have used water-in-toluene microemulsions. The extraction properties of  $C_n V^+$ , where n = 8-18, into the continuous phase of toluene are poor. Other organic solvents such as ethyl acetate or anisole appear to extract effectively these radical ions. Recently,<sup>21</sup> we have demonstrated that  $C_8V^+$  undergoes an induced disproportionation reaction (eq 7) in a two-phase system of

$$2C_8V^+ \rightleftharpoons C_8V: + C_8V^{2+} \tag{7}$$

water-ethyl acetate and have utilized the two-electron reductant,  $C_8V^+$ , in reduction of dibromostilbenes. This disproportionation equilibrium is unfavored in a homogeneous phase. It is forced toward the two-electron reductant,  $C_8V$ : due to the opposite solubility properties of  $C_8V^{2+}$  and  $C_8V$ : in the water-ethyl acetate phases. Thus, application of a water-in-oil microemulsion media

for the production of two-electron reductants via single-electron-transfer reactions, followed by an induced disproportionation, seems feasible. Consequently, the utilization of the doubly reduced product in the fixation of substrates being solubilized in the organic phase is conceivable. Such experiments utilizing this principle in the fixation of valuable products, i.e., reduction of ketones and  $CO_2$  reduction, are now under way in our laboratory.

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Registry No. C1V2+, 3240-78-6; C4V2+, 32449-18-6; C6V2+, 6198-51-2;  $C_8V^{2+}$ , 36437-30-6;  $C_{14}V^{2+}$ , 33243-09-3;  $C_{18}V^{2+}$ , 90179-58-1; (NH<sub>4</sub>)<sub>3</sub>EDTA, 15934-01-7; Ru(bpy)<sub>3</sub><sup>2+</sup>, 15158-62-0.

# Pressure and Temperature Dependence of the Reaction $NO_2 + NO_3 + M \rightarrow N_2O_5 + M$

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The kinetics of the reaction  $NO_2 + NO_3 + M \rightarrow N_2O_5 + M$  (1) were studied with flash photolysis/visible absorption by monitoring the disappearance of NO<sub>3</sub> under pseudo-first-order conditions over the temperature range 236-358 K and pressure range 20-700 torr of helium and nitrogen. Reaction 1 was found to be in the falloff region between second- and third-order kinetics in this range. Falloff parameters were obtained by fitting the experimental data to the falloff equation of Troe and co-workers. When one uses a published temperature-dependent broadening factor  $(F_c)$ , the data are described by  $k_0(N_2) = 4.5 \times 10^{-30}$  cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup> and  $k_{\infty} = 1.65 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K with T dependencies of  $T^{-3.4}$  and  $T^{-0.4}$ for  $k_0$  and  $k_{\infty}$ , respectively. This expression was used in conjunction with recent measurements of the rate constant for  $N_2O_5$ thermal decomposition to obtain an improved measurement  $\Delta H_f^{\circ}(298)$  for NO<sub>3</sub>, which was determined to be 17.3  $\pm 0.7$ kcal mol<sup>-1</sup>. From these data the recommended equilibrium constant expression is  $K_{eq} = k_1/k_{-1} = 2.31 \times 10^{-8} \exp(11350/T)$  $(atm^{-1}).$ 

## Introduction

The nitrate radical, NO<sub>3</sub>, is an important member of the  $NO_x$ family in both the troposphere and lower stratosphere. Although its daytime concentration is limited to a few parts per trillion (ppt) due to rapid photolysis in the visible, nighttime concentration measurements have been reported at levels up to several hundred parts per trillion in both the urban and nonurban troposphere.<sup>1-4</sup>

More significantly, the NO<sub>3</sub> lifetime has been observed to be considerably shorter<sup>1,4-6</sup> than that expected on the basis of the simple scheme in which  $NO_3$  is formed by the reaction

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

and removed via the equilibrium

$$NO_2 + NO_3 (+M) \rightleftharpoons N_2O_5 (+M)$$
 (1,-1)

This discrepancy can result from three sources: (1) incorrect rate or equilibrium constant data for reaction 1; (2) additional NO<sub>3</sub> loss processes such as reactions with aldehydes, alkenes, and aromatics; (3) additional losses for  $N_2O_5$ , possibly via the reaction

