Alkane- and areneoxodiazonium ions: experimental results leading to an *ab initio* theoretical investigation

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ABSTRACT: Alkaneoxodiazonium ions $(R\!-\!N\!=\!N\!=\!O)^+$ and $(R\!-\!O\!-\!N_2)^+$, which are closely analogous to alkanediazonium ions $(R\!-\!N_2)^+$, were detected as reactive intermediates in acid-catalysed reactions of nitroso-hydroxylamines and deamination-type reactions. The isomers were compared by high-level MO investigations of the reactions of nitrous oxide with cationic electrophiles H^+, CH_3^+, Me_3C^+ and $PhCH_2^+$. Strongly bonded species are formed in reactions with the powerfully electrophilic H^+ and CH_3^+, and the resulting ions differ considerably in stabilities; less stable species are formed with Me_3C^+ and $PhCH_2^+$ and the complexes so formed have similar stabilities. Two isomers of $Ph(N_2O)^+$, analogous to phenyldiazonium ion, PhN_2^+, are calculated to be stable ions with the end-N-bonded isomer being preferred over the O-bonded ion at the MP4(SDQ)/6–311G(d,p)//MP2(fc)/6–31G(d,p) and G3 levels of theory. Both are non-planar with the phenyl ring at 90° to the non-linear N_2O residue. Syntheses of salts of $Ar(N_2O)^+$ are now planned. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: *ab initio* calculations; dediazoniation; diazonium ion; deamination; oxodiazonium ion; carbenium ion; carbocation

INTRODUCTION

Salts of arenediazonium ions **1** in Scheme 1, e.g. tetra-fluoroborates, are relatively stable in either aqueous or alcoholic solution, or as crystalline solids. They have been used as intermediates in the synthesis of a wide range of materials from the laboratory up to the industrial scale.[1] In contrast, alkanediazonium ions **2** are known only as reactive intermediates in deamination-type reactions.[2] There is an effect of substituents X upon the stability of **1** but this is understood,[3] and is modest compared with the difference in stability between arene- and alkanediazonium ions. The difference in stability had been attributed earlier to the delocalization of positive charge into the arene ring corresponding to appreciable contributions by the various resonance forms **1c**, etc., as illustrated in Scheme 1, but Glaser and Horan[4] have recently shown that the parent benzenediazonium ion is best regarded as a phenyl cation linked to a nitrogen molecule by a dative bond. It follows that the difference in stability between arene- and alkanediazonium ions
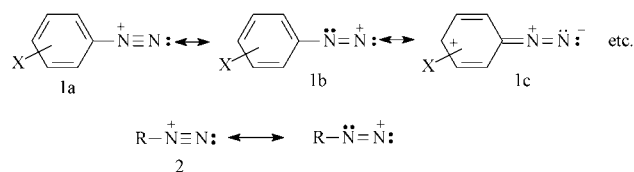
Scheme 1. Electronic configurations of arene- and alkane-diazonium ions

cannot lie principally in conjugative interactions between the arene ring and the diazonium group.

The experimental observation that compounds **1** fragment much more slowly than compounds **2** is represented by reaction profiles for loss of dinitrogen from arene- and alkanediazonium ions in Scheme 2. Chemical reactivity
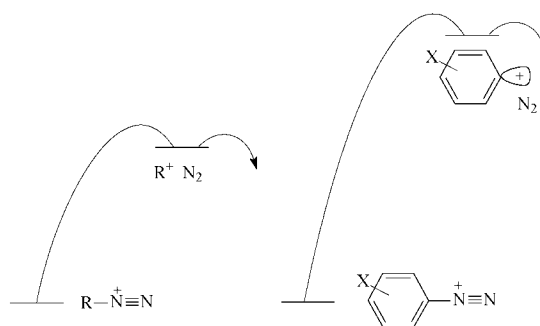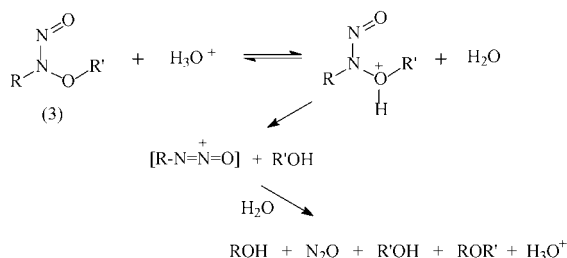

