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LETTERS

Direct Observation of Spin Forbidden Proton-Transfer Reactions: $^3NO^- + HA \rightarrow {}^1HNO + A^-$

Gordon A. Janaway and John I. Brauman*

Department of Chemistry Stanford University, Stanford, California 94305-5080

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The reaction $^3NO^- + HA \rightarrow {}^1HNO + A^-$ requires a spin conversion for transformation of ground-state reactants to ground-state products. The proton-transfer efficiencies of $^3NO^-$ with several acids (CF_3CO_2H, HCl, CH_3CO_2H, H_2S, $(CH_3)_3CSH$, CH_3NO_2, CH_3SH, $CF_3(CH_3)CHOH$, CFH_2CH_2OH, and CH_3OH) in the gas phase have been measured using Fourier transform ion cyclotron resonance (FT-ICR) spectrometry. Proton-transfer efficiency was found to vary dramatically with both the structure and acidity of HA. This variation is attributed to different lifetimes of the collision complex.

Exothermic proton-transfer reactions between anions and neutral acids generally occur at close to the encounter rate,[1] both in solution and in the gas phase, due in part to the presence of a low-energy transition state stabilized by considerable hydrogen bonding character. When a significant barrier to reaction does exist, as, for example, in proton transfers involving resonance stabilized anions, reaction rates are consequently reduced.[2,3]

We report a set of reactions in the gas phase in which the proton-transfer rate is measurable but slow because they require a spin change in order to convert to products.[4−9] These reactions have very different kinetic constraints than reactions with conventional energy barriers. The results reported here demonstrate the importance of structure-dependent dynamics as well as energetics in determining the overall consequences of spin conversion.

Proton-transfer reactions of nitric oxide anion, $^3NO^-$, with most simple acids, eq 1, require a spin conversion.[10−13] We previously reported[14] the isolation and characterization of $FH \bullet {}^3NO^-$, an intermediate in the gas-phase proton-transfer reaction of $^3NO^-$ with HF. The reactivity of this intermediate strongly suggested that spin conversion within the ion−molecule complex occurs with high efficiency.

$$^3NO^- + HA \rightarrow {}^1HNO + A^- \qquad (1)$$

In the work reported here, isolated $^3NO^-$ ion was allowed to react directly with a series of acids, and the efficiency for proton transfer was measured for each acid. The proton transfer rates vary dramatically even for similarly acidic species, in strong contrast to those of most spin-allowed proton-transfer reactions. Specifically, the strong acid H_2S (hydrogen sulfide) does not transfer a proton, while the slightly weaker acid *tert*-BuSH (*tert*-butyl mercaptan) transfers a proton with measurable efficiency.

Experiments were carried out in an IonSpec OMEGA Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer using impulse excitation.[15] $^3NO^-$ was generated from N_2O via O^- as shown in eq 2.[16−18]

$$N_2O + e^- \rightarrow O^-$$
$$O^- + N_2O \rightarrow {}^3NO^- \qquad (2)$$

$^3NO^-$ is bound by only 0.026 eV (0.60 kcal/mol) relative to electron detachment,[17] and both collisional and radiative excitation leads to nonreactive $^3NO^-$ ion loss. A rapid decrease in $^3NO^-$ signal was indeed observed in our experiments, similar to that described by previous investigators.[19−21] Rate constants for collisional $^3NO^-$ loss were measured against several colliders, N_2O, CH_4, $CH_2{=}C(CH_3)_2$, and found to be identical

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* Corresponding author.

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TABLE 1: Thermochemistry and Reaction Efficiency for $^3NO^- + HA \rightarrow X + A^-$ [a,b]

HA	ΔH_{acid} (kcal/mol)[c]	$\Delta H°$ ($^3NO^- + HA \rightarrow X + A^-$)		proton-transfer efficiency
		$X = {}^1HNO$	$X = {}^3HNO$	
CF_3COOH	323.8	−38.7	−20.6	>90%
HCl	333.4	−29.1	−11.0	>90%
CH_3COOH	348.1	−14.4	+3.7	40−50%
H_2S	350.7	−11.8	+6.3	not observed
$(CH_3)_3CSH$	352.0	−10.5	+7.6	30−40%
CH_3NO_2	356.4	−6.1	+12.0	not observed
CH_3SH	357.6	−4.9	+13.2	not observed
$CF_3(CH_3)CHOH$	360.3	−2.2	+15.9	not observed
CH_2FCH_2OH	371.2	+8.7	+26.8	not observed
CH_3OH	380.6	+18.1	+36.2	not observed

[a] All energies in kcal/mol. [b] ΔH_{acid} (HNO) = 362.5 kcal/mol. [c] Ref 27.

within experimental error. Our value of $4 \pm 1 \times 10^{-11}$ cm^3 s^{-1} is quantitatively consistent with the work of Viggiano[22] and Ferguson,[23] who found that polyatomics are generally more efficient for electron detachment than are rare-gas atoms. Noncollisional ion loss, independent of background pressure, varied from 7.3 to 8.6 s^{-1}.[24] The combined rapid $^3NO^-$ loss rate allowed us to observe only relatively fast proton-transfer reactions, and made precise efficiency measurements difficult.

