

92. Photolysis of Dimethylnitrosamine in the Gas Phase

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Dedicated to Prof. Dr. *Conrad Hans Eugster* on the occasion of his 60th birthday

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Summary

Photodecomposition of dimethylnitrosamine in the gas phase (~ 1 Torr) has been investigated following irradiation into the S_1 ($n\pi^*$) $\leftarrow S_0$ (363.5 nm) and S_2 ($\pi\pi^*$) $\leftarrow S_0$ (248.1 nm) transitions at room temperature. With a quantum yield of unity, excitation into the S_1 state yields the fragments $(CH_3)_2N^{\cdot}$ and NO which then recombine leaving no photoproducts. The addition of O_2 results in only one photoproduct, $(CH_3)_2NNO_2$. Irradiating into the S_2 state, the products $CH_2=N-CH_3$, $(CH_2=N-CH_3)_3$, $CH_2=NOH$, N_2O , NO, H_2 , and N_2 were identified by capillary gas chromatography mass spectrometry. In the presence of N_2 as a buffer gas the photoproducts are only $CH_2=N-CH_3$, $(CH_2=N-CH_3)_3$, N_2O , and H_2 . For both excitation conditions a mechanism is proposed involving cleavage of the N, N-bond as the main primary photolytic process.

Introduction. – Nitrosamine molecules possess an interesting chemical structure characterized by the existence of an electron donating group (R_2N) directly bonded to an electron accepting group (NO). These compounds, often present in our food, have received considerable attention following the discovery of their highly carcinogenic nature [1]. Moreover, the potential of nitrosamine formation in polluted urban atmospheres has recently triggered investigations in simulated polluted atmospheres where the formation of nitrosamines has been observed [2], [3].

The interesting structural properties of nitrosamines as well as the question of their degradation, if these compounds indeed occur in the atmosphere, have stimulated us to study their photochemical behavior in the gas phase. In this communication we report results on the photochemistry of dimethylnitrosamine (DMN) one of the simplest and most common nitrosamines. The photolysis of DMN at a pressure of ~ 1 Torr was carried out with and without a foreign gas (nitrogen or oxygen) irradiating into the first and second excited singlet state. Based on the products obtained under these different conditions, a photochemical reaction mechanism for DMN is proposed.

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Experimental part. – DMN was photolyzed in quartz cells (80–6000 ml), with suprasil windows using a 500 W mercury high pressure lamp (*Osrham* HBO 500 W/2) and a *Spex Minimate* monochromator ($f/4.0$, $\Phi 220$ mm). The GC/MS-system employed to analyze the photoproducts consisted of a gas chromatograph (*Carlo Erba* Mod. 4160-01) equipped with a 50 m long open tubular glass column (UCON LB 550X, *Jaeggi*, Trogen, Switzerland) and a quadrupole mass spectrometer (*Balzers* QMG 511). A detailed description of this sensitive detector system is given elsewhere [4].

Dimethylnitrosamine (*Merck*) was purified to $\geq 99.5\%$ by high vacuum distillation at 77 K. ^{15}NO with an isotopic purity $\geq 99.5\%$ (*Prochem.*, London) was used as received. Formaldoxime, $\text{CH}_2=\text{NOH}$, was obtained by dissolving its trimer [5] in a 3% hydrochloric acid solution. *N*-Methylidene-methylamine, $\text{CH}_3-\text{N}=\text{CH}_2$, was identified in the mass spectrometer with the aid of its trimer [6]. The latter has been synthesized according to a published procedure [7].

Results. – 1. *Absorption spectrum.* The gas-phase-absorption spectrum of DMN [8] exhibits a weak band (oscillator strength $f=0.009$) between 24,500 and 30,000 cm^{-1} with a maximum at 27,500 cm^{-1} ($\epsilon_{\text{max}}=68 \text{ M}^{-1} \text{ cm}^{-1}$). This band shows a distinct vibrational progression of $\sim 900 \text{ cm}^{-1}$. The next higher absorption band is strong ($f=0.12$) and unstructured with a maximum at 44,000 cm^{-1} ($\epsilon_{\text{max}}=4600 \text{ M}^{-1} \text{ cm}^{-1}$). Based on an INDO/S-CI calculation [9] using the well established DMN geometry [10] and 57 singly excited configurations, these absorption bands were assigned to the $\text{S}_1 (\pi\pi^*) \leftarrow \text{S}_0$ (calc. 20,000 cm^{-1} , $f=0.004$) and the $\text{S}_2 (\pi\pi^*) \leftarrow \text{S}_0$ transitions (calc. 41,800 cm^{-1} , $f=0.39$). The lowest triplet state T_1 was predicted at 14,000 cm^{-1} . Applying Förster's formula [11], the reciprocal of the natural lifetime of the S_1 state was estimated to be $k_f=1.7 \times 10^5 \text{ s}^{-1}$.

