A Pulsed Laser Photolysis−Pulsed Laser Induced Fluorescence Study of the Kinetics of the Gas-Phase Reaction of OH with NO_2

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The kinetics of the recombination reaction, $OH+NO_2+(M)\rightarrow HNO_3+(M)$ have been investigated by the pulsed laser photolysis−pulsed laser induced fluorescence (PLP−PLIF) technique in air, nitrogen, oxygen, and helium buffer gases at room temperature and as a function of pressure (30−700 Torr). Additional measurements in nitrogen at 273 K (100−700 Torr) are reported. The third-body efficiency of water vapor has also been investigated. Our values for the absolute rate coefficient in nitrogen at room temperature and at 273 K are in excellent agreement with the JPL 1994 recommendation but lie substantially above the current JPL 2000 recommendation. Our rate coefficients in helium agree with previous literature studies, suggesting that systematic errors are small. Oxygen is found to be about 20% less efficient than nitrogen, and we see no significant enhancement in recombination in the presence of water vapor. Our results suggest that formation of the pernitrous acid isomer cannot explain the discrepancies in the current experimental database.

Introduction

The three-body recombination of OH with NO_2 plays a critical role in both tropospheric and stratospheric chemistry.

$$OH + NO_2 + (M) \rightarrow HNO_3 + (M) \qquad (1)$$

In the troposphere, reaction 1 can act as a major sink for OH, while in the stratosphere it acts to control partitioning among the HO_x and NO_x families with a consequent impact on catalytic ozone cycles.[1] The reaction plays a particularly important role in tropospheric ozone formation in polluted environments, acting as a sink for NO_2. Over the range of pressures and temperatures encountered in the atmosphere, the rate coefficient for this association reaction lies in the falloff region between second- and third-order kinetics. A description of the observed falloff behavior in terms of a simple termolecular association, i.e., proceeding on a single potential energy surface to form a single product, does not seem consistent with the experimental database. Robertshaw and Smith drew early attention to this, suggesting that isomer formation or reaction to form a weakly bound electronically excited state might be contributing to the thermal rate coefficient at high pressure.[2] More recent experimental and theoretical work has focused on the potential role of the pernitrous acid isomer on the recombination.[3−6] Two recent theoretical papers have examined this possibility, reaching very different conclusions.[5,6] Despite its atmospheric importance, there is a very limited amount of experimental data on the association rate coefficient in N_2, O_2, or air at pressures above 200 Torr. An accurate value of the rate coefficient is especially important for models of urban ozone formation. Bergin et al.[7] found that the uncertainty in the rate coefficient for reaction 1 was the largest single contributor to the uncertainty in the calculated "incremental reactivity" or ozone forming potential of volatile organic compounds. However, at atmospheric pressure the IUPAC 1997[8] recommendation suggests a value for the absolute rate coefficient for reaction 1 that is almost twice the value recommended by the current JPL expression.[9] The significant discrepancy between the recent JPL recommendations, JPL 1994,[10] JPL 2000,[9] and the IUPAC 1997 recommendation[8] show the need for additional data in N_2 and air. To the best of our knowledge there are no measurements in air available in the current literature and, with the exception of a single competitive rate study,[11] the collisional efficiency of water vapor has not been investigated. In this work we report a series of measurements of the rate coefficient of reaction 1 with several buffer gases, nitrogen, air, oxygen, and helium, over the pressure range 60−700 Torr together with a study of the effect of water vapor. An additional series of measurements in nitrogen at 273 K are also reported.

Experimental Section

Our experimental approach has been described in detail elsewhere[12,13] and utilized the PLP−PLIF technique to measure temporal profiles of OH under pseudo first-order conditions. OH radicals were produced by photolysis of a precursor, either H_2O_2 or HNO_3, directly in the reaction chamber using the 266-nm fourth harmonic output from a Nd:YAG laser.

$$HNO_3 + h\nu_{266\ nm} \rightarrow OH + NO_2 \qquad (2)$$

$$H_2O_2 + h\nu_{266\ nm} \rightarrow 2OH \qquad (3)$$

The OH radical was then excited by a Nd:YAG pumped, frequency doubled, tunable dye laser. OH radicals were excited at ∼282 nm via the $A^2\Sigma^+-X\ ^2\Pi$ (1−0) transition followed by observation of fluorescence from the (1−1) and (0−0) bands at 308−316 nm. The fluorescent light was monitored with a photomultiplier tube, using appropriate filters to minimize scattered light. The photomultiplier output was appropriately terminated and fed to a 500-MHz digital oscilloscope to obtain the integrated voltage averaged for (typically) 100 laser shots.