Scheme 2. Profiles for heterolysis of alkane- and arenedia-zonium ions

$$[R-N=N=O]^+ + R'OH$$

$$\xrightarrow{H_2O} ROH + N_2O + R'OH + ROR' + H_3O^+$$

Scheme 3. Stepwise acid-catalysed fragmentation of *N*-nitrosohydroxylamines

depends upon there being a reaction path so, regardless of thermodynamic aspects, a compound with no accessible reaction path is necessarily *kinetically* stable. This appears to be the basis of the stability of arenediazonium ions. The only credible unimolecular decomposition route involves heterolysis of the carbon–nitrogen bond, and even the stability of the dinitrogen molecule does not adequately compensate for the instability of the aryl cation (which has been extensively explored[5]). Secondary and tertiary alkyl cations, in contrast, are relatively stable reactive intermediates, hence the instability, i.e. reactivity, of the corresponding diazonium ions. Primary alkanediazonium ions do not lead to such stable carbenium ions, but are kinetically unstable because they have low-energy solvent-induced concerted bimolecular reaction paths (S_N2 or $E2$) which are not available to the arenediazonium ion analogues.
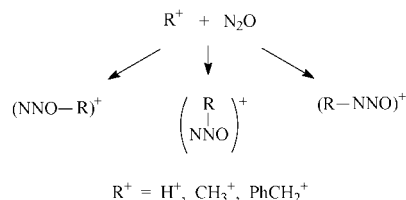
We have shown recently that *N*-nitroso-*N,O*-dialkyl-hydroxylamines (**3**) undergo stepwise acid-catalysed fragmentation involving alkaneoxodiazonium ion intermediates, $(R-N=N=O)^+$, as shown in Scheme 3.[6] These intermediates, which have previously been implicated by White in a range of reactions closely related to deamination,[2,7] are exactly analogous to alkanediazonium ions, $(R-N_2)^+$, in deaminations, and their structure follows directly from the atom connectivity of the substrate. In contrast, the solvolytic decomposition of alkyl azoxyarenesulfonates (**4**) illustrated in Scheme 4 occurs by an initial synchronous concerted fragmentation to give the carbocation intermediate directly, i.e. the carbocation's potential precursor in these reactions, $(RN_2O)^+$, is by-passed.[8] However, $(PhCH_2-ON_2)^+$ with bonding to oxygen is formed at least to some extent in the solvolysis of benzyl azoxytosylate, by capture of the benzyl cation by nitrous oxide subsequent to the initial fragmentation; it then reacts further itself.[9]

