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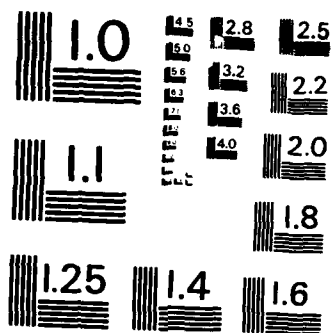
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) In order to obtain a detailed characterization of the chemistry and energetics of the processes which constitute the first stages of the decomposition of the model propellants nitromethane and methyl nitrite, three types of experiment were pursued. In the first series of studies, infrared spectra were obtained for the products of the ultraviolet photodissociation of these two compounds isolated in solid argon at 14 K. Infrared spectra were also obtained for the products of H-atom abstraction from nitromethane and methyl nitrite, including the first spectroscopic observation of the nitromethyl free radical. A summary.			

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20 (cont'd). of the information obtained regarding the chemical reaction mechanism for the first stages of the decomposition of nitromethane and methyl nitrite is presented. In the second series of experiments, the characteristics of a CO₂ laser with a uniquely well defined radiation pulse were tested and this laser was used together with laser-induced fluorescence detection to obtain the energy distribution in the resulting NO when methyl nitrite was dissociated. A marked preference for one spin-orbit state of the NO was observed. Conclusions were possible regarding the source of energy release in the detonation of methyl nitrite. The third series of experiments was concerned with the infrared multi-photon dissociation of a pulsed beam of methyl nitrite or nitromethane coupled with matrix isolation sampling and infrared study of the resulting decomposition products. Because of difficulty in matching the duty cycles of the pulsed beam and the laser and because of inadequate sensitivity of the available infrared instrumentation, this series of experiments yielded no new information regarding the early stages of the decomposition of these model propellants.

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FREE RADICAL DETECTION AND DYNAMICS IN PROPELLANT
IGNITION AND COMBUSTION SYSTEMS

Final Report

Marilyn E. Jacox and John C. Stephenson

21 May 1984

U. S. Army Research Office
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National Bureau of Standards
Washington, D. C. 20234

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Scientific Objectives

The common goal of these experiments is to obtain a detailed characterization of the chemistry and energetics of the processes which constitute the first stages of the decomposition of model propellants, in order to provide a molecular basis for improved control of sensitization and inhibition.

Three types of experiment were used in the pursuit of this goal. The first of these, matrix isolation sampling with infrared spectroscopic detection, has provided a powerful tool for the direct observation and spectroscopic characterization of free radicals and molecular ions. The second, application of laser-induced fluorescence (LIF) to probe the time dependence of product formation and the energy content of the products of infrared multiphoton decomposition (IRMPD) of molecules in the gas phase, has yielded much valuable information on the patterns and rates of energy redistribution in chemical systems. The third type of experiment, proposed and tested as a part of this project, combined IRMPD of a pulsed beam of the propellant molecule, mixed with a large excess of argon, with matrix isolation sampling and infrared spectroscopic study of the resulting solid deposit. Successful conduct of these experiments would permit determination of the importance of various primary dissociation channels in the thermal decomposition of propellants and other energetic materials, modelled by the IMRPD process.

Prototype propellant molecules studied in this project were nitromethane and methyl nitrite. The vapor pressures of these species are sufficiently great for gas-phase sampling. Furthermore, their isotopically substituted counterparts are

readily available, making possible the positive identification of products in the matrix isolation experiments.

Scientific Accomplishments

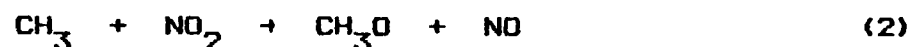
Matrix Isolation Studies

The matrix isolation studies conducted during the period of this proposal have yielded a substantial body of information regarding the chemistry of the first stages of decomposition of nitromethane, summarized in the following discussion.

Under a wide range of conditions, the primary reaction in the decomposition of nitromethane is known to be



Because molecular diffusion is effectively inhibited in an argon matrix, recombination of the free radical products of Reaction (1) is expected. Such recombination must also play an extremely important role in the decomposition of nitromethane at higher pressures or in the condensed phase. Previous gas-phase studies [1-3] have demonstrated that the reaction



predominates. At high pressures and in condensed media, Reaction (2) would be followed by the recombination

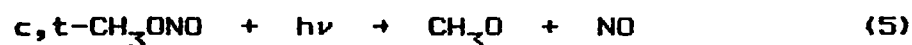


or disproportionation



Consistent with this gas-phase reaction sequence, when nitromethane was photolyzed in an argon matrix the infrared absorptions of both cis- and trans- CH_3ONO appeared, and absorptions of H_2CO and HNO became prominent [4].

