

difficulties in making H atom concentration measurements. The hydrogen atoms are probably trapped in multiple sites with different relaxation times at the different sites.¹¹ Since some of these sites are saturated, intensity measurements using our present apparatus are unreliable. When the microwave power is reduced to a low level, the HCO signal is reduced below the threshold detection level without completely alleviating the H atom saturation.

Although other mechanisms cannot be ruled out, it is postulated that reaction mechanisms 3 and 4, the H

atom abstraction from formaldehyde and the recombination of H atoms and CO molecules, are the most probable mechanisms for the increase of formyl radicals at 87°K.

Acknowledgment. The author wishes to acknowledge with thanks the many suggestions that were rendered to him by Dr. Kevin White in the preparation of this report.

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Photolysis of Solid Dimethylnitramine: Nitrogen-15 Study and Evidence for Nitrosamine Rearrangement

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Publication costs assisted by the Feltman Research Laboratories, Picatinny Arsenal

The photolysis of solid dimethylnitramine with 2537-Å light results in the formation of dimethylnitrosamine as a major product. The mechanism of bond-breaking in this photolytic reaction has been investigated *via* a ¹⁵N tracer technique. Photolysis of a *ca.* 1:1 mixture of doubly ¹⁵N-labeled and unlabeled dimethylnitramine followed by mass spectrometric analysis gave the following isotopic distribution in product dimethylnitrosamine: *m/e* 74:75:76 = 1:2:1. While the product showed efficient isotopic mixing, the unconverted dimethylnitramine in the photolyzed sample showed *no* mixing. A 1:1 mixture of doubly ¹⁵N-labeled dimethylnitramine and unlabeled dimethylnitrosamine gave efficient (almost 100%) light-induced isotopic equilibration. The results show that (a) dimethylnitrosamine arises from dimethylnitramine as a result of N–O bond breakage and (b) dimethylnitrosamine after being formed undergoes almost 100% light-induced rearrangement involving the bond between the two nitrogen atoms.

Introduction

Nitramines, compounds that contain the >N–NO₂ function, are important as explosives. Dimethylnitramine (I) is the simplest member of the secondary nitramines.

In this paper photolysis of dimethylnitramine in the solid state with 2537-Å uv light from a low-pressure mercury lamp is shown to result in the formation of dimethylnitrosamine (II) as a major product. The mechanism of bond breaking in this photolytic step has been investigated with the aid of ¹⁵N in both nitrogen positions of dimethylnitramine and the results of this study form the principal subject of this paper.

Thermal decomposition of dimethylnitramine in the gas phase is reported¹ to give dimethylnitrosamine by a process involving radicals produced by breakage of the N–N bond. In the only previously reported² photo-

chemical study of nitramines, *N*-methyl-*N*-nitro-1-naphthylamine was photolyzed in solution with uv light of wavelength greater than 3600 Å and found to yield the rearranged products, 2- and 4-nitro-*N*-methyl-1-naphthylamines. It was proposed that the photodecomposition, by analogy with thermal decomposition,² proceeded *via* heterolytic fission of the N–N bond followed by an intramolecular migration of NO₂. However, the primary photochemical processes in nitramines are not as well characterized as in the case of C-nitro compounds.³

(1) (a) J. M. Flournoy, *J. Chem. Phys.*, **36**, 1106 (1962); (b) B. L. Korsunskii, F. I. Dubovitskii, and G. V. Sitonina, *Dokl. Akad. Nauk SSSR*, **174**, 1126 (1967).

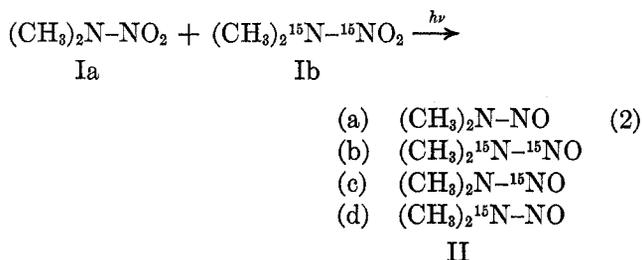
(2) D. V. Banthorpe and J. A. Thomas, *J. Chem. Soc.*, 7158 (1958).