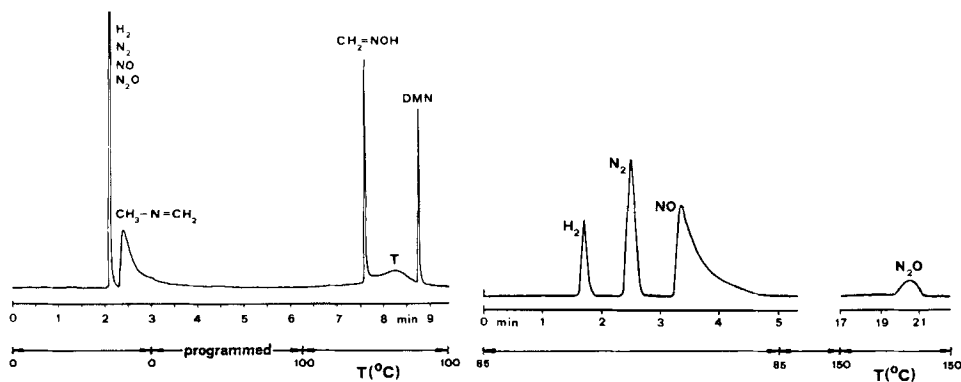
2. *Irradiation into the $\text{S}_1 (\pi\pi^*) \leftarrow \text{S}_0$ transition.* Even after prolonged irradiation into the first electronic transition of dimethylnitrosamine ($p \approx 1$ Torr) at 363.5 nm neither photoproducts nor a decrease in the initial compound pressure is observed. Since under such excitation conditions (330 kJ/Einstein) a N,N-bond ($\sim 170 \text{ kJ/mol}$ [12]) is expected to dissociate forming $(\text{CH}_3)_2\text{N}^\cdot$ and NO, a mixture of 1 Torr DMN and 4.5 Torr ^{15}NO was photolyzed. Mass spectrometric analysis showed the production of $(\text{CH}_3)_2\text{N}^{15}\text{NO}$ [8]. Using this isotopic exchange reaction, the dissociation quantum yield in terms of the number of absorbed photons to the number of produced $(\text{CH}_3)_2\text{N}^{15}\text{NO}$ molecules (which is equal to the number of dissociated $(\text{CH}_3)_2\text{NNO}$ molecules as long as $[\text{NO}] \ll [^{15}\text{NO}]$) was determined and found to be $\Phi_{\text{diss}}(363.5 \text{ nm})=1.03 \pm 0.10$. The addition of 100 Torr N_2 as a buffer gas did not alter this result.

Photolysis of 1 Torr DMN in the presence of 150 Torr O_2 , resulted in only one photoproduct, dimethylnitramine $(\text{CH}_3)_2\text{NNO}_2$. When the oxygen pressure was lowered below 5 Torr, no photoproducts were found.

Both, stationary and time resolved emission measurements revealed no emission signal. Based on the sensitivity of the employed apparatus the emission quantum yield of DMN is $< 5 \cdot 10^{-4}$. With the estimated value of $k_f=1.7 \times 10^5 \text{ s}^{-1}$ the rate constant of the S_1 deactivation is $> 8.5 \times 10^9 \text{ s}^{-1}$.

3. *Irradiation into the $\text{S}_2 (\pi\pi^*) \leftarrow \text{S}_0$ transition.* Following irradiation into the second excited singlet state the gas chromatogram of the partially photolyzed sample showed four distinct new peaks (Fig. 1). Based on their mass spectrograms and retention times on the column (t_r) as well as comparison with synthesized compounds, *N*-methylidene-methylamine ($\text{CH}_2=\text{N}-\text{CH}_3$), its trimer, and

formaldoxime ($\text{CH}_2=\text{NOH}$) have been identified. Since the peak with the shortest retention time appeared to be a superposition of several product peaks, an additional column (4.5 mm diam. $\times$ 2 m, molecular Sieve 5A, 60–80 mesh) was used allowing – as demonstrated in Figure 1 – the separation of four gases: NO (67 Vol. %), H_2 (13) N_2 (13) and N_2O (7). Moreover, at high detector sensitivity small amounts of ethane have been observed.



Capillary GC. separation of the photoproducts of dimethyl-nitrosamine (~ 1 Torr) irradiated at 248.1 nm obtained by the TIC method. In the left chromatogram the peak denoted by T indicates the trimer ($\text{CH}_2=\text{N-CH}_3$)₃. Using an additional column, the highly volatile products were also separated right.

