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The Gas-Phase Reaction of Nitronium Ion with Ethylene. An Experimental and Theoretical Study

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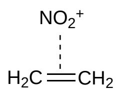
Abstract: The addition of NO_2^+ to ethylene, the prototypal electrophilic nitration of a π system and the focus of considerable theoretical interest as a model of aromatic nitration, has been studied in the gas phase by FT-ICR, MIKE, and CAD mass spectrometry, complemented by ab initio calculations at the MP2/6-31+G* level of theory. The results provide a clearcut answer to the principal mechanistic question addressed, showing that the reaction yields a O-nitroso product, probably CH_3CHONO^+, rather than a C-nitrated product.

Introduction

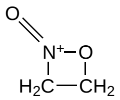
The addition of nitronium ion to ethylene

$$NO_2^+ + C_2H_4 \rightarrow [C_2H_4NO_2]^+ \tag{1}$$

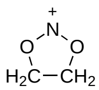
has elicited a considerable theoretical interest, being the most simple example of electrophilic nitration of a π system, and a useful starting point to model electrophilic aromatic nitration. In the past two decades reaction 1 has been investigated with a variety of *ab initio* and semiempirical methods. Following an early study at the HF/STO-3G level of theory,[1] the system has been examined at the HF/3-21G and HF/6-31G*//HF/3-21G levels.[2] More recently, a study has been performed at the HF/6-31G**//HF/4-31G level, complemented by single-point MP2/4-31G//HF/4-31G calculations, as well as by semiempirical MNDO and MINDO/3 calculations.[3] Finally, a comprehensive *ab initio* study using SCF, SCF/MP2, QCISD, and MCSCF techniques has been reported, aimed at investigating the conceivable paths of reaction 1, its products, and their relative stability.[4] The connectivity of the species identified as critical points at the MP2/6-31+G* level of theory is reported below together with that of nitrosated acetaldehyde **XIV**, a possible reaction product not considered in the theoretical analyses. For convenience, the numeration adopted is the same utilized in ref 4, denoting the true minima and the transition states with bold and italic numerals, respectively.



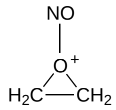
IV, **VI**



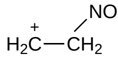
I



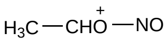
VIII



V, *XIII*



III, *X*, *XI*



$H_3C-CH\overset{+}{O}-NO$

XIV

It should be mentioned that, owing to the specific features of the NO_2^+/C_2H_4 system, characterized by a relatively flat energy hypersurface in many relevant regions, the theoretical analysis of the reaction paths provides no clearcut answer to the fundamental question concerning the nature of the covalently bound product(s) of (1), namely nitro forms containing a $C-NO_2$ group, or *O*-nitrito forms containing a C−O−NO group.

To the best of our knowledge, no experimental study of reaction 1 has been reported, which contrasts with the attention devoted to the related reaction of NO_2^+ with benzene.[5−8] This state of affairs is even more surprising if one considers that the available mass spectrometric techniques, although unable to measure bond angles and distances in gaseous ions, as required for a full structural characterization, nevertheless allow satisfactory definition of the connectivity of moderately complex ions, such as the product(s) formed from reaction 1. This, in principle, could provide an experimental answer to the mechanistically relevant question concerning the nature of the charged adduct(s) formed from the reaction of NO_2^+ with ethylene. In this work we have addressed the problem with a combination of structurally diagnostic techniques including FT-ICR, MIKE, and CAD mass spectrometry.

Results

FT-ICR Mass Spectrometry. Reaction 1 was performed in the external CI ion source of the spectrometer, operated at pressures up to 10^{-4} Torr, utilizing NO_2^+ ions obtained by charge exchange from the ionization of mixtures containing NO_2/N_2 in the 1:1 molar ratio. For comparison purposes,

