

[FHNO]⁻: An Intermediate in a Spin-Forbidden Proton Transfer Reaction

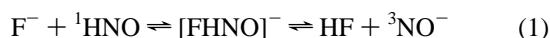
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Proton transfers between anions and neutral acids are among the most ubiquitous reactions in chemistry. They are generally very fast, often encounter controlled. This is due in part to the relatively large stabilization associated with the half-transferred proton—a consequence of strong hydrogen bonding. Some proton transfer reactions, especially those involving resonance stabilized anions, can have substantial barriers to reaction, and these reactions occur at slower rates.^{1,2}

In this paper we report studies of an intermediate complex³ in a proton transfer reaction, eq 1, that must involve a spin change. Although the details of the proton transfer reaction are not fully worked out, we present evidence for the structure of the intermediate complex and a description of some of its chemical reactivity. Proton transfer reactions in which the adiabatic, ground state surface involves a spin change have only recently been observed.^{4,5}



Kinetic experiments were carried out in an Ionspec OMEGA Fourier-transform mass spectrometer with use of impulse excitation.⁶ Electron photodetachment experiments were carried out in a CW-ion cyclotron resonance spectrometer equipped with a capacitance bridge detector.⁷ The light source was a Ti-Sapphire laser (Lexel) pumped with all lines of a 20-W Coherent argon ion laser. [FHNO]⁻ was synthesized as described by King, Maricq, Bierbaum, and DePuy⁸ from the reaction of F⁻ (from electron impact on NF₃, obtained from Ozark Mahoning) with neopentyl nitrite. The neopentyl nitrate was never completely free of neopentyl alcohol; consequently background reactions involving neopentyl alcohol were observed when other reactions were very slow.

A schematic potential surface for this reaction is shown in Figure 1. The energetics of the ground state reaction (¹HNO is the stable isomer)⁹ are known from heats of formation of the ions and neutrals.^{9–12} Although the electron affinity of ground state NO is very small,¹¹ 0.61 kcal/mol, the overall reaction is about 8 kcal/mol exothermic owing to the very strong bond in

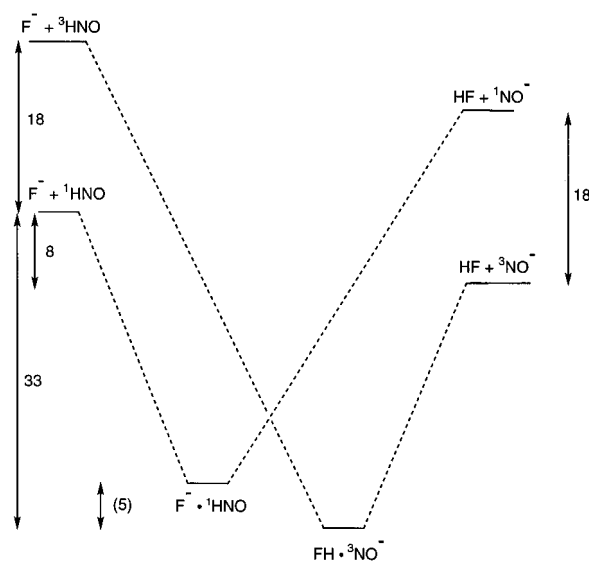


Figure 1. Energies in kcal/mol. The energy difference between the two complexes is taken from *ab initio* calculations, and all other energies represent experimental values (see text for references). The singlet–triplet curve-crossing is calculated to occur about 3 kcal/mol above the energy of F⁻·¹HNO.

HF. The energy of ³HNO is known from photoelectron experiments on HNO⁻ by Ellis and Ellison.¹³ ¹NO⁻ is not a bound state; its energy has been assigned from electron scattering experiments on NO.^{14,15}

Although the importance of spin in these reactions has not been explicitly recognized, there have been previous attempts to explore some of the chemistry of NO⁻. Rinden, Maricq, and Grabowski were unable to observe the slightly exothermic (6 kcal/mol) proton transfer reaction of NO⁻ with nitromethane,¹⁶ although Ferguson and co-workers¹⁷ had previously been able to observe a rapid proton transfer reaction with HCl (35 kcal/mol exothermic). Interestingly, the reaction observed by Ferguson is sufficiently exothermic so that ³HNO could have been produced.

