

Gas Phase Identification of the Elusive *N*-Hydroxyoxaziridine (*c*-H₂CON(OH)): A Chiral Molecule

Santosh K. Singh, Tang-Yu Tsai, Bing-Jian Sun, Agnes H. H. Chang,* Alexander M. Mebel, and Ralf I. Kaiser*

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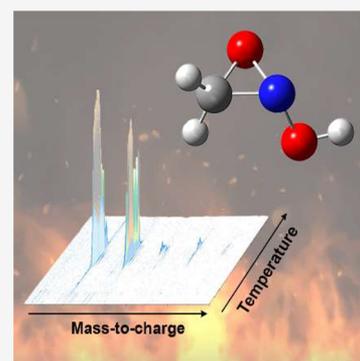
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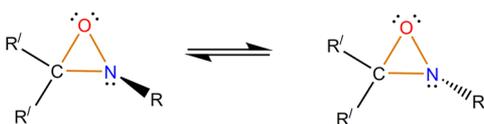
Supporting Information

ABSTRACT: The hitherto elusive *N*-hydroxyoxaziridine molecule (*c*-H₂CON(OH)), a chiral, high energy isomer of nitromethane (CH₃NO₂) and one of the simplest representatives of an oxaziridine, is detected in the gas phase. Electronic structure calculations propose an impending synthesis eventually via addition of carbene (CH₂) to the nitrogen–oxygen double bond of nitrous acid (HONO). The oxaziridine ring demonstrates an unusual kinetic stability toward ring opening compared to the isoelectronic cyclopropane (C₃H₆) counterpart. This system defines a fundamental benchmark to explore the formation and stability of racemic derivatives of strained oxaziridines (*c*-H₂CONH) and changes our perception how we think about fundamental decomposition and isomerization mechanisms in (model compounds of) energetic materials.



Over the past six decades, oxaziridines, a class of organic molecules whose chemical and physical properties are dictated by the presence of two electronegative atoms (oxygen, nitrogen) within a strained three-membered ring (Scheme 1),

Scheme 1. Three Membered Ring Moiety of Oxaziridine Depicting the Nitrogen Inversion Process^a



^a“R” represents an (in)organic group.

have received substantial attention from the synthetic organic, physical organic, and theoretical chemistry communities from a fundamental point of view due to their chirality and distinct chemical bonding along with exotic ring inversion processes.^{1–3} Although oxaziridines do not carry an asymmetric carbon atom and thus lack the classical definition of chirality,⁴ oxaziridines represent a benchmark of optical active strained heterocyclic ring compounds in which the nitrogen inversion barrier of up to 133 kJ mol⁻¹ can be attributed to an increased repulsion of the lone pair of electrons of the adjacent carbon and nitrogen atoms in the transition state favoring sp³ rather than sp² hybridization.^{5–8} Considering the chemical resistance to air and augmented stability compared to dioxiranes,⁹ oxaziridines have been widely exploited as chiral reagents in oxidative transformations and single atom transfer reagents such as Sharpless asymmetric epoxidations¹⁰ and sulfide

oxidation,¹¹ in which the outcome of the chemical reaction is driven by the electrophilic character of the atomic oxygen transfer reagent. The synthesis of chiral oxaziridines in transition metal complexes like cobalt chloride (CoCl₂) and cobalt salicylaldehyde (Co[salicylaldehyde]₂) highlights the significance in preparative, synthetic chemistry.¹²

Despite the significance of oxaziridines, the simplest representative of oxaziridines, the oxaziridine stem compound oxaziridine (*c*-H₂CONH) along with *N*-hydroxyoxaziridine (*c*-H₂CON(OH); **1**), which is a derivative of oxaziridine in which the hydrogen atom on the nitrogen is replaced by a hydroxyl group (OH) (Figure 1), has not been synthesized to date. This is due to previously insurmountable experimental difficulties in preparing appropriate precursor molecules eventually leading to (*N*-hydroxy)oxaziridine upon, for instance, photoprocessing.^{13,14} As a structural isomer of nitromethane (CH₃NO₂; **2**), *cis/trans*-methyl nitrite (CH₃ONO; **3a**, **3b**), *cis/trans*-aci-nitromethane (H₂CN(OH)-O; **4a**, **4b**), *cis/trans*-nitrosomethanol (HOCH₂NO; **5a**, **5b**), and *cis/trans*-hydroxy(methyleneoxonio)amide (CH₂ONOH; **6a**, **6b**), the elusive *N*-hydroxyoxaziridine molecule **1** is connected via a substantial barrier ranging between 197 and 223 kJ mol⁻¹ to the thermodynamically favored aci-nitro-

