FULL PAPER

R(Ar)O–N$_2$$^+$ vs. R(Ar)–N$_2$O$^+$: Are Alkoxy-(Aryloxy-)diazonium Ions or Alkyl-(Aryl-)N-nitroso-onium Ions Formed in the Gas-Phase Reactions of N$_2$O with H$^+$, Me$^+$, Ph$^+$, PhCH$_2$$^+$, Tr$^+$ and PhCO$^+$?

Liliane G. Cabrini,[a] Mario Benassi,[a] Marcos N. Eberlin,*[a] Takao Okazaki,[b] and Kenneth K. Laali*[b]

Dedicated to Prof. George Olah for many wonderful contributions to this area

Gas-phase reactions of N$_2$O with H$^+$, Me$^+$, Ph$^+$, PhCH$_2$$^+$, Tr$^+$ (the tropylium ion) and PhCO$^+$ were studied by pentaquadrupole mass spectrometry. Collision-induced dissociation (CID) of the product ions establishes that, in the diluted solvent and counterion-free MS environment, gaseous Me$^+$ and Ph$^+$ ions form preferentially Me(Ph)O–N$_2$$^+$ (electrophilic attack at oxygen), whereas PhCH$_2$$^+$ forms preferentially PhCH$_2$–N$_2$O$^+$ (electrophilic attack at nitrogen). The nascent phenoxydiazonium ion PhO–N$_2$$^+$ dissociates promptly by N$_2$ loss to form PhO$^+$ as the observable addition product. The PhCO$^+$ and Tr$^+$ ions are unreactive towards addition to N$_2$O. The CID and ion/molecule chemistry of [N$_2$O + H]$^+$ are inconclusive with regard to connectivity, because the ion is rather resistant towards dissociation and reacts essentially as a proton donor species. Gaseous MeO–N$_2$$^+$ is not only efficient as a methylating agent towards ethers, heteroaromatics and nitriles, but also displays a rich chemistry that includes polar [4+2$^+$] stepwise cycloadditions with representative dienes and polar transacetalization with cyclic acetals. Relative energies and geometries of various RO–N$_2$$^+$/R–N$_2O^+$ isomeric pairs were evaluated by MP2 and DFT calculations.

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Introduction

In a landmark paper in 1986,[1] Olah, Herges, Laali and Segal reported on the first generation of a persistent alkoxydiazonium ion, that is MeO–N$_2$$^+$. The methoxydiazonium ion was formed in solution by methylation of N$_2$O with MeF/SbF$_5$/SO$_2$F$_2$ at low temperature, as well as by transmethylation of N$_2$O with [MeOSOClF]$^+$ (*O*-methylated SO$_2$ClF) (Scheme 1).

$$N_2O + MeF/SbF_5/SO_2F_2 \longrightarrow MeO\text{-}N_2^+$$

Scheme 1. Generation of the methoxydiazonium ion under superacid conditions.

The MeO–N$_2$$^+$ connectivity for the solvated ion was unambiguously established by low temperature multinuclear NMR (including ^{15}N), whereas chemical reactivity studies in quenching experiments with aromatics characterized MeO–N$_2$$^+$ as a methylating agent. Therefore in solution, Me$^+$ transfer (accompanied with N$_2$O loss) was shown to be preferred over MeO$^+$ transfer (via dediazoniation). Ab initio calculations supported the observed reactivity of solvated MeO–N$_2$$^+$ because they underscored a weak C–O bond for the gaseous ion. Attempts to generate the prototype hydroxydiazonium ion HO–N$_2$$^+$ through N$_2$O protonation were unsuccessful, and even in the strongest available superacid it was impossible to detect [N$_2$O + H]$^+$ as a distinct species (by NMR or FT-IR).[1] Later, by using ab initio calculations, Olah et al.[2] concluded that failure to directly observe protonated N$_2$O is probably due to the fast equilibrium formation of both *O,N*-diprotonated species undergoing intermolecular exchange with HO–N$_2$$^+$. As an integral part of the study by Olah et al.,[1] solvolytic approaches were also considered for in situ generation and trapping of MeO–N$_2$$^+$ by ionization of methylazoxy triflate (Scheme 2, a).

Solvolytic studies by Maskill and Jencks[3] on benzylazoxy tosylate also provided evidence that PhCH$_2$O–N$_2$$^+$ was formed as a long-lived intermediate (Scheme 2, b), but

[a] ThoMSon Mass Spectrometry Laboratory, Institute of Chemistry, State University of Campinas,
13083-970 Campinas, SP Brazil
[b] Department of Chemistry, Kent State University,
Kent, OH 44242, USA
Fax: +1-330-6723816
E-mail: klaali@kent.edu
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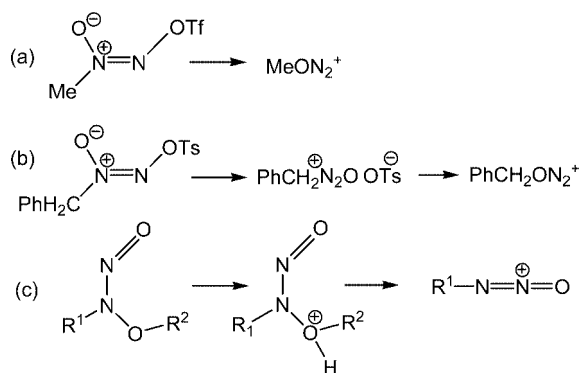
Scheme 2. Solvolytic approaches to RO–N$_2$$^+$ and R–N$_2$O$^+$.