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Kinetic information was obtained by varying the delay between the photolysis and the probe lasers using a digital delay generator. Experiments were carried out under "slow-flow" conditions. Flows were monitored using calibrated mass flow meters. NO_2 was purified by freeze-pump cycles at 77 K. Mixtures containing approximately 2.5% NO_2, together with the buffer gas of interest, were prepared manometrically in 20 L glass bulbs. NO_2 concentrations were measured in situ by UV photometry using the 365 nm lines from a Hg lamp, absorption cells of various lengths, and a band-pass filter/photomultiplier combination situated either upstream or downstream of the cell. In some kinetic experiments, the absorption cell was situated upstream and an optical multichannel analyzer (OMA) was situated downstream. The measured NO_2 concentrations were in excellent agreement. Agreement between measured in-situ concentrations and concentrations based on flows and bulb concentration were excellent. The OMA was also used to characterize the UV spectrum of the purified NO_2 and of the gas mixture in the bulbs. Spectra were taken with the OMA in the region between 200 and 380 nm and compared with literature references,[14] to verify the purity of the NO_2. Comparing our OMA measurements with reference spectra of HNO_3 and NO, we estimate an upper limit of 0.1% for these impurities.

The absorption cross section was measured using the same Hg lamp and band-pass filter. The value that we obtained was identical with the 5.75×10^{-19} cm^2 reported by Wine et al. in 1979.[15] The pure gases and chemicals used in this study had the following stated minimum purities: N_2, 99.999%; O_2, 99.99%, helium 99.99%. Air was zero grade, <1 ppm total hydrocarbons. They were used without any further purification.

Results and Discussion

The kinetic runs were performed under pseudo first-order conditions $[M] \gg [NO_2] \gg [OH]_0$. The concentration of NO_2 was varied between $5 \times 10^{14} < [NO_2] < 2 \times 10^{16}$, in large excess with respect to the $[OH]_0$, which was typically 1×10^{12} molecules cm^{-3}. OH radical temporal profiles were analyzed assuming simple first-order exponential behavior to determine k_1.

$$[OH]_t = [OH]_0 \exp(-k't) \qquad (I)$$

where $k' = k_1[NO_2] + k_d$, k_1 is the bimolecular rate for reaction 1 at any pressure, and k_d is the background loss of OH with the nitric acid precursor, impurities, and via diffusion.

The OH decays were typically monitored over 2−3 orders of magnitude, and some typical decays at 600 Torr in N_2 are shown in Figure 1. The OH A state fluorescence is quenched efficiently by N_2, O_2, and H_2O, hence the fluorescence yield and consequently the s/n ratio degrades as the pressure increases. This has no effect on the accuracy of the pressure dependent rate coefficients but may make them less precise. The quality of the data presented here is well represented by Figures 1 and 2. In all cases we saw good exponential behavior with a typical 2σ uncertainty of 3% in the pseudo first-order rates. The second-order rate coefficients were obtained from linear fits of the plot of k_1 vs $[NO_2]$ for each pressure, as shown in Figure 2, again at 600 Torr in N_2. Typically the pseudo first-order decay rates varied between 400 and 300 000 s^{-1}, and the 2σ measures of precision were less than 5%. The experimental conditions and second-order rate coefficients are summarized in Table 1.

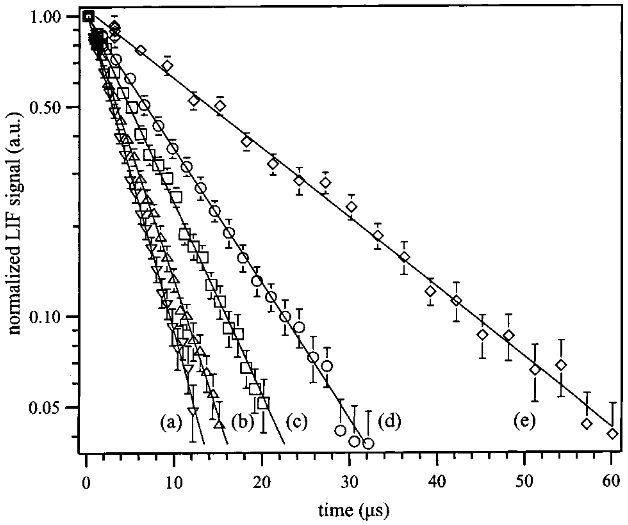

Figure 1. OH temporal profiles in 600 Torr of N_2 at 298 K. NO_2 concentrations (in units of 10^{16} molecule/cm^3) measured in-situ were: (a) 2.9, (b) 2.5, (c) 2.0, (d) 1.5, (e) 1. Solid lines show linear least-squares fits which give pseudo-first-order rates (in s^{-1}): (a) 293 000 ± 5400, (b) 246 000 ± 4800, (c) 146 000 ± 3000, (d) 104 000 ± 3800, (e) 103 000 ± 2200; (errors are 2σ).