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \tag{2}$$

which may be either homogeneous<sup>7</sup> or heterogeneous.<sup>3-5</sup> Errors in the equilibrium constant result only in changes in the partitioning of species in the NO<sub>x</sub> family with little effect on the overall  $NO_x$  budget. On the other hand, if the short lifetime arises from the rapid loss of either  $NO_3$  or  $N_2O_5$  by other processes, then these losses may constitute a removal mechanism for NO<sub>x</sub> which is more important that those already known, such as the formation of  $HNO_3$  via the OH +  $NO_2$  + M recombination. The discrepancy

in the NO<sub>3</sub> lifetime would then reflect a fundamental uncertainty in the atmospheric loss rate of  $NO_x$ .<sup>2,7</sup>

A first step in the resolution of this question, then, is the establishment of accurate kinetic data for reaction 1. In previous evaluations of the rate constant for reaction 1,<sup>8,9</sup> rate data for the N2O5 decomposition step have been combined with thermodynamic estimations of the equilibrium constant to obtain  $k_1$ . The accuracy of this method has been limited by uncertainties in the thermochemistry of NO<sub>3</sub>, and in the kinetic data for reaction -1. As a result, previous estimates of  $k_1$  in the low-pressure limit span a factor of 3 ((1.4–3.7) ×  $10^{-30}$  cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup>) and a factor of 7 in the high-pressure limit ((6.8–50)  $\times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup>  $s^{-1}$ ). In a more recent study over a limited pressure range at 298 K, Fowles et al.<sup>10</sup> derived values for  $k_1$  and  $k_{-1}$  from a comparison

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of experimentally measured, column integrated NO<sub>3</sub> concentrations with those calculated from a model reaction scheme. The values of  $k_1$  and  $k_{-1}$  obtained in that study were a factor of 3 larger than the accepted literature values.

In this study, the pressure and temperature dependences of reaction 1 were investigated by using the flash photolysis/visible absorption (FP/V) technique. NO<sub>3</sub> was formed in the photolysis of Cl<sub>2</sub>-ClONO<sub>2</sub> mixtures and the pseudo-first-order decay of NO<sub>3</sub> was observed at 662 nm in the presence of excess NO<sub>2</sub>. This is the first direct determination of  $k_1$  made without reference to the kinetics of N<sub>2</sub>O<sub>5</sub> thermal decomposition. In addition, an improved estimate of the enthalpy of formation of NO<sub>3</sub> was obtained by combining our measurements of  $k_1$  with the most recent experimental results on  $k_{-1}$ .

## **Experimental Section**

The experimental apparatus has been described in detail previously.<sup>11,12</sup> Briefly, NO<sub>3</sub> radicals were generated by flash photolysis using a Pyrex flash lamp/reaction cell and were monitored spectrophotometrically in the (0,0) band at 661.8 nm. The spectrophotometer system consisted of a xenon arc lamp or tungsten lamp equipped with a Corning 3-66 cutoff filter, a 0.5-m monochromator with a 0.64-nm spectral band-pass and a Corning 2-63 cutoff filter in front of the entrance slit, and a Hamamatsu R955 photomultiplier tube. The absorption path length from eight traversals of the reaction cell was about 7 m. Kinetic decays from 25-50 flashes were averaged to achieve a minimum detectable absorption of about 0.1% which corresponded to a detection limit for NO<sub>3</sub> of  $8 \times 10^{10}$  molecules cm<sup>-3</sup>. The flash energy was varied between 350 and 700 J/flash. The temperature of the photolysis cell was adjusted by circulating ethylene glycol or methanol through the cell's temperature control jacket.

NO<sub>3</sub> radicals were produced from the photolysis of  $Cl_2$ -ClONO<sub>2</sub> mixtures at wavelengths longer than 300 nm:

 $Cl_{2} + h\nu (\lambda > 300 \text{ nm}) \rightarrow 2Cl$   $Cl + ClONO_{2} \rightarrow Cl_{2} + NO_{3}$ (3)

 $k_3 = 6.3 \times 10^{-12} \exp(150/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (\text{ref } 13)$ 

Sufficient ClONO<sub>2</sub> ((2.0-35) × 10<sup>14</sup> molecules cm<sup>-3</sup>) was used to ensure that NO<sub>3</sub> was always formed on a time scale at least 10 times faster than its loss by reaction with NO<sub>2</sub> and that the scavenging of chlorine atoms by NO<sub>2</sub>

$$Cl + NO_2 + M \rightarrow ClNO_2 + M$$

could not compete with reaction 3.  $Cl_2$  and  $NO_2$  concentrations were varied over the ranges  $(2.5-25) \times 10^{15}$  and  $(0.8-25) \times 10^{14}$ molecules cm<sup>-3</sup>, respectively. Initial NO<sub>3</sub> concentrations varied from  $2 \times 10^{12}$  to  $15 \times 10^{12}$  molecules cm<sup>-3</sup>. Under these conditions, NO<sub>2</sub> was always present in large excess over NO<sub>3</sub>, resulting in good pseudo-first-order conditions. The NO<sub>3</sub> loss rate in the absence of NO<sub>2</sub> (due to NO<sub>3</sub> + NO<sub>3</sub> and NO<sub>3</sub> wall losses) was negligibly slow compared to reaction 1.

