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Experimental and theoretical study of the reaction of HO⁻ with NO

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Hydroxide ion (HO⁻) reacts with nitric oxide by slow reactive electron detachment with a rate coefficient $\sim 4 \times 10^{-12}$ cm³ s⁻¹ at 298 K. The detachment process is presumably associative detachment forming nitrous acid and an electron. Observations, data analysis, and alternative explanations for these observations are discussed. The associative detachment reaction was also investigated theoretically through calculations of the geometries, relative energies, and normal-mode vibrational frequencies of the relevant species HO⁻, HO, NO, cis- and trans-HONO, and cis- and trans-HONO⁻. These calculations indicate that in the ion HONO⁻, the *cis* conformer is more stable, while in the neutral HONO, the *trans* conformer is more stable. The HO-NO bond in HONO, which is formed in this reaction, is much stronger than the HO⁻-NO bond in HONO⁻ with an energy of 198.7 ± 1.8 kJ mol⁻¹ for cis-HONO [J. Phys. Chem. Ref. Data 14, 1 (1985)] and 52.2 ± 5 kJ mol⁻¹ for cis-HONO⁻ at 0 K. HONO⁻ is bound with respect to HONO. The adiabatic electron detachment energy resulting from detachment from *cis*-HONO⁻ forming the same conformer of the neutral molecule cis-HONO is 0.29 ± 0.05 eV. The HO–NO equilibrium bond distance in HONO⁻ is considerably longer than that in HONO, with values of 1.750 and 1.640 Å for trans- and cis-HONO⁻, respectively, and 1.429 and 1.392 Å for trans- and cis-HONO, respectively. These geometric and energetic characteristics of HONO⁻ and HONO are combined with calculations of relative energies of these species at nonequilibrium/distorted HO-NO bond lengths to give a qualitative picture of the potential energy curves for these species along the reaction coordinate. While no significant energy barrier to autodetachment of HONO⁻ is present, the Franck-Condon wave function overlap for autodetachment is small and is likely the reason for the observed inefficiency. The maximum calculated rate constant for associative detachment is 4×10^{-12} cm³ s⁻¹, in good agreement with the observed value.

INTRODUCTION

Reaction between hydroxide ion and nitric oxide has never been reported, yet the ion-molecule chemistry of both of these species has been investigated in detail.¹ We found evidence of their reaction when trying to quantify the NO₂ impurity level in our NO sample. Specifically, we attempted to use the efficient charge transfer reaction between hydroxide ion and nitrogen dioxide^{2,3} to calibrate the NO₂ impurity level in the NO sample by evaluating the apparent reaction rate coefficient with NO. We found that the hydroxide ion attenuation observed with added NO (containing NO₂ impurity) could not be entirely accounted for by the NO₂⁻ formed, even when relative detection sensitivity was taken into account. In this study, we have quantitatively accounted for known impurity levels and have discussed and rejected alternative explanations for our observations. We conclude that hydroxide ion reacts, although inefficiently, with nitric oxide via associative detachment

$$HO^- + NO \Rightarrow HONO + e.$$
 (R1)

Nitrous acid, the presumed product in the reaction of HO^- with NO, may be formed, in part, by the title reaction in combustion processes. It is found in both indoor and outdoor polluted environments in the troposphere.⁴⁻⁶ However, the small efficiency of this reaction coupled with typically small ion concentrations makes it unlikely that this reaction is an important source of atmospheric nitrous acid.

EXPERIMENTAL DETAILS

The reported measurements were made with a selected ion flow drift tube which has been described in detail previously.^{7,8} The reactant ions HO⁻ are formed in a remote high pressure ($\sim 0.1-1$ Torr) ion source principally by electron impact on water forming H⁻ followed by reaction

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with water, or by dissociative electron attachment to nitrous oxide (N₂O) to form O⁻ followed by reaction with methane. The HO⁻ ions are mass selected and injected into the reaction flow tube. These ions are carried through the flow tube by a laminar flow of helium and may react with the neutral reagent which is injected through one of two inlets. At the end of the flow tube, the gas flow impacts on a truncated cone, at the center of which is a 0.2 mm sampling orifice. The sampled ions are mass analyzed and counted with a particle multiplier.

The blunt end plate of the cone containing the orifice is electrically isolated from the rest of the cone and vacuum housing, and is connected to an electrometer. We will refer to this plate as the sampling plate. Ion current reaching the sampling plate can be measured and monitored to give an indication of changes in total ion density in the flow tube. In this work, such measurements help to confirm the assignment of signal loss to a reactive electron detachment reaction.

The nitric oxide was Matheson CP grade [99.0% min., typically 99.7% (Ref. 9)] and was purified further before introduction into the flow tube. In the first set of experiments, the NO first passed through Ascarite before entering the flow tube. For the remainder of the paper, we will call the experiments using this procedure the Ascaritetrapped experiments. The active ingredient in Ascarite is sodium hydroxide, which will trap acids, NO_2 , and CO_2 . Despite this treatment, we observed evidence of a NO_2 (or HNO₂) impurity present in the injected neutral flow, possibly because of the large mass flow rate (and therefore short trapping time) needed for investigation of this slow reaction. In the second set of experiments, the NO flow passed through the Ascarite-filled line and subsequently through a U tube which was filled with molecular sieves (4) Å pore) and immersed in a dry ice-methanol bath (196 K). These experiments will be called Ascarite and dry icetrapped experiments. The dry ice bath is expected to trap impurities of low vapor pressure, including nitric acid, NO₂, and water. In the Ascarite and dry ice-trapped experiments, no product ions were detected upon addition of the NO reactant neutral to the flow tube, indicating the elimination of the NO2/HNO2 impurity and possibly other complicating impurities.