for alkylazoxy tosylates, solvolytic studies pointed to a synchronous concerted fragmentation that produces N$_2$O and an ion-pair, with the [RN$_2$O]$^+$ cation being by-passed.[4] On the contrary, acid-catalyzed fragmentation of *N*-nitroso-*N*,*O*-dialkyl-hydroxylamines was reported to lead directly to an alkyl-*N*-nitroso-onium ion (R–N$_2$O)$^+$ as the key intermediate (Scheme 2, c).[5]

In regard to protonated N$_2$O, it has been detected by high-resolution gas-phase IR, but it could not be determined which isomer, H–N$_2$O$^+$ or HO–N$_2$$^+$, was formed.[6] Subsequently, based on computational data, it was suggested that the species detected in IR study was likely the hydroxydiazonium ion HO–N$_2$$^+$.[7] Mass spectrometric collision-induced dissociation (CID) data have seemingly provided evidence for the formation of a mixture of HO–N$_2$$^+$ and H–N$_2$O$^+$, and mainly MeN$_2$O$^+$ (from the reaction of Me$^+$ with N$_2$O), based on dissociation to NO$^+$.[8] However, as far as we could verify, no actual data have been provided to substantiate these claims.

Ab initio calculations at various levels have indicated that both H–N$_2$O$^+$ or HO–N$_2$$^+$ are viable, but their relative stabilities greatly depend on the level of electron-correlation.[9] More recently, Eckert-Maksic and co-workers[10] reported a high-level MO study on RO–N$_2$$^+$/R–N$_2O^+$ pairs at various levels, with R = H$^+$, Me$^+$, *t*Bu$^+$ and Ph$^+$. They concluded that H$^+$, Me$^+$ and Ph$^+$ bind strongly to N$_2$O to either nitrogen or oxygen, and with the relative energies of the resulting cations being dependent on the calculation level, but *t*Bu$^+$ and PhCH$_2$$^+$ were found to from weakly bound adducts with N$_2$O.

In the present study, we have employed MS^2 and MS^3 experiments, by using a pentaquadrupole mass spectrometer,[11] to make ions resulting from the reactions of H$^+$, Me$^+$, Ph$^+$, PhCH$_2$$^+$, Tr$^+$ (the tropylium ion) and PhCO$^+$ with N$_2$O. After isolating the product ions by quadrupole filtering, CID experiments were employed to determine the connectivities of the [N$_2$O + R(Ar)]$^+$ adducts formed in the diluted (solvent- and counterion-free) MS environment. Therefore, the main question was whether (Ar)RO–N$_2$$^+$ or (Ar)R–N$_2$O$^+$ were formed, and how would these ions behave in the diluted gas-phase environment. As the main result of our investigation, the unprecedented gaseous methoxydiazonium ion MeO–N$_2$$^+$ has been formed and char-

acterized, and several of its ion/molecule reactions are herein reported. These reactions demonstrate the potential of gaseous MeO–N$_2$$^+$ not only to act as a methylating agent (perhaps the most expected reactivity), but also to participate in polar transacetalization and [4+2$^+$] stepwise cycloadditions. For comparison, relative energies and geometries of RON$_2$$^+$/RN$_2O^+$ pairs were computed at the MP2/6-31+G(d,p) and by B3LYP/6-31++G(d,p) levels.

Results and Discussion

Methyl Iodide Chemical Ionization of N$_2$O: Under CH$_3$I chemical ionization (CI) of N$_2$O, both its protonated (*m/z* 45) and methylated forms (*m/z* 59) were observed. To investigate the connectivity of these gaseous species, both ions were filtered and then subjected to low-energy (15–20 eV) collision-induced dissociation (CID) with argon.

[N$_2$O + H]$^+$: The double-stage (MS^2) product ion mass spectrum of [N$_2$O + H]$^+$ of *m/z* 45 (not shown) shows, not surprisingly, that the ion is very resistant towards low energy CID. Minor ions eventually observed in the spectrum were those of *m/z* 19, 29, 30 and 32. Formation of this set of fragment ions is inconclusive with regard to connectivity of the parent ion; although highly pure argon is used, the ion of *m/z* 32 may arise from electron abstraction from residual O$_2$ and that of *m/z* 19 from proton transfer to residual water molecules. The minor ion of *m/z* 30 could be attributed to dissociation that forms NO$^+$ via NH loss from H–N$_2$O$^+$, but this assignment is rather unreliable due to the very weak signal obtained and the resistance of the parent ion towards dissociation.

[N$_2$O + CH$_3$]$^+$: The [N$_2$O + CH$_3$]$^+$ cation of *m/z* 59 (Figure 1, a) dissociates preferentially and extensively by N$_2$ loss, generating the product ion of *m/z* 31 (probably CH$_3$O$^+$ as the nascent ion), and this loss was confirmed by forming and dissociating at near the same conditions the [D$_3$]isotopologue ion [N$_2$O + CD$_3$]$^+$ of *m/z* 62 (Figure 1, b). N$_2$ loss is, therefore, consistent with the unprecedented and nearly exclusive formation of the gaseous methoxydiazonium ion MeO–N$_2$$^+$.

