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FREE RADICAL DETECTION AND REACTIONS IN THE
DECOMPOSITION OF ENERGETIC MA (U) NATIONAL
STANDARDS WASHINGTON DC MOLECULAR SPECTROS

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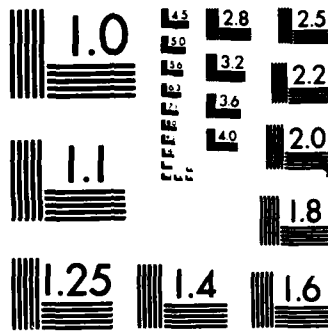
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ABSTRACT (Continue on reverse side if necessary and identify by block number) Infrared and ultraviolet absorption spectra have been obtained for a number of reaction intermediates which are expected to play important roles in the decomposition and combustion of energetic materials. In order to prevent molecular diffusion and subsequent reactions, the species of interest was trapped in a large excess of solid argon at cryogenic temperatures. The vibrational spectrum previously reported for the nitromethyl free radical has been further analyzed to give additional information on the structure and chemical bonding properties of that species. The first infrared spectrum of H ₂ CN, expected to be an impor-		

20. ABSTRACT CONTINUED

tant intermediate in nitramine decomposition, has been obtained and analyzed. Previous reports of the ultraviolet spectrum of this species have been confirmed and extended. The combustion intermediates t-HOCO, HC₂, and CHN₂ have also been studied. The infrared spectrum of t-HOCO has been obtained for the isolated molecule, eliminating complications which resulted from hydrogen bonding in an earlier study. The first survey of the absorption spectrum of the A-X transition of HC₂ between 3600 and 7800 cm⁻¹ has been reported. Studies of the CHN₂ reaction intermediate(s) have not yet been completed.

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FREE RADICAL DETECTION AND REACTIONS
IN THE DECOMPOSITION OF ENERGETIC MATERIALS

Final Report

Marilyn E. Jacox

30 July 1987

U. S. Army Research Office

Proposal 21495-CH

(MIPR 157-84; 105-85; 131-85; 105-86)

Molecular Spectroscopy Division
National Bureau of Standards
Gaithersburg, Maryland 20899

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Scientific Objectives

The research described in this report has as its ultimate objective the improvement of our understanding of the early stages of the decomposition and combustion of energetic materials, in order to promote efficient utilization of these materials and to aid in the design of systems which will minimize the hazards associated with handling them. Because of the difficulties in detecting them, heretofore little has been known about the properties of the molecular fragments which are produced in the early stages of energetic material decomposition. The subsequent reactions of these species, many of which are highly reactive free radicals, lead to the release of energy and to the formation of stable, more readily detected final products.

Spectroscopy is an especially useful tool for studying molecular reaction intermediates, since it is a sensitive, specific technique for the positive identification of molecular species. Analysis of the spectral data provides information on the structure and chemical bonding properties of the molecule. Once the molecular energy levels are known, it becomes possible to develop laser diagnostics which permit remote sensing of chemical reaction systems with both spatial and time resolution capabilities.

The studies described in this report have used the matrix isolation technique in order to obtain survey spectra in both the infrared and the ultraviolet spectral regions for free radicals which are expected to be important in the decomposition and combustion of energetic materials. A dilute solid solution of the species of interest is prepared using a rare gas or nitrogen as the solvent, or matrix, and a temperature sufficiently low that, although at least limited atomic diffusion is still possible, molecular diffusion does not occur. For covalently bonded species isolated in solid argon, the vibrational fundamentals and the band origins of electronic transitions involving the valence electrons typically are shifted by less than about 1% from the corre-

sponding gas-phase values.¹⁻³ Free radicals are stabilized by ultraviolet or vacuum ultraviolet photolysis of a precursor molecule or are trapped among the products of the interaction of species such as H atoms or electronically excited argon atoms, produced in a low-power microwave discharge, with the molecule of interest. In certain systems, photodecomposition products trapped in adjacent sites in the solid may undergo further reaction, yielding information on the early stages of reactions which may occur in solid energetic materials or in their reactions at relatively high pressures. Studies of the threshold and products of photodecomposition of the initially-formed free radicals provide further information on the range of stability of these species.

Scientific Accomplishments

Analysis of the Vibrational Spectrum of Nitromethyl

In an earlier phase of this program, supported by the U. S. Army Research Office under Proposal 17710-C, the reaction of F atoms with nitromethane trapped in solid argon was found⁴ to lead to the appearance of prominent infrared absorptions of the nitromethyl free radical, CH_2NO_2 . Although nitromethyl had long been known to be formed by the reaction of CH_3 with CH_3NO_2 ,⁵⁻⁸ one of the early reactions in nitromethane decomposition, there had been no previous optical detection of it. Electron spin resonance spectra of nitromethyl^{9,10} suggested that the molecule might be nonplanar. However, both the early INDO calculations¹¹ and the recent MCSCF calculations of McKee¹² were consistent with a planar structure. McKee has suggested that the molecule may experience in-plane distortion to a C_s structure. In a later paper, McKee¹³ calculated vibrational frequencies for CH_2NO_2 and proposed a vibrational assignment which differed somewhat from the tentative assignment which had been suggested in the experimental study.

