



A mechanistical study on non-equilibrium reaction pathways in solid nitromethane (CH₃NO₂) and D3-nitromethane (CD₃NO₂) upon interaction with ionizing radiation



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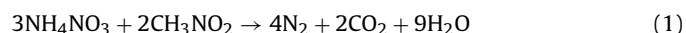
ABSTRACT

Thin films of homogeneously mixed nitromethane (CH₃NO₂) and D3-nitromethane (CD₃NO₂) ices were exposed to energetic electrons and Lyman α photons. The isotopically mixed reaction products were probed in situ via reflectron time-of-flight mass spectrometry coupled with pulsed photoionization during temperature programmed desorption. This study provides compelling evidence on three high energy pathways, which have not been observed under collisionless conditions in the gas phase. These are decomposition of nitromethane (CH₃NO₂) via atomic oxygen loss to nitrosomethane (CH₃NO), fragmentation of nitromethane (CH₃NO₂) and/or methylnitrite (CH₃ONO) via carbene (CH₂) loss, and carbon–hydrogen bond rupture processes in nitromethane (CH₃NO₂) and/or methylnitrite (CH₃ONO).

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1. Introduction

The nitromethane molecule (CH₃NO₂) is the simplest representative of an organic nitro compound carrying a resonance stabilized functional group (nitro). Considering the resonance stabilization, nitromethane (CH₃NO₂) is exploited as a one carbon building block in organic synthesis due to its acidity yielding the H₂CNO₂[−] anion upon deprotonation [1]. The nucleophilic character of the H₂CNO₂[−] anion leads to a widely utilized reagent in the presence of base catalysts upon reactions with aldehydes and ketones via 1,2-addition reactions [2]. Besides classical organic synthesis, nitromethane is also of interest as a monopropellant in high-speed engines exploiting rich air-fuel mixtures since nitromethane delivers the combustion process even in the absence of atmospheric oxygen [3–6]. Although pure nitromethane represents an insensitive explosive with a velocity of detonation of only 6300 ms^{−1} [7,8], mixtures with ammonium nitrate (NH₄NO₃) as an oxidizing agent forms a highly explosive blend [reaction (1)] [9].



An experimental investigation of the decomposition mechanisms of nitromethane (CH₃NO₂) have been mainly restricted to gas phase processes utilizing ultraviolet photodissociation (UVPD) [10–14]

and infrared multi photon dissociation (IRMPD) [15–17]. These studies – often carried out under collision-less conditions in molecular beams and combined with electronic structure calculations [15,18–23] – revealed three key channels: the unimolecular decomposition of nitromethane (CH₃NO₂) to the methyl radical (CH₃) and nitrogen dioxide (NO₂) [reaction (2)] and a roaming-mediated nitromethane (CH₃NO₂)–methylnitrite (CH₃ONO) isomerization followed by the unimolecular decomposition via a radical pathway to the methoxy radical (CH₃O) plus nitrogen monoxide (NO) [reaction (3a)] and through a molecular elimination pathway forming formaldehyde (H₂CO) plus nitrosylhydride (HNO) [reaction (3b)].

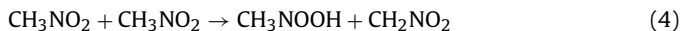


Until very recently, only a few studies have investigated the decomposition of nitromethane in the condensed phase. More than half a century ago, photolysis studies of liquid nitromethane and pure nitromethane ice at 77 K proposed a unimolecular decomposition of nitromethane (CH₃NO₂) in analogy to reaction (2) in the gas phase under collision-less conditions yielding the methyl radical (CH₃) plus nitrogen dioxide (NO₂) [24,25]. Further works exposed the isomerization of nitromethane (CH₃NO₂) to cis- and trans-methylnitrite (CH₃ONO) [26–29], which – upon extended photolysis – resulted in the appearance of formaldehyde (H₂CO) and nitrosylhydride (HNO) [reaction (3b)] and also

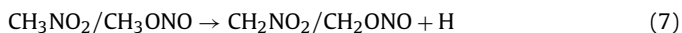
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nitrosomethanol (ONCH₂OH). Multiple experimental and simulation approaches were applied lately to study nitromethane condensed phase decomposition related to detonation conditions [30–40]. Recent molecular dynamics calculations [41,42] predicted besides the traditional nitromethane (CH₃NO₂) to methylnitrite (CH₃ONO) isomerization also intermolecular hydrogen atom transfer processes leading to N-hydroxy-nitrosomethane (CH₃NOOH) plus a nitromethyl (CH₂NO₂) radical at elevated temperatures (3000 K) [reaction (4)] along with formation of isomerization to aci-nitromethane (H₂C=N(O)OH) [reaction (5)]. These simulations predicted further that the decomposition of nitromethane leads to complex organics of hitherto unknown structure accounting for up to 70% of the total carbon and nitrogen budget.