The complex [FHNO]⁻ was allowed to react with a variety of neutrals in order to see if its structure could be inferred from chemical reactions.¹⁸ We observe that reaction with alcohols gives F⁻ transfer. The reaction with neopentyl alcohol is relatively efficient; reaction with methanol, however, is about 1% efficient. These results suggest that F⁻ binding in this complex is about equal to F⁻ binding to neopentyl alcohol (~33 kcal/mol based on binding to *tert*-butyl alcohol¹⁹) and stronger than binding to methanol (29.6 kcal/mol).¹⁹ Reaction with HCN also gives fluoride transfer. Although these results might be taken to indicate a complex structure of the form F⁻·HNO, reactions with other neutrals are more consistent with a structure of FH·NO⁻. Thus, reaction with NO gives NO⁻ transfer, producing N₂O₂⁻, an ion known from the work of Posey and

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(3) The complexes in this reaction, [FHNO]⁻ and its neutral counterpart [FHNO], may be found in the literature as [NOHF]⁻ and [NOHF], respectively. We have written them as shown here not to imply any particular structure but to make the logic of the presentation clear.

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(18) Using mass spectrometric reactions, it is sometimes possible to infer the structure of an ion from its chemical reactivity. See, for example: DePuy, C. H.; Kass, S. R.; Bean, G. P. *J. Org. Chem.* **1988**, *53*, 4427. Chyall, L. J.; Brickhouse, M. D.; Schnute, M. E.; Squires, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 8681–8690.

(19) Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1983**, *105*, 2944. Some of the anchor points on this scale have recently been remeasured and found to be different: Wenthold, P. G.; Squires, R. R. *J. Phys. Chem.* **1995**, *99*, 2002–2005. The values for the part of the scale that we have used, however, should be largely unchanged.

Johnson and Neumark and co-workers to be quite stable.²⁰ $[\text{FHNO}]^-$ reacts slowly with SF_6 to give SF_6^- , consistent with the well-known low reactivity of SF_6 in electron transfer processes.^{21–23} Reaction with O_2 gives an ion with $m/z = 52$, presumably $\text{O}_2^- \cdot \text{HF}$, that appears to result from electron transfer to O_2 followed by HF transfer. Reaction with SO_2 is somewhat more complex, but the major products are electron transfer and electron transfer plus HF transfer to give SO_2^- and $\text{SO}_2^- \cdot \text{HF}$, as well as a small amount of F^- transfer which gives SO_2F^- . It is clear from these experiments that the structure of $[\text{FHNO}]^-$ cannot be unambiguously assigned on the basis of its chemical reactions.

Electron photodetachment spectroscopy can be a powerful tool in determination of both structure and energetics. We have made use of this technique previously in showing that ROHF^- has the structure $\text{RO}^- \cdot \text{HF}$ when ROH is a stronger acid than HF.^{24,25} The same reasoning is useful in this case. The neutral species $\text{FH} \cdot \text{NO}$ should be much more stable than the isomeric complex $\text{F} \cdot \text{HNO}$,^{26–28} because of the weak NH bond vs the strong HF bond.²⁹ On the basis of the stability of $[\text{FHNO}]^-$ that we have deduced from the fluoride transfer reactions, the adiabatic detachment energy should be about 22 kcal/mol.³⁰ To reach the more stable structure via an optical transition, the Franck–Condon overlap between $[\text{FHNO}]^-$ and $\text{FH} \cdot \text{NO}$ must be reasonably large.³¹ Observation of electron photodetachment occurring somewhere near this adiabatic energy requires that the structure of the ion³¹ be $\text{FH} \cdot \text{NO}^-$. If the complex structure were $\text{F}^- \cdot \text{HNO}$, the only Franck–Condon accessible neutral would be $\text{F} \cdot \text{HNO}$, and photodetachment would not be observed until a much higher energy, ~ 70 kcal/mol (< 380 nm). The photodetachment spectrum shows an onset at about 975 nm (29 kcal/mol), clearly in the vicinity that we expect for a complex bound at about 33 kcal/mol with respect to fluoride loss (25

