

HNO₃ Forming Channel of the HO₂ + NO Reaction as a Function of Pressure and Temperature in the Ranges of 72–600 Torr and 223–323 K

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A high-pressure turbulent flow reactor coupled with a chemical ionization mass-spectrometer was used to determine the branching ratio of the HO₂ + NO reaction: HO₂ + NO → OH + NO₂ (1a), HO₂ + NO → HNO₃ (1b). The branching ratio, $\beta = k_{1b}/k_{1a}$, was derived from the measurements of “chemically amplified” concentrations of the NO₂ and HNO₃ products in the presence of O₂ and CO. The pressure and temperature dependence of β was determined in the pressure range of 72–600 Torr of N₂ carrier gas between 323 and 223 K. At each pressure, the branching ratio was found to increase with the decrease of temperature, the increase becoming less pronounced with the increase of pressure. In the 298–223 K range, the data could be fitted by the expression: $\beta(T,P) = (530 \pm 10)/T(\text{K}) + (6.4 \pm 1.3) \times 10^{-4}P(\text{Torr}) - (1.73 \pm 0.07)$, giving $\beta \approx 0.5\%$ near the Earth’s surface (298 K, 760 Torr) and 0.8% in the tropopause region (220 K, 200 Torr). The atmospheric implication of these results is briefly discussed.

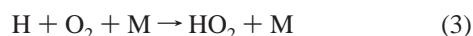
1. Introduction

We have recently reported the observation of a minor channel forming HNO₃ (1b) in the gas-phase reaction of the HO₂ radical with NO:¹



The study was carried out in a turbulent flow reactor (TFR) coupled with a chemical ionization mass-spectrometer (CIMS). The channel (1b) was quantified by direct detection of HNO₃ at pressure $P = 200$ Torr in the reactor, and a value of 0.18% was obtained for the branching ratio k_{1b}/k_{1a} at $T = 298$ K. A negative temperature dependence was found for this branching ratio with a value of 0.9% at 223 K.

Reaction 1 is a very important atmospheric reaction. It plays a key role in controlling the interconversion between OH and HO₂ radicals in the troposphere through the cycle



Reaction 1a is also a major source of tropospheric ozone through the conversion of NO to NO₂ followed by NO₂ photolysis to NO and O-atoms, these latter combining with O₂ to produce ozone. The efficiency of the above cycle is decreased by chain termination reactions, one of the most important being



Reaction 1b is another chain termination reaction suggested to be significant in the upper troposphere.¹ Regarding the potential importance of reaction 1b in the whole atmosphere, it is necessary to determine the branching k_{1b}/k_{1a} over the whole ranges of atmospheric pressures and temperatures.

In the present work, measurements of the branching ratio for reaction 1 was extended to the pressure range of 72–600 Torr in the temperature range 223–323 K to provide a parametrization equation to be used to assess the role of reaction 1b in model calculations of the atmospheric composition. To increase the HNO₃ signal-to-noise ratio, “chemical amplification” according to reactions 1–3 was utilized in the TFR with the chain length of the order of ten. A linear pressure dependence for the branching ratio k_{1b}/k_{1a} was found, and a negative temperature dependence, previously observed at $P = 200$ Torr,¹ was confirmed for the whole range of the indicated pressures between 323 and 223 K.

2. Experimental Section

2.1. Chemical Reactor. The experimental setup consisting of a high-pressure turbulent flow reactor coupled to a chemical ionization mass spectrometer was similar to that used in our first study of the HO₂ + NO reaction.¹ A scheme of the apparatus is presented in Figure 1. The flow in the TFR was created by N₂ carrier gas evaporating from a liquid nitrogen tank. The pressure in the TFR was controlled by regulating the throttling valve of the reactor pump and varying the main N₂ flow. The Reynolds numbers were in the range from 4900 to 11000 at flow rates from 64 to 145 SLPM corresponding to pressures from 70 to 600 Torr. Reactor temperature was controlled by combined effects of cooling via passing the main flow through the metal coil immersed into a Dewar with liquid N₂ and heating using a CB100 digital controller (RKC Instrument). This controller also allowed heating the reactor up to 50 °C.

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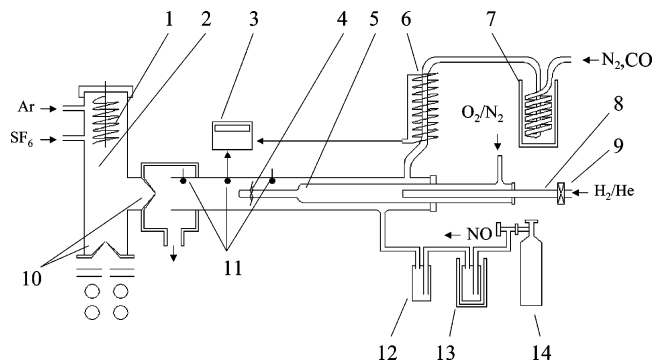
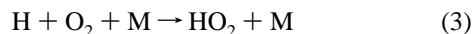


Figure 1. Experimental setup: 1, ion source; 2, ion-molecule reactor; 3, temperature controller; 4, «turbulizer»; 5, injector; 6, resistance; 7, cooling bath; 8, discharge tube; 9, microwave discharge; 10, sampling cones; 11, temperature sensor; 12, Fe^{II}(SO₄) filter; 13, cool bath; 14, NO cylinder.