In view of the wealth of spectral data for CH_2NO_2 obtained in the earlier study, it was decided to conduct a least-squares force constant fit of the experimentally determined vibrational frequencies using a sophisticated normal coordinate analysis program and the NBS Cyber computer facility. As the analysis proceeded, the results were shared with scientists at the U. S. Army Ballistic Research Laboratory, who were also interested in calculating the properties of nitromethyl. The complete normal coordinate analysis is presented in a paper which is scheduled to be published later this summer.¹⁴ An excellent fit to the observed data was obtained for a planar, C_{2v} structure. Several prominent absorptions could also be assigned to combination bands in Fermi resonance with vibrational fundamentals, providing a check on the proposed vibrational assignment. The magnitude of the CN-stretching force constant derived from the analysis is consistent with a C-N single bond.

Products of the Photodecomposition of Benzene and Nitrobenzene

The emphasis in the proposal which forms the subject of this report was on the characterization of transient molecules which may be formed in the decomposition of the nitrobenzenes. Because so little is known about the properties of even the simplest molecules in this series, it was necessary to build a set of experimental data which included the spectra of species such as phenyl, phenoxy, and the nitrophenyl free radical.

The first experiments in this series were concerned with the infrared spectra of the products of the photodecomposition of benzene. Radiation sources included a medium-pressure mercury arc (253.7 nm), a hydrogen-atom discharge lamp (121.6 nm) and an argon discharge (104-107 nm). Evidence was obtained for four different products--phenyl, benzyne (C_6H_4), a species which photolyzes on subsequent 254-nm photolysis of the sample, and a species which is photolytically stable in the presence of radiation from the medium-pressure mercury arc.

Since the objective was the spectral characterization of nitroaromatic species, it was decided next to survey the products of the photodecomposition of nitrobenzene trapped in an argon matrix. The operation of the cage effect would also permit the stabilization of the heretofore unidentified species phenyl nitrite in this system. In experiments using the medium-pressure mercury arc and the argon discharge as the photolysis sources, the infrared spectrum showed no evidence for the formation of photolysis products. These negative results, together with the emphasis given by the ARO workshops on the need for an improved understanding of the decomposition and combustion of the nitramines, led to the concentration of subsequent work on the characterization of free radicals of potential importance to the nitramine problem. This work was greatly facilitated by the use of a new experimental setup which included the Molecular Spectroscopy Division Bomem DA3.002 Bomem Fourier transform system. Infrared spectra with a greatly improved signal-to-noise ratio were obtained at a resolution of 0.2 cm^{-1} . The near infrared spectral region was also accessible, permitting the recording of the first survey spectra of HC_2 , an important combustion reaction intermediate.

Spectrum of H_2CN

The recent analysis of nitramine decomposition by Melius and Binkley¹⁵ suggests that, following the initial loss of NO_2 , the amine radical readily fragments into H_2CN and $\text{CH}_2=\text{N}-\text{NO}_2$ monomer units, which in turn produce $\text{H}_2\text{CN} + \text{NO}_2$. A key element in the subsequent chemistry is the weakness of the CH bond of H_2CN , which readily fragments into $\text{H} + \text{HCN}$. The H atom reacts with another nitramine molecule, leading to the production of HONO and to a similar fragmentation of the resulting amine radical. Thus, because of the properties of H_2CN , autocatalytic decomposition of nitramine occurs.

Despite many experimental and theoretical studies, heretofore the spectral data available for H_2CN were very limited. Electron spin resonance spectra^{16,17} had demonstrated that H atoms can react with HCN at cryogenic temperatures to form a CH_2N product with two equivalent H atoms. This species had also been detected by Morgan and Beyer¹⁸ in the electron spin resonance spectrum of the products of the low-temperature pyrolysis of HMX. Studies^{19,20} of the flash photolysis of $(\text{CH}_2\text{N})_2$ and of $\text{H}_2\text{C}=\text{NOH}$ had yielded a pair of absorption bands between 281 and 285 nm which were attributed to H_2CN . Higher resolution flash photolysis studies^{21,22} of normal and deuterium-substituted $(\text{CH}_2\text{N})_2$ demonstrated the presence of two H atoms in the molecule and yielded short progressions for the deuterated species. A vibrational assignment was not attempted, and the bands were too diffuse for the appearance of rotational structure. The most detailed ab initio calculations of the properties of ground-state H_2CN were those by Bair and Dunning²³, who found a small barrier for the reaction to form H_2CN , for which the depth of the potential minimum is approximately 30 kcal/mol, consistent with the calculations by Melius and Binkley.¹⁵ The species *t*-HCNH was found also to be accessible by the H + HCN reaction, but was somewhat less stable than H_2CN . The stability of *c*-HCNH is marginal. Calculations by Adams and co-workers²⁴ focused on the problem of assigning the electronic bands attributed to H_2CN , for which evidence had been presented favoring the contribution of these bands by two different transitions, separated by only about 600 cm^{-1} .

