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^{15}N NMR Spectroscopic Investigation of Nitrous and Nitric Acids in Sulfuric Acid Solutions of Varying Acidities[1]

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Both nitrous and nitric acids were studied in sulfuric acid solutions of varying acid strengths by ^{15}N NMR spectroscopy. The study gives new insights into the nature of intermediates present at different acid strengths. Furthermore, we have also discovered a novel redox reaction between NO_2^+ and NO^+ ions involving the intermediacy of their respective acids. A mechanism is proposed to explain the observed results.

Introduction

Nitric (HNO_3) and nitrous (HNO_2) acids are the main sources of nitronium (NO_2^+) and nitrosonium (NO^+) ions, respectively.[2,3] Although nitric acid and nitronium and nitrosonium ions are well-known[2,3] and are characterized as stable entities, considerable controversy exists about the nitrous acid equilibria in sulfuric acid solutions and the amenability of the system to proper spectroscopic characterization. Nitric as well as nitrous acid equilibria in sulfuric acid solutions of varying acid strengths have been probed by spectroscopic techniques.[2,3] However, no ^{15}N NMR spectroscopic study has been undertaken thus far to study these systems.

We report ^{15}N NMR spectroscopic investigation of nitrous and nitric acid in sulfuric acid solution. These studies give valuable insights into the nature of the species present at different acid strengths. Furthermore, we also report a unique redox reaction between nitronium and nitrosonium ions involving the intermediacy of their respective acids. The choice method of obtaining ^{15}N NMR data is by ^{15}N enrichment whenever possible and economically feasible. Therefore, for the systems studied herein, easily accessible ^{15}N-enriched compounds were employed to follow the intermediate species formed by the direct examination of the nitrogen reaction center.

Results and Discussion

Nitrous Acid–Nitrosonium Ion System. The nitrous acid–nitrosonium ion equilibrium had been the subject of controversy[4-6] due to uncertainties of the involvement of the nitrosoacidium ion (eq 1) and the onset decomposition of nitrogen(III) species.

$$H^+ + HNO_2 \rightleftharpoons H_2NO_2^+ \rightleftharpoons NO^+ + H_2O \qquad (1)$$

The methods employed for the investigation of this equilibrium were UV–vis[4a-e] and Raman spectroscopy[4f] of sodium nitrite solutions in aqueous sulfuric acid of various strengths. Bayliss[5] and Seel[6] independently arrived at the conclusion that there was no detectable amount of nitrosoacidium ion present in their sample mixtures examined by UV–vis spectroscopy, which were accordingly best described as acid-catalyzed two-particle equilibria (eq 2).

$$H^+ + HNO_2 \rightleftharpoons NO^+ + H_2O \qquad (2)$$

In order to obtain consistent, reproducible results, however, corrections for the loss of nitrogen(III) had to be made. Bayliss and Watts went on to investigate the kinetics of the decomposition reactions under the conditions of their UV–vis measurements and found first-order dependence on nitrite concentration.[7] Decomposition was fastest at 55% (by weight) sulfuric acid and slowed down both at lower and higher acidities. Evaluation of the data led to the following mechanism of the decomposition with k_2 as the rate determining step:

$$H^+ + HNO_2 \xrightleftharpoons[k_{-1}]{k_1} H_2NO_2^+ \xrightleftharpoons[k_{-2}]{k_2} NO^+ + H_2O \qquad (1)$$

$$NO^+ + HNO_2 \xrightleftharpoons[k_{-3}]{k_3} N_2O_3 + H^+ \qquad (3a)$$

$$N_2O_3 \xrightleftharpoons[k_{-4}]{k_4} NO + NO_2 \qquad (3b)$$

Table I. ^{15}N NMR Chemical Shifts of $H^{15}NO_2$–$^{15}NO^+$ in Aqueous Sulfuric Acid

