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Constraining the Mechanism of OH + NO_2 Using Isotopically Labeled Reactants: Experimental Evidence for HOONO Formation[†]

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The reaction of OH with NO_2 is central to atmospheric chemistry, and its dynamics can be constrained by studying the kinetics of isotopically labeled ^{18}OH with NO_2. This labeling opens an isotopic scrambling pathway in the reaction coordinate for nitric acid formation, providing experimental constraints on the high-pressure behavior of the reaction with data obtained at low pressures. This reaction, however, is complicated by the presence of a second product isomer, peroxynitrous acid (HOONO), which does not have a scrambling pathway. We present data for the reaction of ^{18}OH with NO_2 at room temperature between 4 and 200 Torr. The reaction is rapid and independent of pressure. We also locate the H-atom isomerization transition state and show that the isomerization rate constant is at least an order of magnitude faster than adduct dissociation. These results allow us to accurately constrain the formation rate constant of $HONO_2$, which is a factor of 5 slower than the observed OH removal rate constant at high pressure. We conclude that the difference is due to HOONO formation. Our conclusion is consistent with recent theoretical predictions of this branching, and also provides the only self-consistent reconciliation of the high-pressure data with the remainder of the experimental data set.

Introduction

Not only does the reaction of NO_2 with OH play a central role in atmospheric chemistry,[1,2] it also has highly complicated and confounding reaction dynamics, comprising multiple vibrationally excited intermediates prone to collisional stabilization.[3−5] Consequently, evaluation of the pressure dependent rate constant for this reaction has proven to be difficult, despite a data set nearly without parallel in either scope or quality.[6,7] The high pressure limit has been especially troublesome, both because the small size of the reactive phase space forces this limit to exceedingly high pressures[8,9] and because it has proven difficult to reconcile the existing high-pressure data with data obtained at lower pressures.[10,11]

These mechanistic complexities have tangible effects. They are the root cause of substantial disagreements between published extrapolation functions for this reaction, which in turn profoundly influence model results throughout the troposphere and stratosphere. The lower stratosphere is a case in point. The uncertainty in this rate constant affects assessments of impact of aircraft effluents on ozone,[12,13] and, conversely, recent in situ field measurements of the coupled HO_x-NO_x system have pointed to inadequacies in the recommendation for this rate constant.[14] Here we shall address these issues by exploiting isotopes to separate the elementary steps comprising the complex reaction mechanism.

It has been proposed that many of the vexing features of this system can be explained by the presence of a moderately stable reaction product, peroxynitrous acid (HOONO).[15,16] This is an extension of an earlier suggestion that excited electronic states of $HONO_2$ could be responsible for the unusually broad falloff curve of this rate constant.[17] The anomalously low isotopic scrambling rate of $^{18}OH + NO_2$ also led to speculation that HOONO could play an important role in the kinetics of the OH + NO_2 reaction,[18] though this appeared to run counter to a lack of direct experimental evidence for HOONO formation in the gas phase.[19]

Because HOONO should be much less stable than the major product, nitric acid ($HONO_2$), it should have a substantially smaller density of states near the reactant energy than will nitric acid, a correspondingly shorter excited state lifetime, and a lower third-order rate constant. However, it is entropically favored, both because attack on either oxygen atom of NO_2 will lead to its formation and because there are several stable conformers corresponding to several allowed approach geometries, while $HONO_2$ is confined to a single, planar geometry. Finally, there is nothing about the frontier orbital structure of NO_2 to suggest that either reaction path (leading to HOONO or $HONO_2$) should have a significant barrier. Thus, the high-pressure limit for HOONO formation could well be much higher than that for nitric acid formation, though given its relative instability HOONO could have a very short thermal lifetime.