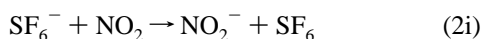
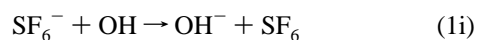
HO₂ radicals were produced in the TFR by the reaction



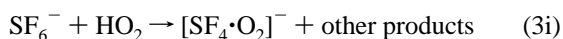
with H-atoms generated by a microwave discharge in H₂/He gas mixtures flowing through a quartz tube concentrically connected to the movable injector. The flows of N₂ in the injector and of He in the discharge tube were optimized for maximum H-atoms production. He (AlphaGaz 2) was purified by passing through molecular sieves cooled by liquid N₂. Tank grade H₂ (AlphaGaz 2) was used without further purification. NO was introduced into the TFR upstream of the tip of the injector. The tank grade NO (AlphaGaz N20) passed successively through ethanol/liquid nitrogen cooled traps and Fe^{II}(SO₄) filter to remove NO₂ and heavier nitrogen oxides. NO flow rate of about 0.6 SCCM was maintained using a TYLAN flow controller. O₂ (AlphaGaz 2) and CO (AlphaGaz N47) were added into the main N₂ stream using CELERITY flow controllers. The maximum distance from the injector tip to the orifice of the inlet cone of the ion-molecule reactor was $L = 50$ cm, which corresponded to a reaction time in the TFR of about $t = 30$ ms at $P = 200$ Torr and $T = 298$ K.

2.2. CIMS Detection and Sensitivity. Gas mixtures from the TFR were sampled through a Teflon cone with orifice diameter of 0.5 mm into the ion-molecule reactor (IMR) located perpendicular to the TFR. The flow rate of the Ar carrier gas in the IMR was 3.6 SLPM at the typical pressure of 0.7 Torr. The primary Ar⁺ ions and electrons were generated in the ion source by a heated filament. The emission current from the filament was always stabilized during the measurements. SF₆ was continuously introduced into the IMR downstream of the ion source. The primary SF₆⁻ negative ions were produced by attachment of thermalized electrons to SF₆.

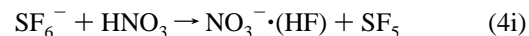
OH radicals and NO₂ were detected as OH⁻ (m/e 17) and NO₂⁻ (m/e 46) ions formed by electron transfer from SF₆⁻:²



HO₂ radicals were detected at m/e 140 using the reaction³



HNO₃ was detected using the reaction with SF₆⁻, giving the peak at m/e 82:⁴



The branching ratio of reaction 1, $\beta = k_{1b}/k_{1a}$, was obtained by measuring the concentration ratio of the HNO₃ and NO₂ products from channels 1b and 1a, respectively. To convert the measured intensity ratio of the products, $\Delta I_{82}/\Delta I_{46}$, to the concentration ratio, it is necessary to know the ratio of the apparatus sensitivities to HNO₃ and NO₂, $S_{\text{HNO}_3}/S_{\text{NO}_2}$. The $S_{\text{HNO}_3}/S_{\text{NO}_2}$ ratio and the absolute sensitivities themselves are determined by a number of parameters which vary with changing the pressure in the TFR. The most important parameters include pressure and flow velocity in the IMR, sampling conditions at the interface between the TFR and IMR, optimum potentials applied to the sampling cone, and the ion optics elements behind it. To account for the dependence of the sensitivities on the pressure in the TFR, the following approach was adopted. At $P = 200$ Torr, the absolute and relative sensitivities were determined using a calibration method described in our previous study.¹ In brief, the three-step procedure consisted of (1) NO₂ calibration using a standard NO₂ gas mixture, (2) OH calibration using reaction 5 at short reaction times and low NO₂ concentrations, and (3) calibration of nitric acid by measuring the kinetics of the OH decay and appearance of HNO₃ in reaction 4:



The advantages of such “chemical” calibration are (i) in situ production of HNO₃ that eliminates the problems connected with the introduction of HNO₃ into the reactor and (ii) absence of the errors connected with the determination of NO₂ concentration, as these errors vanish in the sensitivity ratio $S_{\text{HNO}_3}/S_{\text{NO}_2}$. This procedure was also used in some experiments at $P = 100$, 300, 400, and 500 Torr. However, to avoid potential problems related to increasing formation of peroxyxynitrous acid, HOONO, with pressure in reaction 4⁵ and to simplify the calibration procedure for other pressures in the TFR, the $S_{\text{HNO}_3}/S_{\text{NO}_2}$ ratios were derived from the changes of NO₂ and HNO₃ sensitivities relative to those at 200 Torr determined from direct introduction of HNO₃ and NO₂ into the TFR.

The change of S_{HNO_3} with pressure was determined by flowing gaseous HNO₃ from the mixture of HNO₃ (Aldrich, 69%) and H₂SO₄ (Sigma-Aldrich, 90%) aqueous solutions (10:1 volume ratio) into the reactor. Gaseous HNO₃ was transported by a He flow bubbling through the solution mixture in a glass trap. The trap was kept below 16 °C to avoid saturation of the HNO₃ signal. The helium flow was varied by means of a CELERITY mass flow controller with 10 SCCM maximum flow rate. A dilution by larger He flow regulated using a 250 SCCM TYLAN flow controller took place shortly downstream of the trap. The trap was connected to the reactor via a PFA tube. At each pressure S_{HNO_3} was determined from the linear increase of the signal intensity at m/e 82 with the flow rate of He passing through the bubbler. The HNO₃ partial pressure over the solution, P_{HNO_3} , was not known, but this was not critical because only the sensitivities relative to those at 200 Torr, S_P/S_{200} (HNO₃) = $S_{\text{HNO}_3}(P)/S_{\text{HNO}_3}(200)$, were used. A rough estimation using the average ratio $S_{\text{HNO}_3}/S_{\text{NO}_2} \approx 4$ from the chemical calibration at 200 Torr gave $P_{\text{HNO}_3} \approx 0.03$ Torr at 15 °C.