In order to gain insight into the relative stabilities of
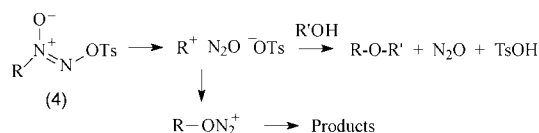
the isomeric cations, $R(N_2O)^+$, i.e. to understand why the reaction of Scheme 3 is stepwise via $(R-N=N=O)^+$ whereas its structural isomer with R bonded to the central nitrogen is by-passed in the decomposition of **4** in Scheme 4, isomers of $(RN_2O)^+$ were investigated theoretically for $R^+ = H^+$ (**5**), Me^+ (**6**) and $PhCH_2^+$ (**7**) (Scheme 5).[10] It was shown that only the ions with R^+ bonded to the terminal atoms of N_2O correspond to energy minima; the ion with R^+ bonded to the central nitrogen is the transition structure for the interconversion of the two stable isomeric ions. About this time, Olah and colleagues reported the preparation and structural characterisation of $(Me-ON_2)^+$ from the reaction of methyl fluoride and nitrous oxide under super-acid conditions at $-80\,°C$,[11] and McMahon and colleagues reported mass spectrometric and theoretical results on gas-phase reactions of nitrous oxide with H^+ and CH_3^+ which indicated preferential bonding of the electrophiles to the terminal nitrogen.[12] Moreover, Amano[13] reported the high-resolution infrared spectrum of protonated N_2O which, based on subsequent *ab initio* studies by Vincent and Hillier,[14] Rice and colleagues,[15] and Yamashita and Morokuma,[16] was interpreted in terms of the *O*-protonated isomer. This was corroborated by a millimetre wave spectroscopy study of protonated and deuterated N_2O.[17] More recently, detailed *ab initio* studies of protonated N_2O using various correlation methods were reported by Del Bene *et al.*[18] and Ekern *et al.*[19] These studies have unequivocally shown that the preferred site of protonation is very sensitive to the level of electron correlation. At the MP3, MP4(SDQ) and QCISD(T) levels (and also within G1 and G2 models), electron correlation indicates that oxygen protonation is preferred, whereas at the HF, MP2 and MP4(SDTQ) levels, N protonation prevails. Thus, regardless of detail, alkane-oxodiazonium ions bonded either through oxygen or the terminal nitrogen are viable species even though they are very reactive towards nucleophiles, i.e. they appear to be closely similar to alkanediazonium ions. The question arose, therefore, of whether areneoxodiazonium ions, $Ar(N_2O)^+$, are stable species, like arenediazonium ions, ArN_2^+, but which have not previously been sought. We now report an *ab initio* MO investigation of the reactions of N_2O with H^+, CH_3^+, $PhCH_2^+$ and Me_3C^+ using more rigorous computational methods than we previously used,[9] and of the reaction of N_2O with Ph^+ to inform a planned experimental search for stable salts of $(ArN_2O)^+$.

Scheme 4. Concerted solvolytic fragmentation of alkyl azoxytosylates

$$R-ON_2^+ \longrightarrow Products$$

$$(4) \quad \xrightarrow{} R^+ \, N_2O \, \overline{O}Ts \xrightarrow{R'OH} R-O-R' + N_2O + TsOH$$

Scheme 5. Reactions of cations R^+ with nitrous oxide

$$R^+ + N_2O$$

$$(NNO-R)^+ \quad \left(\begin{array}{c} R \\ | \\ NNO \end{array}\right)^+ \quad (R-NNO)^+$$

$$R^+ = H^+, \, CH_3^+, \, PhCH_2^+$$

$$R(N_2O)^+$$

5, R = H; **6**, R = Me; **7**, R = PhCH$_2$; **8**, R = t-Bu; **9**, R = Ph

Scheme 6

COMPUTATIONAL METHODS

Geometry optimisation of all species under investigation was carried out by the MP2[20] and Becke 3LYP[21] methods using 6–31G(d,p) and 6–311G(d) basis sets, respectively, within the Gaussian 94[22] suite of programs. Stationary points were optimised without any symmetry constraints and then characterised by calculation of the frequencies using the analytical gradient procedure at the same theoretical levels used in the geometry optimisation. The calculated frequencies were also used to determine zero-point vibrational energies (ZPVE) which were used after scaling (0.9661 for MP2 while the B3LYP ZPVEs were used unscaled) as zero-point corrections for the electronic energies calculated at these and subsequent higher levels of theory. The latter calculations were performed using MP4(SDQ) (**5–9**), QCISD(T) (**5, 6**) and CCSD(T) (**5, 6**) methods with the 6–311G(d,p) basis set at the MP2/6–31G(d,p) optimised geometries, where the systems studied are given within parentheses (Scheme 6). For all these calculations, only valence shell electrons were correlated. Additionally, calculations for some of the species were executed by utilizing G3 (**5, 6, 9**), CBS-Q (**5, 6**) and CBS-APNO (**5, 6**) computational procedures. Each dissociation energy (E_{diss}) was calculated as the difference between the total energy of the substituted oxodiazonium cation and the sum of the total energies of its fragments (i.e. N$_2$O and R$^+$). All calculations were carried out on Pentium III PCs or a cluster of Pentium III and Athlon MP PCs at the Ruđer Bošković Institute in Zagreb.

