



Review of the Photodecomposition of Some Important Energetic Materials

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Abstract: The photodecomposition mechanisms of energetic materials vary with molecular structure, photodissociation wavelength, the phase of the material, experimental pressure and temperature etc. In this paper, the significant progress on photodecomposition studies of some important energetic materials achieved in recent years is introduced in detail, including nitromethane, DMNA (dimethylnitramine), TATB (1,3,5-triamino-2,4,6-trinitrobenzene), RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine), HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane) and CL-20 (2,4,6,8,10,12-hexanitrohexaazaisowurtzitane). The difficulties and prospects of photodecomposition research of energetic materials are also indicated.

Keywords: photodecomposition mechanisms, energetic materials

Introduction

Energetic materials play an important role in both military and civil fields due to their wide application as explosives, propellants and fuels. Many energetic materials have vast landscapes of decomposition pathways that change depending on the initiation process, such as photo, thermal, shock and spark initiation [1-3]. Over recent decades, thermally induced decomposition has been studied extensively both theoretically and experimentally, whereas photo-induced decomposition has not been studied so extensively. In thermal decomposition, the absorbed energy is converted to internal and translational energy, the excited molecules rapidly undergo internal conversion to the ground state with a high degree of vibrational energy from which decomposition occurs, whilst in the photochemical decomposition process the absorbed light energy is converted to internal conversion or intersystem crossing to another excited state from which the molecule may return to the ground state or couple to a dissociative state resulting in a chemical reaction that is unique and unlike the thermal pathway.

A better understanding of the photodecomposition mechanisms of condensed energetic materials helps to understand how shock waves and impact can initiate the rapid exothermic chemical reactions that lead to detonation in explosive solids. Meanwhile, studies on gas phase energetic materials may reveal the properties and reactions of energetic materials at a molecular level, as well as determine the decomposition mechanisms and the corresponding dynamics [4-15]. The photodecomposition of energetic nitro compounds was first studied in 1936 by analyzing the end products. Since then several efforts have been devoted to revealing the photodecomposition mechanisms of energetic materials [16]. In the present paper, the significant advances achieved in recent years in the studies of photodecomposition mechanism of some typical energetic materials are presented, including CH_3NO_2 (nitromethane), DMNA (dimethylnitramine), TATB (1,3,5-triamino-2,4,6-trinitrobenzene), RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine), HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazacyclotane), CL-20 (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane).

Photodecomposition of nitromethane

As the simplest member of the energetic nitro compounds group, the photodecomposition of nitromethane has been investigated for many years. The nitromethane molecule exhibits two electronic bands in the ultraviolet (UV) region. The first strong band is centered at about 198 nm assigned to a $\pi \rightarrow \pi^*$

transition localized on the NO₂ moiety. The second, much weaker band is centered at around 270 nm, and assigned to an n→π* transition from a nonbonding electron of an O atom [7]. Since 1936, studies of the continuous photodecomposition of nitromethane have generally attracted people's attention. A number of reactions have been proposed as the primary photodecomposition process of nitromethane.

Reaction (1) has been proposed as the primary process for the photolysis of nitromethane by Pimentel and Rollefson [17]. They observed a strong absorption spectrum of the methyl radical immediately after flash photolysis (μs) of nitromethane. Their results showed that during the photodecomposition of nitromethane gas a small quantity of methyl nitrite was produced, as a result of the recombination of the methyl radicals and nitrogen dioxide. According to the studies of Haugen and Butler [18], the NO₂ fragment was observed when nitromethane was excited at 193 nm in the π→π* transition, which also suggested that reaction (1) was the primary process. By analysing the dynamics of NO₂ formation, Schoen and his co-workers [19] found that the dissociation was accomplished via reaction (1) in less than five picoseconds after the excitation of the n→π* transition at 264 nm. The C-NO₂ bond rupture was subsequently considered as the main primary process of the photodecomposition of nitromethane gas, which was in agreement with the mechanism of thermal decomposition.