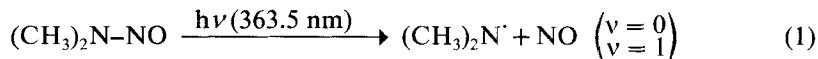
When the photolysis was performed at 0°C and -10°C the $\text{CH}_2=\text{N-CH}_3$ peak which is weak at room temperature greatly increases. In a separate experiment the formation of $\text{CH}_2=\text{N-CH}_3$ and its trimer from a mixture of formaldehyde (1 Torr) and methylamine (1 Torr) was monitored with the mass spectrometer at different intervals following mixing. While the mass peak $m/z=43$ of $\text{CH}_2=\text{N-CH}_3$ rapidly increased during the first few minutes, that of the trimer ($m/z=128$) appeared delayed. These results clearly indicate that the photoproduct $\text{CH}_2=\text{N-CH}_3$ further reacts forming the trimer. This polymer has been found to strongly adsorb on the cell walls.

To obtain further details concerning the formation of formaldoxime, we photolyzed ($\lambda_{\text{ex}}=248.1$ nm) a sample of 2 Torr CH_3I in the presence of 3 Torr NO thereby expecting the photoproduct $\text{CH}_3\cdot$ to be scavenged by NO. In the gas chromatogram two new peaks appeared, a small one with $t_r \sim 150$ s and a relatively large one with $t_r \sim 480$ s. These peaks were identified as CH_3NO and $\text{CH}_2=\text{NOH}$, respectively. The time dependence of these product concentrations showed that formation of $\text{CH}_2=\text{NOH}$ from $\text{CH}_3\cdot$ radicals and NO involves the intermediate CH_3NO (*vide infra* reaction 8). By photolyzing DMN we were not able to encounter CH_3NO . A possible dimer of nitrosomethane was also not observed [13].

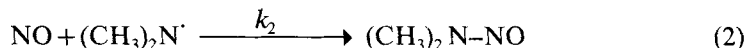
Using N_2 as a buffer gas (1 Torr DMN) the number of photoproducts is reduced. At 100 Torr N_2 we detected $\text{CH}_2=\text{N-CH}_3$, $\text{CH}_2=\text{NOH}$, N_2O , and H_2 . With increasing buffer gas pressure the amount of formaldoxime decreases till, at 500 Torr N_2 , essentially only three photoproducts $\text{CH}_2=\text{N-CH}_3$, N_2O , and H_2 were observed.

Photolysis of 1 Torr DMN in the presence of 150 Torr oxygen resulted in the formation of dimethylnitramine $(\text{CH}_3)_2\text{NNO}_2$, nitromethane CH_3NO_2 , methyl nitrite CH_3ONO , and formaldehyde H_2CO . Some minor peaks in the gas chromatogram could not be identified. It is noted that contrary to irradiation of DMN alone, no volatile gases were produced when O_2 is present.

Discussion. – Irradiation into the first absorption band of DMN leads to the cleavage of the weak N, N-bond with a dissociation quantum yield of unity according to the reaction

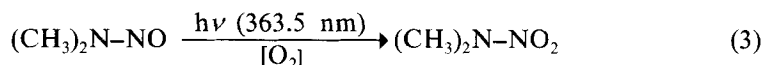


Using the excitation energy of ~ 330 kJ/Einstein, the bond dissociation energy with respect to the ground state potential surface is exceeded by ~ 160 kJ/mol. Without significant collisional deactivation between excitation and dissociation or predissociation, this energy is partitioned among the fragments leaving a fraction of the NO molecules in a vibrationally excited state [8]. The complete reversibility of reaction 1

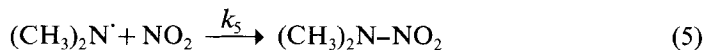


and the low stationary concentration of the fragments produced ($\sim 4.5 \times 10^{15}$ absorbed photons $\cdot \text{l}^{-1} \cdot \text{s}^{-1}$) imply a long radical lifetime. Assuming $k_2 \leq 10^6 \text{ Torr}^{-1} \text{ s}^{-1}$ [8] the lifetime of $(\text{CH}_3)_2\text{N}^\cdot$ is estimated to be > 0.5 s.

In the presence of oxygen only one photoproduct is found which has been clearly identified as dimethylnitramine.



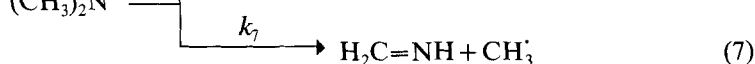
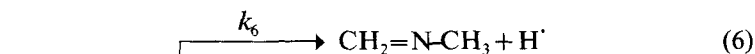
Based on this 'clean' photoreaction and consistent with previous results [14][15], a direct reaction between O_2 and the $(\text{CH}_3)_2\text{N}^\cdot$ radical is considered unlikely. Instead the following mechanism is proposed