At the MP2/6-31+G(d,p) level, H–N$_2$O$^+$ and HO–N$_2$$^+$ are both minima (C_s geometry), (Figure S1, supporting information, see also the footnote on the first page of this article), with H–N$_2$O$^+$ computed to be only 1.2 kcal mol^{-1} more stable (Table S1, supp. inf.). A difference of 1.8 kcal mol^{-1} was previously computed at the MP2/6-31G(d,p) level.[10] An opposite stability order favoring HO–N$_2$$^+$ was reported at other levels, including MP4(SDQ) and QCISD(T). Figure S1 shows their optimized geometries, computed by MP2/6-31+G(d,p) in the present study.

At the MP2/6-31+G(d,p) level, Me–N$_2$O$^+$ and MeO–N$_2$$^+$ are both minima (C_s geometry) (Figure S1), with MeN$_2$O$^+$ computed to be 8.9 kcal mol^{-1} more stable (Table S1). A difference of 9.4 kcal mol^{-1} was previously computed at the MP2/6-31G(d,p) level.[10] There is a considerable energy barrier connecting the two isomers via a TS placed 35.6 kcal mol^{-1} above MeO–N$_2$$^+$ (Table S1 and Figure S2).

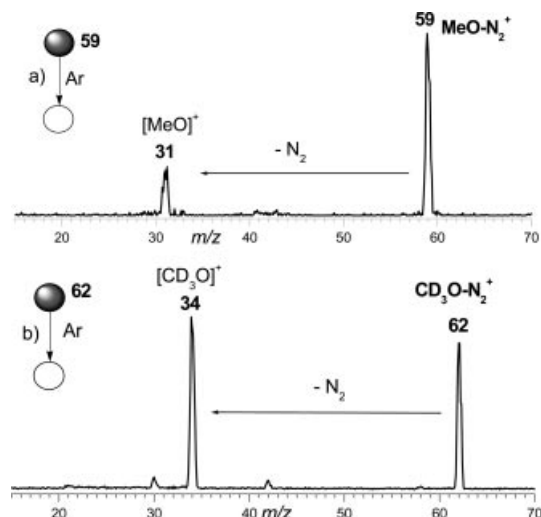L. G. Cabrini, M. Benassi, M. N. Eberlin, T. Okazaki, K. K. Laali

Figure 1. Double-stage (MS^2) product ion mass spectrum for CID of a) $[N_2O + Me]^+$ of m/z 59 and b) $[N_2O + CD_3]^+$ of m/z 62.

The optimized geometries of the *O*-methylated and *N*-methylated cations computed by MP2/6-31+G(d,p) (Figure S1) differ somewhat (in particular for bond-angles) to those reported at the QCISD/6-311G(d,p) level (with MeN$_2$O$^+$ being preferred by 3.6 kcal mol^{-1} at this level).[10]

Ion-Molecule Chemistry of $[N_2O + H]^+$ and MeO–N$_2^+$

The ion/molecule chemistry[12] observed for $[N_2O + H]^+$ of m/z 45 towards all neutral reactants (same compounds as those tested for its methyl homologue; see below), was unfortunately dominated by proton transfer. This rather trivial reactivity is therefore inconclusive in regard to connectivity and will not be discussed in details. The gaseous methoxydiazonium ion MeO–N$_2^+$ was, however, found to display a quite rich and novel chemistry as summarized below.

a) MeO–N$_2^+$ as Methylating Agent: The potential of the gaseous methoxydiazonium ion to act as an effective methylating agent (Me$^+$ transfer) is clearly manifested in its reaction with acetonitrile (Figure 2, a) and pyridine (Figure 2, b), because prominent *N*-methylated onium ions of m/z 56 and m/z 94 are formed, respectively. Protonated molecules of the neutral reactants are also concurrently formed, as N$_2$ can be thought as a (very good) leaving group, which allow the methyl group to be deprotonated with concomitant N$_2$ elimination. Computed ΔΔG values (see below) at the B3LYP/6-31+G(d,p) level [Equations (1), (2) and (3)] suggest that proton transfer from MeON$_2^+$ is rather favorable in the gas phase.
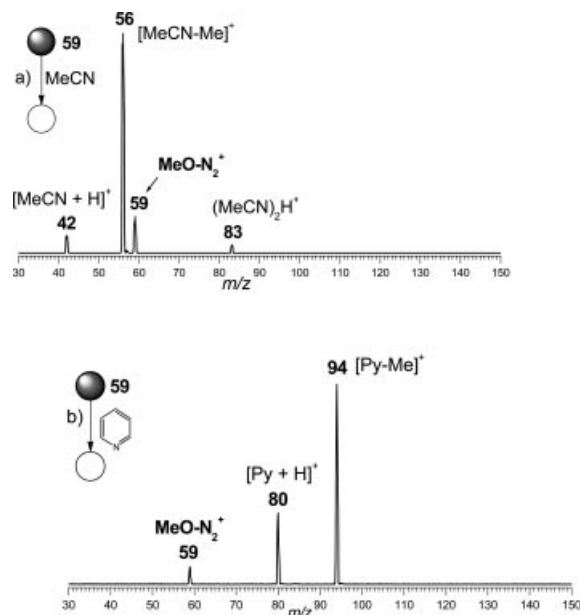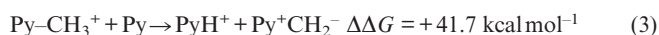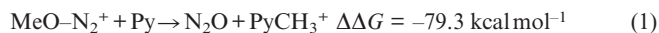
$$\text{MeO–N}_2^+ + \text{Py} \rightarrow \text{N}_2\text{O} + \text{PyCH}_3^+ \quad \Delta\Delta G = -79.3 \text{ kcal mol}^{-1} \quad (1)$$

$$\text{MeO–N}_2^+ + \text{Py} \rightarrow \text{CH}_2\text{O} + \text{N}_2 + \text{PyH}^+ \quad \Delta\Delta G = -126.7 \text{ kcal mol}^{-1} \quad (2)$$

$$\text{Py–CH}_3^+ + \text{Py} \rightarrow \text{PyH}^+ + \text{Py}^+\text{CH}_2^- \quad \Delta\Delta G = +41.7 \text{ kcal mol}^{-1} \quad (3)$$