The major shortcoming of these suggestions remains the lack of any experimental evidence for HOONO formation in the gas phase. Two attempts have been made to isolate this isomer, both of which were carried out between room temperature and approximately 220 K.[5,19] The second experiment was carried

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out in our lab and is described in a companion paper. Neither experiment revealed any evidence for HOONO formation at any temperature. The possibility remains that HOONO is formed but has a very short thermal lifetime, or that the branching ratio is relatively small (and distributed among several conformers). However, our recent experiment, in particular, places severe constraints on these possibilities; we observe $HONO_2$ production with a 90% yield (within error of unity) with a 20 ms experimental time scale.[5]

Given the complexity and importance of this system, it is essential that we obtain additional experimental constraints on its behavior. Isotopic scrambling is one avenue. When OH adds to the nitrogen in NO_2, forming vibrationally excited $HONO_2$, the hydrogen atom can be transferred to either of the other two oxygen atoms. If this transfer is facile, the vibrationally excited intermediate can be considered as an $[H{\cdot}NO_3]$ complex. If the complex lifetime is sufficiently long, when it decomposes back to reactants (which it will do at low pressure, lacking a third body to remove the vibrational energy) the departing oxygen atom will be randomly selected from among the three candidates. Ordinarily, this is a null process, as the atoms are indistinguishable. However, if the oxygen atom on the attacking OH is isotopically labeled, the exchange reaction will be observable. In the perfect case so far described, the disappearance rate constant of the labeled radical at low pressure will be two-thirds of the high-pressure limit for the reaction with or without the label (assuming that mass-dependent effects associated with the labeling are negligible).

This isotopic scrambling experiment has twice been applied to the OH + NO_2 reaction in low-pressure discharge-flow measurements of ^{18}OH removal kinetics.[20,18] The results are in good agreement, but like virtually all aspects of this reaction they are not easy to reconcile with other characteristics of the system. In particular, the resulting rate constants are too low for the simple explanation provided here to hold. Greenblatt and Howard[18] offered HOONO formation as a possible explanation for the discrepancy between their low pressure (2 Torr) scrambling data and the high-pressure data, but without any quantitative analysis of the aggregate kinetics and pressure falloffs. Some time ago (in 1994), we measured the rate constant for the $^{18}OH + NO_2$ reaction as a function of nitrogen pressure from 4 to 200 Torr at 298 K. Here we shall present these data, together with an interpretation that is consistent with all known facts about the reaction. The general notion that both isomers of HNO_3 contribute to the high-pressure kinetics data is strongly supported by our observations.

Experimental Results

We measured rate constants for ^{18}OH disappearance in the presence of excess NO_2 in a high-pressure flow system (HPFS). All details of this experiment have been described extensively in the literature,[21] including application to the unlabeled OH + NO_2 reaction[10] and to isotopic scrambling in the $^{18}OH + H_2O$ reaction.[22] The measurements described here were carried out between 4.5 and 212 Torr of nitrogen at 299 ± 2 K. They are summarized in Table 1.

As a test of our overall accuracy, we also measured the rate for the reaction ^{18}OH + ethane → products over the same pressure range. We found a pressure independent rate constant of $(2.5 \pm 0.15) \times 10^{-13}$ cm^3 $molec^{-1}$ sec^{-1}, which agrees well with the accepted rate for ^{16}OH + ethane at room temperature.

Theoretical

To better constrain the H-atom transfer associated with isotopic scrambling, we have located the pertinent transition state using density functional theory (B3LYP/6-31G**). An extensive portion of the reaction coordinate for the total system is shown in Figure 1. These calculations are discussed in greater detail in a related paper,[5] but we shall summarize the germane features here, in particular focusing on isotopic scrambling. We shall then compute some rate constants based on this surface to demonstrate that isotopic scrambling is much more rapid than adduct dissociation and should thus be complete at low pressure.

TABLE 1: Rate Constants for $^{18}OH + NO_2$ vs Pressure

P Torr	k ($\times 10^{12}$) cm^3/sec
4.49	13.5 ± 1.5
4.49	8.8 ± 1.2
9.53	11.1 ± 1.0
9.58	11.5 ± 1.1
21.96	10.2 ± 0.9
40.41	10.9 ± 1.1
73.11	9.3 ± 1.0
73.04	9.3 ± 1.0
134.40	9.5 ± 0.9
211.90	8.8 ± 0.7