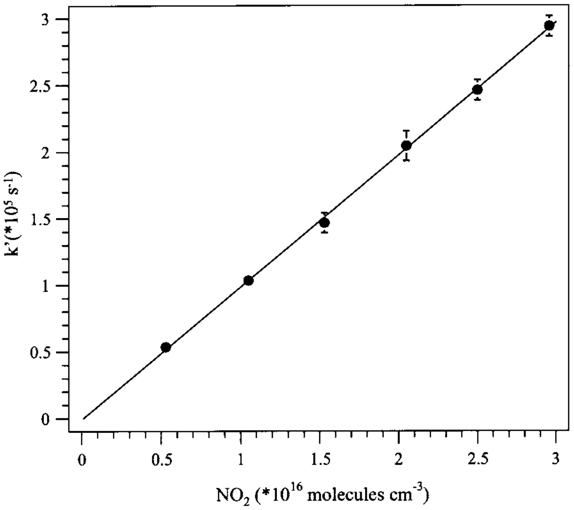

Figure 2. Plot of pseudo first-order rate versus $[NO_2]$ in 600 Torr total pressure of N_2 at 295 K. The solid line shows the linear least-squares fit to the data and gives a second-order rate coefficient of $k = (11.5 \pm 0.53) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} (error is 2σ).

The most likely sources of systematic error in our measurements would be errors in the absorption coefficient for NO_2 or the presence of an unknown impurity. It should be noted that an error in the absorption coefficient would produce an "offset" on the pressure dependent falloff curves, i.e., an error that would be independent of either pressure or the identity of the bath gas. This would also be the case for an impurity that reacted with OH with a pressure independent rate. Of the potential impurities that might react with a pressure dependent rate, NO can be excluded for measurements in air and oxygen as any NO would be rapidly converted to NO_2 by the O_2 in the bulb mixtures. Any significant formation of HNO_3 can also be excluded as it produces an increase in the OH LIF signal, and no such increase was observed.

To ensure that our data set was free of any significant systematic error, we performed a series of measurements in helium buffer gas where the literature database at higher pressure is rather more extensive. Figure 3 shows a comparison of the pressure dependence obtained in this work together with prior studies[15−18] in helium. In an extensive study of reaction 1 in

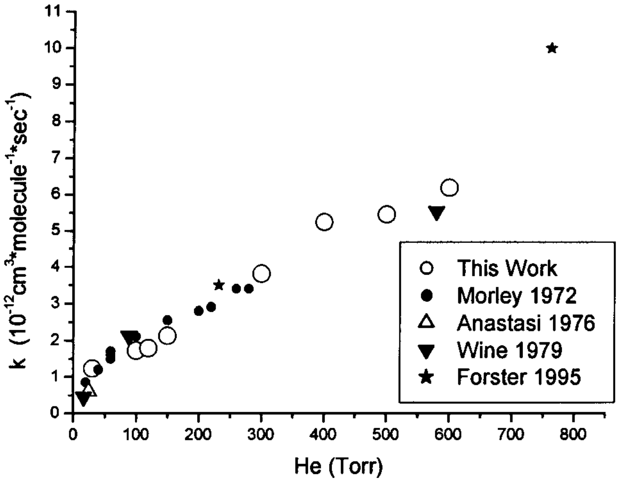

Figure 3. Second-order rate coefficients for reaction 1 in He at 298 K, together with prior literature data.