(3) H. A. Morrison, "The Chemistry of Nitro and Nitroso Groups," Part 1, H. Feuer, Ed., Wiley-Interscience, New York, N. Y., 1969, Chapter 4.

The present ^{15}N -isotope tracer experiments are designed to determine if the chief photolysis product dimethylnitrosamine is formed by the breakage of the N-N bond, as in thermal decomposition of the vapor, or by the rupture of an N-O bond. The latter may be an obvious one-step process



The doubly ^{15}N -labeled, Ib, and the unlabeled, Ia, dimethylnitramine are mixed in *ca.* 1:1 ratio and subjected to photolysis followed by a mass spectrometric analysis. Of the four possible isotopic species of the nitrosamine, IIa-d, strictly a and b would be formed in the event of reaction without N-N fission. Contribution of c and d would indicate the degree of partici-



pation of the N-N fission process.

Experimental Section

Materials. Dimethylnitramine obtained from K and K Laboratories was sublimed before use. Dimethylnitrosamine (Puriss grade) from Aldrich Chemical Co. was used without further purification.

Dimethyl- ^{15}N -nitro- ^{15}N -amine. The ^{15}N -labeled compound was synthesized starting with dimethylamine- ^{15}N (99% enriched, Isomet Corp., Palisades, N. J.) and K^{15}NO_3 (99% enriched, Prochem Ltd., Lincoln Park, N. J.). K^{15}NO_3 was first treated with concentrated H_2SO_4 on a vacuum line to generate H^{15}NO_3 which was later distilled *in vacuo* into a stoichiometric amount of dimethylamine- ^{15}N held at low temperature in a receiver. The mixture thus obtained was thawed gradually to allow salt formation. The doubly labeled dimethylammonium nitrate was then dehydrated by treatment with anhydrous acetic anhydride and zinc chloride⁴ at 35° for 15 hr.

Irradiation Procedure. For convenience in mass spectrometric determination of isotopic distribution among products, the irradiations were carried out with samples (5 to 10 mg) contained in quartz capillaries (1 mm i.d. \times 4-5 cm long) sealed at both ends. Air was not removed by pumping prior to irradiation. Each capillary with sample was irradiated for 120 min at the center of a helical (4.5 cm diameter \times 5 cm high and consisting of six turns; 90 W output) low-pressure mercury lamp (chiefly 2537- \AA wavelength).

Mass Spectrometric Analysis. The spectra were obtained by introducing the samples into the mass spectrometer (Consolidated 21-104, single focusing) *via*

the gas inlet system rather than the solid probe since the vapor pressure of the samples was found to be inconveniently high. The capillary containing the sample was placed in a demountable tube which was then attached to the inlet system. The tube containing the sample was flushed with nitrogen, cooled to 77°K , and then pumped down. The 3-l. expansion volume was filled to approximately 300 μ with sample vapor.

The different experimental runs consisted of (i) pure dimethylnitramine, (ii) *ca.* 1:1 mixture of doubly ^{15}N -labeled and unlabeled *dimethylnitramine* (prepared by intimate mixing in a mortar as well as by coprecipitation from ether), and (iii) *ca.* 1:1 mixture of the labeled dimethylnitramine (Ib) (24.0 mg) and unlabeled *dimethylnitrosamine* (20.3 mg). The last mentioned mixture was a pale yellow solution but still for the sake of uniformity, the above capillary sampling procedure was used. The 10- μ l samples were transferred to the quartz capillaries using a Hamilton syringe and then handled in the same way as the solid samples.