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Table 1. Collision-Induced Dissociation and the Reaction with $(C_2H_5)_2CO$ of $[C_2H_4NO_2]^+$ Ions from Various Sources

	resonance cell				
external source gas mixture	primary ion isolated	pulsed valve gas	ion reisolated	fragments (% intensity)	product(s) from[a] reaction 6
$N_2/C_2H_4/NO_2$	$[C_2H_4NO_2]^+$	Ar	$[C_2H_4NO_2]^+$	$NO^+(100)$, $C_2H_3O^+(10)$	$NuNO^+$
$CH_4/CH_3ONO_2/C_2H_4$	$[C_2H_4NO_2]^+$	Ar	$[C_2H_4NO_2]^+$	$NO^+(100)$, $C_2H_3O^+(3)$	$NuNO^+$
$\overline{O{-}CH_2{-}C}H_2/NO$	$[C_2H_4NO_2]^+$	Ar	$[C_2H_4NO_2]^+$	$NO^+(100)$	$NuNO^+$
CH_3CHO/NO	$[C_2H_4NO_2]^+$	Ar	$[C_2H_4NO_2]^+$	not examined	$NuNO^+$
CH_4/CH_3ONO_2	$[CH_3OHNO_2]^+$	C_2H_4	$[C_2H_4NO_2]^+$		$Nu{\cdot}C_2H_3O^+(100)$
CH_4/CH_3ONO_2	$[CH_3O(NO_2)_2]^+$	C_2H_4	$[C_2H_4NO_2]^+$	$NO^+(100)$, $C_2H_3O^+(5)$	$Nu{\cdot}C_2H_3O^+(100)$, $NuNO^+(6)$

[a] In the reactivity experiment the $[C_2H_4NO_2]^+$ ions have not been thermalized with Ar.

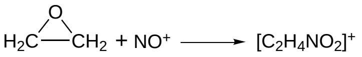
nitration of ethylene was carried out also according to the reaction

$$CH_3OXNO_2^+ + C_2H_4 \rightarrow CH_3OX + [C_2H_4NO_2]^+ \quad (2)$$
$$(X = H, NO_2)$$

performed by ionizing a $CH_4/C_2H_4/CH_3ONO_2$ mixture in the external CI ion source, utilizing as the nitrating agents the cations obtained from the sequence:

$$\underset{(n = 1, 2)}{C_nH_5^+} \xrightarrow[-C_nH_4]{+CH_3ONO_2} CH_3OHNO_2^+ \xrightarrow[-CH_3OH]{+CH_3ONO_2} CH_3O(NO_2)_2^+ \quad (3)$$

Finally, model ions were obtained upon addition of nitrosonium ion formed upon ionization of diluted NO/N_2 mixtures to oxirane or to acetaldehyde in the external ion source, according to the reactions



$$H_2C(O)CH_2 + NO^+ \longrightarrow [C_2H_4NO_2]^+ \quad (4)$$

$$CH_3CHO + NO^+ \longrightarrow [C_2H_4NO_2]^+ \quad (5)$$

Irrespective of the formation process, the $[C_2H_4NO_2]^+$ ions obtained from reactions 1, 2, 4, and 5 were driven into the resonance cell where their identity was established by exact mass measurements. Following isolation by selective-ejection techniques, the $[C_2H_4NO_2]^+$ ionic populations were subjected to structural assay by different techniques. The first approach was based on the determination of the fragmentation pattern of $[C_2H_4NO_2]^+$ ions following collision with Ar, contained in the cell at a low stationary pressure. The results, summarized in Table 1, show that only two charged fragments are produced, namely NO^+ and $C_2H_3O^+$, whose elemental composition was established by exact mass measurements. The results show that, irrespective of their source, the $[C_2H_4NO_2]^+$ ions give the same fragments. In addition, they display similar fragmentation patterns, characterized by a predominant NO^+ peak, with but a minor (<10%) $C_2H_3O^+$ peak. Most significantly, one does not observe the loss of NO_2^+, or of neutral NO_2, which would be expected from non-covalent $C_2H_4{\cdot}NO_2^+$ complexes or from covalently bound $[C_2H_4NO_2]^+$ species containing the $C{-}NO_2$ group.

The second set of FT-ICR experiments involved preparation of $[C_2H_4NO_2]^+$ ions according to reactions 1, 4, and 5, their collisional thermalization by Ar, introduced to a peak pressure up to 10^{-4} Torr via a pulsed valve,[9] their isolation by "soft" selective-ejection techniques, followed by reaction with a nucleophile, Nu, present at a low stationary pressure in the resonance cell. In all cases, the following process occurs

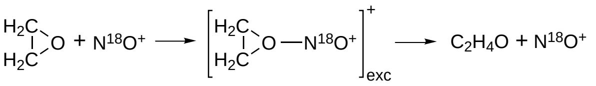
$$[C_2H_4NO_2]^+ + Nu \rightarrow NuNO^+ + C_2H_4O \quad (6)$$