RESULTS AND DISCUSSION

Whereas the highest level calculations used in this study provide an accurate insight into structural and energetic features of investigated species, their use has been limited to the protonated and methylated ions because of the complexity of the higher analogues. Therefore, our first task in this work was to locate stationary structures of all potential ions at a level of theory applicable to all ions. For this purpose, we made use of the MP2(fc)/6–31G(d,p) method. In each case, three minima were located on the MP2 potential energy surface, corresponding to the isomers with an electrophile attached to the end-N, central-N and O atoms. It turned out that linkage of the electrophiles to the central nitrogen leads to high-energy species lying above the dissociation limit. For instance, the dissociation energy (E_{diss}) of the centrally methylated N$_2$O cation calculated at G3 and CBS-APNO levels of theory are −65.8 and −62.9 kJ mol^{-1}, respectively, the negative signs indicating that the total energies of the species are above the sums of the total energies of their fragments (Me$^+$ and N$_2$O). The same holds for other centrally substituted derivatives; consequently, they will not be considered any further.

In the next step, protonation and methylation of N$_2$O were studied in detail using the wide range of methods of varying degrees of sophistication specified above. The results of energy calculations on the reaction between N$_2$O and H$^+$ in Eqn. (1) are summarized in Table 1.

$$(H\underline{N}NO)^+ \rightleftharpoons N_2O + H^+ \rightleftharpoons (NN\underline{O}H)^+ \quad (1)$$
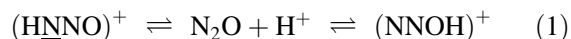
We see that the species with the proton bonded to the oxygen atom is more stable than that with the proton bonded to the terminal nitrogen by all computational methods except MP2 and B3LYP. However, the energy difference between the two isomers varies considerably depending on the method used. The best agreement with

Table 1. Total energies, energies of dissociation of (HN$_2$O)$^+$ and (HON$_2$)$^+$ and their relative energies calculated at various levels of theory

Method	(HN$_2$O)$^+$		(HON$_2$)$^+$		ΔE_{tot}[b] (kJ mol^{-1})
	E_{tot}[a] (a.u.)	E_{diss} (kJ mol^{-1})	E_{tot} (a.u.)	E_{diss} (kJ mol^{-1})	
CBS-APNO (0 K)	−184.86638	560.9	−184.86912	568.1	7.2
CBS-Q (0 K)	−184.65909	555.9	−184.66415	569.2	13.3
G3 (0 K)	−184.79030	560.1	−184.79482	572.0	11.9
CCSD(T)[c]	−184.49790	568.7	−184.50636	590.9	22.2
QCISD(T)[d]	−184.50032	570.1	−184.50766	589.3	19.2
MP4(SDQ)[e]	−184.47114	563.8	−184.48426	598.3	34.4
MP2/6–31G(d,p)	−184.40823	562.9	−184.40522	555.0	−7.9
B3LYP/6–311G(d)	−184.91228	551.8	−184.90935	544.1	−7.7

[a] ZPV energies are included in E_{tot}.
[b] $\Delta E_{tot} = E_{tot}(HN_2O^+) - E_{tot}(HON_2^+)$.
[c] CCSD(T)/6–311G(d,p)//MP2(fc)/6–31G(d,p).
[d] QCISD(T)/6–311G(d,p)//MP2(fc)/6–31G(d,p).
[e] MP4(SDQ)/6–311G(d,p)//MP2(fc)/6–31G(d,p).

Figure 1. Structures of *N*- and *O*-protonated N_2O obtained by geometry optimization at the QCISD/6–311G(d,p) level of theory (CBS-APNO)