$^3NO^-$ was isolated and allowed to react individually with a series of neutral acids, Table 1.[25,26] Enthalpies of reaction are calculated from known thermochemistry.[27] The reactants are structurally varied and span a wide range of acidity. For purposes of this discussion, the $^3NO^-$ proton-transfer results in Table 1 can be divided into four groups.

HA = CF_3CO_2H, HCl. Reaction of $^3NO^-$ with these acids can produce either ^1HNO or ^3HNO in an overall exothermic reaction. Since both product spin states are energetically accessible, observation of product ions does not require a spin conversion. In our experiments, CF_3COO^- and Cl^- were produced very near the calculated ion−molecule capture rate,[26] in quantitative agreement with Ferguson's reported rate constant for proton transfer with HCl.[28,29] These results demonstrate that proton-transfer reactivity is observable on the time scale allowed by $^3NO^-$ autodetachment, and that proton transfer can compete with other ion loss channels.[30] We do not have any information regarding the spin state of the products.

HA = CH_2FCH_2OH, CH_3OH. Production of both ^1HNO and ^3HNO is endothermic; only collisional detachment was observed. These control experiments confirm that product ions are derived from reactive collisions with $^3NO^-$ and not through another ionization mechanism, such as reaction of residual O^- ion with the neutral alcohol.

HA = CH_3NO_2, CH_3SH, $CF_3(CH_3)CHOH$. Proton transfer with $^3NO^-$ is exothermic only to form ^1HNO. No product ion was observed when $^3NO^-$ was allowed to react with these acids, in agreement with Grabowski's observation that collisional detachment is the only reaction between $^3NO^-$ and CH_3NO_2.[31] These reactions are moderately exothermic and would be expected to be efficient if spin conversion were not required for proton transfer.

HA = CH_3CO_2H, H_2S, $(CH_3)_3CSH$. Proton transfer with $^3NO^-$ is exothermic only to form ^1HNO. In marked contrast to the less exothermic reactions discussed above, proton transfer occurred with acetic acid and *tert*-BuSH, comprising the first unequivocal observations of simple spin-forbidden proton-transfer reactions involving $^3NO^-$. The reaction between H_2S and $^3NO^-$, however, does not give any observable proton transfer.

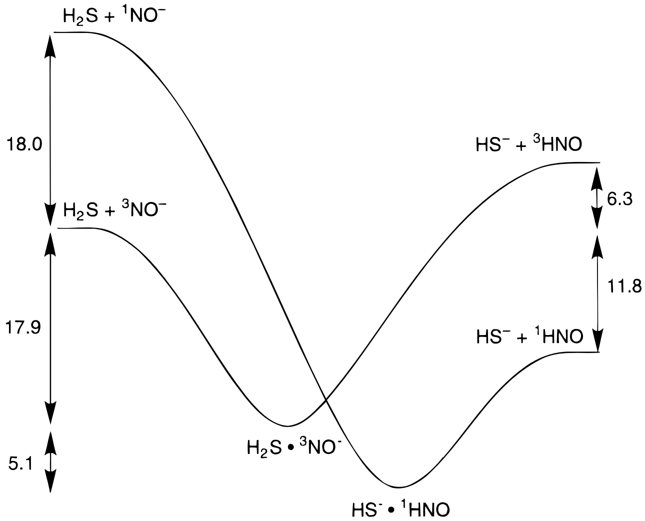

Figure 1. Potential energy surface for the spin−forbidden proton-transfer reaction $H_2S + {}^3NO^-$ (energies in kcal/mol). The experimental exothermicity for this reaction is −11.8 kcal/mol. Well depths are taken from ab initio calculations.

The proton-transfer potential surface for $H_2S + {}^3NO^-$ is shown in Figure 1. Reactant and product energies are known experimentally,[27] and complexation energies are taken from our ab initio calculations.[32−34] The curve crossing point represents the highest energy species separating the reactant and product complexes, and this curve crossing is calculated to occur only 2 kcal/mol above the reactant well. The lowest energy geometry on the triplet potential surface has the proton significantly transferred from H_2S toward $^3NO^-$, suggesting that this curve is best described as having a single minimum. The energetic barrier to proton transfer within the triplet complex is therefore expected to be very small. The singlet curve is very exothermic (30 kcal/mol), and the lowest energy singlet complex shows the hydrogen atom completely transferred to ^1HNO.

The acidities of H_2S and *tert*-BuSH are similar, and the diabatic proton-transfer potentials for H_2S and *tert*-BuSH are almost the same. Consequently, the singlet and triplet curve crossings should also be very similar for these two reactions. This suggests that the more efficient proton-transfer reaction of *tert*-BuSH is a consequence of thermal reaction dynamics, rather than some electronic factor.

