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ABSTRACT

Studies have continued in vacuum ultraviolet photolysis of hydrazine. Results have been obtained which show that 80% of the nitrogen formed is through a molecular elimination and not through previously considered radical-radical combination. Shock tube studies have concentrated on developing suitable instrumentation for measuring simultaneously the absorption of the C_2 Swan and Deslandres systems behind the shock front. Flash lamp development for producing intense Phillips emission has started and results to date are discussed.

INVESTIGATORS

The investigations described in this report have been carried out through the efforts of the following personnel:

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1. PHOTOCHEMISTRY: MOLECULAR ELIMINATION OF NITROGEN IN THE PHOTOLYSIS OF HYDRAZINE

The following section has been submitted for publication to the Journal of Chemical Physics.

VACUUM-ULTRAVIOLET PHOTOCHEMISTRY. V. MOLECULAR ELIMINATION OF NITROGEN IN THE PHOTOLYSIS OF HYDRAZINE*

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The photochemistry of hydrazine has been reviewed[1-3] in terms of two possible primary events

$$N_2H_4 + h\nu \rightarrow N_2H_3 + H \quad (1)$$

$$\rightarrow 2NH_2 \quad (2)$$

with nitrogen formation being attributed to radical-radical reactions

$$2N_2H_3 \rightarrow N_2 + 2NH_3 \quad (3)$$

$$2NH_2 \rightarrow N_2 + 2H_2 \quad (4)$$

We wish to report results of experiments using mixtures of hydrazine and hydrazine-N^{15} which provide evidence for an entirely different mechanism for the formation of nitrogen in the photolysis of hydrazine. Other aspects of hydrazine photolysis will be considered elsewhere.[4]

Hydrazine and hydrazine-N^{15} were prepared by photolysis of ammonia and ammonia-N^{15} (97.3% N^{15} - Merck, Sharp & Dohme of Canada Ltd.) respectively. Based on the nitrogens formed in the photolysis of hydrazine-N^{15} alone (table 1), the compound is better than 90% N^{15}. Isotopic nitrogens produced were analyzed in a Consolidated 21-130 mass spectrometer. Other experimental details are the same as given previously.[5]

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*This research was supported by the National Aeronautics and Space Administration under Contract NASw-890.

1. D. Husain and R.G.W. Norrish, Proc. Roy. Soc. A273, 145 (1963).
2. L. F. Audrieth and B. A. Ogg, "The Chemistry of Hydrazine," John Wiley and Sons, Inc., New York, N. Y., 1951.
3. W. A. Noyes, Jr. and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publishing Corp., New York, N. Y., 1941.
4. L. J. Stief, V. J. DeCarlo, and R. J. Mataloni (to be published).
5. L. J. Stief, V. J. DeCarlo, and J. J. Hillman, J. Chem. Phys. 43, 2490 (1965).

The principal results are summarized in table 1. From the very low yield of N_2^{29} it is evident that the major portion of the nitrogen produced in the photolysis of hydrazine is formed by molecular elimination. We have also photolyzed mixtures of hydrazine and hydrazine-N^{15} using the Kr resonance lines (1165Å and 1236Å) and with a hydrogen discharge lamp fitted with a quartz window (λ >1850 Å). Qualitatively similar results were obtained in both cases with somewhat higher yields of N_2^{29}. Secondary photolysis of ammonia contributed somewhat to the increased randomization observed in the 1236Å experiment.

The small amount of randomization observed in these experiments (13% when correction is made for N^{14} in the hydrazine-N^{15}) is not consistent with any of the previously suggested mechanism of N_2 formation. Combination of NH_2 radicals (reaction 4) leads to 100% randomization in N_2. Combination of N_2H_3 radicals (reaction 3) probably proceeds via an intermediate formation of tetrazane (N_4H_6) and can lead to from 50 to 100% randomization depending on the mechanism of N_2 elimination from tetrazane.[6,7]

If corrections are made for N^{14} present in our hydrazine-N^{15} and if the mechanism of N_2H_3 combination leading to 50% randomization is accepted,[7] molecular formation of N_2 in the photolysis of hydrazine accounts for 80% of the N_2 formed. This estimate is not raised or lowered by more than 10% if other mechanisms of N_2H_3 combination are used or if the correction for N^{14} in the hydrazine-N^{15} is neglected.

Molecular formation of N_2 is thus estimated to account for 80 ± 10% of the N_2 formed in the photolysis of hydrazine. The overall mechanism for molecular elimination of N_2 from hydrazine may be represented as

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6. W.C.E. Higginson and D. Sutton, J. Chem. Soc., p. 1402 (1953).
7. J. W. Cahn and R. E. Powell, J. Am. Chem. Soc. 76, 2568 (1954).

$$N_2H_4 + h\nu \rightarrow N_2 + H_2 + 2H \quad (5)$$

The first step may be either removal of H or H_2 followed by decomposition of excited N_2H_3 or N_2H_2. The overall process

$$N_2H_4 + h\nu \rightarrow N_2 + 2H_2 \quad (6)$$

would not be consistent with our observation[4] that the ratio of N_2 to H_2 formed in the photolysis of N_2H_4 in the presence of C_2D_4 is unity. The process

$$N_2H_4 + h\nu \rightarrow N_2 + 4H \quad (7)$$

is energetically possible only below 1545Å and would not explain the results at higher wavelengths.

