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Photodecomposition of Energetic Nitro Compounds

J. C. Mialocq

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TRANSLATION:

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Abstract. - The photodecomposition of energetic nitrocompounds depends on the excitation energy, the light intensity which determines the mono-, bi- or multiphotonic character of the initial process and their gaseous, liquid or solid state. The initial processes of the photodecomposition of nitromethane and nitroalcanes are reviewed and their relevance to the initiation of energetic nitrocompounds detonation is discussed. The case of nitramines (dimethylnitramine and tetryl) is also briefly introduced.

1. INTRODUCTION

The study of the photodecomposition of energetic molecules is useful for understanding the mechanisms of initiation of the decomposition reactions of explosives at elevated temperature or under the effect of a shock wave. Monochromatic light excitation in effect makes it possible to bring the molecules from a known fundamental vibrational and electronic state to a well-defined excited vibration state whose development is, in principle, possible to describe. Understanding dissociation processes is more difficult in polyatomic molecules than in diatomic ones, however, because of the greater number of vibrational degrees of freedom. In addition, knowing that the excitation energy of a molecule is greater than the threshold of dissociation does not allow us to conclude that this molecule is going to dissociate, since we do not *a priori* know the coordinate of the reaction and how the energy will be exchanged between the vibration modes.

In this review, we shall attempt to present the recent significant results on the photodecomposition of some explosives. For example, the photolysis of

nitromethane, the simplest member of the nitroparaffin family, is still not understood in spite of the many studies done since the historical works of Hirschlaff and Norrish [1]. The photolysis of other nitro compounds, among which we shall examine the case of nitramines, is also quite complex [2].

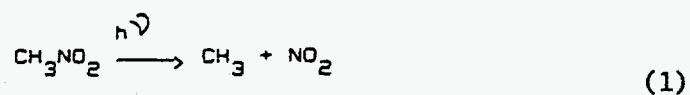
2. PHOTODECOMPOSITION OF NITROMETHANE

We shall distinguish the case of the gas phase, where the nitromethane molecule undergoes processes characteristics of the isolated molecule, and the case of the condensed phase, where the processes may be more complex.

2.1. UV Photolysis of Gaseous Nitromethane

Since 1936 [1], studies on the continuous photolysis of nitromethane based on the analysis of the end products have generally led to comparisons with thermal decomposition. A number of reactions have been proposed as the primary process:

2.1.1. Cleavage of the C-NO₂ Bond



Observing the formation of small amounts of methyl nitrite during the photolysis of nitromethane gas, Pimentel and Rollefson [3] concluded that there was cleavage of the C-NO₂ bond, followed by recombination into CH₃NO₂* or CH₃ONO*, this latter then dissociating to yield CH₃O and NO radicals. The C-NO₂ cleavage had been proposed back in 1950 by Cottrell and Reid in the thermal decomposition of nitromethane [4]. This cleavage was subsequently considered the main primary process of the UV photolysis of nitromethane gas

[5-22]. But rearrangement processes could be involved to a lesser extent. According to Honda et al. [11], at 313 nm the quantum yield of Reaction (1) is 0.6 via the excited triplet stage ($n-\pi^*$) with an energy greater than 3.4 eV. In addition, Spears and Brugge estimated the vibrational populations of the NO_2 fragment in a laser-induced fluorescence (LIF) microsecond experiment, by exciting the nitromethane at 252.2 nm and the NO_2 fragment at 505 nm [14]. IR chemiluminescence of the NO_2 fragment showed them that the ν_3 mode was highly excited [15]. According to Haugen and Steinmetz [16], the NO_2 fragment does not form when nitromethane is excited at 249 nm in the $n \rightarrow \pi^*$ transition, at low pressure and in a defocussed beam. NO_2 appears, on the other hand, after excitation at 193 nm in the $\pi \rightarrow \pi^*$ transition. Likewise, the study by Kwok et al. [17] on the photodissociation of CH_3NO_2 at 266 nm in a molecular jet indicates that there is no dissociation in the absence of collision. Schoen et al. [18], moreover, analyzed the kinetics of NO_2 formation and found that the dissociation is accomplished in less than five picoseconds, with a quantum yield of 0.70 at 264 nm. At 193 nm, the efficiency of the dissociation was amply confirmed, since the quantum yield is 1 in a molecular jet [19] and some of the internal energy of the fragments is the electronic energy of the excited state ${}^2\text{B}_2$ of NO_2^* , observed in fluorescence [19, 20].