In the low-temperature studies of the H + HCN reaction conducted under this proposal, five of the six vibrational fundamentals of H_2CN were identified, together with one infrared absorption which had isotopic substitution behavior consistent with its assignment to the in-plane CNH deformation fundamental of *c*- or *t*-HCNH. The HCNH species has a photolysis threshold in the visible region of the spectrum, whereas H_2CN photolyzes when the sample is

exposed to radiation of wavelength shorter than 290 nm, consistent with the observation of diffuse absorption bands for H_2CN in the earlier flash photolysis studies. The isotopic data were sufficient to permit a detailed normal coordinate analysis for H_2CN . This analysis was consistent with a planar molecular structure with partial triple bond character for the CN bond. The direction and magnitude of the shift in the absorptions observed for D_2CN from the calculated values is consistent with highly anharmonic vibrations involving motion of the deuterium atoms. The shallow potential well calculated by Melius and Binkley¹⁵ and by Bair and Dunning²³ for the ground state of H_2CN implies large anharmonic corrections to the hydrogen-atom stretching and deformation vibrations.

The same two bands as had been observed in the gas-phase flash photolysis studies on more complex molecules were detected in ultraviolet absorption studies of the products of the $\text{H} + \text{HCN}$ reaction in solid argon, confirming the assignment of these two bands to H_2CN and excluding the contribution of one of them by a "hot band" in the gas-phase studies. These observations are consistent with the results of the calculations by Adams and co-workers.²⁴ In the argon matrix studies, weak absorption bands of H_2CN were also observed at shorter wavelengths than the two previously assigned bands, and it was possible to propose a tentative vibrational band assignment for the $\text{H}_2\text{CN } ^2\text{A}_1 - \text{X } ^2\text{B}_2$ band system. A paper has been prepared presenting the detailed results of these studies.²⁵

Infrared Spectrum of t-HOCO

Another important free radical for which spectroscopic data have been obtained during this project is t-HOCO. It has long been postulated that the HOCO reaction intermediate is formed in the reaction of OH with CO, the principal process by which CO is converted into CO_2 in hydrocarbon combustion. Stu-

dies in this laboratory some time ago explored the infrared spectrum of the products of the vacuum-ultraviolet photolysis of H_2O isolated in solid CO , resulting in the assignment of most of the vibrational fundamentals of both *c*- and *t*-HOCO.²⁶ However, these products can hydrogen-bond to the CO matrix. Because OH cannot diffuse through an argon matrix, the yield of HOCO in $Ar:CO:H_2O$ photolysis experiments was below the detection limit, and the extent of perturbation of the HOCO absorptions by hydrogen bonding could not be assessed. In the new series of experiments, *t*-HOCO was produced in good yield by H-atom abstraction from formic acid. A significant role for HOCO in nitramine decomposition may thus be anticipated not only because of the $OH + CO$ reaction, which is general to combustion systems, but also because of the presence of formic acid, which Beyer and DeWilde²⁷ have detected among the products of the pyrolysis of HMX.

The first studies of H-atom abstraction from formic acid were conducted using the $F + HCOOH$ reaction. A good yield of *t*-HOCO was obtained, consistent with the results of *ab initio* calculations²⁸ which indicate that the *trans*-structure is the lowest energy configuration. As expected, the vibrations which had been assigned to modes involving the OH group were shifted considerably (150 cm^{-1} for the OH stretch and 50 cm^{-1} for the in-plane OH deformation) upon elimination of the hydrogen-bonding to a CO matrix. However, in this system HF was also produced, and approximately half of the *t*-HOCO was stabilized in sites in which the carbonyl end of the molecule was hydrogen-bonded to HF . There resulted a doubling of the CO -stretching absorption, a mode which would be particularly useful for the development of infrared diagnostics for *t*-HOCO in gas-phase reaction systems. In order to distinguish between the absorptions of *t*-HOCO and those of *t*-HOCO... HF isolated in solid argon, the interaction with HCOOH of excited argon atoms produced in a low-power microwave discharge was used as an alternate source of *t*-HOCO. Four of the vibrational

fundamentals of the isolated molecule were assigned. The results of these experiments are of interest not only to the combustion scientist but also to those concerned with hydrogen bonding, since the infrared spectrum of t-HOCO has now been observed not only for the isolated molecule but also for t-HOCO which is hydrogen-bonded through either its OH or its CO group. Detailed isotopic substitution experiments were also conducted, and the results were used in a normal coordinate analysis of the vibrational spectrum of t-HOCO. A paper presenting the full account of these studies is in preparation.