A rate coefficient is determined from the attenuation of the reactant ion count rate as a function of reactant neutral flow rate. This attenuation is measured separately for each of two neutral inlet positions to determine the end correction, or the effective neutral mixing distance. A single end correction was evaluated from all the data collected, since the experimental conditions were essentially identical. The reported rate coefficients for the differing trapping strategies are an average of at least ten measurements (five at each inlet). The reactant ion was formed from H₂O in most of the experiments, but four rate coefficient measurements were made when the HO⁻ was formed from N₂O and CH₄ for comparison. These four measurements were made using the Ascarite-trapped NO. Random error in the reported rate coefficients is estimated to be $\pm 20\%$, while absolute error is estimated to be $\pm 30\%$. This is slightly

larger than our typical error limits of $\pm 15\%$ and $\pm 25\%$ due to the complications of the impurities and small rate constants.¹⁰

For reactions which have only reactive electron detachment channels, the attenuation of the current to the sampling plate with neutral flow rate will be an additional measure of the rate coefficient for the reaction, assuming that electrons are not detected or are only inefficiently detected by the sampling plate and that diffusion coefficients do not change dramatically with reactant neutral flow rate. The lack of curvature in the kinetic plots [ln(sampling current) vs reactant flow] derived from our data supports these assumptions. In addition, experimental evidence for inefficient sampling of electrons in our apparatus has been shown for other detachment reactions.^{11,12} The inefficient detection of electrons is due to the large diffusional loss of these species to the flow tube wall. The advantage of ion current data over ion count rate data is that detector sensitivity is not an issue for the former. The disadvantage is that ion current measurements in our experiments are typically much less precise than are ion count rate data. Therefore, we will use the ion current data as ancillary data which support the conclusions of the ion count rate data.

In the Ascarite-trapped experiments, some NO_2^- was observed upon addition of the NO reactant neutral to the flow tube. Formation of NO_2^- cannot arise from the direct reaction of HO⁻ with NO at thermal energies; this process is endothermic by $\sim 75 \text{ kJ mol}^{-1}$. Therefore, observation of NO_2^- indicates that an impurity of NO_2 or possibly HNO₂ is being introduced into the flow tube with the nitric oxide. We can determine the relative contributions to the HO⁻ reactivity for formation of NO₂⁻ and for reactive electron detachment as described below. The branching fraction for formation of NO_2^- , defined as the fractional contribution to the total observed rate coefficient (k_{obs}) by the reaction of HO⁻ with impurities responsible for formation of NO₂⁻, is given by $f \cdot k_{imp}/k_{obs}$, where $k_{obs} = k_{NO}$ $+f \cdot k_{imp}$, and k_{imp} is the rate coefficient for reaction of HO^- with the impurity NO_2/HNO_2 , f is the fraction of NO₂ plus HNO₂ in the NO flow, and $k_{\rm NO}$ is the rate coefficient for the reaction of HO⁻ with NO. If we assume that reaction of HO⁻ with the impurity (NO₂/HNO₂) proceeds with a rate coefficient (k_{imp}) of 1.1×10^{-9} cm³ s⁻¹ which is the known value for the reaction of HO⁻ with NO_2 at room temperature,^{2,3} then we can evaluate *f*. The branching fraction for formation of NO₂⁻ also allows us to determine the reaction rate coefficient of interest $k_{\rm NO}$.

The branching between formation of ionic products and detachment products may be determined from the fraction of reactant ion signal lost which cannot be accounted for by ionic products gained. This procedure requires that all ionic products are identified and that detection sensitivity for each ionic product has been taken into account. NO_2^- was the only ionic product observed upon addition of the neutral flow to the flow tube. Relative detection sensitivity is evaluated by comparing the detected ion count rate with the sampling plate current for each ion of interest. In this evaluation, each ion species is injected into the flow tube in the absence of all other ion species.



FIG. 1. Detection sensitivity. Detected counts/second for HO^- (solid circles) and NO_2^- (solid squares) as a function of sampling plate current (see the Experimental Details section).

The measured relative detection sensitivity for HO⁻ and NO_2^- was the same within our measurement precision (see Fig. 1). The lack of discrimination between detection of HO^- and NO_2^- supports the assertion that all ionic products in the flow tube have been identified. If ions other than HO^- and NO_2^- had been present in the flow tube as a result of reaction of HO⁻ with impurities, e.g., NO₃⁻ from HNO₃, these ions would have been detected under these low discrimination conditions. The branching fraction evaluated is plotted as a function of the NO reactant neutral flow rate and extrapolated to the zero flow rate to account for possible secondary reactions. For the set of experiments where NO₂⁻ was observed, no significant change in branching fraction with NO flow rate was observed, and so an average of the fractions at each flow rate was taken as the branching fraction.

The branching between formation of ionic products and detachment products may also be determined from sampling plate current measurements as a function of NO flow rate. For reactions involving ionic product channels as well as reactive electron detachment channels, the sampling plate current is not proportional to the reactant ion signal because it reflects product ions as well. In this case, branching fractions for reactive electron detachment channels can be readily determined from a comparison of the initial current to the final current at reaction completion.¹³ However, for slow reactions such as the reaction of interest, driving the reaction to completion may not be possible. In this case, one can evaluate the branching fraction from the attenuation of sampling plate current with flow as compared with the reactant ion attenuation as

$$\frac{(I_0 - I_i)}{I_0} \left\{ \frac{[\text{HO}^-]_0}{([\text{HO}^-]_0 - [\text{HO}]^-_i)} \right\} = \frac{k_{\text{NO}}}{(k_{\text{NO}} + f \cdot k_{\text{imp}})}, \quad (1)$$

where I is the current measured, $[HO^{-}]$ is the reactant ion count rate, and the subscripts 0 and *i* denote the absence of neutral reactant and the presence of neutral reactant with flow rate *i*, respectively. The rate coefficients *k* and factor *f* are as defined above.

THEORETICAL METHODS

Calculations of molecular total energies and molecular geometries were carried out *ab initio* with use of the CRAY version of Gaussian 90.¹⁴ Fully optimized geometries were obtained for HO(²II), HO⁻(¹Σ⁺), NO(²II), *cis*-HONO(¹A'), *trans*-HONO(¹A'), *cis*-HONO⁻(²A''), and *trans*-HONO⁻(²A'') at the second-order Møller–Plesset (MP2)(FU)/6-31+G(d) level of calculation employing analytical gradients.^{15,16} Bond lengths were optimized to 0.001 Å and bond angles to 0.1°. Normal-mode vibrational frequencies were computed with equilibrium structures.

In order to obtain insight into the energetics involved in the title associative detachment reaction (R1), we calculated the total energies of the HONO and HONO⁻ species as a function of the initial reaction coordinate, the HO-NO bond distance (denoted as $R_{\rm O-N}$ henceforth), thereby estimating the shape of the potential energy vs $R_{\rm O-N}$ curves for *cis*-HONO and *cis*-HONO⁻ and the position at which the curves cross. In each of these MP2/6-31 +G(d) calculations, the O-N bond length was held constant in the HO-NO species and the remaining parameters were optimized.

