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The Elusive Formaldonitrone, $CH_2{=}N(H){-}O$. Preparation in the Gas Phase and Characterization by Variable-Time Neutralization−Reionization Mass Spectrometry, and Ab Initio and Density Functional Theory Calculations

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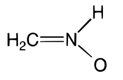
Abstract: Formaldonitrone, $CH_2{=}N(H){-}O$ (**1**), the hitherto elusive simplest organic nitrone, has been prepared transiently in the gas phase by femtosecond collisional neutralization of its cation radical, $CH_2{=}N(H){-}O^{+\bullet}$ ($\mathbf{1}^{+\bullet}$). Ion $\mathbf{1}^{+\bullet}$ was generated by dissociative ionization of 1,2-oxazolidine and characterized by collisionally activated dissociation mass spectra and augmented Gaussian 2(MP2) calculations. Nitrone **1** showed negligible dissociation upon collisional neutralization and was distinguished from its tautomers formaldoxime (**2**) and nitrosomethane (**3**). **1** was calculated to be more stable than its isomers $CH_2{-}O{-}NH$ (**5**) and oxaziridine (**6**). The enthalpy of formation of **1** was calculated from enthalpies of atomization and two isodesmic reactions as $\Delta H_{f,298}(\mathbf{1}) = 58 \pm 1$ kJ mol^{-1}. The adiabatic and vertical ionization energies of **1** were calculated as $IE_a = 9.40$ eV and $IE_v = 9.42$ eV, the vertical recombination energy of $\mathbf{1}^{+\bullet}$ was $RE_v = 9.35$ eV. Formation of **1** by collisional electron transfer was accompanied by negligible Franck−Condon effects. The potential energy surfaces for the formation, isomerizations, and dissociations of **1** and $\mathbf{1}^{+\bullet}$ were investigated by ab initio calculations.

Introduction

Nitrones,[1] $R_1R_2C{=}N(R_3){-}O$, are 1,3-dipolar compounds that undergo facile thermal cycloadditions with a variety of dipolarophiles.[2] In addition to the considerable synthetic utility of nitrone 1,3-dipolar cycloadditions,[3] the mechanisms of these reactions have been of historical[4,5] and recent interest.[6,7] Nitrones are intrinsically reactive compounds that readily oligomerize in the condensed phase unless stabilized by bulky substituents.[3b] *N*-Methylnitrone, $CH_2{=}N(CH_3){-}O$, has been generated transiently in solution by condensation of *N*-methylhydroxylamine with formaldehyde and trapped by alkene dipolarophiles.[8] However, the simplest member of the nitrone family, formaldonitrone (**1**), cannot be generated in the same manner because condensation of formaldehyde with hydroxylamine produces formaldoxime (**2**) instead.[9] Therefore, nitrone **1** has been elusive so far.[3b] Formaldonitrone tautomers **2** and nitrosomethane (**3**) are also reactive compounds in the condensed phase; **2** undergoes facile oligomerization,[10−12] whereas **3** forms a dimer[13] and isomerizes to **2**.[12]



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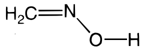

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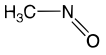

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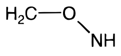

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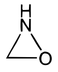

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Computational studies of nitrone **1** and its tautomers **2** and **3** indicated that these isomers were comparable in energy. Those studies concluded that structure **1** should be intrinsically stable in the absence of bimolecular reactions.[14−21] In addition, early ab initio calculations by Adeney et al.,[14] and recent density functional theory calculations indicated that **1** was separated from **2** and **3** by substantial potential energy barriers, 179−195 and 212−225 kJ mol^{-1}, respectively.[18,19] Other N−O bond containing isomers of **1** (e.g., oxaziridine and isonitrosomethane) were calculated to be substantially less stable than **1**.[18−21]

We report here the first preparation of nitrone **1** in the rarefied gas phase. We used collisional neutralization of the stable cation radical $\mathbf{1}^{+\bullet}$ to generate the elusive molecule **1** and characterized

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it by neutralization−reionization mass spectrometry (NRMS).[22] NRMS has been used previously to generate a variety of intrinsically stable but highly reactive molecules, as previously reviewed.[23] Gaussian 2(MP2) calculations[24] that were augmented in the geometry optimization procedure[25] were used to provide ion and neutral energies and isomerization barriers. We show that a combination of high-level theoretical calculations and experiment resulted in an accurate prediction of a kinetically controlled formation of ion **1**$^{+\bullet}$ from a stable precursor and allowed for characterization of neutral **1** formed by vertical electron transfer.

Experimental Section

Methods. Neutralization−reionization (NR) mass spectra were measured on a tandem acceleration−deceleration mass spectrometer as described previously.[26] Samples were introduced into the ion source from a glass liquid inlet maintained at or below room temperature. The hydrogen−deuterium (H/D) exchange to prepare 1,2-oxazolidine-2-*d* (**4**-*d*) was performed in the ion source that was conditioned with D_2O at 10^{-5} Torr for 30 min before and then during the measurements. 1,2-Oxazolidine-2-*d* thus prepared contained >95% d_1 by electron ionization (EI) mass spectrometry. Charge-exchange (CE) ionization with carbonylsulfide was performed in a tight chemical ionization source at COS/**4** ratios of >100. Precursor ions were extracted from the ion source, focused by a radio frequency (rf)-only quadrupole analyzer, and accelerated to 8250 eV kinetic energy. Collisional neutralization of fast ions was performed with dimethyl disulfide that was admitted to the first collision cell at a pressure to achieve 70% transmittance of the precursor ion beam. Neutral intermediates were reionized after 3.2 μs by collisions with oxygen at pressures that achieved 70% transmittance of the precursor ion beam. The ions were decelerated to 80 eV kinetic energy, energy-filtered, and mass analyzed by a second quadrupole analyzer operated at unit mass resolution. Typically, 20−40 scans were accumulated and averaged to give an NR mass spectrum, and the measurements were reproduced over a period of several weeks. Collisional activation of neutral intermediates (NCR) was performed by admitting helium into the neutral drift region at pressures allowing 70, 50, and 30% precursor ion transmittance. The drift region was floated at +250 V to reject any ions formed there. Variable-time measurements were carried out as described previously.[27] The neutral intermediate lifetimes were varied in steps at 0.20, 0.92, 1.53, and 2.14 μs.