experimentally determined results is achieved by CCSD(T)/6–311G(d,p)//MP2(fc)/6–31G(d,p) calculations; the result is only ca 4 kJ mol^{-1} lower than the experimental value of 26 ± 2 kJ mol^{-1}.[23,24] Somewhat disappointingly, other relatively high levels of theory such as CBS-APNO, CBS-Q and G3 provide poor energy differences (ΔE_{rel}) between the two isomers (7.2, 13.3, and 11.9 kJ mol^{-1}, respectively) which are considerably less than the experimental value. It is also noteworthy in this respect that the value calculated by the G3 method is in less satisfactory agreement with experiment than values calculated by G1 (13.9 kJ mol^{-1}) and G2 (14.2 kJ mol^{-1}).[19] On the other hand, proton affinities of the oxygen site offered by these three computational procedures (572.4, 573.5, and 576.3 kJ mol^{-1}, respectively) are in excellent agreement with the experimental value (572.5 kJ mol^{-1}).[24] Apparently, all these methods overestimate the stability of the *N*-protonated species due to the effect of triple electron excitations taking place in the electron correlation calculations within each of the three composite models. This drawback of the electron correlation methods with triple excitations has been discussed earlier by Ekern *et al.*,[19] and Del Bene *et al.*,[18] and was ascribed to the larger contribution of biradical configurations to the description of the N protonated isomer relative to the O protonated form.[19] Finally, we note in passing that use of the B3LYP formalism does not lead to an improvement in the predicted energy difference compared with use of MP2. Use of different basis sets within the B3LYP formalism does not affect the accuracy either.*

The structural effects of protonation are as expected (Fig. 1). At the CBS-APNO level [optimization of geometry at the QCISD/6–311G(d,p) level], we find that both ions are non-linear and the N—H and O—H bond lengths are in the expected range, indicative of strong bonding. Bonding of the proton to the oxygen atom shortens slightly the N—N bond (by 0.020 Å) but appreciably lengthens the O—N bond (by 0.089 Å) compared with in N_2O (the related N—N and N—O bond lengths in N_2O are 1.129 and 1.189 Å, respectively). In contrast, bonding of the proton to the nitrogen leads to an N—N bond elongation by 0.022 Å, whereas the O—N bond is shortened by 0.054 Å. Calculations at the MP2 level predict the same trend for the *O*-protonated ion, whereas in the *N*-protonated species the N—N bond is slightly shortened compared with N_2O.

Table 2 summarises energetic data for bonding between N_2O and CH_3^+ (which, like H$^+$ is an extremely reactive electrophile). In contrast to our earlier findings,[10] and to the relative energies of the protonated isomers, the N-bonded ion is now found to be the more stable at all levels of theory although the difference again depends upon the computational method. The present result that

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* ΔE_{tot} for Me(N$_2$O)$^+$ ions calculated at B3LYP employing 6-31G(d), 6-311G(d), and 6-311+G(d,p): -26.7, -32.3, and -31.3 Kj mol^{-1}, respectively.

Table 2. Total energies, dissociation energies and relative energies of N- and O-bonded methyloxodiazonium ions calculated at various levels of theory

Method	(MeN$_2$O)$^+$		(MeON$_2$)$^+$		
	E_{tot}[a] (a.u.)	E_{diss} (kJ mol^{-1})	E_{tot} (a.u.)	E_{diss} (kJ mol^{-1})	ΔE_{tot}[b] (kJ mol^{-1})
CBS-APNO (0 K)	-224.17096	201.9	-224.16320	181.5	-20.4
CBS-Q (0 K)	-223.90823	201.6	-223.90049	181.2	-20.4
G3 (0 K)	-224.08252	196.9	-224.07596	179.6	-17.3
CCSD(T)[c]	-223.70318	190.5	-223.69818	177.3	-13.2
QCISD(T)[d]	-223.70557	191.7	-223.69977	176.5	-15.2
MP4(SDQ)[e]	-223.67194	181.5	-223.67047	177.7	-3.8
MP2/6–31G(d,p)	-223.58652	203.8	-223.57138	164.1	-39.7
B3LYP/6–311G(d)	-224.23504	203.8	-224.22273	171.5	-32.3

