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Protonated methyl nitrite. A theoretical investigation on the structure and stability of $(MeO–NO)H^+$ and the proton affinity of RO–NO (R = H, Me)

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Abstract

Ab initio calculations have been performed on the structure and stability of $(MeO–NO)H^+$ and the proton affinity (PA) of RO–NO (R = H, Me). At the MP4/6-311G**//MP2(FULL)/6-31G* level of theory, the ion–dipole adduct $MeOH–NO^+$ **1** is by far the most stable protomer. At the G2 level, the dissociation enthalpy into MeOH and NO^+ is computed as 25.3 kcal mol^{-1} and the PAs of MeO–NO and HO–NO amount to 187 and 188 kcal mol^{-1}, respectively. This finding marks a departure from the expected order and parallels the anomalous trend recently ascertained in the PAs of the strictly related $RO–NO_2$ (R = H, Me).

1. Introduction

The experimental [1–4] and theoretical [5,6] contributions to the recent debate concerning gaseous protonated $RO–NO_2$ (R = H, Me) convincingly support the conclusion that the most stable form of protonated $RO–NO_2$ is a complex between ROH and NO_2^+. More significantly, the proton affinity (PA) of nitric acid is accepted as larger than the PA of methyl nitrate by several kcal mol^{-1}. This counter-intuitive departure from the general observation that PA (MeO–X) > PA (HO–X) [1] may arise from different factors whose role is still open to question. They include the ion–dipole character of the ROH/NO_2^+ complexes and the binding energies (BE) of ROH and NO_2^+, the stability of the neutral $RO–NO_2$, and the RO–H and $RO–NO_2$ bond dissociation energies. As a continuation of our experimental and theoretical investigation of gaseous protonated X–NO (X = H, [8,9] OH [10], F [11]), we report here the results of a theoretical study on the structure and stability of protonated MeO–NO and the PA of RO–NO (R = H, Me). Our findings suggest that methyl nitrite is also *less basic* than nitrous acid and provide new evidence for the explanation of such anomalous trends in the PAs of gaseous molecules.

2. Computational details

The ab initio calculations were performed using a IBM RISC/6000 version of the GAUSSIAN 94 set

[1] All the thermochemical data are taken from Ref. [7].

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of programs [12]. The geometries of the investigated species were optimized at the MP2/6-31G* level of theory (used without frozen orbitals and denoted as MP2(FULL)) and their zero-point vibrational energies were obtained by the corresponding analytical frequencies. The relative stability of all the investigated molecules and ions was subsequently evaluated by MP4/6-311G** single-point calculations. In addition, we have calculated approximate QCISD(T)/6-311 + G(3df,2p) energies of selected species using the Gaussian-2(G2) procedure [13] routinely implemented in Gaussian 94. The 0 K total energies of the investigated species, G2 (0 K), were corrected to 298.15 K, G2 (298.15 K), by adding the rotational ($\frac{3}{2}RT$ or RT), translational ($\frac{3}{2}RT$) and vibrational contributions at this temperature. According to the G2 theory, the last term was calculated by standard statistical mechanics [14] formulas using the scaled (0.8929) HF/6-31G* vibrational frequencies. As a final, the 298.15 K energy differences were corrected to enthalpy differences by assuming ideal gas behaviour and adding the proper ΔnRT contribution.

3. Results and discussion

3.1. Structure and stability of MeO–NO

We have preliminarily investigated the structure and stability of different conformers of MeO–NO by optimizing their geometries at the MP2(FULL)/6-31G* level of theory. Fig. 1 shows the connectivity of the syn and the anti MeO–NO conformers which we have located and characterized as true minima on the surface. The full list of their optimized parameters is given in Table 1. The differences in the structures of the two conformers are fully consistent with the results of the numerous already available ab initio studies [15–17]. From Table 2, which collects the total energies of all the presently investigated molecules and ions, at the MP4/6-311G**//MP2(FULL)/6-31G* level of theory, the syn conformer of MeO–NO is more stable than the trans by 1.3 kcal mol^{-1}. This finding is in line with previous theoretical predictions [15–17] and with a recent experimental estimate of 749 ± 29 cal mol^{-1} [17] obtained from a variable temperature