An alternate explanation for the randomization in the N_2 formed in the photolysis of hydrazine-hydrazine-N^{15} mixtures would be the disproportionation of N_2H_3 radicals

$$N_2H_3 + N_2H_3 \rightarrow N_2H_2 + N_2H_4 \quad (8)$$

followed by decomposition of N_2H_2

$$N_2H_2 \rightarrow N_2 + H_2 \quad (9)$$

The relative importance of direct molecular elimination and disproportionation of N_2H_3 can not be evaluated at present. However, it should be noted that if disproportionation of N_2H_3 leads to no randomization in N_2 and combination of N_2H_3 leads to 50% randomization,[7] the observed 13% randomization requires that if these reactions are the only source of N_2, the ratio of disproportionation to combination for N_2H_3 is 2.8. This ratio will be even higher if combination of N_2H_3 leads to greater than 50% randomization or if combination of NH_2, which leads to 100% randomization, contributes appreciably to N_2 formation. Even the minimum value of 2.8 is very high in comparison with that of the analogous hydrocarbon radical, C_2H_5,[8] which has a disproportionation to combination ratio of 0.14.

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8. J. A. Kerr and A. F. Trotman-Dickeson, Progr. Reaction Kinetics, 1, 111 (1961).

Regardless of the relative contribution of these two mechanisms, it is evident that - contrary to previous suggestions - the major portion of the nitrogen formed in the photolysis of hydrazine is eliminated from a single molecule and not formed by radical-radical combination.

We wish to thank Mr. Walter Payne for his assistance in conducting the experiments and Dr. J. R. McNesby for advice and comments.

Table 1

NITROGEN FORMATION IN THE PHOTOLYSIS OF HYDRAZINE

Pressure (millitorr) $N_2{}^{30}H_4$	$N_2{}^{28}H_4$	λ(Å)	Relative Abundance $N_2{}^{28}$	$N_2{}^{29}$	$N_2{}^{30}$
420	---	1470[a]	6.8	7.3	100
250	250	1470[a]	79.2	16.8	100
250	250	1470[a]	95.0	18.9	100
200	200	>2000[b]	140.0	24.5	100

a. Xe resonance lamp, sapphire window.
b. Medium pressure Hg lamp, quartz envelope.

2. SHOCK TUBE STUDIES - COLLISIONAL ENERGY TRANSFER IN FREE RADICALS

Introduction

The gases present in the coma of a comet are extremely rarefied and until recently the environment has been considered to be collision free by many investigators.[1] This collisionless environment has very recently come under question.[2] The rates of some collisional processes that would effect the observational data are necessary in order to evaluate the importance of collisions in the coma. The collisional efficiency of a singlet-triplet crossing for NH and C_2 as well as the efficiency of vibrational relaxation of C_2 are two such processes. Since the only observed emissions for NH and C_2 originate in triplet systems, a knowledge of the efficiency of the singlet-triplet collisional interchange coupled with observational data would help set an upper limit on the number of possible collisions. This is particularly true of C_2 where a recent estimate has resulted in the conclusion that if the singlet and triplet systems were equilibrated in the coma, emission of the Phillips system should be more intense than the Swan system.[3] Also, a knowledge of the relaxation time for C_2 would help evaluate the potential success of attempting to spectroscopically observe discrepancies in the vibrational populations of the C_2 radical in the inner coma.[4]

A shock tube program has been initiated this year to measure the rates of the above processes. Initial work is concerned with the triplet-singlet interchange for C_2. Specifically, the work is directed toward measuring the rates of the following processes:

$$C_2X^3\Pi u \xrightarrow{(M)} C_2a^1\Sigma_g{}^+$$

$$C_2X^3\Pi u \xrightarrow{(M)} C_2b^1\Pi u$$

Directed toward this aim, simultaneous absorption measurements of the Swan and Deslandres systems of C_2 are being conducted behind the shock front. The shock tube and associated electronic and optical components have been further modified

this quarter in order to circumvent several experimental problems that have become apparent under actual operation. Work has produced absorption of the Swan bands in the reflected shock region but has failed to show definitive absorption in the incident shock. The flash lamps developed last quarter to produce the Swan and Deslandres systems of C_2 in emission have been studied in hope of producing the Phillips system.