Figure 2. Double-stage (MS^2) product ion mass spectrum for reactions of MeO–N$_2^+$ of m/z 59 with a) acetonitrile and b) pyridine.

The alkylation ability of MeO–N$_2^+$ is further demonstrated in ion/molecule reactions with propylene oxide (Figure 3, a) and with epichlorohydrin (Figure 3, b). For propylene oxide, Me$^+$ transfer to oxygen to form the oxonium ion of m/z 73 is the major process. Two other product ions of m/z 57 and 41 are also formed, which correspond to methane loss (m/z 57) and methanol loss (m/z 41) from the Me$^+$ adduct of m/z 73. With epichlorohydrin, a product ion of m/z 71 was formed almost exclusively. A plausible mecha-
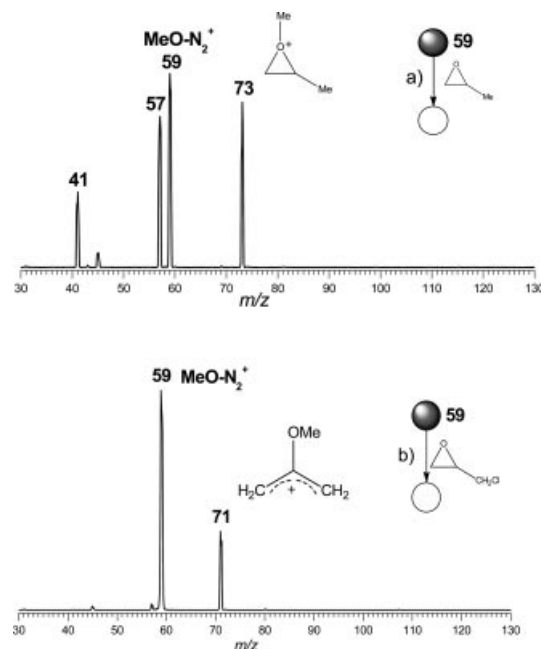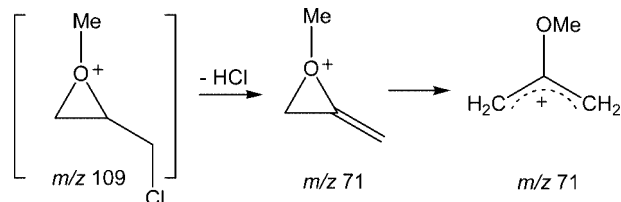

Figure 3. Double-stage (MS^2) product ion mass spectrum for reactions of MeO–N$_2^+$ of m/z 59 with a) propylene oxide and b) epichlorohydrin.

nism for its formation (Scheme 3) involves initial *O*-methylation followed by HCl loss and ring opening to form the stable 2-methoxyallyl cation.

Scheme 3. Formation of product ion of *m/z* 71 via the unstable *O*-methylated primary product of *m/z* 109, in the reaction of MeO–N$_2^+$ and epichlorohydrin.

b) Transacetalization of MeO–N$_2^+$ with Cyclic Acetals: Reaction of the methoxydiazonium ion with 2-methyl-1,3-dioxolane (Figure 4) forms the ion of *m/z* 103, and this reactivity demonstrates that gaseous MeO–N$_2^+$ ions display the amphoteric properties required for polar transacetalization reactions with cyclic acetals.[13] A product ion of *m/z* 103 was also formed in reactions with 2,2-dimethyl-1,3-dioxolane (spectrum not shown). Scheme 4 rationalizes a mechanism for this reaction, based on the well-established mecha-
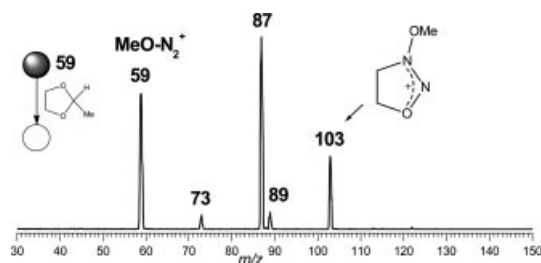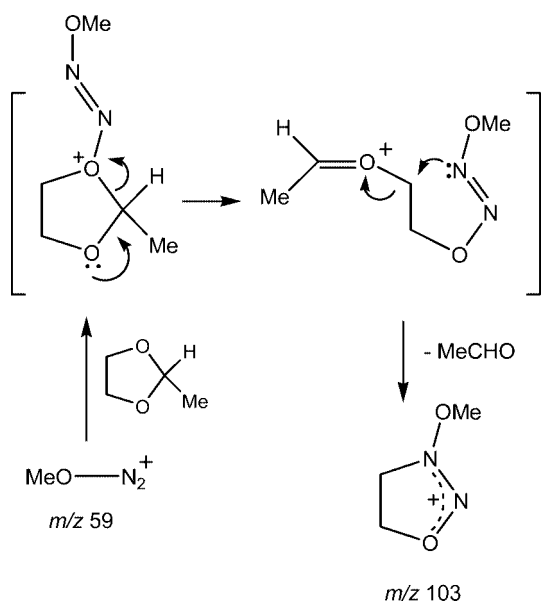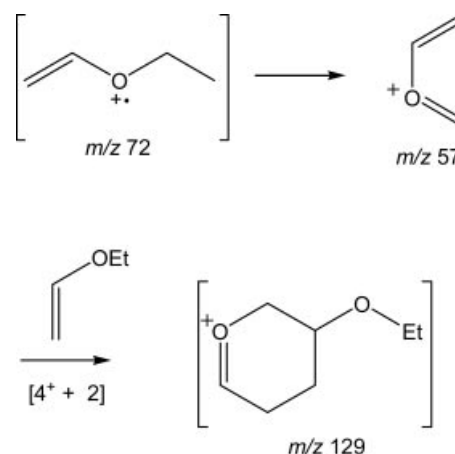