The law of conservation of energy in effect allows us to write the relation:

$$E_{\text{avail}} = h\nu + E_{\text{int}} - D(\text{R} - \text{NO}_2) = E_e + E_T + E_V + E_R$$

where the available energy E_{avail} is the sum of the energy of the excitation photon and of the internal energy of the molecule E_{int} , minus the dissociation energy of the $\text{R}-\text{NO}_2$ bond, $D(\text{R}-\text{NO}_2) = 60.1$ kcal/mol. The available energy

includes the electronic, translational, vibrational, and rotational energies of the fragments that Buttler et al. were able to measure [20].

In addition, they demonstrated that the dissociation took place before the relaxation of NO_2 by the alkyl group, since after light excitation localized on NO_2 , the fluorescence spectrum of NO_2^* did not depend on the nature of the alkyl group [20].

In the vicinity of 266 nm, the efficiency of dissociation becomes a source of conflict, with Buttler et al. [20] estimating that the quantum yield of dissociation was less than 0.03 in the study by Kwok et al. [17], while Mialocq and Stephenson [24, 25] found a yield of (0.17 ± 0.11) and showed that the dissociation yield did not depend on the nature of the alkyl group ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, 1 \text{ -- } \text{C}_3\text{H}_7$ and $2 \text{ -- } \text{C}_3\text{H}_7$). The dissociation kinetics (< 6 psec) that they observed, like that obtained by Schoen et al. [18], is in agreement with the rate constant that they calculated according to the RRKM theory, within the limits of temporal resolution: $k = 4.8 \times 10^{12} \text{ sec}^{-1}$, or $\tau = 0.21$ psec.

Quite recently, Greenblatt et al. [26] did not observe the production of the NO_2 fragment for a nitromethane excitation at 282 nm. It therefore seems that a threshold of cleavage of the C- NO_2 bond is involved toward $38,000 \text{ cm}^{-1}$: we must take into account the energy of the excitation photon and the internal energy of the nitromethane, which is different in a cell and in a molecular jet. But other factors may play a role, such as the lower sensitivity of detection for NO_2 than for OH, which has been observed, moreover, in very low concentrations. We have summarized the quantum yields of NO_2 formation in Table 1.

TABLE 1. QUANTUM YIELDS OF FRAGMENT FORMATION
IN THE UV PHOTOLYSIS OF CH₃NO₂ GAS (IN %).

λ (nm)	NO ₂	OH	HNO
313	60 [11]		20 [11]
282	0 [26]	0,5-2* [26]	
266	< 3 [20]		
	(17±11) [25]	0,4 [27]	
264	70 [18]		
193	100 [19]		

*In nitroethane, nitropropane, and *tert*-nitrobutane.

2.1.2. Intramolecular Rearrangements

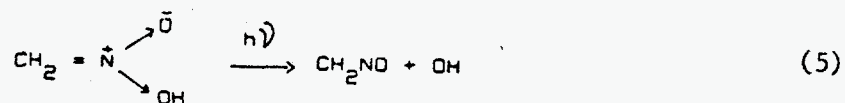
Intramolecular elimination reactions involve a ring with four or five sites [members?] in the case of nitromethane [1, 8] and the higher nitroalkanes [6, 21]:



This reaction, proposed in 1936 by Hirschlaff and Norrish, is no longer of more than historical interest, since it is HNO which is eliminated [8], in Reaction (3).