Using in particular $(C_2H_5)_2CO$ as the nucleophile, one observes NO^+ transfer which is a fairly efficient process, ($k_6 = 6.5 \pm 2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, about 10% of the ADO collision rate constant), whereas the NO_2^+ transfer

$$[C_2H_4NO_2]^+ + Nu \nrightarrow NuNO_2^+ + C_2H_4 \quad (7)$$

does not occur. This observation is structurally informative, since $(C_2H_5)_2CO$ has a high NO_2^+ affinity, 27.6 kcal mol^{-1}, and it has been found that the complexes formed by NO_2^+ with a variety of ligands undergo fast nitronium ion transfer to 3-pentanone.[10] In order to allow meaningful comparison with the MIKE and CAD spectrometric results presented in the next section, it should be noted that the external CI source of the FT-ICR spectrometer is operated in a low-pressure range, typically around 5×10^{-5} Torr, where collisional deactivation of excited ions is inefficient. Hence, the ions formed in the exothermic process 1 undergo extensive fragmentation and/or isomerization in the relatively long time, ca. 10^{-5} s, required for their transfer into the resonance cell, where collisional thermalization occurs.

Kinetic Energy (MIKE) and Collisionally Activated Dissociation (CAD) Spectra of Mass Selected Ions. Reaction 1, 2, 4, and 5 were performed in the CI ion source of a ZAB-2F spectrometer operated in the pressure range from 0.1 to 0.4 Torr, and the MIKE spectra of the $[C_2H_4NO_2]^+$ ions formed were recorded (Figure 1). Only two Gaussian-shaped metastable peaks are present in the MIKE spectra of the ions formed in processes 2 and 4, the $C_2H_3O^+$ fragment at m/z 43 being the predominant one. As is apparent from Figure 1, the metastable NO^+ peak from the fragmentation of the $[C_2H_4NO_2]^+$ ion formed in reaction 4 is particularly narrow, suggestive of a small kinetic energy release, typical of a simple bond fission. Replacing NO^+ with $N^{18}O^+$ in reactions 4 and 5 gives $[C_2, H_4, N, {}^{16}O, {}^{18}O]^+$ adducts which undergo metastable loss of $N^{18}O^+$, or of $HN^{18}O$, but not of $N^{16}O^+$, nor of $HN^{16}O$. These findings exclude the occurrence of ^{18}O isotopic mixing in the nitrosated adduct, e.g.



(8)

The CAD spectra of the $[C_2H_4NO_2]^+$ ions obtained from reactions 1, 4, and 5 are closely similar (Table 2), displaying the $C_2H_4O^+$ fragment, m/z 44, arising from the NO loss, as the

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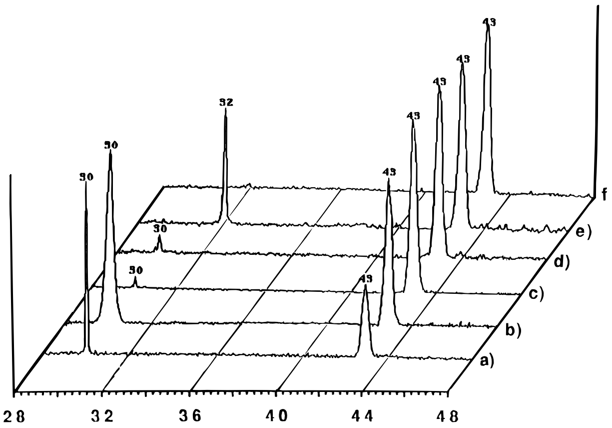

Figure 1. MIKE spectra of $(C_2H_4NO_2)^+$ ions from various sources: (a) reaction 4, (b) reaction 2, (c) reaction 5, (d) reaction 1, (e) reaction 4 with $N^{18}O^+$, (f) reaction 5 with $N^{18}O^+$.

Table 2. CAD Spectra of $[C_2H_4NO_2]^+$ Ions from Various Sources

	relative intensity[a]			
m/z	reaction 1	reaction 2	reaction 4	reaction 5
14	3.8	3.8	3.1	3.4
15	7.8	9.4	9.5	7.0
29	30.3	49.8	31.9	30.8
42	12.6	9.8	7.7	14.7
44	45.5	8.6	47.8	44.1
46	*b*	18.6	*b*	*b*

[a] Normalized with respect to the sum of the intensities. The peaks arising from unimolecular fragmentation are not considered. Standard deviation of relative intensities ±10%. [b] Below detection limit, ca. 1%.

major peak. Only the $[C_2H_4NO_2]^+$ ions obtained from reaction 2 undergo loss of NO_2^+, *m/z* 46, which is structurally informative, suggesting the existence of a NO_2 group in the species assayed, whereas loss of NO is much less significant than in the fragmentation of $[C_2H_4NO_2]^+$ ions obtained from other sources.