The chlorine nitrate used in this study was obtained from Molina and Molina<sup>14</sup> and was handled as described previously<sup>13</sup> to reduce the formation of impurities in the flow system (e.g.,  $Cl_2O$ ), photolysis by stray light, and thermal decomposition. ClONO<sub>2</sub> was introduced into the cell in a manner similar to that described by Margitan.<sup>13</sup> A part of the carrier gas flow was diverted through a saturator containing ClONO<sub>2</sub> at -78 °C at which temperature the ClONO<sub>2</sub> vapor pressure is about 1 torr.<sup>15</sup>

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Figure 1. Relative absorption of the  $Br_2/Cl_2/BrCl$  (—) and Coumarin 485 (---) photolysis filters. Shown for comparison are the absolute absorption spectra of  $Cl_2$  (---) and  $NO_2$  (---).

The ClONO<sub>2</sub> concentration in the flow exiting the saturator is measured by using a spectrophotometer consisting of a Zn lamp (214 nm), 30-cm absorption cell, prism monochromator, and solar-blind PMT (EMR 542G). The ClONO<sub>2</sub> absorption cross section was taken to be  $3.6 \times 10^{-18}$  cm<sup>2</sup> molecule<sup>-1</sup> at 214 nm.<sup>16</sup>

 $NO_2$  was prepared by reacting NO with a large excess of  $O_2$  in a storage bulb at room temperature and allowing sufficient time (>12 h) for conversion. Cl<sub>2</sub> and NO were used as received without additional purification. He and N<sub>2</sub> were passed through molecular sieve traps at 77 and 195 K, respectively.

To reduce the photolysis of  $NO_2$  relative to  $Cl_2$  and thus minimize any possible complications due to the  $NO_3 + NO$  reaction, two different photolysis light filters were used in the filter jacket of the reaction cell. For temperatures above 290 K, an equilibrium mixture consisting of 110 torr of Br<sub>2</sub>, 174 torr of BrCl, and 35 torr of Cl<sub>2</sub> was employed. Because Br<sub>2</sub> condensation can occur at lower temperatures, a liquid filter consisting of a  $10^{-4}$ M solution of Coumarin 485 dissolved in methanol was used below 290 K. As indicated in Figure 1, both filters have absorption spectra similar to that of  $NO_2$  and absorb a significant fraction of the photolysis energy above 350 nm where the  $NO_2$  cross section is increasing and the  $Cl_2$  cross section is decreasing. The use of these filters reduced the NO<sub>2</sub> photolysis relative to Cl<sub>2</sub> photolysis by a factor of 10. The NO<sub>2</sub> photolysis was measured both with and without these filters and found to be 0.1% and 2% per flash, respectively. A slight enhancement in NO<sub>3</sub> loss due to the NO + NO<sub>3</sub> reaction was observed when the filters were not used.

The lower and upper temperature limits over which this study could be performed were determined by the dimerization of NO<sub>2</sub> and the thermal decomposition of N<sub>2</sub>O<sub>5</sub>, respectively. The lowest temperature used, 236 K, was determined by using the criterion that less than 10% of the NO<sub>2</sub> should be dimerized at the highest concentration used.<sup>17</sup> The criterion applied at the highest temperature, 358 K, was that the first-order rate constant for the thermal decomposition of the nascent N<sub>2</sub>O<sub>5</sub> should be less than 10% of the first-order rate constant for NO<sub>3</sub> disappearance,  $k_1$ -[NO<sub>2</sub>], at the lowest NO<sub>2</sub> concentration employed. These criteria were fairly conservative and ensured that first-order conditions for NO<sub>3</sub> loss were rigorously adhered to over the allowed temperature range. Corrections were not made for either of these effects, although experiments performed at temperatures significantly higher than 358 K did result in curved decay plots.

