Methyl-Cation Shuttles: Xe- and N₂-Catalyzed Isomerization of CH₃NO₂⁺ to CH₃ONO⁺
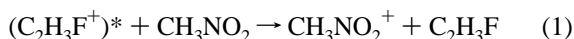
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The isomerization of protonated molecules can be catalyzed by molecules which transport or "shuttle" the proton from a high-energy site to a lower-energy site on the protonated molecule.[2] Such catalysis recently has been characterized in the gas phase for the isomerization of protonated CO,[3] CN,[4] N₂O,[5] and SiO[6] in which the proton is transported by H₂, CO and CO₂, and NO and CO as well as N₂ and SO, respectively. Proton-transport catalysis has also been invoked in the isomerization of anions in the gas phase[7] and is fundamental to reactions in solution such as acid- and base-catalyzed pyrolysis of amides and keto–enol isomerization of carbonyl compounds.[8] Here we report what we believe to be the first observation of an analogous catalysis involving the transport of a methyl cation, viz. the isomerization of CH₃NO₂⁺ to CH₃ONO⁺ which has a barrier of 14.8 kcal mol⁻¹ (see Figure 1) catalyzed by Xe and by N₂. The catalysis was achieved within the reaction region of a selected-ion flow tube (SIFT) mass spectrometer,[10] and the two isomers were distinguished using multi-collision induced dissociation (CID).[11]

CH₃NO₂⁺ and CH₃ONO⁺ ions were produced in separate experiments upstream in flowing He carrier gas at 0.35 ± 0.01 Torr by electron transfer from nitromethane (IE = 11.02 ± 0.04 eV)[12] and methylnitrite (IE = 10.38 ± 0.03 eV)[12] to $C_2H_3F^+$ according to reactions 1 and 2, respectively.

$$(C_2H_3F^+)^* + CH_3NO_2 \rightarrow CH_3NO_2^+ + C_2H_3F \quad (1)$$

$$C_2H_3F^+ + CH_3ONO \rightarrow CH_3ONO^+ + C_2H_3F \quad (2)$$

$C_2H_3F^+$ ions were produced by electron impact on vinyl fluoride (IE = 10.363 ± 0.015 eV)[12] in a conventional ion source at electron energies of 40 eV and 30 eV, respectively, and mass-selected and injected upstream into the flow tube. The upstream addition of nitromethane and methylnitrite was minimized to avoid secondary association reactions. The CH₃-NO₂⁺ and CH₃ONO⁺ ions were allowed to thermalize with ca.

Figure 1. Potential-energy diagram for the isomerization and fragmentation of the nitromethane and methylnitrite ions based on the results of a threshold photoelectron–photoion coincident (TPEPICO) mass-spectrometer study.[9a] Not shown are the dissociations of CH₃ONO⁺ into CH₃NO⁺ + O, NO⁺ + CH₂OH, and CH₂OH⁺ + NO which should be kinetically unfavorable.[9b,c]
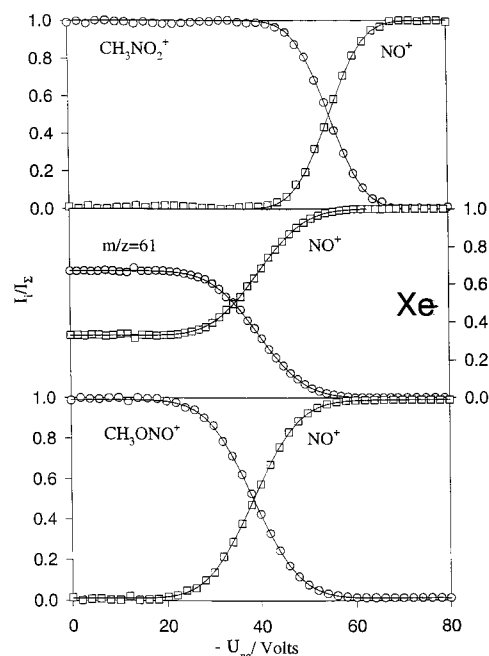
Figure 2. Multicollision CID spectra for CH₃NO₂⁺ derived from nitromethane (top), for the *m/z* 61 ion derived from the reaction of CH₃NO₂⁺ with ca. 10¹⁹ molecules s⁻¹ of Xe (middle), and for CH₃-ONO⁺ derived from methylnitrite (bottom). The NO⁺ initially present in the experiment with Xe (middle) can be attributed to the dissociation of CH₃ONO⁺ into NO⁺ + CH₃O after isomerization since the shuttle reaction can produce internally excited (CH₃ONO⁺)* if it is fast compared to collisional thermalization with He.