However, Hirschlaff and Norrish [16] performed a preliminary study of the decomposition of nitromethane in the gas phase using UV radiation of 200-300 nm. They suggested that the primary process for the photolysis of nitromethane proceeded as shown in Reaction (2). Nevertheless, the pathway described in Reaction (2) has not aroused a lot of interests, since HNO was eliminated in Reaction (3), and the nitro-nitrite isomerization was proposed to be involved in the primary process. In addition, several minor dissociation pathways, such as O atom elimination (CH₃NO+O), OH formation (CH₂NO+OH) and C-H bond cleavage (CH₂NO₂+H) etc have all been suggested to be the primary processes for the photodissociation of nitromethane.



In 1958, Brown and Pimentel [20] studied the photolysis of nitromethane in a solid argon matrix at 20 K. They observed that the HNO radical was one of the primary products and suggested that the nitro-nitrite isomerization was

the primary process. Cundall and co-workers [21] studied the photolysis of nitromethane in the liquid phase at 254 nm, and considered that the O atom elimination process might be involved in the primary process. Quite recently Guo and co-workers [7] made a complete interpretation of these different mechanisms. They investigated the photolysis of nitromethane at 226 and 271 nm under both collisionless and collisional conditions at nanosecond and femtosecond time scales. Their results showed that at 226 and 193 nm the C-NO₂ bond rupture was the main primary process for the photolysis of nitromethane following the $\pi \rightarrow \pi^*$ excitation. Their observation of the formation of OH and CH₃NO species with low quantum yields proved that OH formation and O atom elimination were minor channels for the dissociation of nitromethane after $\pi \rightarrow \pi^*$ excitation. In nanosecond 271 nm ($n \rightarrow \pi^*$) photolysis experiments, CH₃, NO₂, CH₃O, and OH were not observed, whilst in femtosecond 271 nm laser experiments, the nitromethane parent ion was observed with major intensity, together with CH₃, NO₂, and NO fragment ions with only minor intensity.

In conclusion, the photo-induced decomposition pathways of nitromethane depend on the phase of the material, experimental temperature and photodissociation wavelengths. Among these different mechanisms, the most accepted photodecomposition mechanism is the formation of NO₂ after C-NO₂ bond cleavage.

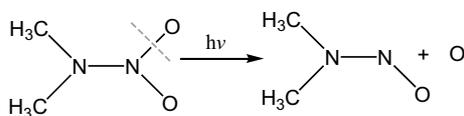
Photodecomposition of DMNA

Since the photodecomposition of energetic materials is an extremely complicated reaction, the mechanisms and dynamics of the dominant decomposition reactions are still a challenge [8]. Due to these difficulties, the photodecompositions of CH₃NO₂ (nitromethane) and DMNA (dimethylnitramine) have been studied extensively as model compounds due to their simple molecular structures and since they are expected to exhibit some processes which are important in the complex decomposition of other energetic materials.

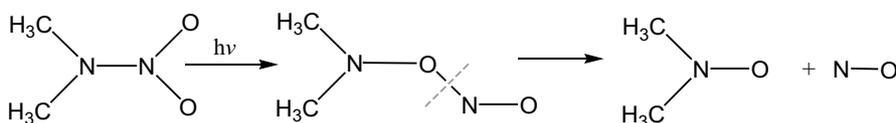
The photodecomposition of gas-phase DMNA with UV radiation at 266 nm has been studied by Mialocq and Stephenson [22]. Their results showed that the mechanisms were the formation of both ground state and electronically excited NO₂. McQuaid et al. [23] investigated the photodecomposition of gas-phase DMNA with 248 nm laser radiation, using laser-induced fluorescence and emission spectroscopy. They observed NO₂ elimination as the major decomposition pathway, with some evidence for minor pathways such as HONO elimination and nitro-nitrite isomerization. Sausa and co-workers [24] dissociated DMNA in a molecular beam using both 226 and 193 nm laser radiation and

concluded that NO_2 elimination was the major decomposition pathway of DMNA at these two excitation wavelengths. However, Bernstein's results [8] showed that DMNA decomposed at 226 nm through a nitro-nitrite isomerization mechanism as the major channel from the excited electronic state.

