

# UV-induced photodecomposition of 2, 2', 4, 4', 6, 6'-hexanitrostilbene (HNS)

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HNS (2, 2', 4, 4', 6, 6'-hexanitrostilbene) is a heat-resistant photosensitive explosive widely used in the booster charge. Investigation of the photodecomposition mechanism may provide important information for controlling and enhancing the detonation performance, also for the lifetime prediction. The UV-induced photodecomposition of HNS has been subjected to experimental studies. The UV-Vis spectra, X-ray photoelectron spectroscopy (XPS) and electron paramagnetic resonance spectra (EPR) demonstrate the formation of NO<sub>2</sub> free radicals and nitroso derivatives of HNS upon UV irradiation, which proves well known facts that C–NO<sub>2</sub> breaking and removal of oxygen from the nitro group take part in the photodecomposition of HNS.

Keywords: HNS; photodecomposition; C–NO<sub>2</sub> breaking; removal of oxygen

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## 1. Introduction

The photo-induced decomposition of energetic materials has long been of interest in the scientific and military community. Determination of the photodecomposition mechanism, photolytic degradation kinetics, the degradation products and identification of intermediates are very important for better prediction of explosives lifetime [1]. Additionally, understanding the photodecomposition mechanisms and dynamics allows for better control and improvement of the performance of energetic materials for combustion and explosion [2].

The photodecomposition of energetic materials is an extremely complicated process and studying the decomposition reaction is still a challenge [3]. Because of these difficulties, the photodecomposition of CH<sub>3</sub>NO<sub>2</sub> (nitromethane) and DMNA (dimethylnitramine) was studied extensively in the early stage. The compounds can be considered as

a model due to their simple molecular structure and the possibility to reveal some of the processes important in complex energetic material photodecomposition. Several different mechanisms were proposed as an initial step for the photo-induced decomposition, such as C–NO<sub>2</sub> breaking, O atom elimination, OH formation, and nitro-nitrite isomerization reaction [3–7].

Based on these results, several efforts have been devoted to revealing the photodecomposition mechanism of some complex energetic materials involving both cyclic and noncyclic compounds such as TATB (1, 3, 5-triamino-2, 4, 6-trinitrobenzene), HMX (1, 3, 5, 7-tetranitro-1, 3, 5, 7-tetrazacyclooctane), RDX (1, 3, 5-trinitro-1, 3, 5-triazacyclohexane), CL-20 (2, 4, 6, 8, 10, 12-hexanitro-2, 4, 6, 8, 10, 12-hexaazaisowurtzitane) and many others. The photo-induced decomposition of TATB has been considered very interesting for the color change from yellow to green when it is exposed to light. Sharma et al. [8] used photoelectron spectroscopy to study the changes of TATB structure upon UV irradiation. Their measurements showed that the N 1s and O 1s peaks

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of the nitro group decreased when TATB was exposed to UV light and indicated that C–NO<sub>2</sub> bond cleavage was the primary decomposition pathway upon photoexcitation. Kakar et al. in their experiment [9] also indicated that white light irradiation of TATB resulted in ejection of the NO<sub>2</sub> group from the molecule. Williams and Both Britt [1, 10] used electron paramagnetic resonance spectra to confirm that the photo-degradation product of TATB was a free radical and the solid free radical persisted for longer than two years at room temperature. McDonald et al., using time-of-flight secondary ion mass spectrometry [11], have shown an increase in the peak in the 242 amu feature which was assigned to TATB minus oxygen for the UV irradiated samples. They demonstrated that the photodecomposition mechanism might be associated with forming mono-nitroso derivatives due to oxygen loss from the TATB molecule. For cyclic nitramines RDX, HMX and CL-20, the Bernestin's research group [2, 12–14] have done several useful and informative experiments to study the initial steps in the photodissociation of RDX, HMX and CL-20 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. The results showed that NO molecule was a major decomposition product of the three energetic materials and the intensity of the NO ion signal from energetic materials was proportional to the number of nitramine functional groups in the molecule. They suggested two possible mechanisms for the generation of the NO molecule: (1) the nitro-nitrite isomerization of the energetic material molecule with subsequent release of NO; (2) N–N bond fission of the unstable nitrosamine intermediate, which occurs after an O atom loss from the energetic material molecule. Additionally, Pace et al. [15] used electron paramagnetic resonance spectra to identify the •NO<sub>2</sub> free radical formation during ultraviolet photolysis of HMX and RDX single crystals. The difference was that the formation of •NO<sub>2</sub> free radical occurred at only one of the N–N bond positions of β-HMX, while UV photolysis of single crystals of RDX under the same conditions produced

•NO<sub>2</sub> at each N–N bond position of the molecule. Hawari et al. [16] used liquid chromatogram-mass spectrum (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 involving sequential homolysis of N–NO<sub>2</sub> bond and the other involving photorearrangement prior to hydrolytic ring cleavage and then decomposition in water.