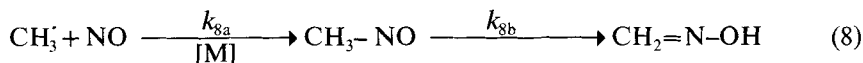
In the case of the $\text{NH}_2^\cdot$ radical ($> 10^{-5}$ Torr) no reaction with O_2 (500 Torr) has been observed [14]. Furthermore, *Lindley et al.* [15] have recently shown that the reactivity of the $(\text{CH}_3)_2\text{N}^\cdot$ radical with oxygen is indeed very low, about 10^6 times less efficient than with NO or NO_2 . Although reaction 4, which probably involves the intermediate ONOO [16], is also relatively slow with a reported $k_4 = 1.56 \times 10^8 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ [17], it can compete with reaction 2 as long as the O_2 pressure is higher than 5 Torr. Since during photolysis the ratio $[\text{DMN}]/[\text{NO}_2] > 10^4$ and the

ε (363.5 nm) values of both compounds are roughly the same, no direct photolysis of NO_2 is expected.

When DMN is excited into the $S_2(\pi\pi^*) \leftarrow S_0$ transition at 248.1 nm the excitation energy, 485 kJ/mol, exceeds the C–N bond energy of ~ 350 kJ/mol [12]. However, the photoproducts found lead one to propose that even under these excitation conditions the main primary photochemical step is the dissociation of the very weak N, N-bond (see equ. 1). Without collisions the amine radical possesses a considerable amount of excess vibrational energy. Prior to vibrational relaxation and/or recombination with NO (see equ. 2), this hot radical decays according to the competing paths



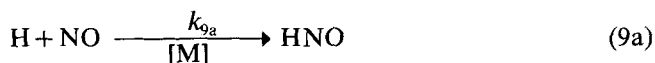
While *N*-methylidene-methylamine and its final reaction product $(\text{CH}_3-\text{N}=\text{CH}_2)_3$ have both been identified as major photoproducts, the formation of $\text{HN}=\text{CH}_2$ has not yet been unambiguously ascertained. This molecule is believed to polymerize and adsorb on the cell walls. Being the source of $\text{CH}_3^{\cdot}$ radicals further supports reaction 7. As has been demonstrated, this radical reacts with NO from reaction 1 to form the other major product via the intermediate step

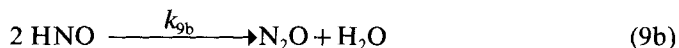


The first step in this reaction is known to be efficient with a rate constant (averaged) $k_{8a}(\infty) = 1.5 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [18]. In view of the fact that only traces of CH_3-CH_3 product were found, most of $\text{CH}_3^{\cdot}$ radicals must be 'scavaged' by NO preventing substantial self-recombination of $\text{CH}_3^{\cdot}$ even though this process has a $k = 3.4 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [19]. The partial pressure of the $\text{CH}_3^{\cdot}$ radical during photolysis is therefore considerably smaller than that of NO and consequently $k_6(\text{E}) > k_7(\text{E})$ under our experimental conditions.

The increase of the buffer-gas pressure decreases the amount of $\text{CH}_2=\text{N}-\text{OH}$ produced and practically suppresses it at 500 Torr N_2 . When the excited DMN molecule and/or the amine radical are partly vibrationally deactivated by collisions with N_2 , thus reducing the excess energy of the $(\text{CH}_3)_2\text{N}^{\cdot}$ radical, the branching ratio changes in favor of reaction 6 and indirectly reaction 2.

Whether or not a buffer-gas was used H_2 and N_2O have been found as products. While H_2 is probably formed by recombination of the $\text{H}^{\cdot}$ radicals from reaction 1, N_2O , on the other hand, is very likely to be produced from $\text{H}^{\cdot}$ (equ. 6) and NO (equ. 1) by the well established mechanism [20] [21]





Reactions 6–9 were further examined by photolyzing DMN (1 Torr) in the presence of an excess of ^{15}NO (6 Torr), thereby expecting the H and CH_3 radicals to be scavenged by the isotopic species. In agreement with these proposed reaction steps the mass spectrometric analysis of the photolysed sample showed the mass peaks $^{15}\text{N}_2\text{O}$ (equ. 9) and $\text{CH}_2=^{15}\text{NOH}$ (equ. 8).

For the small amount of N_2 detected no simple mechanistic explanation can be given.

With 150 Torr O_2 one of the major photoproducts detected is $(\text{CH}_3)_2\text{NNO}_2$, paralleling the observation and the formation mechanism of this compound after excitation at lower energy. (It seems that the vibrational energy content of the dissociating species has been lowered by O_2 collisional energy transfer creating the conditions of $\lambda_{\text{exc}} \sim 363 \text{ nm.}$) The other products CH_3NO_2 , CH_3ONO , and H_2CO indicate the existence of complicated oxidation paths possibly involving $\text{OH}^\cdot$ radicals [21]. Without quantitative data at hand or the identification of intermediates, postulation of such mechanism at this time would be highly speculative. Further work on this endeavor is currently in progress.

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