#### **Results and Discussion**

The reaction between NO<sub>3</sub> and NO<sub>2</sub> was studied as a function of total pressure (20-700 torr), diluent gas ( $M = He, N_2$ ), and temperature (236-358 K). Plots of ln (NO<sub>3</sub> absorbance) vs. time were linear over 3-4 1/e times over the entire range of experimental conditions (Figure 2). The slopes of these plots are the

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TABLE I:	<b>Rate Constants</b>	for the	Reaction	$NO_1 +$	NO <sub>1</sub> H	- M →	$N_2O_5 +$	M
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		1	$0^{13}k_1$ , cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-</sup>	1		
press., torr	236 K	267 K	298 K	343 K	358 K	
		М	$I = N_2$			
20	$7.04 \pm 0.4$	$6.08 \pm 0.4$	$4.26 \pm 0.4$	$2.46 \pm 0.2$	$2.34 \pm 0.2$	
35			$5.59 \pm 0.4$			
60	$10.0 \pm 0.4$	$8.81 \pm 0.5$	6.61 ± 0.6	$4.38 \pm 0.8$	$4.21 \pm 0.3$	
100			$8.30 \pm 0.6$			
150	$12.2 \pm 0.6$	$11.9 \pm 0.7$	$9.21 \pm 0.7$	5.92 ± 0.6	$5.79 \pm 0.4$	
225			$10.1 \pm 0.7$			
350		$13.6 \pm 0.9$	$10.3 \pm 0.9$	$8.63 \pm 0.6$	$8.31 \pm 0.9$	
500		$13.6 \pm 0.7$				
700			$11.4 \pm 0.9$	$10.4 \pm 0.9$	$9.64 \pm 0.8$	
		М	[ = He			
20	$6.05 \pm 0.3$	$5.25 \pm 0.3$	$2.74 \pm 0.3$		$2.04 \pm 0.3$	
50	$7.91 \pm 0.4$	$7.62 \pm 0.5$	$5.23 \pm 0.5$		$3.20 \pm 0.4$	
150	$10.3 \pm 0.5$	$9.90 \pm 0.5$	$6.99 \pm 0.5$		$4.53 \pm 0.3$	
350	$13.2 \pm 0.7$	$12.1 \pm 0.7$	$8.80 \pm 0.7$		$6.38 \pm 0.4$	
600	$13.1 \pm 0.9$	$14.0 \pm 0.8$				
700		$13.5 \pm 0.8$	$10.3 \pm 0.8$		$8.59 \pm 0.5$	

<sup>*a*</sup> Quoted uncertainties are  $1\sigma$ .



**Figure 2.** First-order decay of NO<sub>3</sub> in the presence of excess NO<sub>2</sub>. Reactant concentrations were (in molecules cm<sup>-3</sup>) [NO<sub>2</sub>] =  $1.15 \times 10^{15}$ , [NO<sub>3</sub>]<sub>0</sub> ~  $1.3 \times 10^{13}$ , [Cl<sub>2</sub>] =  $1.4 \times 10^{16}$ , [ClONO<sub>2</sub>] =  $1.1 \times 10^{15}$ ;  $p_{N_2}$  = 20.6 torr, T = 298 K. The observed first-order rate constant was 488 s<sup>-1</sup>.

pseudo-first-order rate constants, k'. No residual absorption was observed after the reaction was completed, consistent with the negligible absorbance of N<sub>2</sub>O<sub>5</sub> at 661.8 nm.

Bimolecular rate constants for reaction 1 were obtained from plots of k' vs. [NO<sub>2</sub>] at constant temperature and total number density. These plots were linear with negligibly small y intercepts (Figure 3) over a tenfold range in [NO<sub>2</sub>]. The observed rate constants are listed in Table I and show a significant pressure dependence. As expected from studies on the unimolecular decomposition of N<sub>2</sub>O<sub>5</sub>,<sup>18-22</sup> reaction 1 is in the falloff region in the



Figure 3.  $k' vs. [NO_2]$  for the reaction  $NO_2 + NO_3 + N_2 \rightarrow N_2O_5 + N_2$  as a function of total pressure between 20 and 700 torr at 358 K.