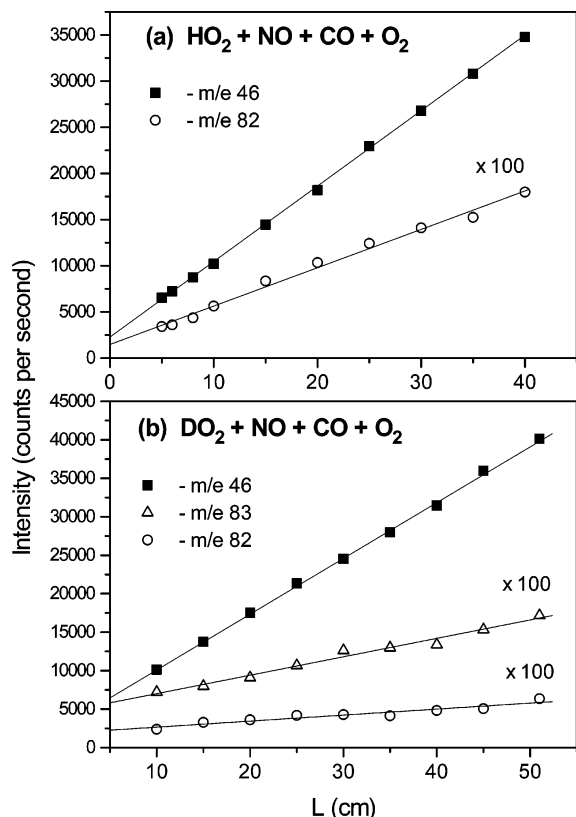


Figure 2. Chemical amplification in the HO₂/NO/CO/O₂ (a) and HO₂/NO/CO/O₂ (b) systems at 200 Torr and 298 K: (a) [HO₂] = 4.8 × 10¹¹, [NO] = 5.9 × 10¹³, [O₂] = 1.8 × 10¹⁶, and [CO] = 2.2 × 10¹⁷ molecule cm⁻³ (chain length 5.6); (b) [DO₂] = 8 × 10¹¹, [NO] = 3 × 10¹³, [O₂] = 1.2 × 10¹⁶, [CO] = 3 × 10¹⁷ molecule cm⁻³ (chain length 4.6).

Calibration of the NO₂ signal was made by flowing a commercial NO₂ gas mixture (Alpha Gaz, 5000 ppm in N₂) into the TFR. The mixture flow rate was measured by a TYLAN-2900 mass flow controller. The NO₂ sensitivities, S_{NO_2} , were obtained from the slopes of the linear dependence of the signal intensity at m/e 46 on the concentration calculated from the flow rate. The signal intensities were measured in the range of [NO₂] = 3 × 10¹¹ to 2 × 10¹³ molecule cm⁻³ for which a good linearity was observed at each pressure. Similarly to HNO₃, the pressure dependence was expressed relative to that at $P = 200$ Torr, $S_P/S_{200}(\text{NO}_2) = S_{\text{NO}_2}(P)/S_{\text{NO}_2}(200)$. The sensitivities for NO₂ and HNO₃ exhibited different pressure dependences, which very likely resulted from different formation mechanisms of product ions. Both were found to decrease with increasing pressure in the TFR keeping all the other parameters unchanged as it was the case in these experiments. Finally, having made calibrations for NO₂ and HNO₃, a pressure factor $f_P = [S_P/S_{200}(\text{HNO}_3)]/[S_P/S_{200}(\text{NO}_2)]$ was determined for the calculation of the HNO₃ to NO₂ concentration ratio.

Change of the temperature in the TFR at a constant pressure has no noticeable influence on the signal intensities of NO₂ and HNO₃ as was shown in test experiments at 200 Torr. In these experiments, NO₂-He and HNO₃-He mixtures were continuously introduced into the reactor where the temperature was lowered from 300 to 239 K while constant pressure was maintained by regulating the reactor pumping.

3. Results

3.1. Chemical Amplification of HNO₃ formation in the HO₂/NO/CO/O₂ System. Use of the chemical amplification (1a–3) in the TFR allowed an increase of the signal intensities

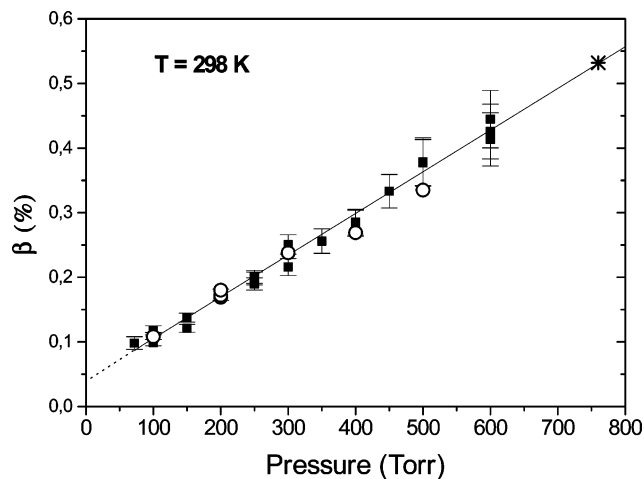
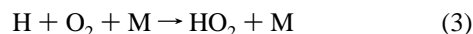
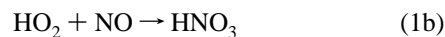
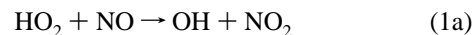