A recent experimental study on the interaction of cryogenic films of nitromethane (CH₃NO₂) and of D3-nitromethane (CD₃NO₂) films with energetic electrons and photons (Lyman α ; 10.2 eV) [43] exposed that besides the classical gas phase pathways [reactions (2) and (3)] and the predicted hydrogen transfer processes [reactions (4) and (5)], nitromethane (CH₃NO₂) might undergo non-traditional (high energy; non-equilibrium), highly endoergic decomposition routes [reactions (7)–(9)]. These involve the decomposition of nitromethane and/or the methylnitrite isomer to the nitromethyl radical (CH₂NO₂) and/or CH₂ONO plus suprathreshold atomic hydrogen (H) [$\Delta_{\text{R}}G=+461 \text{ kJ mol}^{-1}$; $\Delta_{\text{R}}G=+472 \text{ kJ mol}^{-1}$] [reaction (7)], to nitrosomethane (CH₃NO) plus atomic oxygen (O) [$\Delta_{\text{R}}G=+363 \text{ kJ mol}^{-1}$] [reaction (9)], and to singlet carbene (CH₂) plus nitrous acid (HONO) [$\Delta_{\text{R}}G=+430 \text{ kJ mol}^{-1}$] potentially via methylnitrite (CH₃ONO).



In the present study, we test experimentally these novel reaction mechanisms and expose thin films of homogeneously mixed nitromethane (CH₃NO₂) and of D3-nitromethane (CD₃NO₂) to ionizing radiation in form of energetic electrons and monochromatic photons (Lyman α ; 10.2 eV) at 5 K. After the radiation exposure, the radiolyzed samples undergo temperature programmed desorption (TPD) to 300 K; the subliming species are simultaneously analyzed via reflectron time of flight mass spectrometry (Re-TOF-MS) coupled with fragment-free soft photoionization exploiting vacuum ultraviolet photons at an energy of 10.49 eV. Ultimately – based on the shifts of the masses of the reaction products by deuteration and a cross correlation of isotopically mixed products – we present compelling evidence of the validity of three key non-equilibrium pathways [reactions (7)–(9)] leading to complex organic molecules via radical-radical reactions and well-defined molecular growth processes unobservable under collisionless conditions in the gas phase.

2. Experimental

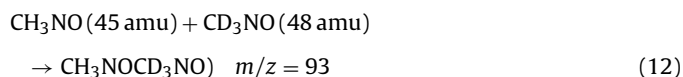
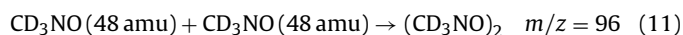
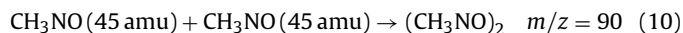
The experiments were conducted in an ultra-high vacuum (UHV) chamber operated at base pressures of a few 10^{-11} torr [43]. Mixed nitromethane (CH₃NO₂, TCI AMERICA, 99+%) and D3-nitromethane (CD₃NO₂, Aldrich, 99+% D) ices were condensed via vapor deposition of premixed gases (1:1) onto a cryogenically cooled silver wafer at 5 K exploiting a glass capillary array at a pressure of 5×10^{-8} torr for 2 min resulting in ice samples of $380 \pm 10 \text{ nm}$ thickness. The thickness of the samples were

extracted via helium-neon laser (632 nm) interferometry using an index of refraction of the ices of $n_{632\text{nm}} = 1.39 \pm 0.02$ [43,44]. In separate experiments, the CH₃NO₂–CD₃NO₂ ices were exposed to monochromatic Lyman α vacuum ultraviolet (VUV) photons at $122 \pm 5 \text{ nm}$ for 60 h with $3.5 \pm 0.5 \times 10^{12} \text{ photons s}^{-1} \text{ cm}^{-2}$ or monoenergetic electrons (5 keV) for 60 min at electron currents of 15 nA yielding dose of $4.1 \pm 0.4 \text{ eV}$. After the irradiation, the sample was kept at 5 K for one hour before temperature programmed desorption (TPD) studies were carried out by heating the irradiated ices at a rate of 0.5 K min^{-1} to 300 K. The subliming molecules were photoionized via single photon ionization and probed in a reflectron time-of-flight mass spectrometer (ReTOF). The molecules were ionized following single photon ionization exploiting pulsed (30 Hz) coherent vacuum ultraviolet (VUV) light at 118.2 nm (10.49 eV) [43]. Briefly, the third harmonic (354.6 nm) of a Nd:YAG laser (Spectra Physics, PRO-250; 30 mJ per pulse) was exploited to produce the VUV photons via frequency tripling ($\omega_{\text{VUV}} = 3\omega_1$) in xenon (Xe) gas (99.999%; Specialty Gases of America) as the nonlinear medium. The resulting VUV flux was $10^{13} \text{ photons cm}^{-2} \text{ s}^{-1}$ depicting a conversion efficiency of about 10^{-4} . The 10.49 eV light was separated exploiting an off-axis lithium fluoride (LiF) lens. The ions resulting from the photoionization were extracted into a reflectron time-of-flight mass spectrometer (Re-TOFMS).