Experimental

A diagram of the electronic and optical equipment associated with the 15' aluminum shock tube is represented in the previous quarterly report.[5] Initial experiments demonstrated that the Bausch & Lomb Monochromators used in the original arrangement were not of adequate resolution to completely separate the 3852.2Å band head corresponding to the 0-0 transition of the Deslandres system from the intense 3871.3Å band head of CH also present in the lamp emission. Because of this difficulty these monochromators were replaced by a single Bass-Kessler grating spectrograph having a dispersion of 26 Å/mm in second order. A pair of traveling exit slits fitted to the spectrograph were set at the desired wavelengths and the absorption intensities again monitored with two 1P21 photomultiplier tubes. The 125 micron exit slits presently in use result in a resolution of 3.3Å and the instrument has capacity for further resolution if required.

Using the above spectrograph, runs have been conducted to measure absorption of the Swan and Deslandres bands. Varying compositions of ethylene in argon behind the incident shock and acetylene in argon behind both the incident and reflected shock have been investigated. The flash lamps developed last quarter were re-investigated in an attempt to produce Phillips band emission. Spectrographic records for the lamp emissions under varying conditions

of gas composition, total pressure and geometry were recorded on I-N spectroscopic plates. A new lamp containing carbon electrodes filled to 20 Torr of hydrogen was also examined using I-N hypersensitized plates.

Results and Discussion

Studies this quarter demonstrated that the experimental equipment was operational. However, no absorption could be detected in the initial runs with ethylene-argon mixtures. In these runs, a high enough concentration of C_2 for absorption measurements would not be produced unless the particle travel time at these temperatures was sufficient to allow appreciable dehydrogenation of the ethylene to occur before the heated gases reached the observation window. Because of this possibility, subsequent absorption work was conducted using mixtures of acetylene in argon even though the use of acetylene would result in more extensive soot formation in the shock tube and therefore more frequent disassembly and cleaning. However, subsequent work with acetylene again failed to produce any measurable absorption. Experiments conducted in the reflected shock region of higher density has more recently produced appreciable absorption ($I_o/I \sim 2$). These measurements in the incident and reflected shock therefore demonstrate that the sensitivity of the equipment is presently inadequate for the necessary measurements in the incident shock region. This could be due to either the fact that the concentration of C_2 in the shocked gas is inadequate to produce appreciable absorption or the spectral light of the flash lamp being used for absorption contains intense rotational lines corresponding to levels that are not appreciably populated in the shock tube. These points will be examined more carefully in order to eliminate this present difficulty.

Absorption of the Swan and Deslandres systems in the shock tube will result in information on the temporal behavior of the $X^3\Pi u$ and the $b^1\Pi u$ states of C_2. Absorption of the Phillips bands in the shock heated gas would yield information on the ground state $C_2{}^1\Sigma_g{}^+$ and therefore the role of this state in singlet-triplet collisional interchange could be directly studied. Measurement of this system in absorption would be facilitated by development of the characteristic emission in an intense lamp. Work has therefore proceeded to develop this system in lamps similar to those used for the Deslandres and Swan systems as well as a new lamp incorporating carbon electrodes and filled with hydrogen.

Enhanced formation of the Phillips system in a lamp would result from the production of a higher concentration of $b^1\Pi u$ in an atmosphere where the rate of collisional quenching of the state was smaller than the rate of the radiative transition. The fact that this system is weaker than either the Swan or Deslandres systems suggests that the upper $b^1\Pi u$ state is longer lived than either the $c^1\Pi g$ or the $a^3\Pi g$ states. Work was therefore carried out at lower total pressures in the lamps in order to decrease the rate of a possible collisional deactivation process but this direction did not produce enhanced or observable Phillips emission.

Experiments were also conducted in an attempt to increase the rate of production of the $b^1\Pi u$ state directly by discharging various organics in the lamp as well as by employing different rare gases that might be more effective in collisionally exchanging the triplet states to singlet states. The efficiency of these collisions would be enhanced by the heavier rare gases with lower excitation levels. A flashed carbon arc in hydrogen similar to the steady state lamp used by Ballik and Ramsey[6] has also been studied for this emission.

The efforts this quarter on production of an intense characteristic line source lamp for Phillips emission have not proven fruitful. The lack of sensitivity of spectrographically recording this near infrared radiation coupled with a lack of knowledge of the relative transition probabilities for the different vibrational bands constitute two reasons for this difficulty. Future work will require use of more sensitive plates in hope of seeing the lower vibrational transition of potentially higher strength.

References

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2. L. Bierman and E. Trefftz, C. A. 63, 17314e (1965); B. Donn, private communication.
3. Claude Arpigny, Ann. Rev. Astron. and Astrophys. 3, 351 (1965).
4. B. Donn, private communication.
5. Melpar Quarterly Report, Contract No. NASw-890, November 1965.
6. E. A. Ballik and D. A. Ramsey, Astrophys. J. 137, 84 (1963).