TABLE 1: Summary of Kinetic Data for OH + NO_2 → Products

buffer gas	P [Torr]	$k \times 10^{12}$ [cm^3 molecule^{-1} s^{-1}]	T [K]
nitrogen	30	2.23 ± 0.32	298
	50	2.62 ± 0.57	
	100	4.06 ± 0.42	
	200	6.44 ± 0.21	
	300	7.48 ± 0.24	
	400	7.92 ± 0.19	
	500	9.78 ± 0.21	
	600	10.86 ± 0.8	
	700	10.90 ± 0.33	
nitrogen	100	5.46 ± 0.35	273
	200	6.25 ± 0.06	
	300	7.85 ± 0.11	
	400	9.20 ± 0.45	
	500	9.75 ± 0.5	
	600	11.50 ± 0.53	
	700	11.7 ± 0.2	
oxygen	50	2.16 ± 0.12	298
	200	4.25 ± 0.05	
	300	5.45 ± 0.35	
	400	6.97 ± 0.05	
	500	7.16 ± 0.12	
	600	8.67 ± 0.34	
helium	30	1.23 ± 0.05	298
	100	1.72 ± 0.05	
	120	1.79 ± 0.05	
	150	2.13 ± 0.07	
	300	3.82 ± 0.05	
	400	5.24 ± 0.05	
	500	5.46 ± 0.03	
	600	6.20 ± 0.08	
He+H_2O	110 + 20	1.7 ± 0.2	298
	140 + 10	2.1 ± 0.1	
	130 + 20	2.35 ± 0.1	
air	100	3.32 ± 0.13	298
	200	5.59 ± 0.15	
	300	7.31 ± 0.17	
	400	7.9 ± 0.08	
	500	9.28 ± 0.08	
	600	10.5 ± 0.50	
	700	11.3 ± 0.20	

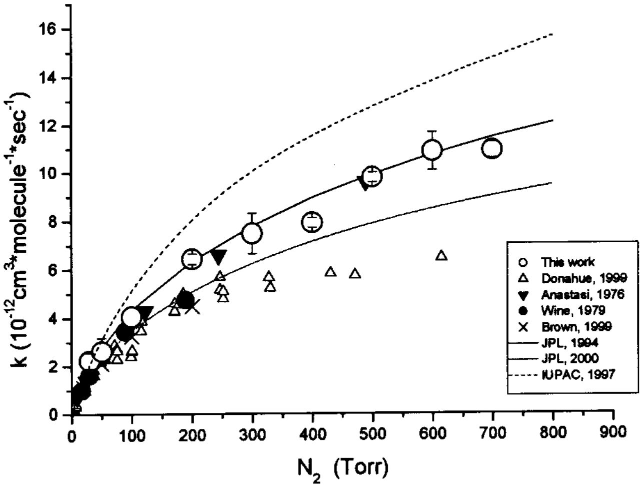

Figure 4. Second-order rate coefficients for reaction 1 in N_2 at 298 K, together with prior literature data. The solid and dotted lines show the JPL 2000, IUPAC 1997, and JPL 1994 recommendations.

He buffer, Forster et al.[16] noted an "irregularity" in the data between 50 and 760 Torr, which lie below the experimental falloff curve obtained by combining low-pressure data with their results for 1−150 atm. Over the range of pressures studied here, 40−600 Torr, the agreement between our data and prior studies is quite good, including the data points at 300 and 700 Torr reported by Forster et al., although, as we discuss below, our results in N_2, air, and O_2 do not seem consistent with the "jump" in k_1. We hope to perform further experiments in He to investigate the pressure dependence at higher pressures and extend the range of overlap with the ultrahigh-pressure studies.[16,19] As we note below, Hippler and co-workers plan to report new data on this reaction that will remove this discrepancy.[20]

Figure 4 shows variation in the rate coefficient for reaction 1 in N_2 over the pressure range 30−700 Torr, together with previous data[15,18,21,22] and recent JPL and IUPAC recommendations. At pressures below 100 Torr the data sets agree within the respective error bars, but at 200 Torr they form two groups. Our results are in excellent agreement with the data of Anastasi and Smith[18] but lie approximately 30% above the data of Wine et al.,[15] Brown et al.,[22] and Donahue et al.[21] Our results at pressures above 200 Torr are in excellent agreement with the JPL 1994[10] recommendation and the data of Anastasi and Smith[18] on which it is based, but are significantly faster than the recent measurements reported by Donahue et al., which were obtained using a high-pressure flow-tube technique.

A fit of our data to the JPL formulation of the three-body roll-off expression would give $k_0 = (2.5 \pm 0.3) \times 10^{-30}$ cm^6 molecule^{-2} s^{-1} and $k_\infty = (2.4 \pm 1.7) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, compared with the values $k_0 = (2.6 \pm 0.3) \times 10^{-30}$ cm^6 molecule^{-2} s^{-1} and $k_\infty = (2.4 \pm 1.2) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} reported in the 1994 compilation.