species	solvent	*t*, °C	color	$\delta(^{15}N)$	line shape
NO_2^-	D_2O	−25	none	610	sharp
HNO_2	D_2O/3% D_2SO_4	+25	none	575	sharp
HNO_2	D_2O/0.5 M HCl	+25	none	576	sharp
NO^+	HSO_3F	+25	none	383	sharp
NO^+	98% D_2SO_4	+25	none	377	sharp
HNO_2	10% D_2SO_4	−5	none	575	sharp
HNO_2	20% D_2SO_4	−5	none	575	slightly br
HNO_2	30% D_2SO_4	−5	none	573	br
HNO_2	40% D_2SO_4	−5	blue	570	v br
NO^+	40% D_2SO_4	−5	blue	361	sharp
HNO_2	50% D_2SO_4	−10	blue	565	v br
NO^+	50% D_2SO_4	−10	blue	355	sharp
HNO_2	50% D_2SO_4	0	blue tint	566	v br, dec
NO^+	50% D_2SO_4	0	blue tint	355	sharp
HNO_2	50% D_2SO_4	+10	none	565	extremely br
NO^+	50% D_2SO_4	+10	none	354	sharp
NO^+	50% D_2SO_4	+20	none	354	sharp

Before the measurements were taken, the mixture was flushed with dry dinitrogen to eliminate all gaseous byproducts, and a linear first-order rate law in nitrogen(III) disappearance was observed. As admitted by the authors, their rate expression could not be applied to the critical acid concentration range, where decomposition was fastest. The decomposition was also found to increase rapidly with increasing temperature.[7]

The key to understanding the nitrous acid–nitrosonium ion system is the study of the range of greatest instability. We, therefore, undertook such a study and monitored the nitrous acid–nitrosonium ion system by ^{15}N NMR spectroscopy. There are two ways to monitor changes in this system. One can slowly increase the acidity of the mixture and thus approach the critical range or maintain a fixed acidity close to the critical range with as low a temperature as possible and subsequently raise the temperature.

Table I summarizes the ^{15}N chemical shifts measured (referenced to external liquid NH_3) for all the species involved at different acid concentrations and different temperatures.

After recording of the NMR spectra, the 40 and 50% sulfuric acid solutions were added to cold 96% sulfuric acid to increase their overall acidity to 92% H_2SO_4. This permits the distinction to be made between NO^+ and any possible formation of NO_3^-

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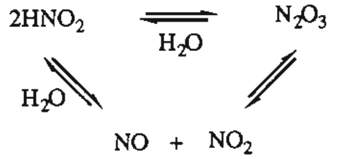
from disproportionation of HNO_2 (eq 4a), since NO_3^- absorbing at 377 ppm, in close proximity to NO^+, is completely converted to NO_2^+ ($\nu(^{15}N)$ of 251 ppm; vide infra) in 92% H_2SO_4[8,9] (eq 4b).