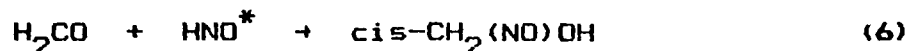
The key role of methyl nitrite in the reaction sequence for the decomposition of nitromethane dictated a series of detailed studies of this species. The first of these [5] yielded a complete vibrational assignment for both cis- and trans-methyl nitrite, facilitated by studies of the relative rates of photolysis of these two rotamers trapped in solid argon. The second study [6] explored the photodecomposition of methyl nitrite over a wide range of photon energy. The results are consistent with the occurrence of the primary photodecomposition reaction



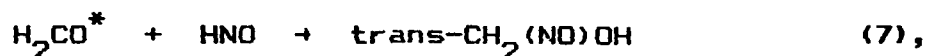
over the range from the photodecomposition threshold, near 365 nm, to 105 nm. Since Reaction (4) has a high probability of occurring in a single molecular collision [7,8], in an argon matrix very prominent infrared absorptions of H_2CO and HNO appear. These studies indicate that models of the chemistry of the decomposition of nitromethane at relatively high pressures and in the condensed phase need to take into account the formation of substantial concentrations of CH_3O and HNO in the early stages of the reaction and to include the roles of these highly reactive molecules in the later stages of the decomposition.

A number of other infrared absorptions, attributable to at least three previously unidentified products, are common to the spectra which result from the photodecomposition of nitromethane and methyl nitrite in solid argon. In a study of the photo-induced reaction of hydrogen-bonded H_2CO and HNO , produced by prolonged 365-nm irradiation of methyl nitrite in an argon matrix, Muller and Huber [9,10] demonstrated the stabilization of

the previously unobserved species cis- and trans-nitrosomethanol by the reactions



and



where 645-nm radiation was used for the photoexcitation of HNO and 345-nm radiation for the photoexcitation of H_2CO . Reversible, photoinduced interconversion between these two rotamers was also observed.

Detailed studies in this laboratory of the 254-nm photolysis of nitromethane in solid argon [4] demonstrated that one of the previously unidentified products was trans-nitrosomethanol, produced by Reaction (7) from H_2CO and HNO formed in the earlier stages of the reaction sequence. A smaller concentration of cis-nitrosomethanol was also identified. Since electronically excited HNO and H_2CO will play significant roles at the high energies typically attained in the decomposition of nitromethane, the chemistry of nitrosomethanol must also be considered in the search for a detailed understanding of these systems.

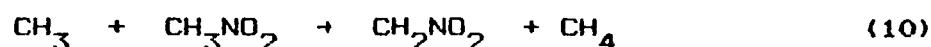
On extended photolysis of nitromethane in solid argon [4], still further decomposition occurs by the reaction



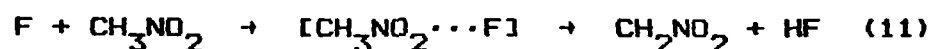
HCNO, stabilized in solid argon, in turn undergoes photoisomerization to HNCO:



Because methyl radicals characteristically abstract hydrogen atoms, the reaction

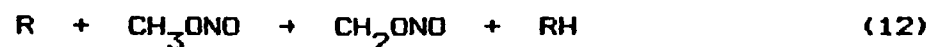


is expected to be an important secondary process in the decomposition of nitromethane. The extent of Reaction (10) and the role played by CH_2NO_2 in the later stages of the reaction would be enhanced in the condensed phase. A number of other atoms and small free radicals, including O, OH, NH_2 , and CH_3O , which are present in propellant and detonation reaction systems also characteristically abstract H atoms and would further enhance the role of CH_2NO_2 in the thermal decomposition of nitromethane under practical conditions. Experiments in which F atoms were used to abstract H atoms from nitromethane, with rapid quenching of the primary reaction products in an excess of solid argon at 14 K, have yielded the first spectroscopic detection of CH_2NO_2 , the nitromethyl radical [11].



The initially-formed F-atom addition complex decomposes by a tunnelling mechanism. These observations suggest that addition complexes of nitromethane with some of these other H-atom abstractors may play significant roles in the chemistry and energy exchange processes in the early stages of nitromethane decomposition. A detailed, computer-based analysis of the vibrational spectrum of CH_2NO_2 is in progress and may yield further information on the properties of its chemical bonds.