Figure 3. Pressure dependence of $\beta = k_{1b}/k_{1a}$ at 298 K. Open circles denote measurements with chemical HNO₃ calibration; star is the extrapolation to atmospheric pressure (760 Torr).

of produced nitric acid that was a critical factor in reducing experimental uncertainties, and confirmation of the previously measured branching ratio k_{1a}/k_{1b} .¹ Amplification of the signal was achieved by adding into the TFR high concentrations of CO and O₂, creating a chain mechanism that includes termination reaction 1b:



At the same time, CO in reaction (2) served as a scavenger of OH radicals preventing formation of nitric acid in the secondary reaction (4):



Figure 2a illustrates the increase of the NO₂ and HNO₃ concentrations with the increase of the distance L between the injector tip and the interface cone in the HO₂/NO/CO/O₂ system. This run was done at $P = 200$ Torr, $T = 298$ K, and initial concentrations [HO₂] = 4.8 × 10¹¹; [NO] = 5.9 × 10¹³; [O₂] = 1.8 × 10¹⁶; and [CO] = 2.2 × 10¹⁷ molecule cm⁻³. The initial concentration of HO₂ was determined by measuring the NO₂ concentration formed in the reaction in the absence of CO. The maximum NO₂ concentration formed in the presence of CO was 2.8 × 10¹² molecule cm⁻³, corresponding to a chain length of 5.8. The chain length was regulated by NO concentration, the limiting step being reaction 1a. It was necessary to limit the chain length in order to make the rate of reaction (4) negligible and thus to control the rate ratio of reactions 4 and 2, which is the probability of HNO₃ formation in reaction 4. In the given example, for maximum distance $L = 50$ this ratio was $\alpha = k_4[\text{NO}_2]_{\text{tot}}/k_2[\text{CO}] = 1.8 \cdot 10^{-4}$. [NO₂]_{tot} is the mean total NO₂ concentration in the reactor equal to [NO₂]_{react}/2 + [NO₂]_{bgr}, where [NO₂]_{react} is the NO₂ concentration produced in the reaction at maximum L and [NO₂]_{bgr} is the background concentration originating mainly from the NO inlet system. The rate constants k_2 and k_4 were taken from ref 6. A linear amplification was observed for both NO₂ and HNO₃ products described by the equations $I_{46} = (814 \pm 11)L + 2282$ and I_{82}

TABLE 1: Determination of $\beta = k_{1b}/k_{1a}$ at Different Pressures and 298 K Using Chemical Calibration of HNO_3^a

P Torr	N^b	$S_{\text{NO}_2}^c$	S_{OH}^c	$S_{\text{HNO}_3}^c$	$\Delta I_{82}/\Delta I_{46}$ 10^{-4}	b_{82}/b_{46}^d 10^{-4}	β_{int}^e %	β_{slope}^f %	α^g %
10^{-8} cps/molecule cm^{-3}									
200	1	1.23	2.32	3.79	51.9 ± 2.8	51.5 ± 1.8	0.169 ± 0.023	0.167 ± 0.022	0.018
	2	1.74	3.31	7.63	75.5 ± 4.3	72.9 ± 5.3	0.172 ± 0.024	0.166 ± 0.024	0.019
	3	1.98	2.90	6.80	61.7 ± 5.5	63.6 ± 5.6	0.180 ± 0.028	0.185 ± 0.030	0.028
	4	0.93	1.67	6.67	113 ± 5.4	111 ± 4.9	0.169 ± 0.023	0.166 ± 0.022	0.016
Average:							0.173 ± 0.010	0.171 ± 0.016	
100	1	1.75	4.49	12.0	74.2 ± 4.5	73.1 ± 4.8	0.108 ± 0.015	0.107 ± 0.016	0.012
300	1	1.49	1.66	4.57	73.1 ± 3.5		0.238 ± 0.037		0.012
400	1	1.97	2.08	2.10	28.7 ± 3.9		0.269 ± 0.043		0.013
500	1	1.07	1.32	1.16	37.4 ± 4.0	35.0 ± 3.8	0.345 ± 0.077	0.345 ± 0.074	0.008

^a Calibration using $\text{H} + \text{NO}_2$ and $\text{OH} + \text{NO}_2$ reactions. ^b Experiment number. ^c S_X denotes sensitivity to species X . ^d b_M is the slope of the linear dependence of signal intensity at m/e M versus reaction time. ^e Values from the intensities. ^f From the slopes. ^g $\alpha = k_5[\text{NO}_2]_{\text{tot}}/k_3[\text{CO}]$ is the upper limit for the probability of HNO_3 formation in the side $\text{OH} + \text{NO}_2$ reaction.

