

# The Structures of the [M-H] Anions of the CH<sub>3</sub>NO<sub>2</sub> Isomers Nitromethane and Methyl Nitrite

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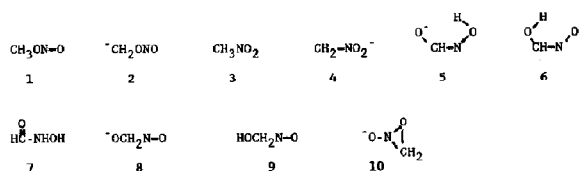
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The 60-u anion observed in the ion/molecule chemistry of methyl nitrite is shown to have the structure O=NCH<sub>2</sub>O<sup>-</sup>, and not that of the expected deprotonation product <sup>-</sup>CH<sub>2</sub>ONO, by the use of mass-analyzed ion kinetic energy spectrometry, ion/molecule reactivity, and ab initio calculations. (*J Am Soc Mass Spectrom* 1990, 1, 295-300)

Methyl nitrite **1** is commonly used in chemical ionization mass spectrometry (CIMS) and ion-molecule reaction studies as a source of methoxide, which is generated by thermal electron dissociative attachment [1, 2]. Further reaction of methoxide with **1** yields an [M-H] anion at 60 u. This ion has been represented [3] as **2**, a dipole-stabilized carbanion [4]. On the basis of the acidities of methanol [5] and other known dipole-stabilized anions [4], however, it seemed likely to us that the reaction of methoxide with **1** to form **2** should be considerably endothermic. If anion **2** is envisioned in the geometry that is most favorable for most dipole-stabilized anions, with the lone pair of the carbanion *syn* to a transoid nitrosyl group [4], then there is a lone pair on the nitrosyl group proximate to the carbanion. Such a structure should be destabilized with respect to a carbonyl-stabilized carbanion. There are two possibilities that may explain the presence of a 60-u anion. **1** might be rearranging in the vacuum system to the isomeric nitromethane **3**, with deprotonation by methoxide now 24 kcal/mol exothermic [5], or the [M-H]<sup>-</sup> ion may not be the straightforward deprotonation product of **1** but rather some rearranged structure.

There are other possible isomers of the formula CH<sub>2</sub>NO<sub>2</sub><sup>-</sup> that could reasonably be accessed in such a rearrangement, such as **5** and **6** from neutral formyl hydroxamate **7**, or nitrosomethoxide **8** from the (unstable) nitrosomethanol **9**. The barrier for the rearrangement of methyl nitrite to nitromethane has been shown to be 53 kcal/mol [6] and calculated at a very high level of CI to be 67 kcal/mol [7]. This implies that the rearrangement probably does not occur for the neutral species, but rather occurs during the course of the ion-molecule chemistry. Therefore, the structures of the 60-u anions from **1** and several isomers have been examined by mass-analyzed ion kinetic energy spectrometry (MIKES) experiments, gas-phase

ion-molecule reactions, and molecular orbital (MO) calculations. The results indicate that **8** is the structure of the 60-u anion produced from **1**.