3. Results and discussion

3.1. Nitrosomethane channel

Previous experiments on the decomposition of pure nitromethane (CH₃NO₂) and D3-nitromethane (CD₃NO₂) ices at 5 K upon exposure to energetic electrons and Lyman α photons monitored signal at $m/z=45$ (CH₃NO; 45 amu; IE=9.3 eV) and $m/z=48$ (CD₃NO; 48 amu; IE=9.3 eV) peaking at temperatures of 110, 160 and 280 K [43]. This was attributed to nitrosomethane likely formed via atomic oxygen loss of nitromethane (CH₃NO₂; 61 amu) and D3-nitromethane (CD₃NO₂; 64 amu), respectively. Further evidence on the atomic oxygen loss channel was presented based on the identification of the ‘dimers’ of nitrosomethane and D3-nitrosomethane at $m/z=90$ and 96, respectively, in the temperature range from 250 K to 300 K. Here, nitrosomethane (CH₃NO) was found to rapidly dimerize forming (E)-azodioxymethane (IE=8.6 eV). These previous conclusions lead us to predict that in the irradiated mixed nitromethane (CH₃NO₂) and D3-nitromethane (CD₃NO₂) ices, we should form (CH₃NO)₂ ($m/z=90$), (CD₃NO)₂ ($m/z=96$), and also (CH₃NOCD₃NO) ($m/z=93$) [reactions (10)–(12)]. As a matter of fact, an inspection of the TPD profiles of $m/z=90$, 93, and 96 supports the formation of (E)-azodioxymethane from the corresponding (D3)-nitrosomethane monomers both during the exposure of the ices with energetic electrons and photons from about from 250 K to 300 K (Fig. 1). Minor signal at $m/z=92$ and 91 within the temperature regime of 250–300 K at levels of less than 10% compared to signal at $m/z=93$ likely originates from the CH₃NO₂–CD₂HNO₂ and CH₃NO₂–CH₂DNO₂ dimerization. This in turn proposes the existence of CH₂DNO₂ and CD₂HNO₂ (see below). Therefore, the explicit identification of signal at $m/z=90$ and 96, and in particular at $m/z=93$ verifies the existence of (E)-azodioxymethane synthesized from (isotopically substituted) nitrosomethane formed via atomic oxygen loss from their nitromethane precursor [reaction (8)].