To assess the possible role of CH_2ONO in the decomposition of methyl nitrite, the reaction of F atoms with methyl nitrite was also studied [12]. By analogy with Reaction (10), the H-atom abstraction reaction



should play an important role in this system, as well. However, the infrared spectrum of the primary F-atom reaction products indicates that, even with rapid low-temperature quenching, CH_2ONO is marginally stable.



For $\text{R} = \text{F}$ atoms, evidence was obtained for the formation of a cyclic intermediate in Reaction (12). A second primary reaction channel,



involving the abstraction of NO, was also important. Because the end O atom would be more exposed than the central N atom, F-atom attack, the appearance of prominent infrared absorptions previously attributed to FON as well as of the absorptions of the more stable FNO isomer supports the previous spectroscopic identification of FON. Infrared absorptions of CH_3O were not detected; presumably they are relatively weak.

Gas-Phase IRMPD Studies

In order to obtain quantitative information on the infrared multiphoton decomposition (IRMPD) of molecules, a carbon dioxide laser was constructed which produced pulses for which the intensity vs. time profile was a square wave of selectable duration. Pulses from this laser, combined with time-resolved tunable dye laser-induced fluorescence and a highly automated data acquisition system, were used to study the IRMPD of selected molecules in the gas phase under single collision conditions.

The much-studied IRMPD of $\text{CF}_2\text{CFC1}$ and HCC1F_2 provided test cases, yielding several new conclusions [13,14]:

- (a) The energy content of the products does not depend simply on the laser intensity, I , but also on the pulse duration or fluence, F .
- (b) The time necessary for the reactants to absorb 40 photons ($\text{CF}_2\text{CFC1}$) or 20 photons (HCC1F_2) and to reach a "steady state" reaction rate is between 2 and 20 nsec, depending on I .
- (c) The observed "I dependence" (at constant F) for the decomposition of HCC1F_2 is a yield proportional to $I^{1/2}$, consistent with simple laser power broadening in the lower discrete levels. Earlier work with poorly defined intensity had yielded incorrect absorption cross sections for $\text{CF}_2\text{CFC1}$ and HCC1F_2 , and the low pressure yield vs. intensity curves could not be fitted by a rate equation description of IRMPD.

Methyl nitrite may fragment either to form methoxy and nitric oxide (Reaction (5)) or directly by the reaction



which, although energetically more favorable, involves a significant nuclear rearrangement. Studies in this laboratory of the IRMPD of methyl nitrite under collision-free conditions demonstrated that the decomposition, which requires the absorption of 20 photons, occurs exclusively by Reaction (5). The observed "I dependence" at constant F was, once again, a yield proportional to $I^{1/2}$. The NO product was formed cold; its rotational temperature varied between 320 and 560 K, increasing

slightly with I, its vibrational temperature was ≤ 800 K, and its Doppler-width translational temperature was ≤ 140 K (center of mass).

In another series of experiments, CH_3ONO in a pulsed supersonic molecular beam was vibrationally excited by CO_2 laser pulse of well characterized intensity and fluence. The LIF probe used for these experiments has pressure-scanned intra- and inter-cavity etalons, so that its spectral bandwidth is very narrow. The initial distribution of NO formed in different rotational and spin-orbit levels (about 90 NO A-X ro-vibronic transitions were probed) has been determined. Also, the Doppler widths of many NO transitions have been measured with about 0.04 cm^{-1} resolution. (For a thermal velocity distribution, $\Delta\nu = 0.04 \text{ cm}^{-1}$ corresponds to a translational temperature resolution of $T = 50$ K.) Because the reactants are in a beam, they have essentially no initial translational energy in the direction of propagation of the laser, and so deconvolution to account for motion of the parent molecule is unnecessary.

In these recent studies, we discovered several effects not previously observed in IRMPD on other unimolecular decomposition reactions. The NO may be formed in either of two electronic spin-orbit states, $^2\Pi_{1/2}$ or $^2\Pi_{3/2}$; the latter state ($\Omega = 3/2$) is 124 cm^{-1} higher than the former state ($\Omega = 1/2$). For reasons not yet understood, in Reaction (5) the NO is formed preferentially in the $\Omega = 1/2$ state. Specifically, the sum over all nuclear rotational angular momentum levels for the lower state divided by the sum in the upper state ($\sum_K ^2\Pi_{1/2}(K) / \sum_K ^2\Pi_{3/2}(K)$) varies from 7 at

