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# Identification of Elusive Keto and Enol Intermediates in the Photolysis of 1,3,5-Trinitro-1,3,5-Triazinane

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**ABSTRACT:** Enols have emerged as critical reactive intermediates in combustion processes and in fundamental molecular mass growth processes in the interstellar medium, but the elementary reaction pathways to enols in extreme environments, such as during the decomposition of molecular energetic materials, are still elusive. Here, we report on the original identification of the enol and keto isomers of oxy-s-triazine, as well as its deoxygenated derivative 1,3,5-triazine, formed in the photodecomposition processes of 1,3,5-trinitro-1,3,5-triazinane (RDX)—a molecular energetic material. The identification was facilitated by exploiting isomer-selective tunable photoionization reflectron time-of-flight mass spectrometry (PI-ReTOF-MS) in conjunction with quantum chemical calculations. The present study reports the first experimental evidence of an enol intermediate in the dissociation domain of a nitramine-based



energetic material. Our investigations suggest that the enols like 1,3,5-triazine-2-ol could be the source of hydroxyl radicals, and their inclusion in the theoretical models is important to understand the unprecedented chemistry of explosive materials.

ver the last decades, the fundamental understanding of the chemistry of enols, reactive intermediates formally consisting of an alkene and a hydroxyl group connected to a carbon atom of the carbon-carbon double bond, has gained considerable interest from the physical organic, computational, combustion, and astrochemical communities to unravel the formation mechanisms, keto-enol equilibria, and the kinetics of their formation in combustion, atmospheric, and interstellar environments.<sup>1–10</sup> The simplest enol, vinyl alcohol [H<sub>2</sub>C=C-(OH)H] (Figure S1), was firmly detected via microwave spectroscopy by Saito<sup>11</sup> nearly a century after its postulation as a highly reactive, short-lived transient by Erlenmeyer.<sup>1</sup> Chemically more complex enols such as propenol [CH<sub>3</sub>C-(H)=C(OH)H and butenol  $[CH_3CH_2C(H)=C(OH)H]$ were detected in hydrocarbon flames (Figure S1).<sup>1-4</sup> Vinyl alcohol  $[H_2C=C(OH)H]$ , propenol  $[CH_3C(H)=C(OH)H]$ , and 2-hydroxyacrylic acid  $[CH_2=C(OH)COOH]$ —the enol of the biologically important pyruvic acid [CH<sub>3</sub>COCOOH]have emerged as tracers of a galactic cosmic ray-mediated nonequilibrium chemistry in interstellar analogue ices exploiting isomer-selective photoionization (PI) coupled with reflectron time-of-flight mass spectrometry (ReTOF-MS) (Figure S1).<sup>8,9</sup>

Despite the identification of enols as critical intermediates in hydrocarbon oxidation processes<sup>1–3</sup> and their fundamental role in molecular mass growth processes of complex organic molecules on icy interstellar grains,<sup>8,9</sup> enol transients have only been hypothesized in the decomposition of energetic materials such as of 1,3,5-trinitro-1,3,5-triazinane (RDX; 1; Scheme 1). Behrens and co-workers predicted the existence of both the

keto (C<sub>3</sub>H<sub>3</sub>N<sub>3</sub>O; 2a) and enol (C<sub>3</sub>H<sub>2</sub>N<sub>3</sub>OH; 2b) tautomers of oxy-s-triazine (OST) in the thermal decomposition of RDX (1) (Scheme 1).<sup>13,14</sup> Successive studies exploiting photolysis,<sup>15</sup> electron exposure,<sup>16</sup> and pyrolysis<sup>17–20</sup> of RDX detected signal at m/z = 97, i.e., the molecular parent ion of C<sub>3</sub>H<sub>3</sub>N<sub>3</sub>O, upon nonisomer selective ionization of the decomposition products in the gas phase but failed to unambiguously assign the structural isomer(s). Therefore, despite the potentially critical role of the tautomer pair 2a-2b in the elucidation of the underlying decomposition mechanisms of RDX, the identification of 2a and 2b is still elusive. An identification of these transient species is fundamental in our understanding of the dominating decomposition chemistry of complex organic molecules, including molecular energetic materials like RDX.<sup>21-31</sup> Transients such as 2a and 2b could be a key source of hydroxy (OH) radical;<sup>23,24,31</sup> thus, the identification of enols would critically constrain and impact our knowledge on the decomposition mechanisms of nitramine-based energetic materials.

