Relative Stability of Isomeric Methyl Nitrate Cations $(CH_3NO_3)H^+$

Fernando Bernardi
Dipartimento di Chimica 'G. Ciamician,' Via Selmi 2, 40126 Bologna, Italy
Fulvio Cacace *
Università di Roma 'La Sapienza', P. le A. Moro 5, 00185 Roma, Italy
Felice Grandinetti
Istituto di Chimica Nucleare del C.N.R., Area della Ricerca di Roma, 00016 Monterotondo Stazione, Roma, Italy

The structure and the relative stability of isomeric $(CH_3NO_3)H^+$ ions have been investigated using *ab initio* computational techniques. The results, both at the STO-3G and at the 4-31G level of calculation, show that protonation of the nitro group is energetically favoured. However, when the effects of solvation by single neutral molecules were included, the cation obtained by protonation of the ether oxygen was more stable, thus indicating that differential solvation can appreciably influence the intrinsic relative stability of the title compounds.

Protonated alkyl nitrates are effective nitrating agents, long used in liquid-phase preparative reactions, especially those involving activated arenes.[1] Recently, a gas-phase study based on the co-ordinated application of mass spectrometric and radiolytic techniques has characterized protonated methyl nitrate as the first example of a well behaved nitrating cation, the substrate and positional selectivity of which conform to solution-chemistry trends.[2–5] Formation of the reagent by proton transfer (1), characterized by exothermicity[6] of 44

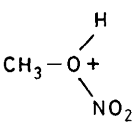
$$C_nH_5^+ + CH_3NO_3 \longrightarrow C_nH_4 + (CH_3NO_3)H^+ \quad (1)$$

($n = 1$) and 13 ($n = 2$) kcal mol^{-1}, has been directly demonstrated by methane chemical ionization (CI) mass spectrometry, and its heat of formation, 161 kcal mol^{-1}, has been estimated using the proton affinity (PA) of CH_3NO_3 from i.c.r. equilibrium measurements, 175.8 kcal mol^{-1}. However, the structure of protonated methyl nitrate, of considerable interest in the mechanistic study of gas- and liquid-phase aromatic nitration, could not be established from the experimental data and this prompted the present theoretical study.

The geometry, energy, and charge distribution of methyl nitrate (**I**), of methyl nitrate protonated at the ether oxygen (**II**), and of the isomeric cation protonated at the oxygen of the nitro group (**III**) have been computed using the GAUSSIAN 80 program.[7] Full geometry optimization with gradient techniques has been carried out at the STO-3G[8] and 4-31G[9] levels. Calculated geometries and charge distributions, optimized at the 4-31G level, are reported respectively in Figure 1 and 2, and the energies calculated both at the STO-3G and 4-31G levels are given in the Table. Considerable differences do exist between the results obtained at the two levels. In fact, while protonation at the nitro group appears energetically favoured in both cases, *i.e.* (**III**) is more stable than (**II**), the stability difference, as high as 36.3 kcal mol^{-1} at the STO-3G level, reduces to 6.7 kcal mol^{-1} at the more accurate 4-31 G level. Using the 4-31G energies of NO_2^+, CH_3OH, and (**III**), one can calculate the binding energy of NO_2^+ to methanol, 33.1 kcal mol^{-1}, the difference of which from the value deduced from experimental data, *ca.* 24 kcal mol^{-1}, is not intolerably large, taking into account the cumulative uncertainties of both computational and experimental data.

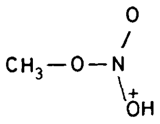
CH_3ONO_2

(I)



$CH_3{-}\overset{\displaystyle H}{O^+}{-}NO_2$

(II)



$CH_3{-}O{-}N(=O){-}\overset{+}{O}H$

(III)

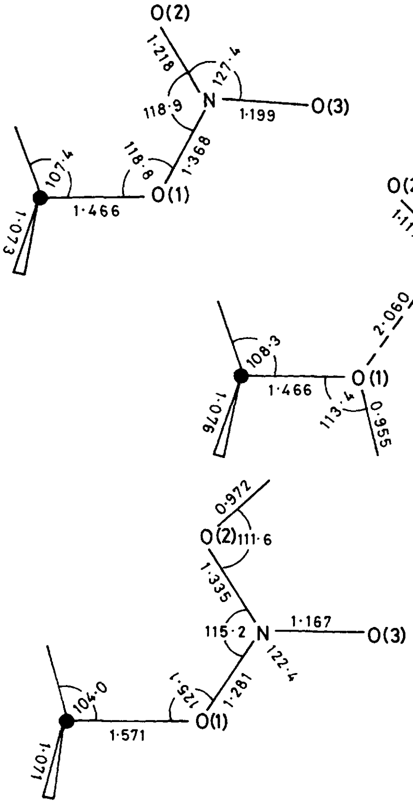


Figure 1. From top to bottom, calculated structures, optimized at 4-31 G level, for species (**I**)—(**III**), respectively. Distances are in Å, angles in °.