Finally, the CAD spectrum of the $[C_2H_4NO_2]^+$ ion formed upon EI ionization of 1-nitropropane, recorded for comparison purposes, displays NO_2^+, *m/z* 46, as the most intense fragment which suggests that the $C-NO_2$ bond present in the neutral parent molecule is preserved in the $[C_2H_4NO_2]^+$ fragment, making the CAD spectrum of the latter distinguishable from those of isomeric species containing a C−O−NO group instead.

Thermochemical Measurements. The difference of the NO^+ binding energy (BE) in the water−NO^+ and oxirane−NO^+ complexes was evaluated at 298 K utilizing the general ligand-exchange equilibrium

$$\mathrm{Nu_1NO^+ + Nu_2 \rightleftharpoons Nu_1 + Nu_2NO^+} \tag{9}$$

under the assumption that $\Delta G°_9 \cong \Delta H°_9$. In the systems of interest, the results obtained from the kinetic method[11] based on the unimolecular dissociation of $Nu_1(NO^+)Nu_2$ adducts support those obtained from the equilibrium approach, as discussed in detail elsewhere.[12] The equilibria investigated concerned the following ligands, arranged in order of increasing NO^+ BE: H_2O, C_2H_5Cl, CH_3ONO_2, *i*-C_3H_7Cl, $C_2H_5ONO_2$, CH_3OH, *i*-$C_3H_7ONO_2$, CH_3NO_2, oxirane, $C_2H_5NO_2$, C_2H_5CN, and CH_3CHO. The relevant result of the interlaced equilibrium measurements, namely BE(oxirane−NO^+) − BE(water−NO^+) = 8.4 ± 0.5 kcal mol^{-1}, was utilized to evaluate the absolute NO^+ BE of oxirane, based on the available water−NO^+ BE value of 18.5 ± 1.5 kcal mol^{-1} from a direct experimental determination,[13] supported by the results of a previously reported theoretical study at the MP4(SDTQ)//6-311G**/MP2(FU)//6-31G** + level of theory.[14] In this way one obtains an oxirane−NO^+ BE of 26.9 ± 2 kcal mol^{-1} and, utilizing available thermochemical data,[15,16] a heat of formation of **V** of 195.8 ± 2 kcal mol^{-1}.

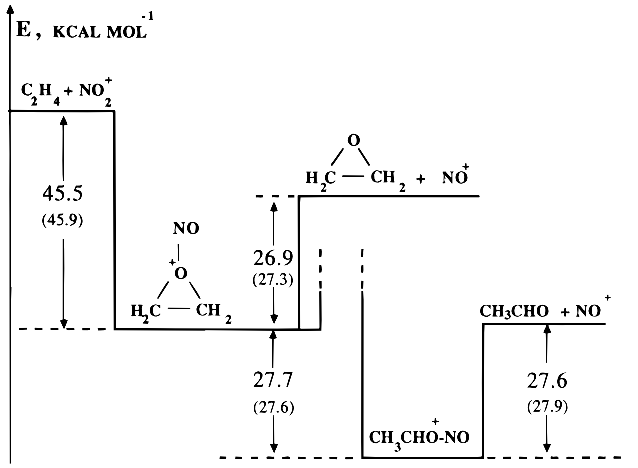

Figure 2. Schematic energy diagram of the relevant region of the $[C_2, H_4, N, O_2]^+$ system. The theoretical values are those taken from ref 4 and corrected for the ZPE contribution, except those concerning $CH_3CHO-NO^+$, calculated in the present work.

The NO^+ BE of acetaldehyde is higher by 0.7 kcal mol^{-1} than that of oxirane, which combined with the large stability difference between the two neutral ligands[15] makes **XIV** a deep local minimum on the energy hypersurface, laying 27.7 kcal mol^{-1} below ion **V**, as illustrated in the energy diagram of Figure 2.