Here, we report the first detection of the keto and enol tautomers of oxy-s-triazine (2) prepared via the photolysis of 1. The identification was made possible by combining isomer-

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Scheme 1. Decomposition of 1,3,5-Trinitro-1,3,5-triazinane (RDX; 1) to Oxy-s-triazine Isomers (2a  $[C_3H_3N_3O]$  and 2b  $[C_3H_2N_3OH]$ ) and 1,3,5-triazine ( $C_3H_3N_3$ ; 3a)



Figure 1. Structures of oxy-s-triazine (2) and 1,3,5-triazine (3) isomers along with their calculated relative energies ( $\Delta E$ ) in kJ mol<sup>-1</sup> and adiabatic ionization energies (IE) range in eV. Coordinates of the structures are provided in Table S5, and their geometrical parameters are depicted in Figures S11 and S12.

selective tunable vacuum ultraviolet (VUV) photoionization (PI) and reflectron time-of-flight mass spectrometry (ReTOF-MS) with quantum chemical calculations. In contrast to conventional electron impact ionization, PI-ReTOF-MS represents a versatile approach to selectively photoionize distinct isomers based on their adiabatic ionization energies (IEs).<sup>32-36</sup> We further explore the role of the keto-enol tautomers **2a** and **2b** in the formation of 1,3,5-triazine  $(C_3H_3N_3; 3a)$ , a deoxygenated derivative of oxy-*s*-triazine  $(C_3H_3N_3O)$ ,<sup>18-20,37,38</sup> and also unravel the significance of three consecutive nitrous acid (HONO) eliminations leading to 1,3,5-triazine  $(C_3H_3N_3; 3a)$  (Scheme 1).<sup>25,39-42</sup> Overall,



Figure 2. PI-ReTOF-MS data collected during the sublimation phase as a function of temperature at photon energies of (a and b) 10.49, (c) 10.12, and (d) 9.90 eV. Spectra in panels (a, c, and d) and (b) are measured after irradiation of RDX films at 254 and 206 nm photons, respectively.

our study provides compelling evidence for the formation of 1,3,5-triazine (3a) along with the keto-enol tautomers of oxys-triazine (2a, 2b).

The experiments were performed in an ultrahigh vacuum (UHV) surface science machine at a base pressure of a few  $10^{-10}$  Torr (Figure S2).<sup>43,44</sup> A silver substrate coated with a thin film of RDX (99.99%) at a thickness of  $16 \pm 1 \ \mu m$  was cooled to 5.0  $\pm$  0.1 K. Ultrahigh purity RDX was prepared through recrystallization of production-grade RDX and characterized through NMR, UV, and FTIR spectroscopy (Figures S3–S5).<sup>15</sup> The bond dissociation processes were triggered by exposing distinct films of RDX in separate experiments to 254 nm (4.88 eV) and 206 nm (6.02 eV) light accessing the  $n \to \pi^*$  and  $\pi_R \to \pi^*$  transitions of RDX, respectively (Table S1).<sup>45</sup> These photon energies are well below the adiabatic ionization energy of RDX in the condensed phase, which has been calculated to range from 9.9 to 10.2 eV.<sup>46,47</sup> The photolysis was performed at doses of 10.7  $\pm$  1.0 and 22.3  $\pm$  2.0 eV molecule<sup>-1</sup> at 254 (4.88 eV) nm and 206 (6.02 eV) nm wavelengths, respectively (Table S2). Fourier transform infrared (FTIR) spectra of the films were collected in situ before, during, and after the irradiation to monitor the chemical changes in the samples. The photolysis products formed in the exposed RDX were annealed from 5 to 320 K at a rate of 1 K min<sup>-1</sup> (temperature-programmed desorption; TPD). The subliming neutral molecules were ionized