Accurate ion masses, metastable-ion, and collisionally activated dissociation (CAD) spectra were measured on a JEOL HX-110 double-focusing mass spectrometer operated at 10 kV. For accurate mass measurements, the mass resolution was >10 000 (10% valley definition). The CAD spectra were obtained with air as collision gas at 70 and 50% transmittance of the precursor ion beam. The mass resolution was >500 and the products were detected by linked magnet-electrostatic sector (B/E) scan.

Materials. 1,2-Oxazolidine (**4**) was prepared from *N*-hydroxyurethane and 1,3-dibromopropane (both Aldrich) by a two-step procedure according to King,[28] and characterized by EI mass spectrometry.[29] The one-step procedure reported by Hine and Evangelista[30] did not yield 1,2-oxazolidine in our hands. Formaldoxime (**2**) was prepared according to Dunstan and Bossi.[9] Monomeric **2** was sampled into the mass spectrometer by gently heating the partially polymerized sample in a liquid inlet system.

Calculations. Standard ab initio calculations were performed by using the Gaussian 98 suite of programs.[31] Geometries were optimized with density functional theory calculations using Becke's hybrid B3LYP functional[32] and the 6-31+G(d,p) basis set. For selected species, geometries were also optimized with Møller−Plesset theory calculations[33] truncated at second order, MP2(FULL)/6-31+G(d,p), as discussed later. Spin unrestricted calculations (UB3LYP and UMP2) were performed for open-shell species. Spin contamination in UB3LYP calculations was small, as judged from the $\langle S^2 \rangle$ expectation values that ranged between 0.75 and 0.77. Spin contamination in UMP2 calculations was low to moderate for most species, $\langle S^2 \rangle = 0.77-0.97$. The contamination was partially corrected by Schlegel's annihilation procedure[34] that decreased the total energies by 2−17 millihartree (8 millihartree rmsd). The optimized structures were characterized by harmonic frequency analysis as local minima (all frequencies real) and first-order saddle points (single imaginary frequency). The B3LYP frequencies were corrected by 0.963,[35] and the MP2(FULL) frequencies were corrected by 0.931 and used to calculate zero-point vibrational corrections and 298 K enthalpies. Complete optimized geometries (Cartesian coordinates), uncorrected harmonic frequencies, and total energies for all species are available as Supporting Information. Optimized geometries of some $[C,H_3,N,O]$ neutral[17−21] and ion isomers[20] have been reported previously. Single-point energies were calculated at two levels of theory. The composite G2(MP2) procedure[24] was used to provide reference energies for all systems of interest. In addition, B3LYP energies were calculated with the 6-311+G(3df,2p) basis set

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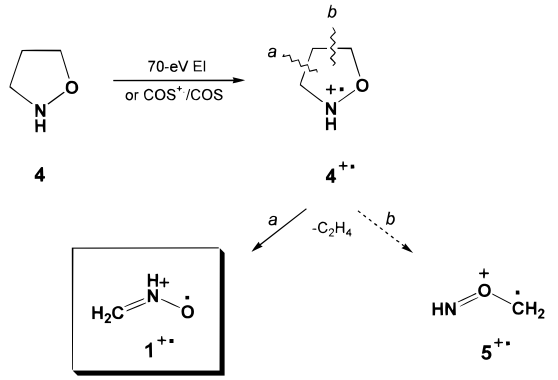
Scheme 1



and averaged with the PMP2/6-311+G(3df,2p) energies available from the G2(MP2) calculations.[36] Comparisons of B3LYP and PMP2 relative energies can be indicative of pathological behavior of the molecular or cation radical system under study.[36] The G2(MP2) energies were substantially less sensitive to spin contamination. The differences in UMP2- and PMP2-based G2(MP2) energies were within 0.4 millihartree (rmsd), with a maximum of 1.7 millihartree for the energy of $\mathbf{1}^{+\bullet}$ that was based on a B3LYP-optimized geometry.

Rice−Ramsperger−Kassel−Marcus (RRKM) calculations were performed with direct count of quantum states using Hase's program,[37] as reported previously.[38]

Results and Discussion

Ion Formation and Energies. NRMS relies on an unambiguous generation of a precursor ion that is then converted by a fast collision lasting a few femtoseconds to the neutral species of interest.[23c] Therefore, precursor ion characterization is an important step in the generation of elusive neutral species. We reasoned that ring cycloreversion in 1,2-oxazolidine cation radical ($\mathbf{4}^{+\bullet}$) can yield ion $\mathbf{1}^{+\bullet}$ or an isomer $\mathbf{5}^{+\bullet}$ (paths a and b, Scheme 1). Electron ionization of **4**[29] produced an abundant ion at *m*/*z* 45, which consisted mostly of $[C,H_3,N,O]^{+\bullet}$ (91.5%, measured 45.0214, calc. 45.0215) with minor admixtures of $C_2H_5O^+$ (8.2%, measured 45.0338, calc. 45.0340)[39] and $C_2H_7N^{+\bullet}$ (0.3%, measured 45.0579, calc. 45.0578). The $[C,H_3,N,O]^{+\bullet}$ ion from $\mathbf{4}^{+\bullet}$ was characterized by the CAD spectrum, which was significantly different from the CAD spectra of several known isomers,[20,41] notably, tautomeric ions $\mathbf{2}^{+\bullet}$ and $\mathbf{3}^{+\bullet}$ (Table 1).[42] The most distinguishing features of the CAD spectrum of $\mathbf{1}^{+\bullet}$ were the peak of NO^+ at *m*/*z* 30, which was much less abundant in the spectrum of $\mathbf{2}^{+\bullet}$, and the NHO^+ ion at *m*/*z* 31 (NDO^+, *m*/*z* 32, from **1-d**$^{+\bullet}$), which was absent in the CAD spectrum of $\mathbf{3}^{+\bullet}$. Even more unambiguous distinction was made through NR mass spectra, which are discussed later. Hence, the ion $\mathbf{1}^{+\bullet}$ formed by dissociation of $\mathbf{4}^{+\bullet}$ was different from $\mathbf{2}^{+\bullet}$ and $\mathbf{3}^{+\bullet}$. However, structures $\mathbf{1}^{+\bullet}$, $CH_2{-}O{-}NH^{+\bullet}$ ($\mathbf{5}^{+\bullet}$), and oxaziridine cation radical ($\mathbf{6}^{+\bullet}$) may be difficult to distinguish through ion dissociations.