Discussion

The results outlined in the previous sections provide a clearcut experimental answer to the principal question addressed in this study, showing that the charged product from (1) has a C−O−NO, rather than a $C-NO_2$ connectivity. This finding characterizes the gas-phase addition of nitronium ion to ethylene as a *O*-nitrosation, rather than a *C*-nitration reaction. This conclusion rests on the mutually supporting evidence from the CAD spectrum of the $[C_2H_4NO_2]^+$ adduct from (1) compared to those of model ions, and from its reactivity pattern, characterized by the NO^+ transfer to a gaseous nucleophile in the ligand-exchange process studied by FT-ICR mass spectrometry. The evidence on the exact structure of the *O*-nitrosated species obtained from (1) is less conclusive, in that neither CAD spectrometry of the $[C_2H_4NO_2]^+$ adduct nor its reactivity pattern allow clearcut discrimination between the two most likely candidates, namely ions **V** and **XIV**, although circumstantial evidence for the latter can be found in the close similarity between the MIKE spectra of the products from reactions 1 and 5. Furthermore, as previously noted, ion **XIV** is considerably more stable than **V**. Hence, even assuming that the latter is formed as a primary ("kinetic") product from (1), it can be expected to isomerize into **XIV** in the relatively long time, some 10 μs, before structural characterization by FT-ICR

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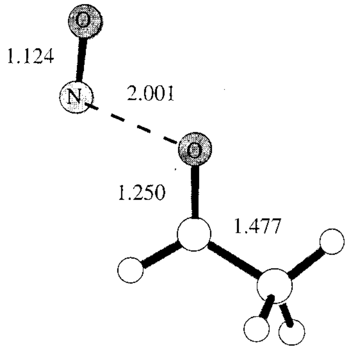
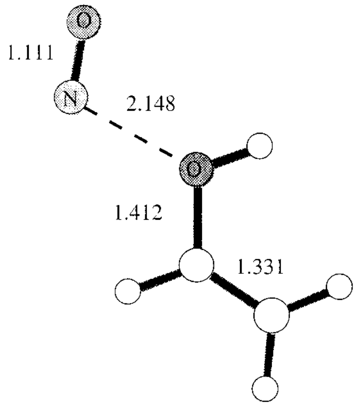
or CAD spectrometry. A necessary condition is obviously that its internal energy content allows overcoming the activation barrier for **V** → **XIV** conversion. This is most likely the case, in view of the large exothermicity, nearly 50 kcal mol^{-1}, of reaction 1 leading to formation of **V** from NO_2^+ and C_2H_4 (Figure 2), and of the inefficiency of collisional deactivation in the low-pressure range typical of the mass spectrometric techniques utilized. In conclusion, we are inclined to believe that when subjected to structural assay, i.e. some 10^{-5} s after its formation, the charged product from (1) has the connectivity of nitrosated acetaldehyde **XIV**, although such an assignment must be regarded as tentative.

Comparison with the most recent theoretical study of reaction 1 shows an excellent general agreement, in that ion **V**, the only *O*-nitrito species taken into account in the theoretical analysis, is found to be the most stable $[C_2H_4NO_2]^+$ product from (1) at the MP2/6-31+G* level, and furthermore its formation from NO_2^+ and C_2H_4 is characterized as a barrierless process.[4] From the quantitative standpoint, the agreement is also excellent, in that the exothermicity of reaction 1 yielding **V** amounts to 47.4 kcal mol^{-1} at 0 K according to calculations performed at the MP2 level of theory.[4] Taking into account the zero-point energy (ZPE) correction, we now find that the theoretically computed exothermicity of (1) amounts to 45.9 kcal mol^{-1} at 298 K, which compares very well with the experimental value of 45.5 kcal mol^{-1} at 298 K (Figure 2).

Because of this satisfactory agreement between computational and experimental results, we extended the theoretical investigation of the potential energy surface for reaction 1 to part of the *O*-nitrito region not previously considered in ref 4. The calculations were performed at the MP2/6-31+G* level of theory using the GAUSSIAN-94[17] quantum chemistry package. Full geometry optimization was performed, followed by characterization of the resulting stationary points and calculation of their zero-point correction to the energy by means of analytic Hessian-matrix calculations. Two new minimum geometries were found that have not been previously reported in ref 4. These structures correspond to the nitrosated acetaldehyde ion **XIV** and its corresponding nitrosated enol form **XV** (see Figure 3). As can be seen from the values reported in Table 3, structure **XV** is slightly more stable than structure **V**, while structure **XIV** is 27.6 kcal mol^{-1} more stable than structure **V**, and is the global minimum of the whole potential energy surface. This latter result is again in excellent agreement with the experimentally-derived value of 27.7 kcal mol^{-1} reported earlier in this work. This result strongly supports the previously-made tentative assignment of nitrosated acetaldehyde structure **XIV** to the $[C_2H_4NO_2]^+$ ion detected and as the final product of reaction 1.