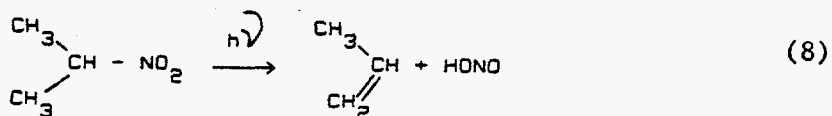
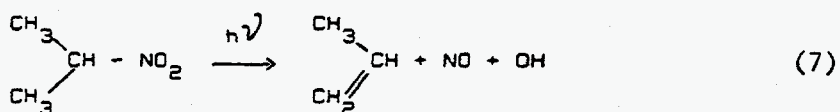
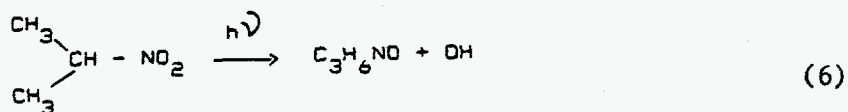


The appearance of the OH spectrum immediately after the excitation led Napier and Norrish to propose the photolysis of a nitromethane isomer [10]:



The quantum yield of Reaction (3) would be 0.2 at 313 nm according to Honda et al. [11], via the lowest excited singlet state ($n-\pi^*$).

Wittig et al. [21] showed that 2-nitropropane excited at 222, 249, or 308 nm yielded OH radicals as well as the more important nitrous acid radical HONO, via a five-membered ring. The OH radical ($\chi^2\pi$) may be produced directly or may arise from the decomposition of HONO when its excess energy is 48 kcal/mol. In addition, the $[\text{HONO}]/[\text{NO}_2]$ ratio increases by a factor of 2 when the excitation wavelength goes from 222 to 308 nm: the elimination of HONO is in effect the most exothermic process [21].



The quantum yield of OH formation at 266 nm is (0.004 ± 0.001) in the absence of collision [27], but at 282 nm the formation of OH, which occurs efficiently in nitroethane, nitropropanes, and *tert*-nitrobutane, does not come into play in the case of nitromethane according to Greenblatt et al. [26], since the participation of a five-membered ring is necessary and proven by

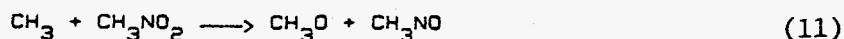
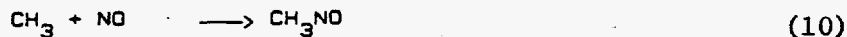
the formation of OH and not of OD from $\text{CH}_3\text{CD}_2\text{NO}_2$. The quantum yields of formation are low, however (0.5-2%) [26].

2.1.3. Production of CN, C_2 , CH, and NO Fragments

At high laser intensity, Haugen and Steinmetz demonstrated that CN, C_2 , and CH fragments form in consecutive absorption processes at 193 nm [16], and the intermediate stages pass through CH_2 or CH_3 [22]. Under these high fluence conditions, NO fragments are also observed [23].

2.2. UV Photolysis of Nitromethane in the Condensed Phase

Brown and Pimentel [28] showed that the photolysis of nitromethane in an argon matrix of 20 K yielded methyl nitrite by cage recombination of CH_3 and NO_2 fragments [3]. In the liquid phase as well, the main product is methyl nitrite [6, 29], and in a matrix of water or carbon tetrachloride at 77 K, the EPR spectra of NO_2 and CH_3 were observed after photolysis of CH_3NO_2 [30]. The effect of oxygen on the yield of methyl nitrite was interpreted as proof of the existence of an excited state lasting long enough to react with the oxygen [29]. Nitrosomethane is also formed in significant proportions [29]. It is the result of secondary reactions:

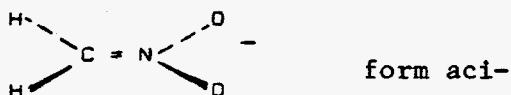


Reaction (11), posed as an hypothesis by Cundall et al. [29], is considered

by Tran-Dinh-Son and Sutton as playing a very important role [31]. These authors determined the quantum yield of nitromethane decomposition at 253.7 nm -- $\phi \geq (0.22 \pm 0.03)$ -- from the quantum yields of formation of the main products, CH_3ONO , HCHO , CH_3NO , N_2 , NO , and N_2O .