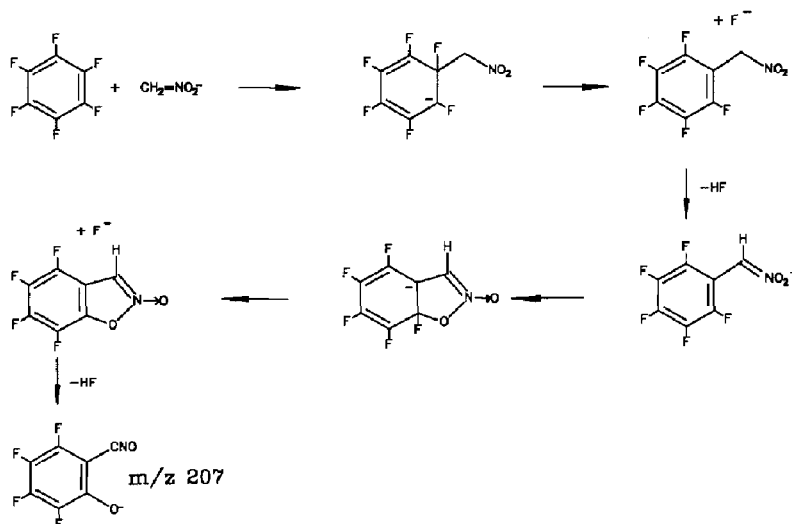
## Experimental

The negative chemical ionization (NCI) mass spectra and MIKES were obtained on a VG ZAB-EQ instrument with reverse geometry controlled by a VG 11-250J computer system. Ammonia was used as the CI gas for nitromethane experiments, either methane or nitrogen was used as the CI gas for methyl nitrite experiments, and methane was used as the CI gas for formyl hydroxamate experiments. Typical CI gas pressure was 1 × 10<sup>-4</sup> to 5 × 10<sup>-4</sup> torr. For MIKES with collision-induced dissociation (CID), helium was used at 1-5 μtorr, giving 50-80% reduction of the parent peak. All gases were reagent grade.

The ion-molecule work was performed on a home-built pulsed ion cyclotron resonance (ICR) mass spectrometer run by a dedicated IBM PC [8]. A 1-in. cubic cell and 1 T field strength were used. Sample pressures of about 1-5 μtorr were typical. Data were obtained by the rapid scan technique [9]. Nitrogen trifluoride (NF<sub>3</sub>), which produces fluoride upon electron impact, was used to generate the [M-H] anion of MeNO<sub>2</sub>.

Methyl nitrite was synthesized *in situ* by mixing isoamyl nitrite and methanol [2]. The existence of methyl nitrite in the vapor phase above this mixture was confirmed by Fourier transform infrared (FT IR) analysis of the headspace gas; the spectrum obtained agreed with the published spectrum of methyl nitrite [10]. In addition, on the basis of vapor pressure data [11], one would expect the vapor above an

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Scheme I

employing the 6-31+G//6-31+G basis set [24] have been done on a number of the anions of interest here and their corresponding conjugate acids. Correlation energy will probably make some difference in the relative energies of these structures, owing to the appreciably different bonding types involved. At an uncertainty level of  $\sim 5$  kcal/mol, however, we believe that the pre-Hartree-Fock level calculations given here are sufficient to guide our interpretation of the energetics. As shown in Tables 5 and 6, the calculations indicate that deprotonation of methyl nitrite by methoxide to form **2** is 25 kcal/mol endothermic. This calculated acidity is close to that observed experimentally for  $\text{CH}_3\text{OCH}_3$  [25] at 407 kcal/mol. In both  $\text{CH}_3\text{OCH}_2^-$  and **2**, the carbanion is attached to an oxygen atom, so polar effects should be comparable. There is no possibility of any extra "dipolar stabilization" in  $\text{CH}_3\text{OCH}_2^-$ , however, so it is unlikely that there is any dipolar stabilization involved in **2**. In absolute energies, carbanion **2** is the least stable; then methyl nitronate **4** and nitrosomethoxide **8** are comparable and 51 kcal/mol more stable than **2**. Finally, **6** is 30 kcal/mol more stable than **4** and **8**. For the conjugate acids, the calculations place methyl nitrite at

$-1.8$  kcal/mol (more stable) from nitromethane, while experimentally it is *less* stable by  $+2.0$  kcal/mol [26]. The calculated acidity of nitrosomethanol **9** agrees well with the observed bracketed acidity of the 60-u anion from methyl nitrite, though we note that no zero-point energy correction has been applied to convert the calculated  $\Delta E$  to  $\Delta H$  [24]. The calculations thus support **8** as the structure of the 60-u anion from **1**.

One further line of information arises from linear free energy relationships. The acidity of  $\text{HOCH}_2\text{N}=\text{O}$  as an alcohol can be predicted from the  $\rho_1$  for the gas-phase acidities of  $\text{RCH}_2\text{OH}$  [27]. Using a revised value of  $\rho_1$  of 20.3 kcal/mol [5] and  $\sigma_1(\text{NO}) = 0.37$  [28], a  $\Delta H_{\text{acid}}$  of 364.5 kcal/mol is calculated, quite close to the observed acidity of  $368 \pm 4$  kcal/mol for the 60-u anion from **1** and the calculated  $\Delta E_{\text{acid}}$  of 364.8 kcal/mol.