Figure 4. Double-stage (MS^2) product ion mass spectrum for reactions of MeO–N$_2^+$ of *m/z* 59 with 2-methyl-1,3-dioxolane.

Scheme 4. Reaction of MeO–N$_2^+$ with the cyclic acetal 2-methyl-1,3-dioxolane, leading to the polar transacetalization product ion of *m/z* 103.

nism for polar transacetalization with acylium ions and analogs.[14] The product ions of *m/z* 73, 89 and 87 correspond formally to methyl loss, proton transfer and hydride abstraction from/to 2-methyl-1,3-dioxolane, respectively. Note that an analogous ion, NO$_2^+$, has recently been observed to display similar polar transacetalization reactivity.[15]

c) Electron Transfer to MeO–N$_2^+$: Another exception to the more commonly observed methylating reactivity (Me$^+$ transfer) of the methoxydiazonium ion was encountered in its reaction with ethyl vinyl ether. For this enol ether, the major product ions detected were those of *m/z* 129, 57 and 72 (spectrum not shown). These products indicate that the major primary reaction channel was electron abstraction (charge-exchange) that forms the radical cation of ethyl vinyl ether of *m/z* 72 (Scheme 5). This ion further undergoes methyl radical loss to form the fragment of *m/z* 57, which adds in turn to ethyl vinyl ether to form the ion of *m/z* 129, probably via [4$^+$+2] cycloaddition.

Scheme 5. Formation of the product ion of *m/z* 129 from self-reactions of neutral/ionized ethyl vinyl ether.

MeO–N$_2^+$ as an Effective Dienophile in [4+2$^+$] Cycloadditions: Ion/molecule reactions with isoprene, butadiene and 2,3-dimethyl-1,3-butadiene demonstrate the intrinsic potential of gaseous methoxydiazonium ion MeO–N$_2^+$ as an effective 2$^+$ dienophile in polar [4+2$^+$] gas-phase cycloadditions.[16] Its reaction with isoprene (Figure 5, a) yields two major product ions of *m/z* 81 and 82, which can be ascribed to stepwise cycloaddition, forming the heterocyclic pyrrole ring in its ionized or protonated forms. Initial *N*-addition would be followed by ring closure, followed either by loss of a neutral [MeONO] species or a [MeONO]$^-$ radical species, to form either protonated or ionized methyl pyrrole of *m/z* 82 and 81, respectively (Scheme 6). Similar pathways are apparently followed in reactions with butadiene (not shown) and with 2,3-dimethyl-1,3-butadiene (Figure 5, b).

Reaction of PhCH$_2^+$ with N$_2$O: In an effort to prevent rearrangement to the more stable tropylium ion,[17] we aimed to form a relatively cold benzyl cation and to promote its reaction with N$_2$O under self-CI conditions. The approach used was to form PhCH$_2^+$ ions by protonation of
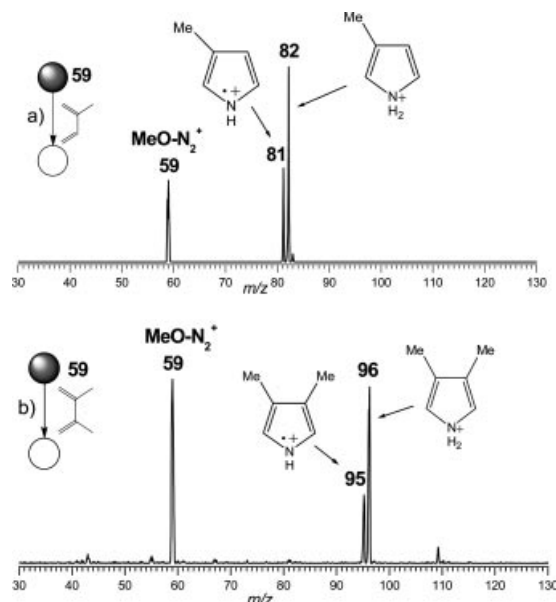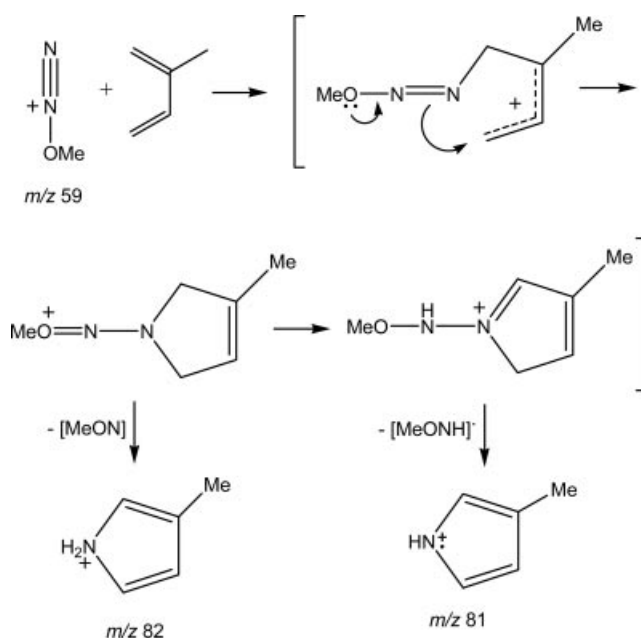
Figure 5. Double-stage (MS²) product ion mass spectrum for reactions of MeO–N$_2^+$ of m/z 59 with a) isoprene and b) 2,3-dimethyl-1,3-butadiene.