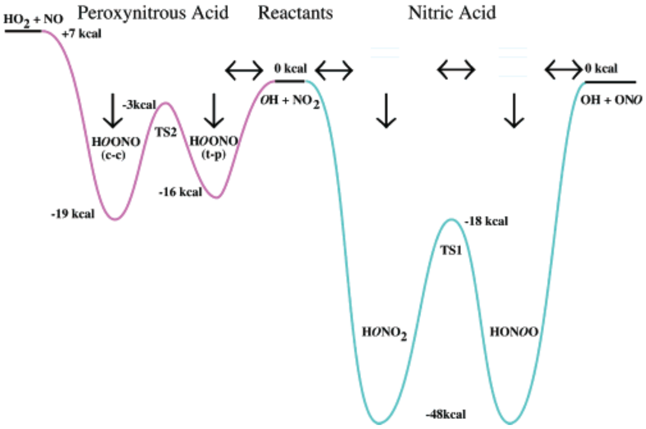

Figure 1. Theoretical potential energy surface for the title reaction. The isotopically labeled reactants are shown in the middle. The ^{18}O is indicated with an italicized *O*. Formation of $HONO_2$ proceeds to the right, first through $H^{18}ONO_2$, then to $HONO^{18}O$, and finally to OH + $NO^{18}O$. Formation of HOONO proceeds to the left, where each of several conformers can be formed directly but no isotopic scrambling is facile. Note that the critical barrier to H-atom transfer (TS1) sits well below the reactants (by 18 kcal/mol).

This surface agrees well with another recently published surface,[4] though ours is the first to describe the isomerization transition state under consideration here. Figure 1 is best read out from the middle, where one finds the reactants. Formation of nitric acid is shown to the right of the reactants. The barrier to isomerization lies 18 kcal/mol below the reactant energy. Isotopically scrambled reactants, which are a product from the perspective of radical decay, are shown on the right-hand edge of the figure. Formation of HOONO is also possible. This will not have any facile isotopic scrambling pathway and will thus behave nearly identically for ^{18}OH and ^{16}OH. This process is shown to the left of the reactants (note that any conformer of HOONO may be formed directly from OH and NO_2, and only the two most stable are shown).

Our primary objective is to assess whether isotopic scrambling is indeed fast compared to dissociation of vibrationally excited nitric acid. To achieve this, we need to know the unimolecular isomerization and dissociation rates at roughly the reactant energy. We shall present a simple calculation, using an average dissociation rate based on the observed rate constant and a microcanonical isomerization rate constant at approximately the reactant energy. This is easy to understand and amply demonstrates the facility of isomerization.

TABLE 2: B3LYP Frequencies for Species (in cm^{-1}) (energies in kcal/mole)

mode	$OH + NO_2$	$HONO_2$	TS1
ν_1	3705	3717	2333
ν_2	1709	1766	1684
ν_3	1396	1354	1349
ν_4		1322	1098
ν_5		901	1063
ν_6	749	766	840
ν_7		649	724
ν_8		581	614
ν_9		479	1918*i*
I_a		0.207	0.213
I_b		0.401	0.376
I_c		0.429	0.493
E	0	−48.8	−17.6
E_{zp}	10.8	−32.3	−3.8

First we shall calculate the average dissociation rate constant. In the Lindemann−Hinshelwood model, the excited state lifetime may be easily inferred from the observed high and low pressure rate constants. The low pressure rate constant is approximately

$$k_0 = \beta k^{II} \frac{k_\infty}{k_d} \tag{1}$$

where β is the collisional efficiency of the bath gas (approximately 0.4 for nitrogen), k^{II} is the second-order collision rate constant (3×10^{-10} cm^3 sec^{-1}), and k_d is the unimolecular dissociation rate of the adduct. Solving for k_d we find

$$k_d = \beta k^{II} \frac{k_\infty}{k_0} \tag{2}$$

Using the JPL recommendation for the high and low-pressure limits (the reason for this choice will become clear), we find $k_d \sim 8 \times 10^8$ sec^{-1}.

We need to compare this dissociation rate constant with the unimolecular isomerization rate constant to see which process will dominate. For this we shall simply calculate the microcanonical rate constant near the reactant zero point energy. We summarize the energies and vibrational frequencies for the reactants, nitric acid, and the transition state, TS1, in Table 2. Note that the transition state energy is −14.6 kcal/mol relative to the reactant zero point, while the nitric acid ground-state lies at −43.1 kcal/mol. Calculation of the microcanonical rate constant for isomerization as a function of energy is straightforward. We calculate a simple sum over density of states, neglecting anharmonicity and assuming that external rotations are active:[23]

$$k(E) = \frac{\sigma W^*(E - E_0)}{h\rho(E)} \tag{3}$$

We count rovibrational states explicity.[24] The result is shown in Figure 2. Actual loss of the excited $H^{18}ONO_2$ will be twice as rapid because of the two identical pathways (not treated in the RRKM calculation), and the actual eigenvalue for equilibration of the isomers will be faster by $\sqrt{6}$. Isomerization of the vibrationally excited adduct is clearly at least an order of magnitude faster than dissociation, and we may safely assume that isotopic scrambling is rapid.