The MP2/6-31+G(d) optimum structures were used to compute single-point energies at the MP2(FC)/6-311+ +G(3df,3pd) level.^{17,18} The latter calculational level was chosen since only reliable relative energies are required for this part of the project. Previous studies have shown that for systems with small spin contamination, electron detachment energies calculated at the MP2 or fourth-order Møller–Plesset (MP4) level with a moderately sized basis set, e.g., 6-311+G(d,p), are within 0.2 eV of the experimental values.¹⁹⁻²¹

Since accurate relative energies are required we systematically examined the thermochemistry of the equilibrium geometries of HONO, HONO⁻, HO+NO, and HO⁻+NO using both the Gaussian-1 (G1) and Gaussian-2 (G2) methods. The development of a predictive *ab initio* thermochemistry model that is reliable to $5-10 \text{ kJ/mol}^{-1}$ has been the goal of computational chemistry for some time. Early models by Pople and co-workers were based on calculated energy differences at the MP4 level of theory for prescribed isogyric processes.²²⁻²⁴

More recently, a systematic procedure for prediction of molecular energies, referred to as G1 theory, has been proposed by Pople *et al.*²⁵ In this method, systematic corrections for both basis set deficiencies and the level of correlation treatment are applied to the energies calculated at the QCISD(T)/6-311G(d,p)//MP2(FU)/6-31G(d) level of theory. The G1 energy can be written as

 $E_{0}(G1) = E_{\text{QCISD}(T)/6-311G(d,p)} + (E_{\text{MP4}(\text{FC})/6-311+G(d,p)} - E_{\text{MP4}(\text{FC})/6-311G(d,p)}) + (E_{\text{MP4}(\text{FC})/6-311G(2df,p)} - E_{\text{MP4}/6-311G(d,p)}) - 0.00614n_{\text{pair}} - 0.00019n_{\text{os}} + E_{\text{ZPE}}.$ (2)



FIG. 2. Reactant ion counts/second (solid circles) and sampling plate current (open diamonds) as a function of reactant neutral flow. Current values have been normalized to counts/second values at zero flow for comparison. Lines drawn represent the least squares fits to the data.

A suggested improvement to the method, referred to as the G2 theory,²⁶ further corrects for nonadditivity effects in the treatment of the basis set

$$E_{0}(G2) = E_{0}(G1) + (E_{MP2/6-311+G(3df,2p)} - E_{MP2/6-311G(2df,p)}) - (E_{MP2/6-311+G(d,p)} - E_{MP2/6-311G(d,p)}) + 0.00114n_{pair}.$$
 (3)

Pople and co-workers have demonstrated better than 8 $kJ \text{ mol}^{-1}$ accuracy for these methods in calculations on a large number of first row elements.

EXPERIMENTAL RESULTS AND ANALYSIS

Observations

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The average rate coefficients for reaction of HO⁻ with NO measured with the two trapping strategies were identical within experimental precision and are equal to 4.1 $\times 10^{-12}$ and 4.0×10^{-12} cm³ s⁻¹ for the Ascarite-trapped and Ascarite and dry ice-trapped experiments, respectively. These identical values indicate that NO₂/HNO₂ and other possible impurities present in the Ascarite-trapped experiments and absent in the Ascarite and dry ice-trapped experiments represent a negligible fraction of the total NO flow. In addition, the measured rate coefficient was the same within experimental precision whether the reactant ion was formed from H₂O or from N₂O and CH₄, with values of 4.1×10^{-12} and 4.2×10^{-12} cm³ s⁻¹, respectively, for the Ascarite-trapped experiments. These data indicate that any small leak of source gas into the flow tube did not interfere with our measurements and, most importantly, was not responsible for the reactant ion attenuation. Finally, the relative attenuation observed in the sampling plate current was the same as the relative reactant ion attenuation in the Ascarite and dry ice-trapped experiments (see Fig. 2). A rate coefficient using sampling plate current data was not evaluated because of the uncertainty in these values.



FIG. 3. Reactant ion (solid circles) and product ion (solid squares) counts/second as a function of reactant neutral flow. NO_2^- product ions were observed in the Ascarite-trapped experiments only (see the Experimental Details section) and are presumed to arise from reaction with an impurity.

 $\rm NO_2^-$ observed in the Ascarite-trapped experiments represented ~15% of the total reaction "products," or made a contribution of ~15% to the observed reaction rate coefficient. This value, taken together with the observed rate coefficient, leads to an estimated impurity level of ~0.05% in NO for the Ascarite-trapped experiments (see the Experimental Details section). Subtracting the contribution of this known impurity from the observed rate coefficient leads to a value of 3.5×10^{-12} cm³ s⁻¹ for $k_{\rm NO}$, in agreement with the value obtained in the Ascarite and dry ice-trapped experiments within experimental precision.

Evidence for reactive electron detachment reaction

The small rate coefficient measured, lack of ionic products formed, and difficulty in obtaining a pure sample of nitric oxide make it necessary to consider carefully the evidence available before ascribing the reactivity to associative detachment. We list and discuss below the important experimental indications that the reactant ion attenuation is a result of a reactive electron detachment reaction with nitric oxide.

(1) The reactant ion signal loss was much greater than the product ion signal gained. In the Ascarite and dry icetrapped experiments, reactant ion signal loss was observed with no product ions detected. Detection discrimination between the reactant ion and possible product ions cannot account for the signal loss observed because this discrimination was measured and shown to be negligible (see the Experimental Details section and Fig. 3). Diffusion coefficient differences arising either from the addition of the neutral reagent or from differences between the reactant and product ions cannot explain the apparent ion signal loss. Diffusional loss of ions to the flow tube walls will be reduced in a mixture of helium and added NO neutral from what it is in the helium flow alone. In addition, diffusional loss generally decreases with increasing ionic mass,²⁷ and all conceivable ionic products (from reaction

with impurities) are of higher mass than the reactant ion. Therefore, if all reactions of the reactant ion form product ions (as opposed to electrons), we would expect an increase in total ion signal upon reaction.

(2) The current measured at the sampling plate decreased with increasing reactant neutral flow rate. Such a decrease indicates that total ion signal in the flow tube is decreasing and that reaction involves production of electrons, which are not detected efficiently.^{11,12} In the Ascarite and dry ice-trapped experiments, where no ionic products were observed, this attenuation was identical to the reactant ion attenuation, as expected for reaction exclusively by reactive electron detachment (Fig. 2).