Results

When dimethylnitramine (I) was irradiated in the solid form (as a thin layer or in a "capillary") the white solid turned into a viscous yellow liquid. The latter was analyzed by gas chromatography using a P.E. Model 154D instrument equipped with a flame-ionization detector. A 6 ft \times $1/4$ in. S.S. column containing firebrick coated with Ucon polyglycol (P.E. LB-550x) was operated at 140° and 10 psig helium pressure. Under these conditions dimethylnitrosamine (II) could be readily separated from (I) and identified by elution times (II, 9 min; I, 20 min). The conversion to nitrosamine was of the order of 35%. No other products were detectable by the above method or by an nmr analysis (Varian T-60). The nmr spectrum of (I) in acetone- d_6 showed a triplet at δ 3.4 (measured from TMS). The nitrosamine (II), however, gave two peaks, δ 3.0 and δ 3.8 corresponding to the trans and the cis methyl groups, respectively. The nitramine (I) after a 110-min irradiation clearly showed strong absorptions at δ 3.0, 3.4, and 3.8. An ir spectrum of the neat yellow liquid obtained after irradiation was consistent with dimethylnitrosamine since it showed peaks at 842 (m), 682 (m), and 1048 (vs) cm^{-1} . The uv absorption spectrum had a maximum at 345 nm corresponding to the nitrosamine band in addition to the short wavelength band around 240 nm which appeared in the spectra of both nitramines and the nitrosamines. The mass spectral data discussed in detail here provide additional confirmation for the nitrosamine as the main photoproduct.

Tables I and II show the mass spectral data pertinent to the molecular ions of the dimethylnitramine and the nitrosamine. The isotopic distribution derived

(4) W. J. Chute, K. G. Herring, L. E. Toombs, and G. F. Wright, *Can. J. Chem.*, Sect. B, **26**, 89 (1948).

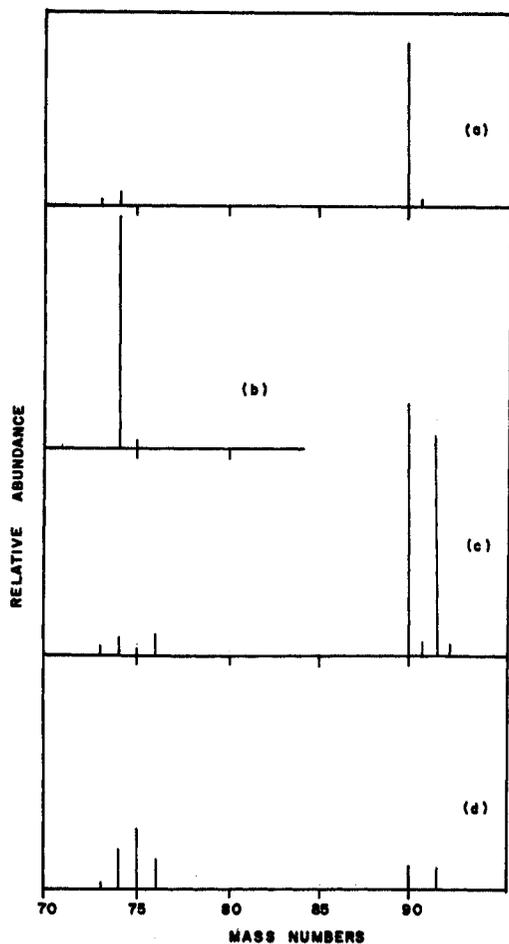


Figure 1. Observed mass spectra: (a), $(\text{CH}_3)_2\text{N}-\text{NO}_2$; (b), $(\text{CH}_3)_2\text{N}-\text{NO}$; (c), ca. 1:1 mixture of $(\text{CH}_3)_2\text{N}-\text{NO}_2$ and $(\text{CH}_3)_2\text{N}^{15}\text{N}^{16}\text{O}_2$ —unirradiated; (d), mixture in (c)—after irradiation. Relative sensitivity: $\times 10$ for (a), (b), (c) and $\times 1$ for (d).

from these data is shown in Table III. Figure 1 shows the corresponding mass spectra of the above and those of irradiated and unirradiated mixtures (ca. 1:1) of dimethylnitramine and its doubly tagged analog.