$= (4.19 \pm 0.13)L + 14.8$. The top panel of Table 1 presents the branching ratios calculated from this experiment (first line) and three other similar experiments carried out at 200 Torr with chemical calibration. In these experiments, the product intensity ratios, $\Delta I_{82}/\Delta I_{46}$, were determined both from the slopes of the amplification kinetics and by averaging the $\Delta I_{82}/\Delta I_{46}$ values for different positions of the injector. The average value is $\beta = (0.173 \pm 0.008)\%$. Taking into account the systematic errors in calibration, the final result can be expressed as $\beta = (0.17 \pm 0.03)\%$.

Chemical amplification of the deuterated nitric acid, DNO_3 , was obtained in the isotopic $\text{DO}_2/\text{NO}/\text{CO}/\text{O}_2$ system, when the discharge in D_2/He mixture was used to produce D-atoms. Figure 2b shows the results of the kinetic measurements for NO_2 , DNO_3 and HNO_3 at $P = 200$ Torr, $T = 298$ K, and initial concentrations $[\text{DO}_2] + [\text{HO}_2] = 9.5 \times 10^{11}$; $[\text{NO}] = 2.9 \times 10^{13}$; $[\text{O}_2] = 1.2 \times 10^{16}$; $[\text{CO}] = 2.5 \times 10^{17}$ molecule cm^{-3} . Appearance of HNO_3 ($m/e = 82$) is explained by the formation of OH and H-atoms from the dissociation of H_2O traces in He carrier gas. The initial ratio of $[\text{H}]/[\text{D}] = 0.14$ was obtained by the titration of the discharge products with NO_2 . Isotopic DNO_3 also exhibits linear kinetics proving that the nitric acid observed in the $\text{HO}_2 + \text{NO}$ reaction is not a product of the surface reaction of NO_2 with H_2O . Assuming similar sensitivities to HNO_3 and DNO_3 , the observed DNO_3 signal intensity indicates that the branching ratio for the isotopic $\text{DO}_2 + \text{NO}$ reaction would be a factor of ~ 2 lower than for reaction 1.

3.2. Pressure Dependence of the Branching Ratio at Room Temperature. At room temperature, the kinetics of the formation of NO_2 and HNO_3 products were measured in the presence of CO as described above at different pressures ranging from 72 to 600 Torr. The bottom panel of Table 1 contains the results obtained using chemical calibration at 100, 300, 400, and 500 Torr and Table 2 contains the results from the six experiments with variable pressure using direct calibration of HNO_3 . In most experiments, the $\Delta I_{82}/\Delta I_{46}$ ratio was determined from the slopes of the amplification kinetics. Some experiments were done at a fixed L making several measurements of NO_2 and HNO_3 with the discharge switched on and off (experiment 5 in Table 2). The measured intensity ratios were corrected by sensitivity pressure factor f_P determined with respect to 200 Torr as described in the Experimental Section. Then, division of the corrected intensity ratios by that for 200 Torr gives β/β_{200} , the reaction branching ratio at a given pressure relative to that at 200 Torr which is a known value:

$$\beta(P) = [\Delta I_{82}/\Delta I_{46}(P)/\Delta I_{82}/\Delta I_{46}(200)]f_P\beta_{200} \quad (\text{Eq1})$$

TABLE 2: Determination of the Pressure Dependence of $\beta = k_{1b}/k_{1a}$ at 298 K Using Sensitivity Pressure Factor^a

N^b	P Torr	$[\text{NO}_2]_{\text{bgr}}$ 10^{11}	$\Delta[\text{NO}_2]$ 10^{12}	$[\text{CO}]$ 10^{17}	f_P^a	$\Delta I_{82}/\Delta I_{46}$ 10^{-4}	β/β_{200}^c	β %	α^d %
1	100	1.6	2.0	1.9	0.62	47.7	0.57	0.097	0.012
	150	2.4	2.5	2.2	0.73	49.7	0.70	0.118	0.020
	200	2.7	2.5	2.5	1	51.9	1	0.169	0.017
2	200	4.0	4.2	2.5	1	61.7	1	0.180	0.028
	250	3.9	3.0	2.8	1.24	57.0	1.15	0.206	0.020
	300	3.6	2.3	3.1	1.61	55.5	1.45	0.261	0.016
	350	4.2	0.54	3.3	2.12	47.1	1.62	0.280	0.008
3	200	2.0	2.4	2.1	1	75.5	1	0.173	0.018
	400	4.2	1.6	3.2	2.55	47.4	1.64	0.282	0.012
	500	4.2	1.1	3.5	3.60	46.1	2.19	0.378	0.010
	600	4.8	0.43	3.4	4.59	42.1	2.57	0.441	0.008
4	200	1.9	2.4	2.4	1	57.0	1	0.173	0.016
	600	4.7	0.72	6.0	4.59	30.5	2.45	0.425	0.005
5	172	2.3	3.3	2.7	0.73	40.8	0.95	0.164	0.018
	200	2.4	2.8	2.7	1	34.3	1	0.173	0.017
	250	1.8	1.4	2.3	1.24	32.0	1.16	0.201	0.013
	300	2.4	1.6	2.8	1.61	26.5	1.25	0.216	0.012
	350	3.0	1.4	3.3	2.16	23.5	1.48	0.256	0.012
	400	3.6	1.7	3.7	2.61	21.7	1.65	0.285	0.012
	500	3.6	1.1	3.5	3.71	20.1	2.18	0.377	0.010
600	4.3	0.78	4.2	4.59	17.8	2.39	0.413	0.008	
6	72	1.3	1.3	2.5	0.51	48.4	0.57	0.098	0.005
	100	1.6	2.3	2.5	0.62	48.1	0.68	0.118	0.010
	150	2.2	3.0	2.5	0.73	43.8	0.76	0.132	0.017
	200	3.5	4.6	3.7	1	43.6	1	0.173	0.020
	250	2.9	4.1	4.0	1.24	41.0	1.10	0.189	0.019
	450	2.7	1.5	7.2	1.81	27.7	1.95	0.337	0.006

^a See Experimental Section for determination of pressure correction factor f_P using external source of HNO_3 . ^b Experiment number. ^c Branching ratio with respect to that at 200 Torr. ^d Upper limit for the probability of HNO_3 formation in the $\text{OH} + \text{NO}_2$ side reaction. Concentrations are in molecule cm^{-3} .