(3) The rate coefficients determined for the reaction of HO^- with NO, with the NO purified using two different trapping strategies, were essentially identical. The observation of NO₂⁻ product ion in one case and its absence in the other indicates that the impurity levels in NO are different when NO is passed through the two different trapping systems. The agreement of the rate coefficients in these two cases supports the assertion that the HO⁻ reaction observed is with the major neutral reagent NO. This agreement also specifically eliminates reaction with NO₂ impurity as an explanation for the observed reactivity.

(4) Independent investigation suggests similar results. In preliminary experiments, Bierbaum and Barlow²⁸ measured a rate coefficient of 4×10^{-12} cm³ s⁻¹ for the reaction of HO⁻+NO, but made no attempt to identify products or to purify further the commercially available NO sample. Rate coefficients are measured as a function of distance in their²⁹ selected ion flow tube (SIFT), so that possible problems associated with changing neutral reactant flow rates are eliminated.

(5) Other likely impurities cannot account for reaction. Nitrous oxide is formed in the disproportionation reaction of NO at high pressures³⁰ and was used as a reactant ion source gas in some experiments. This possible impurity, however, reacts with HO⁻ only via slow oxygen atom exchange, which cannot be observed in the reaction of isotopically unenriched reactants. Similarly, water vapor, which could be present from leakage from the source chamber or as an impurity in the helium buffer gas, reacts by atom exchange,^{31,32} which would not be observed, and will cluster with hydroxide ion,³³ but no ionic clusters were observed. One expects nitric acid (HNO₃) and nitrous acid (HNO_2) , possible impurities in the neutral reactant, to react efficiently with HO⁻ by proton transfer, forming the ions NO_3^- and NO_2^- , respectively, based on the relative gas phase acidities of water and these species.³⁴ No NO₃⁻ was observed, and the NO₂⁻ observed in one set of experiments accounted for only 15% of the observed rate coefficient. Quoted concentration limits9 for ammonia, carbon monoxide, carbon dioxide, and halogens in the NO sample are too small to account for the observed rate coefficient in the cases where reaction does occur. Finally, N_2O_3 and $(NO)_2$, if present, are expected to be of negligible concentration in the flow tube. Even if present in the NO reservoir, they are weakly bound³⁰ and therefore would be expected to dissociate rapidly in the flow tube.

Assignment to associative detachment

We assign the reactive electron detachment reaction of HO⁻ with NO to associative detachment

$$HO - + NO ⇒ cis-HONO + e,$$

$$\Delta H_{298}^{0} = -23.4 \text{ kJ mol}^{-1} \text{ (Ref. 35)}, \qquad (R1a)$$

$$HO - + NO ⇒ trans-HONO + e,$$

$$\Delta H_{298}^{0} = -25.5 \text{ kJ mol}^{-1} \text{ (Ref. 35)} \qquad (R1b)$$

because formation of all other possible detachment products is endothermic.³⁵

Reaction efficiency

Associative detachment involves the formation of a temporary negative ion followed by autodetachment of the electron from this anion to form the corresponding neutral and a free electron $HO^- + NO \Rightarrow [HONO^-] \Rightarrow HONO$ +e. The inefficiency of the present associative detachment reaction indicates that the interaction lifetime of the reactants is much shorter on average than the lifetime against autodetachment of the negative ion or ion-dipole complex formed. This situation may arise from (1) an inefficiency of forming the temporary negative ion; (2) an energy barrier to autodetachment; or (3) poor overlap between the temporary negative ion and neutral wave functions in the autodetaching region. There are no general methods for estimating the efficiency of forming the temporary negative ion. It has been shown, e.g., that application of symmetry arguments to predict the fraction of collisions that may result in complex (temporary ion) formation are not generally applicable to low energy ion-molecule reactions.^{36,37} In the theoretical investigation that follows, we probe relevant portions of the potential energy surfaces involved in the title associative detachment reaction for energetic and overlap constraints.

THEORETICAL RESULTS AND ANALYSIS

Molecular total energies

Total energies (E_T) calculated using various calculational levels are given in Table I along with vibrational zero-point energies (ZPEs). Total energies calculated with the G1 and G2 methods include zero-point energies; the other reported total energies do not. The reported zeropoint energies are unscaled, except those used in the G1and G2 methods, which are scaled by 0.8929. The trans conformer is more stable for HONO, while the cis conformer is more stable for HONO⁻. For both the neutral and anionic systems, increasing the size of the basis set and utilizing full fourth-order Møller-Plesset perturbation theory (MP4SDTQ) stabilizes the trans conformer more than the cis conformer. All our calculations indicate that for HONO, the *trans* conformer is more stable than the *cis*, ranging from -1 to -4 kJ mol⁻¹: -1.3 kJ mol⁻¹ [MP2/ 6-31+G(d)], -4.3 kJ mol⁻¹ [MP4SDTQ/6-311] ++G(d,p)], -1.6 kJ mol⁻¹ [MP2/6-311++G(3df, 3pd], -3.4 kJ mol^{-1} (G1), and -2.5 kJ mol^{-1} (G2).

TABLE I. Total energies (E_T) and zero-point energies (ZPE).