The IUPAC recommendation for the absolute rate coefficient of reaction 1 in air generates values 25 to 100% above the ones obtained using the current JPL expression in the range of pressures of tropospheric interest. The difference between those curves does not depend on the slightly different format used by the two panels, but rather on the fact that the IUPAC expression uses the high-pressure limit obtained in the very high-pressure laboratory measurements in He obtained by Hippler and co-workers.[16,19]

We used the JPL format to fit our data and the previous available studies in nitrogen, obtaining for nitrogen and air $k_0 = 2.5 \times 10^{-30}$ cm^6 molecule^{-2} s^{-1} and $k_\infty = 2.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. In this study we found that the fit is extremely dependent on fixed parameters that we used as F_c and k_0. This dependence may explain why the high-pressure limit extrapolated with the Kassel procedure from the data by Anastasi and Smith in 1976 is only 1.6×10^{-11} cm^3 molecule^{-1} s^{-1}, while these data lie on the 1994 JPL recommendation with $k_\infty = 2.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

TABLE 2: Comparison of the High Pressure Limits Reported for $OH + NO_2 + (M) \rightarrow$ Products

formalism	k_∞ [cm^3 molec^{-1} s^{-1}]	method	buffer gas	ref
no fit	$>1.6 \times 10^{-11}$	recombination	SF_6, 586 Torr	15
Kassel procedure	1.6×10^{-11}	recombination	N_2, 586 Torr	18
no fit	3.0×10^{-11}	recombination	CF_4, 8.4 atm	2
IUPAC, F_c=0.43	7.5×10^{-11}	recombination	He, 145 atm	16
	$>1.5 \times 10^{-11}$	isotopic exchange	He, 1−2.5 Torr	30
	1.1×10^{-11}	isotopic exchange	He, 1−2.5 Torr	31
no fit	4.8×10^{-11}	vibrational relaxation	Ar, 18 Torr	23
Troe expression	4.7×10^{-11}	recombination	N, 615 Torr	21
	1.3×10^{-11}	vibrational relaxation		32
IUPAC F_c=0.41	7.5×10^{-11}	recombination	He, 769 atm	19
NASA F_c=0.6	2.5×10^{-11}	recombination	He, N_2, O_2, and air up to 700 Torr	this work
NASA	1.7×10^{-11}	fit	n/a	9
IUPAC	7.5×10^{-11}	fit	n/a	8

The results of our fit can reproduce, within the experimental error, the data points of Wine et al.[15] and Anastasi and Smith.[18] Both studies were performed before the introduction of a standardized format for data fitting and do not report high-pressure limits based on the JPL or IUPAC formats. Our fitting parameters are also consistent within the experimental errors with the 1982 measurements by Robertshaw and Smith[2] in 8.4 atm of CF_4. In addition to extrapolation from low-pressure data, isotopic exchange[3] and vibrational deactivation[23] techniques have been used to evaluate the high-pressure limit for this reaction. Table 2 gives a summary of the high-pressure limits reported in the current literature.

The low-temperature database for reaction 1 in N_2 consist of four studies respectively by Dransfield,[24] Brown et al.,[22] Anastasi and Smith,[18] and Wine et al.[15] None of these studies reported measurements at pressures above 250 Torr. We measured the rate coefficient for reaction 1 in N_2 at 273 K in the pressure range 30−600 Torr. Figure 5 shows our results together with the 265 K data of Anastasi and Smith and Dransfield et al. and the 1994 and 2000 JPL recommendations. Again our kinetic data at 273 K show a very good agreement with the JPL 1994 recommendation but lie above the current recommendation. The association of NO_2 to form N_2O_4 is enhanced at low temperature;[22] however, we calculated that the fraction of the $[NO_2]_0$ that dimerized at 273 K varied between 0.1 and 1% and this should have a negligible effect on our results.

We also measured k_1 as a function of pressure in air and O_2 at room temperature. Our room-temperature data in O_2 were obtained over the pressure range 30−600 Torr, while data in air were obtained over the pressure range 100−700 Torr. These results, together with our room-temperature N_2 data, are shown in Figure 6. Our rate coefficients in oxygen are 15−20% lower than those obtained at the same pressure in nitrogen. These experiments confirm a slightly lower efficiency of O_2 as third body for reaction 1 as suggested by Brown et al.[22] based on their results in 20 and 50 Torr of O_2. At the precision of our data, the results in N_2 and air are not distinguishable. The 700 Torr results do not seem compatible with the rate coefficient reported by Hippler and co-workers for reaction 1 in 760 Torr of He at room temperature.[16,19] They reported a value, $(1.0 \pm 0.3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, that is similar to the values we obtain in N_2 or O_2; however, as we note below, these results will be revised.