Table 1. CAD Spectra of $\mathbf{1}^{+\bullet}$, $\mathbf{2}^{+\bullet}$, and $\mathbf{3}^{+\bullet}$

	rel intensity[a]			
m/*z*	$\mathbf{1}^{+\bullet b}$	**1-d**$^{+\bullet}$	$\mathbf{2}^{+\bullet}$	$\mathbf{3}^{+\bullet}$
44	13.7	9.7	16.2	22.4
43	4.7	6.4	6.6	10.6
42		3.9	1.6	7.2
32		5.2		
31	7.3		1.6	
30	(193)[c]	(82.5)[c]	15.5	(158)[c]
29	3.2	24.8	2.3	11.6
28	49.7	17.7	40.6	12.4
27	12.0	9.6	17.2	9.0
26		5.2	3.5	2.8
18	1.2		2.4	
17	1.2	4.0	2.3	
16	2.9	4.7	2.2	2.8
15	0.1			9.3
14	1.8	4.9	2.0	5.7
13	1.2		1.5	2.6
12	1.2		0.7	3.4

[a] Relative to the sum of CAD fragment ions excluding *m*/*z* 30. [b] The relative intensities in the CAD spectrum of $\mathbf{1}^{+\bullet}$ were corrected for contributions from $CH_3CH{=}OH^+$ that were scaled to minimize the H_3O^+ peak at *m*/*z* 19. [c] These peaks contained contributions from metastable ion dissociations.

To characterize the formation of $\mathbf{1}^{+\bullet}$ from $\mathbf{4}^{+\bullet}$ we studied by ab initio calculations the various paths for 1,2-oxazolidine ring openings and the product threshold energies (Figure 1). Dissociation of the C-3−C-4 bond in $\mathbf{4}^{+\bullet}$ required an activation barrier of 171 kJ mol^{-1} in the transition state (**TS1**) to form open-ring intermediate $\mathbf{7}^{+\bullet}$, which can equilibrate with its more stable anti−anti rotamer $\mathbf{8}^{+\bullet}$. The threshold energy for the formation of $\mathbf{1}^{+\bullet}$ and C_2H_4 was 269 kJ mol^{-1} above $\mathbf{4}^{+\bullet}$. When combined with the calculated adiabatic ionization energy of **4** ($IE_a = 7.76$ eV), the appearance energy (AE) of $\mathbf{1}^{+\bullet}$ from **4** was 10.55 eV. Competitive dissociation of the C-4−C-5 bond in high-energy $\mathbf{4}^{+\bullet}$ could proceed through transition states **TS2** and **TS3** that differed in the dihedral angles about the N−O and C-3−N bonds. The energies for **TS2** and **TS3** (223 and 247 kJ mol^{-1}, respectively) were substantially greater than that for **TS1**. Following ring rupture through **TS2** and **TS3**, the putative open-ring intermediates, $^\bullet CH_2CH_2NH{-}O{=}CH_2^+$, collapsed by closing a three-membered ring to form an ion−molecule complex of aziridine cation radical with formaldehyde, $\mathbf{9}^{+\bullet}$ (Figure 1). Dissociation of the latter formed an aziridine cation radical ($\mathbf{10}^{+\bullet}$) and formaldehyde that were 149 kJ mol^{-1} above $\mathbf{4}^{+\bullet}$.

The reaction flux through **TS1**−**TS3** was estimated by RRKM calculations. As expected from the different activation energies, ring opening through **TS1** was consistently faster than those proceeding through **TS2** and **TS3**. Importantly, at the threshold for the formation of $\mathbf{1}^{+\bullet}$ and C_2H_4 (269 kJ mol^{-1}), ring opening via **TS1** had a unimolecular rate constant, log $k_1 = 7.28$, that was >3 orders of magnitude larger than those for **TS2** (log $k_2 = 4.1$) and **TS3** (log $k_3 = 2.15$). Hence, dissociation through **TS1** was preferred kinetically.

The thresholds for elimination of C_2H_4 to produce $\mathbf{5}^{+\bullet}$ or the oxaziridine cation radical ($\mathbf{6}^{+\bullet}$) were 344 and 334 kJ mol^{-1} above $\mathbf{4}^{+\bullet}$, respectively, implying that the respective AE values for $\mathbf{5}^{+\bullet}$ and $\mathbf{6}^{+\bullet}$ from **4** were ≥11.32 and 11.22 eV, respectively. Ionization of **4** in the energy interval 10.55−11.22 eV should, therefore, produce $\mathbf{1}^{+\bullet}$ and not $\mathbf{5}^{+\bullet}$ or $\mathbf{6}^{+\bullet}$. The CE ionization of **4** with carbonyl sulfide ($COS^{+\bullet}/COS$) falls within this energy

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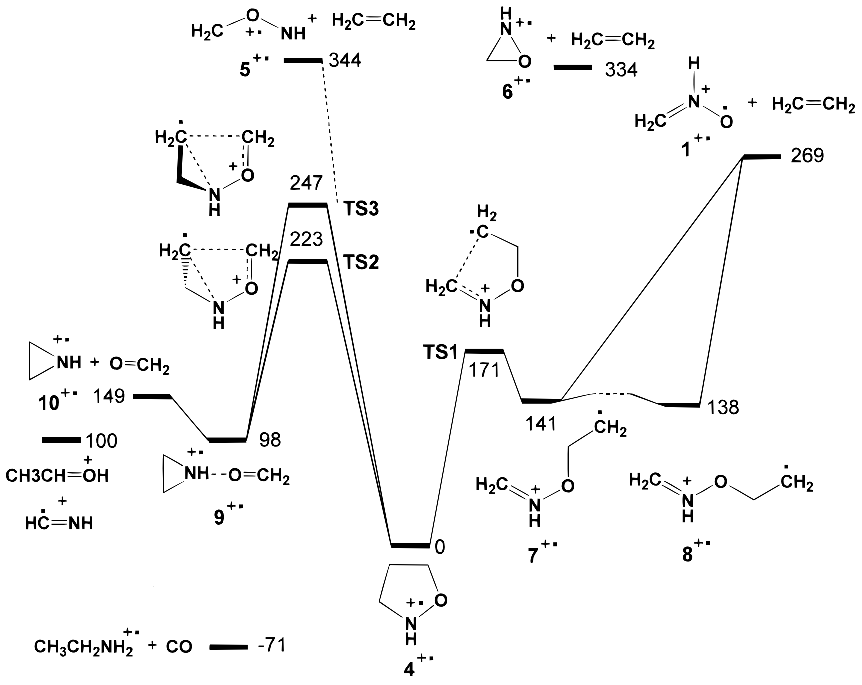

Figure 1. G2(MP2) potential energy diagram for dissociations of oxazolidine cation radical. All energies are in kJ mol^{-1} at 0 K.