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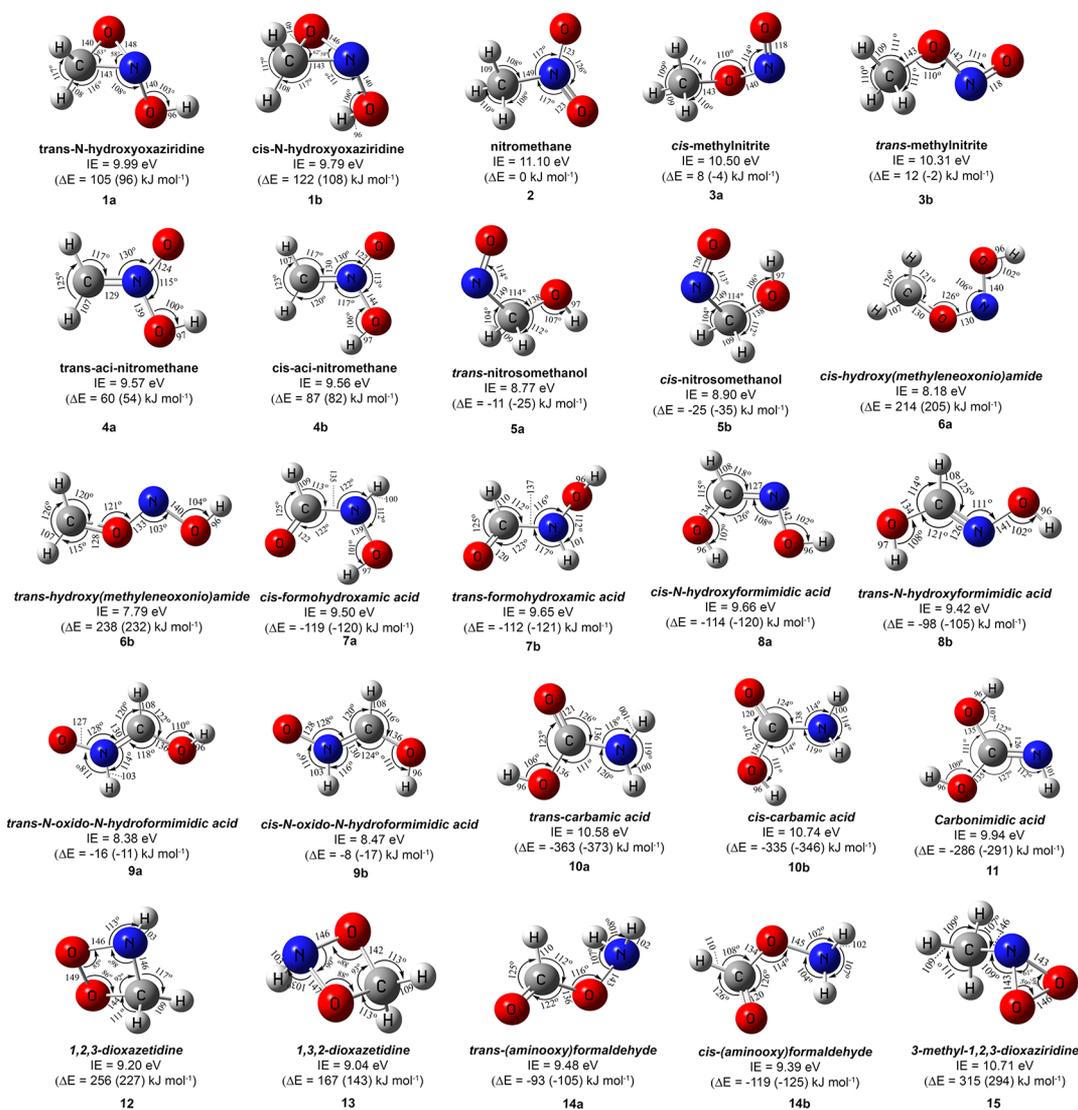


Figure 1. Structures of nitromethane (CH_3NO_2) isomers along with their adiabatic ionization energies (IE) and relative energies (ΔE) calculated at the B3LYP//CCSD(T)/CBS level of theory with CCSD/cc-pVTZ//MRCI/CBS energies provided in parentheses. The Cartesian coordinates of the structures are provided in Table S9 of the Supporting Information. Bond lengths and angles are given in picometers and degrees, respectively.

methane ($\text{H}_2\text{CN}(\text{OH})\text{O}$; 4). Formally, this isomerization involves a rotation of the CH_2 moiety perpendicularly to the $-\text{NOH}$ fragment followed by a migration of the oxygen atom to form a carbon–oxygen σ bond and hence a three-membered ring through a [1,2] sigmatropic shift.^{15–18} However, the kinetic and thermodynamical stability of aci-nitromethane ($\text{H}_2\text{CN}(\text{OH})\text{O}$; 4) compared to that of *N*-hydroxyoxaziridine ($\text{c-H}_2\text{CON}(\text{OH})$; 1) along with the preferred isomerization of aci-nitromethane ($\text{H}_2\text{CN}(\text{OH})\text{O}$; 4) to nitroso-methanol (HOCH_2NO ; 5) through a hydroxyl group migration from the nitrogen atom to the carbon atom via a barrier of 240 kJ mol^{-1} in an overall exoergic reaction ($\Delta_{\text{R}}G = -85 \text{ kJ mol}^{-1}$)¹⁸ reveals the necessity of an alternative synthetic route to *N*-hydroxyoxaziridine ($\text{c-H}_2\text{CON}(\text{OH})$; 1).