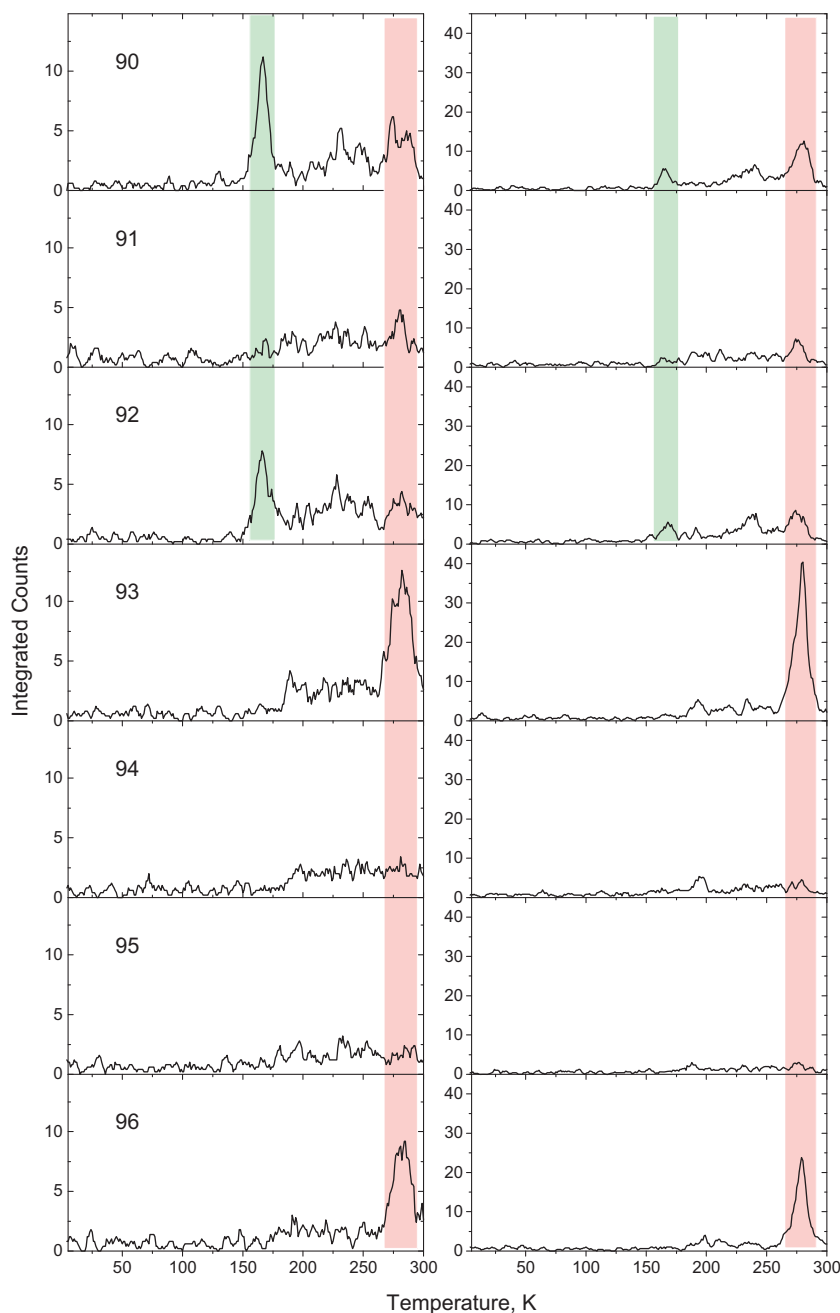


Figure 1. Temperature programmed desorption profiles of products formed in Lyman α (left) and electron (right) irradiated 1:1 mixture of nitromethane (CH_3NO_2) and D3-nitromethane (CD_3NO_2). Mass-to-charge ratios of the sublimating products are indicated in the top left corner. At around 280 K (red) (CH_3NO_2), $\text{CH}_3\text{NO-CD}_3\text{NO}$ and (CH_3NO_2) desorb. The peak at 160 K (green) is likely representing the co-desorption of $\text{CH}_2\text{N}_2\text{O}_3$ and $\text{CD}_2\text{N}_2\text{O}_3$ with the matrix. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.2. Carbene channel

Our studies on the nitromethane (CH_3NO_2) and D3-nitromethane (CD_3NO_2) ices proposed a molecular mass growth process by 14 amu (CH_3NO_2) and 16 amu (CD_3NO_2) via the reaction of precursor molecules with carbene (CH_2) and D2-carbene (CD_2), respectively [43]. This recommended mass growth process was based on detected mass-to-charge ratios of 45 (CH_3NO ; 45 amu; IE=9.3 eV) versus 59 ($\text{CH}_3\text{CH}_2\text{NO}$; 59 amu; IE=10.1 eV) and 61 (CH_3ONO ; 61 amu; IE=10.44 eV) versus 75 ($\text{CH}_3\text{CH}_2\text{ONO}$; 75 amu; IE=10.53 eV) from the exposed nitromethane samples, which is also matched with the mass-to-charge ratios of 48 (CD_3NO ; 48 amu; IE=9.3 eV) versus 64 ($\text{CD}_3\text{CD}_2\text{NO}$; 64 amu; IE=10.1 eV)

and 64 (CD_3ONO ; 64 amu; IE=10.44 eV) versus 80 ($\text{CD}_3\text{CD}_2\text{ONO}$; 80 amu; IE=10.53 eV) in the D3-nitromethane ices reaching peak sublimation rates at about 160 K. Note that the ionization energy of ethylnitrite of 10.53 eV is slightly above the photon energy of 10.49 eV; as demonstrated earlier, the effective electric field of the repeller plate in Re-TOFMS can lower the ionization energy by at least 0.04 eV.

First, if this mechanism is valid, in the mixed nitromethane (CH_3NO_2) – D3-nitromethane (CD_3NO_2) ices, we should also monitor signal from the reaction of carbene (CH_2) with D3-nitrosomethane (CD_3NO) and of D2-carbene (CD_2) with nitrosomethane (CH_3NO) at $m/z=62$ and 61, respectively. As a matter of fact, in the mixed samples, signal was observed at $m/z=59$