Scheme 6. Proposed mechanism for cycloaddition of MeO–N$_2^+$ with isoprene, leading to protonated or ionized 3-methyl pyrrole.

benzyl methyl ether followed by its dissociation by methanol loss, and to promote its addition to N$_2$O under the stabilizing (relatively high-pressure) CI conditions. The expected benzylated adduct of m/z 135 was indeed formed, and its product ion mass spectrum for CID with argon (Figure 6) shows dissociation mainly to [PhCH$_2$N]$^+$ of m/z 105. The observed NO loss indicates therefore that the N-benzylated adduct PhCH$_2$–N$_2$O$^+$ was preferentially formed.
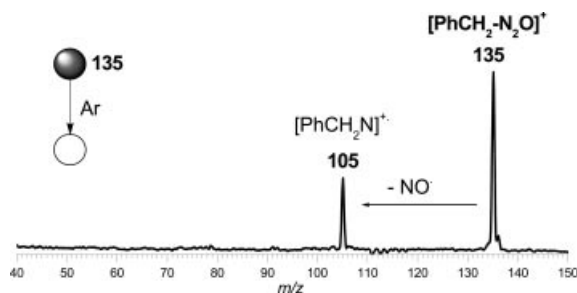

Figure 6. Double-stage (MS²) product ion mass spectrum for CID of the ion of m/z 135 formed in reactions of PhCH$_2^+$ with N$_2$O under CI conditions.

At the B3LYP/6-31++G(d,p) level, the N-benzylated and O-benzylated ions have very close energies (Table S1, supp. inf.). For PhCH$_2$–N$_2$O$^+$ two minima (structures **A** and **B**) and for PhCH$_2$O–N$_2^+$ three minima (**C**, **D** and **E**) were located at this level (Figure S3), with **A** for PhCH$_2$–N$_2$O$^+$ and **C/D** for PhCH$_2$O–N$_2^+$ being slightly more favored. Structures **A** and **C** correspond to the previously reported ones by MP2(fc)/6-31G(d,p). The resulting structures represent, however, weakly bonded ion/molecule complexes, with dissociation energies of 18.7 kJ mol^{-1} (for **A**) and 14.5 kJ mol^{-1} (for **C**) by MP2/6-31G(d,p).[10]

Alternative Approaches to [PhCH$_2$ + N$_2$O]$^+$ Generation: On the basis of standard conditions used to generate C$_7$H$_7^+$ isomers,[17] the benzyl cation was generated from benzyl bromide using 15-eV electron ionization. The ion was then filtered by Q$_1$ and allowed to react in q$_2$ with N$_2$O. Under the lower pressure, less stabilizing (by quenching) q$_2$ conditions (as compared to CI), moderate reaction took place. The PhCH$_2$–N$_2$O$^+$ adduct was however not observed, probably because it dissociated promptly by NO loss to form [PhCH$_2$N]$^+$ of m/z 105 as a minor product ion (spectrum not shown).

Reaction of Tr$^+$ with N$_2$O: C$_7$H$_7^+$ ions generated by 70-eV EI of toluene[17] were very modestly reactive towards N$_2$O. The resulting adduct of m/z 135 escaped direct detection, producing [C$_7$H$_7$N]$^+$ ions of m/z 105 by rapid NO loss. The latter ion proved to be quite stable and no fragment ions were observed upon 15–50 eV CID. As the tropylium ion is known to be rather unreactive,[17] we interpret this result as evidence that the majority of the C$_7$H$_7^+$ population, which is known to be dominated by Tr$^+$, is unreactive towards N$_2$O, and that the minor product ion at m/z 105 arises in fact from the reactions of PhCH$_2^+$ present as a minor fraction in the C$_7$H$_7^+$ population.