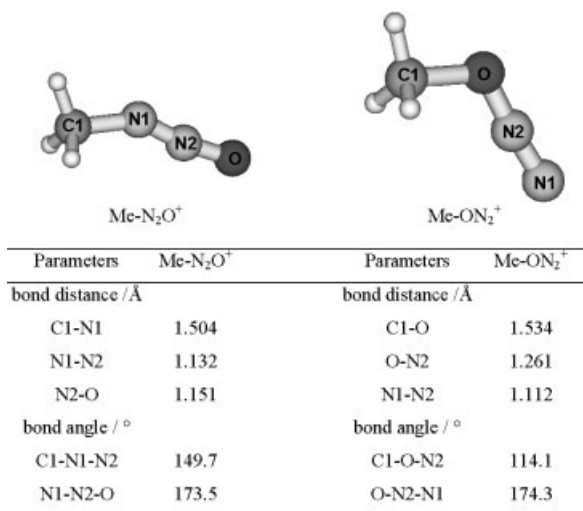[a] ZPV energies are included in E_{tot}.
[b] $\Delta E_{tot} = E_{tot}(\text{MeN}_2\text{O}^+) - E_{tot}(\text{MeON}_2^+)$.
[c] CCSD(T)/6–311G(d,p)//MP2(fc)/6–31G(d,p).
[d] QCISD(T)/6–311G(d,p)//MP2(fc)/6–31G(d,p).
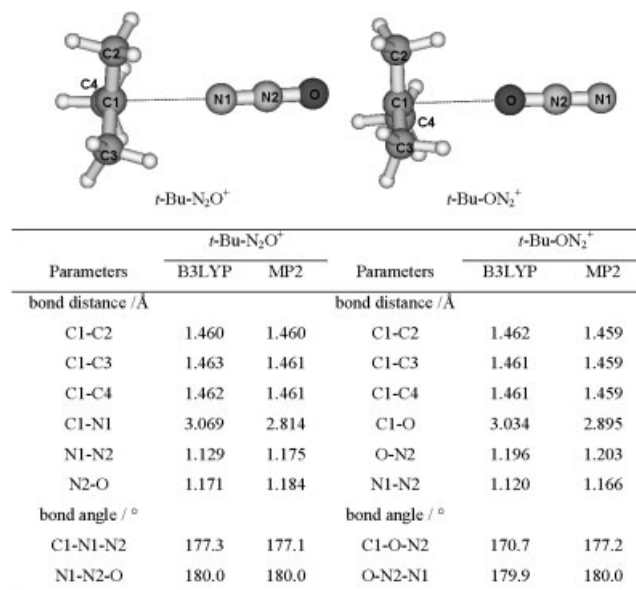[e] MP4(SDQ)/6–311G(d,p)//MP2(fc)/6–31G(d,p).

Figure 2. Optimized structures of MeN_2O^+ and $MeON_2^+$ at the QCISD/6–311G(d,p) level of theory (CBS-APNO)

Figure 3. Structures of isomeric *tert*-butyloxodiazonium ions calculated at the MP2(fc)/6–31G(d,p) and B3LYP/6–311G(d) levels of theory

the N-bonded ion is of lower energy is in accord with conclusions from gas phase work by McMahon and Kebarle,[12] but not with solution results by Olah and colleagues.[11] Structures of the two ions optimized at the QCISD/6-311G(d,p) level, as required within the CBS-APNO formalism are shown in Fig. 2; the C—O and C—N bond lengths are normal, the methyl in both cases being essentially tetrahedral, but the non-linearity is greater for the O-bonded ion in accordance with the trend observed for the protonated species. Correspondingly, the effect of the bonding of the electrophile upon the N—N and N—O bond lengths is similar to that for the protonated species.

We next turn to complexes of N_2O and Me_3C^+ (which is a much less reactive electrophile) and there are now marked differences (Table 3 and Fig. 3). The larger size of the complexes prevented the use of the most rigorous methods which were applied to the protonated and methylated species. In both *tert*-butylated ions, the bonding is rather weak, the C—N and C—O interatomic distances very large (2.814 and 2.895 Å, respectively, at the MP2 level), the central carbon of the *tert*-butyl group is virtually trigonal and the NNO residues are practically linear and only negligibly different from the neutral N_2O

molecule. However, it is interesting that the CON and CNN bond angles are less than 180°. Furthermore, these two complexes have similar stabilities with the oxygen-bonded *t*-Bu ion being slightly preferred (except by the MP2 method). However, the MP2 result should be taken with caution due to the limitations of MP2 calculations for this type of ion, as mentioned above.