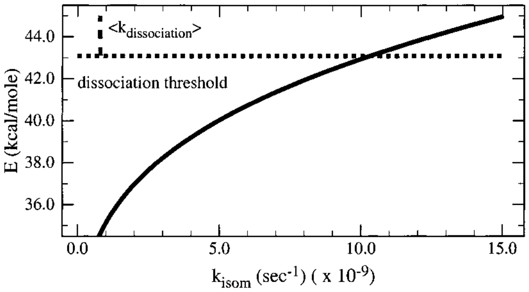

Figure 2. RRKM isomerization rate vs $HONO_2$ energy. Zero energy is the zero-point energy of $HONO_2$. The dissociation threshold is shown as a horizontal dashed line at 43.1 kcal/mol, while the experimentally constrained mean dissociation rate constant is shown as a vertical dashed line at 8×10^8 sec^{-1}. Clearly, isomerization is at least an order of magnitude faster than dissociation.

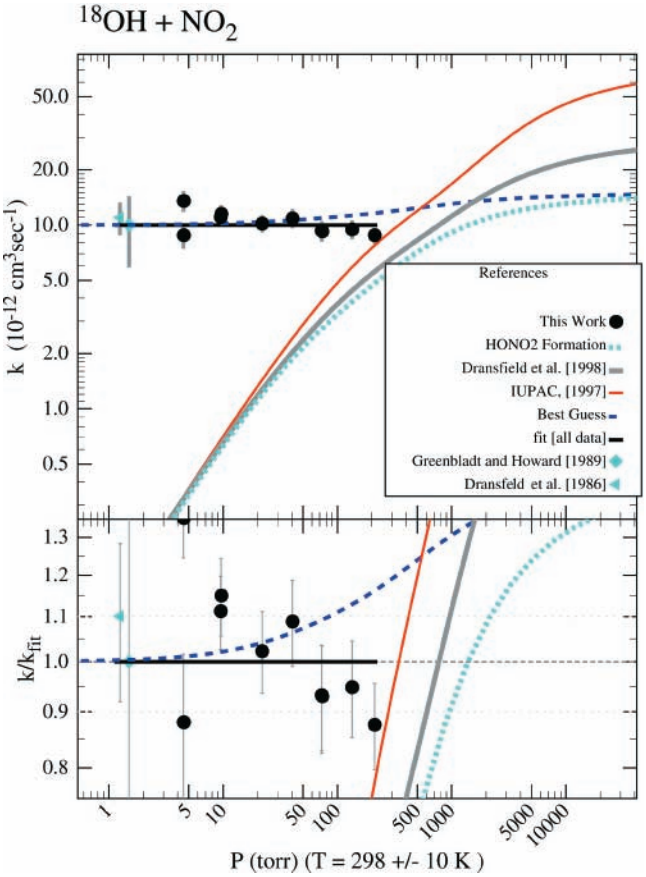

Figure 3. Experimentally determined rate constants for the reaction $^{18}OH + NO_2 \rightarrow$ products plotted vs pressure. Literature values are also shown, along with several functions. The straight line is a simple average of all the data, while the sigmoid curve is a combination of this average at low pressure and the lowest of the three falloff curves. The falloff curves are recommended curves for the unlabeled $OH + NO_2$ rate constant. The lower curve is the current JPL recommendation[6] with a slightly reduced high-pressure limit, the middle curve is from our recent study,[11] and the upper curve is the current IUPAC recommendation.[7] Residuals are shown relative to the simple average.