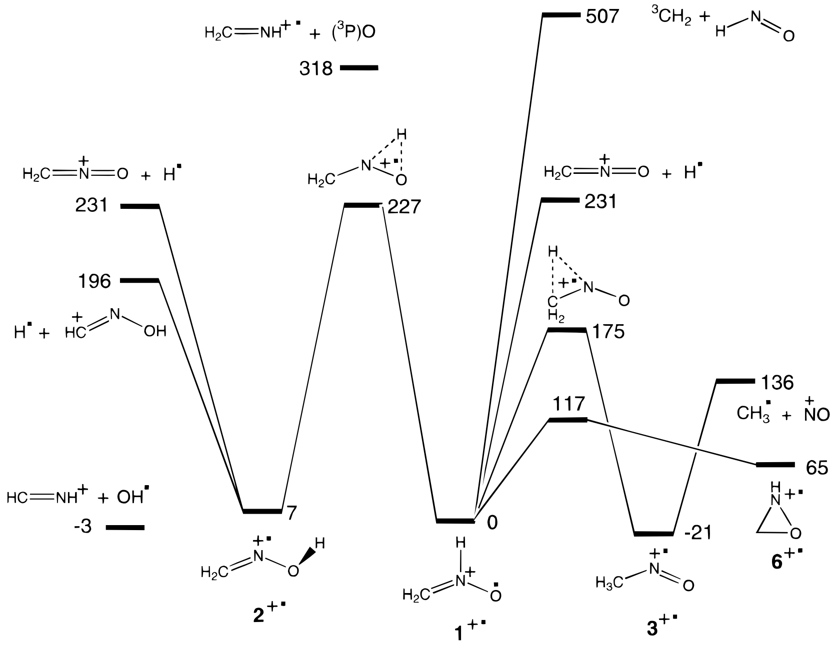

Figure 2. G2(MP2) potential energy diagram for $[C,H_3,NO]^{+\bullet}$ isomers. All energies are in kJ mol^{-1} at 0 K.

interval because $RE(COS^{+\bullet}) \approx IE(COS) = 11.17$ eV.[43] The CE ionization with $COS^{+\bullet}$ yielded a 4:1 mixture of $\mathbf{1}^{+\bullet}$ and $CH_3CH{=}OH^+$. After correcting for the presence of the latter,[44] the CAD and NR mass spectra of the CE-produced ion were very similar to those of the $[C,H_3,N,O]^{+\bullet}$ ion prepared by EI of **4**. Hence, the $[C,H_3,N,O]^{+\bullet}$ cation radical formed by cycloreversion of **4** was nitrone $\mathbf{1}^{+\bullet}$ and not an isomer.

It is worth noting that the formations from $\mathbf{4}^{+\bullet}$ of $CH_3CH{=}OH^+ + HC{=}NH^\bullet$ and $CH_3CH_2NH_2^{+\bullet} + CO$ were 100 kJ mol^{-1} endothermic and 71 kJ mol^{-1} exothermic, respectively, and represented the energetically most favorable ion dissociations (Figure 1). The fact that these dissociations competed poorly with the much more endothermic ring cleavage leading to $\mathbf{1}^{+\bullet}$ indicated kinetic preference for the latter dissociation.

The potential energy surface for unimolecular dissociations and isomerizations of $\mathbf{1}^{+\bullet}$ was also studied by G2(MP2) calculations (Figure 2). Ion $\mathbf{1}^{+\bullet}$ was found to reside in a deep potential energy well. The lowest-energy dissociation involved a rearrangement by hydrogen migration to form $\mathbf{3}^{+\bullet}$, which required 175 kJ mol^{-1} above $\mathbf{1}^{+\bullet}$. However, the transition state energy was 39 kJ mol^{-1} *above* the dissociation threshold to CH_3 and NO^+. Hence, isomerization of $\mathbf{1}^{+\bullet}$ to $\mathbf{3}^{+\bullet}$ must be

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(43) Wang, L.; Reutt, J. E.; Lee, Y. T.; Shirley, D. A. *J. Electron Spectrosc. Relat. Phenom.* **1988**, *47*, 167.

(44) Contamination with $CH_3CH{=}OH^+$ was much less apparent in the NR mass spectrum of $\mathbf{1}^{+\bullet}$ than on CAD. This result may be due to a lower cross section for electron transfer to $CH_3CH{=}OH^+$ than to $\mathbf{1}^{+\bullet}$. The reference NR mass spectrum of $CH_3CH{=}OH^+$ prepared from 2-propanol was as follows: *m/z* (rel abundance $\%\Sigma I_{NR}$) 45(13.2), 44(12.4), 43(13.0), 42(3.9), 41(0.8), 31(0.2), 30(3.8), 29(13.8), 28(6.8), 27(3.1), 26(5.8), 25(2.6), 24(0.9), 19(0.2), 18(0.5), 17(0.7), 16(1.2), 15(6.6), 14(4.7), 13(2.7), 12(2.1).