On the basis of all these lines of argument, we conclude that the 60-u anion from **1** has structure **8**. There are two reasonable mechanisms for formation of **8**. As shown in Scheme II, path A involves initial formation of **2** in an ion-molecule complex followed by unimolecular rearrangement through a cyclic intermediate **10**, which breaks the ring N—O bond to

Table 5. Ab initio calculations on  $[\text{M} - \text{H}]$  anions from isomers of  $\text{CH}_3\text{NO}_2$ 

Neutral Species		$\Delta\Delta E_i^a$	Anion		$\Delta\Delta E_i^a$	$\Delta E_{\text{acid}}^b$	$\Delta H_{\text{acid}}$ (exptl)
$\text{CH}_3\text{NO}_2$	<b>3</b>	(0.0)	$\text{CH}_2 = \text{NO}_2^-$	<b>4</b>	(0.0)	351.8	356.4 <sup>c</sup>
$\text{CH}_3\text{ONO}$	<b>1</b>	-1.8	$^-\text{CH}_2\text{ONO}$	<b>2</b>	51.3	405.0	
$\text{HOCH}_2\text{NO}$	<b>9</b>	-13.1	$^-\text{OCH}_2\text{NO}$	<b>8</b>	-0.2	364.7	(368) <sup>d</sup>
$\text{OCHNHOH}$	<b>7</b>	-46.8	$^-\text{OCH} = \text{NOH}$	<b>6</b>	-30.5	368.1	

<sup>a</sup> 6-31+G//6-31+G, Gaussian 86. All values are kcal/mol relative to the first compound in the column.

<sup>b</sup>  $\Delta E(\text{anion}) - \Delta E(\text{neutral}) + 365.7$ .

<sup>c</sup> Ref 5.

<sup>d</sup> This work.

**Table 6.** Calculated thermochemistry for possible 60-u anion structures

Reaction	$\Delta E_{\text{rxn}}^{\circ}$
MeO <sup>-</sup> + MeONO → MeOH + <sup>-</sup> CH <sub>2</sub> ON=O (2)	+ 25
MeOH + CH <sub>2</sub> =NO <sub>2</sub> <sup>-</sup> (4)	- 26
MeOH + <sup>-</sup> OCH <sub>2</sub> N=O (8)	- 26
MeOH + <sup>-</sup> OCH=NOH (5)	- 57

\* 6-31+G//6-31+G, Gaussian 86, kcal/mol [24].

give the final oxyanion 8. It might be argued that 10 could just as easily cleave a C—O bond to open to 4, of comparable stability to 8. To examine this point, we have used semiempirical MO calculations to explore the reaction pathways postulated here. These were employed because of the prohibitive cost of investigating reaction surfaces of this complexity with ab initio calculations. Most existing semiempirical methods are notorious for not obtaining reasonable energies when dealing with N—O bonds: The MNDO method\* [29] calculates 1 to be -40 kcal/mol (more stable) from 3 (experimental: +2 kcal/mol less stable), whereas AM1 [30], an improved version of MNDO, results in 1 being -22 kcal/mol from 3. These methods are clearly not appropriate to the present problem. The recent PM3 Hamiltonian [31], however, places 1 at +6.8 kcal/mol from 3, in the right direction and of the right order of magnitude. We have thus used this newer method\*\* to examine various reasonable pathways on the reaction surface. For the isomerization of <sup>-</sup>CH<sub>2</sub>ONO [ $\Delta H_f(\text{PM3}) = -10.7$  kcal/mol] to <sup>-</sup>OCH<sub>2</sub>NO [ $\Delta H_f(\text{PM3}) = -38.7$  kcal/mol], a barrier of 7.6 kcal/mol is found. The geometry of the transition state is roughly that of 10, but with the nitrogen of the NO group 2.0 Å from both the C and the O in the nominal three-member ring. This is not an exact transition state (based on one negative frequency), because the C—O—N bond angle in 2 was simply reduced until a maximum in energy was found, at 89.5°. Structure 10 at the PM3 level is not an intermediate; no stable point could be found on the reaction surface for such a cyclic structure, using any reasonable bond lengths. No simple transition state for the isomerization of 2