Here, we report on the very first synthesis and detection of the hitherto elusive *N*-hydroxyoxaziridine ($\text{c-H}_2\text{CON}(\text{OH})$; 1) molecule in the gas phase. Our experiments are combined with electronic structure calculations to propose the underlying reaction mechanism(s) of *N*-hydroxyoxaziridine ($\text{c-H}_2\text{CON}(\text{OH})$; 1). Considering the molecular structure of *N*-hydroxyoxaziridine ($\text{c-H}_2\text{CON}(\text{OH})$; 1), we follow the

premise that the latter can be synthesized in low temperature ices eventually via cycloaddition of carbene (CH_2) to the nitrogen–oxygen double bond of nitrous acid ($\text{H}-\text{O}-\text{N}=\text{O}$) with the latter formed through the recombination of a hydrogen atom (H) with the nitrogen dioxide (NO_2) radical. Therefore, experiments were carried out in an ultrahigh vacuum (UHV) surface science machine operated at a base pressure of a few 10^{-11} Torr (Supporting Figure S1).^{19,20} Binary ices of methane (CH_4), methane- d_4 (CD_4), or ^{13}C -methane ($^{13}\text{CH}_4$) with nitrogen dioxide (NO_2) were prepared in separate experiments with thicknesses of $550 \pm 50 \text{ nm}$ at $4.9 \pm 0.2 \text{ K}$ at ratios of $1.2 \pm 0.4:1$ (Supporting Figures S2–S4, Tables S1–S3). Bond-cleavage processes in (isotopically labeled) methane were initiated by exposing these ices to energetic electrons at doses of $1.2 \pm 0.2 \text{ eV}$ per molecule on average (Supporting Table S4). Fourier transform infrared (FTIR) spectra of the ices were collected *in situ* before and after the irradiation (Supporting Figures S2 and S3). The low irradiation dose together with overlapping infrared absorptions of functional groups of nitrogen–oxygen carrying (in)organic molecules excludes an identification of *N*-hydroxyoxaziridine

(*c*-H₂CON(OH); **1**) via classical FTIR spectroscopy (Table S5), and a novel approach is required.²¹

After the irradiation, the ices were annealed at a rate of 1 K min⁻¹ to 300 K (temperature-programmed desorption, TPD). During the TPD phase, the subliming neutral molecules were ionized via tunable vacuum ultraviolet (VUV) photoionization (PI), mass resolved in a reflectron time-of-flight mass spectrometer (PI-ReTOF-MS), and assigned via their arrival times by a multichannel plate via their mass-to-charge ratios. By systematically tuning the photoionization energies from 10.49 eV via 10.20, 9.80, and 9.70 eV (Supporting Table S8), specific isomers **1**–**15** can be (selectively) ionized on the basis of their adiabatic ionization energies (IE; Figure 1; Supporting Table S6)²¹ to eventually determine which isomer(s) is(are) formed. This strategy leads ultimately to the identification of *N*-hydroxyoxaziridine (*c*-H₂CON(OH); **1**). It shall be noted that a comparison of experimentally available benchmarks with IEs computed at the B3LYP/cc-pVTZ//CCSD(T)/CBS level of theory suggests that the calculated ionization energies can be lower or higher by 0.08 eV (Table S6).^{18,22,23} Further, in the present setup, calibration experiments revealed that the electric field of the extraction plate of the ion optics reduces the ionization energy by 0.03 eV.²⁴ A comparison of experimental and computed IEs of various molecules further supports the former statement (Table S7).