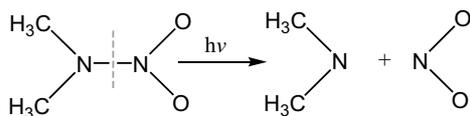
Based on the reported results, most scientists supported NO_2 elimination as the major decomposition channel of DMNA from excited states, but inconsistencies still existed between the nitro-nitrite isomerization and NO_2 elimination mechanisms. On the basis of the available experimental results, the possible photodecomposition channels of DMNA were shown in Figure 1 [8].



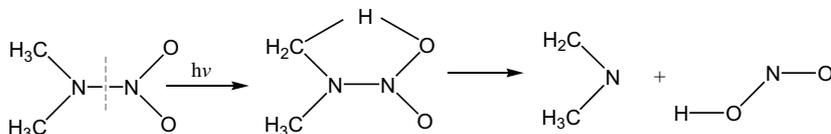
- (1) Initial elimination of O with formation of the nitrosamine: major channel, solid DMNA at room temperature, photodecomposition at 253.7 nm



- (2) Nitro-nitrite isomerization: major channel, molecular beam, photodecomposition at 226 and 193 nm



- (3) NO_2 elimination: major channel, gas-phase DMNA at room temperature, photodecomposition at 266 and 248 nm



- (4) HONO elimination: minor channel, molecular beam, photodecomposition at 226 nm; minor channel, gas-phase DMNA at room temperature, photodecomposition at 248 nm

Figure 1. Different decomposition channels observed for DMNA under different experimental conditions.

Photodecomposition of TATB

TATB, the most common, insensitive, high explosive, has excellent shock resistance and thermal stability. The photo-induced decomposition of TATB has been considered to be very interesting as its colour changes from yellow to green when exposed to light.

Sharma et al [5] used photoelectron spectroscopy to study the change of the TATB structure upon UV irradiation. Their measurements showed that the N 1s and O 1s peak of the nitro group decreased when TATB was exposed to UV light and indicated that C-NO₂ bond cleavage was the primary decomposition pathway, as shown in Figure 2. Kakar et al's experiment [25] also indicated that white light irradiation of TATB resulted in ejection of an NO₂ subsistent from the molecule. Both Britt [26] and Williams [1] have employed electron paramagnetic resonance spectroscopy to confirm that the photo-degradation product of TATB was a free radical and that this solid free radical persisted for more than two years at room temperature. McDonald et al's Time-of-Flight Secondary Ion Mass Spectrometry study [6] has shown an increase in the 242 amu peak which was assigned to TATB minus oxygen for the UV irradiated samples. They demonstrated that the photodecomposition mechanism would be associated with forming mono-nitroso derivatives due to a loss of oxygen from the TATB molecule, as shown in Figure 3.

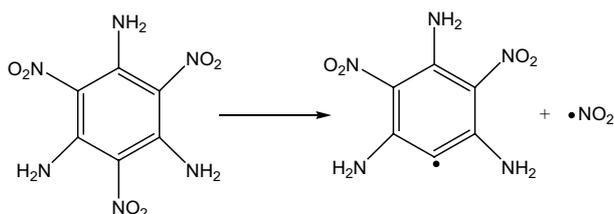


Figure 2. The possible photodecomposition pathway of TATB: C-NO₂ bond cleavage.