Faust et al. obtained an absorption spectrum in the picosecond laser photolysis of liquid nitromethane at 266 nm; the increase in this spectrum had not stopped after 13 nanoseconds [32]. Although the effective absorption cross section of NO_2 is low, these authors attributed the absorption to NO_2 , and they explained the formation kinetics by the existence of a precursor: the nitromethane triplet or an isomer such as the aci- form already proposed by Napier and Norrish [10].

Quite recently, another product -- nitrosomethanol $\text{CH}_2(\text{NO})\text{OH}$ -- was detected by Jacox [33] using IR spectroscopy, in the photodecomposition of nitromethane in an argon matrix at 14 K. Finally, Engelke et al. [34] used ^{13}C -NMR to show that the UV irradiation of nitromethane produces the aci- ion, while no detectable quantity of methyl nitrite was observed.



2.3. UV Photolysis of Nitromethane in Solution

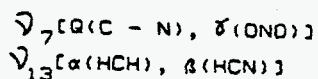
The reactivity of nitroalkanes excited in UV light is modified a little in dilute solution. In solvents which readily give up a hydrogen, such as alcohols, $\text{RNO}_2\text{H}^\bullet$ radicals are produced in Reaction (12) [35, 36]:



In aqueous solution, the photolysis of nitromethane or nitroethane gives the EPR spectrum of the $\text{RNO}_2^{\cdot-}$ radical anion, but this spectrum is more intense in a basic medium, necessary for neutralizing the conjugated acid RNO_2H [37]. In cyclohexane also, the excited NO_2^* group takes a hydrogen from the solvent [38, 39]. Jarosiewicz et al. [40], however, believe that this process is negligible ($\phi = \text{ca. } 10^{-2}$) in comparison with the cleavage of the C-N bond. The role of the solvent is nonetheless important, since its polarity and its polarizability are manifested in the cage effect which leads to the recombination of the CH_3 and NO_2 radicals, in competition with the creation of stable products [40]. In solution, the quantum yield of CH_3NO_2 photodecomposition should therefore be less than in the gas phase [40].

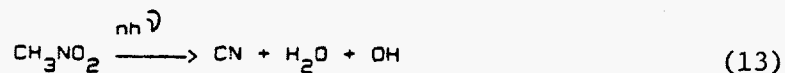
2.4. Multiphotonic Photolysis in Infrared Light, in the Gas Phase

With the development of lasers delivering high luminous intensities in the infrared region, many IR photolysis experiments were done. They showed that the molecules could dissociate in the absence of collision, after having stored the vibration energy by absorbing a large number of IR photons. In the case of nitromethane gas, NO_2 , CH , CN , C_2 , OH , O_2 , and NH fragments were observed in fluorescence after excitation of the ν_7 (921 cm^{-1}) and ν_{13} modes (1097 cm^{-1}) [41-44]:

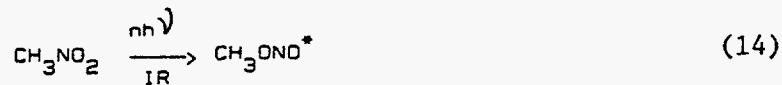


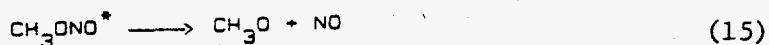
The multiphotonic IR dissociation of CH_3NO_2 produces NO_2 fragments in the fundamental electronic state which Avouris et al. [44] analyzed in laser-induced fluorescence (LIF). But they also observed the direct fluorescence of electronically excited NO_2^* fragments resulting from a vibration-electronic

energy transfer (V + E) [44]. According to these authors, CN* fragments could be produced from a very organized excited state of CH₃NO₂ in Reaction (13):



