J. Phys. Chem. **1993,** 97, 9141-9148 **9141**

Measurement of Rate Coefficients for the Unimolecular Decomposition of N_2O_5

Christopher A. Cantrell,[*] Richard E. Shetter, Jack G. Calvert, Geoffrey S. Tyndall, and John J. Orlando

Atmospheric Kinetics and Photochemistry Group, Atmospheric Chemistry Division, National Center for Atmospheric Research,[†] P.O. Box 3000, Boulder, Colorado 80307-3000

Received: April 14, 1993; In Final Form: June 21, 1993[⊗]

The kinetics of the decomposition of dinitrogen pentoxide (N_2O_5) in the presence of excess nitric oxide (NO) in a bath of nitrogen was studied as a function of temperature and pressure using Fourier transform infrared spectroscopy to monitor the N_2O_5 concentration. The available data encompassing temperatures from 253 to 384 K and third-body concentrations from 4.3×10^{14} to 1.1×10^{20} molecule^{-3} have been analyzed, although rate coefficients over the entire range of pressures have not been measured at all temperatures. The following recommendations are made to fit parameters to the Troe expression for $k(N_2O_5 + M)$: $k_{0,2} = 1.04 \times 10^{-3}(T/300)^{-3.5} \exp(-11000/T)$ cm^3 molecule^{-1} s^{-1}, $k_{\infty,2} = 6.22 \times 10^{14}(T/300)^{-0.2} \exp(-11000/T)$s^{-1}, $F_c = 2.5 \exp(-1950/T) + 0.9 \exp(-T/430)$. These parameters, when combined with data for $k(NO_2 + NO_3 + M)$, yield N_2O_5 equilibrium constant values ($k(N_2O_5 + M)/k(NO_2 + NO_3 + M)$) systematically higher than recent evaluations of direct measurements by 19–37% but closer to earlier measurements. With these new recommendations, calculated atmospheric decomposition lifetimes for N_2O_5 are decreased slightly ($\sim$15% to 20%), compared to current ones, at ground level and in the upper stratosphere.

Introduction

The odd nitrogen chemistry of the atmosphere has been extensively studied though laboratory and field measurements. The exchange between and interaction among the members of this family (NO, NO_2, NO_3, and N_2O_5) constitute an important group of reactions which are, directly or indirectly, responsible for ozone generation and destruction, the formation of nitric acid, creation of organic nitrate compounds, and other significant effects. The NO_2 and NO_3 radical species associate to form the odd nitrogen reservoir, N_2O_5:

$$NO_2 + NO_3 \xrightarrow{M} N_2O_5 \qquad (1)$$

This reaction has been studied several times in the laboratory over a range of N_2, O_2 and He pressures and temperatures.[1-6] N_2O_5 decomposes thermally to reform NO_2 and NO_3:

$$N_2O_5 \xrightarrow{M} NO_2 + NO_3 \qquad (2)$$

This reaction has also been studied in the laboratory,[7-13] and these studies have been evaluated and reviewed.[14,15] There remains some question as to the best rate coefficients for this reaction (see e.g., Johnston *et al.*[15]), although the mechanism and approximate values for the rate coefficients have been known for more than 40 years. The rate of this reaction is slow for many conditions encountered in the troposphere, with lifetimes toward thermal decomposition ($1/k_2(T,M)$) of N_2O_5 ranging from about 20 s at 298 K and 1 atm pressure (earth's surface), to 7 h at 250 K and 380 Torr pressure (middle troposphere), to 1.2 years at 215 K and 90 Torr pressure (tropopause). Atmospheric lifetimes toward thermal decomposition could be longer because N_2O_5 can be reformed through reaction 1. In any case, photolytic or heterogeneous processes certainly could control the N_2O_5 lifetime for the conditions of low temperature and pressure found in the lower stratosphere and upper troposphere. It is still important, however, that accurate data be available for reaction 2 over a range of conditions, in order to check for consistency between the kinetics of reactions 1 and 2 and the value for the equilibrium constant for the N_2O_5 chemical system (k_2/k_1), as well as to understand the diurnal cycles of NO_2, NO_3, and N_2O_5 for warmer lower tropospheric and upper stratospheric conditions. We discussed earlier[16] that some inconsistencies apparently exist between the available kinetic and equilibrium constant data for the N_2O_5 system. Since then, new evaluations of the equilibrium constant ($K_{1,2}$) have been reported.[17-19] Here, we present new measurements of the rate coefficient for reaction 2 and evaluate the degree of agreement between various features of the N_2O_5 equilibrium system (k_1, k_2, and $K_{1,2}$).

Experimental Procedures

Conditions and Considerations for This Study. All of the experiments reported here were performed in a 48-L stainless steel cell equipped with multiple pass optics that have been described previously.[16,20] The optics were adjusted to yield a 48.6-m optical path. The infrared spectra were collected with a BOMEM DA3.01 Fourier transform spectrometer system configured with a KBr beam splitter, SiC heated rod source, and HgCdTe narrow-band (750–5000 cm^{-1}) infrared detector cooled with liquid nitrogen. The infrared beam entered the cell through BaF_2 windows employing an evacuable optical path to and from the spectrometer. The cell mirrors and transfer optics were constructed of aluminum-coated quartz with a SiO protective layer. Temperature control of the cell was achieved through circulation of either water or ethanol through a jacket around the cell. The cell and jacket were surrounded by an evacuable Dewar. The temperature control was sufficient that maximum variations throughout the cell were much less than ±0.5 °C, typically of order ±0.1 °C. Dinitrogen pentoxide and other gases were added to the cell through a glass vacuum system. Calibrated volumes and capacitance manometer pressure transducers (MKS Baratron) allowed accurate addition of known amounts of the gases under study. N_2O_5 was synthesized by the method of Davidson *et al.*[21] and modified as described by Cantrell *et al.*,[22] which involves the exhaustive oxidation of NO by O_3, and then it was stored at 196 K. The level of NO_2 decomposition product in the N_2O_5 was negligible. Nitric oxide (Linde, 98.5%) was used as received. The nitric oxide contained a nitrogen dioxide contamination of approximately 1%, but this did not affect the kinetic determinations because the rate of loss of N_2O_5 was monitored in an excess of NO.

[†] The National Center for Atmospheric Research is funded by the National Science Foundation.

[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1993.