XIV



XV

Figure 3. Optimized geometries of nitrosated acetaldehyde **XIV** and the corresponding nitrosated enol form **XV**.

Table 3. Energies (*E*), Zero-Point Energy (ZPE) Corrections, and Relative Energies (Δ*E*) Calculated at the MP2/6-31+G* Level of Theory

	E (hartrees)	ZPE (hartrees)	*E* + ZPE (hartrees)	Δ*E*(MP2) (kcal mol^{-1})
reactants	−282.53753[a]	0.06322	−282.47431	73.5
V	−282.61317[a]	0.06578	−282.54739	27.6
XV	−282.61404[b]	0.06265	−282.55139	25.1
XIV	−282.65541[b]	0.06401	−282.59140	0.0

[a] From ref 4. [b] This work.

A final remark concerns the reaction of ethylene with gaseous NO_2^+ carriers, e.g. protonated methyl nitrate, $[CH_3OHNO_2]^+$, in essence a nitronium ion solvated by a methanol molecule.[17,18] The CAD spectrum of the $[C_2H_4NO_2]^+$ ions from reaction 2 provides the only experimental evidence obtained in this study for *C*-nitration of ethylene, suggested by the loss of the NO_2^+ fragment, a peak not displayed by the CAD spectra of the $[C_2H_4NO_2]^+$ adducts from all other reactions. It appears that *C*-nitration is a distinctive feature of the reactivity of $[CH_3OHNO_2]^+$, and probably of other “solvated” forms of NO_2^+, that promote formation of a $C-NO_2$ bond, in contrast with the behavior of free NO_2^+, which promotes instead formation of a $C-ONO$ bond. In this respect, ethylene behaves like benzene, whose reaction with free NO_2^+ yields an oxygen-containing radical cation, arising from the decomposition of a *O*-nitroso species,[5] whereas the reaction with $[CH_3OHNO_2]^+$ gives protonated nitrobenzene, as shown by theoretical and experimental gas-phase studies.[18−21]

Experimental Section

Materials. Ethylene was obtained from Fluka AG with a stated purity exceeding 99.8% mol %. The other gases, C_2H_4, NO, and NO_2 purchased from Matheson Gas Products Inc., had a stated purity in excess of 99.95 mol %. All chemicals used in the ICR experiments as

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well as in MIKE and CAD spectrometry were research products obtained from Aldrich Co. Methyl nitrate and methyl nitrite were synthesized and purified according to standard procedures, whereas acetaldehyde monomer was obtained by heating the trimer in the presence of sulfuric acid. $N^{18}O^+$ ions were obtained by injecting into the CI source of the ZAB-2F spectrometer a solution prepared by dissolving unlabeled NO_x oxides into $H_2{}^{18}O$.

Experimental Procedures. MIKE and CID spectra were recorded using a ZAB-2F mass spectrometer from VG Micromass Ltd. Typical operation conditions were as follows: source temperature 160 °C, emission current 0.5−1 mA, repeller voltage 0V, accelerating voltage 8 kV. MIKE spectra of the nitrosonium complexes were recorded by using a specially built cooling system, to achieve a source temperature not exceeding 50 °C. MIKE and CAD spectra represent a sum of at least 40 scans, acquired with an energy resolution of 4000 fwhm. Helium, used as the collision gas to record CAD spectra, was admitted into the cell adjusting its pressure to the lowest value required to achieve a spectrum with a good signal-to-noise ratio, which typically required reducing the beam intensity to 30%. The FT-ICR experiments were performed in a 47e APEX spectrometer from Bruker Spectrospin AG, equipped with an external ion source, operated at a total nominal pressure not exceeding 7×10^{-5} Torr. The ion of interest, *m/z* 74, was driven into the resonance cell and thermalized by collisions with Ar, introduced via a pulsed valve. After isolation, the ions were allowed to decompose upon collisions with Ar, or to react at 25 °C, at total pressures ranging from 5×10^{-8} to 5×10^{-7} Torr, with the neutral reagents, or their premixed mixture prepared from weighed amounts of the components.

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