or from a sequential excitation with the intermediate CH₃NO resulting from the cleavage of an NO bond (72 kcal/mol). CH* and C₂* fragments result from bimolecular reactions [44]. Another method of analyzing the NO₂ and CH₃ fragments is multiphotonic ionization spectroscopy of the NO₂, which proves their rotational excitation [45, 46]. Rockney and Grand thus concluded that the relaxation leads to a high translation energy of the fragments [46]. Quite recently, Wodtke et al. also observed CH₃O and NO fragments arising from the dissociation of the very hot isomer CH₃ONO of nitromethane, obtained by multiphotonic IR excitation in a molecular jet [47, 48]. These authors measured the flight times [*sic*; lifetimes? -- *Tr. Ed.*] of the ions coming from the species NO₂, CH₃, NO, and CH₃O, which they ionized by electron impact. They thus determined the translation energy probability distribution of these fragments. For CH₃ and NO₂, the results show that there is a simple cleavage without any exit energy barrier, and a low translation energy. With respect to the NO fragment, the results showed that two reaction pathways are involved: Reaction (1), since the ionization of NO₂ leads to the NO⁺ ion, and Reaction (14) of nitromethane isomerization, followed by dissociation (15) of the methyl nitrite, whose internal energy is sufficient:





The peak of the HCO^+ ion coming from the CH_3O fragment shows that this latter has a high translation energy, which these authors explained by the reaction pathway (14)-(15). The branching ratio of Reactions (1) and (14) is $k_{14}/k_1 = 0.6$, in favor of (1). For nitroethane, they showed that in competition with Reaction (1), Reaction (4), whose activation energy is 45 kcal/mol, liberates a strong translation energy from the products C_2H_4 and HONO . For 2-nitropropane, they arrived at the same conclusion, i.e., the existence of Reaction (8), and the branching ratio of Reactions (1) and (8) is $k_8/k_1 = 0.5$, in favor of the C-N cleavage.

Wodtke et al. calculated the energy of the potential barrier of the process of CH_3NO_2 isomerization; it is between 51.5 and 55.5 kcal/mol. The energy of the barrier for the process of HONO elimination is (46 ± 1.5) kcal/mol for nitroethane, and 3-5 kcal/mol lower for 2-nitropropane. In these two compounds, they noted the absence of the process of isomerization and formation of alkoxy radicals and NO [48].

The multiphotonic IR ionization of nitromethane is also possible, but it requires a much higher energy (11.3 eV) than that needed for dissociation [49].

3. KINETICS OF DISSOCIATION OF THE C-N BOND

Rockney et al. [46] calculated that it would take 20 photons at 9.6 μm (R(20) ray of the CO_2 laser), at an energy of 3.08 kcal/mol, to bring a molecule of CH_3NO_2 above the threshold of dissociation ($E_0 = 58.8$ kcal/mol). The RRKM theory makes it possible to calculate the rate of dissociation of a

molecule excited above the threshold of dissociation E_0 . Measurement of the dissociation times between 1 and 100 nanoseconds gives the rate constant of dissociation $k(E^*)$, which makes it possible to deduce the excess energy E^* and then the energy (E^*-E_0) which will be distributed in the degrees of freedom of the fragments. In the RRKM theory, the model takes into account the "activated complex" or "critical molecular configuration". Rockney et al. thus found 14 vibration frequencies -- those of CH_3NO_2 , among which the C-N elongation vibration disappears and six other vibrations are weakened. They obtained an Arrhenius constant of $A = 1.5 \times 10^{16} \text{ sec}^{-1}$ at 900 K and $1.9 \times 10^{16} \text{ sec}^{-1}$ at 1,400 K. The RRKM rate constants which they calculated for 1-4 excess IR photons are given in Table 2 [46].