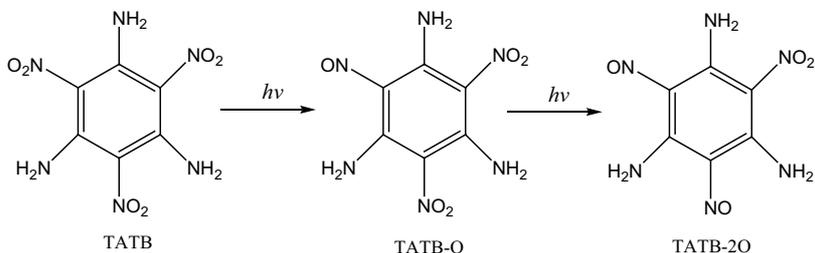


Figure 3. The possible photodecomposition pathway of TATB: O atom elimination.

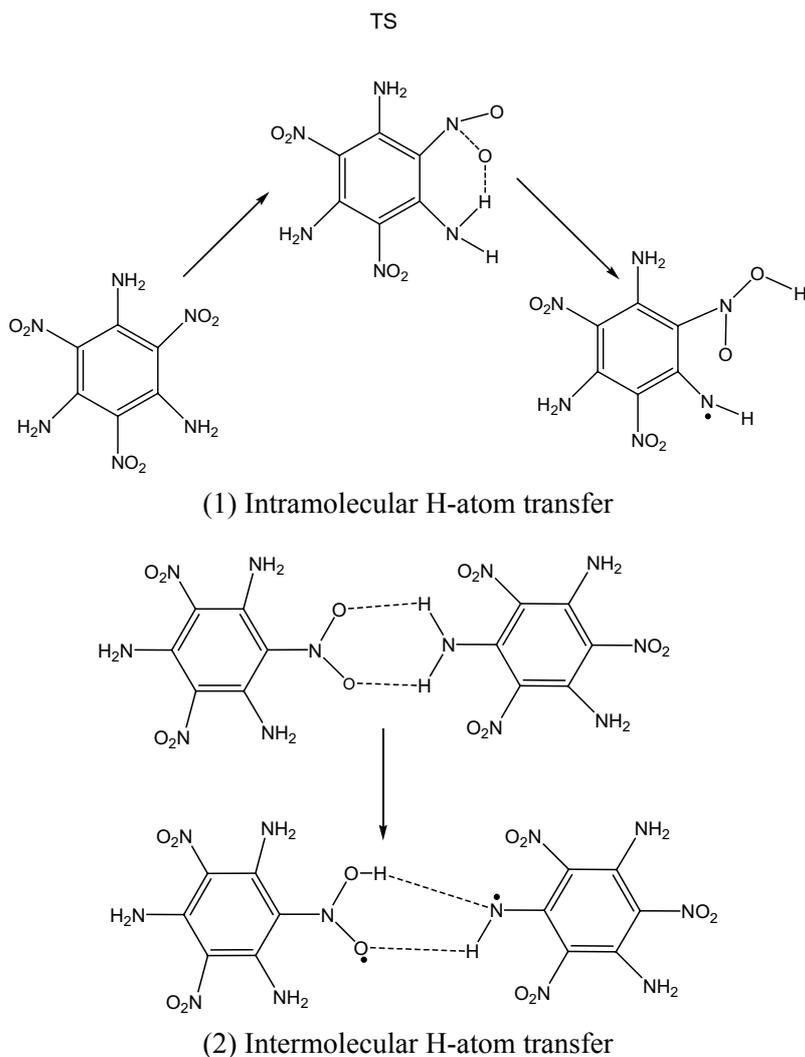


Figure 4. The possible photodecomposition pathways of TATB: H-atom transfer reactions.

Recently, Glascoe et al. [3] investigated the photodecomposition of TATB both at ambient pressure and 8 GPa. They probed TATB and its products after photoexcitation with a 5 ns pulse of 532 nm light by using ultrafast time-resolved infrared and steady-state Fourier transform IR spectroscopy. The ambient-pressure results indicated that no water was formed during or upon completion of

the decomposition reaction, while the 8 GPa-pressure results revealed a small but consistent proportion of water after photoexcitation. Comparison of the ambient and elevated pressure results provided direct evidence that the mechanism of photo-induced TATB decomposition changes dramatically as the pressure is elevated and indicated that the contentious water-formation mechanisms, in part, depended on the initial pressure. It was suggested that pressure may facilitate the H-atom transfer (as shown in Figure 4) or inhibit the C-NO₂ bond homolysis process.