0022-3654/93/2097-9141$04.00/0

A typical experiment involved the addition of a known pressure of N_2O_5 to one of the calibrated volumes and addition of a known pressure of NO to another volume. The gases were swept into the cell simultaneously. The amounts of the two gases were selected such that the initial $[NO]/[N_2O_5]$ ratio in the cell was greater than 20, with typical cell concentrations of about 4×10^{14} and 2×10^{13} molecules cm^{-3} for NO and N_2O_5, respectively. Nitrogen from liquid boil-off was used as the bath gas. The amount added was such that nitrogen was in excess of the other gas components (N_2O_5, NO_2, NO, and NO_3) by factors of 26 at low total pressures to greater than 1000 at the highest pressures studied. This minimized possible errors introduced by corrections necessary for the enhanced collision efficiencies of NO_2, NO, and N_2O_5 compared to N_2.[9,10] The enhancement amounted to 5–9% at the very lowest cell pressures (0.3–0.4 Torr), 0.6–2% at slightly higher pressures (0.5–1.5 Torr), and less than 0.5% at higher pressures. These corrections were applied to the cell pressures reported in this study; an effective N_2 concentration was calculated by adding the actual nitrogen concentration and the equivalent contribution of the other gases. Infrared spectra were collected by averaging 1–200 interferometer scans, amounts which were determined by the constraints on the time necessary to collect one interferogram and the rate of decay of the N_2O_5. Typically, 10 infrared spectra with resolution of 5 cm^{-1} were collected over approximately two N_2O_5 lifetimes. We performed experiments at cell temperatures varying from 253 to 323 K and cell pressures from about 0.3 to 3000 Torr, attempting to overlap the conditions of other recent studies[12,13] as much as possible. The infrared band of N_2O_5 near 1250 cm^{-1} was integrated and converted to concentration with band intensities measured in this laboratory.[23] However, because the decomposition of N_2O_5 is a first-order reaction ($d(\ln[N_2O_5])/dt$ = constant) for a given set of conditions, the final rate coefficients are independent of the choice of absorption cross section. We also performed integrations of the infrared band of NO_2 near 1600 cm^{-1}. These integrated areas were converted to cell concentrations through band strengths measured in our laboratory.

The amounts of N_2O_5 reacted and NO_2 produced agreed, to well within experimental uncertainty (±5%), with the overall stoichiometry proposed by Smith and Daniels (1947)[24] and confirmed by others:

$$N_2O_5 + NO = 3NO_2 \tag{3}$$

This arises from reaction 2 followed by reaction 4:

$$NO_3 + NO \rightarrow 2NO_2 \tag{4}$$

The rate equation for this mechanism (reactions 1, 2, and 4) is

$$-\frac{d[N_2O_5]}{dt} = k_2[N_2O_5]\left[\frac{k_4[NO]}{k_4[NO] + k_1[NO_2]}\right] \tag{a}$$

If $k_4[NO]$ is much greater than $k_1[NO_2]$, then the rate expression reduces to

$$-\frac{d[N_2O_5]}{dt} = k_2[N_2O_5] \tag{b}$$

Since k_4 is more than a factor of 10 larger than k_1, [NO] need only be larger than or equal to $[NO_2]$ for eq b to hold with reasonable accuracy. All rate coefficients measured here had errors of less than 2% (usually much less) due to the contribution of reaction 1. These small corrections were not made to the data. The unimolecular decomposition of NO_3[15,25] does not affect the measurement because the NO_3 lifetime is already so short ($\tau <$ 0.1 ms) due to reaction 4. This would, in any case, make the approximation indicated in relation b even better.

Treatment of the Data from This Study and Others. Sample N_2O_5 decays from this study near room temperature (292.8–293.9 K) are shown in Figure 1. The points represent individual relative N_2O_5 determinations, and the lines are the linear least-squares fit of the logarithm of the relative N_2O_5 concentration versus reaction time. Nonlinear exponential fits were tested for a few cases and were found to yield identical values for the first-order rate coefficients. The reaction time associated with each spectrum was taken as the elapsed time from the beginning of the experiment to the halfway point of the collection period. The rate coefficients (corrected for heterogeneous loss, discussed below) are given in Table I, and plotted in Figure 2, along with the recommended fit.

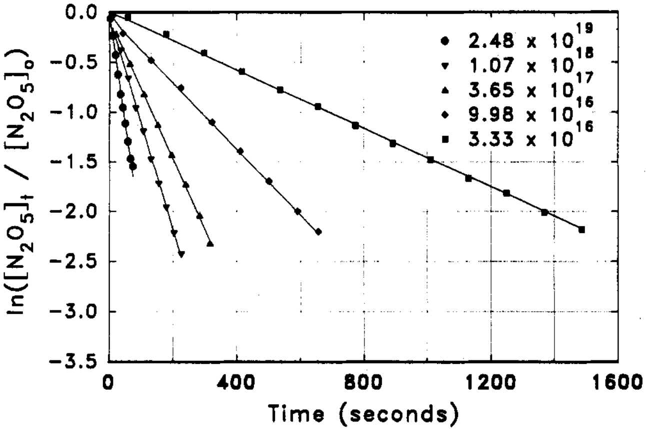

Figure 1. Sample decays of N_2O_5, plotted as the logarithm of the relative concentration versus reaction time for cell temperatures near 293 K, and $[N_2]$ (molecule cm^{-3}) as shown.

The decay of N_2O_5 was presumed to be dominated by gas-phase and heterogeneous losses. The gas-phase rate coefficients for reaction 2 were assumed to follow the Troe expression,[26–31] a semiempirical relationship between the rate coefficient at any temperature and third-body concentration using four fit parameters and a broadening factor at the center of the fall-off curve, F_c. A heterogeneous wall loss coefficient (k_5) was also added.

$$k_{meas}(T,M) = \left[\frac{k_{0,2}(T)[M]}{1 + k_{0,2}(T)[M]/k_{\infty,2}(T)}\right]F_c^{\,z} + k_5 \tag{c}$$

where z is defined as

$$z = \left(1 + \left[\frac{\log(k_{0,2}(T)[M]/k_{\infty,2}(T))}{N}\right]^2\right)^{-1}$$

where $N = 0.75 - 1.27 \log_{10} F_c$. Here, $k_{meas}(T,M)$ is the measured rate coefficient; $k_{0,2}(T)$ and $k_{\infty,2}(T)$ represent the fitted low-pressure- and high-pressure-limiting rate coefficients, which are functions of temperature and are represented in the form $k = A(T/300)^n \exp(B/T)$; [M] is the concentration of the third-body gas, expressed in terms of equivalent $[N_2]$ in this case; and T is the absolute temperature. The temperature exponents, n, were taken from measurements of reaction 1.[6] The broadening factor, $F_c^{\,z}$, is the strong collision factor introduced by Troe[28] to account for broadening caused by the energy-dependent $k(E)$ determined by fitting the results of RRKM calculations. The wall loss term is not part of the original Troe formulation but has been included here to take into account its possible occurrence in the various studies of reaction 2. The wall loss could have been determined by low-temperature measurements of the rate of decay of N_2O_5 in the absence of NO, but this was not done in the present study. It should be pointed out that the number of fit parameters is effectively larger than the six mentioned above, because the empirical functions for F_c and N implicitly include factors derived from the fitting of experimental data (e.g., the 0.75 and 1.27 in the expression for N). As with all fitting procedures, the results of the final expressions should be used with caution outside the range of the observations.