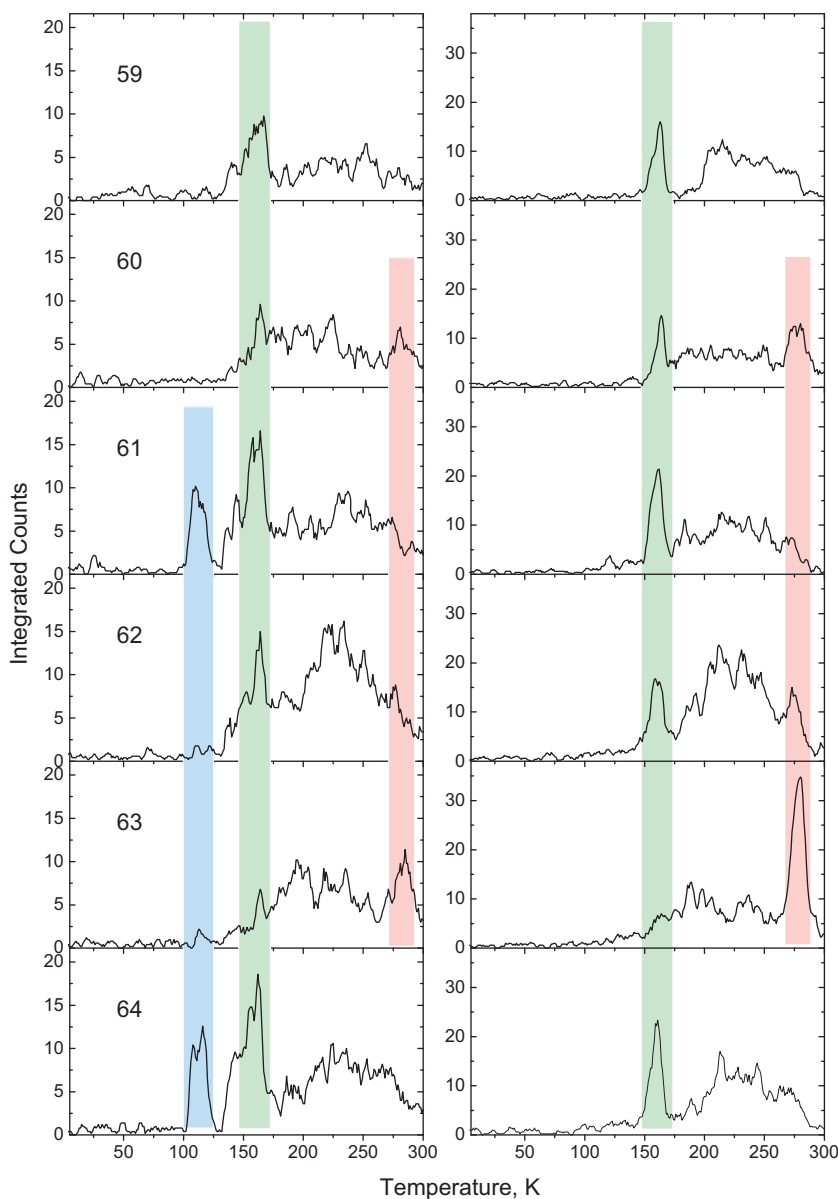
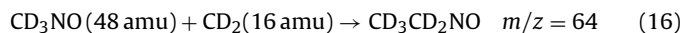
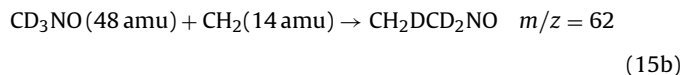
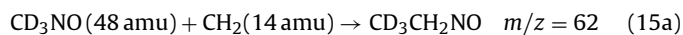
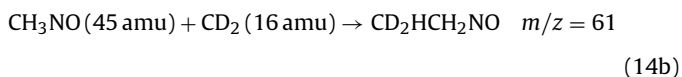
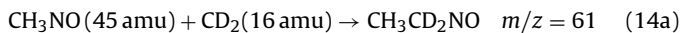
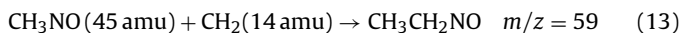


Figure 2. Temperature programmed desorption profiles of $m/z = 59\text{--}64$ products formed in Lyman α (left) and electron (right) irradiated 1:1 mixture of nitromethane (CH_3NO_2) and D3-nitromethane (CD_3NO_2). Mass-to-charge ratios of the sublimating products are indicated in the top left corner. The peaks at 160 K (green) correspond to $\text{CH}_3\text{CH}_2\text{NO}$ and its deuterated variants co-desorbing with the $\text{CH}_3\text{NO}_2/\text{CD}_3\text{NO}_2$ matrix. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

($\text{CH}_3\text{CH}_2\text{NO}$) and 64 ($\text{CD}_3\text{CD}_2\text{NO}$) and most importantly at m/z 62 and m/z 61 as predicted based on the carbene (CH_2) and D2-carbene (CD_2) insertion with ion counts peaking at about 160 K (Fig. 2). Note that small ion counts visualized at 160 K at m/z 63 and 60 likely origin from reaction of D2-carbene (CD_2) and carbene (CH_2) with CD_2HNO and CH_2DNO , respectively. It is important to highlight that the insertion of singlet carbene can occur into a carbon–hydrogen and also into the carbon–nitrogen single bond. In case of the reaction of nitrosomethane (CH_3NO) and D3-nitrosomethane (CD_3NO) with D2-carbene (CD_2) and carbene (CH_2), respectively, this can lead to distinct isotopomers [reactions (14) and (15)].