$$3HNO_2 \rightleftharpoons HNO_3 + 2NO + H_2O \tag{4a}$$

$$HNO_3 + H^+ \rightleftharpoons NO_2^+ + H_2O \tag{4b}$$

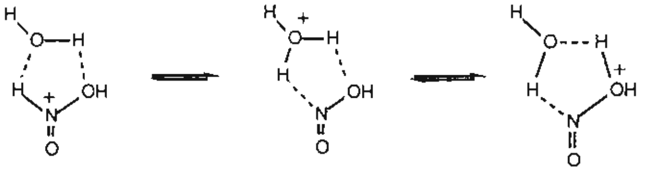
After acidification, no nitronium ion peak was found and disproportionation of HNO_2 according to eq 4a can be discarded as a competing side reaction. Analysis of the data in Table I shows identical trends when the acidity is increased at constant temperature and the temperature is elevated at constant acidity. In either case, the nitrous acid resonance starts to broaden as its intensity decreases with higher acidity or temperature, whereas the nitrosonium ion peak remains sharp throughout all experiments. Both the HNO_2 and the NO^+ signals are shielded at intermediate acidities/temperature by about 10 and 30 ppm, respectively. In contrast to the NO_2^+–HNO_3 system, which is a true two-particle equilibrium with a nitroacidium-like transition state or intermediate (vide infra),[8] the NO^+–HNO_2 system displays different behavior. The fact that the NO^+ line shape remains sharp suggests that its formation (and consumption) must be slow on the NMR time scale in accordance with the kinetic analysis of Bayliss and Watts.[7] Nitrous acid, however, must be involved in an equilibrium (or exchange) at higher acidities/temperature that is fast on the NMR time scale and does not include NO^+ to account for the line broadening effect. There are two species that could conceivably be responsible for the observed exchange, namely N_2O_3 (or its decomposition products NO and NO_2) or the elusive nitrosoacidium ion. If the former were the exchanging species by spontaneous formation and decomposition of HNO_2 (eq 5), a second-order rate dependence in nitrite instead of a first-order rate law should have been observed.[7] Likewise, invoking the presence of NO and NO_2 radicals to account for the line broadening of the HNO_2 signal should have resulted in a broadened peak for NO^+ too, as well as some formation of NO_3^- (eq 4a), neither of which was observed.



(5)

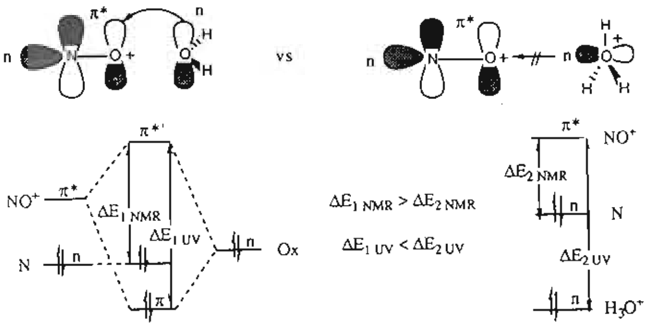
The only possible explanation seems to be a protonation–deprotonation equilibrium between nitrous acid and the elusive nitrosoacidium ion, according to eq 1, which is perturbed by the slow, continuous depletion of the latter to form nitrosonium ion. This would account for the first-order rate behavior as well as the broadened HNO_2 signals and the gradual increase of the NO^+ concentration. At low acidities and/or temperatures this equilibrium has a very small contribution from the nitrosoacidium ion, resulting in only a slightly broadened line for the HNO_2 peak. As the acidity and/or temperature is increased, the concentration of the nitrosoacidium ion increases, providing more NO^+ cation by dehydration, which assumes increasing steady-state concentration, relative to HNO_2, i.e. more extensive line broadening. At this point decomposition of nitrogen(III) species is most rapid, since NO^+ and HNO_2 are both present in comparable amounts to accelerate the formation of N_2O_3 (eq 3a), which may or may not further decompose to NO and NO_2 (eq 3b). The lack of formation of brown gas (NO_2) and the absence of NO_3^- would indicate that the reaction depicted in eq 3b does not occur to any major extent under these conditions. The nitrosoacidium ion, however, cannot be observed as a separate entity. Its elusiveness has been the subject of controversy in the interpretation of UV–vis spectroscopic data.[4] It was invoked to explain the anomalous shift of the nitrous acid UV absorption to higher wavelength with increasing acidity,[4a] but later reports[4c] preferred to explain this phenomenon by decreased availability of the lone electron pair on nitrogen in HNO_2 for the n → π* transition due to stronger hydrogen bonding in more concentrated sulfuric acid solutions. The shielding of the ^{15}N NMR chemical shift of HNO_2 at higher acidities is in accordance with an increased interaction between the sulfuric acid and the nitrogen lone pair due to an increased contribution of the local paramagnetic shielding constant, σ_{para} (greater HOMO–LUMO gap), to the overall shielding constant.[3] Whether the nitrogen is fully protonated to form small concentrations of the nitrosoacidium ion, which is in equilibrium with its deprotonated conjugate acid, or engages in stronger hydrogen bonding, as invoked to explain the bathochromic shift, cannot be discerned by UV–vis or ^{15}N NMR spectroscopy. Both sets of data can be explained in terms of tight coordination of a water molecule to HNO_2 that could assist the proton transfer from the nitrogen to the oxygen preceding the dehydration. This would account for the shielding and extensive broadening of the ^{15}N NMR signal of HNO_2 as well as its bathochromic shift in the UV–vis experiments upon acidification (Scheme I).