		Calculational		ZPE°
Molecule	State	level ^a	E_T (hartrees) ^b	$(kJ mol^{-1})$
HO ^d	² Π	MP2/6-31+G(d)	-75.531 99	22.2
		MP2/6-311 + +G(3df, 3pd)	-75.620 62	
		<i>G</i> 1	-75.642 14	
		<i>G</i> 2	-75.643 91	21.3
HO-q	$^{1}\Sigma^{+}$	MP2/6-31 + G(d)	-75.590 84	22.1
		MP2/6-311 + +G(3df, 3pd)	-75.692 07	
		Gl	- 75.709 99	
	_	G2	75.712 76	20.0
NO ^d	² Π	MP2/6-31+G(d)	- 129.573 06	23.1
		MP2/6-311 + +G(3df, 3pd)	- 129.693 67	
		<i>G</i> 1	- 129.739 12	
		<i>G</i> 2	- 129.739 95	11.9
Trans-HONO ^d	¹ A'	MP2/6-31+G(d)	-205.191 68 ^e	51.8
		MP2/6-311 + +G(3df, 3pd)	205.405 47	
		<i>G</i> 1	205.459 71	
		G2	-205.461 79	54.1
Cis-HONO ^d	¹ A'	MP2/6-31+G(d)	-205.191 20 ^e	52.0
		MP2/6-311 + +G(3df, 3pd)	- 205.404 85	
		Gl	- 205.458 42	
		G2	-205.460 82	54.3
Trans-HONO ^{-d}	² A11	MP2/6-31+G(d)	-205.189 21 ^e	45.1
		MP2/6-311 + +G(3df, 3pd)	-205.407 20	
		<i>G</i> 1	-205.468 21	
•		G2	205.474 09	43.9
Cis-HONO ^{-d}	² A''	MP2/6-31+G(d)	-205.191 70 ^e	45.9
		MP2/6-311 + +G(3df, 3pd)	205.408 43	
		Gl	-205.469 00	
		G2	-205.471 43	46.4
Trans-HONO ^f		MP2/6-31+G(d)	-205.184 96	
$R_{\rm NO} = 1.640$		MP2/6-311 + +G(3df, 3pd)	-205.397 85	
Trans-HONO ^f		MP2/6-31+G(d)	-205.189 30	
$R_{\rm NO} = 1.540$		MP2/6-311 + +G(3df, 3pd)	-205.402 49	
Cis-HONO ^g		MP2/6-311 + +G(3df, 3pd)	-205.379 08	
Cis-HONO ^f		MP2/6-31+G(d)	-205.180 85	
$R_{\rm NO} = 1.640$		MP2/6-311 + +G(3df, 3pd)	-205.393 51	
Cis-HONO ^r		MP2/6-31+G(d)	-205.187 56	
$R_{\rm NO} = 1.516$		MP2/6-311 + +G(3df, 3pd)	-205.400 44	
Cis-HONO ^f		MP2/6-31+G(d)	-205.180 10	
$R_{\rm NO} = 1.250$		MP2/6-311 + +G(3df, 3pd)	-205.396 44	
Cis-HONO ⁻¹		MP2/6-31+G(d)	-205.190 27	
$R_{\rm NO} = 1.750$		MP2/6-311 + +G(3df, 3pd)	-205.407 78	
Cis-HONO ⁻¹		MP2/6-31+G(d)	-205.190 38	
$R_{\rm NO} = 1.540$		MP2/6-311 + +G(3df, 3pd)	205.407 47	
Cis-HONO ⁻¹		MP2/6-31+G(d)	205.189 68	
$R_{\rm NO} = 1.516$		MP2/6-311 + +G(3df,3pd)	205.406 94	
Cis-HONO-		MP2/6-31+G(d)	-205.185 21	
$K_{\rm NO} = 1.429$		MP2/6-311 + +G(3df, 3pd)	205.403 48	
CIS-HONO ⁻		MP2/6-31+G(d)	-205.181 98	
$K_{NO} = 1.392$		MP2/0-311 + + G(3af, 3pd)	205.400 82	

^aMP2 calculations are MP2/6-31+G(d)//MP2/6-31+G(d) or MP2/6-311++G(3df,3pd)//MP2/6-31+G(d).

^bMP2 total energies E_T do not include ZPE, while G1 and G2 do.

^cReported zero-point energies are unscaled, except those used in the G1 and G2 methods, which are scaled by 0.8929 times the value calculated at the HF/6-31G(d) level.

^dEquilibrium geometries.

 $^{\circ}MP4SDTQ/6-311++G(d,p)//MP2/6-31+G(d)$ total energies are -205.322 96 and -205.321 31 hartrees for *trans*-HONO and *cis*-HONO, respectively, and -205.321 31 and -205.321 44 hartrees for *trans*-HONO⁻ and *cis*-HONO⁻, respectively.

^fNO bond length fixed, remaining parameters optimized at the MP2/6-31+G(d) level.

⁸ E_T calculated with equilibrium geometry of *cis*-HONO⁻. MP4SDTQ/6-311++G(*d*,*p*)//MP2/6-31 +G(*d*) total energies are -205.321 31 and -205.322 96 hartrees for *cis*-HONO and *trans*-HONO, respectively, and -205.321 44 and -205.321 31 hartrees for *cis*-HONO⁻ and *trans*-HONO⁻, respectively.

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These results are in good agreement with other theoretical values and the experimental values.^{38,39} Bongartz *et al.*³⁸ measured the UV absorption spectrum of gaseous nitrous acid and found this energy difference to be -2.7 ± 0.20 kJ mol⁻¹. The MP4SDQ/6-311G(*d*,*p*) calculations of Coffin and Pulay³⁹ gave a difference of -4.6 kJ mol⁻¹. For HONO⁻, the *cis* conformer is more stable than the *trans* by between -0.3 to -6.5 kJ mol⁻¹: -6.5 kJ mol⁻¹ [MP2/6-31+G(*d*)], -0.3 kJ mol⁻¹ [MP4SDTQ/6-311++G(3df,3pd)], -2.1 kJ mol⁻¹ (*G*1), and -2.5 kJ mol⁻¹ (*G*2). No independent data exist for HONO⁻ with which we can compare our results.

Molecular geometries

The MP2/6-31+G(d) equilibrium geometries of HO, HO⁻, NO, *cis*- and *trans*-HONO, and *cis*- and *trans*-HONO⁻ may be found in Table II and are compared with experimental values where possible.^{40,41} The optimum parameters for *cis*- and *trans*-HONO found in the MP4SDQ/ 6-311G(*d*,*p*) study of Coffin and Pulay³⁹ are also given in the table. The MP2/6-31+G(d) bond lengths calculated in this study are within 0.025 Å of the experimental lengths. The worst agreement occurs for the HO and N=O bonds in *trans*-HONO and the N=O bond in *cis*-HONO.⁴⁰ This is in contrast to Coffin and Pulay's results³⁹ for HONO, where the worst variation from the experimental results occurred for the O–N bond. With respect to the bond angles, only ∠HON in *cis*-HONO varies significantly from the experimental value (by 1.7°).⁴⁰

Table III presents the MP2/6-31+G(d) normal-mode vibrational frequencies for HO, HO⁻, NO, cis- and trans-HONO, and *cis*- and *trans*-HONO⁻. The vibrational frequencies are unscaled. The experimental frequencies^{42,43} and the unscaled frequencies obtained by Coffin and Pulay³⁹ are also given. The frequencies calculated for HO and HO^- are within 25 cm⁻¹ of the experimental values. In contrast, the unrestricted second-order Møller-Plesset (UMP2)/6-31+(d) harmonic vibrational frequency for NO is in error by 1952 cm^{-1} . As previously observed by Jensen,⁴⁴ this large difference is an artifact of the UMP2 method, occurring when the geometrical derivative of $\langle S^2 \rangle$ is large, as it is for NO. Recently developed perturbation methods based on the restricted open-shell Hartree-Fock (ROHF) wave function, such as the restricted Møller-Plesset (RMP) method of Knowles et al.,⁴⁵ do not exhibit this behavior, as the ROHF wave function is a proper eigenfunction of S^2 . Using the RMP2/6-31+G(d) energies calculated with Gaussian 92,46 we find from finite differences a value of 1898 cm^{-1} for the NO harmonic vibrational frequency, a result in close agreement with experiment.