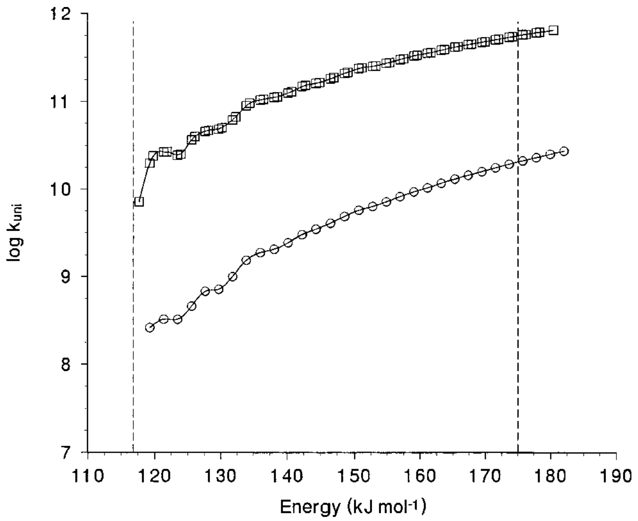

Figure 3. RRKM rate constants (log k_{uni}) for unimolecular isomerization of $\mathbf{1}^{+\bullet} \rightarrow \mathbf{6}^{+\bullet}$ (log k_1, circles) and $\mathbf{6}^{+\bullet} \rightarrow \mathbf{1}^{+\bullet}$ (log k_{-1}, squares). The energy scale is relative to $\mathbf{1}^{+\bullet}$. The left dashed vertical line is at the G2(MP2) transition state energy for $\mathbf{1}^{+\bullet} \rightarrow \mathbf{6}^{+\bullet}$ (117.3 kJ mol^{-1}). The right dashed vertical line is at the G2(MP2) threshold energy for $\mathbf{1}^{+\bullet} \rightarrow \mathbf{3}^{+\bullet} \rightarrow CH_3^{\bullet} + NO^+$ (174.9 kJ mol^{-1}).

followed by fast dissociation of the latter, so that *nondissociating* $\mathbf{1}^{+\bullet}$ and $\mathbf{3}^{+\bullet}$ could not equilibrate. Likewise, the potential energy barrier for isomerization to $\mathbf{2}^{+\bullet}$ (227 kJ mol^{-1}) was 31 kJ mol^{-1} above the threshold for loss of a hydrogen atom from $\mathbf{2}^{+\bullet}$ to form $HC{=}N{-}OH^+$ (Figure 2). This result implied that *nondissociating* $\mathbf{1}^{+\bullet}$ and $\mathbf{2}^{+\bullet}$ could not equilibrate either. Note that rate constants for simple-bond cleavage dissociations typically have steeper dependence on internal energy than do rate constants for rearrangements, so that ions $\mathbf{2}^{+\bullet}$ and $\mathbf{3}^{+\bullet}$ possessing internal energies 31−39 kJ mol^{-1} or higher above dissociation thresholds will dissociate rapidly without rearranging back to $\mathbf{1}^{+\bullet}$.

Isomerization by ring closure of $\mathbf{1}^{+\bullet}$ to form $\mathbf{6}^{+\bullet}$ was also studied computationally. The transition state for the ring opening was located at 117 kJ mol^{-1} above $\mathbf{1}^{+\bullet}$ and 52 kJ mol^{-1} above $\mathbf{6}^{+\bullet}$ (Figure 2). This result means that $\mathbf{1}^{+\bullet}$ and $\mathbf{6}^{+\bullet}$ can equilibrate at energies below that of the lowest barrier to rate-determining isomerization to $\mathbf{3}^{+\bullet}$ (175 kJ mol^{-1}, vide supra). The rate constants for the reaction $\mathbf{1}^{+\bullet} \rightarrow \mathbf{6}^{+\bullet}$ (k_1) and its reverse (k_{-1}) were calculated by RRKM (Figure 3) and used to determine the equilibrium populations of $\mathbf{1}^{+\bullet}$ and $\mathbf{6}^{+\bullet}$, $K_{eq} = k_{-1}/k_1 = [\mathbf{1}^{+\bullet}]/[\mathbf{6}^{+\bullet}]$, in the critical energy region between 117 and 175 kJ mol^{-1}. The calculations showed $[\mathbf{1}^{+\bullet}]/[\mathbf{6}^{+\bullet}]$ ratios to be in the range 80−27 for the energy range just mentioned. This result clearly indicated that *nondissociating* $\mathbf{1}^{+\bullet}$ should be >96% pure even if a fraction equilibrated with the less stable oxaziridine ion $\mathbf{6}^{+\bullet}$. The fact that $\mathbf{1}^{+\bullet}$ prepared with <60 kJ mol^{-1} internal energy[45] by dissociative charge−exchange ionization of **4** afforded an NR mass spectrum that was closely similar to that of presumably more energetic ion from 70-eV ionization of **4** was perfectly consistent with the calculated equilibrium. Even for equilibrating but nondissociating $\mathbf{1}^{+\bullet}$, the fraction of $\mathbf{6}^{+\bullet}$ would not exceed 4%, which may not be observable in the NR spectra. Conversely, preparation of nonequilibrating ion $\mathbf{6}^{+\bullet}$ would represent a challenge because of the lack of a stable precursor and the narrow energy limits for the existence of pure $\mathbf{6}^{+\bullet}$ (52 kJ mol^{-1}, vide supra).

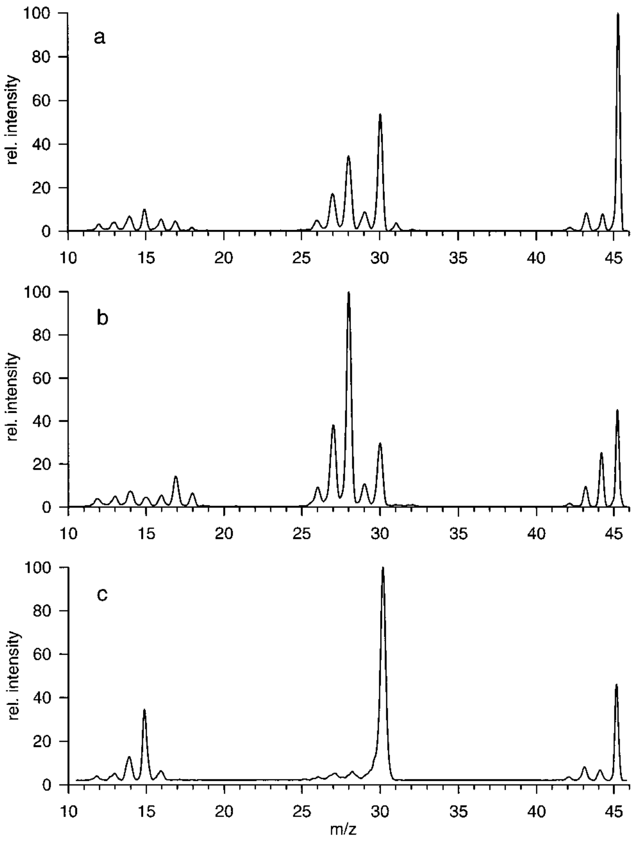

Figure 4. Neutralization (CH_3SSCH_3, 70% transmittance)−reionization (O_2, 70% transmittance) mass spectra of (a) $\mathbf{1}^{+\bullet}$, (b) $\mathbf{2}^{+\bullet}$, and (c) $\mathbf{3}^{+\bullet}$.