Discussion

Our data for the reaction $^{18}OH + NO_2 \rightarrow$ products are plotted in Figure 3, along with the other data from the literature[20,18] and several functional curves. Our measurements are in nearly perfect agreement with the literature values, but they extend the pressure range to 200 Torr. Over the full range from 1 to 200 Torr, there is nothing in the data to suggest any significant pressure dependence in the rate constant. If anything there is a slight decrease in the observed rate constant with pressure, though this is within the (1-σ) uncertainties of the individual measurements. The weighted average of all the available data is $k = 1.0 \pm 0.04 \times 10^{-11}$ cm^3 $molec^{-1}$ sec^{-1}. At first blush this is surprising, as the unlabeled reaction is known to be strongly pressure dependent. Several recommendations for the pressure dependence of that rate constant are shown as well in Figure 3. Clearly, the rate constant for the isotopically labeled reaction is much faster than that for the unlabeled reaction at low pressures, but the two rate constants converge with increasing pressure.

The observed behavior can be understood easily in the context of the simple model presented in the Introduction; at low pressures, isotopic scrambling causes adduct decomposition to remove the reactant ^{18}OH radical 2/3 of the time, but as pressure increases a certain fraction of the vibrationally excited intermediate is also collisionally stabilized, until eventually all of the intermediates are stabilized and the labeled reaction behaves identically to the unlabeled one (from the perspective of radical removal). If the unlabeled reaction has a rate constant $k(\mathrm{p})$, we expect the labeled reaction to have a rate constant $k'(\mathrm{p}) = 2/3k(\infty) + 1/3k(\mathrm{p})$. In this case, we use the average value obtained above to predict a high-pressure limit of 1.5×10^{-11} cm^3 molec^{-1} sec^{-1}, which we use along with the JPL recommendation for the falloff function, $k(\mathrm{p})$. The resulting sigmoid-shaped function (labeled "best guess") is shown in Figure 3, and while the data do not show the gentle increase with pressure suggested by the function, the scatter is such that this is not surprising. The rate constant should have increased by only 15% at 200 Torr from the low pressure limit. The only modification to the JPL recommendation required in this exercise is a slight reduction in the high-pressure limit, from 1.67 to 1.5×10^{-11} cm^3 molec^{-1} sec^{-1}.

This would settle the matter if the JPL recommendation described the data at high pressures, but it does not. The other two functions shown in Figure 3 are more representative of the high pressure data. The middle curve, from our earlier work[11] is based on all data except the very high pressure data of Forster[8] and Fulle,[9] while the upper curve is the IUPAC recommendation,[7] which reasonably fits those high-pressure data but overestimates the observed rate constants at intermediate pressures. One possibility is that HOONO formation is responsible for this evident increase in the high-pressure rate constant.

If we accept this postulate, we can assume that the difference between the high-pressure limit inferred from our scrambling data (1.5×10^{-11} cm^3 molec^{-1} sec^{-1}) and the high pressure limit of the data is due to HOONO formation. The high pressure limit for OH removal has been measured in two independent ways: by extension of kinetics measurements to extremely high pressures[8,9] ($k_\infty = 7.5 \times 10^{-11}$ cm^3 molec^{-1} sec^{-1}), and by measurements of the quenching rate constant for vibrationally excited OH, which should preferentially lose its quantum of vibration to NO$_2$ during a collision[25] ($k_\infty = 4.8 \pm 0.8 \times 10^{-11}$ cm^3 molec^{-1} sec^{-1}). These results are in reasonable agreement; certainly there is consensus that the high-pressure limit is very fast. Because the high-pressure kinetics data are more direct and because they extend well into the falloff region and can thus be compared to a falloff function over some range, we shall use those data to constrain the high-pressure value, giving a high-pressure limit for HOONO formation of 6×10^{-11} cm^3 molec^{-1} sec^{-1}.

This leaves the low pressure limit of this channel as the sole remaining parameter to constrain. The data are reasonably reproduced with a low-pressure rate constant for HOONO formation of 4×10^{-31} cm^6 molec^{-1} sec^{-1}. This may be compared with our low-pressure rate constant for HONO$_2$ formation of 2.4×10^{-30} cm^6 molec^{-1} sec^{-1}. The separate formation rate constants and the sum of both channels are all shown in Figure 4, along with the available data. Almost all of the measured rate constants fall between the curve for HONO$_2$ formation and the curve for the total rate constant, which is consistent with the suggestion that experimental time scales are influencing the kinetics observations.