The above mentioned studies have thus discussed the photodecomposition reaction of some energetic materials. However, as to 2, 2', 4, 4', 6, 6'-hexanitrostillbene (HNS, C<sub>14</sub>H<sub>6</sub>N<sub>6</sub>O<sub>12</sub>, see Fig. 1), which is widely used in booster charges, mild detonating fuses, and heat-stable explosives, due to its excellent thermal stability, high detonation sensitivity and low critical diameter, no related investigation about its photodecomposition has been reported in detail since HNS has been considered as a typical photosensitive explosive for which the photodecomposition appears to be easily achieved.

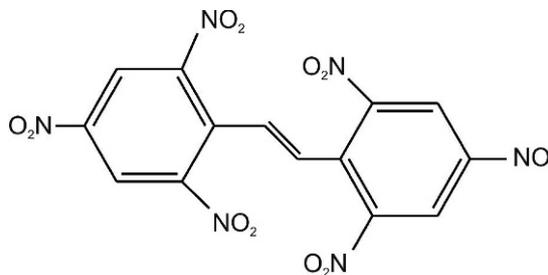


Fig. 1. The molecular structure of HNS.

In the present work, the photodecomposition of HNS was preliminary studied by comparing the UV-Vis spectra, electron paramagnetic resonance (EPR) spectra, X-ray photoelectron spectra (XPS) of HNS before and after UV-irradiation.

## 2. Experimental

The HNS sample (purity 99.5 % determined by HPLC) with an average particle size of 20 μm was offered by the Institute of Chemical Materials, China Academy of Engineering Physics. The acetonitrile used in the experiment was of AR grade.

The solid state HNS powders were irradiated using a 24 W monochromatic UV lamp (365 nm, Beijing Bingyang Scientific). They were stirred 3 times per hour to provide uniform UV exposure. The experiment was conducted at ambient temperature (nominally 24 °C) in a dark room.

UV-visible spectra of acetonitrile were measured and registered using VARIAN CARY 100 UV-visible spectrophotometer in the 190 – 900 nm region, in the presence of a solvent as a background. The EPR measurements of HNS powders before and after irradiation were made on Bruker E500 at room temperature. The XPS measurements were carried out with a Thermo VG Escalab250 photoelectron spectrometer, employing Al K Alpha for excitation. The instrument was operated in the constant analysis energy (CAE) mode with the pressure below  $2 \times 10^{-7}$  Pa.

### 3. Results

#### 3.1. UV-Vis spectra

The absorption spectra for HNS in acetonitrile are shown in Fig. 2, indicating that the maximum absorption peak, appearing at 231 nm, can be attributed to the  $\pi \rightarrow \pi^*$  transition region of the trans-stilbene, the base chromophore group of HNS. For HNS,  $\pi \rightarrow \pi^*$  transition is expected to dominate the absorption, however it is also possible that lower intensity  $n \rightarrow \pi^*$  transition associated with the  $\text{NO}_2$  groups may occur in the extended red tail for the non-planar ground-state of the HNS molecule [17]. When the acetonitrile solutions of HNS are irradiated, two additional absorption processes occur: an intense absorption in the 310 – 340 nm range with a maximum at 330 nm, and a small well-defined band in the 345 – 365 nm range, centered at 350 nm. The maximum at  $\sim 330$  nm may be an artifact originating from too high concentration of the applied solution. The new peak which appeared in the 345 – 365 nm range may be due to the photochemical reaction of the applied solution. It is known that many stilbene compounds undergo a photodecomposition of trans-cis photoisomerisation reaction; however it should not affect the photodegradation of HNS which is attributed

to the large intramolecular steric hindrance in HNS molecule.

On the basis of the results, we have tried to identify the intermediate products during photolysis of HNS using liquid chromatogram-mass spectrum (LC-MS) method. Unfortunately, no information was available for the low concentration of photodecomposition products to enable detection. So we used XPS and EPR technique to measure the core-level peaks of different atoms of the molecule and detect intermediate free radical molecules as a function of UV irradiation [18, 19].