Consider the curve crossing region of the potential surface shown in Figure 2, in which HA = H_2S or *tert*-BuSH. The collision complex formed between $^3NO^-$ and HA has two[35] energetically accessible exit channels: dissociation to separated reactants, k_{diss}, and spin-forbidden proton transfer, k_{pt}.[36] The proton-transfer efficiency is the ratio of k_{pt} to the sum of the rate constants for both exit channels from the reactant well, eq 3.

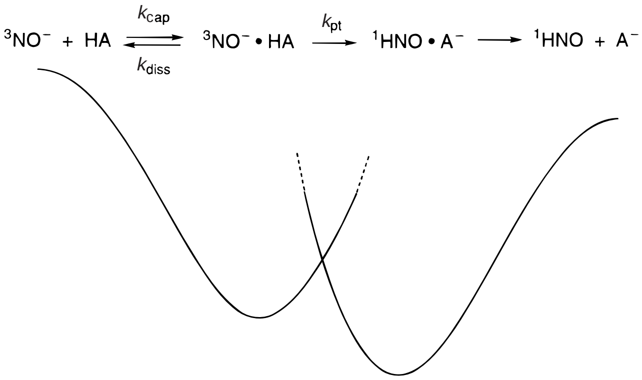

Figure 2. Schematic potential for proton transfer. Proton-transfer efficiency is determined by the fraction of activated ion−molecule complexes that undergo spin conversion/proton transfer relative to reaction through all exit channels. This branching ratio is determined by the values of k_{pt} and k_{diss}. k_{diss} for H_2S is estimated to be 10^3 times that for *tert*-BuSH (see text).

$$\text{efficiency} = k_{pt}/(k_{diss} + k_{pt}) \tag{3}$$

Whatever the factors are that determine the rate of spin conversion,[37,38] we expect they will not differ greatly for these two complexes with similar well depths, curve crossing energies, and S−H as a proton donor.

The dissociation rate constant k_{diss} can be estimated using statistical reaction rate theory.[39−42] RRKM calculations have been performed for these two complexes;[43] the dissociation rate for *tert*-BuSH•$^3NO^-$ is calculated to be 2.7×10^5 s^{-1}, about 10^3 times slower than that for H_2S•$^3NO^-$. This difference is a consequence of the increased number of internal vibrational and rotational modes within the larger species, and manifests itself as a 10^3-fold increase in the lifetime of the *tert*-BuSH•$^3NO^-$ complex compared to that of the smaller H_2S•$^3NO^-$ complex.

tert-BuSH transfers a proton to $^3NO^-$ with an estimated efficiency of 30−40%. From the RRKM dissociation rate constant, the first-order rate constant for spin-forbidden proton transfer within the reactant complex must be about 1.5×10^5 s^{-1}. With a similar value for k_{pt}, proton transfer from H_2S to $^3NO^-$ would have an efficiency of only 0.1%, too slow for us to observe.

Acetic acid has a similar acidity and a similar number of internal modes as *tert*-BuSH and would also have a longer lifetime toward dissociation than does $^3NO^- \bullet H_2S$. These differences in lifetimes, as estimated using RRKM statistical reaction rate theory, are sufficient to explain the observed pattern of spin forbidden proton-transfer reactivity of $^3NO^-$.

In the $^3NO^- \bullet HCl$ complex, there is essentially no barrier to proton transfer on the exothermic triplet surface. The lifetime of this complex is therefore limited by the rate of spin-allowed proton transfer rather than the ion−molecule dissociation rate. This suggests that proton transfer between $^3NO^-$ and HCl may well give only ^3HNO, because the lifetime of this collision complex would be too short for efficient intersystem crossing to occur. Similarly, the reaction of $^3NO^-$ with CF_3COOH to form ^3HNO would be expected to produce mostly ^3HNO.

In summary, the spin change requirement in the $^3NO^-/^1HNO$ system clearly causes several very exothermic (<−12 kcal/mol) proton-transfer reactions to become too slow for us to observe. However, reaction of $^3NO^-$ with strong acids that have many internal degrees of freedom shows measurable proton transfer. We attribute the observation of a measurable spin-forbidden proton-transfer rate of $^3NO^-$ with CH_3CO_2H and *tert*-BuSH to a longer lifetime of the collision complex, which allows enough time for spin conversion to occur.

Acknowledgment. We thank the National Science Foundation for support of this research and Michael Chabinyc and Colleen Regan for assistance with ab initio and RRKM calculations.

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(25) Efficiency is defined as k_{pt}/k_{cap}. k_{pt} is the measured proton-transfer rate constant, and k_{cap} is the capture rate constant for $^3NO^-$ and HA, calculated using the modified ADO formalism of Su and Chesnavich.[26]

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(35) We assume that the rate of barrier recrossing is negligible, consistent with the exothermicity of the reaction, Figure 1, and the spin change required for the reverse reaction.

(36) Collisional detachment comprises an additional channel for disappearance. On the basis of results of our collisional detachment studies (see text), the $^3NO^-$ loss rates would not be expected to differ significantly between the two thiol complexes.

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