exploiting tunable vacuum ultraviolet (VUV) photoionization (PI); the ions formed were mass resolved in a reflectron timeof-flight mass spectrometer (ReTOF-MS). Upon systematically tuning the photon energies to 10.49, 10.12, 10.01, and 9.90 eV, isomers of oxy-s-triazine  $(C_3H_3N_3O; 2a-b)$  and 1,3,5-triazine (C3H3N3; 3a) were selectively photoionized based on their adiabatic ionization energies. This approach eventually elucidates which isomer(s) is(are) formed.<sup>8,9,48</sup> The computed structures of most possible cyclic and acyclic isomers of oxy-striazine and 1,3,5-triazine are depicted in Figure 1. Their simplified structures are depicted in Figure S6. To identify these isomeric forms, we used SciFinder's web-based structure search program. Considering the fact that the product at m/z =97 is formed at the early stage of RDX decomposition,<sup>15</sup> its structure must retain the -N-C-N-C-N- or -C-N-C-N-N- skeletal framework of RDX. Therefore, we selected only those cyclic and acyclic isomeric species that have the aforementioned structural backbone, are neutral, and possess functional groups similar to those of proposed structures of products at m/z = 97 and 81. It is important to stress here that the calculated (CCSD(T)/CBS//B3LYP/cc-pVTZ) adiabatic ionization energies (IEs) of the isomers can be lower by 0.02 eV or higher by 0.06 eV. This error range was determined by comparing experimental and computed IEs of the multiple molecular systems as benchmarks (Table S3). Further, ReTOF-MS calibration experiments revealed that the electric



**Figure 3.** Left PI-ReTOF mass spectra measured at m/z = 97 as a function of temperature at photon energies of (a and c) 10.49, (b and d) 10.12, (e) 10.01 and (f) 9.90 eV. Right PI-ReTOF mass spectra recorded at m/z = 81 at photon energies of (g and i) 10.49 and (h and j) 9.90 eV. Spectra (a, b, e, f, i, and j) and (c, d, f, g, and h) are collected after photolysis of RDX films at 206 and 254 nm, respectively.

field of the extraction plate of the ion optics lowers the ionization energies by 0.03 eV.  $^{36}$ 

Infrared (IR) difference spectra of RDX (1) measured at 5 K after exposure to 254 and 206 nm lights are displayed in Figure S7. A decrease in vibrational band intensities of 1 (RDX) due to photolysis is apparent from the absorptions observed on the negative scale. In contrast, the upbeat "absorptions" imply vibrational features of small product species (Table S4);<sup>21,49-54</sup> among these, observation of nitrous acid (HONO) absorption at 1689 cm<sup>-1</sup> implies that the HONOelimination process that could lead to 2a-b and 3a (Scheme 1) must have facilitated during the decomposition. However, explicit identification of higher molecular weight species such as 2a-b and 3a by FTIR would be problematic because of the complex mixture of several oxygen-nitrogen-carrying species formed in the photolysis, which would result in overlapping infrared absorptions from similar frequencies of the functional groups. Therefore, a novel analytical approach is essential.