20–700 torr pressure range with collision efficiencies increasing in the order He <  $N_{\rm 2}.$ 

*Falloff Parameters*. Troe and co-workers have shown that the rate constant falloff curves of addition reactions can be described by the expression

$$k([\mathbf{M}],T) = \frac{k_0[\mathbf{M}]}{1 + k_0[\mathbf{M}]/k_{\infty}} F_c^{[1+[(1/N) \log (k_0[\mathbf{M}]/k_{\infty})]^2]^{-1}}$$
(I)

where  $k_0(T) = k_0^{300}(T/300)^{-n}$ , the low-pressure limiting rate constant;  $k_{\infty}(T) = k_{\infty}^{300}(T/300)^{-m}$ , the high-pressure limiting rate constant, and  $N = 0.75 - 1.27 \log F_c$ . This expression incorporates both the pressure and temperature dependence of k and provides

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TABLE II: Falloff Parameters for the Reaction  $NO_2 + NO_3 + M \rightarrow N_2O_5 + M^a$ 

ref	F <sub>c</sub>	$10^{30}k_0^{300}$ , cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup>		$10^{12}k_{-}^{300}$		
		M = He	$M = N_2$	cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	n	m
this work	ref 8	$2.7 \pm 0.6$	$4.5 \pm 1.1$	$1.65 \pm 0.15$	$3.4 \pm 1.3$	$0.4 \pm 0.5$
this work	0.60	$1.2 \pm 0.4$	$2.0 \pm 0.5$	$1.40 \pm 0.14$	$4.3 \pm 1.3$	$0.5 \pm 0.5$
7	0.60		$2.2 \pm 1.1$	$1.0 \pm 0.8$	$2.8 \pm 1.0$	$0 \pm 1.0$
8	ref 8		3.7	1.6	4.1	0.2

<sup>*a*</sup> Quoted uncertainties are  $1\sigma$ .

a useful format for reporting kinetic data obtained in the falloff regime. It is also particularly useful for atmospheric modeling studies where rate constants must be calculated as a function of altitude.

Equation I contains five parameters:  $k_0^{300}$ ,  $k_\infty^{300}$ , n, m, and  $F_c$ . The curve-fitting method used to determine these parameters has been described in detail previously.<sup>23–25</sup> In order to limit the number of independent parameters, values of  $k_0^{300}$ ,  $k_\infty^{300}$ , n, and m were determined by using two different functions for the broadening factor at the center of the falloff curve,  $F_c$ . For the first, we used the theoretical values calculated by Malko and Troe.<sup>9</sup> These were obtained from the empirical function

$$F_{c} = 0.565 - 0.000697T$$

where T is the temperature in kelvin. This is a more exact expression than the biexponential function

$$F_c = \exp(-T/250) + \exp(-1050/T)$$

used by Malko and Troe over the temperature range 236-358 K where  $F_c$  varied from about 0.4 to 0.3. In the second case, a temperature-independent value for  $F_c$  of 0.6 was used to be consistent with the parameters employed in the NASA rate constant evaluation.<sup>8</sup> The results are indicated in Table II. (See also Figure 4.) Since the 20-700-torr pressure regime is close to the high-pressure limit, parameters relating to  $k_{\infty}$  are much more accurately determined than those relating to  $k_0$ . As a result,  $k_{\infty}^{300}$  is fairly insensitive to the function defining  $F_{\rm c}$ , lying in the range  $(1.4-1.6) \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> over wide variations in the broadening parameter.  $k_0^{300}$ , however, is quite sensitive to  $F_c$ , varying by more than a factor of 2 between the two cases. Similarly, the best fit for m, the temperature dependence of  $k_{\infty}$ , is insensitive to  $F_{\rm c}$  and varies between 0.4 and 0.5 while the corresponding parameter for  $k_0$  changes significantly, between 3.4 and 4.3. Since the variable  $F_c$  method is the more realistic of the two, the parameters derived from this case are preferred over the ones determined by using the fixed value of  $F_c$ .

As indicated in Table II, there are two recent evaluations of the falloff parameters for reaction  $1.^{8,9}$  Both evaluations are based primarily on the N<sub>2</sub>O<sub>5</sub> thermal decomposition data of Connell and Johnston,<sup>21</sup> and Viggiano et al.;<sup>22</sup> however, the NASA review<sup>8</sup> uses a fixed  $F_c$  of 0.6 while Malko and Troe<sup>9</sup> estimated  $F_c$  by using the method of Troe and co-workers.<sup>26,27</sup> In the high-pressure limiting region where our data are the most applicable, the best agreement is with the recommendation of Malko and Troe who obtain  $1.6 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for  $k_c$ .<sup>300</sup>. The value of (1.0  $\pm 0.8) \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> from the NASA review<sup>8</sup> is somewhat lower than our data indicate, although the uncertainty on their estimate encompasses the experimental value. For the low-pressure limit,  $k_0$ .<sup>300</sup> (M = N<sub>2</sub>), both evaluations are in excellent agreement with our work when common  $F_c$  functions are used. To accurately establish the low-pressure limit, however, experimental data below 10 torr must be obtained.