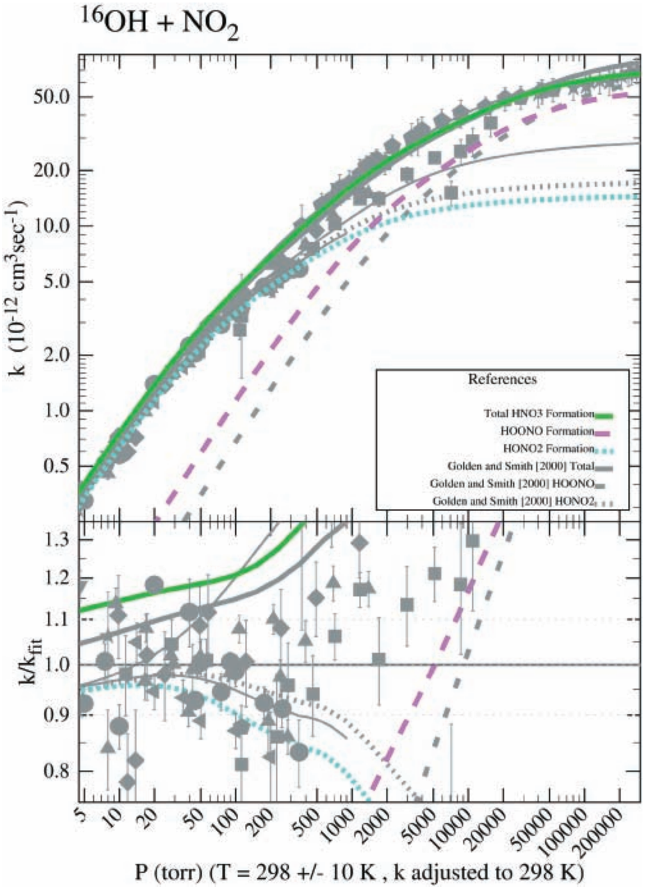

Figure 4. Falloff curves for the unlabeled OH + NO$_2$ reaction. Literature data are plotted in gray (see Dransfield).[11] The falloff curves show are for HONO$_2$ formation (cyan), HOONO formation (magenta), and the aggregate rate constant (green). These curves are directly products of the data. The HONO$_2$ formation rate constant is determined from the isotopically labeled rate constants, while the HOONO formation rate is left as a difference so that the aggregage rate matches the available high pressure data. These curves are very similar to those recently proposed by Golden and Smith.[13] However, the constraints are independent; our branching is constrained by the ^{18}OH kinetics, while theirs is constrained by a hindered-Gorin RRKM calculation.

Our measurements and analysis strongly support the results of both recent theoretical predictions,[15,16] adding the additional constraint of isotopic labeling to the problem. They also confirm the suggestion by Greenblatt and Howard[18] that the unusually low rate constant for the scrambling reaction is due to the HOONO formation channel. We stress that our analysis is based entirely on experimental results; we have used our calculated isomerization rate constant to help build the case that isomerization is facile, but it in no other way enters the calculation. The critical data are the pressure-dependent rate constants for the isotopic scrambling reaction. Because the scrambling rate constant is blind to HOONO formation, we can infer the high-pressure limit for HONO$_2$ formation from these results, provided that isomerization indeed far outpaces decomposition for the vibrationally excited intermediate. With a second assumption that HONO$_2$ formation dominates at low pressure, we can completely describe the HONO$_2$ formation rate constant and then, by subtraction, the HOONO formation rate constant.

Our results are quantitatively closer to those of Golden and Smith[16] than those of Matheu et al.[15] Indeed, the consistency of the curves plotted in Figure 4 is striking; they are within 20% of each other over the entire pressure range. While the master equation simulations of Matheu et al.[15] do not produce simple Lindemann−Hinshelwood type rate expressions, in general terms their results suggest a much shorter lifetime for HOONO and a correspondingly smaller third-order rate constant for this channel. Thus we conclude that our results substantially confirm those of Golden and Smith,[16] with the only interdependence being that each result is in part constrained by the data for the unlabeled reaction.