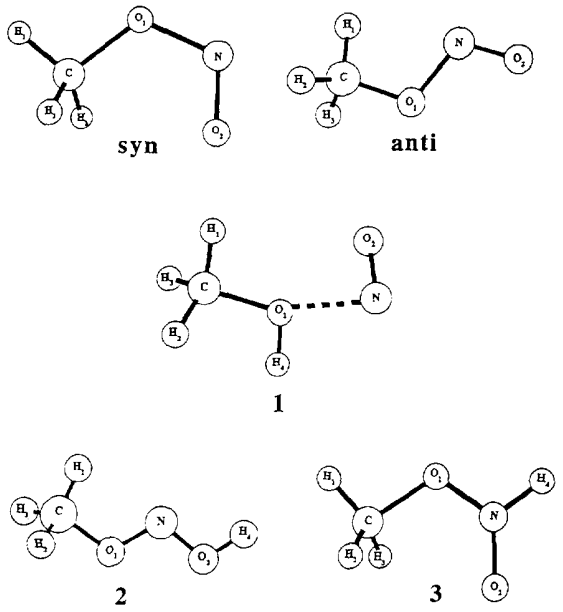

Fig. 1. Connectivity of the MeO–NO conformers and the (MeO–NO)H$^+$ ions.

study of the relative infrared intensities of ν(N–O_2) of the two conformers. Therefore, we will refer the calculation of the PA of MeO–NO (vide infra) to the more stable syn conformer.

3.2. Structure and stability of isomeric (MeO–NO)H$^+$

The available studies [18,19] on the gas phase chemistry of protonated methyl nitrite indicate that it serves as an excellent precursor of NO^+ complexes and suggest the formation of a weekly bound MeOH–NO^+ adduct as the most stable (MeO–NO)H$^+$ protomer. This experimental evidence is not inconsistent with a MINDO semiempirical prediction of MeOH–NO^+ as more stable than MeO–N–OH^+ by ca. 10 kcal mol^{-1} [20]. However, high-level of theory calculations are required to provide firmer support to the conclusion from the experiments. At the best of our knowledge, such detailed calculations have not yet been reported. As an extension of our previous interest in the strictly related protonated HO–NO [10], we decided to perform post-SCF ab initio calculations, up to the G2 level of theory, on the structure and stability of protonated methyl nitrite.

Table 1
MP2(FULL)/6-31G * optimized parameters of MeO–NO and $(MeO–NO)H^+$. The symmetry is given in parentheses and the labeling of the atoms is detailed in Fig. 1

Species	Bond length (Å)	Bond angle (°)	Dihedral angle (°)
syn-MeO–NO (C_s)	$C–O_1$: 1.441 $O_1–N$: 1.393 $N–O_2$: 1.210 $C–H_1$: 1.087 $C–H_2$: 1.092	$C–O_1–N$: 114.6 $O_1–N–O_2$: 114.1 $H_1–C–O_1$: 104.0 $H_2–C–O_1$: 110.7	$H_2–C–O_1–H_1$: 119.3
anti-MeO–NO (C_s)	$C–O_1$: 1.438 $O_1–N$: 1.419 $N–O_2$: 1.198 $C–H_1$: 1.092 $C–H_2$: 1.091	$C–O_1–N$: 109.1 $O_1–N–O_2$: 110.7 $H_1–C–O_1$: 109.5 $H_2–C–O_1$: 108.4	$H_2–C–O_1–H_1$: 120.2
$MeOH–NO^+$ (1, C_1)	$C–O_1$: 1.457 $O_1–N$: 1.986 $N–O_2$: 1.122 $C–H_1$: 1.091 $C–H_2$: 1.090 $C–H_3$: 1.090 $O_1–H_4$: 0.981	$C–O_1–N$: 116.8 $O_1–N–O_2$: 108.3 $H_1–C–O_1$: 106.3 $H_2–C–O_1$: 111.0 $H_3–C–O_1$: 107.9 $H_4–O_1–N$: 109.4	$H_1–C–O_1–H_4$: 168.0 $H_2–C–O_1–H_4$: 47.2 $H_3–C–O_1–H_4$: 284.7 $H_4–O_1–N–O_2$: 200.9 $C–O_1–N–O_2$: 328.1
$MeO–N–OH^+$ (2, C_s)	$C–O_1$: 1.507 $O_1–N$: 1.260 $N–O_2$: 1.291 $C–H_1$: 1.087 $C–H_2$: 1.087 $O_2–H_4$: 0.994	$C–O_1–N$: 113.0 $O_1–N–O_2$: 107.6 $H_1–C–O_1$: 108.1 $H_2–C–O_1$: 103.7 $N–O_2–H_4$: 105.5	$H_2–C–O_1–H_1$: 121.1
$MeO–NH–O^+$ (3, C_s)	$C–O_1$: 1.499 $O_1–N$: 1.284 $N–O_2$: 1.210 $C–H_1$: 1.085 $C–H_2$: 1.089 $N–H_4$: 1.044	$C–O_1–N$: 114.7 $O_1–N–O_2$: 126.3 $H_1–C–O_1$: 101.8 $H_2–C–O_1$: 107.7 $H_4–N–O_1$: 111.1	$H_2–C–O_1–H_1$: 119.2