The mass spectra of the species subliming from the processed RDX films are recorded as a function of temperature exploiting PI-ReTOF-MS at photon energies of 10.49, 10.12, and 9.90 eV (Figure 2a-d). Measurement at 10.49 eV reveals observable signals at m/z = 97 (C<sub>3</sub>H<sub>3</sub>N<sub>3</sub>O; Figure 3a) and 81  $(C_3H_3N_3;$  Figure 3g); additionally, noticeable traces were detected at m/z = 30 (NO), 31 (CH<sub>5</sub>N), 42 (C<sub>2</sub>H<sub>2</sub>O), 44  $(N_2O)$ , 45  $(CH_3NO)$ , 46  $(NO_2)$ , 57  $(C_2H_3NO)$ , 58  $(C_2H_6N_2)$ , 59  $(C_2H_5NO)$ , 60  $(N_2O_2)$ , 71  $(C_2H_5N_3)$ , 72  $(C_2H_4N_2O)$ , 73  $(C_2H_7N_3)$ , 74  $(CH_2N_2O_2)$ , 75  $(C_2H_5NO_2)$ , 87 (C<sub>3</sub>H<sub>9</sub>N<sub>3</sub>), 88 (CN<sub>2</sub>O<sub>3</sub>), 89 (CH<sub>3</sub>N<sub>3</sub>O<sub>2</sub>), 98 (C<sub>2</sub>H<sub>2</sub>N<sub>4</sub>O), 99 ( $C_3H_5N_3O$ ), 105 ( $C_2H_7N_3O_2$ ), 117 ( $C_3H_7N_3O_2$ ), 118  $(C_2H_6N_4O_2)$ , 119  $(C_2H_5N_3O_3)$ , 128  $(C_3H_4N_4O_2)$ , 130 (C<sub>3</sub>H<sub>6</sub>N<sub>4</sub>O<sub>2</sub>), 146 (C<sub>3</sub>H<sub>6</sub>N<sub>4</sub>O<sub>3</sub>), 149 (C<sub>4</sub>H<sub>11</sub>N<sub>3</sub>O<sub>3</sub>), and 191  $(C_3H_5N_5O_5)$  (Figure S8). It is important to highlight that data collected at 10.49 eV in control experiments for non-irradiated RDX films did not unveil any ion signal, revealing that the ion

count references above originate from molecules formed during the photolysis of the RDX films successively subliming into the gas phase (Figure S9).

Let us focus first on the structural isomers of 2 and the TPD profiles extracted at m/z = 97 (Figure 3a-f). The TPD profile recorded at 10.49 eV displays two sublimation events peaking at 290 and 310 K (Figure 3a,c). At 10.49 eV, all isomers 2a-i can be photoionized. Upon lowering the photon energy to 10.12 eV, isomers 2a-g can still be ionized, but the ionization energies of isomers 2h and 2i are greater than 10.12 eV; therefore, these isomers cannot be ionized. The TPD profile extracted at 10.12 eV still exhibits both sublimation events. However, the integrated areas of the deconvoluted peaks<sup>35</sup> at 310 and 290 K of 2.9  $\pm$  0.3:1 (10.49 eV) and 1.5  $\pm$  0.1:1 (10.12 eV) differ. This suggests that two distinct isomers of **2a**-g contribute to the ion signal at m/z = 97 (Figure 3b,d). We further tuned the photon energy to 9.90 eV to separate the target isomers 2a-b from the remaining isomers 2c-g; at 9.90 eV, the latter-if formed-can still be ionized, but the former cannot. At 9.90 eV, we observed the disappearance of the complete ion signal, implying that isomers 2c-g are not formed (Figure 3f). Thus, we can conclude that only the keto (2a) and (or) enol isomers (2b) of oxy-s-triazine contribute(s) to the ion counts at mass channel 97. To discriminate between 2a and 2b isomers, we extracted the TPD profile at a photon energy of 10.01 eV, which is lower than the IE of the enol form (2b); the data revealed the disappearance of the first sublimation peak at 290 K, while the second sublimation peak is still present albeit with lower ion counts (Figure 3e). These data signify that the first sublimation event peaking at 290 K contributes to the enol form (2b) of the oxy-s-triazine, whereas the keto form (2a) sublimes at a higher temperature (310 K).

Having confirmed the formation of both the keto and enol isomers of oxy-s-triazine, we focused our attention on 1,3,5-

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Figure 4. Calculated decomposition pathways of RDX (1), leading to oxy-s-triazine isomers (2a and 2b) and 1,3,5-triazine (3a). The CCSD(T)/cc-pVTZ//B3LYP/cc-pVTZ energies are given in kJ mol<sup>-1</sup> relative to 1 (RDX). Coordinates and energies of the depicted species are provided in Tables S6 and S7.