The mass spectra of the molecules subliming from the irradiated methane–nitrogen dioxide ices are presented in Figure 2 as a function of temperature recorded at photon

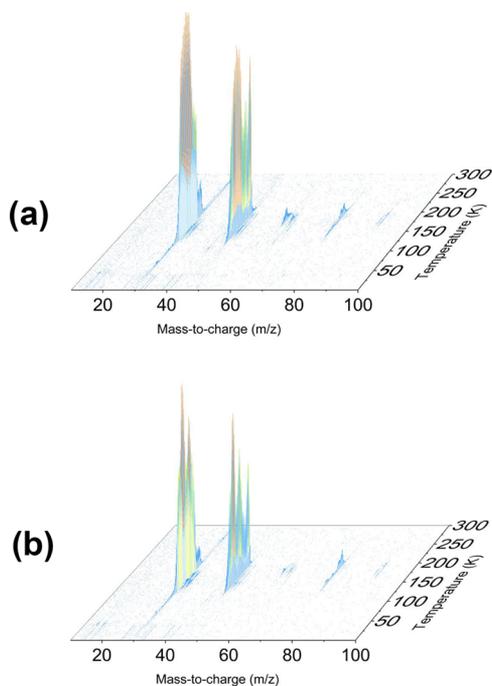


Figure 2. PI-ReTOF-MS data of the molecules subliming from an irradiated CH₄–NO₂ ice mixture as a function of temperature at a photon energy of (a) 10.49 eV and (b) 10.20 eV.

energies of 10.49 and 10.20 eV. Considering the experiments at 10.49 eV, a comparison of the data of the nonirradiated ice mixtures (blank; Supporting Figure S5) with the exposed ices exposes the formation of new molecules. In addition to the precursor nitrogen dioxide (NO₂) (*m/z* = 46; IE = 9.58 eV) and prominent signal at *m/z* = 30 (NO), 59 (C₂H₅NO), 89

(C₃H₇NO₂), and 90 (C₂H₆N₂O₂) (Supporting Figure S6), the PI-ReTOF-MS data recorded for the CH₄–NO₂ system at 10.49 eV disclose a distinct trace at mass-to-charge (*m/z*) of 61 (Figure 3); this graph exhibits two sublimation events peaking at 122 and 176 K (Figure 3a). The mass-to-charge ratio of *m/z* = 61 is consistent with the molecular formula CH₃NO₂.

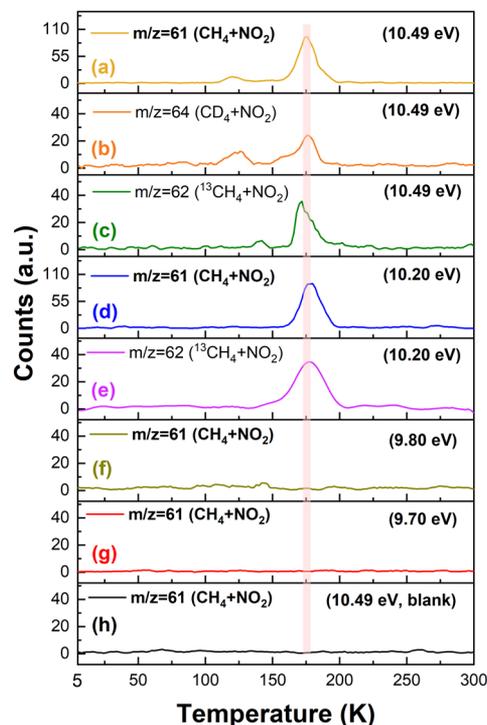


Figure 3. Temperature program desorption (TPD) profiles at (a) *m/z* = 61 (CH₄ + NO₂), (b) *m/z* = 64 (CD₄ + NO₂), and (c) *m/z* = 62 (¹³CH₄ + NO₂) using a photon energy of 10.49 eV. (d) TPD profiles of *m/z* = 61 and (e) at *m/z* = 62 at 10.20 eV. TPD profiles of *m/z* = 61 (f) at 9.80 eV and (g) at 9.70 eV. The blank experiment is recorded at 10.49 eV (h). Errors in the photon energies are ±0.0001 eV.

At a photon energy of 10.49 eV, all isomers depicted in Figure 1 can be photoionized, except for **2**, **10**, and **15**. It is important to note that signal at *m/z* = 61 is absent in the control experiment (Figure 3h), revealing that ion counts at *m/z* = 61 are linked to the radiation exposure of the binary ice mixture, but do not originate from the photoionization laser and/or gas phase ion–molecule reactions of the subliming molecules. To corroborate that the species monitored at *m/z* = 61 are connected to a molecule with the formula CH₃NO₂, two additional isotopic experiments were conducted by replacing methane (CH₄) in separate experiments with methane-*d*₄ (CD₄) and ¹³C-methane (¹³CH₄). The TPD profiles recorded at *m/z* = 64 and 62 are shifted by 3 and 1 amu in the D and ¹³C-labeled ices, respectively (Figure 3b,c). These data propose that at least at the sublimation event peaking at 176 K, the molecule of interest carries three hydrogen atoms and a single carbon atom, a finding that is consistent with the molecular formula CH₃NO₂. It is important to mention here that spectra measured at *m/z* = 64 and *m/z* = 62 in methane-*d*₄ and ¹³C-methane experiments, respectively, the shape of the second sublimation peak is slightly broadened near the region 150–