Photodecomposition of RDX and HMX

Since they are widely used, the nitramine high explosives, RDX and HMX have been widely investigated both theoretically and experimentally. It has been proposed that N-NO₂ bond cleavage was the initial step of the photodecomposition of RDX and HMX. Pace et al. [27, 28] used electron paramagnetic resonance spectroscopy to identify the formation of $\times\text{NO}_2$ free radicals during ultraviolet photolysis of HMX and RDX single crystals. The difference between the two was that the $\times\text{NO}_2$ free radical was formed at only one of the N-N bond positions of β -HMX, whilst UV photolysis of single crystals of RDX under the same conditions produced $\times\text{NO}_2$ at each N-N bond position of the molecule.

In the study of the photodecomposition of RDX at 248 nm [29], one interesting initial step has been proposed through the observation of OH emission. The most plausible mechanism for OH production was unimolecular decomposition of RDX via the formation of a five-member ring (OHCNN), as shown in Figure 5. The immediate precursor of OH in this mechanism was probably the primary fragment of HONO.

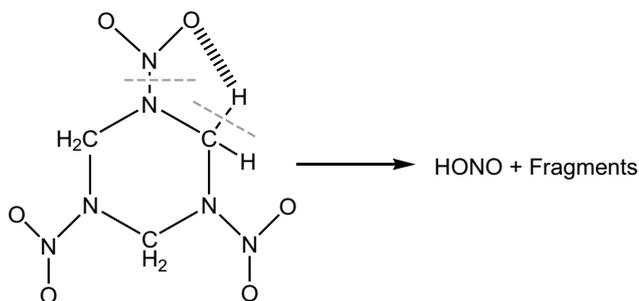


Figure 5. The possible photodecomposition mechanism of RDX: formation of a five-member ring (OHCNN) to generate an HONO intermediate.

The Bernestin group [9-11] has performed some useful and informative experiments to study the initial steps in the photodissociation of RDX and HMX from their first excited electronic states, by employing laser-induced fluorescence spectroscopy, nanosecond mass resolved excitation spectroscopy and femtosecond pump-probe spectroscopy in the UV spectral region. Their results showed that the NO molecule was a major decomposition product of the two energetic materials and that the intensity of the NO ion signal was proportional to the number of nitramine functional groups in the molecule. They suggested two possible mechanisms for the generation of NO molecules: (1) the nitro-nitrite isomerization of the energetic molecule with subsequent release of NO; (2) N-N bond fission of the unstable nitrosamine intermediate, which occurs after O atom loss from the energetic molecule.

Photodecomposition of CL-20

The newly developed, polycyclic, energetic nitramine CL-20 has been used for a wide range of military and civil purposes due to its high energy and high density. The basic structure of CL-20 consists of N-NO₂ functional groups, which is similar to that of RDX and HMX. Therefore, the three energetic materials of RDX, HMX and CL-20 were expected to exhibit some of similarities in their chemical reactions [30].

Pace and Kalyanaraman [31] reported the cleavage of the N-NO₂ bond during CL-20 photodecomposition by trapping the generated NO₂ in dimethyl sulfoxide, followed by detection of the spin adduct using electron spin resonance spectroscopy.

Hawari et al. [32] used Liquid Chromatography-Mass Spectrometry (LC-MS) to detect the key intermediates carrying important information on the initial steps involved in the photodegradation of CL-20 and indicated that CL-20 degraded via at least two initial routes: one involved sequential homolysis of an N-NO₂ bond and the other involved photo-rearrangement prior to hydrolytic ring cleavage and then decomposition in water.