As is the case with HONO, both conformers of HONO⁻ are minima on the potential energy surface (no imaginary frequencies). The MP2/6-31+G(d) frequencies are within 10% of the experimental and MP4SDQ/6-311G(d_{xp}) values. The discrepancies in the three sets of data for HONO can be explained by the differences in the equilibrium geometries.

Electron affinity and HO-NO bond dissociation energy

From the data in Table I, we can calculate the electron detachment energy of HONO⁻ and the O-N bond dissociation energy in HONO⁻ to form HO⁻ + NO. We believe the G1 and G2 values are accurate to ± 5 kJ mol⁻¹ based on comparisons with experimental values for HO and HONO discussed below.

The electron detachment energies of cis-HONO⁻ and HO⁻ are listed in Table IV. The adiabatic electron detachment energies were calculated from the difference between the lowest quantum level of the negative ion and the corresponding neutral using the G1 and G2 methods. In the case of cis-HONO⁻, the reported value corresponds to the difference between the lowest quantum level of the negative ion and the corresponding neutral of the same conformation cis-HONO. The good agreement of the calculated values for HO⁻ with the experimental electron detachment energy indicates that the G1 and G2 methods will provide fairly accurate values for the electron detachment energy of cis-HONO⁻. The anion cis-HONO⁻ is bound relative to cis-HONO by approximately 0.3 eV. The MP2/6-311+ +G(3df, 3pd) adiabatic electron detachment energies are within 0.13 eV of the G1 and G2 energies. The vertical detachment energy, for electron detachment of cis-HONO⁻ to form *cis*-HONO, is significantly larger than the adiabatic value [estimated to be ~ 0.8 eV using MP2/ 6-311 + +G(3df, 3pd) calculations] because of the significant difference in molecular geometry, especially the O-N bond distance.

The bond enthalpies (ΔH^0) for dissociation of HONO to HO+NO and dissociation of HONO⁻ to HO⁻+NO are listed in Table V. The experimental enthalpy of dissociation for cis-HONO was calculated using standard enthalpies of formation of the molecular species involved at 0 K.³⁵ The calculated bond dissociation energy of *cis*-HONO to HO+NO is in excellent agreement with the experimental value, indicating that the value calculated for cis-HONO⁻ is also good. The much smaller bond dissociation energy for cis-HONO⁻ as compared with cis-HONO reflects the smaller electron affinity of cis-HONO as compared with HO. While the bond dissociation energy of cis-HONO⁻ is larger than the electron detachment energy, the inefficiency of autodetachment reflected by the small efficiency of the associative detachment reaction of $HO^- + NO$ indicates that it may be possible to stabilize HONO⁻ formed in this reaction at high pressures.

Reaction efficiency

When the negative ion and neutral have different geometries, as is the case for HONO⁻ and HONO, autodetachment will generally occur in the region where the two potential energy curves cross, and the efficiency of autodetachment will be given by the characteristics of the crossing region.⁴⁷ In what follows, we use our calculations to investigate this crossing region and the resulting autodetachment efficiency.

The relevant portions of the potential curves of cis-

TABLE II. Molecular geometries.^a

Molecule	Geometrical parameter	Calculated value (This work)	Calculated value (Coffin and Pulay) ^b	Experimental value	Molecule	Geome	etrical neter	Calculated value (This work)	Calculated value (Coffin and Pulay) ^b	Experimental value
HO₅ HO₋c HOc	R _{HO} R _{HO} R _{NO}	0.981 0.977 1.143 1.127 ^e 1.176 ^f		0.970 ^d 0.97 ^d 1.151 ^d	$C_{is}-HONO^{i}$ $R_{O-N}=1.$ $C_{is}-HONO^{i}$ $R_{O-N}=1.$	h 1 640 1 2 h 1 516 1	$R_{N=0}$ R_{HO} CONO CONO $R_{N=0}$ R_{HO}	1.170 0.988 112.9 101.7 1.187 0.989		
Trans-HONG	C^{c} R_{O-N} $R_{N=O}$ R_{HO} $\angle ONO$ $\angle HON$	1.429 1.194 0.982 110.5 102.3	1.405 1.175 0.963 110.6 102.1	1.432 ^g 1.170 ^g 0.958 ^g 110.7 ^g 102.1 ^g	$Cis-HONO1$ $R_{O-N}=1.$	2 h 1 250 1 2	$R_{N=0}$ R_{HO} R_{HO}	112.7 103.6 1.228 1.001 114.5		
Cis-HONO [®]	R_{O-N} $R_{N=O}$ R_{HO} $\angle ONO$ $\angle HON$	1.392 1.208 0.992 113.1 105.7	1.376 1.186 0.973 105.0 113.1	1.392 ^g 1.185 ^g 0.982 ^g 104.0 ^g 113.6 ^g	Cis-HONO R _{O-N} =1.	h 1 750 1 2	HON R _{N=0} R _{HO} CONO HON	108.3 1.223 0.981 109.2 100.4		
Trans-HONO	$\begin{array}{c} \sum R_{O-N} \\ R_{N=O} \\ R_{HO} \\ \angle ONO \\ \angle HON \end{array}$	1.750 1.218 0.979 108.5 99.1			C_{is} -HONO $R_{O-N} = 1.$ C_{is} -HONO	-11 1 540 1 2 -h 1	R _{N=0} R _{HO} ONO HON R _{N=0}	1.280 0.984 107.7 97.9 1.285		
Cis-HONO ⁻	$\begin{array}{c} \circ \qquad R_{\rm O-N} \\ R_{\rm N=O} \\ R_{\rm HO} \\ \angle \rm ONO \\ \angle \rm HON \end{array}$	1.640 1.258 0.982 108.1 96.9			$R_{O-N} = 1.$ Cis-HONO $R_{O-N} = 1.$	516] 2 h] 429]	R _{HO} ONO HON R _{N=0} R _{HO}	0.985 107.7 98.3 1.301 0.987		
$\frac{Trans-HONG}{R_{O-N}=1.64}$	$ D^h = R_{N=0} $ $ 0 = R_{HO} $ $ \angle ONO $ $ \angle HON $	1.164 0.983 109.7 99.5			Cis-HONO R _{O-N} =1.	2 -h 392 1	ONO HON R _{N=0}	107.9 100.0 1.308 0.989		
$\frac{Trans-HONO}{R_{O-N}} = 1.54$	D^{h} $R_{N=0}$ 0 R_{HO} $\angle ONO$ $\angle HON$	1.177 0.983 110.0 100.7				2	ONO HON	108.1 100.8		