In the mass spectrum of dimethylnitramine the relative abundance of the ion (this ion has been previously postulated⁵ to be $(\text{CH}_3)_2\text{N}-\text{N}^+=\text{O}$) at m/e

Table I: Relative Abundance^a of Selected Ions in the Mass Spectra of Dimethylnitramine before and after Uv Irradiation (Irradiation Time: 120 min)

Sample no.		Relative abundance					
		(m/e) 74	75	76	90	91	92
1	Unirradiated	5.8	0.3	0.2	100	3.6	0.5
2		3.2	0.3	0.2	100	3.2	0.5
1	Irradiated	179	4.6	0.7	100	3.1	0.7
2		148	4.6	0.3	100	3.0	0.6
3		129	3.5	0.3	100	3.3	0.6

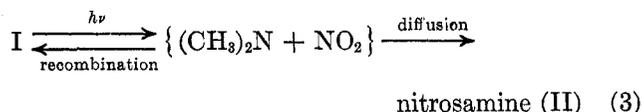
^a Each set is average of two mass scans.

74 is about 6% while in the nitrosamine the molecular ion at m/e 74 has a relative abundance of 96%. The formation of nitrosamine in the dimethylnitramine is therefore readily followed by a measurement of m/e 74. The ^{15}N isotopic isomers would then move to m/e 75 and 76, respectively.

In using the data of Tables I and II to get isotopic distribution some corrections have to be applied. In the spectrum of dimethylnitramine (Ia) (Table I, lines 1 and 2) the m/e 91 arises from the natural ^{13}C content and likewise the m/e 93 in the spectrum of Ib (Table II) is due to natural carbon-13. Of the m/e 91 values shown in Table II about 2% of each is due to the ^{14}N impurity in the doubly tagged dimethylnitramine (1% at each position) and the remainder is due to the ^{13}C . The ratios of m/e 90 and 92 in the spectra of the unirradiated mixtures of Ia and Ib (Table II, lines 1 and 2 in Batch 1 and line 1 in Batch 2) give the ratios of the unlabeled and doubly ^{15}N -labeled species actually present in the mixture used for photolysis. These ratios were used to determine the statistical distribution to be expected of m/e 74, 75, and 76 if complete isotopic equilibration took place. For an equimolar mixture of Ia and Ib the ratio would be 1:2:1. The observed and the "calculated" ratios are summarized in Table III.

Discussion

The data presented in Table II reveal that there is extensive contribution of m/e 75 in addition to the normal increase in m/e 74 and 76 subsequent to photolysis. Prior to photolysis m/e 75 appeared to be less than 2% which indicated that no isotope exchange was caused by electron impact. Furthermore, the ratio of 74:75:76 was nearly statistical as shown in Table III. One obvious conclusion which may be drawn from this excellent agreement with statistical distribution would be that the photolysis involves an initial N-N bond fission. However, the spectra failed to show any increase in m/e 91 above the initial levels. This indicated no isotopic exchange between Ia and Ib. The conclusion that the N-N bond undergoes a cleavage in the photolysis is inconsistent with no isotope exchange taking place in the nitramine itself. For, in order to account for the rather high conversion to nitrosamine (35% as determined by nmr analysis)



the radicals formed on N-N fission have to *escape*, by *diffusion*, the highly favored geminate recombination in the solid state and also not lead to bulk recombination and isotopic exchange in (I). It seemed likely, there-

(5) S. Bulusu, T. Axenrod, and G. W. A. Milne, *Org. Mass. Spectrom.*, **3**, 13 (1970).