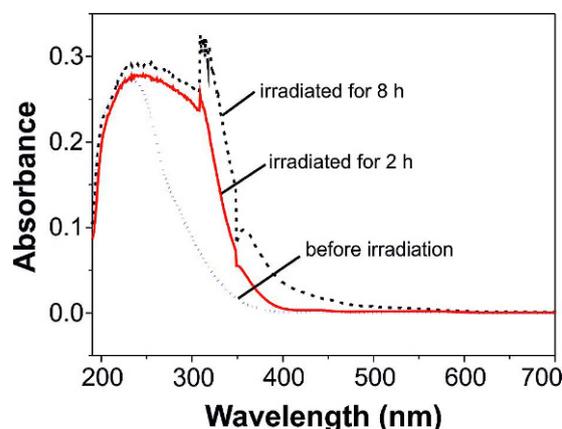


Fig. 2. UV-Vis spectra of HNS before and after UV irradiation.

#### 3.2. XPS spectra

In HNS there is no nitrogen in the ring and only one nitrogen peak arising from  $\text{NO}_2$  group is observed in the XPS spectra at  $\sim 405$  eV. This peak is shown in Fig. 3 for both the UV irradiated and unirradiated samples of HNS. The data show that in the irradiated sample, a new peak occurs at the low binding energy of 401 eV, which grows as the irradiation time increases. The appearance of the new peak at 401 eV can be attributed to the chemical state of N 1s of the nitroso derivative of HNS in the photolytic decomposition [18]. A similar change is also observed on the O 1s peak, as shown in Fig. 3. In the XPS O 1s spectra, the peak at about 532 eV is observed in both the UV irradiated and unirradiated samples of HNS, which can be attributed to the chemical state of O 1s of the  $\text{NO}_2$  group. After UV irradiation, a new peak has occurred on