Similarly for the weakly electrophilic benzyl cation, bonding to N_2O is weak, C—N and C—O interatomic distances are large (2.763 and 2.696 Å, respectively, at the MP2 level), the carbon which bonds to the N_2O remains virtually trigonal and the N_2O residues are linear (Fig. 4). These structural results suggest that the two complexes are of similarly low stability, as is confirmed by energy calculations (Table 4). A similarly weak interaction was found between the benzyl cation and nitrogen.[25]

Figure 5 and Table 5 show results for the combination of the powerfully electrophilic phenyl cation with nitrous oxide through the terminal nitrogen. The plane of the

Table 3. Total energies, dissociation energies and relative energies of N- and O-bonded *tert*-butyloxodiazonium ions calculated at various levels of theory

Method	$(t\text{-BuN}_2\text{O})^+$		$(t\text{-BuON}_2)^+$		
	E_{tot}^a (a.u.)	E_{diss} (kJ mol^{-1})	E_{tot} (a.u.)	E_{diss} (kJ mol^{-1})	ΔE_{tot}^b (kJ mol^{-1})
MP2/6–31G(d,p)	−341.09778	26.9	−341.09626	22.9	−4.0
MP4(SDQ)^c	−341.26139	21.7	−341.26417	29.0	7.3
B3LYP/6–311G(d)	−342.17421	14.9	−342.17600	19.6	4.7

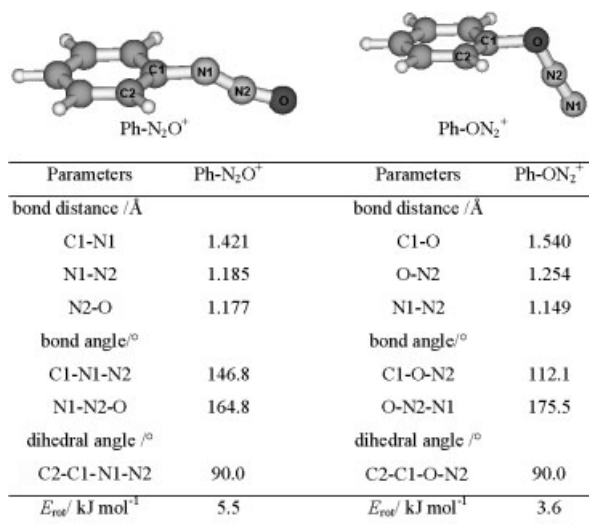[a] ZPV energies are included in E_{tot}.
[b] $\Delta E_{\text{tot}} = E_{\text{tot}}(t\text{-BuN}_2\text{O}^+) - E_{\text{tot}}(t\text{-BuON}_2^+)$.
[c] MP4(SDQ)/6–311G(d,p)//MP2(fc)/6–31G(d,p).
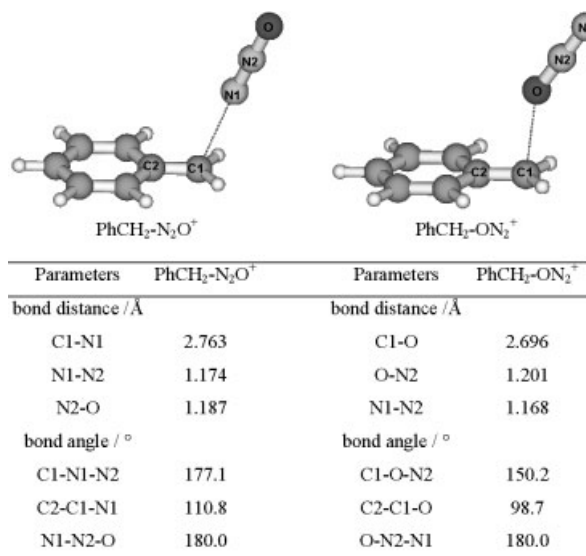
Figure 4. Structures of benzyloxodiazonium ions calculated at the MP2(fc)/6–31G(d,p) level of theory