Table 2
Total energies (atomic units) and zero-point energy (ZPE, kcal mol^{-1}) of the investigated molecules and ions

Species	MP2(FULL)/6-31G *	MP4/6-311G * * [a]	G2 (298.15 K)	ZPE [b]
syn-MeO–NO	−244.33911	−244.51060	−244.67182	31.2
anti-MeO–NO	−244.33520	−244.50789		30.8
$MeOH–NO^+$ (1)	−244.65061	−244.83965	−244.96743	37.6
$MeO–N–OH^+$ (2)	−244.61263	−244.79755		39.4
$MeO–NH–O^+$ (3)	−244.61770	−244.79619		40.0
HO–NO	−205.17335	−205.30879	−205.45860	12.6
$H_2O–NO^+$	−205.48882	−205.64044	−205.75581	18.5
MeOH	−115.35330	−115.46848	−115.53154	33.0
H_2O	−76.19924	−76.27607	−76.32921	13.5
NO^+	−129.24817	−129.32641	−129.39652	3.0

[a] At the MP2(FULL)/6-31G * optimized geometry and including ZPE.
[b] MP2(FULL)/6-31G *.

Protonation of MeO–NO could in principle occur at three different centres. Fig. 1 and Table 1 show the MP2(FULL)/6-31G* optimized geometries of the most stable conformers of $MeOH–NO^+$, MeO–N–OH^+ and MeO–$NH–O^+$. These ions, henceforth indicated as **1**, **2**, and **3**, respectively, were ascertained to be true minima on the potential energy surface. As the most significant result, protonation at O_1 strongly affects the geometrical parameters of MeO–NO. The obtained $MeOH–NO^+$ ion **1** closely resembles an ion–dipole complex between MeOH and NO^+. The bond distance computed between the two moieties, whose structural features are not substantially different from those computed for the free MeOH and NO^+, is as large as 1.986 Å. In addition, from Table 2, ion **1** is by far the most stable among the $(MeO–NO)H^+$ protomers. The MP4/6-311G** energy difference with the oxygen-protonated isomer **2** is computed as large as 28.2 kcal mol^{-1}. The latter species is practically degenerate with the nitrogen-protonated isomer **3**, less stable than **2** by only 1.5 kcal mol^{-1}. Thus, our ab initio calculations convincingly support the suggestion, based on experimental evidence, of the formation in the gas phase of $MeOH–NO^+$ as the most stable $(MeO–NO)H^+$ protomer. The comparison with our previous results concerning gaseous protonated HO–NO [10] provides a coherent description of the structure and the relative stability of isomeric $(RO–NO)H^+$. Thus, at the MP4/6-311G** level of theory, the $H_2O–NO^+$ ion–dipole complex was found to be significantly more stable than the almost degenerate $HO–NH–O^+$ and $HO–N–OH^+$ protomers. In addition, consistent with the theoretical prediction, it was the only isomer successfully detected and characterized by structurally diagnostic mass spectrometric techniques [10].

3.3. The PA of RO–NO (R = H, Me)

Having ascertained the significantly larger stability of the $MeOH–NO^+$ protomer we have subsequently calculated the PA of methyl nitrite, i.e. the minus enthalpy change of the reaction

$$MeO–NO + H^+ \rightarrow MeOH–NO^+ \quad (1)$$

and the stability of $MeOH–NO^+$ with respect to the dissociation

$$MeOH–NO^+ \rightarrow MeOH + NO^+. \quad (2)$$

To this end, we performed an accurate evaluation of the total energies of $MeOH–NO^+$, the syn conformer of MeO–NO, and MeOH and NO^+. We have selected the G2 computational procedure [13], amply recognized as able to reproduce or predict unknown thermochemical data (atomization energies, ionization potentials, electron affinities, and proton affinities) of compounds containing first- and second-row atoms with a target accuracy of ± 2 kcal mol^{-1}. Thus, from the G2 (298.15 K) energies reported in Table 2, the PA of MeO–NO is evaluated as $-\Delta H_1 = 187 \pm 2$ kcal mol^{-1}. The only experimental estimate currently available, 190.5 ± 1.0 kcal mol^{-1}, has been so far obtained by Farid and McMahon [18] by ion cyclotron resonance (ICR) spectrometry. It must be corrected to 193.1 ± 1.0 kcal mol^{-1} to achieve consistency with the current value of 204.0 kcal mol^{-1} for the PA of the reference NH_3. The appreciable discrepancy between the theoretical and the experimental value does not reflect an unexpected and unusual failing of the G2 procedure in predicting the PA of a simple molecule. Rather, it likely arises from the large combined uncertainties associated with the ICR bracketing technique employed for the experimental determination [18]. This conclusion is supported by the following considerations.