In the only previous study of the effects of water vapor on reaction 1, Simonaitis and Heicklen[11] used a competitive rate technique and derived an expression for the low-pressure limit for reaction 1 of 1.1×10^{-29} cm^6 molecule^{-2} s^{-1} with water as the third body. That would suggest that water is more efficient as a third body by a factor of 4 than is air. Evenseck and co-workers[25] used a density functional approach to examine the recombination of OH with NO_2 in the presence of water vapor. They found that in a three-body encounter of OH, NO_2, and H_2O, the presence of H_2O dramatically lowers the activation energy for recombination of OH and NO_2 on a triplet surface that can then intersystem cross to the singlet product surface. Since the probability of such a three-body collision is negligible

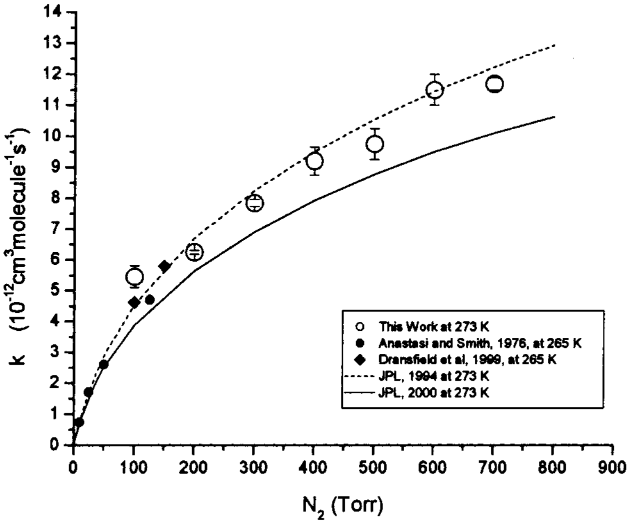

Figure 5. Second-order rate coefficients for reaction 1 in N_2 at 273 K, together with prior literature data. The solid and dotted lines show the JPL 2000 and JPL 1994 recommendations.

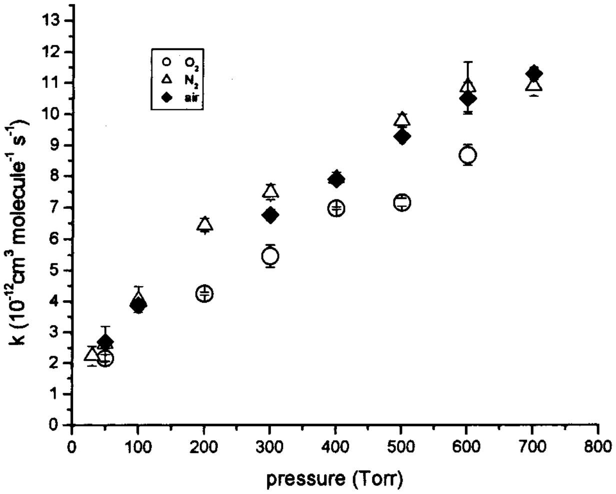

Figure 6. Second-order rate coefficients for reaction 1 in N_2, O_2, and air at 298 K.

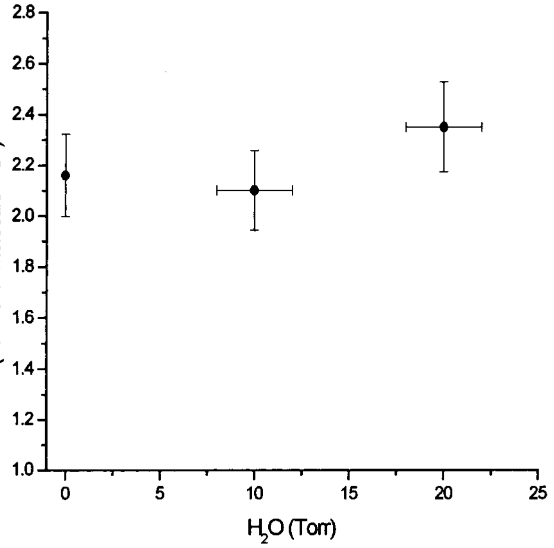

Figure 7. Second-order rate coefficients for reaction 1 as a function of the partial pressure of water vapor at a constant total pressure of 150 Torr in He buffer at 298 K.