The rate coefficients were fit to the Troe expression, using a nonlinear weighted least-squares program based on the Simplex algorithm,[32] which iteratively minimizes relative root mean square deviations of the data from the fitted surface. The weights in the

TABLE I: Summary of Data from This Study for Reaction 2

temp (K)	k_2[a]	[M][b]	95%[c]
253.1	0.000 086	3.854E19[d]	1.0
253.1	0.000 062	1.149E20	1.0
263.5	0.000 174	3.715E18	1.0
263.5	0.000 289	1.108E19	1.0
263.5	0.000 333	2.771E19	0.82
263.5	0.000 384	3.753E19	1.0
263.5	0.000 592	1.068E20	0.45
263.8	0.000 218	3.700E18	0.22
263.8	0.000 429	1.096E20	0.44
264.2	0.000 398	2.770E19	0.21
272.9	0.000 461	4.193E17	1.0
272.9	0.000 677	1.052E18	0.90
272.9	0.001 03	3.570E18	0.48
272.9	0.001 45	1.056E19	0.65
272.9	0.001 67	2.701E19	0.27
272.9	0.001 81	3.609E19	0.21
272.9	0.002 27	9.714E19	0.45
273.2	0.000 166	9.560E16	0.22
273.2	0.000 416	3.200E17	0.21
273.2	0.000 742	1.050E18	0.20
273.6	0.001 02	3.780E18	0.20
274.0	0.001 79	1.050E19	0.20
283.0	0.000 48	4.850E16	0.20
283.0	0.000 835	9.730E16	0.20
283.3	0.000 157	1.300E16	1.0
283.3	0.000 485	5.125E16	1.0
283.3	0.000 771	1.055E17	1.0
283.3	0.001 60	3.520E17	0.28
283.3	0.003 21	1.021E18	0.23
283.3	0.005 00	3.431E18	0.31
283.3	0.004 64	1.021E19	0.24
283.3	0.006 52	2.603E19	0.31
283.3	0.007 67	3.485E19	0.24
283.3	0.007 6	9.800E19	0.23
283.3	0.005 32	1.027E20	0.46
292.8	0.001 21	2.296E16	0.42
292.8	0.001 33	3.330E16	0.20
292.8	0.001 58	3.585E16	0.43
292.8	0.002 82	9.809E16	0.46
292.8	0.025 4	3.336E19	0.20
292.8	0.026 6	1.008E20	0.23
292.9	0.010 7	1.070E18	0.20
292.9	0.022 1	2.480E19	0.21
293.9	0.001 10	2.248E16	0.73
293.9	0.001 98	4.073E16	0.43
293.9	0.002 72	9.983E16	0.38
293.9	0.006 84	3.651E17	0.20
293.9	0.011 4	9.920E17	0.20
293.9	0.017 8	3.254E18	0.20
293.9	0.022 8	1.007E19	0.20
293.9	0.027 0	2.470E19	0.21
293.9	0.028 8	2.474E19	0.20
303.0	0.082 6	2.400E19	0.20
303.0	0.086 0	3.160E19	0.21
303.9	0.002 91	1.735E16	0.20
303.9	0.009 11	9.012E16	0.20
303.9	0.019 0	3.184E17	0.20
303.9	0.037 4	1.169E18	0.20
303.9	0.053 6	3.150E18	0.20
303.9	0.073 0	9.441E18	0.20
303.9	0.102	2.470E19	0.58
312.9	0.008 02	2.459E16	0.20
312.9	0.014 0	4.980E16	0.20
312.9	0.022 7	8.817E16	0.20
312.9	0.051 6	3.683E17	0.20
312.9	0.096 4	9.386E17	0.20
312.9	0.146	3.139E18	0.29
321.8	0.056 9	9.120E16	0.20
322.0	0.122	3.130E17	0.20
322.2	0.195	1.070E18	0.21
322.5	0.011 9	1.364E16	0.20
322.5	0.020 4	2.918E16	0.20

[a] Rate coefficient units are s^{-1}. [b] N_2 concentration in molecules cm^{-3}. [c] Approximate 95% confidence interval uncertainty; the inverse was used as the weight in the fitting to the Troe expression. [d] Read 3.854E19 as 3.854×10^{19}.

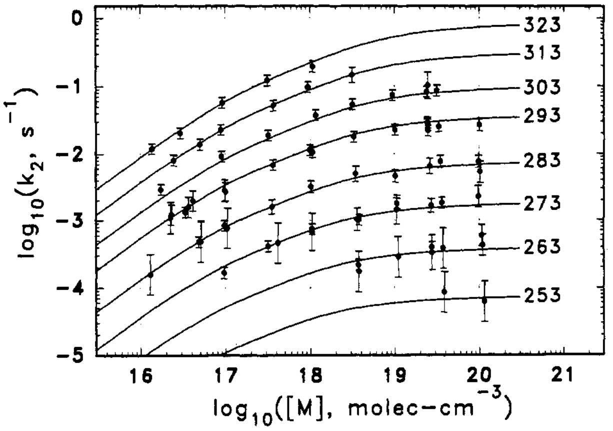

Figure 2. Falloff curves for the unimolecular decomposition of N_2O_5 from this study. Fits are from eq d.

fit were the inverse of the 95% confidence interval estimates of the relative uncertainty in the individual rate coefficient determinations, determined from the quadrature addition of the uncertainties associated with the decay fitting (variable from 1% to 100%), the heterogeneous loss (20% of the wall loss coefficient), and other possible unknown sources of uncertainty (10%). The parameters derived from this fit are presented and discussed below. Other iterative methods (for example, grid, gradient, or gradient expansion) of minimizing the deviations of the data from the fit gave results identical to those of the Simplex method (see, e.g., refs 33–35).

The n_0 and n_∞ values are temperature exponents for $k_{0,2}$ and $k_{\infty,2}$, respectively. They were constrained using those determined through analysis of k_1 data and reported by Orlando *et al.*[6] For most of the fits, values of −3.5 and −0.2 were used for n_0 and n_∞, respectively. Values of −4.3 and +0.3 were also used, which were derived from fits to data which included the high-pressure results of Croce de Cobos *et al.*[2] The B value can be constrained by measured equilibrium constant data (−11 100 ± 400 K), but it was used as a fit parameter here. On average, B was typically close to −11 000 K, varying from about −11 000 to −11 100 K, depending on the conditions of the fit. Values of F_c used in our analysis were those recommended by Malko and Troe (1982),[14] $\exp(-T/250) + \exp(-1050/T)$; Orlando *et al.* (1991),[6] $2.5\cdot\exp(-1950/T) + 0.9\exp(-T/430)$; and DeMore *et al.* (1992),[19] 0.6. Thus, a fit for a given set of conditions yielded the following parameters: A_0, A_∞, B, and k_5.

It is well-known that heterogeneous effects can cause an overestimate of the rate coefficient for reaction 2[8,12,24] due to reaction of N_2O_5 at the vessel walls:

$$N_2O_5 + \text{wall} \rightarrow \text{products} \qquad (5)$$

The heterogeneous loss in a given cell, after conditioning, can usually be adequately represented as a first-order loss which is nearly independent of temperature and pressure.[12] However that does not mean its contribution is easy to determine, because the lowest pressure studies are usually not in the second-order region (where $k \approx k_2$) and because uncertainties in F_c make the curvature in the falloff difficult to quantify. The heterogeneous wall loss assessment for the data of this study and the others was accomplished by performing fits of the various data sets to the Troe expression at various values of F_c. The average value for k_5 from these preliminary fits was subtracted from the data before further analysis. These k_5 values are reported in the discussion of the individual studies.