The obtained pressure dependence is shown in Figure 3. It is a linear function of pressure expressed by

$$\beta(P) = (6.4 \pm 0.3) \times 10^{-4}P(\text{Torr}) + (4.2 \pm 0.8) \times 10^{-2} \quad (\text{Eq2})$$

with 2σ uncertainty limits. Extrapolation to atmospheric pressure gives $\beta(760) = 0.53\%$, which is indicated by a star symbol in Figure 3. It is worth noting that the obtained dependence has a positive zero intercept. Assuming $\beta \rightarrow 0$ when $P \rightarrow 0$, the measurements indicate that there should be a nonlinear dependence at low pressures.

3.3. Temperature Dependence of the Branching Ratio at Different Pressures. Temperature dependence of β was measured by keeping a constant mass flow rate of the carrier gas and the reactants at a given pressure. The constant pressure

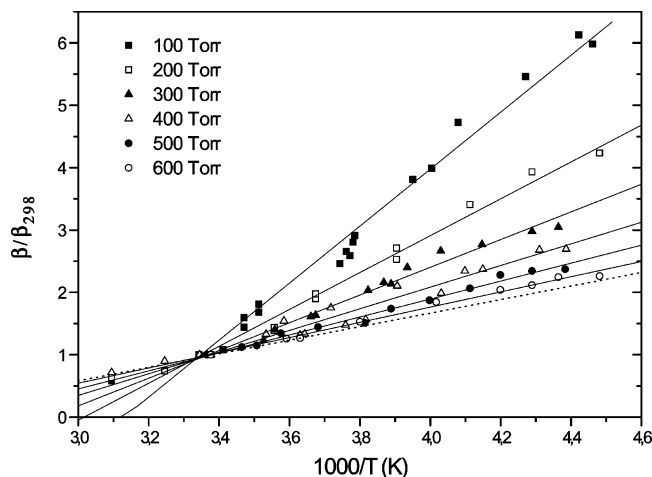


Figure 4. Normalized temperature dependence of $\beta = k_{1b}/k_{1a}$ at different pressures. Dotted line is the extrapolation to 760 Torr.

during the cooling was maintained by regulating the throttling valve of the reactor pump. As a rule, the measurements were done at a fixed position of the injector, corresponding to $L = 50$ cm. Table 3 gives the measured signal intensity ratios and the ratios normalized to the room-temperature value, which is identical to the normalized branching ratio, β/β_{298} . The concentrations of NO, O₂, and CO given in Table 3 correspond to $T = 298$ K. Figure 4 presents a summary of the normalized branching ratios as a function of $1000/T$. The observed plots could be rather well approximated by a linear fit. These fits are shown in Figure 4 by solid lines (the data obtained above 298 K were excluded from the linear regression analysis). The slopes of the linear fit monotonically decrease with the increase of

pressure. The extrapolation to atmospheric pressure (black dotted line) was obtained from the power function fit for this decrease.

When the normalized temperature curve for every pressure is multiplied by the corresponding β coefficient given by eq 1, we obtain a full picture for the branching ratio, as shown in Figure 5. In the 298–223 K range temperature dependences for different pressures present a set of nearly parallel and equidistant straight lines. The linear fit fails at temperatures higher than 298 K, where curvatures were observed for $P = 100, 200,$ and 400 Torr. Below 298 K the whole set of data can be described by the simple three-parameter expression of the general form

$$\beta(P, T) = a/T + bP + c \quad (\text{Eq3})$$

Coefficient a was found by averaging the slopes of the observed temperature dependencies, coefficients b and c were determined by standard two-parameter least-square fit of the data. The numerical expression can be written as

$$\beta(P, T) = (530 \pm 20)/T(\text{K}) + (6.4 \pm 1.3) \times 10^{-4}P(\text{Torr}) - (1.73 \pm 0.07) \quad (\text{Eq4})$$

(with 2σ uncertainties). In Figure 6 the pressure dependence for HNO₃ production is reported at four temperatures: 298, 263, 249, and 228 K, with the nearest available experimental points taken in the vicinity of these temperatures. The straight lines were calculated using eq 4. Extrapolated to zero pressure, they exhibit larger intercepts for lower temperatures.