Scheme I



I II III

Chart I



Increasing acidity enhances the protonation power of the assisting H_2O molecule necessary for the protonation of an oxygen lone pair (prior to dehydration) rather than a more basic nitrogen lone pair. This would be consistent with an increased shielding (partial lengthening of the ON–OH_2^+ bond) and line broadening via contribution of an additional particle to the ongoing equilibrium. These equilibrating species, I–III, are not expected to display UV maxima very different from HNO_2 itself, since the electronic n → π* transition is only slightly perturbed (increased HOMO–LUMO gap), being in accord with the observed shift to higher wavenumbers. In this context the elusive nitrosoacidium ion would be better represented as a resonance hybrid between structures I–III, i.e. $HNO_2 \cdot H_3O^+$, instead of $NO_2H_2^+$. As seen by comparison between our ^{15}N NMR and the UV–vis data,[6] the magnitude of the shifts involved are small compared to the shielding of ^{15}N chemical shift and the UV maxima shifts for NO^+.[10] The deshielding of approximately 30 ppm observed in the ^{15}N NMR spectra between free NO^+ (383 ppm) and coordinated NO^+ (355 ppm) stems from a decrease in the ΔE term (HOMO–LUMO separation), $n_N \rightarrow \pi^*_{NO^+}$, with increasing acidity resulting in a smaller contribution to the σ_{para} shielding constant[9,10] (Chart I).

The hypsochromic shift (10000 cm^{-1}) in the electronic spectra, however, does not originate from the electronically forbidden $n_N \rightarrow \pi^*_{NO^+}$ transition, but from an intermolecular $n_{H_2O} \rightarrow \pi^*_{NO^+}$ transition, where the ionization potential of the donor water

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molecule increases with increasing H-bonding interaction with the solvent H_2SO_4 (i.e. acidity).[6] In terms of MO description, this means that the remaining lone pair on oxygen is lowered in energy, becoming incompatible for mixing with the π^* of NO^+ as the acidity increases (Chart I).

Finally, the dual role of water as proton and electron donor is reflected in the observed data as well. At low acidities, the position of equilibrium 1 and the decomposition rate are dependent on the activity of HNO_2 and the acid, H_3O^+, to protonate HNO_2, generating "$HNO_2 \cdot H_3O^+$", the common intermediate, whereas at higher acid concentrations (<60% H_2SO_4), the decomposition rate decreases parallel to the activity of water, i.e. decreasing electron donor ability. The fact that Bayliss and et al.[5] as well as Seel[6] found their ratios of NO^+:HNO_2 to account for all nitrous material (after correction for the decomposition) is understood, considering they included the species responsible for the absorptions shifted to higher wavenumbers at the critical acid range in the HNO_2 mole fraction thereby adding the equilibrium contribution of $HNO_2 \cdot H_3O^+$ to the HNO_2 contribution, leaving these mixtures as a two-particle system.