TABLE 2. RATE CONSTANTS AND LIFETIMES CALCULATED FOR THE DISSOCIATION OF CH_3NO_2 , AS A FUNCTION OF THE EXCESS ENERGY ABOVE THE DISSOCIATION THRESHOLD. KEY: (a) excess energy, cm^{-1} ; (b) rate constant, sec^{-1} ; and (c) lifetime, sec.

Energie en excès (cm^{-1}) (a)	Constante de vitesse (S^{-1}) (b)	Durée de vie (S) (c)	Référence
979	$1,66 \times 10^7$	$6,03 \times 10^{-8}$	[46]
2 057	$1,71 \times 10^8$	$5,85 \times 10^{-9}$	[46]
3 154	$8,82 \times 10^8$	$1,13 \times 10^{-9}$	[46]
4 211	$3,16 \times 10^9$	$3,16 \times 10^{-10}$	[46]
7 695	$3,3 \times 10^{10}$	$3,0 \times 10^{-11}$	[48]
16 813	$4,8 \times 10^{12}$	$2,1 \times 10^{-13}$	[25]

Forst's approach, on the other hand, does not require knowing the vibration frequencies of the reactant CH_3NO_2 , nor those of the transition state [51].

Mialocq and Stephenson also used the Forst equation

$$k(E) = \frac{A_0 N(E - E_0)}{N(E)}$$

where A_{∞} and E_{∞} are the Arrhenius parameter and activation energy, and $N(E)$ and $N(E - E_{\infty})$ are the densities of state of the reactant, which can be calculated from the vibration frequencies according to the Whitten-Rabinovitch method. With $A_{\infty} = 1.78 \times 10^{16} \text{ sec}^{-1}$, $E = 37,594 \text{ cm}^{-1}$, and $E_{\infty} = 20,778 \text{ cm}^{-1}$, they found $k_{16,813 \text{ cm}^{-1}} = 4.8 \times 10^{12} \text{ sec}^{-1}$, or a lifetime of 0.21 psec [25]. The value of A_{∞} is subject to argument, however, since the excitation energy is greatly over the threshold. The RRKM calculation done by Wodtke et al. [48] gives a lifetime of 30 psec for an excess energy of 7695 cm^{-1} . These latter values are also shown in Table 2, for comparison. We see that the values calculated by Mialocq and Stephenson for a monophotonic luminous excitation at 266 nm are in good agreement with the kinetics of formation of the NO_2 fragment [18, 25].

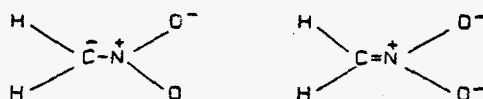
4. THOUGHTS ON THE INITIATION OF NITROMETHANE DETONATION

Nitromethane is a rocket fuel which detonates under the effect of a shock wave [53, 54], and a less powerful explosive than the nitroethers, but its greater chemical stability is an advantage [55]. Its critical detonation diameter is 12-20 mm and the initiation pressure for detonation is on the order of 90 kbars [55]. The capacity for detonation is increased by the addition of inorganic acids, water, organic bases, and di- and triethylamines [55-58]. For example, Kondrikov et al. [55] noted that 0.025% of amine was enough to cut the critical diameter to half its initial value. UV light also contributes to the sensitivity of nitromethane [34, 57-58].

A number of authors have therefore suggested that the basic anionic species CH_2NO_2^- [57-58] and the protonated species $\text{CH}_2\text{NO}_2\text{H}$ [59] were the initial species causing the detonation sensitization. According to Engelke et al.

[57], the detonation rate of nitromethane is proportional to the concentration of the anionic form (aci- ion). Considering that the pressure increases the autoionization of weak acids, they calculated that at 50 kbars and 400 K, the concentration of CH_2NO_2^- was multiplied by 80 in comparison to normal conditions, and they rejected even the hypothesis that the initial species of liquid nitromethane chemistry under the effect of a shock wave were radicals.