One problem remains. The hindered-Gorin RRKM calculations of Golden and Smith[16] show a long lifetime for HOONO at 230 K. In a companion paper we report a product study of the unlabeled reaction revealing no sign of HOONO at 230 K and 375 torr.[5] It is difficult to reconcile this with the evidence presented here, which suggests that the yield of HOONO should be up to 30%, unless the HOONO lifetime is less than the experimental time scale of 0.2 s even at 230 K. We should note that any HOONO produced would be dispersed among several conformers, so individual IR absorption bands may be quite weak. It is also possible that we have overestimated the HOONO formation rate; using vibrational deactivation to constrain the high pressure limit for this channel reduces the rate by nearly 40%. A combination of these effects could render the HOONO itself quite difficult to observe and the difference of the $HONO_2$ branching ratio from unity difficult to discern.

A second possibility could explain the isotopic scrambling data: if H-atom transfer is not facile but is instead in competition with adduct decomposition, the observed low-pressure limit of the title reaction would indeed be lower than the expected 2/3 of the high-pressure limit. While a model based on incomplete scrambling can explain the ^{18}OH kinetics, the general consistency of our current explanation with the other available facts strongly favors the simpler explanation we have already presented.

Several additional experimental constraints can and should be brought to bear on this problem. First, temperature-dependent data for the isotopic scrambling would allow us to extend this analysis away from room temperature and down to temperatures relevant to the upper troposphere and lower stratosphere. Second, measurements with ^{18}OD would quickly reveal whether H-atom transfer is truly facile in this system. If it is, the primary isotope effect should be only modest. Third, measurement of the formation rate constant for ^{16}OH would directly constrain the scrambling rate constant. Fourth, a product study of the reaction should reveal a statistical (2:1) distribution of nitric acid isomers at low pressure that starts to become biased strongly toward $H^{18}ONO_2$ at approximately 200 Torr. Fifth, kinetics measurements of the $^{16}OH + NO_2$ reaction at the appropriate time scale should reveal biexponential behavior in the OH decays if these conjectures are correct. Except at very high pressure, the effect would be subtle because the two eigenvalues would be the sum of the rate constants and the $HONO_2$ formation rate constant alone, which do not differ by a factor of 2 until 2000 Torr. Finally, direct observations of the various HOONO conformers, and in particular their thermal lifetimes, would close the final loophole in these calculations.

Atmospheric Implications

The title reaction may play an important role in the stratosphere by causing strong mass-independent fractionation of OH. Under many conditions, the NO_x-NO_y system including OH, NO_2, and $HONO_2$ is in a rough diurnal steady state. The process described here should work to enrich NO_2 in oxygen isotopes at the expense of OH (and $HONO_2$). Consequently, ^{18}OH should be depleted in the stratosphere, and ^{18}ONO enriched, unless other feedbacks diminish the effect. Because of the many radical feedback loops in the stratosphere, the ultimate fractionation can only be predicted by a complete photochemical model.

Our results suggest that, while HOONO is probably formed in significant quantities in the atmosphere, it is probably lost just as quickly through thermal decomposition. These results strongly support the conclusion of Golden and Smith[16] that the rate constants appropriate to atmospheric chemistry modeling (i.e., for $HONO_2$ formation) are those generally following the lower bound of the available rate constant data (the current JPL recommendation). In fact, the $HONO_2$ formation rate constant presented here is 5% lower than the current JPL recommendation at room temperature and pressure. The chain termination rate due to $OH + NO_2$ is thus probably overestimated in current photochemical models; this will significantly affect ozone assessments and the interpretation of field data.

Conclusions

We have presented a consistent explanation for the unusual kinetics of the $OH + NO_2$ reaction. Our experimental data on the scrambling rate constant for oxygen isotopes show that the pressure dependence (none) for this process is quantitatively consistent with facile H-atom transfer in the vibrationally excited complex. This in turn confirms that the high-pressure limit for $HONO_2$ formation is well below the observed high pressure limit for OH disappearance, leaving HOONO formation as the only likely explanation for those observations. These results support recent predictions that arrived at the same general conclusion[15,16] using master equation and RRKM computations on the theoretical surface constrained by the kinetics of the unlabeled reaction. Continued failure to observed HOONO under any experimental conditions[5] remains a perplexing problem, but this result may be due to a difference between the thermal lifetime of HOONO and the experimental time scale of the product studies.

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