The binding energy from this study is in substantial agreement with that from an early MINDO study,[10] which however predicted isomer (**II**) to be *more* stable than (**III**) by *ca.* 20 kcal mol^{-1}.

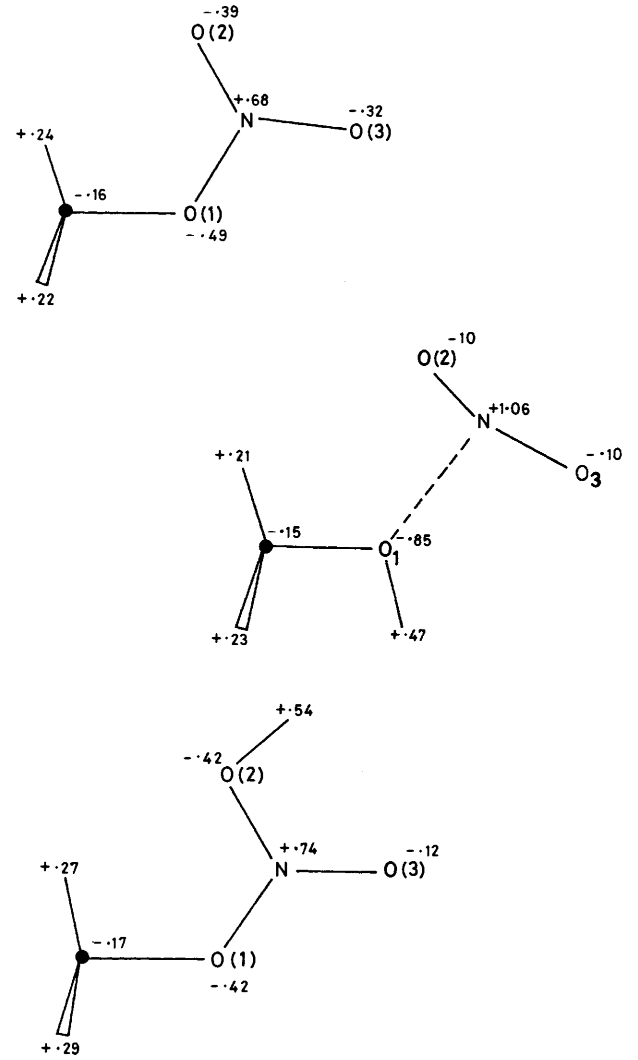


Figure 2. From top to bottom, calculated atomic charges, in electron units, for species (I)–(III), respectively.

Table. Relative stability of protonated methyl nitrate isomers.

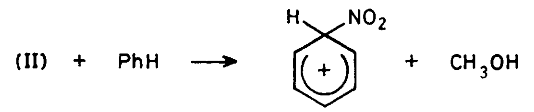
Species	STO-3G Energy[a]	4-31G Energy[a]	ΔE^b STO-3G	ΔE^b 4-31G
(I)	−314.253 81	−317.966 39		
(II)	−314.587 13	−318.233 26	+36.3	+6.7
(III)	−314.645 07	−318.243 98		
(II) + $2H_2O$		−470.108 48[c]		−2.7
(III) + $2H_2O$		−470.104 12[c]		

[a] Energies in atomic units. [b] Energy differences in kcal mol^{-1}. [c] Calculations performed by optimizing the N–OH_2 distance and the H_2O molecules orientation, but retaining the same geometrical parameters used for isolated ions (II) and (III). The two molecules resulted symmetrically disposed with respect to the molecular plane at a distance of 2.415 Å from nitrogen atom with the HOH plane bisecting the ONO angle.

In order to investigate solvation effects, 4-31G calculations have been performed on the clusters obtained by arranging two water molecules perpendicularly to the molecular plane of ions (II) and (III), at the optimized distance from the nitrogen atom. The results indicate that the hydrated cation (II) is *more* stable than hydrated cation (III) by 2.7 kcal mol^{-1}, showing that differential solvation effects can appreciably alter the intrinsic stability order of protonated methyl nitrate isomers.