Monitoring the nitrous acid–nitrosonium ion system by ^{15}N NMR spectroscopy provides additional insight into this complex system. Due to the slow time scale relative to UV–vis or Raman spectroscopy, exchange and equilibria phenomena could be detected that allow acquisition of a better picture of the nature of the controversial, elusive nitrosoacidium ion.[4-6]

Nitric Acid–Nitronium Ion System. In contrast to the previously discussed nitrous acid–nitrosonium ion system, the nitric acid–nitronium ion system has been well studied.[2] A number of spectroscopic techniques such as UV, Raman, and ^{14}N NMR spectroscopy have been used to determine the fractional conversion of HNO_3 into NO_2^+ ion as a function of the acidity of the medium.[2,8,11,12]

Marziano et al.,[12] on the basis of Raman spectroscopic studies, showed that the acidity dependence of the HNO_3–NO_2^+ ion equilibrium is adequately described in terms of the Mc acidity function. Ross, Kuhlmann, and Malhotra[8] have utilized ^{14}N NMR spectroscopy to determine fractional conversions in HNO_3–NO_2^+ equilibrium. These authors were also able to determine the rate constants for the formation of the NO_2^+ ion as well as for its hydration. We have now utilized ^{15}N NMR spectroscopy to complement the ^{14}N results. Figure 1 shows the ^{15}N NMR spectra of sodium nitrate (95% ^{15}N enriched) at various H_2SO_4 concentrations. At an acid strength of 84.1 wt %, only nitric acid is observed. At 88.5 wt % of acid concentration, both nitric acid as well as nitronium ion are observed. At 96.4 wt %, only nitronium ion is observed. These observations are in accord with the previous results.

$^{15/14}N$ Exchange of $^{15}NO_2^+$ with $^{14}NO^+$ in Sulfuric Acid Solution. It has long been established that nitrites are oxidized by dilute nitric acid, a reaction thought to occur according to eqs 6–8.[13]