The potential energy surface for $\mathbf{1}^{+\bullet}$ further pointed to the most favorable dissociations being $\mathbf{1}^{+\bullet} \rightarrow \mathbf{3}^{+\bullet} \rightarrow NO^+ + CH_3^{\bullet}$, $\mathbf{1}^{+\bullet} \rightarrow HC{\equiv}NH^+ + OH^{\bullet}$, $\mathbf{1}^{+\bullet} \rightarrow CH_2{=}N{=}O^+ + H^{\bullet}$, and $\mathbf{1}^{+\bullet} \rightarrow \mathbf{2}^{+\bullet} \rightarrow HC{=}NOH^+ + H^{\bullet}$, the ion products of which were observed experimentally (Table 1).

Summarizing the ion chemistry part, $\mathbf{1}^{+\bullet}$ was formed selectively by dissociation of 1,2-oxazolidine cation radical $\mathbf{4}^{+\bullet}$; the ring cleavage was controlled kinetically. Nondissociating $\mathbf{1}^{+\bullet}$ did not isomerize to its tautomers $\mathbf{2}^{+\bullet}$ or $\mathbf{3}^{+\bullet}$.

Neutral Formaldonitrone. Nitrone **1** was formed by collisional neutralization of $\mathbf{1}^{+\bullet}$ and characterized by NR mass spectra (Figures 4a and 5a−c). Neutral **1** was remarkably stable under NR conditions and, following collisional reionization, it furnished an abundant survivor ion that amounted to 35% of the sum of NR ion intensities (ΣI_{NR}, Figure 4a).[44] The NR of ions $\mathbf{1}^{+\bullet}$ prepared by EI and CE dissociative ionization of **4** gave very similar spectra that showed little dissociation (Figures 4a and 5a). Nitrone **1** was clearly distinguished from its tautomers **2** and **3** that gave distinctly different NR mass spectra (Figure 4b,c).[20,41] In particular, **2** showed a less abundant survivor ion and more abundant $HC{=}NOH^+$ (*m*/*z* 44) and $HC{\equiv}NH^+$ (*m*/*z* 28) fragments than did **1**. NR of $\mathbf{3}^{+\bullet}$ resulted in a $[NO^+]/[\mathbf{3}^{+\bullet}]$ abundance ratio (3.3) that was substantially different from that for $[NO^+]/[\mathbf{1}^{+\bullet}]$ (0.56). The NR spectrum of $\mathbf{1\text{-}d}^{+\bullet}$ prepared by dissociative ionization of oxazolidine-*N*-*d* is shown in Figure 5b. Deuterium labeling resulted in mass shifts that were analogous to those observed for ion dissociations of $\mathbf{1\text{-}d}^{+\bullet}$ (Table 1), namely, NHO (*m*/*z* 31) → NDO (*m*/*z* 32) and $CH_3 \rightarrow CH_2D$.

Collisional activation with He of **1** resulted in a decrease of reionized $\mathbf{1}^{+\bullet}$ relative intensity (Figure 5c). For example, at 30% precursor ion transmittance due to 70% dissociation and/or scattering of the precursor beam, the relative abundance of

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[45] This follows from the difference of $RE(COS^{+\bullet}) - AE(\mathbf{1}^{+\bullet}) = 0.62$ eV. A part of the excess energy is carried away by the neutral fragment, and ion $\mathbf{1}^{+\bullet}$ is likely to be further cooled by several tens of collisions with COS in the ion source. The fully thermalized $\mathbf{1}^{+\bullet}$ would have 14.3 kJ mol^{-1} internal energy at 523 K.

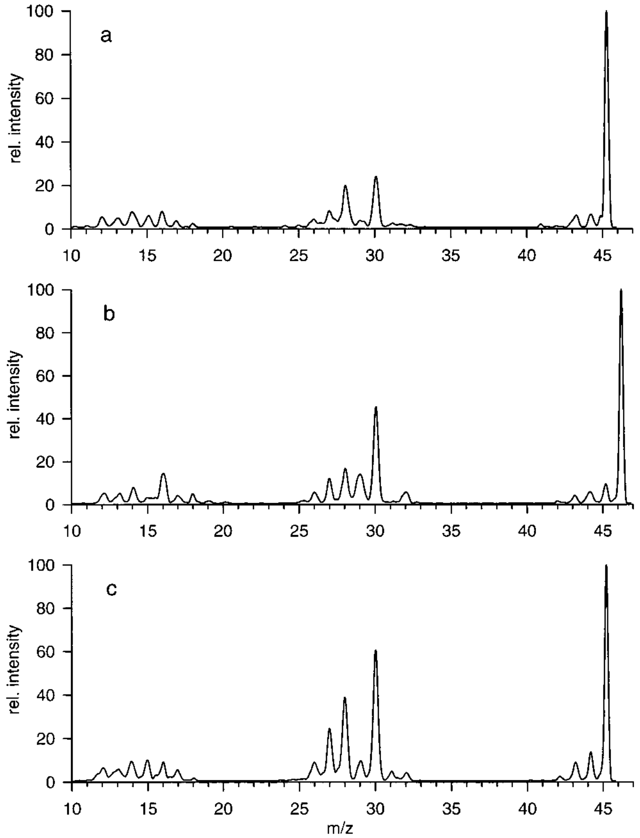

Figure 5. Neutralization (CH_3SSCH_3, 70% transmittance)–reionization (O_2, 70% transmittance) mass spectra of (a) $\mathbf{1}^{+\bullet}$ from charge-exchange ionization of **4**. (b) **1-d**$^{+\bullet}$ by 70-eV EI of **4-d**. (c) Neutralization–collisional activation (He, 50% transmittance)–reionization spectrum of $\mathbf{1}^{+\bullet}$.