triazine in the pool of RDX decomposition products. To distinguish the target isomer **3a** from isomers **3b** and **3c**, we analyzed the data obtained at 10.49 and 9.90 eV. At a photon energy of 10.49 eV, all isomers of **3** can be ionized. At 9.90 eV, isomers **3b** and **3c**—if formed—can still be ionized, but **3a** cannot. A close inspection of the data revealed that the TPD profile extracted at m/z = 81 at a photon energy of 10.49 eV shows a single sublimation event centered at 270 K (Figure 3g); this ion signal disappears when the photon energy is lowered to 9.90 eV (Figure 3h). These data indicate that molecule **3a** is formed. It is important to note that ion signal at m/z = 81 is not observed at 10.49 and 9.90 eV after photodecomposition at 206 nm (Figure 3i,j), implying that the pathway leading to 1,3,5-triazine is preferable at lower photon energy accessing the  $n \rightarrow \pi^*$  transition.

Our experiments provide conclusive evidence on the formation of 1,3,5-triazine (3a) along with the keto-enol tautomers of oxy-s-triazine (2a, 2b) upon photolysis of RDX (1). We propose now likely formation mechanisms employing quantum chemical calculations. At this stage, it is important to discuss the excited-state dynamics of 1. Excited-state calculations performed by Bernstein and co-workers<sup>55</sup> suggest that after electronic excitation via UV photons, the excited

molecules of 1 undergo internal conversion to the ground state  $(S_0)$  from the excited states  $(S_1/S_2)$  through conical intersection (CI) and finally dissociate in the  $S_0$  state. In the ground state, a number of fragmentation channels could open. Previous gas-phase computational analyses identified four primary fragmentation channels of RDX that could occur in the ground state: (1)  $N-NO_2$  fission yielding nitrogen dioxide along with an N-centered radical, (2) a molecular elimination channel producing nitrous acid (HONO) and unsaturated ring species, (3) a nitro-nitrite rearrangement followed by nitrogen monoxide (NO) loss leading to an O-centered radical, and (4) a ring-opening pathway (Figure S10).<sup>25,39-42,55</sup> Goddard and co-workers established that 3a (1,3,5-triazine) could originate from 1 through three consecutive nitrous acid (HONO) elimination steps.<sup>24</sup> These fragmentation pathways rationalize the formation of 1,3,5-triazine and are widely accepted. On the other hand, thermal and photochemical routes to keto (2a) and enol (2b) forms of oxy-s-triazine along with their isomerization processes have not been firmly established computationally. Goddard et al. proposed that 2a could evolve from a mononitro intermediate 1-nitro-1,2-dihydro-1,3,5triazine (C<sub>3</sub>H<sub>4</sub>N<sub>3</sub>O<sub>2</sub>; 128 amu) via HNO (nitrosyl hydride) elimination,<sup>25</sup> but detailed energetics of this pathway have

been absent in the literature. Therefore, we performed quantum chemical calculations at the CCSD(T)/cc-pVTZ//B3LYP/cc-pVTZ level of theory to determine potential molecular elimination channels (HONO, nitrous acid; HNO, nitrosyl hydride) that could lead to 1,3,5-triazine (3a) and keto–enol tautomers (2a and 2b) of oxy-s-triazine (Figure 4).