$$3NaNO_2 + 3HNO_3 \rightleftharpoons 3HNO_2 + 3NaNO_3 \qquad (6)$$

$$3HNO_2 \rightleftharpoons HNO_3 + 2NO + H_2O \qquad (7)$$

$$3NaNO_2 + 2HNO_3 \rightleftharpoons 3NaNO_3 + 2NO + H_2O \qquad (8)$$

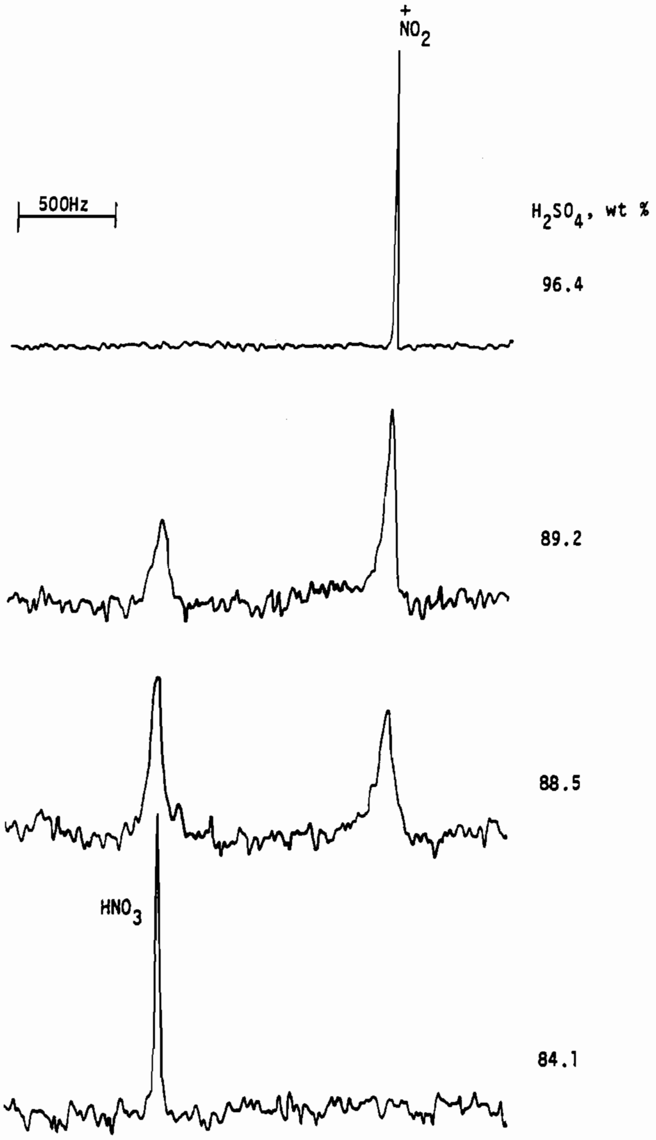

Figure 1. 20.82-MHz ^{15}N NMR spectra of 0.8 M solutions of $NaNo_3$ (95% ^{15}N) in aqueous sulfuric acid at ambient temperature.

Nitric acid, however, does not seem to react as an oxidizing agent, but merely as a proton source to protonate nitrite anion, giving the conjugate acid base pair in a common acid–base reaction (eq 6). As the nitrous acid concentration increases, it starts to decompose by the disproportionation mechanism discussed in the previous section. The nitrogen(V)-containing species (HNO_3 and $NaNO_3$) do not participate in the disproportionation at all, since using sulfuric acid instead of nitric acid to generate nitrous acid from its conjugate base nitrite anion eventually results in the same disproportionation reaction of HNO_2 into NO and HNO_3.

In order to discern whether nitrogen(III) can be oxidized by nitrogen(V) species under acidic conditions, which are required for nitrogen(V) to act as an oxidizer, one has to convert the unstable nitrous acid into the acid-stable nitrosonium ion. Concentrated nitric acid would be acidic enough to accomplish this conversion, but it is prone to disproportionation and does not lend itself to quantitative analysis of this redox equilibrium. The only acid-stable nitrogen(III) and nitrogen(V) species are the nitrosonium and the nitronium ion, NO^+ and NO_2^+, respectively.

Consequently, we investigated the reaction of NO^+ with NO_2^+ in concentrated sulfuric acid where neither ion undergoes decomposition and, hence, any change in the composition of the mixture must be due to a redox reaction between nitrogen(V) and nitrogen(III) species. To this end, we reacted a solution of ^{15}N-labeled $Na^{15}NO_3$ in 98% concentrated D_2SO_4 (checked to contain $^{15}NO_2^+$ cation only) with a solution of unlabeled $^{14}NO^+$ of the same acid strength. When the sealed mixture is monitored by ^{15}N NMR spectroscopy over the course of 3 weeks, slow exchange of the ^{15}N label is observed. The initial NMR recording taken after mixing the solutions showed no NO^+ resonance, only NO_2^+ at 251 ppm (referenced to liquid NH_3). After 24 h a peak at 377 ppm emerges, known to correspond to the $^{15}NO^+$ cation (independently determined by dissolution of ^{15}N-labeled $Na^{15}NO_2$ in concentrated D_2SO_4). The peak at 377 ppm steadily grows in intensity, and its integrated area was recorded over time and normalized against the NO_2^+ absorption at 251 ppm. Since both

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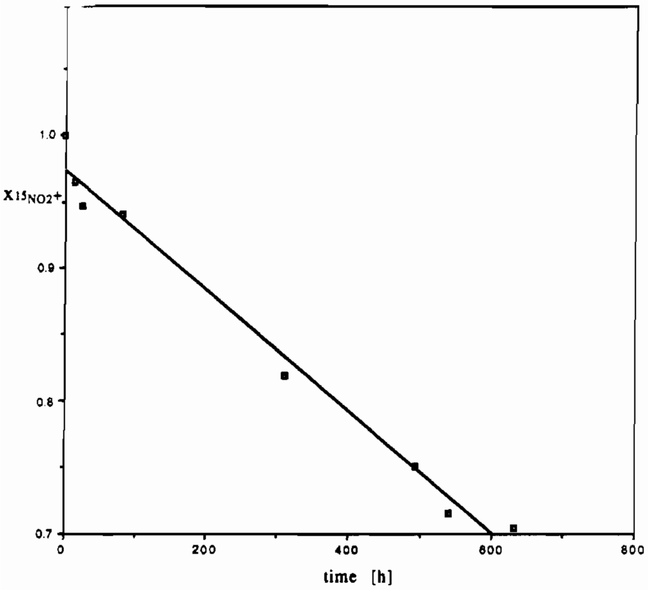