Table 2. Rate Parameters for Dissociations of Neutral **1** and Reionized $\mathbf{1}^{+\bullet}$

product	$10^5 k_N$ (s^{-1})[a]	k_i	product	$10^5 k_N$ (s^{-1})[a]	k_i
NO	0.2	5.1	O	0.2	1.4
CH_3	0.1	1.1	HNO	0.0	0.5
CH_2N	0.3	3.1	CH_2	0.0	4.3
OH	0.0	0.9	CH_2NO[b]	0.0	1.3
CH_2NH	0.1	1.4			

[a] ±20%. [b] The complementary H^+ could not be measured because of the quadrupole analyzer low-mass cutoff.

Table 3. Relative and Dissociation Energies of **1** and Isomers

	rel energy[a]			
species/reaction	G2(MP2)	B3LYP	PMP2	av[b]
1	0	0	0	0
syn-**2**	−24	−19	−20	−20
anti-**2**	−45	−38	−40	−39
3	4	15	11	13
5	159	168	178	173
6	36	53	35	44
TS(**1** → *anti*-**2**)	176	179	179	179
TS(**1** → **3**)	212	212	218	215
1 → $CH_2{=}N{-}O^\bullet + H^\bullet$	313 301[c]	289	306	297
1 → $^\bullet HC{=}NH{-}O + H^\bullet$	504 492[c]	483	485	484
1 → $^3CH_2 + HN{=}O$	481	461	449	455
1 → $CH_2{=}NH + (^3P)O$	279 267[c]	278	290	284
1 → $CH_2{=}NH + (^1D)O$	469[d] 457[c,d]	468[d]	480[d]	474[d]

[a] At 298 K in units of kJ mol^{-1}. [b] Averaged B3LYP/6-311+G(3df,2p) and PMP2/6-311+G(3df,2p) relative energies. [c] 298 K dissociation energies without empirical "high level" corrections.[24] [d] Adjusted for the experimental difference in $(^1D)O$ and $(^3P)O$ energies (189.79 kJ mol^{-1} [55]).

reionized $\mathbf{1}^{+\bullet}$ was 18% ΣI_{NR}, which is a <50% decrease. This result showed that **1** was a very stable molecule that did not dissociate readily upon collisional activation.

The unimolecular dissociations of neutral **1** and reionized $\mathbf{1}^{+\bullet}$ were distinguished by variable time measurements that provided the respective rate parameters, k_N and k_i (Table 2). The data clearly showed that dissociations of neutral **1** were negligible, and most of the NR products were formed *after collisional ionization*. The stability of gaseous **1** was in sharp contrast with the high reactivity of aliphatic nitrones in solution.[8]

In view of the remarkable stability of isolated **1** in the gas phase, it was of interest to establish its enthalpy of formation $\Delta H_{f,298}(\mathbf{1})$. The latter was calculated with G2(MP2) from the enthalpy of atomization (eq 1) and enthalpies of two isodesmic reactions (eqs 2 and 3).[46,47]

$$\mathbf{1} \rightarrow (^3P)C + (^4S)N + (^3P)O + 3(^2S)H \qquad (1)$$

$$\Delta H_{r,0} = 2007.7 \text{ kJ mol}^{-1};\ \Delta H_{r,298} = 2034.5 \text{ kJ mol}^{-1};\ \Delta H_{f,298}(\mathbf{1}) = 58.1 \text{ kJ mol}^{-1}$$

$$\mathbf{1} + CH_3NO \rightarrow CH_2{=}NH + CH_3NO_2 \qquad (2)$$

$$\Delta H_{r,298} = -122.4 \text{ kJ mol}^{-1};\ \Delta H_{f,298}(\mathbf{1}) = 57.6 \text{ kJ mol}^{-1}$$

$$\mathbf{1} + NO \rightarrow CH_2{=}NH + NO_2 \qquad (3)$$

$$\Delta H_{r,298} = -27.3 \text{ kJ mol}^{-1};\ \Delta H_{f,298}(\mathbf{1}) = 58.1 \text{ kJ mol}^{-1}$$

The enthalpies of formation calculated from eqs 1–3 agreed very well and provided an estimate for **1** as $\Delta H_{f,298}(\mathbf{1}) = 58 \pm 0.3$ kJ mol^{-1}.[46,50] The G2(MP2) 298 K enthalpy of atomization of **1** was 2036.2 kJ mol^{-1} when based on the MP2(FULL)/6-31+G(d,p) optimized geometry of **1**, which is considered a very reasonable agreement with the value in eq 1. Interestingly, eqs 2 and 3 indicated that **1** would exothermically oxidize the nitroso group. This prediction is in line with the known oxidizing properties of stable nitrones that served as oxygen donors in oxidations of several substrates.[3b,51]

Unimolecular dissociations of **1** were predicted to be substantially endothermic (Table 3). Cleavage of the N–H bond was the lowest-energy spin-allowed dissociation that nevertheless required 313 kJ mol^{-1}. Cleavages of the C–N, C–H, and N–O bonds were all >450 kJ mol^{-1} endothermic. Isomerization to *anti*-**2** was the lowest-energy unimolecular reaction of **1** that required 176 kJ mol^{-1} in the transition state. Isomerization to form **3** had a higher activation energy, $E_{TS} = 212$ kJ mol^{-1}.

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(46) A previous, slightly higher estimate that was based on relative G2-(MP2) energies of **1** and formamide was $\Delta H_{f,298}(\mathbf{1}) = 67$ kJ mol^{-1}.[20]

(47) Thermochemical data for $(^3P)C$, $(^2S)H$, $(^4S)N$, $(^3P)O$, NO, NO_2, and CH_3NO_2 were taken from ref 48. The other enthalpies of formation were $\Delta H_{f,298}(CH_2{=}NH) = 88$ kJ mol^{-1})[49] and $\Delta H_{f,298}(CH_3NO) = 72$ kJ mol^{-1}.[20]

(48) *NIST Chemistry Webbook, NIST Standard Reference Database*, No. 69; Mallard, W. G., Lindstrom, P. J., Eds.; NIST: Gaithersburg, MD, 1998; http://webbook.nist.gov/chemistry.