Corrections to the third-body concentrations are necessary if the reaction is performed in pure N_2O_5 and NO or in a bath gas other than nitrogen because of the different collision efficiencies of these species as compared to N_2,[9,10] although it appears that O_2 and N_2 have nearly equal efficiencies.[5] A linear correction ($[N_2]_{\text{effective}} = [M]_{\text{expt}}(\beta(M)/\beta(N_2))$, where $\beta(M)$ is the collision efficiency of bath gas M relative to the strong collision limit) to the collider concentrations neglects the effect of collider efficiency on the shape of the falloff curve ($F_c \propto \beta^{0.14}$, see, e.g., ref 14).

TABLE II: Summary of Regressions to N_2O_5 + M Data Using Results from This Study and Others in the Literature[i]

data[a]	k_0[b]		k_∞						
	A_0	n_0	A_∞	n_∞	B	F_c[c]	RMS difference[d]	k_0^{298}	k_∞^{298}
N, CJ, V[e]	1.04	–3.5	6.22	–0.2	–11 000	O	16.0	0.99	0.058
N, CJ, V	1.06	–4.3	6.20	+0.3	–11 000	O	16.1	1.01	0.058
N, CJ, V[f]	1.31	–3.5	6.66	–0.2	–11 040	O	17.1	1.09	0.054
N, CJ[g]	1.09	–3.5	8.09	–0.2	–11 110	D	20.1	0.72	0.052
N, CJ, V	1.52	–3.5	7.51	–0.2	–11 000	M	19.7	1.45	0.070
N, CJ, V	1.03	–3.5	7.18	–0.2	–11 040	P	17.8	0.85	0.058
N, CJ, V, JP	1.06	–3.5	7.13	–0.2	–11 030	O	23.6	0.91	0.060
N, CJ, V, JP, SD	0.957	–3.5	6.44	–0.2	–11 000	O	23.4	0.91	0.060
N, CJ, V[h]	1.14	–3.5	6.75	–0.2	–11 020	O	17.0	1.02	0.059

[a] Investigator shorthand: N, this study; CJ, Connell and Johnston;[12] V, Viggiano *et al.*;[13] SD, Schott and Davidson;[11] JP, Johnston and Perrine.[7] [b] Values in table have been multiplied by the following factors: A_0, 10^3; A_∞, 10^{-14}; k_0^{298}, 10^{19}; units for k_0 values are cm^3 molecule^{-1} s^{-1} and for k_∞ values are s^{-1}. [c] F_c values shorthand: O, Orlando *et al.*;[6] D, fixed at 0.6 as recommended by DeMore *et al.*;[19] M, Malko and Troe;[14] P, fit parameter yielded 0.50. [d] Estimates of the relative root mean square differences (1σ) between fits and the data, multiplied by 1×10^2. [e] See eq d, which is the best-fit recommendation. [f] Unweighted fit. [g] Data at temperatures less than 298 K only, so as to approximate atmospheric conditions. [h] See eq h, which is the equilibrium and kinetically consistent recommendation. [i] Using $k = A(T/300)^n \exp(B/T)$ for $k_0(T)$ and $k_\infty(T)$.

However, this effect is relatively small (a factor of 2 change in collision efficiency results in a 10% change in F_c). Of course, in a mixture of more than one gas, the contribution of each is summed to arrive at the total effective nitrogen concentration. In this paper, we have assumed a linear scaling of the third-body concentration with collision efficiency to calculate $[N_2]_{\text{effective}}$ for much of the data obtained from experiments performed either in pure reagents or bath gases other than nitrogen. These corrections, when performed, are detailed in the discussion of the appropriate studies below. Due to the fact that the data from the present study and those of Connell and Johnston[12] and Viggiano *et al.*[13] were performed in nitrogen, appropriate for atmospheric chemistry considerations, and because of the uncertainty in making collision efficiency corrections, the fits were performed primarily on these data and compared to corrected versions of data from some of the other studies.

A value of 1.1×10^{-4} s^{-1} for k_5 was subtracted from all the results of this study before subsequent analyses. The rate of reaction 5 was relatively large in this study (reported k_5 values for other studies are between about 4×10^{-4} and 2×10^{-5} s^{-1}), probably due to the stainless steel absorption cell. Cells made of glass with similar surface to volume ratios typically have much lower wall loss rates.

In the study of Viggiano *et al.*[13] (hereafter, V), the N_2O_5 decays were carried out in flow-through cells followed by detection using ion–molecule reactions in a flowing afterglow apparatus, between 285 and 384 K at eight pressures from 10 to 1000 Torr. Heterogeneous loss of N_2O_5 was small compared to gas-phase loss. V reported individual rate coefficients and also summarized the results using Arrhenius expressions at each pressure studied. Since there is no reason to expect an Arrhenius behavior to hold for a decomposition reaction in the falloff region, we fit the individual data points to the Troe expression. For the further analysis of these data, the results of this fit of the V data only were used to calculate rate coefficients at the eight pressures of their study, at the temperatures of this study where they overlap, and at 10-deg intervals at higher temperatures. This was done to facilitate visual comparison between these data and the fitted curves. The results are shown in Figure 3a.

The Connell and Johnston[12] (hereafter, CJ) study was performed under conditions of low to moderate pressure (about 0.01–760 Torr) and relatively low temperature (262–307 K). The reported rate coefficients ranged from about 4×10^{-6} to 1×10^{-2} s^{-1}. The rate coefficients were measured at six temperatures, with most of the data acquired at 268 and 295 K. The loss rate of N_2O_5 was determined by monitoring its concentration using infrared absorption spectroscopy at 1245 cm^{-1}. Connell and Johnston subtracted 2×10^{-5} s^{-1} from their data before their analysis. Clearly, if too large a heterogeneous rate was subtracted from the raw rate coefficients, the results would be systematically low. Malko and Troe (1982)[14] concluded in their evaluation of $k_2(T,\text{M})$ that the lower temperature and lower pressure data of CJ were systematically low. This is possibly due to the subtraction of too large a heterogeneous rate. We first added 2×10^{-5} s^{-1} to all the data as reported, in order to retrieve the original data, and then performed the heterogeneous analysis as described above. Fitted k_5 values ranged from 6×10^{-6} to 1.1×10^{-5} s^{-1}, with an average of 8×10^{-6} s^{-1}. While this analysis is not unambiguous, it appears that the proper value for k_5 for the CJ study may be smaller than the value they utilized. These corrected data are shown in Figure 3b along with the data as originally reported. This reevaluation of the heterogeneous component does not affect the overall fit much because of the low weight applied to the data at low temperature and pressure, as suggested by the authors.