to 4 could be found, either, but, on the basis of an extensive survey of geometries, we believe that any pathway must involve a minimum  $\Delta H^{\ddagger} > 50$  kcal/mol. This is consistent with the need to break a C—O bond, costing energy, before the CH<sub>2</sub> group can rotate, to stabilize the charge by resonance delocalization. For the isoelectronic neutral system, NH<sub>2</sub>ONO rearranging to NH<sub>2</sub>NO<sub>2</sub>, a barrier of 22 kcal/mol has been calculated at the MCSCF/6-31G\*\*//4-31G level [32].

Another more likely mechanistic possibility is path B in Scheme II, an E<sub>2</sub>-type elimination in the ion-molecule complex, followed by nucleophilic addition of NO<sup>-</sup> to the carbonyl group. The net reaction to free NO<sup>-</sup> and formaldehyde is estimated to be exothermic by -3.8 kcal/mol [5], but if the NO<sup>-</sup> bonds to the formaldehyde to give 8, the reaction enthalpy is ~-26 kcal/mol. In such a complex, there is no simple pathway for the intermediates formaldehyde and NO<sup>-</sup> to go to CH<sub>2</sub>=NO<sub>2</sub><sup>-</sup>. The E<sub>2</sub> pathway B seems more likely than the rearrangement pathway A for energetic reasons also. On the basis of ab initio calculations plus a reasonable estimate of the complexation energy of 15 kcal/mol for MeOH plus <sup>-</sup>CH<sub>2</sub>ONO, the ion-molecule complex for the nonrearranged MeOH...<sup>-</sup>CH<sub>2</sub>ONO has been determined to be ~10 kcal/mol endothermic relative to the reactants methoxide and methyl nitrite. This energy barrier would have to be overcome by rearrangement of the carbanion during proton transfer, which seems unlikely. In contrast, the E<sub>2</sub> pathway should be mechanistically facile and result in a product ion-molecule complex considerably more stable than the reactants. For MeOH...<sup>-</sup>OCH<sub>2</sub>NO, we estimate that the complex is ~45 kcal/mol more stable than the reactants, thus providing the driving force for the reaction. All points on path B should be exothermic relative to the reactants.

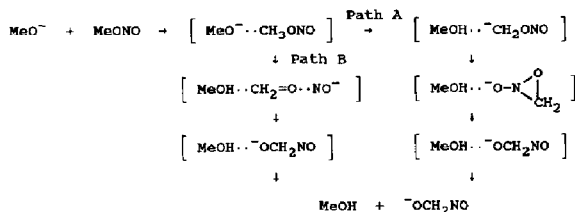
## Conclusions

Different fragmentation and reactivity pathways indicate that the structures of the [M-H] anions from nitromethane and methyl nitrite are not the same. For the [M-H]<sup>-</sup> ion from methyl nitrite, the structures outlined in Table 6 have been considered. All but 8 have been ruled out because of calculated energetics and reactivity and fragmentation experiments. No distinctive reaction of the alkoxide structure expected for 8 was found, other than its apparent proton affinity.

These results raise a serious question with regard to the practice of measuring approximate acidities by the bracketing method. Were such a test applied here, the acidity obtained for methyl nitrite would be wrong by at least 25 kcal/mol. It is imperative that the structure of anions produced in this fashion be verified by the various reaction techniques available.

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Scheme II

\*Program No. QCMPO4, Quantum Chemistry Program Exchange, Indiana University, Bloomington, IN 47405, with extensive modifications by the present authors for more efficient PC operation. See also ref. 29.

\*\*Mopac 5.0, Program No. QCPE 455, Quantum Chemistry Program Exchange, Indiana University, Bloomington, IN 47405.

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