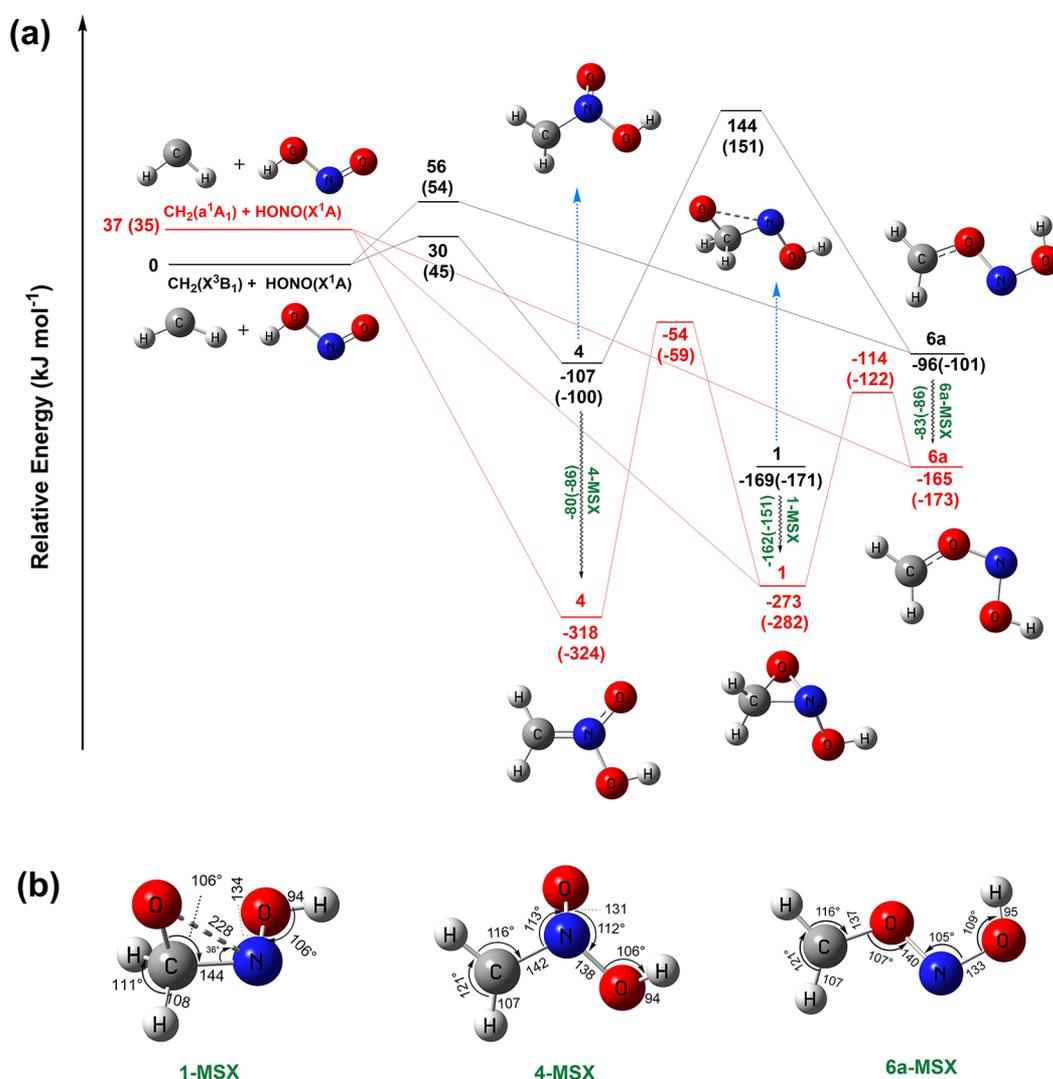


Figure 4. (a) Theoretically predicted reaction pathways of singlet (red) and triplet (black) carbene (CH₂) with nitrous acid (HONO). The CCSD/cc-pVTZ//CCSD(T)/CBS energies are given in kJ mol⁻¹ with respect to the separated reactants. The CCSD/cc-pVTZ//MRCI/CBS energies are provided in parentheses. The CPMCSCF/TZVPP//CCSD(T)/CBS minimum-energy crossing points (MSX) are shown for intersystem crossing (ISC) pathways as waved arrows. The CPMCSCF/TZVPP//MRCI/CBS energies are provided in parentheses. (b) Structures of 1-MSX, 4-MSX, and 6a-MSX. Geometrical parameters are provided in Figures S11–S13 and coordinates are tabulated in Table S10. Bond lengths and angles are given in picometers and degrees, respectively.

160 K. This is due to ion counts from species holding molecular formula N₂H₂O₂, whose weak signal has been detected at $m/z = 62$ in nonisotopic labeled experiments (Figure S7).