^aBond lengths are in Angstroms, bond angles are in degrees.

^bMP4SDQ/6-311G(d,p) calculation (Ref. 39).

cMP2/6-31+G(d) equilibrium geometries.

^dReference 41.

HF/6-31G(d) calculation (Ref. 56).

fRMP2/6-31-G(d) calculation.

^gReference 40.

^hNO bond length fixed, remaining parameters optimized at the MP2/6-31+G(d) level.

HONO⁻ and *cis*-HONO in this reaction as well as the asymptotic energy limits for the separated species $HO^- + NO$ and HO + NO are plotted in Fig. 4, where an energy value of zero is defined as the classical minimum of the negative ion. We have chosen to plot the relative energies of *cis*-HONO⁻ and *cis*-HONO because the ground state of HONO⁻ has the *cis* conformation and there is a barrier to rotation from *trans*- to *cis*-HONO of about 40 kJ mol^{-1.48,49} Therefore, we expect autodetachment from *cis*-HONO⁻ to form *cis*-HONO. [Calculations on *trans*-HONO as a function of R_{O-N} result in a potential similar to that of *cis*-HONO, but positioned at a slightly lower energy and slightly larger R_{O-N} (see Tables I and II).] The relative potential energy values of the species at equilibrium

molecular geometries were determined from the G2 calculations described above, while the energy of the distorted geometries relative to the equilibrium values were determined from the MP2/6-311++G(3df, 3pd) calculations. The potential curves given in Fig. 4 were fit to the Hulburt-Hirschfelder form⁵⁰ in order to uniformly extend them to the dissociating region. While the O-N central stretch is not a normal-mode vibration of either the neutral HONO molecule or the anion, the potential energy curves in Fig. 4 for stretching along the O-N bond can be interpreted as the minimum energy pathway for the concerted decomposition of the molecule or molecular anion into HO+NO or HO⁻+NO, respectively. Furthermore, since the physical process is initially the attraction of

TA.	BLE	III.	Vibrational	frequencies	(ω_e)	in	cm ⁻	•

Molecule	Normal- mode symmetry	ω _e (calc) (This work) ^a	$\omega_e(\text{calc})$ (Coffin and Pulay) ^b	$\omega_e(\text{expt})$
НО		3713		3735°
HO-	-	3702		3700°
NO		3856		1904°
		2221 ^d		
		1898°		
Trans-HONO	A"	592	602	544 ^f
	A'	612	664	596 ^f
	A'	819	896	790 ^f
	A'	1303	1351	1263 ^f
	A'	1656	1767	1700 ^f
	A'	3665	3844	3591 ^f
Cis-HONO	A'	638	680	609 ^f
	A"	703	694	640 ^f
	A'	904	947	852 ^f
	A'	1340	1383	g
	'A'	1612	1746	1641 ^f
	A'	3496	3699	3426 ^f
Cis-HONO	A"	279		
	A'	388		
	A'	715		
	A'	1179		
	A'	1504		
	A'	3618		
Trans-HONO	A'	150		
	A"	171		
	A'	485	•	
	A'	961		
	A'	2102		
	A'	3680		

 $^{a}MP2/6-31+G(d).$

^bMP4SDQ/6-311G(*d*,*p*) calculation (Ref. 39).

^cReference 42. ^dHF/6-31G(d) calculation (Ref. 56).

 $^{\circ}RMP2/6-31-G(d)$ calculation (Ref. 56).

^fReference 43.

^gNot observed experimentally.

 $HO^- + NO$ with thermal energy of ~300 K, it can be argued that the reaction initially follows along this minimum energy reaction coordinate. At some separation (~1.4-1.5 Å), the negative ion and neutral potential energy curves will cross, and it is in this region that electron detachment may occur.

The autodetachment efficiency can be reduced by the presence of an energy barrier at the potential energy curve crossing. However, the potential energy curves for *cis*-HONO and *cis*-HONO⁻⁻ in Fig. 4 suggest that autodetachment, and consequently the title associative detachment reaction, are not inhibited by an energy barrier. The absence of a significant energy barrier despite the large difference in equilibrium O-N bond distance for the two species can be attributed in part to the weak R_{O-N} dependence of the *cis*-HONO⁻ potential. Apparently the energy gained from ion-dipole and ion-induced dipole forces is offset by repulsive forces which keep the bond distance long and the total energy small in the negative ion.

The autodetachment efficiency may also be affected by the overlap of anion and neutral wave functions. Although autodetachment in a low energy ion-molecule reaction is

TABLE IV. Electron detachment energies (ΔE).

Molecule	Calculational level	$\Delta E_{calc} (eV)^{a}$	$\Delta E_{expt}(eV)$
HO ⁻	$MP2/6-311 + +G(3df, 3pd)^{b}$	1.944	1.827 672 0°
	<i>G</i> 1	1.846	
	G2	1.874	
Cis-HONO ^{-d}	$MP2/6-311 + +G(3df, 3pd)^{b}$	0.160	
	<i>G</i> 1	0.288	
	G2	0.289	
Cis-HONO ^{-e}	$MP2/6-311 + +G(3df, 3pd)^{b}$	0.799	

*Adiabatic electron detachment energy unless otherwise noted.

 $^{b}MP2/6-311 + +G(3df, 3pd)//MP2/6-31+G(d)$ calculation.

^cReference 57.

^dAdiabatic electron detachment energy for detachment from *cis*-HONO⁻ to form *cis*-HONO.