Results and Discussion

Effect of n_0, n_∞, and F_c on the Falloff Curves. We have evaluated the effect of different forms of F_c, T^n dependencies of $k_{0,2}$ and $k_{\infty,2}$, the inclusion of weighting, and the makeup of the data set on which the fit is performed. Results of some of the fits are shown in Table II and summarized in the following discussion. The quality of the fits, estimated through root mean square differences between the data and the fitted surfaces, is also presented. For easy comparison of the fits, the room temperature $k_{0,2}$ and $k_{\infty,2}$ values are tabulated. A "base case" was selected with which to compare the other results. This case utilizes the data of this study, of V, and of CJ; the F_c recommendation and n dependencies for k_0 and k_∞ of –3.5 and –0.2, respectively from Orlando *et al*;[6] and a fitted exponential temperature coefficient. These parameters are given in Table II. This set of conditions resulted in the lowest residual differences between the data and the fit of all the options we tested. The base case fitting parameters are shown in eq d:

$$k_{0,2}(T) = 1.04 \times 10^{-3}\left(\frac{T}{300}\right)^{-3.5} \times \exp\left(-\frac{11000}{T}\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_{\infty,2}(T) = 6.22 \times 10^{14}\left(\frac{T}{300}\right)^{-0.2} \exp\left(-\frac{11000}{T}\right) \text{ s}^{-1}$$

$$F_c = 2.5 \exp\left(-\frac{1950}{T}\right) + 0.9 \exp\left(-\frac{T}{430}\right) \qquad \text{(d)}$$

In Table II, it is shown that changing n_0 and n_∞ has little effect on the fit compared to the base case. The rate coefficients calculated using n_0 of –4.3 and n_∞ of +0.3 are changed by less that 2% compared to eq d. Assigning equal weights to all the data causes a slight increase (up to 10%) in calculated rate coefficients at low pressures and a slight decrease (up to 8%) at high pressures compared to the base case. These changes are primarily due to the low weight assigned to the low-pressure, low-temperature data of CJ in the weighted fits.

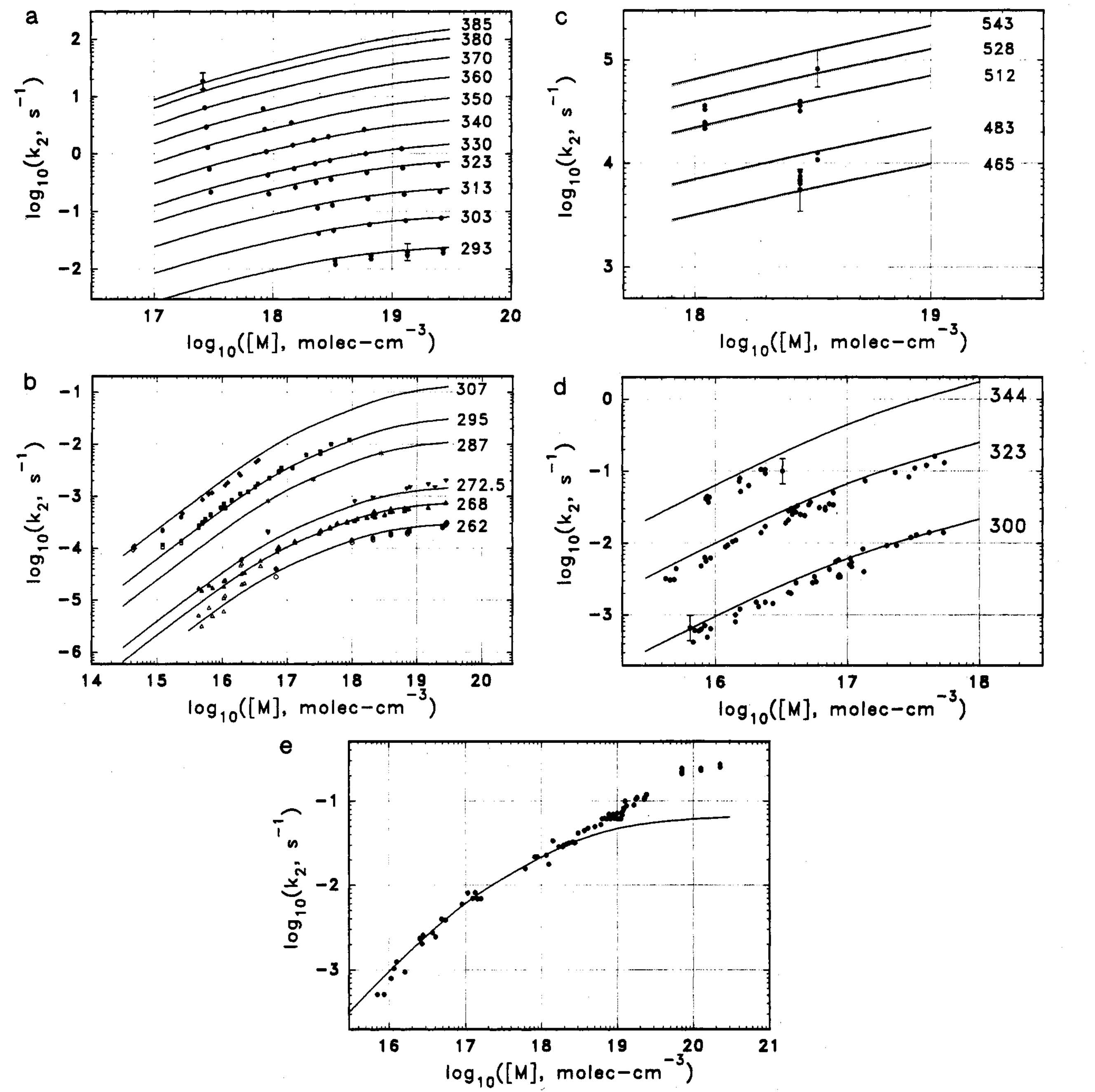

Figure 3. Data for reaction 2 from previous studies: (a) Viggiano *et al.*;[13] (b) Connell and Johnson,[12] solid symbols are corrected for heterogeneous wall loss (see text) and hollow symbols are as reported; (c) Schott and Davidson;[11] (d) Johnston and Perrine;[7] (e) Mills and Johnston,[8] at 300 K, corrected for heterogeneous wall loss as suggested by Johnston and Perrine. In all cases, the solid line indicates the fit calculated from eq d. For part c, the dashed line indicates the fit which includes the SD data.