In the only other study of reaction 1 which monitored NO<sub>3</sub> directly, Fowles et al.<sup>10</sup> measured  $k_1$  between 80 and 160 torr of O<sub>2</sub> at 298 K. A steady-state flow of NO<sub>2</sub> and O<sub>3</sub> was used to generate NO<sub>3</sub> which was monitored by absorption at 662 nm



Figure 4. Temperature and pressure dependence of the rate constant for the  $NO_2 + NO_3 + N_2$  reaction. Dotted points (•) are curve fits to the data using the falloff equation (eq 1) and the parameters in Table II.

giving an average NO<sub>3</sub> concentration for the integrated column down the length of the flow tube. A computer model was used to fit the observed dependence of this  $[NO_3]_{av}$  on  $[NO_2]$  by using  $k_1$  as a variable parameter. At the higher NO<sub>2</sub> concentrations used, the thermal decomposition of  $N_2O_5$  (regenerating  $NO_3$ ) could not be neglected, requiring that  $k_{-1}$  also be treated as an experimental parameter. In their study, a value of  $(2.0 \pm 0.8)$ × 10<sup>-12</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> was obtained for  $k_1[M]$  at [M] = 2.7 $\times 10^{18}$  molecules cm<sup>-3</sup>. This can be compared with a value of  $7.0 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> obtained in this study by using eq 1 to interpolate to the same conditions, and the parameters in Table II for  $M = N_2$ . At these pressures, the reaction is so close to the high-pressure limit that there is virtually no M effect between O2 and  $N_2$ , contrary to the suggestion of Fowles et al. The value for  $k_{-1}$  obtained by Fowles et al. is also about a factor of 3 higher than the recommendation of Malko and Troe.<sup>9</sup> Thus, the ratio  $k_1/k_{-1}$  obtained by Fowles et al. is consistent with previous estimations of the equilibrium constant, but the large discrepancies in the measured values of  $k_1$  and  $k_{-1}$  suggest a possible systematic error in the Fowles et al. work.

Thermodynamics of  $NO_3$ . The rate constant data obtained in this study may be combined with data on the thermal decomposition of  $N_2O_5$  to obtain the equilibrium constant for the reaction pair

$$NO_2 + NO_3 + M \rightleftharpoons N_2O_5 + M$$

as well as the standard entropy and enthalpy of formation of NO<sub>3</sub>. Studies of  $N_2O_5$  decomposition have been carried out for many years, with the earlier data being summarized by Baulch et al.<sup>28</sup> Recently, two additional studies have been reported which use

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<sup>(27)</sup> R. G. Gilbert, K. Luther, and J. Troe, Ber. Bunsenges. Phys. Chem., 87, 169 (1983).

<sup>(28)</sup> D. L. Baulch, D. D. Drysdale, and D. G. Horne, "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the  $H_2$ - $N_2$ - $O_2$  System", Butterworths, London, 1973.



Figure 5. Plot of  $\ln (K_{eq}, \operatorname{atm}^{-1})$  vs. 1/T for the equilibrium NO<sub>2</sub> + NO<sub>3</sub> + M  $\rightleftharpoons$  N<sub>2</sub>O<sub>5</sub> + M. Kinetic data for  $k_{-1}$  were obtained from the data of Viggiano et al. (•) and from Connell and Johnston ((+) plotted for each temperature with slight variations in 1/T for clarity). The corresponding values of  $k_1$  were calculated from eq 1. The central line is the best-fit least-squares line to all the data with the y intercept constrained by the literature  $\Delta S_0$  for the reaction. The upper and lower lines represent the  $2\sigma$  limits of the slope (with the constrained  $\Delta S_0$ ).

more sensitive detection methods for N2O5 and are therefore less likely to be affected by secondary chemistry due to the lower N2O5 concentrations employed. Connell and Johnston<sup>21</sup> observed the thermal decomposition of  $N_2O_5$  in a static cell by long-path infrared absorption over the pressure range  $4 \times 10^{14}$ – $2.8 \times 10^{19}$ molecules cm<sup>-3</sup> between 262 and 307 K. Viggiano et al.<sup>22</sup> observed the decomposition of  $N_2O_5$  in slowly flowing  $N_2O_5$ -NO- $N_2$ mixtures by using a chemical ionization technique to ionize  $N_2O_5$ prior to mass-spectrometric detection. This study was carried out between 10 and 800 torr, over the temperature range 285-384 K. The results of these studies have been summarized and evaluated by Malko and Troe,<sup>9</sup> who note that the agreement between the experimental falloff curves over the range of temperature overlap is good but that discrepancies exist between the extrapolated low- and high-pressure limits. Nevertheless, these are probably the most reliable data on N<sub>2</sub>O<sub>5</sub> thermal decomposition in the temperature range near 300 K.