A-X Transition of HC₂

The first survey absorption spectrum of the near-infrared electronic transition of HC₂, an important combustion reaction intermediate, was reported²⁹ during the term of this proposal. Because this species is formed during the high-temperature degradation of hydrocarbons in oxygen-deficient combustion systems, it may be expected to play a significant role in the later stages of solid propellant combustion, when the binder--often a long carbon-chain species--begins to participate in the chemistry of the system. The interaction of a beam of excited argon atoms with acetylene was used as the HC₂ source, and the Bomem Fourier transform system was used to obtain spectra in the 700-7900-cm⁻¹ spectral region. In addition to several absorptions of fundamentals and combination bands in the infrared region, a prominent, complicated pattern of absorptions of HC₂ was observed between 3600 and 7800 cm⁻¹. The great complexity of the HC₂ band system is a consequence of extensive perturbation of energy levels of the $\bar{A} \ 2\Pi$ state by high vibrational levels of the ground $2\Sigma^+$ state. The previous assignment^{30,31} of three gas-phase absorptions of HC₂ between 3780 and 4110 cm⁻¹ to ground-state combination bands was confirmed. The observed matrix shifts were relatively small. Therefore, these studies may be useful in the development of near-infrared laser diagnostics for

HC₂ in gas-phase reaction systems. Furthermore, because all of the HC₂ absorptions observed in an argon matrix must originate in the $\bar{X}(000)$ state, the argon-matrix observations may be helpful in the detailed gas-phase assignment of this very complicated band system.

CH + N₂ Reaction Products

A long-lived intermediate is known to be important in the reaction of CH with N₂.³² This process is of general importance whenever air is present in the combustion system and is implicated in the fixing of nitrogen to form NO early in the reaction sequence.³³⁻³⁶ An ultraviolet band system of HNCN was characterized some time ago by Herzberg and Warsop.³⁷ Another band system at somewhat shorter wavelengths was tentatively attributed to an HCN₂ species by Kroto and co-workers.³⁸ Experiments on this reaction system were initiated during the period of this proposal, but have not yet been completed. Although several discharge sampling configurations were tried, the highest product yield was obtained using the H-discharge (121.6 nm) photolysis of methane isolated in a nitrogen matrix. The previously identified ultraviolet band system of HNCN was prominent, as was a second band system between 280 and 330 nm with a band spacing of approximately 1050 cm⁻¹. These bands parallel those reported by Kroto and co-workers. Survey infrared scans indicate that several absorptions are present which may be contributed by an HCN₂ species. Further infrared studies using the Bomem system and isotopically substituted samples are planned. Studies of the photodecomposition thresholds of the initially-formed species, using mercury-arc radiation and various filters, will aid in determining whether more than one species contributes to the observed spectrum.

Electronic Energy Level Data Compilation

Although not a part of this proposal, another project conducted by the Principal Investigator during this period may be of interest to readers of this report. With partial support from the National Bureau of Standards Office of

Standard Reference Data, a compilation of the electronic energy levels and their vibrational structure for transient molecules which possess from three to six atoms is being prepared. Preliminary tables for a number of these species which are expected to be important in nitramine decomposition were included in the Report of the ARO Workshop on Combustion Probes for Solid Nitramines, held in Livermore, California, in June 1986. The compilation, which now includes more than 430 molecules, is approaching completion and will be submitted to the Journal of Physical and Chemical Reference Data.

Publications

- "The $\bar{A} \ 2\Pi - X \ 2\Sigma^+$ Transition of HC_2 Isolated in Solid Argon," M. E. Jacox and W. B. Olson, J. Chem. Phys. 86, 3134 (1987).
- "Analysis of the Vibrational Spectrum of the Nitromethyl Free Radical," M. E. Jacox, J. Phys. Chem., in press.
- "Vibrational and Electronic Spectra of the $H + HCN$ Reaction Products Trapped in Solid Argon," M. E. Jacox, J. Phys. Chem., in review.
- "The Vibrational Spectrum of t-HOCO Trapped in Solid Argon," M. E. Jacox, in preparation.

Participants in ARO Research

- Dr. Marilyn E. Jacox, Principal Investigator
- Dr. W. Bruce Olson, NBS staff member (collaborator in one of the above papers; no salary charged to this project)

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