Figure 5. Optimized structures of PhN_2O^+ and $PhON_2^+$ and barriers to rotation about the central bonds calculated at the MP2(fc)/6–31G(d,p) level of theory

phenyl group is at 90° to that of the non-linear N_2O residue, and the C—N bond is normal in accord with the strong bonding, similar in fact to that in PhN_2^+ (1.391 Å).[4] There is slight elongation of the N—N bond and shortening of the N—O bond compared with nitrous oxide. The barrier to rotation about the C—N bond is 5.5 kJ mol^{-1}. Figure 5 and Table 5 also include results for the ion formed by bonding of Ph$^+$ with the oxygen of

N_2O; overall, it is similar to the N-bonded isomer with the C—O bond length normal, again indicating strong bonding. Compared with N_2O, the N—N bond is short and the N—O bond is long, and the barrier to rotation about the C—O bond is only 3.6 kJ mol^{-1}. From the energetic point of view, the complex with the phenyl group bonded to the terminal nitrogen appears to be slightly more stable compared with the oxygen-bonded

Table 4. Total energies, dissociation energies and relative energies of N- and O-bonded benzyloxodiazonium ions calculated at various levels of theory

Method	$(PhCH_2N_2O)^+$		$(PhCH_2ON_2)^+$		
	E_{tot}[a] (a.u.)	E_{diss} (kJ mol^{-1})	E_{tot} (a.u.)	E_{diss} (kJ mol^{-1})	ΔE_{tot}[b] (kJ mol^{-1})
MP2/6–31G(d,p)	−453.88217	18.7	−453.88057	14.5	−4.2
MP4(SDQ)[c]	−454.06120	12.9	−454.06291	17.4	4.5
B3LYP/6–311G(d)	−455.30134	11.1	−455.30233	13.7	2.6

[a] ZPV energies are included in E_{tot}.
[b] $\Delta E_{tot} = E_{tot}(PhCH_2N_2O^+) - E_{tot}(PhCH_2ON_2^+)$.
[c] MP4(SDQ)/6–311G(d,p)//MP2(fc)/6–31G(d,p).

Table 5. Total energies, dissociation energies and relative energies of N- and O-bonded phenyloxodiazonium ions calculated at various levels of theory

Method	$(PhN_2O)^+$		$(PhON_2)^+$		
	E_{tot}[a] (a.u.)	E_{diss} (kJ mol^{-1})	E_{tot} (a.u.)	E_{diss} (kJ mol^{-1})	ΔE_{tot}[b] (kJ mol^{-1})
G3 (0 K)	−415.69534	129.1	−415.68913	112.8	−16.3
MP2(fc)/6–31G(d,p)	−414.70079	156.4	−414.68040	102.9	−53.5
MP4(SDQ)[c]	−414.84471	119.0	−414.84463	118.8	−0.2
B3LYP/6–311G(d)	−415.97471	135.4	−415.95642	87.4	−48.0

[a] ZPV energies are included in E_{tot}.
[b] $\Delta E_{tot} = E_{tot}(PhN_2O^+) - E_{tot}(PhON_2^+)$.
[c] MP4(SDQ)/6–311G(d,p)//MP2(fc)/6–31G(d,p).

isomer at both the MP4(SDQ)/6–311G(d,p)//MP2(fc)/6–31G(d,p) and the G3 level of theory. It should be noted, however, that MP2/6–31G(d,p) and B3LYP/6–311G(d) calculations erroneously predict that bonding of the phenyl group to the nitrogen end of the N_2O is strongly preferred, in accordance with previously discussed drawbacks of these methods.

CONCLUSIONS

Highly reactive electrophiles H^+, CH_3^+, and Ph^+ bond strongly to either the terminal nitrogen or the oxygen atom of nitrous oxide, but not to the central nitrogen. Weaker electrophiles t-Bu^+ and $PhCH_2^+$ bond only weakly. On the evidence of our results for $Ph(N_2O)^+$, and by analogy with the relative stabilities of alkane- and arenediazonium ions (the former being reactive intermediates in deamination-type reactions and the latter being cations of stable salts), we propose that $Ph(N_2O)^+$ (or substituted variants) may be sufficiently stable to be isolable as, for example, tetrafluoroborate salts.

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