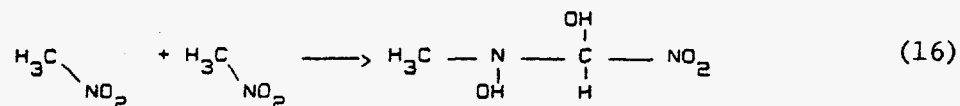
In aqueous solution, the pK_a of CH_3NO_2 is 10.2 at 25°C, and the CH_2NO_2^- anion which is isoelectronic with the nitramine $\text{H}_2\text{N}-\text{NO}_2$ shows an absorption band at 233 nm which suggests intramolecular charge transfer between the CH_2^- electron donor group and the NO_2 electron acceptor group. These two groups are represented in the nonplanar form of the molecule, which is less stable than the planar form with the double bond [61]:



The initiation of detonation in solid nitromethane probably involves a multiphonon excitation of the internal vibrations of the molecule [62], and according to Peyrard et al. [62, 63], the C-N cleavage propagates in a cooperative mechanism.

With respect to theory, recent calculations are in favor of a rearrangement of the nitromethane into methyl nitrite, the dissociation of which is easier [64]. At 700°C, this rearrangement predominates over the C-N cleavage, which will become predominant only at a higher temperature [64]. A quantum mechanical study of the C-N cleavage has just shown the existence of resonances and high oscillations of the photofragmentation rate as a function of the total energy [65].

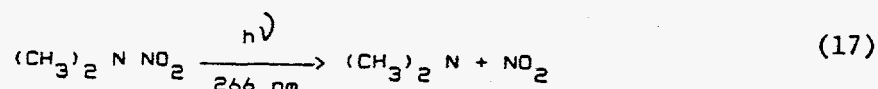
It is still too early, however, to say that one or more of the unimolecular Reactions (1), (3), (4), (5), (6), (7), (8), or (9) constitute the initial stages of the ignition of nitromethane subjected to a shock wave, since a very fast bimolecular reaction has just been proposed by Bardo [66] as the initial step. It is a head-to-tail reaction



for which the half-reaction time would be 5×10^{-12} sec at a pressure of 80 kbars and a temperature of 850 K. While the writing of this particular reaction is difficult to justify, the hypothesis of a fast bimolecular reaction involving a CH_2NO_2^- anion seems plausible in the condensed phase.

5. UV PHOTODECOMPOSITION OF NITRAMINES

The study of the photodecomposition of nitramines is motivated by their use as rocket fuels and explosives, such as HMX and RDX [67]. An essential characteristic is the cleavage of the N-N bond, the bond energy of which is 46.2 kcal/mol; it is thus easier than the C-N cleavage [68]. Recently, Mialocq and Stephenson [69] showed that the photodissociation of dimethylnitramine at 266 nm was accomplished in less than 6 psec, with a high quantum yield on the order of 0.48 [25]. A high proportion of electronically excited NO_2^* fragments is also formed, with a quantum yield of 0.06 [25, 69].



The rapid formation of NO_2 in the case of dimethylnitramine is in agreement with the calculation of the rate constant of unimolecular dissociation

according to Forst's approach: $k = 2.5 \times 10^{11} \text{ sec}^{-1}$, or $\tau = \text{ca. } 4 \text{ sec}$ [25].

Likewise, the picosecond laser excitation at 266 nm of a solution of tetryl in methanol showed the appearance in the laser pulse of a strong absorption in the visible region of the spectrum, which could be that of the *N*-methyltrinitroanilino radical resulting from N-NO₂ cleavage [70].

6. CONCLUSION

The monophotonic UV or multiphotonic IR photodissociation of nitro substances is a very fast process which occurs in less than 6 picoseconds in the case of nitromethane and dimethylnitramine in the gas phase. The cleavage of the C-NO₂ or N-NO₂ bonds is not necessarily the primary step in the initiation of the detonation of nitro explosives in the liquid or crystalline phase. Intramolecular rearrangement reactions may be involved as well, as may bimolecular reactions. Additional studies are under way to clarify the mechanism of photodissociation of nitromethane and tetryl in the condensed phase.

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