(49) (a) Holmes, J. L.; Lossing, F. P.; Mayer, P. M. *Chem. Phys. Lett.* **1992**, *198*, 211. (b) Hammerum, S. *J. Am. Chem. Soc.* **1999**, *121*, 6002.

(50) The error limits do not include the uncertainties in the experimental enthalpies of formation that were used to evaluate eqs 1–3.

(51) (a) Rastetter, W. H.; Gadek, T. R.; Tane, J. P.; Frost, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 2228. (b) Eghtessad, E.; Zinner, G. *Arch. Pharm.* **1979**, *312*, 1027. (c) Schaumann, E.; Behrens, U. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 722.

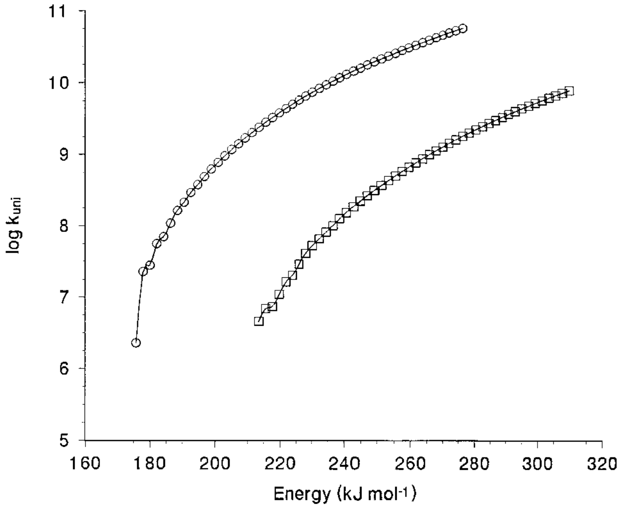

Figure 6. RRKM rate constants (log k_{uni}) for unimolecular isomerizations of **1** → **3** (circles) and **1** → *anti*-**2** (squares). The energy scale is relative to **1**.

These values were in a reasonable agreement with those from recent B3LYP calculations of Vladimiroff[18] who obtained 195 and 225 kJ mol^{-1} for **1** → *anti*-**2** and **1** → **3**, respectively, and in excellent agreement with the results of Alcami et al.[19] who obtained 179 and 212 kJ mol^{-1} for **1** → *anti*-**2** and **1** → **3**, respectively.

The activation barriers for isomerizations of **1** indicated that the route to *anti*-**2** should be preferred. This indication was substantiated by RRKM calculations that showed rate constants for **1** → *anti*-**2** that were 1−2 orders of magnitude greater than those for **1** → **3** (Figure 6).

Could **1** formed by femtosecond electron transfer isomerize to *anti*-**2**? The isomerization barrier was 137 kJ mol^{-1} below the threshold for the lowest-energy spin-allowed dissociation to $CH_2{=}N{-}O^\bullet$ and $H^\bullet$ (Table 3), and the calculated rate constants showed that the isomerization should be fast ($k > 10^7\ s^{-1}$) in **1** having internal energies >180 kJ mol^{-1} (Figure 6). Experimental evidence from NR mass spectra indicated that very little if any **2** was formed, as shown by the relative abundance of dissociation products that were characteristic of **2** (Figure 4b). However, because neutral **1** did not undergo appreciable dissociation and the post-reionization dissociations of $\mathbf{1}^{+\bullet}$ involved rate-determining isomerizations to $\mathbf{3}^{+\bullet}$ and $\mathbf{2}^{+\bullet}$, the spectra alone were insufficient to quantify the extent of neutral isomerization.

We argue on the basis of energy data that isomerizations of **1** were negligible. Vertical electron capture in $\mathbf{1}^{+\bullet}$ was accompanied by unusually small Franck−Condon effects, as documented by very similar adiabatic ionization (IE_a) and vertical recombination energies (RE_v); that is, $IE_a(\mathbf{1}) = 9.40$ eV and $RE_v(\mathbf{1}^{+\bullet}) = 9.35$ eV.[20] Ion $\mathbf{1}^{+\bullet}$ was generated by CE ionization of **4** with <60 kJ mol^{-1} internal energy (vide supra) which, when combined with the Franck−Condon energy upon neutralization, formed neutral **1** with <60 kJ mol^{-1} internal energy. Hence, **1** formed in the ground electronic state should be stable. Formation upon collisional electron transfer of excited electronic states has been documented recently for several systems.[38,52] With **1**, the ultraviolet (UV) absorption spectra of stable nitrones ($\lambda_{\max} \cong 230{-}240$ nm)[53] indicate an excitation energy >5 eV. If converted nonradiatively, this energy should be sufficient to promote fast dissociation of isolated **1**, contrary to experimental observations.

Does **1** isomerize to the less stable oxaziridine isomer **6**? Investigations with MP2(FULL) and B3LYP calculations of the reaction coordinate for the ring-opening in **6** showed a ridge at a bond distance d(C−O) = 2.0 Å, but a first-order saddle point was not found. This result indicated that single-reference calculations, both density functional theory (DFT) and perturbational, were inadequate in treating the bond dissociation in the vicinity of the transition state. The B3LYP energy at the ridge (200 kJ mol^{-1} above **1**) indicated that **1** and **6** were separated by a substantial barrier to ring closure or opening, respectively. By comparison, previous semiempirical calculations reported barriers of 150−250 kJ mol^{-1} for the **1** → **6** isomerization in the ground electronic state,[54] and the very recent B3LYP calculations also reported a substantial barrier (231 kJ mol^{-1}).[19] Therefore, ring closure in low-energy **1** formed by collisional electron transfer appeared unlikely.

Conclusions

The simplest nitrone **1** was generated transiently in the gas phase by collisional neutralization of stable cation radical $\mathbf{1}^{+\bullet}$. Nitrone **1** was remarkably stable in an isolated state in sharp contrast to the high reactivity of aliphatic nitrones in solution. Combined experimental and computational data strongly indicated that **1** formed by collisional electron transfer did not isomerize unimolecularly to other [C,H_3,N,O] molecules.

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Supporting Information Available: Tables of B3LYP/6-31+G(d,p) and MP2(FULL)/6-31+G(d,p) optimized geometries, uncorrected harmonic frequencies, and G2(MP2) total energies (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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