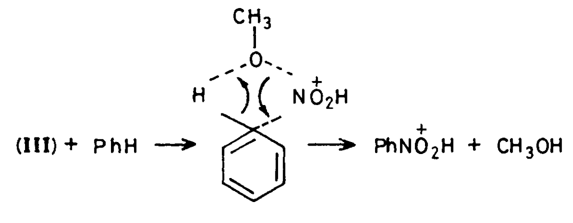
The result is of interest, suggesting that in the liquid phase, *e.g.* in H_2SO_4 solutions, protonation of methyl nitrate, and possibly of other alkyl nitrates, yields (II) as the most stable cation. Since the latter can be regarded as a nitronium ion solvated by methanol, consistent with the large N–O(1) distance, the substantial positive charge of N, and the large O(2)–N–O(3) angle (*ca.* 162°), it is hardly surprising that its attack on aromatic substrates displays mechanistic features typical of nitronium-ion reactivity.[1,11]

Passing to gas-phase nitration, the relative stability of (II) and (III) is relevant, in that their different structures may reflect on the reaction mechanism. Thus, ion (II) is expected to yield a classical σ complex (Wheland intermediate) [reactions (2)]



(2)

while other mechanisms, including a concerted process leading directly to *O*-protonated nitrobenzene (3), could conceivably



(3)

characterize attack by ion (III). In gaseous systems, containing a large excess of CH_3NO_3 over the arenes, and where exothermic proton-transfer reactions involving *n*-type nucleophiles are very fast,* equilibration of (II) and (III) can be expected to occur before attack on aromatic molecules.

The stability difference between (II) and (III) computed in this study is not sufficiently large to exclude the *kinetic* role of (II), especially in view of its preferential stabilization by association processes that could well occur in the gas phase. However, the reversal of the stability order of species (II) and (III) with respect to earlier theoretical results undoubtedly underlines the need for further experimental investigation of the role of process (3), the possibility of which had initially been suggested by the observation that 10^{-5} s after its formation the gaseous nitrated adduct from PhH is the *O*-protonated nitrobenzene.†

Acknowledgements

We are grateful to A. Guarino for interest in this work, and to the Italian National Research Council (C.N.R.) and Ministero della Pubblica Istruzione for financial support.

References

1 K. Schofield, 'Aromatic Nitration,' Cambridge University Press, Cambridge, 1980, p. 94, and references therein.
2 M. Attinà and F. Cacace, *J. Am. Chem. Soc.*, 1986, **108**, 318.

---

* These reactions, unless severely hindered by steric constraints, occur at the collision frequency in the gas phase, *cf.* ref. 12.

† The structure of the nitrated adduct has been established by collisionally induced dissociation (CID) mass spectrometry, using as a model ion, the adduct from the selective *O*-protonation of $PhNO_2$, *cf.* ref. 3.

3 M. Attinà, F. Cacace, and M. Yañez, *J. Am. Chem. Soc.*, 1987, **109**, 5092.
4 M. Attinà, F. Cacace, and G. de Petris, *Ang. Chem., Int. Ed. Engl.*, 1987, **26**, 1177.
5 M. Attinà and F. Cacace, *Gazz. Chim. Ital.*, 1988, **118**, 241.
6 Unless indicated otherwise, thermochemical data of gaseous ions are taken from S. G. Lias, J. F. Liebman, and R. D. Levin, *J. Phys. Chem. Ref. Data*, 1984, **13**, 695.
7 J. S. Binkley, R. A. Whiteside, R. Krishnan, R. Seeger, D. J. De Frees, H. B. Schlegel, S. Topiol, L. R. Kahn, and J. A. Pople, *QCPE*, 1981, **13**, 406.
8 W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, 1969, **51**, 2657.
9 R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, 1951, **54**, 724.
10 M. J. S. Dewar, M. Shanshal, and S. D. Worley, *J. Am. Chem. Soc.*, 1969, **91**, 3590.
11 D. W. Amos, D. A. Baines, and G. W. Flewett, *Tetrahedron Lett.*, 1973, 3191.
12 D. K. Bohme, in 'Interactions between Ions and Molecules,' ed. P. Ausloos, Plenum Press, New York, 1975, p. 489.

Received 2nd *October* 1987; *Paper* 7/00183E