The predicted pathways revealed that 1 (RDX; 222 amu) could undergo a concerted HONO elimination to the dinitro intermediate 4 (C<sub>3</sub>H<sub>5</sub>N<sub>5</sub>O<sub>4</sub>; 175 amu) passing a barrier of 175 kJ mol<sup>-1</sup>. Intermediate 4 (C<sub>3</sub>H<sub>5</sub>N<sub>5</sub>O<sub>4</sub>; 175 amu) can eliminate yet another HONO to generate the mononitro species 5a (C<sub>3</sub>H<sub>4</sub>N<sub>3</sub>O<sub>2</sub>; 128 amu) after overcoming an energy barrier of 126 kJ mol<sup>-1</sup>. Finally, **5a** ( $C_3H_4N_3O_2$ ; 128 amu) may encounter a third HONO elimination yielding eventually 1,3,5-triazine (3a; 81 amu); this reaction requires an energy of 62 kJ mol<sup>-1</sup>. Overall, the dissociation of RDX (1) to 1.3.5triazine (3a) plus three molecules of nitrous acid (HONO) represents an overall exoergic process by 214 kJ mol<sup>-1</sup>. The mononitro product 5a (C<sub>3</sub>H<sub>4</sub>N<sub>3</sub>O<sub>2</sub>; 128 amu) formed could isomerize to its thermodynamically favorable nitrite isomer 5b  $(C_3H_4N_2ONO; 128 \text{ amu})$  through a nitro-nitrite isomerization pathway; this requires passing a barrier of 194 kJ mol<sup>-1</sup>. It is important to note that the signal observed at m/z = 128indicates the formation of a species of the molecular formula  $C_3H_4N_3O_2$  attributed to structures 5a and/or 5b. The mononitrite product **5b** ( $C_3H_4N_2ONO$ ) may further undergo in an exoergic reaction involving nitrosyl hydride (HNO) elimination and formation of keto oxy-s-triazine (2a); this reaction requires 132 kJ mol<sup>-1</sup>. The keto form (2a) of oxy-striazine could isomerize to the enol isomer (2b) through an intramolecular hydrogen migration that involves an energy barrier of 145 kJ mol<sup>-1</sup>. Dissociation of 1 to keto/enol form of oxy-s-triazine plus two nitrous acid (HONO) and a nitrosyl hydride (HNO) is highly exoergic by 249 and 258 kJ mol<sup>-1</sup>. Thus, the formation of oxy-s-triazine from RDX via nitrous acid eliminations followed by nitro-nitrite isomerization and a nitrosyl hydride elimination is feasible under the given experimental conditions. Although oxy-s-triazine (m/z = 97)is observed in high dose experiments at both 254 and 206 nm photolysis, in the case of very low dose (0.10  $\pm$  0.02 eV molecule<sup>-1</sup> at 254 nm and 0.20  $\pm$  0.02 eV molecule<sup>-1</sup> at 206 nm) experiments the signal at m/z = 97 is observed only at 206 nm, suggesting that the formation of oxy-s-triazine is preferential at a higher photon energy.<sup>15</sup> It is important to recall that 1,3,5-triazine represents also a wavelength-selective product, as was observed only during the photolysis at 254 nm (Figure 3g,i). These observations imply that the decomposition branching ratio is wavelength-dependent and that products such as oxy-s-triazine and 1,3,5-triazine could be tracers of wavelength-dependent decomposition pathways.

In summary, we provided the first experimental observation of an enol intermediate in the decomposition of RDX (1). The formation of both the keto (2a) and enol (2b) tautomers of oxy-s-triazine, as well as its deoxygenated derivative 1,3,5triazine (3a) upon photolysis of RDX (1), are contemplated by selective photoionization coupled with ReTOF-MS. The isomer-selective photoionization scheme permits the selective photoionization and discrimination of the target isomers based on their adiabatic ionization energies. Quantum chemical calculations rationalize the formation of keto oxy-s-triazine (2a) from RDX (1) via HONO elimination. The detection of nitrous acid (HONO) in the infrared (IR) spectrum further supports the nitrous acid elimination channels leading to 2a and 3a. The former can isomerize to its enol form 2b through an intramolecular hydrogen shift. The present study represents a critical step toward the unraveling of the complex decomposition mechanisms of molecular energetic materials, revealing key transients such as enols through state-of-the-art laboratory studies merged with quantum chemical calculations. Further structural identification of reaction products employing isomer-selective photoionization schemes in the coming years will be crucial for a detailed understanding of the ignition phenomena of nitramine-based explosives and the development of detailed fundamental decomposition mechanisms.

#### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.1c01610.

Methods (experimental and computational), experimental setup schematic view, VUV generation, dose calculation, NMR spectra, FTIR spectra, FTIR bands assignment, UV-vis spectrum, mass spectra, structures, geometrical parameters, geometrical coordinates, and calculated energies (PDF)

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## Notes

The authors declare no competing financial interest.

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