Second, to support the validity of the carbene insertion pathway, we also probed the mass growth processes from methyl nitrite (CH_3ONO) to ethylnitrite ($\text{C}_2\text{H}_5\text{ONO}$) together with the isotopically labeled counterparts. Here, carbene (CH_2) and D2-carbene (CD_2) reaction with methyl nitrite (CH_3ONO ; 61 amu) and D3-methyl nitrite (CD_3ONO ; 64 amu), respectively, should result in signal at m/z 75 ($\text{C}_2\text{H}_5\text{ONO}^+$) and m/z 80 ($\text{C}_2\text{D}_5\text{ONO}^+$) [reactions (17) and (22)]. Also, insertion of carbene (CH_2) and D2-carbene (CD_2) into the carbon–hydrogen and/or carbon–nitrogen single bonds of D3-methyl nitrite (CD_3ONO ; 64 amu) and methyl nitrite (CH_3ONO ; 61 amu) should result in signal at m/z 78 ($\text{CD}_3\text{CH}_2\text{ONO}^+/\text{CH}_2\text{DCD}_2\text{ONO}^+$) and m/z 77

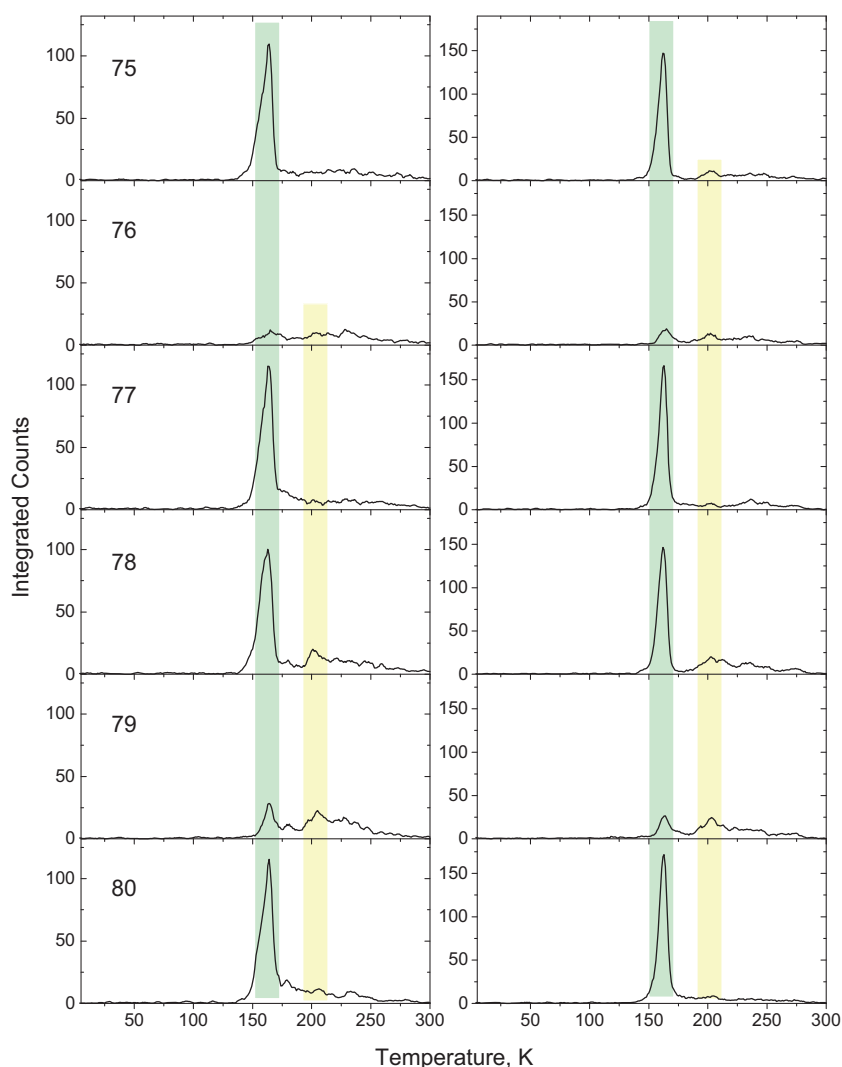
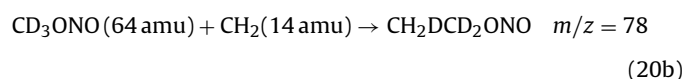
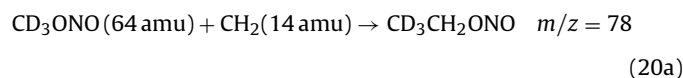
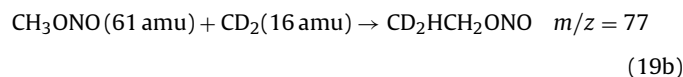
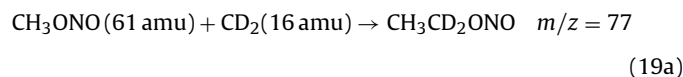
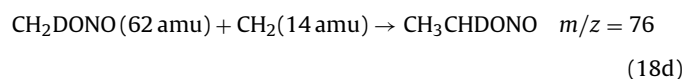
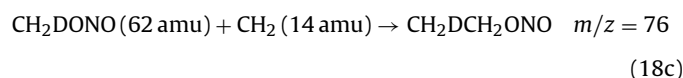
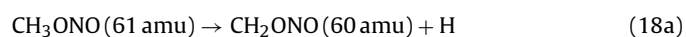
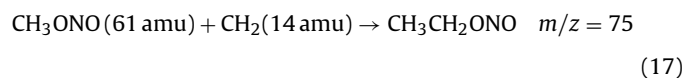
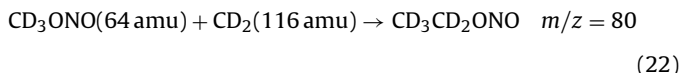
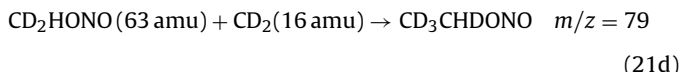
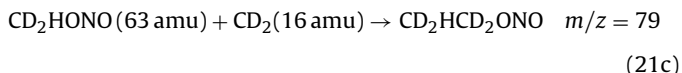
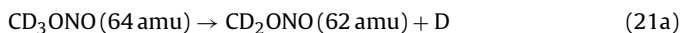