Reaction of Ph-CO$^+$ with N$_2$O: The benzoyl cation (formed by 70-eV EI of acetophenone) failed to produce a detectable adduct with N$_2$O (Figure 7). The product-ion distribution revealed that the reactant ion, even upon the very gentle q$_2$ collision conditions used to favor associative reactions (near zero collision energy) dissociated instead, upon collision with N$_2$O, to form Ph$^+$ of m/z 77. This fragment ion seems, however, to undergo a secondary reaction with N$_2$O mainly by electrophilic attack at oxygen to produce the phenoxydiazonium ion PhO–N$_2^+$. The nascent ad-

duct was probably unstable under the q$_2$ conditions, undergoing rapid dediazoniation (N$_2$ loss) to generate the minor PhO$^+$ ion of *m/z* 93. This ion undergoes further dissociation to form (by CO loss), probably the cyclopentadienyl cation of *m/z* 65 observed in the product ion mass spectrum (Figure 7), whereas Ph$^+$ dissociates by acetylene loss to form the ion of *m/z* 51. The CO loss has been established as the main dissociation route for PhO$^+$.[18] The heat for dissociation is not likely to come from collisions, but rather from the heat liberated in quite exothermic reactions.
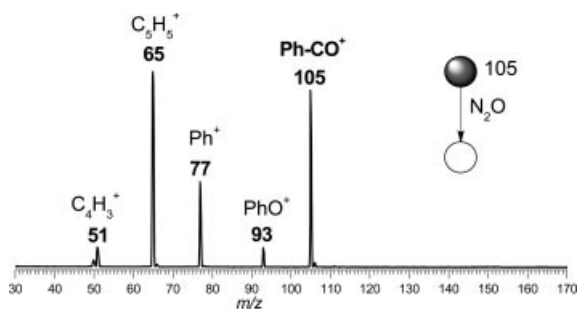

Figure 7. Double-stage (MS^2) product ion mass spectrum for the reactions of PhCO$^+$ of *m/z* 105 with N$_2$O.

Reaction of Ph$^+$ with N$_2$O: In accord with the products detected by reactions of PhCO$^+$ with N$_2$O (Figure 7), gaseous phenyl cation (formed now in the ionization source via 70 eV EI of acetophenone and filtered by Q$_1$) is found to react with N$_2$O to a great extent by electrophilic attack at oxygen (Figure 8). The nascent phenoxydiazonium ion
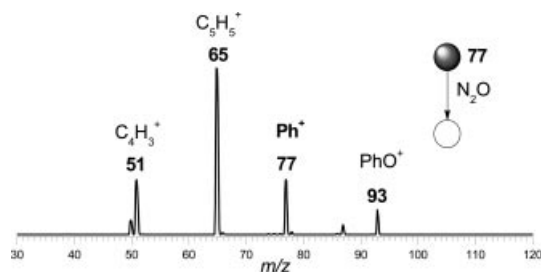

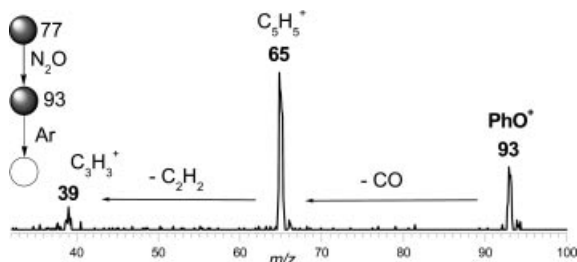Figure 8. Double-stage (MS^2) product ion mass spectrum for the reactions of Ph$^+$ of *m/z* 77 with N$_2$O.

Figure 9. Triple-stage (MS^3) sequential product ion mass spectrum for CID of PhO$^+$ of *m/z* 93 formed by reaction of Ph$^+$ of *m/z* 77 with N$_2$O.

PhO–N$_2$$^+$ of *m/z* 123 seems again to be unstable under the q$_2$ conditions, undergoing dediazoniation to generate PhO$^+$ of *m/z* 93, which further dissociates by CO loss to form probably the cyclopentadienyl cation of *m/z* 65. The reactant ion Ph$^+$ also dissociates considerably by acetylene loss to form the C$_4$H$_3$$^+$ of *m/z* 51. The sequential product ion mass spectrum (MS^3) of the PhO$^+$ of *m/z* 93 (Figure 9) shows it to dissociate by loss of CO (28 Da), to form the ion of *m/z* 65 (most probably the cyclopentadienyl cation).

At the B3LYP/6-31++G(d,p) level, Ph–N$_2$O$^+$ is computed to be more stable than PhO–N$_2$$^+$ by 10.1 kcal mol^{-1} (Table S1; Figure S3), however, they become almost equally favorable at the MP4(SDQ) level.[10]

Overall Summary and Concluding Remarks

The unprecedented gaseous methoxydiazonium ion, viz. MeO–N$_2$$^+$, has been formed by reactions of Me$^+$ with N$_2$O. The connectivity of this stable alkoxy-diazonium ion has been established using tandem mass spectrometric experiments via its CID and characteristic ion/molecule chemistry. The results fully concur with the earlier stable ion solution results of Olah and associates,[1] contradicting the previously mentioned preferential formation in the gas phase of the isomeric nitroso-onium ion Me–N$_2$O$^+$.[8] The CID data for the [N$_2$O + H]$^+$ ion were inconclusive with regard to establishing connectivity, and the ion was found to react mainly as a Brönsted acid. For the gaseous methoxydiazonium ion MeO–N$_2$$^+$, on the other hand, its intrinsic chemistry reveals not only its ability to act as an effective methylating agent; but the ion is found to act also as an amphoteric cation in polar transacetalization reactions as well as an effective dienophile in representative [4+2$^+$] cycloadditions, leading likely to ionized and protonated forms of pyrroles. Preferential formation of MeO–N$_2$$^+$ is surprising however, in view of the computational studies that indicate that isomeric gaseous Me–N$_2$O$^+$ is slightly more favored thermodynamically over MeO–N$_2$$^+$ at all levels, with variable energy differences (between 1 and 9 kcal mol^{-1} depending on the computational method). The computed energy difference between H–N$_2$O$^+$ and HO–N$_2$$^+$ is significantly less, favoring HO–N$_2$$^+$ at most levels, except by MP2/6-31G(d,p).