Table II: Relative Abundance^a of Selected Ions in the Mass Spectra: 1:1 Mixture of (CH₃)₂N-NO₂ (Ia) and (CH₃)₂¹⁵N-¹⁵NO₂ (Ib) before and after Irradiation (Irradiation Time: 120 min)

Sample no.	(m/e)	Relative abundance						
		74	75	76	90	91	92	93
Batch 1								
1	Unirradiated	5.0	1.8	5.3	100	4.3	84	2.2
2		4.0	1.7	4.6	100	4.1	95	2.1
1	Irradiated	134	221	84	100	7.0	70	2.3
2		164	279	133	100	4.8	81	1.9
Batch 2								
1	Unirradiated	8	2	8	100	7	78	3.7
1	Irradiated	208	345	155	100	6	82	4.3
2		232	390	179	100	7	88	3.7
3		357	528	249	100	7	87	4.3
4		299	522	243	100	7	90	3.5

^a Each set is an average of two mass scans. Batch 1: sample mixture prepared by intimate mixing in a mortar. Batch 2: sample mixture prepared by coprecipitation from ether.

Table III: Isotopic (¹⁴N/¹⁵N) Distribution in the Nitramine and Nitrosamine after Photolysis, Derived from Table II

(m/e)		Nitrosamine (II)			Nitramine (I)	
		74	75	76	90	92
Batch 1						
Sample 1	Relative abundance	129	219	79	100	70
	Observed ratio	1.00	1.70	0.61		
	Calculated ratio	1.00	1.70	0.70		
Sample 2	Relative abundance	160	275	128	100	81
	Observed ratio	1.00	1.72	0.82		
	Calculated ratio	1.00	1.81	0.81		
Batch 2						
Sample 1	Relative abundance	200	343	147	100	82
	Observed ratio	1.00	1.72	0.74		
	Calculated ratio	1.00	1.82	0.82		
Sample 2	Relative abundance	224	388	171	100	88
	Observed ratio	1.00	1.73	0.76		
	Calculated ratio	1.00	1.88	0.88		
Sample 3	Relative abundance	349	526	241	100	87
	Observed ratio	1.00	1.51	0.69		
	Calculated ratio	1.00	1.87	0.87		
Sample 4	Relative abundance	291	520	215	100	90
	Observed ratio	1.00	1.79	0.74		
	Calculated ratio	1.00	1.90	0.90		

fore, that the isotope crossover in the photoproduct, nitrosamine, had occurred in a secondary light-induced process *after* its initial formation from the nitramine (I).

In order to test the possibility of a nitrosamine photorearrangement, a 1:1 mixture of (CH₃)₂¹⁵N-¹⁵NO₂ (Ib) and unlabeled nitrosamine was irradiated. The results which are shown in Table IV established clearly that nitrosamine had undergone an efficient light-induced isotopic equilibration. In fact, the 75:76 ratio was higher than 2.4 presumably due to the fact that in the initial stages of the photolysis experiment the concentration of the unlabeled nitrosamine was overwhelmingly large.

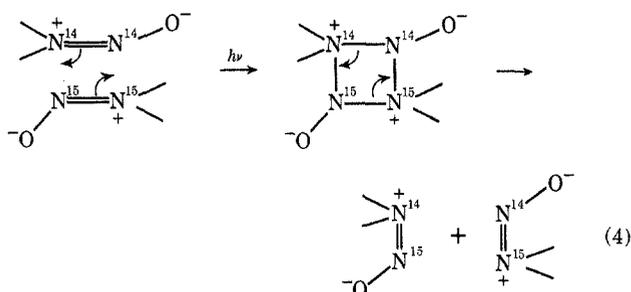
Mechanism of Nitrosamine Photorearrangement. The

Table IV: Relative Abundance of Selected Ions in the Mass Spectra: Mixture (ca. 1:1) of (CH₃)₂¹⁵N-¹⁵NO₂ and (CH₃)₂N-NO Before and After Irradiation (Irradiation time: 120 min)

Sample no.	(m/e)	Relative abundance				
		74	75	76	92	75:76 ^a
1	Unirradiated	393	12.6	8.5	100	
2		409	13.0	8.6	100	
1	Irradiated	441	306	125	100	2.52
2		717	417	176	100	2.36
3		533	335	130	100	2.59

^a The m/e 75 and 76 were corrected for background shown in the control run before 75:76 ratio was computed.

above isotope crossover in nitrosamine may or may not proceed from an initial N–N bond cleavage. However, the extent of the crossover (nearly 100%) is inconsistent with the favored geminate recombination in the condensed phase if the $(\text{CH}_3)_2\text{N}$ and NO radicals are indeed formed first. The following mechanism (4) is now proposed which is consistent with the major experimental observations, *viz.*, a very efficient isotopic crossover in the nitrosamine and almost total preclusion of exchange in the parent nitramine.