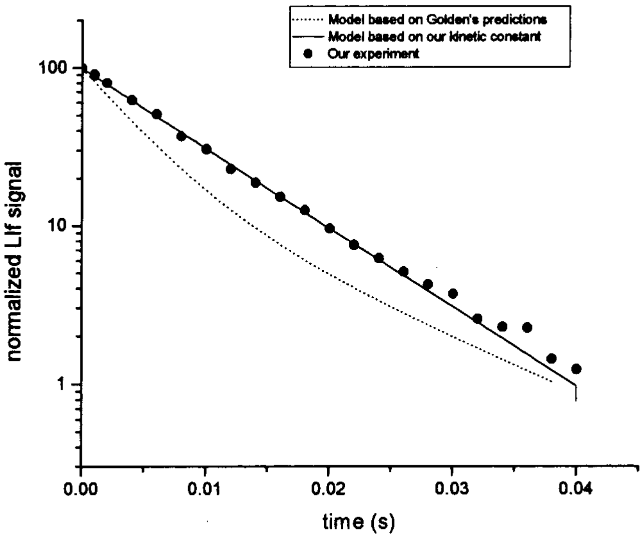

Figure 8. OH temporal profile in 600 Torr of He at 298 K in $[NO_2] = 2.5 \times 10^{13}$ molecule/cm^3. The straight line shows a least-squares fit to the data. The dotted line shows a simulation of the OH temporal profile obtained using the expressions proposed by Golden and Smith for the formation of nitric acid and the formation and decay of pernitrous acid.

in the atmosphere, OH would have to be complexed with H_2O for this mechanism to be operable. We performed measurements in mixtures of He and water vapor at 150 Torr total pressure with 10 and 20 Torr of water vapor, shown in Figure 7. Water vapor was measured in situ by the absorption of the 184.9 nm Hg line.[13] At the precision of our experiments, we found no enhancement in the rate coefficient in the presence of water vapor.

Two recent theoretical studies have examined the role of peroxynitrous acid, a weakly bound isomer of nitric acid, on the recombination reaction and on the potential effects on the results obtained from laboratory studies. Since all laboratory studies monitor the pseudo first-order loss of OH in the presence of a large excess of NO_2, the rate coefficient measured would be the sum of all pathways removing OH. If a channel forming pernitrous acid is significant, its effect on laboratory studies would depend on the time scale of the unimolecular decomposition of the peroxynitrous acid. Golden and Smith[5] have reported the results of RRKM calculations on the OH + NO_2 association, considering channels that proceed via the formation of both the nitric acid ($HONO_2$) and pernitrous acid (HOONO) isomers. They concluded that the association proceeds via both channels, forming nitric acid, which can be collisionally stabilized to form the stable nitric acid end product, and via the formation of pernitrous acid, which can be collisionally stabilized but which is so weakly bound that it redissociates to products on a millisecond time scale at room temperature. They hypothesize that the high-pressure flash photolysis experiments that typically monitor OH decay on a sub-millisecond time scale, monitor both channels and, as a consequence, overestimate the effective rate of the formation of the nitric acid product. They suggest that the high-pressure flow tube experiments of Donahue et al., which monitor OH decays on a longer time scale, monitor only the channel forming nitric acid.

Matheu and Green[6] calculated the formation rates for both channels using an inverse Laplace transform approach and both modified strong collision and the master equation treatments of collisional energy transfer. Their calculations indicate that peroxynitrous acid formation is much slower than nitric acid formation at pressures of up to one atmosphere and that isomer formation should not have an impact on the results of laboratory experiments in this pressure regime.

We have examined the hypothesis of Golden and Smith by monitoring OH decays at very low NO_2 concentrations in He at 500 Torr. At these concentrations it is no longer feasible to directly monitor NO_2 photometrically; however, we can calculate the NO_2 concentrations from flows and we obtain results that are entirely consistent with results obtained at the higher NO_2 concentrations. Figure 8 shows an example of such an OH decay together with the OH temporal profile predicted using the expressions presented by Golden and Smith. To ensure the reliability of the kinetic experiments at very low NO_2 concentration we performed several "blanks" kinetic runs, observing the disappearance of OH due to diffusion, wall loss and reaction with nitric acid. We estimate that in the low NO_2 experiments the contribution of k_d to the overall OH decay is about 60%. On the other hand, the extreme reproducibility of the kinetic constant under those circumstances makes the statistical error in the kinetic constant on the order of 5%.