The effect of different F_c forms was examined by comparing the base case to three cases using (1) the Malko and Troe (1982)[14] recommendation for F_c, (2) a constant F_c of 0.6, and (3) a variable temperature-independent F_c fit parameter. The parameters from these fits are also shown in Table II. In the first case, the high- and low-pressure-limiting rate coefficients are increased substantially (21% and 45%, respectively). Rate coefficients calculated from this fit are up to 10% higher at high pressures (4 atm), 5% lower at intermediate pressures (30 Torr), and up to 35% higher at low pressures. These changes are due to the broadening of the falloff caused by the lower F_c values (0.33 at room temperature) recommended by Malko and Troe. For the F_c of 0.6, only the data of Connell and Johnston and this study near room temperature and below were used to approximate data appropriate for atmospheric conditions. Rate coefficients from this fit are about 10% lower at high pressures, 25% lower at low pressures, and about 5% higher at intermediate pressures. These changes are caused by the narrowing of the falloff with the larger value of F_c. The variable F_c fit yields values about the same as the base case at high pressures, 0–20% higher at intermediate pressures, and 10–15% lower at low pressures. These effects demonstrate the need for accurate values of F_c, although we believe the expression derived by Orlando *et al.*[6] is a reliable representation of the falloff broadening for the N_2O_5 reaction system, which yields F_c of 0.45 at room temperature.

Comparison of $k_2(T,M)$ Data with Least-Squares Fits. An examination of the differences between the recommended fit and the measured rate coefficients is possible through inspection of Figures 2 and 3a–e. To examine differences between the various fits and the available data, two terms are defined below. These are the formulas for the root mean square difference (Δ_{rms}) and the average difference (Δ_{avg}) between the measured data points and the rate coefficients derived from the fits. The root mean square difference is a measure of the differences between the fit and the data regardless of direction. The average difference indicates the degree to which positive and negative differences cancel. While these parameters do not reveal all the systematic differences, they do give some information on the degree of agreement between calculated rate coefficients and those directly measured.

$$\Delta_{\mathrm{rms}} = (1/(N-n))[\sum((k_2(T,\mathrm{M}) - k_{2,\mathrm{fit}})^2)]^{1/2} \quad \text{(e)}$$

$$\Delta_{\mathrm{avg}} = (1/N)[\sum((k_2(T,\mathrm{M}) - k_{2,\mathrm{fit}})/k_{2,\mathrm{fit}})]$$

Here, N is the number of data points, n is the number of fit parameters (usually three), $k_2(T,\mathrm{M})$ are the measured rate coefficients, and $k_{2,\mathrm{fit}}$ are the rate coefficients calculated from the least-squares fits.

For data of this study, the agreement is good, with a few data points noticeably higher than the fit. We did observe that the gas temperature did rise a few degrees during cell pressurization, during some of the experiments, presumably due to the pseudo-adiabatic compression of the initial gas in the cell. Normally, we waited until the temperature had stabilized before commencing with the collection of spectra; however, it is possible that the thermocouples were not completely thermally equilibrated with the cell contents in all instances, and the temperature in some experiments therefore may be slightly underestimated. The temperatures reported in Table I were those measured at the end of the experiment, immediately before the mixture was pumped out. Using fits calculated from eq d, we find Δ_{rms} for this study to be 15.9% and Δ_{avg} to be −0.6%. The latter result indicates that the data are evenly scattered about the fit.

The rate coefficients derived from the data of V are consistently below the fit at lower temperatures, as seen in Figure 3a. Some high-temperature, higher-pressure points are above the fit, although the differences are not large compared to the uncertainty of the measurements. It is possible the study of V was subject to erroneous temperature measurements, although the authors report an accuracy of 0.4–0.5 K. We have found that systematic errors in the rate coefficients can be expected near the temperature extremes in this type of study due to random errors in the I^- signal measurement on which the results are based. This effect is due to the logarithmic transformation of the ratios of the measured signals. These errors result in rate coefficients which are too high at higher temperatures and too low at lower temperatures, which is exactly the trend observed. A look at their reported fit of data to the Troe expression further demonstrates the difference. The k_0^{298} and k_∞^{298} values (4.1×10^{-20} and 0.028, respectively) are about a factor of 2 lower than those obtained in this study, while the temperature dependency $k_{\infty,2}$ seems unreasonably large (−12787 K was reported for B_∞), which will cause values to be systematically high at higher temperatures. The root mean square difference between eq d and their data (as used here) is 12.6%, and the average difference is −4.4%.

The CJ data (Figure 3b) agree very well with the fit with a couple of exceptions. The data at 272.5 and 295 K are systematically above the fit, while the data at nearby temperatures agree fairly well (268 K) or are slightly below the fit (307 K). There are differences between the fit and the data at the lowest pressures at 268 K, where the effect of the heterogeneous component correction is the greatest. However, these data received little weight in the fitting process (relative uncertainties of 0.8) as suggested by Connell and Johnston. The root mean square difference between the fit calculated from equation d and these data is 19.3%, and the average difference is +1.5%.

Schott and Davidson[11] (hereafter, SD) studied N_2O_5 and NO_3 chemistry using shock waves to generate temperatures from 450 to 1200 K. They measured the kinetics of reaction 2 from 463 to 543 K at pressures from about 85 to 305 Torr, by measuring the rate of formation of NO_2 and NO_3 using optical absorption. Their experiments were performed in argon. We take the approximation of Malko and Troe (1982) that $k_{0,2}(\mathrm{Ar}) \approx k_{0,2}(\mathrm{N_2})$ and therefore make no collision efficiency corrections. It had been postulated earlier[16,36] that the SD cross sections for NO_3 were systematically low by about a factor of 2 near 662 nm. Here, however, we take the data as originally reported. The data of SD are shown along with the recommended fit (solid line) in Figure 3c. The curves are calculated for groups of temperatures, but some individual data points are as much as 3 K from the temperature associated with the nearest curve. The agreement between the Schott and Davidson data and the fit is fairly good considering the uncertainties in collision efficiency corrections, in the temperature (about ±10 K), and possible errors in the NO_3 cross sections. The results of a fit which included the SD data are also shown in Figure 3c (dashed line, also see Table II). The root mean square difference between the fit (eq d) and the data is 33.9%, and the average difference is −11.3%.

There were four reports of N_2O_5 decomposition rate data by Johnston and co-workers in the 1950s.[7–10] The reports from 1953 have important information concerning the relative efficiencies of various bath gases to dissociate N_2O_5 but have relatively little data over ranges of temperature and pressure. Thus, no $k_2(T,\mathrm{M})$ data from Johnston[9] and Wilson and Johnston[10] were used in the present evaluation.

Johnston and Perrine[7] report rate coefficients for reaction 2 at three temperatures from 300 to 344 K and pressures from about 0.05 to 10 Torr. They measured the rate of NO_2 formation through visible absorption spectroscopy at 436 nm using a cross section that agrees with the value reported by Davidson *et al.*[37] to within 3%. The rate of formation of NO_2 was converted to the rate of loss of N_2O_5 through the stoichiometry indicated by relation 3. These experiments were performed either in "pure reagents" (an equimolar mixture of N_2O_5 and NO) at pressures below 1 Torr or with CO_2 as the bath gas at pressures above 1 Torr. The experiments in pure reagents have the drawback that the third body changes from N_2O_5 and NO to NO_2 during the course of reaction. It is perhaps fortuitous that the collision efficiency relative to nitrogen of NO_2 ($\approx$3.0) is nearly equal to that of an equimolar mix of N_2O_5 and NO (2.78). This is complicated by the stoichiometry of the reaction (2 mol of reactants yield 3 mol of products), which increases the effective nitrogen concentration during the course of the experiment. The third-body concentrations for the pure reagent experiments were multiplied by 2.78 and for the CO_2 experiments by 1.71, based on data from Johnston.[9] Three outlier points were also eliminated. No modifications to the data were made for possible heterogeneous loss; however, the correction is likely less than $4 \times 10^{-4}\ \mathrm{s}^{-1}$ and would affect only those lowest pressure data measured near room temperature. The collision efficiency corrected data are shown in Figure 3d, and they are systematically below the recommended fit calculated with eq d. The root mean square difference between the fit and these data is −35.1%, and the average difference is −43.6%. It is interesting that the uncorrected data may actually be closer to the fit than the corrected ones, and although the correction is an approximate one it should be closer to reality than the uncorrected data.