The enthalpy of reaction was obtained by determining the slope of a plot of ln K vs. 1/T. Values of  $K(T) = k_1/k_{-1}$  were obtained by ratioing the individual measurements of  $k_{-1}$  from Viggiano et al. and Connell and Johnston, and the corresponding values of  $k_1$  calculated by using eq I with the parameters in Table II. This plot is shown in Figure 5 and indicates that there is excellent consistency between the two thermal decomposition studies over their range of temperature overlap (286-308 K). The points lie on a reasonably straight line although consideration of the Viggiano et al. data alone suggests a slight upward curvature. When combined with the Connell and Johnston data which have somewhat larger scatter, the nonlinearity becomes insignificant. The standard enthalpy  $(\Delta H_0)$  and entropy  $(\Delta S_0)$  changes of reaction 1 at 298 K can be obtained from the slope and y intercept of the best-fit line in Figure 5. Because the extrapolation to obtain the y intercept is very long, and the standard entropies of  $NO_2$ ,



**Figure 6.** Altitude dependence of  $k_1$  using falloff parameter recommendations from the NASA (---, ref 7) and CODATA (---, ref 30) reviews, and this work (--) evaluated by using the standard midlatitude temperature and pressure profiles.

NO<sub>3</sub>, and N<sub>2</sub>O<sub>5</sub> are known with reasonable accuracy, the entropy change determined from our kinetic data, -36.3 eu, is less reliable than the value determined from tabulated quantities,<sup>29</sup>  $\Delta S_0 =$  $-34.9 \pm 1.4$  eu. Therefore, the slope was obtained from linear least-squares analysis by fixing the y intercept at the literature value of  $\Delta S_0/R$ . The 1 $\sigma$  uncertainty of the slope was found from the lines which encompassed about 63% of the points in Figure 5 when the y intercepts were varied by the 1 $\sigma$  limits of  $\Delta S_0/R$ . The value of  $\Delta H_0$  thus obtained is  $-22.5 \pm 0.6$  kcal mol<sup>-1</sup>. Combining this with tabulated standard heats of formation at 298 K for NO<sub>2</sub> and N<sub>2</sub>O<sub>5</sub><sup>29</sup> leads to a value of 17.3  $\pm$  0.7 kcal mol<sup>-1</sup> for  $\Delta H_f^{\circ}(298)$  of NO<sub>3</sub>. This is almost identical with the currently accepted value,<sup>29</sup> 17.0  $\pm$  5 kcal mol<sup>-1</sup>; however, the uncertainty in the current measurement is almost 1 order of magnitude smaller.

The equilibrium constant determined in this study can be compared with that measured by Graham and Johnston using molecular modulation.<sup>30</sup> Our expression, based on the tabulated value of  $\Delta S_0^{\circ}$  is

$$K = 2.31 \times 10^{-8} \exp(11350/T) \operatorname{atm}^{-1}$$

and results in values of K which are about 20% higher than those obtained by Graham and Johnston

$$K = \frac{8.8 \times 10^{-6}}{T} \exp(11180/T) \text{ atm}^{-1}$$

in the temperature range near 300 K.

Atmospheric Implications. The expression for  $k_1([N_2],T)$  obtained in this study may be compared with the evaluations presented in the recent NASA<sup>8</sup> and CODATA<sup>31</sup> reviews of kinetic data for atmospheric chemistry. Both these evaluations are based on N<sub>2</sub>O<sub>5</sub> thermal decomposition data coupled with estimates of the equilibrium constant. Figure 6 shows a plot of  $k_1$  vs. altitude using a typical atmospheric pressure and temperature profile. Excellent agreement between the results from this work and the CODATA recommendation are observed with the NASA recommendation being about 30–40% lower over the altitude range 0–45 km. This stems from the use of a lower value of  $k_{\infty}^{300}$  in the NASA review,  $1.0 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, than that obtained in this study.