low CO_2 laser intensity to 3 at the highest intensity (5.6 W/cm^2). Also, the nascent rotational temperatures for the two spin-orbit states are different: $T_{\text{rot}}(\Omega = 3/2)$ is about 100 K above $T_{\text{rot}}(\Omega = 1/2)$, typically 500 K vs. 400 K. However, for very high values of the nuclear rotational quantum number ($E_{\text{rot}} > 1000 \text{ cm}^{-1}$), these differences disappear. In contrast to the marked preference for one spin-orbit state in the NO product, the two lambda doublet components of NO are statistically populated: $A^+/A^- = 1.0$. The physical significance of the two lambda doublets is that the A^- has the lobes of the π electron cloud localized in the plane of rotation, while for A^+ the π cloud is out of plane, directed along the axis of rotation. The vibrational temperature, T_v , defined by the ratio $\text{NO}(v=1)/\text{NO}(v=0) = \exp(-(1876 \text{ cm}^{-1})/kT_v)$, was determined to be $T_v = 590 \pm 90 \text{ K}$. The rotational energy in the newly formed $\text{NO}(v=1) {}^2\Pi_{1/2}$ molecules is slightly lower than in the ground vibrational level (310 K vs. 500 K).

These detailed new results will be very important in understanding Reaction (5) and other unimolecular dissociations. However, in terms of simply accounting for the net energy released in the decomposition of CH_3ONO , the most significant overall result is that extremely little energy appears in the products (at least in relative kinetic energy or NO internal excitation), even under the most intense CO_2 laser irradiation. Therefore, essentially all the energy released in the detonation of CH_3ONO comes not from the initial bond breaking Reaction (5) but from subsequent radical reactions such as (4).

IRMPD of Pulsed Beam with Matrix Isolation Sampling

A central experiment of this proposal involved the expansion of an energetic molecule in argon carrier gas from a pulsed supersonic beam into a high vacuum chamber, irradiation and decomposition in the gas phase by pulses from a CO_2 TEA laser (IRMPD), condensation of the products isolated in solid argon on a cryogenic observation surface at 14 K, and analysis of the infrared absorptions ($400\text{--}4000\text{ cm}^{-1}$) of the products. $\text{Ar}:\text{CH}_3\text{ONO} = 100$ mixtures were photolyzed by the R(32) line at 983 cm^{-1} , which photolyzes the *cis*- CH_3ONO rotamer preferentially and is most effective at dissociating the rotationally cold reactant. LIF observations of the photolyzed beam showed substantial formation of NO. The only infrared product absorption of the sample condensed on a copper cold finger at 14 K which could be unambiguously identified was that of isolated NO, formed in Reaction (5). After about 5 hours of photolysis and deposition, the NO absorption maximum was only 5%, compared to the 55% absorption at 990 cm^{-1} of unphotolyzed CH_3ONO . No absorptions due to CH_3O were observed. Our earlier failure to observe matrix-isolated CH_3O in the F-atom reaction with CH_3ONO had also suggested that CH_3O is a weak infrared absorber. Nitromethane, CH_3NO_2 , was also photolyzed in this apparatus by the 1081 cm^{-1} R(24) CO_2 laser line. Grant [15] has recently shown that IRMPD of CH_3NO_2 in a pulsed molecular beam leads to CH_3 and NO_2 products. Thermal reaction rate data and thermodynamic data suggested that other reaction channels were possible. Our infrared spectrum of the photolyzed sample showed only a weak absorption of NO_2 .

These experiments were designed to assess the importance of various primary dissociation channels in the decomposition of these energetic materials. Although we have used the existing apparatus to the best of our abilities, the results have not been particularly interesting or definitive. Basically, the duty cycle and pulse energy of the photolysis laser were too low for an efficient match to the pulsed valve, which has the shortest pulse duration (14 μ sec) available. Moreover, the Beckman IR-9 infrared spectrometer was not fast or sensitive enough for the detection of other more interesting decomposition products at the level of photodecomposition attainable under these sampling conditions. We concluded that it would not be useful to attempt more CO₂ laser - pulsed molecular beam - cryogenic sampling experiments with the present equipment.

Publications

"The Vibrational Spectra of Methyl and Deuteromethyl Nitrite," F. L. Rook and M. E. Jacox, J. Mol. Spectrosc. 93, 101 (1982).

"The Photodecomposition of Methyl Nitrite Trapped in Solid Argon," M. E. Jacox and F. L. Rook, J. Phys. Chem. 86, 2899 (1982).

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"Photodecomposition of Nitromethane Trapped in Solid Argon," M. E. Jacox, J. Phys. Chem. 88 (in press).

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