Mills and Johnston[8] report rate coefficients for reaction 2 over a very wide pressure range at 300 K. The measurements were performed in three experimental setups covering different pressure ranges. The experiments were also performed with equimolar amounts of NO and N_2O_5 (no bath gas) or in baths of CO_2 or N_2, and thus collision efficiency corrections are necessary for data in the first two categories. These data, particularly at high pressures, appear to be systematically high compared to other studies by factors of 1.5–5 for unknown reasons. However, these differences are clearly unrelated to the collision efficiency corrections. Johnston and Perrine postulated that the lower pressure data of Mills and Johnston could be used if corrected by a heterogeneous wall loss of $3.6 \times 10^{-4}\ \mathrm{s}^{-1}$, and indeed the data from the low-pressure apparatus and the results at the lower pressures from the intermediate-pressure apparatus are in reasonable agreement with rate coefficients calculated from eq d, shown in Figure 3e. These data were not used for any of the fits reported here. Hisatsune *et al.*[38] measured the loss of N_2O_5 and the formation of NO_2 via infrared absorption spectroscopy.

By performing experiments in varying ratios of $[N_2O_5]$ to [NO], they were able to extract values for $k_2(T,M)$ as well as for the ratio k_2k_4/k_1, at two pressures and three temperatures. The six data points appear reasonable, but correcting the data for the collision efficiencies without knowing the relative amounts of NO and N_2O_5 would prove impossible. We have not used these data in the present evaluation.

The N_2O_5 reaction system was also studied by Linhorst and Hodges[39] and by Smith and Daniels.[24] The experiments of Linhorst and Hodges measured the formation of molecular oxygen from the decomposition of N_2O_5 at low pressures of reactant with no bath gas and no added NO. These results correspond to the first-order irreversible decomposition of N_2O_5.[7,8,15,16] Smith and Daniels measured the rate of reaction in the presence of NO by determining the NO_2 concentration with absorption spectroscopy from 460 to 600 nm. This study established the mechanism for this reaction as well as the overall stoichiometry. We have not directly used data from either of the latter two studies.

Test fits were also performed on expanded data sets (in addition to the data of this study, of CJ, and of V). The first test added the data of JP, and the second included data of both JP and SD. The differences between these new fits and equation d were calculated for the T and M conditions of the this study, CJ and V data only. The effect of including these other data was rather small, of order 5–10%. Both test fits were about 5% higher than eq d at high pressures and about 10% lower than eq d at low pressures. The root mean square difference with the JP data included was 23.6%, and incorporating both JP and SD it was 23.4%, somewhat larger than the difference with the base case data set. The average differences were −7.0% and −5.0%, respectively.

Comparison of Falloff Curves with Malko and Troe Evaluation. We next compare the falloff curves from the present study to those from the detailed evaluation by Malko and Troe (1982).[14] To accomplish this, we used the eq d parameters and the recommended expression from Malko and Troe for temperatures from 200 to 300 K. Values for $k_{2,\text{fit}}(T,M)$ were calculated at the temperatures of this study, V, and CJ (253–384 K) and at third-body concentrations of 1×10^{15}, 1×10^{16}, 1×10^{17}, 1×10^{18}, 1×10^{19}, and 1×10^{20} molecules cm^{-3}. Notice that this matrix of evaluation points includes data outside the range of measured rate coefficients and outside the range of atmospheric conditions. For each T and [M] pair, k_2 values from eq d and from the Malko and Troe recommendations were determined and a ratio was calculated (k from eq d over k from Malko and Troe). The average of these ratios for all conditions surveyed was 0.85 (±0.10, 1σ), but was not very different for subsets of the entire data set. The Malko and Troe formulation for 200–300 K, on average, yields $k_2(T,M)$ values some 18% higher than the present recommendations. The variations in the ratios with temperature and pressure are somewhat systematic. At low pressures, the ratio averages about 0.7, at intermediate pressures it averages 0.98, and at the highest pressures it averages 0.9. At low pressures the ratios increase with temperature, at intermediate pressures they are nearly invariant with temperature, and at high pressures the ratios decrease with increasing temperature. The latter effect is the result of slightly different T^n dependencies and B values in the two evaluations.

Comparison of Falloff Curves with DeMore *et al.* (1992) Recommendations. The recent compilation from the Jet Propulsion Laboratory (DeMore *et al.*, 1992[19]) recommends calculation of rate coefficients for $k_2(T,M)$ using their tabulated parameters for $k_1(T,M)$ and $K_{1,2}$. Defining $K_{1,2}$ as k_2/k_1, $k_2(T,M)$ is then determined from $k_1(T,M) \times K_{1,2}$. We have performed a comparison for the same conditions as described above between eq d and the DeMore *et al.* recommendations. The average of the ratios of eq d to DeMore *et al.* for all the T and [M] conditions was 1.22 (±0.14, 1σ), with slightly better agreement for conditions at room temperature and below (253–295 K), yielding 1.16 (±0.13, 1σ). For standard atmospheric conditions from 0 to 50 km,[40] the average ratio was 1.06 (±0.07, 1σ). The ratios vary systematically with T and [M]. At low pressures, the ratios average 1.43, at intermediate pressures 1.05, and at high pressures 1.20. The ratios increase with temperature at high and low pressures and show almost no variation with temperature at intermediate pressures. These differences give some indication of the degree of disparity between k_1, k_2, and $K_{1,2}$: there are some systematic differences, but they are not great and are certainly well within the errors associated with the measurements of the three parameters.

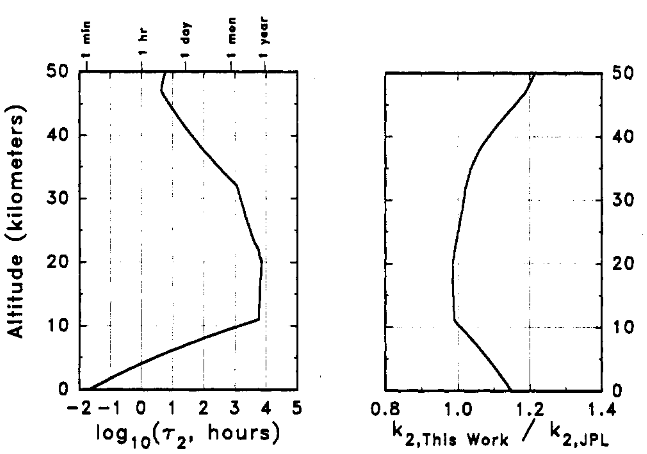

Figure 4. On the left, lifetimes of N_2O_5 toward decomposition ($1/k_2(T/M)$) for standard atmospheric conditions (U.S. Standard Atmosphere[40]) are plotted versus altitude from the present evaluation. On the right, ratios of the present results of $k_2(T,M)$ (eq d) to those of the evaluation of DeMore *et al.*[19] ($k_1(T,M)K_{1,2}$) are plotted for standard atmospheric conditions.