Vertical electron detachment energy for detachment from *cis*-HONO⁻ to form *cis*-HONO.

not likely to involve a strictly vertical transition, we expect the probability for autodetachment to be affected by the vibrational wave function overlap of the anion and neutral in the classical region of detachment. We can locate this region from the position of crossing of the *cis*-HONO and *cis*-HONO⁻ curves in Fig. 4. Autodetachment may occur from the continuum states or bound states of HONO⁻ to bound states of HONO. While HONO⁻ is initially formed in continuum states, quasibound states can result from transfer of translational energy to vibrational energy of the negative ion. Such a situation is common in low energy ion-molecule reactions, as evidenced by the observation of statistical atom exchange in a number of reactions.^{1,36,37}

Estimation of the probability of autodetachment from bound states of HONO⁻ to bound states of HONO involves evaluating the Franck–Condon vibrational wave function overlap of these two species multiplied by the fraction of complexes formed in each of the different vibrational levels. We find, however, that due to the very different O–N bond lengths of these species, overlap is very small $(10^{-2}-10^{-4})$ for all pertinent vibrational levels of *cis*-HONO⁻ and *cis*-HONO. This small overlap suggests that the observed associative detachment reaction must arise from autodetachment of continuum states of HONO⁻.

Initially HONO⁻ will be formed in continuum states and may be better described as a HO⁻+NO collision complex. The possibility of autodetachment from these continuum states to bound states of HONO can be estimated by

TABLE V.	Bond	enthalpies	(ΔH^0)	at O	K.
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Bond ^a	Calculational level	$\frac{\Delta H_{calc}^{0}}{(\text{kJ mol}^{-1})}$	$\frac{\Delta H_{expt}^{0 b}}{(\text{kJ mol}^{-1})}$
ΔH^0 (cis-HO–NO)	Gl	202.6	198.7 ± 1.8
	G2	202.1	
ΔH^0 (cis-HO ⁻ -NO)	G 1	52.2	
	<i>G</i> 2	49.1	

 $^{a}\Delta H^{0}(cis$ -HO–NO) indicates energy to break the HO–NO bond in cis-HONO forming HO+NO.

^bCalculated from standard heats of formation at 0 K from Ref. 35.



FIG. 4. Dissociation potential energy curves for HONO and HONO- to form HO+NO and HO-+NO, respectively.

analysis of the reverse process-dissociative attachment (DA) of e+HONO \Rightarrow HO⁻+NO, since the cross sections are related through detailed balancing. A detailed analysis of DA for e+HONO requires knowledge of the multidimensional potential surface for HONO. The cross section for electron capture in DA is determined by the asymptotic form of the nuclear motion wave function $\xi(R)$. For electrons with initial energy $\hbar^2 k_i^2/(2m)$, we have for the cross section

$$\sigma_{\rm DA} = \frac{4\pi^2 m K}{M k_i} \lim_{R \to \infty} |\xi(R)|^2.$$
⁽⁴⁾

Here $\xi(R)$ represents the nuclear motion wave function along the minimum energy pathway for HO-NO shown in Fig. 4. Treating electron capture as a direct process and neglecting interference with possible electron vibrational excitation processes, we can evaluate Eq. (4), provided some estimate of the capture width for electron attachment can be made for the region of HONO to the left of the crossing point (~ 1.4 -1.5 Å) on the minimum energy reaction surfaces shown in Fig. 4. Using Fermi's golden rule, we estimate the resonance width as

$$\Gamma = 8\pi^2 \overline{k}^2 \sqrt{(2\Delta E)},\tag{5}$$

where ΔE is the calculated vertical separation of the negative ion state and that of HONO, and \overline{k} is an average

value of the coupling matrix element for the electronic states of the neutral and negative ion species. We use an average value of $\Gamma = \sim 0.01$, a value characteristic of weak coupling between the neutral and negative ion states.

For thermal energy collisions of $HO^- + NO$ $(E \sim 0.038 \text{ eV})$ and invoking detailed balance, we find the following estimates of the cross sections for association detachment:

	and the second s
HONO vibration state	$\sigma(\text{cm}^2)$
0	0.6×10 ⁻¹⁸
1	0.3×10^{-17}
2	0.3×10^{-16}
3	0.5×10^{-16}
4	0.5×10^{-17}

The small detachment cross section for v=0 arises from the poor Franck–Condon overlap between HONO (v=0) and the continuum states of HONO⁻. These calculated cross section data correspond to a maximum rate constant of $\sim 4 \times 10^{-12}$ cm³ s⁻¹, in good agreement with the measured rate of 4.1×10^{-12} cm³ s⁻¹.

CONCLUSIONS

Analysis of our reaction kinetic data and consideration of alternative hypotheses lead us to conclude that the hydroxide ion reacts with the nitric oxide via associative detachment, albeit inefficiently, forming nitrous acid and an electron. Our theoretical calculations suggest that this inefficiency arises as a result of the very different geometries of the temporary negative ion HONO⁻ formed and the neutral reaction product HONO, making autodetachment from HONO⁻ to HONO+*e* inefficient as compared with dissociation back to reactants $HO^- + NO$.

Our calculations also indicate that HONO⁻ has a positive electron detachment energy and that the vertical detachment energy is significantly larger than the adiabatic value because of the change in geometry between the anion and neutral. An experimental determination of these values would be instructive, but formation of a stable beam of HONO⁻ could be difficult. The small cross section for autodetachment from bound states of cis-HONO⁻ to bound states of cis-HONO indicate that once formed, the bound state ions should be fairly stable against autodetachment. Indeed, it may be possible to form the stable ions from the title reaction $HO^- + NO$ because of the inefficiency of associative detachment. However, this requires that the temporary negative ion formed can be stabilized by a third body before it dissociates back to reactants.

Slow reactive electron detachment channels (associative detachment or other channels producing neutral species plus an electron) have not commonly been reported in the literature.¹ Recent work in this laboratory, however, has shown that reactive electron detachment channels can be a common reaction channel for ion-molecule reactions and that the efficiency of these channels can range from the most efficient to the very inefficient.^{12,51-55} Identification of slow reactive electron detachment channels or channels competing with ionic product channels requires an ability to monitor total ion signal, relative ion signals, and relative detection sensitivities. A SIFT with the ability to monitor an ion current which is representative of the flow tube ion density, such as used in these experiments, is well suited for such investigations.

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