The "predicted" OH profile was obtained by taking their expressions for the formation of $HONO_2$, which is irreversible, and the formation and decay rates of HOONO and using an efficiency of 0.48 relative to N_2 to predict rates in He. We used Acuchem[27] to simulate the OH temporal profile under these conditions, and it can be seen that the redissociation of HOONO should produce a clearly observable nonexponential temporal profile. Indeed, based on our simulations, such nonexponential behavior should have been observable in the high-pressure flow-tube experiments of Donahue et al. if this mechanism is operative. These results do not rule out the formation of the elusive HOONO under different experimental conditions. However, they clarify two aspects of reaction 1. The first is that the discrepancy between this work and the high-pressure flowtube results of Donahue et al.[3] are not due to the different temporal resolution as suggested by Golden and Smith.[5] The second is that if the HOONO species is stabilized to a significant extent at atmospheric pressure then it should have a lifetime longer then a second under atmospheric conditions, since it was not possible to detect the decomposition of HOONO into OH and NO_2.

The use of the Troe formalism to parameterize third-order rate coefficients provides an extremely convenient functional form for use in atmospheric models and, as noted by Patrick and Golden,[28] provides a useful method of highlighting uncertainties and ambiguities in experimental data. The exact formalism for this parametrization and the physical significance of the values of k_0 and k_∞ are topics of current debate.[29] It now seems reasonable to conclude, based on both the experimental and theoretical data available, that the peroxynitrous acid channel plays some role in the recombination reaction, but that role is extremely uncertain. In our view the parameterization for atmospheric modeling should be based primarily on the available experimental data that has been obtained under atmospheric conditions of gas composition, pressure, and temperature. In more recent work, Donahue et al.[3] have measured the rate coefficient for the reaction of ^{18}OH with NO_2 as a route to the high-pressure limit for reaction 1. They conclude that their results can reconcile the high-pressure data with the remainder of the experimental data set. They note that evaluation of the rate coefficient for reaction 1 has proven difficult "despite a data set nearly without parallel in either scope or quality". We would also note that the database in a pressure region of critical atmospheric interest between 200 and 760 Torr is extremely limited. Our results suggest that the formation of the peroxynitrous acid isomer cannot explain the discrepancies in the experimental database. Given the importance of reaction 1 in tropospheric chemistry, the resolution of these discrepancies in the rate coefficient at one atmosphere pressure in air is a matter of some priority.

Conclusion

Our results suggest that the current JPL 2000 recommendation underestimates the second-order constant for reaction 1 in air at 298 and 273 K. Our results in air and N_2 are in good agreement with the measurements by Anastasi and Smith and are well represented by the JPL 1994 recommendation. If the formation of a weakly bound pernitrous acid intermediate were significant, it could explain the difference between flow tube and flash photolysis studies. Our work suggests that the recent calculations by Golden and Smith on the rates of isomer formation are not consistent with experimental observations and cannot explain these discrepancies. Despite their similar molecular weights, O_2 and N_2 show measurably different third-body efficiencies in the range of pressure between 30 and 600 Torr, O_2 being less efficient than N_2. We find no measurable enhancement in the rate coefficient in the presence of 20 Torr of water vapor at room temperature, suggesting that it does not have an unusually high efficiency as a third body.

Note Added After Review. Since the review of this paper, we have become aware of other work on this reaction. Hippler and co-workers have revisited the reaction at ultrahigh pressure and find that their previous work overestimated these rate coefficients. In addition, they have observed double exponential OH behavior at high temperature and pressure that they believe is direct evidence for formation of both isomers.[20] Golden and Smith are currently revising their RRKM parameters for the reaction in light of these results. Finally, Troe has reanalyzed the data set for the forward and reverse reactions (1, −1) over the temperature range 50−1400 K.[29] He suggests that the use of a temperature independent F_c of 0.4 and values of $k_{1,0} = [N_2]\ 3.0 \times 10^{-30}\ (T/300\ K)^{-3.0}$ cm^6 molecule^{-2} s^{-1} and $k_{1,\infty} = 3.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} are consistent with the experimental database over the range 220−400 K. This expression gives rate coefficients that lie below our data and gives a value of 9.86×10^{-12} cm^3 molecule^{-1} s^{-1} at 700 Torr of nitrogen, 9.5% lower than the value reported here. Using an F_c of 0.4, our data are fit by the values $k_{1,0} = [N_2]\ 3.7 \times 10^{-30}\ (T/300\ K)^{-3.0}$ cm^6 molecule^{-2} s^{-1} and $k_{1,\infty} = 3.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

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