we use "eigenvector following"[15] to locate two possible transition states (TS). Starting from the ground-state geometry, we determine a symmetric and a nonsymmetric pathway (Figure 2). The resulting reaction pathways are characterized as TSs by the presence of a single negative eigenvalue (620 cm^{-1} in both cases) and feature vastly different energetics. The MBPT(2) barriers are 48.0 and 22.8 kcal/mol for the symmetric and nonsymmetric processes, becoming 53.7 and 19.8 kcal/mol after estimation of the zero-point and internal energy corrections. The height of the barrier would suggest that hydrogen pentazole could be potentially isolated under gas-phase conditions. The asymmetric TS cleaves bonds heterolytically, enabling MBPT(2) to offer a good barrier approximation that should only be reduced by a few kilocalories/mole at higher levels of correlation. The homolytic barrier cleavage in the symmetric TS is poorly described by MBPT(2), but the barrier would still be expected to be too great to offer a competitive path.

Substitution by the electropositive atom Li or the electron-donating NH_2 group lowers the activation energy by 3.6 and 7.9 kcal/mol, respectively. As such, pentazoles with electron-withdrawing substituents, such as the known (dimethylamino)phenyl derivative, are more likely to be isolated. This particularly recommends a possible synthesis of the bipentazole molecule shown in Figure 1. Its potential aromaticity poses interesting questions.

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Thermal Decomposition of Solid RDX Begins with N–N Bond Scission

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Cyclic nitramine propellants such as hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazine (HMX) have found wide application as explosives and propellants. Although a great deal of empirical data are available concerning the explosive properties of these materials,[1,2] surprisingly little is known about the detailed mechanism of their combustion.[3,4]

Several recent studies have attempted to identify the *initial* step in the thermal decomposition mechanism. One of the obvious choices for this is scission of one of the N–N bonds. Thermodynamic studies identify this as the weakest bond in the molecule,[5] and results from thermogravimetric mass spectrometry experiments on HMX are consistent with this homolysis mechanism,[6] though these authors also propose that competing bimolecular pathways are required to explain deuterium kinetic isotope effects.[7] Indirect evidence supporting the importance of the N–N bond scission mechanism can be found from thermal decomposition studies of other closely related nitramines.[8,9] Also, ultraviolet photolysis experiments on crystalline RDX have shown that N–N homolysis is a primary reaction pathway,[10] though thermal pyrolysis might not follow the same mechanism.

Zhao et al. proposed an alternative mechanism in which gas-phase RDX molecules each decompose by concerted depolymerization that initially forms three molecules of methylenenitramine,[11] CH_2NNO_2. Under these conditions, the N–N bond scission channel accounts for only about one-third of the product yield. Sewell and Thompson have recently published a classical dynamics study of RDX decomposition[12] that supports the experimental findings of Zhao et al. Also, some of the early thermal pyrolysis work on isotopically substituted RDX supports a mechanism in which the N–N bond is preserved in the decomposition reaction.[13,14]

Our experiment is designed to rapidly quench and trap the initial pyrolysis products following rapid IR laser heating of solid RDX. To do this, we form a thin film (approximately 20 mm in diameter by 5–20 μm thick) of the pure solid material by vapor deposition from a Knudsen oven at 120 °C onto an infrared-transparent window (CaF_2 or CsI) at 77 K inside a vacuum Dewar vessel. The film is warmed to room temperature in order to convert the amorphous solid to a crystalline form of RDX. A second CsI window is then used to cover the sample, and this "sandwich" arrangement is remounted in the vacuum Dewar vessel and recooled to 77 K. The sample is irradiated with a CO_2 laser tuned to the P(20) line at 944 cm^{-1}, which rapidly heats it from 77 K

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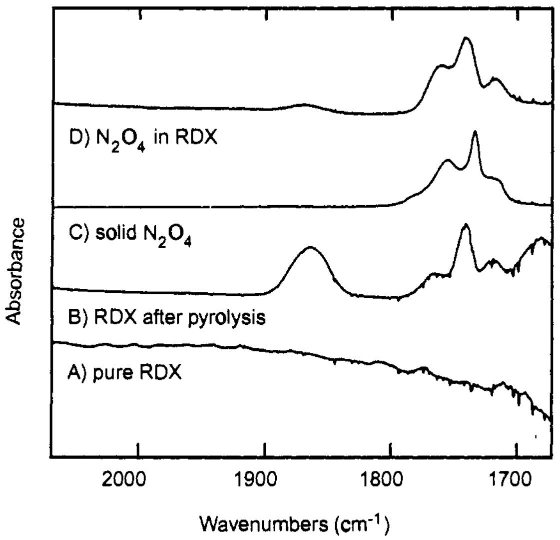