Figure 2. Decrease of $x_{^{15}NO_2^+}$ with time.

particles are linear cations with a sp-hybridized nitrogen atom (comparable magnetic anisotropies) and the experimental conditions such as temperature, magnetic field strength, concentration, and solvent are identical for both ions, their spin–lattice relaxation times may be assumed to be of the same magnitude,[9,10] permitting direct integration of the peak areas to ascertain their respective mole fractions.

When the NO_2^+ mole fraction, $x_{^{15}NO_2^+}$, is plotted versus time a straight line with a correlation coefficient of 0.99 is obtained, indicative of a first-order type rate dependence on the change in NO_2^+ concentration (Figure 2). To rationalize the above result we propose a compatible mechanism.

A direct binary reaction between the two cationic species is incompatible with the first-order type rate dependence as well as the repulsion of like charges. The possibility of a monomolecular decomposition of $^{15}NO_2^+$ to $^{15}NO^+$ by loss of oxygen to account for the observed rate behavior can be discarded, since $^{15}NO_2^+$ in 98% sulfuric acid in the absence of NO^+ cation did not show even traces of $^{15}NO^+$ after 1 week. These considerations and the fact that the presence of NO^+ cation is required and the increase in ^{15}N-labeled $^{15}NO^+$ concentration is paralleled by a corresponding decrease of ^{15}N-labeled $^{15}NO_2^+$ concentration necessitate a multistep mechanism with a bimolecular reaction in the rate-determining step (RDS) that obeys a pseudo-first-order rate law. Furthermore, it has been established that the nitric acid–nitrosonium ion equilibrium in sulfuric acid is only shifted to the latter side at acidities higher than 90% sulfuric acid,[8] which allows for a very small equilibrium concentration of nitric acid even in 98% D_2SO_4. We therefore suggest the mechanism in eqs 9–12.

$$^{15}NO_2^+ + H_2O \overset{\text{RDS}}{\underset{}{\xrightleftharpoons{\text{slow}}}} H^{15}NO_3 + H^+ \tag{9}$$

$$H^{15}NO_3 + {}^{14}NO^+ \xrightleftharpoons{\text{fast}} [HO_2{}^{15}N\text{–}O\text{–}{}^{14}NO]^+ \tag{10}$$

$$[HO_2{}^{15}N\text{–}O\text{–}{}^{14}NO]^+ \xrightarrow{\text{fast}} H^{15}NO_2 + {}^{14}NO_2^+ \tag{11}$$

$$H^{15}NO_2 + H^+ \xrightarrow{\text{fast}} {}^{15}NO^+ + H_2O \tag{12}$$

Once nitric acid is formed it can react with a NO^+ cation in a relatively fast step to generate an intermediate (or a transition state) that contains both ^{15}N-labeled and unlabeled nitrogen. The decomposition of this intermediate (transition state) to exchange the ^{15}N label produces nitrous acid, which is immediately protonated and dehydrated in this highly acidic medium to give ^{15}N-labeled $^{15}NO^+$ cation. Consequently, the net reaction is ^{15}N exchange between labeled $^{15}NO_2^+$ and unlabeled $^{14}NO^+$ cations. The alternative possibility of reaction between NO^+ and D_2O as initial and rate-determining steps to set up the label exchange would not change the observed rate law but seems very unlikely. The nitrous acid–nitrosonium ion equilibrium is totally shifted to the latter side at much lower acidity, (70% H_2SO_4) such that the probability for the existence of HNO_2 in 98% sulfuric acid can be negligible. The exchange of the ^{15}N label in the intermediate (transition state) can be formally considered a reduction of nitric acid by nitrosonium ion and in frontier orbital terms to be an electron transfer from the n electrons of NO^+ into the antibonding empty π^*_z orbital of HNO_3, weakening this N–O bond and resulting in subsequent decomposition of the intermediate. The above exchange mechanism has also been confirmed by reacting $^{15}NO^+$ with $^{14}NO_2^+$ in 98% sulfuric acid medium.