Figure 3. Temperature programmed desorption profiles of $m/z=75$ – 80 products formed in Lyman α (left) and electron (right) irradiated 1:1 mixture of nitromethane (CH_3NO_2) and D3-nitromethane (CD_3NO_2). Mass-to-charge ratios of the sublimating products are indicated in the top left corner. The prominent peaks at 160 K (green) correspond to $\text{CH}_3\text{CH}_2\text{ONO}$ and its deuterated variants co-desorbing with the $\text{CH}_3\text{NO}_2/\text{CD}_3\text{NO}_2$ matrix. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

($\text{CH}_3\text{CD}_2\text{ONO}^+/\text{CD}_2\text{HCH}_2\text{ONO}^+$) [reactions (19) and (20)]. Figure 3 demonstrates the existence of these ions depicting ion signal with almost equal intensity at $m/z=75$, 77, 78, and 80 peaking at about 160 K. It should be noted that smaller signal peaking at 160 K could also be found at $m/z=76$ and 79; this signal could arise from H versus D and D versus H exchange pathways in the methylnitrite/D3-methylnitrite molecules followed by carbene and D2-carbene insertion [reactions (18) and (21)]. Note that the D versus H and/or H versus D exchange can also take place in the nitromethane and D3-nitromethane prior to their isomerization to the (D3)-methylnitrite isomers. Nevertheless, these minor pathways clearly indicate the effectiveness of a carbon–hydrogen bond rupture in either the reactants ((D3)-nitromethane) or the nitrite isomers ((D3)-methyl nitrite) as suggested in reaction (7).



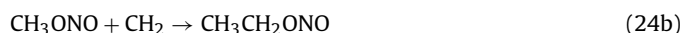


We should mention that a hydrogen atom loss followed by methyl addition could present an alternative to singlet carbene insertion mechanism of the discussed 14–16 amu mass growth process. However, the absence of the methyl radical signature at 608 cm^{-1} [45] in the infrared spectrum of the irradiated sample allows us to exclude this pathway.