Figure 1. (A) Portion of the infrared spectrum of RDX following deposition from a Knudsen oven onto a 77 CsI optical window. The sample was warmed to room temperature and covered with a second CsI window, and the assembly was recooled to 77 K in high vacuum prior to obtaining the spectrum. (B) Infrared spectrum of the same sample as in trace A following CO_2 laser pyrolysis. The beam was rastered over the sample such that each region was subjected to a single laser pulse (4.7 J/cm^2 at 944 cm^{-1}). (C) Infrared spectrum of a thin film of N_2O_4 deposited from the vapor (NO_2/N_2O_4) onto a 77 K CsI window in vacuum. (D) Infrared spectrum of a thin film sample of NO_2/N_2O_4 codeposited with RDX onto a 77 K CsI window.

to an estimated 500 K in 35 μs (the nominal laser pulse width). Because the films are in contact with a relatively massive substrate, they rapidly cool back to 77 K with a characteristic time scale estimated to be 2 ms based on the thermal conductivity of RDX.[2,15] The extent of heating and decomposition can be controlled by changing the laser fluence (energy per unit area per pulse). A complete description of the experimental technique and results for RDX pyrolysis will be presented in a forthcoming paper.

The formation of initial pyrolysis products is detected by obtaining transmission FTIR spectra of the thin films before and after CO_2 laser irradiation. A representative spectrum is shown in Figure 1. Trace A shows a portion of the infrared spectrum of an RDX film prior to photolysis. Although no RDX absorptions are apparent here, other regions of the spectrum show a complicated series of intense absorption bands. The spectrum obtained after laser pyrolysis at high fluence (4.7 J cm^{-2}) shows the appearance of new absorption features centered at 1864 and 1735 cm^{-1} (trace B). The 1864-cm^{-1} band is attributable to nitric oxide on the basis of good agreement with the gas-phase vibrational frequency of NO (1876 cm^{-1}). The triplet of bands centered at 1735 cm^{-1} is similar to an absorption band identified as CH_2O in a previous study of UV photolysis of matrix-isolated RDX by Alix and Collins.[16,17] However, we believe it is actually due to N_2O_4, the dimer of NO_2, which exhibits a strong absorption in this region.[18] Our assignment was easily confirmed by obtaining the FTIR spectrum of a thin solid film of N_2O_4 deposited directly from the vapor (an equilibrium mixture of NO_2 and N_2O_4) onto the IR window at 77 K (shown in trace C). The spectrum of a mixed sample of N_2O_4 in RDX was also obtained (trace D). In each case, the position and shape of the N_2O_4 absorption band closely match those of the photolysis product shown in trace B. In addition to NO and N_2O_4, the IR spectra following high-fluence pyrolysis show evidence for formation of HCN (2086 cm^{-1}), N_2O (2236 cm^{-1}), and CO_2 (2343 cm^{-1}).

The N_2O_4 absorption band was also observed in experiments conducted at lower laser fluence (about 2.4 J/cm^2 per pulse). Under these conditions, only a small fraction of the RDX molecules are dissociated. The absorption bands of N_2O, HCN, and CO_2 were absent, and only a trace of NO was observed. *These experiments provide convincing evidence that N-N bond scission is the first step in the thermal decomposition mechanism of RDX.*

The only other reasonable decomposition channel is the concerted depolymerization observed by Zhao et al.[11] which forms methylenenitramine, CH_2NNO_2. Although the infrared spectrum of this molecule is not known, its vibrational frequencies have been calculated by Mowry et al.[19] Most of the calculated frequencies lie close to absorption bands of RDX and would be difficult to observe in this type of pyrolysis experiment. However, the bands expected at 1220, 896, and 621 cm^{-1} lie in regions of the IR spectrum which are relatively free of interference from RDX and should have been detected using spectral subtraction methods if CH_2NNO_2 were produced by pyrolysis. There is no evidence for any of these bands in the pyrolysis experiments carried out in this study.

Finally, we note that our conclusion that solid RDX dissociates via N-N bond scission is not necessarily in conflict with the conclusion of Zhao et al. that depolymerization dominates in the gas-phase decomposition mechanism. We speculate that the presence of neighboring molecules in the condensed phase strongly inhibits the depolymerization mechanism due to the large positive volume of activation expected for this three-body channel. In contrast, the product molecules separate freely in the analogous gas-phase process. Therefore, both our results and those of Zhao et al. may be correct and compatible with each other. They simply correspond to very different experimental conditions.

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Iron-Mediated [4 + 2] Cycloaddition of 1,3-Butadiene with Ethyne and Propyne in the Gas Phase

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The Diels-Alder reaction is a versatile and convenient route to stereospecific synthesis of six-membered rings.[1] The low reactivity of unactivated alkynes and alkenes as dienophilic reagents, however, is a major limitation of this [4 + 2] cycloaddition process.[2] Transition metal complexes have been found to facilitate intermolecular[3-5] and intramolecular[6] dienyne cycloadditions, presumably via η^3-complex formation and reductive

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