Having established the formation of molecule(s) with the molecular formula CH₃NO₂ (61 amu) together with its ¹³C- and D-substituted counterparts, we elucidate now the nature of the structure isomer formed. This objective is achieved by selectively photoionizing distinct isomers based on their different ionization energies (Figure 1). Previous calculations advocate that isomers 1–6 can be accessed via (multiple step) isomerization of nitromethane (2); although not accessible from 2, isomers 7–15 are presented here for completeness.¹⁸ Lowering the photon energy to 10.20 eV still ionizes isomers 1, 4–9, and 11–14, but not 2, 3, 10, and 15. At a photon energy of 10.20 eV, the TPD profile recorded at $m/z = 61$ reveals striking differences compared to the one at 10.49 eV: the first sublimation event peaking at 122 K disappeared (Figure 3d). This strongly indicates that ion counts detected from 100 to

145 K are linked to *cis/trans*-methyl nitrite (CH₃ONO; 3a/b), which cannot be ionized at 10.20 eV. Previous experiments in our laboratory exploiting PI-ReTOF-MS revealed that *cis/trans*-methyl nitrite (CH₃ONO; 3a/b) sublimed over the range of nearly 90–130 K;²⁵ this range agrees well with the present studies hence supporting that the ion counts in this range originate from *cis/trans*-methyl nitrite (CH₃ONO; 3a/b).

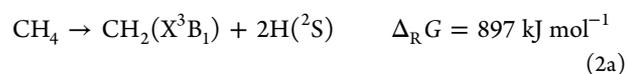
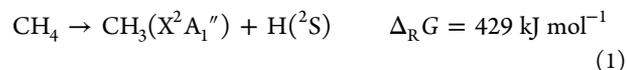
At 10.20 eV, the second sublimation event is still visible (Figure 3d). This trend also holds for the TPD of the ¹³CH₄-NO₂ system recorded at $m/z = 62$ (Figure 3e). To discriminate *N*-hydroxyoxaziridine (c-H₂CON(OH); 1) from the remaining isomers 4–9 and 11–14, two experiments were conducted at a photon energy of 9.70 eV (Figure 3g) and 9.80 eV (Figure 3f). At 9.80 eV, isomers 4–9, and 12–14, if formed, can still be ionized. A close inspection of the data reveals no ion counts at $m/z = 61$ and hence the disappearance of the second sublimation event peaking at 176 K (Figure 3f). Also, no ion counts are visible at 9.70 eV. Therefore, the

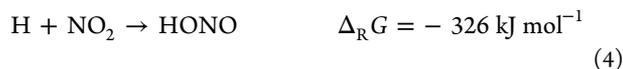
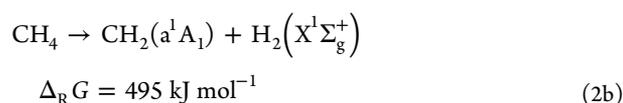
experiments at 9.80 and 9.70 eV reveal that the second sublimation event cannot be associated with 4–9 or 12–14. Thus, for the experiment at 10.20 eV only isomers 1 and 11 remain. Intriguingly, isomer 11 (carbonimidic acid; ((OH)₂CNH) is an enol form of carbamic acid (NH₂COOH; 10). Although formation of carbonimidic acid ((OH)₂CNH; 11) has not been observed previously in the ice matrix, evidence of synthesis of carbamic acid (NH₂COOH; 10) has been reported in the ice mixtures of NH₃/CO₂ and H₂O/CO₂/NH₃ via thermal processing.^{26,27} In these studies, the sublimation temperature of the carbamic acid system during the TPD phase is observed at ≥250 K.^{26,27} The enol form of carbamic acid (NH₂COOH; 10), i.e., carbonimidic acid (C(OH)₂NH; 11), is more polar; it should sublime at a higher temperature relative to the sublimation temperature of its keto form 10. This has been verified for the keto–enol systems acetaldehyde–vinyl alcohol and propanal–1-propenol.²⁸ Therefore, if isomers 10 and 11 had formed in our experiment, ion signals should have been observed at temperature ≥250 K, which is absent in the present study. Further, 9.80 eV is lower than the nominal adiabatic ionization energy of *trans*-*N*-hydroxyoxaziridine (c-H₂CON(OH); 1a) of 9.99 eV with errors of +0.06 and –0.05 eV, thus covering a range from adiabatic ionization energies of 10.05–9.94 eV; therefore, 1a can be ionized at 10.20 eV, but not at 9.80 eV. Within the error limits as discussed below, 9.80 eV might be higher than the adiabatic ionization energy of *cis*-*N*-hydroxyoxaziridine (c-H₂CON(OH); 1b). Therefore, an experiment below the ionization energy of 1b is required. The photon energy of 9.70 eV is lower than the nominal adiabatic ionization energy of *cis*-*N*-hydroxyoxaziridine (c-H₂CON(OH); 1b) of 9.79 eV with errors of +0.06 and –0.05 eV thus comprising the limits of adiabatic ionization energies from 9.85 to 9.74 eV; consequently, 1b can be ionized at 10.20 eV, but not at 9.70 eV. Therefore, the signal of the second sublimation event at 10.20 eV and the absence of any ion counts at 9.80 and 9.70 eV can be associated with subliming *N*-hydroxyoxaziridine (c-H₂CON(OH); 1). The aci-nitromethane (H₂CN(OH)O; 4) isomer has been detected at a photoionization energy of 9.80 eV in our previous study investigating the decomposition of nitromethane (CH₃NO₂).¹⁸ However, lack of signal at 9.80 and 9.70 eV in the present study suggests that aci-nitromethane cannot contribute to any signal at 10.20 eV. Consequently, on the basis of the photoionization studies combined with isotope substitution experiments within the methane–nitrogen dioxide system, *N*-hydroxyoxaziridine (c-H₂CON(OH); 1) is synthesized.