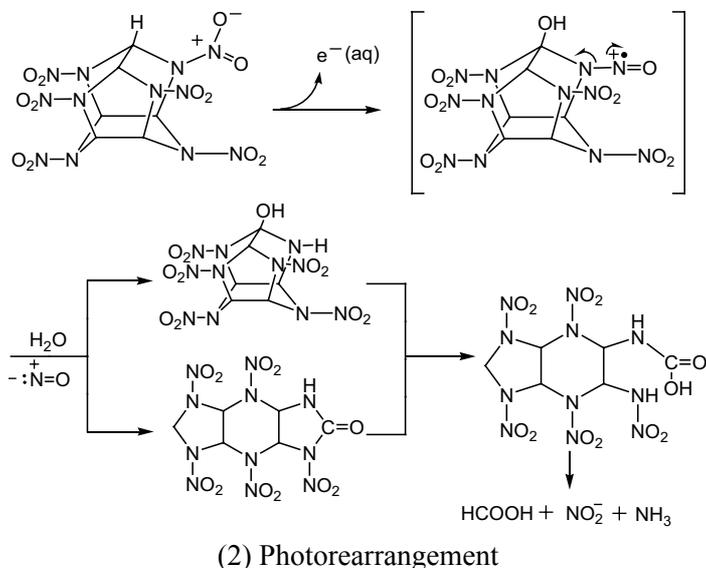
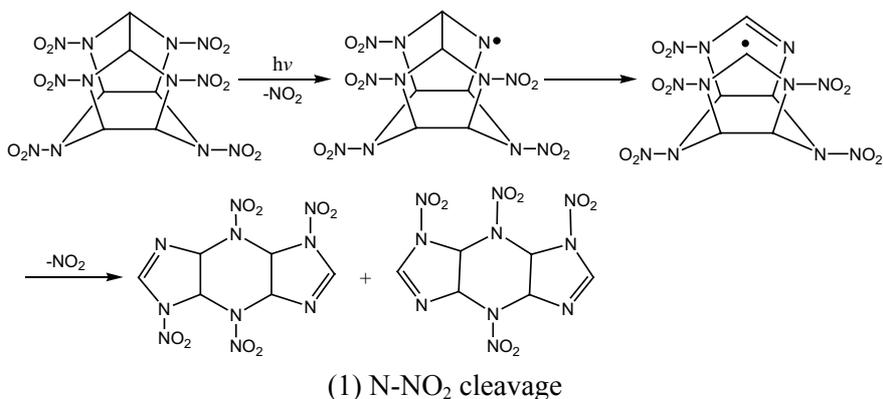


Figure 6. The possible photodecomposition pathways of CL-20.

Guo [14] has compared the photodecomposition mechanism of CL-20 with RDX and HMX using nanosecond mass resolved excitation spectroscopy and femtosecond pump-probe spectroscopy. His experimental observations and theoretical calculations suggested that the NO molecule was an initial product of the decomposition of electronically excited CL-20 and that the UV decomposition of CL-20 followed almost the same decomposition pathway as that of RDX and HMX. The only difference was that CL-20 has a more intense NO ion signal, as listed in Table 1.

Table 1. Comparison of the maximum NO ion intensity for the three energetic materials

Sample	NO ⁺ intensity
CL-20	3.7 V
HMX	2.0 V
RDX	1.5 V

Conclusions

The significant progress in the photodecomposition study of some typical energetic materials was reviewed. The photodecomposition of energetic materials is an ultrafast and complex process, which can be dramatically influenced by different experimental conditions, such as molecular structure, phase, temperature, photodissociation wavelength, energy, and the duration of the laser pulse etc. Because the decomposition dynamics of energetic materials falls within the same time scale as the pulse duration of the light (ps~fs), some new techniques, such as picosecond and femtosecond time-resolved techniques, combined with time-of-flight mass spectrometry (TOFMS), laser-induced fluorescence (LIF) spectroscopy, FT-IR spectroscopy, Raman spectroscopy should be developed to obtain more information on the transient structures of the energetic materials.

Acknowledgments

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