If one compares the theoretical and the experimental values of the PA of the strictly related nitrous acid, HO–NO, the agreement is excellent. Thus, upgrading our previous G1 calculations [10], we have presently evaluated the G2 (298.15 K) PA of HO–NO, with formation of $H_2O–NO^+$, as 188 ± 2 kcal mol^{-1}. The experimental value of 187.7 kcal mol^{-1} is obtained combining the enthalpy of formation of HO–NO, -19 kcal mol^{-1}, H^+, 365.7 kcal mol^{-1}, and $H_2O–NO^+$, so far obtained by Kebarle and coworkers [21] as 159 kcal mol^{-1} from the direct measurement of the enthalpy change of the reaction

$$H_2O–NO^+ \rightarrow H_2O + NO^+ \quad (3)$$

evaluated as $\Delta H_3 = 18.5 \pm 1.5$ kcal mol^{-1}. This value is also in good agreement, within combined uncertainties, with the 19.5 kcal mol^{-1} value obtained using the G2 (298.15) energies of $H_2O–NO^+$, H_2O, and NO^+, reported in Table 2. In addition, the G2 (298.15 K) enthalpy change of reaction (2) is

evaluated as $\Delta H_2 = 25.3$ kcal mol^{-1}, which is significantly lower than the 31.8 kcal mol^{-1} value derived from the experimental PA of MeO–NO [19] and again suggests an inaccuracy in the latter determination.

At the G2 (298.15 K) level of theory, the PA of HO–NO is *larger* than the PA of MeO–NO. This finding parallels the currently accepted order in the PAs of the strictly related RO–NO_2, i.e. PA (HO–NO_2) > PA (MeO–NO_2) [1–6]. However, the difference in the PAs of RO–NO_2, experimentally determined as 4.0 ± 1.2 kcal mol^{-1} [4], is larger than the presently computed difference in the PAs of RO–NO, 1 kcal mol^{-1}. In addition, the latter value falls below the uncertainty expected in the G2 calculations. However, the following considerations provide independent theoretical support for PA (HO–NO) > PA (MeO–NO) and may contribute to enlighten the factors which determine such anomalous trends in the PAs of gaseous RO–NO and RO–NO_2 (R = H, Me).

The simple explanation offered by Lee and Rice [6] for the unexpected trend in the PAs of HO–NO_2 and MeO–NO_2 is based on a correlation between the PA of RO–NO_2 and the difference between the RO–H and RO–NO_2 bond energies. Thus, they focus on the isodesmic reaction

$$\text{HO–NO}_2 + \text{MeOH} \rightarrow \text{H}_2\text{O} + \text{MeO–NO}_2 \qquad (4)$$

and, based on a simple thermochemical cycle, they arrive to the equation

$$\Delta H_4 = \text{PA(MeO–NO}_2\text{)} - \text{PA(HO–NO}_2\text{)} + \text{BE(H}_2\text{O/NO}_2^+\text{)} - \text{BE(MeOH/NO}_2^+\text{)} \qquad (5)$$

and calculate ΔH_4 as -6.9 kcal mol^{-1} (to be compared with an experimental value of -8.1 kcal mol^{-1}). Since the difference in the calculated BEs is only -2.3 kcal mol^{-1}, Eq. (5) furnishes a -4.6 kcal mol^{-1} difference in the PAs of MeO–NO_2 and HO–NO_2, which is consistent with a direct evaluation of -5.6 kcal mol^{-1}. Based on these findings, we have used the same approach to predict the difference between the PA of HO–NO and MeO–NO. Thus, we have evaluated the G2 (298.15 K) enthalpy change of the isodesmic reaction

$$\text{HO–NO} + \text{MeOH} \rightarrow \text{H}_2\text{O} + \text{MeO–NO} \qquad (6)$$

as $\Delta H_6 = -6.8$ kcal mol^{-1}. The favourable comparison with the experimental value, -6.5 kcal mol^{-1}, provides additional reassuring evidence for the accuracy of our G2 calculations. Using the equation

$$\Delta H_6 = \text{PA(MeO–NO)} - \text{PA(HO–NO)} + \text{BE(H}_2\text{O/NO}^+\text{)} - \text{BE(MeOH/NO}^+\text{)} \qquad (7)$$

and the above discussed BEs of H_2O and MeOH to NO^+, we obtain a difference of -1 kcal mol^{-1} in the PAs of MeO–NO and HO–NO. This is fully consistent with the value obtained from the direct calculation of the PAs and reinforces the expectation on the validity of equations like (5) and (7) in predicting unusual trends in the PAs of gaseous molecules.

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