The PhCH$_2$$^+$ cation was found to be unique among the series of gaseous carbocations tested in that it adds to N$_2$O under stabilizing CI conditions at nitrogen, forming the corresponding *N*-nitroso-onium ion PhCH$_2$–N$_2$O$^+$. The isolated PhCH$_2$$^+$ ion generated under EI conditions reacts very modestly with N$_2$O under the quadrupole collision cell (q$_2$) conditions, in which the nascent PhCH$_2$–N$_2$O$^+$ ion rapidly looses NO to form [PhCH$_2$N]$^+$. The present and the earlier reported calculations are in concert, pointing to weakly bonded ion/molecule complexes.

The Tr$^+$ cation is found to be unreactive towards N$_2$O, whereas Ph-CO$^+$ fails to react, probably because of its relatively low energy threshold for CO loss. Hence, dissociation to Ph$^+$ becomes the only observable channel, even upon low energy, near zero eV collisions with N$_2$O.

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Phenyl cation reacts to a considerable extent with N_2O under the q_2 collision conditions to form the phenoxydiazonium ion $PhO–N_2^+$, but the nascent adduct undergoes prompt dediazoniation to form PhO^+. By analogy, formation of FCO^+ and SFO^+ cations by ion-molecule reactions of FC^+ and SF^+ with N_2O, followed by prompt N_2 loss, has been observed previously.[19] Computational study, in the present work, points to strong $[Ph + N_2O]^+$ adducts at all levels, but the relative stability differences vary greatly with the computational level, in many cases favoring $Ph–N_2O^+$.

In dealing with the question, *how can the gas-phase mass spectrometric results, present and previous computational studies, and the earlier experimental data under stable ion and solvolytic conditions be tied together*, the following closing comments could be made: (a) direct generation of $MeO–N_2^+$ in both superacid media and in the gas-phase confirms the stability of alkoxydiazonium ions and the preference of Me^+ to bind to oxygen; (b) calculation energies favoring $Me–N_2O^+$ over the observed $MeO–N_2^+$ may be rationalized if $MeO–N_2^+$ is the kinetically favored ion and there exists a substantial barrier both in solution and in the gas phase for Me^+ migration. As already mentioned, for the isomerization from $MeO–N_2^+$ to $Me–N_2O^+$, MP2/6-31+G(d,p) calculations predict a ΔG^* of 35.6 kcal mol^{-1} in the gas phase (Table S1; Figure S2, supp. inf.), which appears high enough to hamper the intramolecular process; (c) contrasting generation of $PhCH_2O–N_2^+$ under solvolytic conditions and of the isomeric $PhCH_2–N_2O^+$ in the gas phase may be related to solvent and counterion effects, favoring *O*-benzylation. Computational studies aimed at exploring the solvation effects have been initiated in our laboratory.

Mass Spectrometric Methods: MS^2 and MS^3 experiments were performed with an Extrel pentaquadrupole mass spectrometer.[20] The $Q_1q_2Q_3q_4Q_5$ consists of three mass-analyzing quadrupoles (Q_1, Q_3, Q_5) in which ion-mass selection and analysis are performed, and two reaction quadrupoles (q_2, q_4), which are used to perform either low-energy (near zero eV) ion/molecule reactions or 15 eV CID with argon. For the two-stage MS^2 experiments, the ion of interest was filtered by Q_1 and after ion/molecule reactions or CID in q_2, Q_5 was scanned to record the product ion spectra, while operating both Q_3 and q_4 in the non-mass analyzing rf-only mode. For the MS^3 experiments, a q_2-product ion of interest was mass-selected by Q_3 for further 15 eV collision-induced dissociation (CID) with argon in q_4, while scanning Q_5 to record the mass spectrum. The collision energies, calculated as the voltage difference between the ion source and the collision quadrupole, were typically near 1 eV for ion/molecule reactions and 15 eV for CID both in MS^2 and MS^3 experiments.

Computational Protocols: Structures were optimized, using a C_s or C_1 molecular point group, by the second-order Møller–Plesset perturbation theory (MP2) or the density function theory (DFT) method at MP2/6-31+G(d,p), B3LYP/6-31+(d,p) or B3LYP/6-31++G(d,p) level, employing the Gaussian 03 package.[21] All computed geometries were verified by frequency calculations to have no imaginary frequencies. Table S1 summarizes the total energies (*E*), zero point energies (ZPE) and Gibbs free energies (*G*) for the studied molecules, and their geometrical features are summarized in Figures S1 and S3. A transition state structure for rearrangement between CH_3NNO^+ and CH_3ONN^+ was searched by varying the C–N–O angle (Figure S2) at MP2/6-31+G(d,p) level, and the resulting structure was checked by frequency analysis to have one imaginary frequency.

Supporting Information (see footnote on the first page of this article): Energies and geometries (Table S1 and Figures S1–S3) for the optimized structures CH_3NNO^+, CH_3ONN^+, $PhCH_2NNO^+$, $PhCH_2ONN^+$, $PhNNO^+$, $PhONN^+$, $TrNNO^+$ and $TrONN^+$ are available in the Supporting Information.

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