It is inspiring to propose underlying mechanism of the formation of *N*-hydroxyoxaziridine (c-H₂CON(OH); 1) (Figure 4). The electronic structure calculations at both CCSD/cc-pVTZ//CCSD(T)/CBS and CCSD/cc-pVTZ//MRCI/CBS levels of theory have been performed; the latter in particular are carried out to assess multireference effects. It appears these two energies are comparable in this system, an indication that the multiconfiguration nature of CCSD(T) has nearly included the multireference effects (Supporting Table S11). Experiments of neat methane ices exposed to ionizing radiation revealed three decomposition pathways of methane leading to methyl (CH₃) (reaction 1) and singlet/triplet carbene (CH₂) (reactions 2a and 2b).²⁹ The methyl radical and the hydrogen atom can react with nitrogen dioxide barrierlessly if both reagents have a favorable recombination geometry in the ices to nitromethane (CH₃NO₂; 2) (reaction

3) and nitrous acid (HONO) (reaction 4) in exoergic reactions, respectively. The reactivity of carbene (CH₂) with nitrous acid depends on the spin state of carbene. The electronic structure calculations revealed that the singlet carbene adds barrierlessly to the central nitrogen atom and to the terminal oxygen atom of nitrous acid (HONO) leading to aci-nitromethane (H₂CN(OH)O; 4), and intermediate 6a, respectively. This is evident through the intrinsic reaction coordinate (IRC) calculations at the CCSD/cc-pVTZ//CCSD(T)/CBS level (Supporting Figure S8a,b). However, addition of a singlet CH₂ (carbene) to the nitrogen–oxygen double bond of HONO (nitrous acid) leading to *N*-hydroxyoxaziridine (c-H₂CON(OH); 1), may involve a small barrier. Although this barrier does not optimize at the CCSD/cc-pVTZ level, its evidence is observed in IRC calculation, which shows an existence of a maximum at about 7 kJ mol^{–1} with respect to the reactants (Supporting Figure S8c). It is important to note here that the existence of a small barrier in the formation pathway of singlet *N*-hydroxyoxaziridine (c-H₂CON(OH); 1) does not affect the overall reaction mechanism since 1 can be formed in one step from the reactants or via intermediates 4 and/or 6a after isomerization. These molecules are stabilized by 273, 318, and 165 kJ mol^{–1} with respect to the separated reactants. Both 6a and 4 can undergo ring closure to *N*-hydroxyoxaziridine (c-H₂CON(OH); 1). On the triplet surface, triplet carbene has barriers to addition of 30 and 56 kJ mol^{–1} to the central nitrogen and to the terminal oxygen atom of nitrous acid (HONO) leading to triplet 4 and 6a, respectively.

If triplet carbene can be formed with sufficient excess kinetic energy in the decomposition of methane, these barriers might be surmountable, and triplet 4 and 6a can be accessed. These intermediates might undergo intersystem crossing to the singlet manifold via minimal energy crossing points (MSX) depicted in Figure 4. However, despite our attempts to locate the reaction path, it appears triplet reactants do not produce triplet 1 directly. The triplet 1 might be formed (1) in a multistep pathway via oxygen elimination from 4 forming a van-der-Waals complex followed by recombination of atomic oxygen to the methylene group (CH₂) and (2) again via 4 transforming to 5b then eventually to 1 (Supporting Figure S9). The N–O bond length across CH₂ in triplet 1 is very large (233 pm); thus, excluding it from being called a covalent bond and thus triplet 1 does not represent a true cyclic structure (Supporting Figures S9 and S12). Further, no transition states between triplet 1 and triplet 4 as well as triplet 1 and triplet 6a were identified. Overall, the computations suggest that the one-step reaction of singlet carbene with nitrous acid via addition to the nitrogen–oxygen double bond represents a likely pathway to form *N*-hydroxyoxaziridine (c-H₂CON(OH); 1). It is important to highlight that the addition of singlet carbene to a double bond mirrors the reactivity of carbene with ethylene (C₂H₄) leading to the formation of cyclopropane (C₃H₆) in electron irradiated methane–ethylene ices at 5 K.³⁰