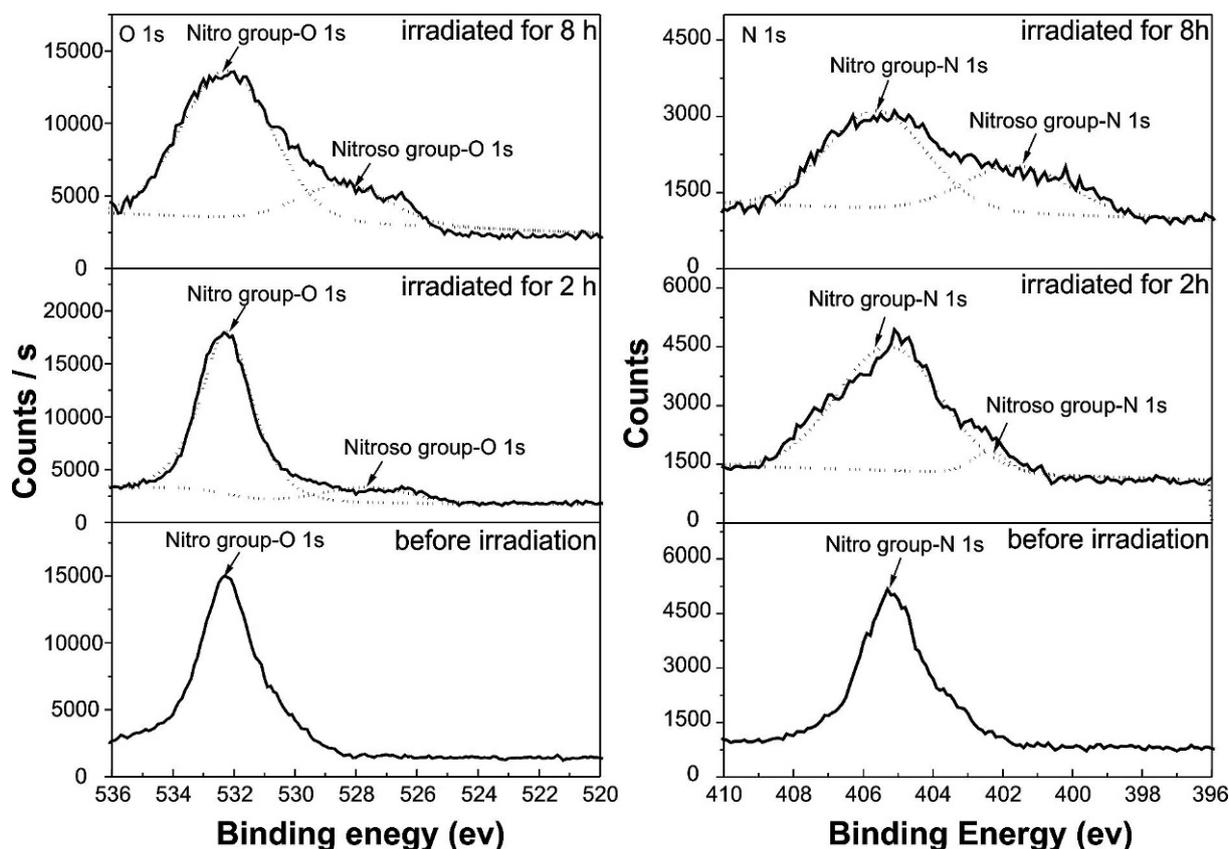


Fig. 3. XPS O1s spectra and N 1s spectra of HNS before and after irradiation, the solid line is the XPS curve, the short dotted line is the fitting curve.

Table 1. XPS analysis results of the content of N 1s and O 1s of HNS before and after UV irradiation.

HNS samples	Content (%)		[O]/[N] ratio
	N 1s	O 1s	
Before UV irradiation	20.81	42.52	2.043
UV irradiation for 8 h	16.76	30.94	1.846

the low binding energy side of about 528 eV, which rose as the irradiation time increased. The appearance of the new peak at 528 eV can be attributed to the chemical state of O 1s of the nitroso derivative of HNS in the photolytic decomposition. The content of N 1s and O 1s of HNS before and after UV irradiation analyzed by XPS is listed in Table 1. Table 1 shows that there is a marked decrease in the content of N 1s and O 1s when HNS is exposed to UV light, which may be associated with the removal of the NO<sub>2</sub> group from the molecule [8].

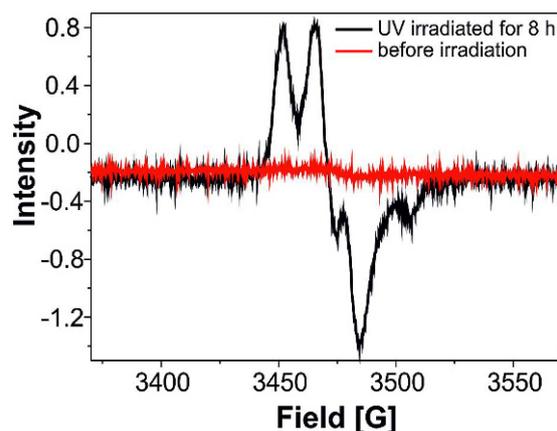


Fig. 4. EPR spectra of HNS before and after UV-irradiation.

Additionally, the [O]/[N] ratio after 8 h UV irradiation also shows a decrease compared with the unirradiated samples. However, the removal of NO<sub>2</sub>