Experimental Section

^{15}N-enriched $Na^{15}NO_3$ (95%) and $Na^{15}NO_2$ (99%) and 99% D-enriched D_2O (99.8%) and D_2SO_4 (98%) were purchased from MSD Isotopes and Aldrich, respectively, and used as received. $NaNO_3$ and $NaNO_2$ are commercially available from Baker (99.9%) and used without further purification. ^{15}N spectra were recorded either on a Varian Associates Model VXR 200 (data system VXR 4000) NMR spectrometer equipped with a 5-mm broad-band variable-temperature probe or a FT-80 NMR spectrometer equipped with a 10-mm broad-band probe and an external lock. ^{15}N chemical shifts were referenced to external liquid NH_3 at $\delta = 0.00$ ppm.

Preparation of the Nitrous Acid Mixtures. A predetermined volume of concentrated D_2SO_4 was injected into an oven-dried 5-mm NMR tube filled with the appropriate volume of D_2O to make up 10–15% sulfuric acid solutions of total volume of 0.5 mL. The NMR tube was sealed with a rubber septum and then degassed by repeated (three times) evacuation and venting with dry argon gas. These degassed solutions were cooled to −10 °C, and approximately 20 mg of ^{15}N-enriched $Na^{15}NO_2$ was added to the NMR tube, which was then degassed again at −10 °C. After complete dissolution of the salt, the tube was inserted into the NMR probe that had been precooled or kept at room temperature, depending on the individual experiment, and the ^{15}N NMR spectra were recorded.

Preparation of Nitric Acid Mixtures. A predetermined amount of concentrated H_2SO_4 was carefully injected into an oven-dried 10-mm NMR tube filled with the appropriate amount of water to make up 80–97% sulfuric acid solutions of total volume of 1.5 mL. The NMR tubes were sealed with a rubber septum, degassed by repeated (three times) evacuations with dry argon gas. To these degassed solutions approximately 25 mg of ^{15}N-enriched $Na^{15}NO_3$ was added, and the resulting solutions were degassed further. After the dissolution of the salt, the ^{15}N NMR spectra were obtained at ambient temperature (23 °C).

Preparation of NO^+ and NO_2^+ in D_2SO_4. Approximately 10 mg of ^{15}N-enriched $Na^{15}NO_3$ or $Na^{15}NO_2$ was dissolved in 0.25 mL of D_2SO_4 in an 5-mm NMR tube. The tube was then sealed with a rubber septum and degassed for 5 min. To this mixture of $^{15}NO_2^+$ or $^{15}NO^+$ cation in 98% D_2SO_4 was added a similar solution of unenriched NO^+ or NO_2^+ in 98% D_2SO_4 prepared analogously, and the combined solution of 0.5 mL total volume was then degassed and sealed again. The ^{15}N NMR spectra recorded immediately only showed resonances for $^{15}NO_2^+$ or $^{15}NO^+$.

Acknowledgment. Support of our work by the Office of the Naval Research is gratefully acknowledged.

Registry No. HNO_2, 7782-77-6; HNO_3, 7697-37-2; NO^+, 14452-93-8; NO_2^+, 14522-82-8; $H_2NO_2^+$, 36180-50-4.