TABLE III: Evaluation of the Equilibrium Constant for the N_2O_5 System and Results of the Kinetic Analysis of This Study

$K_{1,2}(T)$, molecule cm^{-3}	$K_{1,2}(298)$	ref
$1.46 \times 10^{26} \exp(-10815/T)$	2.53×10^{10}	Wayne[17]
$7.94 \times 10^{26} \exp(-11275/T)$	2.94×10^{10}	Atkinson[18]
$2.50 \times 10^{26} \exp(-10930/T)$	2.94×10^{10}	DeMore *et al.*[19]
$3.70 \times 10^{26} \exp(-11000/T)$	3.44×10^{10}	eq f
$4.07 \times 10^{26} \exp(-11020/T)$	3.54×10^{10}	eq g

Atmospheric Lifetimes of N_2O_5 toward Decomposition. The atmospheric lifetimes of N_2O_5 due to decomposition are presented in Figure 4. On the left-hand side, the inverse of $k_2(T,M)$ is plotted versus altitude for the present evaluation (eq d) using atmospheric conditions from the U.S. Standard Atmosphere[40] at altitudes from 0 to 50 km. In the graph on the right-hand side, the ratios of $k_2(T,M)$ values for this evaluation to those from the recommendations of DeMore *et al.*, using $k_1(T,M)$ and $K_{1,2}(T)$, are plotted for the same conditions. This new evaluation implies a shorter lifetime for N_2O_5 of up to 15% in the regions of the atmosphere near the surface and a 2% longer lifetime near the tropopause. A 20% shorter lifetime is calculated for average conditions of temperature and pressure appropriate for 50-km altitude. As described earlier, on average the lifetimes from the present evaluation are about 6% less than those calculated using the DeMore *et al.* recommendations.

Kinetic and Measured Equilibrium Constants. The equilibrium constant ($K_{1,2}$) for the N_2O_5 system has been measured directly[11,16,41-44] and indirectly,[1,36] and these data have been screened and evaluated.[17-19] These recommendations, which are based on laboratory measurements, are shown in Table III. These evaluations will be used to examine the consistency between the kinetic and equilibrium data. To effect this comparison, kinetic equilibrium constants ($K_{1,2;k}$) were generated from ratios of the fits (eq d and Orlando *et al.* recommendations) of the measured rate coefficients of reactions 1 and 2. It is important that these ratios be performed with fits derived using the same F_c and $k(T)$ forms, to minimize any artifacts created by the fitting procedure.

Kinetic equilibrium constants were calculated at the conditions of temperature and pressure of the measurements from this study, V, and CJ. The average ratios of the kinetic equilibrium constants to the evaluations of DeMore *et al.* (1992),[19] Atkinson (1991),[18] and Wayne (1990)[17] were calculated to be 1.18 (±0.02, 1σ), 1.22 (±0.09, 1σ), and 1.36 (±0.07, 1σ), respectively. A least-squares fit to these individual kinetic equilibrium constants results in the following expression:

$$K_{1,2;k} = 3.70 \times 10^{26} \exp\left(-\frac{11000}{T}\right) \text{ molecule cm}^{-3} \qquad \text{(f)}$$

The recommendations for $k_1(T,\mathrm{M})$ and $k_2(T,\mathrm{M})$ are not totally consistent with eq f, because the ratios $k_{0,2}/k_{0,1}$ and $k_{\infty,2}/k_{\infty,1}$ are different, resulting in an apparent dependence of $K_{1,2}$ on pressure. The differences are not extremely large, with the low-pressure ratio yielding an equilibrium constant at 298 K of 3.46×10^{10} molecule cm^{-3} and the high-pressure ratio a value of 3.50×10^{10} molecule cm^{-3}.

As an alternate approach, an expression for $K_{1,2;k}$ is arrived at by fitting the $k_2(T,\mathrm{M})$ data to k fit functions multiplied by an expression for $K_{1,2}$. This results in a truly "kinetically consistent" equilibrium constant expressed as follows:

$$K_{1,2;k} = 4.07 \times 10^{26} \exp\left(-\frac{11020}{T}\right) \text{ molecule cm}^{-3} \qquad \text{(g)}$$

Values for $k_2(T,\mathrm{M})$ are then calculated from the following parameters, determined by multiplying $K_{1,2;k}$ from eq g by $k_1(T,\mathrm{M})$ from Orlando *et al.*:

$$k_{2,0} = 1.14 \times 10^{-3}\left(\frac{T}{300}\right)^{-3.5} \exp\left(-\frac{11020}{T}\right) \text{ cm}^6 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_{2,\infty} = 6.75 \times 10^{14}\left(\frac{T}{300}\right)^{-0.2} \exp\left(-\frac{11020}{T}\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \qquad \text{(h)}$$

The average ratios (over the range of $k_2(T,\mathrm{M})$ measurements) of $K_{1,2;k}$ from eq g to the evaluations of DeMore *et al.* (1992), Atkinson (1991), and Wayne (1990) are 1.19 (±0.03, 1σ), 1.23 (±0.09, 1σ), and 1.37 (±0.08, 1σ), respectively, which are slightly larger than those ratios calculated with eq f. The average ratio of $k_2(T,\mathrm{M})$ values calculated from eq d to those calculated from eq h is 0.98 (±0.01, 1σ) over the range of measurements of this study, CJ, and V. The maximum ratio was 1.00, and the minimum was 0.96. Thus, the best-fit recommendation (eq d) and the equilibrium-constrained fit (eq h) are not very different over the range of the k_2 measurements.

Conclusions

Rate coefficients have been measured for the unimolecular decomposition of N_2O_5. By performing fits on a data set which includes the present and those of some previous studies, we made recommendations for rate coefficients over a range of conditions of temperature and pressure (2.53–384 K, 4.3×10^{14} to 1.1×10^{20} molecule cm^{-3} N_2, but not at all temperatures). Kinetic equilibrium constants were calculated using data from the association reaction. Analysis of these values suggests that an equilibrium constant for the N_2O_5 system that is slightly higher than current recommendations is more consistent with the avilable kinetic data for the forward and reverse reactions of the N_2O_5 system.

Acknowledgment. This work was supported, in part, by the Upper Atmospheric Research Program of NASA under project number W-16042. The authors gratefully acknowledge the helpful comments of Elliot Atlas and Alan Fried in the preparation of this manuscript.

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