Can *N*-hydroxyoxaziridine (*c*-H₂CON(OH); **1**) survive in the gas phase? Considering the average velocity of 247 ms⁻¹ of *N*-hydroxyoxaziridine (*c*-H₂CON(OH); **1**) subliming at 176 K and the distance between the ice and the photoionization laser of 2 mm, the lifetime of the subliming *N*-hydroxyoxaziridine (*c*-H₂CON(OH); **1**) must be at least 8 ± 1 μs to “fly” from the ice to the photoionization region. The kinetic stability of *N*-hydroxyoxaziridine (*c*-H₂CON(OH); **1**) is the direct effect of extensive barriers connected with its unimolecular decomposition ranging between 292 and 336 kJ mol⁻¹ (Supporting Figure S10 and Table S10).

In summary, exploiting single photon vacuum ultraviolet photoionization reflectron time-of-flight mass spectrometry (PI-ReTOF-MS), this study reveals the formation and detection of the *N*-hydroxyoxaziridine (*c*-H₂CON(OH); **1**) molecule, an optically active, high energy isomer of nitromethane (CH₃NO₂; **2**), exploiting tunable photoionization coupled with reflectron mass spectrometry.^{31–34} Nonequilibrium reaction pathways were proposed involving the reaction of carbene with nitrous acid leading to *N*-hydroxyoxaziridine (*c*-H₂CON(OH); **1**). A comparison of the molecular structures of the cyclic moiety of the *N*-hydroxyoxaziridine (*c*-H₂CON(OH); **1**) and cyclopropane (C₃H₆) reveals elongated nitrogen–oxygen (148 pm), carbon–nitrogen (143 pm), and carbon–oxygen (140 pm) bonds compared to the carbon–carbon bond (151 pm) in cyclopropane (Supporting Figure S12).³⁵ The computed bond angles ranging from 58° to 63° deviate from the classically expected 60° and can be compared to 104° found in cyclopropane as indicative of carbon–carbon bonds bent outward; this decreases the bond strain and essentially distorting the sp³ hybridization of the carbon atom resulting in a significant π bond character. It is important to highlight that in *N*-hydroxyoxaziridine (*c*-H₂CON(OH); **1**), the relative orientation of the C–N and O–H bonds result in a *trans* (**1a/1a'**) and *cis* (**1b/1b'**) conformers with respect to the nitrogen–oxygen single bond carrying the hydroxyl functional group with ring inversion barriers calculated to be 267 kJ mol⁻¹ (Supporting Figure S14). Hence, the replacement of two carbene moieties in cyclopropane by an oxygen atom and the N–OH functional group has a profound effect on the structure and chemical bonding of cyclopropane (C₃H₆) compared to the *N*-hydroxyoxaziridine (*c*-H₂CON(OH); **1**) previously searched for by physical (organic) chemists as a reactive intermediate and high energy isomer of methyl nitrite (CH₃NO₂) in energetic materials for the least six decades.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcllett.0c01277>.

Experimental and computational methods, schematic of the ultra-high vacuum chamber, IR spectra, interference

pattern, mass spectra, TPD profiles, calculated potential energy surfaces, IRC calculations, structures, geometrical parameters, IR frequencies, ionization energies, VUV generation scheme, structures coordinates, and relative energies (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Agnes H. H. Chang – Department of Chemistry, National Dong Hwa University, Shoufeng, Hualien 974, Taiwan; Email: hhchang@gms.ndhu.edu.tw

Ralf I. Kaiser – Department of Chemistry and W. M. Keck Research Laboratory in Astrochemistry, University of Hawaii, Honolulu, Hawaii 96822, United States; orcid.org/0000-0002-7233-7206; Email: ralfk@hawaii.edu

Authors

Santosh K. Singh – Department of Chemistry and W. M. Keck Research Laboratory in Astrochemistry, University of Hawaii, Honolulu, Hawaii 96822, United States

Tang-Yu Tsai – Department of Chemistry, National Dong Hwa University, Shoufeng, Hualien 974, Taiwan

Bing-Jian Sun – Department of Chemistry, National Dong Hwa University, Shoufeng, Hualien 974, Taiwan

Alexander M. Mebel – Department of Chemistry and Biochemistry, Florida International University, Miami, Florida 33199, United States; orcid.org/0000-0002-7233-3133

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acs.jpcllett.0c01277>

Notes

The authors declare no competing financial interest.

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