4. Summary

Exposing isotopically mixed nitromethane (CH_3NO_2) and D3-nitromethane ices (CD_3NO_2) to ionizing radiation in form of energetic electrons and Lyman α vacuum ultraviolet photons (10.2 eV), we were able to elucidate the existence of three high energy pathways (7)–(9) in the decomposition of (D3)-nitromethane, which do not occur in the unimolecular decomposition of (D3)-nitromethane under collisionless conditions in the gas phase. *First*, the detection of three azodi-oxy-methanes ($(\text{CH}_3\text{NO})_2$, $(\text{CD}_3\text{NO})_2$, and $\text{CH}_3\text{NOCD}_3\text{NO}$) verifies the presence of the corresponding nitrosomethane isomers, which in turn are formed via atomic oxygen loss from their nitromethane precursor molecules via reaction (8) in strongly endoergic reactions [$\Delta_R G = +363 \text{ kJ mol}^{-1}$]. *Second*, the carbene insertion pathways and the corresponding mass growth processes has been validated by the conversion of (D3)-nitrosomethane ($\text{CH}_3\text{NO}/\text{CD}_3\text{NO}$) to (D5)-nitrosoethane ($\text{CH}_3\text{CH}_2\text{NO}/\text{CD}_3\text{CD}_2\text{NO}$); the isotopically mixed counterparts $\text{CH}_3\text{CD}_2\text{NO}/\text{CD}_2\text{HCH}_2\text{NO}$ as well as $\text{CD}_3\text{CH}_2\text{NO}/\text{CH}_2\text{DCD}_2\text{NO}$ demonstrate the reactions of D2-carbene

and carbene with nitrosomethane and D3-nitrosomethane, respectively. Additional evidence originates from the verification of the reaction of nitrosomethane (CH_3NO_2)/methyl nitrite (CH_3ONO) with carbene leading to nitroethane ($\text{C}_2\text{H}_5\text{NO}_2$)/ethylnitrite ($\text{C}_2\text{H}_5\text{ONO}$) together with their (partially) deuterated counterparts. It should be noted that our investigations cannot decipher if the carbene reacts with nitromethane to form nitroethane followed by isomerization to ethylnitrite or if nitromethane isomerizes first to methyl nitrite followed by reaction with carbene to ethylnitrite (reactions (23) and (24)). However, the mass growth process via carbene insertion is clearly evident. In principle, two pathways can lead to carbene: decomposition of nitromethane (CH_3NO_2) to nitryl hydride (HNO_2) [$\Delta_R G = +464 \text{ kJ mol}^{-1}$] and/or decomposition of methyl nitrite (CH_3ONO) to nitrous acid (HONO) [$\Delta_R G = +430 \text{ kJ mol}^{-1}$] [reactions (25) and (26)].



Finally, we could verify the existence of free hydrogen atoms (3.1/3.2). These free hydrogen atoms were formed via highly endo-ergic carbon–hydrogen bond rupture in nitrosomethane (CH_3NO) (3.1) as well as nitromethane (CH_3NO_2) and/or methyl nitrite (CH_3ONO) (3.2).

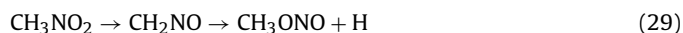
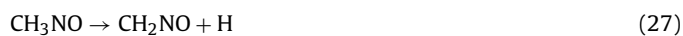


Figure 4 compiles the reaction pathways identified in the decomposition of nitromethane–D3-nitromethane ices upon interaction with ionizing radiation with carbene insertion pathways labeled in blue, hydrogen versus deuterium exchange paths in black, nitromethane reactions via dimerization in red, and nitromethane–methyl nitrite rearrangements expressed in red.

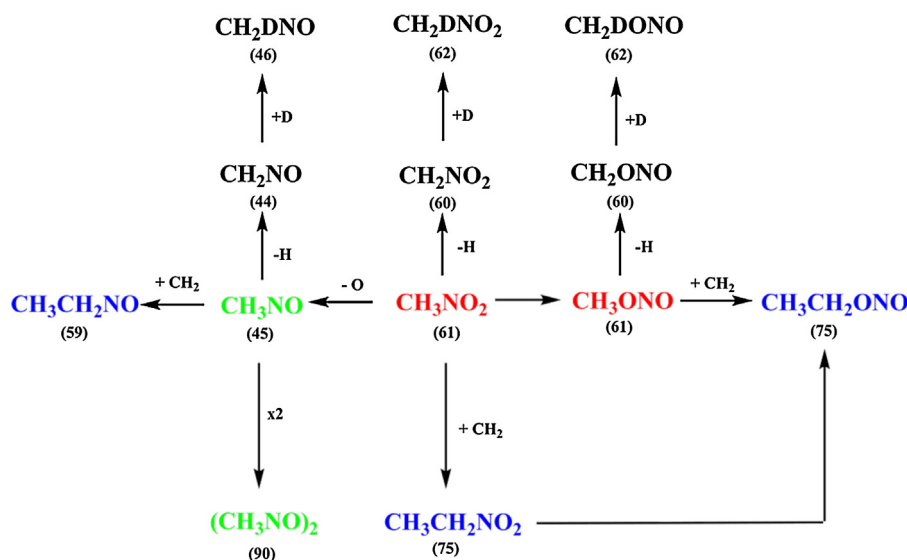


Figure 4. Selected reaction mechanisms taking place in 1:1 mixture of nitromethane (CH_3NO_2) and D3-nitromethane (CD_3NO_2) ice under Lyman α and electron irradiation.

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