5×10^5 He collisions at 294 ± 3 K before being subjected to multi-collision CID downstream at the sampling orifice. The potential of the sampling nose cone (U_{nc}) was varied from 0 to -80 V. Figure 2 shows that NO⁺ is the predominant product ion (>99%) in the dissociation of both isomers over the voltage range employed, but that the measured onsets for the two dissociation reactions 3 and 4 are distinctly different,

$$CH_3NO_2^+ + He \rightarrow NO^+ + CH_3O + He \quad (3)$$

$$CH_3ONO^+ + He \rightarrow NO^+ + CH_3O + He \quad (4)$$

viz. 51 and 29 V, respectively. The measured ratio of onset voltages, 1.8, is comparable to the ratio of the energies required for dissociation, 14.8 kcal mol⁻¹/10.4 kcal mol⁻¹ = 1.4.

Figure 2 also shows that the multi-collision CID spectrum of the *m/z* 61 ion produced when Xe is added to CH₃NO₂⁺

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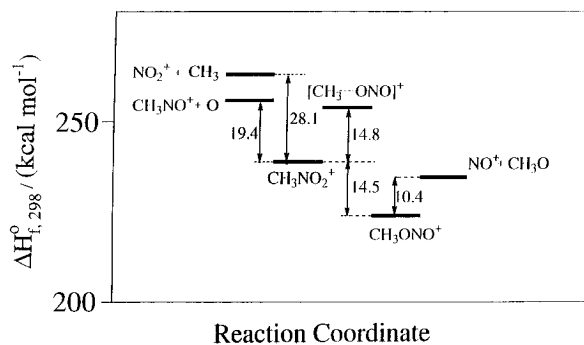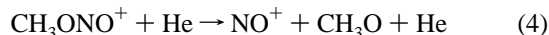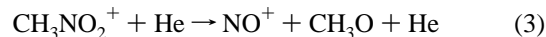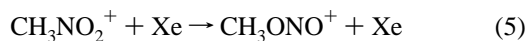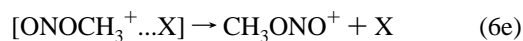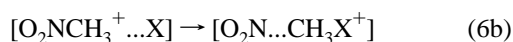
generated upstream by reaction 1 is identical in onset to that for the CH_3ONO^+ ion produced by reaction 2, viz. the onset for NO^+ production is shifted to 29 V. In other words, the addition of Xe has resulted in the following isomerization:

$$CH_3NO_2^+ + Xe \rightarrow CH_3ONO^+ + Xe \qquad (5)$$

A similar result was obtained with N_2, but CO had no measurable effect.

The mechanism which we propose for the observed isomerization of $CH_3NO_2^+$ to CH_3ONO^+, namely

$$CH_3NO_2^+ + X \rightarrow [O_2NCH_3^+...X] \qquad (6a)$$

$$[O_2NCH_3^+...X] \rightarrow [O_2N...CH_3X^+] \qquad (6b)$$

$$[O_2N...CH_3X^+] \rightarrow [ONO...CH_3X^+] \qquad (6c)$$

$$[ONO...CH_3X^+] \rightarrow [ONOCH_3^+...X] \qquad (6d)$$

$$[ONOCH_3^+...X] \rightarrow CH_3ONO^+ + X \qquad (6e)$$
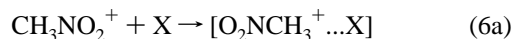
is analogous to that which has been invoked previously for the observed "proton shuttle" isomerization of protonated molecules.[2] In the above mechanism, the species X acts as a "methyl-cation shuttle" by allowing the migration of CH_3^+ from the N atom to the adjacent O atom. If the methyl-cation affinity (MCA) of X is intermediate between MCA($\underline{N}O_2$) and MCA-($\underline{O}NO$), then both of the CH_3^+ transfer steps $\overline{6}b$ and 6d will be exothermic, ostensibly permitting an efficient overall reaction. The methyl-cation affinities MCA($\underline{N}O_2$) = 33 kcal mol^{-1} and MCA($\underline{O}NO$) = 46 kcal mol^{-1} can be obtained from existing thermochemical data;[12] thus the requirement for an efficient methyl-cation shuttle reaction (6) is that 33 kcal mol^{-1} < MCA-(X) < 46 kcal mol^{-1}. This criterion is met by N_2 (MCA = 44 kcal mol^{-1})[13] and, within experimental uncertainty, by Xe (MCA = 46.5 kcal mol^{-1})[13] but is clearly not met by CO (MCA = 79 kcal mol^{-1}).[12] It follows, therefore, that Xe and N_2 are capable of effecting the isomerization of $CH_3NO_2^+$ to CH_3ONO^+ as observed, while the "back-transfer" step (6d) is very endothermic for CO which cannot act as a shuttle reagent in this system.

Our observation of the isomerization reaction (6) involving Xe and N_2 suggests that this mode of catalysis, which has hitherto been reported in the gas phase only for isomerization of protonated species, may be rather general. Attempts have begun to compute details of the potential-energy surface for reaction 6, and we shall extend our experimental study of such reactions to include other possible shuttle atoms and molecules.

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