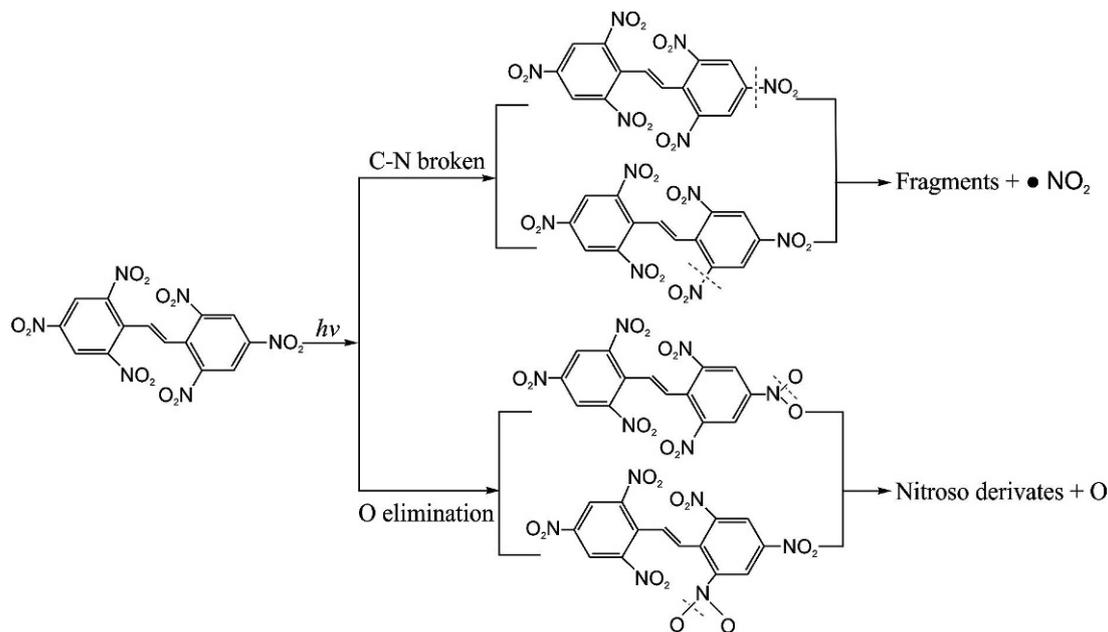


Fig. 5. The possible photodecomposition of HNS: C–NO<sub>2</sub> breaking and the removal of an oxygen of the nitro group.

group does not result in the decrease of the [O]/[N] ratio. Combined with the appearance of the new N 1s peak at 401 eV and O 1s peak at 528 eV, one possible explanation is that another photodecomposition channel still exists, that is the removal of oxygen from the nitro group [18].

### 3.3. EPR spectra

The EPR spectra of the powder HNS sample before and after UV irradiation are shown in Fig. 4. After UV irradiation, the HNS sample produced a stable EPR peak which indicates that the free radicals are produced in the photodecomposition process. The EPR signal of the radicals has a pattern which matches the powder spectrum of randomly oriented  $\bullet\text{NO}_2$  radicals [15]. Therefore, it can be concluded that the photodecomposition mechanism is associated with breaking C–NO<sub>2</sub>.

## 4. Discussion

The results of these experiments provide evidence for some of the specific bonds to be broken. The new absorption at 350 nm in the UV spectra indicates that a photochemical reac-

tion has occurred. The EPR spectra prove that there are some quantities of NO<sub>2</sub> free radicals arising from photo-induced breakup of the constituent molecules, which indicates that the photodecomposition mechanism is associated with C–NO<sub>2</sub> breaking. The XPS measurements also provide some evidence for the existence of the NO<sub>2</sub> as a product of the decomposition. The decrease in the content of N 1s and O 1s when HNS is subjected to UV irradiation indicates that one of the effects of photolysis is the removal of the NO<sub>2</sub> group from the ring. Combined with the experimental results of XPS and EPR spectra, it means that the NO<sub>2</sub> group is ejected from the ring of HNS molecule and breaking of C–NO<sub>2</sub> may occur in the photodecomposition process.

It was also reported that the first step in the photolytic photodecomposition of molecules like TNT and HNS is the so-called “insertion reaction” involving an exchange of the position of a hydrogen atom with an oxygen of the adjacent nitro group [18]. However, the results obtained here do not seem to be consistent with this type of interaction. In our XPS data, the [O]/[N] ratio appears to decrease as a result of the UV irradiation.

The appearances of the new peak of N 1s spectra at  $\sim 401$  eV and the new peak of O 1s spectra at  $\sim 528$  eV are definitely associated with the photo-generation of the nitroso derivative of HNS. Based on these observations, the removal of an oxygen atom of the nitro group is evident in the UV-induced photodecomposition of HNS.

It is of some interest that the decomposition effect of photolysis observed in solid HNS, the breaking of C-NO<sub>2</sub> bond and the removal of an oxygen of the nitro group (as shown in Fig. 5), is different from that of thermal decomposition [20]. Since the first step in the photolytic decomposition is an electronic excitation of the molecule, the difference suggests that the chemical reactions of thermal decomposition may not be the same. Additionally, the photodecomposition of energetic materials is somewhat similar to the shock-induced decomposition; both may cause electronic excitation of energetic material molecule.

## 5. Conclusions

In this work, the UV-induced photodecomposition of HNS has been investigated experimentally by different research methods, including UV-Vis spectra, XPS spectra and EPR spectra. The results show that the chemical structure of HNS molecules has dramatically changed due to the UV irradiation. The breaking of C-NO<sub>2</sub> bond and the removal of an oxygen of the nitro group have been proposed to be the primary decomposition reaction steps in the UV-induced photodecomposition.

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