4. Discussion

Recently, a theoretical examination of the mechanisms on the HNO₃ potential energy surface ($\text{HO}_2 + \text{NO} \rightleftharpoons \text{HOONO} \rightleftharpoons$

TABLE 3: Measurement of the Temperature Dependence of $\beta = k_{1b}/k_{1a}$ at Different Pressures

T K	$\Delta I_{82}/\Delta I_{46}$ 10^{-4}	β/β_{298}^a	T K	$\Delta I_{82}/\Delta I_{46}$ 10^{-4}	β/β_{298}^a	T K	$\Delta I_{82}/\Delta I_{46}$ 10^{-4}	β/β_{298}^a
$P = 100$ Torr; $[\text{NO}] = 4.1 \times 10^{13}$; $[\text{O}_2] = 1.4 \times 10^{16}$; $[\text{CO}] = 2.4 \times 10^{17}$ molecule cm^{-3}								
298	113	1	265	311	2.74	226	695	6.13
293	123	1.08	253	432	3.81	223	678	5.98
288	172	1.52	249	452	4.00	298	97.1	1
285	198	1.75	245	536	4.73	308	71.8	0.74
267	279	2.46	234	618	5.45	323	56.5	0.58
$P = 200$ Torr; $[\text{NO}] = 3.8 \times 10^{13}$; $[\text{O}_2] = 1.2 \times 10^{16}$; $[\text{CO}] = 2.5 \times 10^{17}$ molecule cm^{-3}								
298	38.7	1	243	132	3.41	298	33.7	1
281	53.0	1.45	233	152	3.93	308	24.9	0.74
272	76.4	1.98	223	164	4.24	323	21.3	0.63
256	105	2.71						
$P = 300$ Torr; $[\text{NO}] = 5.4 \times 10^{13}$; $[\text{O}_2] = 1.6 \times 10^{16}$; $[\text{CO}] = 2.9 \times 10^{17}$ molecule cm^{-3}								
298	25.0	1	261	51.0	2.03	241	69.4	2.77
283	30.8	1.23	257	53.5	2.14	233	75.1	2.98
281	35.1	1.40	254	60.1	2.40	229	76.3	3.05
273	40.3	1.61	248	65.1	2.53			
$P = 400$ Torr; $[\text{NO}] = 6.1 \times 10^{13}$; $[\text{O}_2] = 2.1 \times 10^{16}$; $[\text{CO}] = 3.5 \times 10^{17}$ molecule cm^{-3}								
298	31.5	1	256	66.1	2.10	228	84.7	2.69
283	41.8	1.33	250	62.5	1.99	298	16.2	1
279	48.0	1.53	241	74.2	2.36	308	14.6	0.90
266	46.6	1.48	232	84.4	2.68	323	11.6	0.72
$P = 500$ Torr; $[\text{NO}] = 9 \times 10^{13}$; $[\text{O}_2] = 2.7 \times 10^{16}$; $[\text{CO}] = 4.8 \times 10^{17}$ molecule cm^{-3}								
298	14.2	1	272	20.5	1.44	243	29.4	2.07
289	16.0	1.12	262	24.7	1.74	238	32.4	2.28
285	16.3	1.15	255	21.5	1.51	233	33.3	2.34
280	20.2	1.42	250	26.6	1.87	228	33.8	2.37
$P = 600$ Torr; $[\text{NO}] = 4.0 \times 10^{13}$; $[\text{O}_2] = 3.2 \times 10^{16}$; $[\text{CO}] = 4.0 \times 10^{17}$ molecule cm^{-3}								
298	18.9	1	263	28.9	1.53	233	40.0	2.12
278	23.8	1.26	249	34.9	1.85	229	42.5	2.25
275	24.0	1.27	238	38.6	2.04	223	42.8	2.26

^a Branching ratio with respect to that at 298 K.

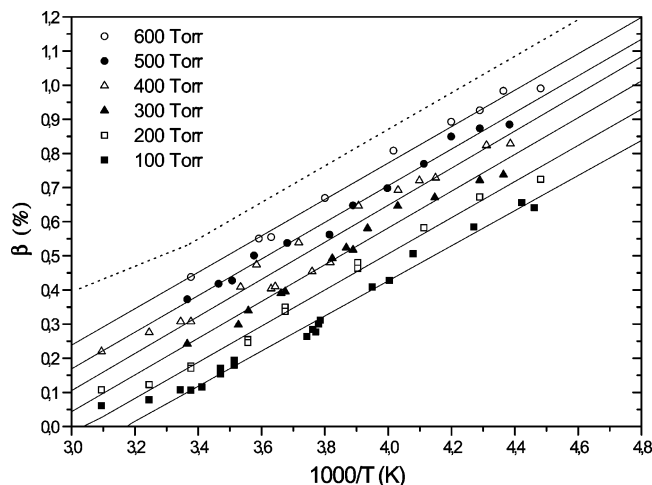


Figure 5. Pressure and temperature dependences of $\beta = k_{1b}/k_{1a}$. Upper dotted line represent extrapolation to $P = 760$ Torr.

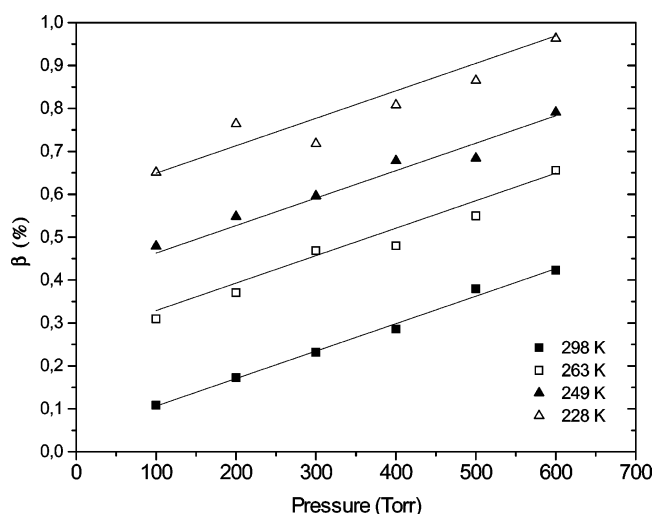


Figure 6. Pressure dependence of $\beta = k_{1b}/k_{1a}$ at different temperatures. Solid curves correspond to eq 3.