Nitrosamines reportedly are resistant to photodecomposition.⁶ Very early studies⁷ of the photolysis of dimethylnitrosamine itself in the gas phase showed dimethylamine and uncharacterized polymeric material as products. Later work on nitrosamines dealt with studies of photolysis in solution.^{6,8} Photodecomposition of dibenzyl nitrosamine in presence of oxygen was observed to yield dibenzylamine, *N*-benzylidene benzylamine, and dibenzylammonium nitrate.⁸ The reported conversion to nitrate is about 0.3% per hour of photolysis. The products were interpreted to arise from radicals generated by breakage of the N–N bond. In solution, breakage of the N–N bond would be favored since the resulting radicals could be stabilized by solvation. To our knowledge, a photorearrangement of nitrosamines such as the one proposed here to explain the present results was never considered. However, this reaction is reminiscent of a recent study⁹ of C-nitroso compounds describing a light-induced shift of the equilibrium, dimer \rightleftharpoons monomer, toward the monomer.

Mechanism of Formation of Nitrosamine from Dimethylnitramine Photolysis in Solid State. From the absence of mass 91 in our experiments with doubly labeled (^{15}N) dimethylnitramine we conclude that the

N–N bond does not break in the solid-phase photolysis. However, since nitrosamine is formed in large yield, it has to result by a one-step process involving cleavage of the N–O bond.

Thermolysis of dimethylnitramine in the gas phase to give nitrosamine was proposed¹ to take place with prior formation of the radicals $(\text{CH}_3)_2\text{N}$ and NO_2 . While in the gas phase and in solution one can visualize formation of these radicals, the mechanism of solid phase photolysis seems to involve preferential breakage of the N–O bond analogous to the case of aromatic C-nitro compounds.³ The stability of the N–N bond is also in line with the observed short N–N bond length (1.26 Å)¹⁰ in solid dimethylnitramine and the attributed double bond character in virtue of it. Detailed crystal structure data¹¹ are, however, lacking to see if the lattice orientation of adjacent molecules of dimethylnitramine is such as to promote the nitrosamine photorearrangement.

Summary and Conclusion

Photolysis of dimethylnitramine carried out in the solid state yields dimethylnitrosamine as the major product. Isotope crossover experiments using mixtures of doubly ^{15}N -labeled dimethylnitramine with unlabeled dimethylnitramine and dimethylnitrosamine, respectively, lead to the conclusion that nitramine converts to nitrosamine as a photoproduct by an N–O bond cleavage. Labeled and unlabeled nitrosamines also undergo a light-induced rearrangement resulting in an efficient isotope crossover.

Acknowledgment. The authors wish to thank Professor B. S. Thyagarajan of the University of Idaho for helpful discussions and Mr. J. R. Autera for much technical assistance.

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(7) C. H. Bamford, *J. Chem. Soc.*, 12 (1939).

(8) T. Axenrod and G. W. A. Milne, *Tetrahedron*, **24**, 5775 (1968).

(9) A. L. Bluhm and J. Weinstein, *Nature (London)*, **215**, 1478 (1967).

(10) W. Costain and E. G. Cox, *ibid.*, **160**, 826 (1947).

(11) In answer to a point raised by one of the referees, it may be said that space group $P2_1/m$ given in ref 10 indicates that the more probable orientation of adjacent molecules in the unit cell is head-to-tail which is consistent with the rearrangement mechanism given in eq 4.