kcal/mol for NO^- loss). We have been able to photodetach a reasonable fraction of the population by using the argon ion laser, showing that essentially all of the $[\text{FHNO}]^-$ ions have this structure or are in rapid equilibrium with it. On this basis we believe that the structure of the complex³¹ is best described as $\text{FH} \cdot {}^3\text{NO}^-$. Bowen and co-workers³² have previously shown that the structure of NO^- complexed with water is $\text{H}_2\text{O} \cdot \text{NO}^-$, a result expected because of the low acidity of H_2O compared with HNO .

Quantum calculations³³ are consistent with these results. We find well-defined minima for $\text{F}^- \cdot {}^1\text{HNO}$ and $\text{FH} \cdot {}^3\text{NO}^-$, the latter being about 5 kcal/mol more stable. The singlet and triplet curves cross about 3 kcal/mol above the singlet minimum. We calculate the binding energy of the complex, the overall energetics of eq 1, and the singlet–triplet splitting in HNO and in NO^- all to within 2 kcal/mol of the experimental values. Thus, we are confident that the calculated complex energies are reasonably accurate. We find that binding an additional alcohol molecule in the complex ($\text{FHNO}^- \cdot \text{ROH}$) lowers the energy of the singlet state more than that of the triplet so that the singlet now becomes the ground state.

The issue of spin dynamics in this system is not fully resolved. The synthesis of ${}^3[\text{FHNO}]^-$ also requires a spin change, since the reaction of F^- with neopentyl nitrite to produce ${}^3[\text{FHNO}]^-$ involves only singlet reactants. We observe that $[\text{FHNO}]^-$ acts not only as a source of electrons or NO^- as expected for the triplet but also as a source of F^- , as expected for the singlet. Thus a spin change is required for some of the reactions of $[\text{FHNO}]^-$. The reaction appears to be quite efficient, especially considering the modest spin–orbit coupling in NO .³⁴ We believe that the energy required to reach the curve crossing region in the proton transfer reaction between $\text{FH} \cdot {}^3\text{NO}^-$ and $\text{F}^- \cdot {}^1\text{HNO}$ is low. The lifetime of the complexes in which F^- is transferred is likely to be reasonably long, and when a molecule of alcohol is complexed to $[\text{FHNO}]^-$ the singlet complex is lower in energy than the triplet. In addition, multiple collisions occur during the lifetime of the complex. Thus, curve crossing may be facilitated in these reactions. More research will be necessary to clarify the details of this interesting process.

In summary, we have studied the intermediate, $[\text{FHNO}]^-$, in eq 1 and showed that its chemistry requires efficient spin changes. The binding energy of F^- to HNO appears to be about 33 kcal/mol, and the most stable structure of this ion appears to be $\text{FH} \cdot {}^3\text{NO}^-$.

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(31) Our calculations suggest that the most stable complex has the structure $\text{FH} \cdot \text{NO}^-$ in which the HF is hydrogen bonded to the nitrogen of NO^- . We find another reasonably low energy form of this complex, $\text{NO}^- \cdot \text{HF}$, in which the HF is hydrogen bonded to the oxygen of NO^- . There is, similarly, a neutral complex with a comparable structure, $\text{NO} \cdot \text{HF}$. Inasmuch as our calculations suggest that $\text{FH} \cdot \text{NO}^-$ is the more stable structure, we have chosen to represent the complex in this way. The experiment itself only shows that the complex looks like NO^- bonded to HF. It does not allow us to distinguish between the alternative geometries.