$\text{OH} + \text{NO}_2 \rightleftharpoons \text{HNO}_3$) has been performed by Zhang and Donahue using a multiple-well master-equation simulation of the system.⁷ To constrain the parameters of the simulation, the authors used the experimental evidence for HNO_3 production in the $\text{HO}_2 + \text{NO}$ reaction,¹ the experimental data on formation and decay of *cis*- and *trans*-conformers of the short-lived HOONO intermediate in the $\text{OH} + \text{NO}_2$ reaction,^{8–10} and on isotopic scrambling in $^{18}\text{OH} + \text{NO}_2$.^{10,11} The calculations show that channel 1b can occur by isomerization of *trans*-HOONO to HONO₂, if a high barrier between *cis* and *trans* conformers and a low barrier for isomerization to HONO₂ are assumed. A good agreement with our branching fraction for HNO_3 formation in reaction 1 at 298 K¹ was obtained with the energy of the transition state for isomerization of approximately 5 kcal mol⁻¹ lower than the energy of $\text{OH} + \text{NO}_2$. The existence of such a low-lying “rotational” transition state was first proposed by Dransfield et al.¹² A search for the transition states for HOONO rearrangements was performed by Zhao et al.¹³ using density functional theory. The authors suggest that O–O cleavage in HOONO may lead to hydrogen-bonded $\text{OH}\cdots\text{ONO}$ complexes which through rotational motion can be reoriented for N–O bond formation and collapse to HONO₂. The complexes and the transition states for isomerization were located at the B3LYP/6-311++G** and CBS-QB3 levels. All these stationary points were found to be very similar in energy, in the range of 1–2

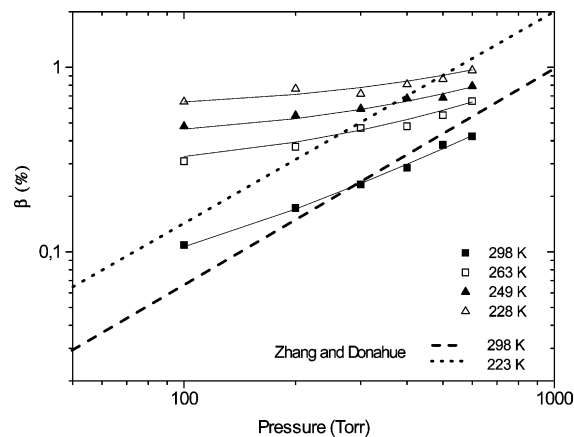


Figure 7. Representation of the Figure 6 in logarithmic scale for comparison with the calculation from Zhang and Donahue⁹ (thick curves).

kcal mol⁻¹ lower than the free OH and NO₂. However, in contrast to ref 9, where the isomerization path was involved to explain the observed decay of *trans*-HOONO, Zhao et al. believe that the isomerization occurs easier from *cis*-HOONO than from *trans*-HOONO conformation.

According to theoretical considerations,⁷ the pressure dependences in Figure 6 can be interpreted as a falloff corresponding to stabilization of the excited HONO₂ formed at the $\text{HO}_2 + \text{NO}$ energy. In Figure 7 we compare our present experimental results with the calculated pressure dependence⁷ presented in logarithmic coordinates. As already mentioned, there is a rather good agreement between the measurements and theory at 298 K, although the theoretical pressure dependence at 298 K is somewhat steeper than the observation. As seen in Figure 7, the linearity of eq 1 breaks when switching to logarithmic scale because, formally, $\beta \neq 0$ at zero pressure. Accordingly, the divergence between the measurements and calculations increases at lower temperatures because of larger intercepts. To summarize, theory does not exclude formation of HNO₃ in reaction 1; at ambient temperature, the observed pressure dependence of β can be reproduced by calculations in a limited pressure range (100–600 Torr). Also, calculations confirm the observed negative temperature dependence of β .

5. Atmospheric Implication

The obtained results confirmed our previous finding of a minor HNO₃ forming channel in the $\text{HO}_2 + \text{NO}$ reaction, with an increase of the HNO₃ yield with decreasing temperature.¹ In addition, they show an increase of this yield with increasing pressure. The atmospheric consequences of this new process has been already considered in our previous paper, predicting a noticeable effect of reaction 1b on the concentrations of HO_x, NO_x, and ozone in the upper troposphere.¹ The plots of Figure 5 show a change of $\beta = k_{1b}/k_{1a}$ roughly from 0.5% near the Earth’s surface (298 K, 760 Torr) to 0.8% in the tropopause region (220 K, 200 Torr). This suggests that reaction 1b could also have a significant effect in the middle and lower troposphere. The effect of reaction 1b on the atmospheric composition can be quantified by including this reaction in atmospheric models with the rate constant calculated using eq 4. Such model calculations have already been done using both 2D and 3D models.¹⁴ The resulting impact of reaction 1b on the chemical composition of the troposphere could even be more significant considering the positive influence of water vapor on the branching ratio β which has been observed in the previous test experiments.¹ This humidity effect is going to be investigated

in more details by measuring β as a function of H₂O concentration in extended ranges of pressure and temperature.

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