The reported discrepancy in the atmospheric lifetime of NO<sub>3</sub> cannot be explained by uncertainties in  $k_1$  or the equilibrium constant for reaction 1 and must result from additional reactions of NO<sub>3</sub> or N<sub>2</sub>O<sub>5</sub>, although the observational data seem to suggest that it must be NO<sub>3</sub> that is scavenged.<sup>2</sup> The significance of these reactions for atmospheric chemistry rests not only on their rates

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<sup>(30)</sup> R. A. Graham and H. S. Johnston, J. Phys. Chem., 82, 254 (1978).
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but on the extent to which they result in a permanent sink for  $NO_x$ . Such mechanistic information can be obtained only from direct studies of the disappearance rates of  $NO_3$  (and  $N_2O_5$ ) and a characterization of reaction products.

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# Specific Rate Constants k(E,J) for the Unimolecular Dissociations of H<sub>2</sub>CO and D<sub>2</sub>CO

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Statistical calculations of J- and E-dependent specific rate constants k(E,J) for the unimolecular complex eliminations H<sub>2</sub>CO  $\rightarrow$  H<sub>2</sub> + CO and D<sub>2</sub>CO  $\rightarrow$  D<sub>2</sub> + CO and the unimolecular simple bond fissions H<sub>2</sub>CO  $\rightarrow$  H + HCO and D<sub>2</sub>CO  $\rightarrow$  D + DCO are presented. RRKM type calculations including the K rotor with proper constraints were applied to the elimination reactions, whereas a simplified statistical adiabatic channel calculation was applied to the bond fission reactions. The J dependences of the specific rate constants are demonstrated in detail. The calculations show "channel switching" for rotationally hot molecules. Representations for k(E,J), including tunneling contributions, are given.

### Introduction

In the dissociation of formaldehyde in its electronic ground state two basically different reaction channels with very close threshold energies compete, the molecular elimination reaction leading to molecular products

$$H_2CO \rightarrow H_2 + CO$$
 (1)

and the simple bond fission reaction leading to radical products

$$H_2CO \rightarrow H + HCO$$
 (2)

The two-channel character of the dissociation has been recognized in thermal dissociation experiments only recently.<sup>1</sup> Earlier results<sup>2</sup> were attributed to a single channel only.

Detailed experiments on the photochemistry of formaldehyde more clearly show the competition between two channels in the threshold range. These experiments as well as highly resolved measurements of fluorescence lifetimes (for an excellent review of the extensive literature on formaldehyde photochemistry see ref 3) have attracted much interest, in particular in the framework of the theory of radiationless transitions. These experiments indicate that photochemical decomposition near the threshold most probably proceeds by a sequential mechanism

$$S_1 \rightarrow S_0^* \rightarrow H_2 + CO$$
 (3a)

In order to clarify whether  $S_1 \rightarrow S_0^*$  or  $S_0^* \rightarrow$  products are the "rate-determining processes", the theory of nonradiative processes was applied<sup>3</sup> to the coupling of single vibronic states in  $S_1$  and the "lumpy continuum" of  $S_0^*$ . Furthermore, the dynamics of unimolecular dissociation of  $S_0^*$  was investigated in a series of model calculations: the S<sub>0</sub> potential energy surface was calculated ab initio;<sup>4</sup> anharmonic vibrational densities of states were de-

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termined;<sup>5</sup> the effect of tunneling was studied in detail;<sup>6,7</sup> for J= 0 mode-selective dissociation was postulated;<sup>8,9</sup> classical trajectory calculations were performed in ref 10.

There have been several RRKM type statistical calculations of the specific rate constants for the molecular elimination channel (eq 1) of the dissociation (see ref 6 and other work cited in ref 3). The simple bond fission channel (eq 2), however, has received much less attention. So far, these calculations do not appear to provide a sufficiently detailed basis for application to thermal and photochemical dissociation experiments. In both cases, the Jdependence of the rate constants is of crucial importance and has to be accounted for explicitly. For the molecular elimination channel, the contributions of the K rotor (in symmetrical top representation) to the rovibrational density of states  $\rho(E,J)$ , as well as to the rovibrational number of activated complex states W(E,J), have to be implemented into a RRKM calculation together with the J dependence of the threshold energy. To our knowledge no explicit calculations of this type for the specific rate constant

$$k(E,J) = \frac{W(E,J)}{h\rho(E,J)}$$
(4)

have been published so far, except for J = 0. The treatment of the J dependence of the specific rate constants k(E,J) for the simple bond fission is much more difficult since complicated angular momentum coupling restrictions have to be accounted for. Based on the detailed statistical adiabatic channel model,<sup>11</sup> we have recently formulated a simplified adiabatic channel model<sup>12,13</sup> which allows for a convenient handling of the angular momentum problem. This model includes all elements of loose phase space theory, but in addition it does not neglect the important angular parts of the interaction potential between the

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