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LBL-8943

The Thermal Dissociation of N_2O_5 in N_2

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Abstract

The thermal decomposition of di-nitrogen pentoxide ($N_2O_5 \rightarrow NO_2 + NO_3$) has been studied in excess nitrogen between 4×10^{14} and 2.8×10^{19} molecules cm^{-3} and between 262 and 307 K. This reaction is an example of unimolecular reaction kinetics, catalyzed by inert gases M, and exhibiting effects of non-equilibrium distributions over reacting energy states. Previous measurements of the limiting low-pressure second-order rate constant have been confirmed and extended to lower temperatures; with $M = N_2$, the combined old and new data give $k_o' = 6.1 \times 10^{-6} \exp[(-9570 \pm 200)/T]$ cm^3 $molecules^{-1}$ s^{-1}. An estimate of the high-pressure first-order rate constant, $k_\infty = 1.78 \times 10^{17} \exp[(-12540 \pm 130)/T]$ s^{-1}, was found to be lower than the previous value at 300 K, and the high-pressure activation energy was found to be larger than the previous estimate. The problem of extrapolating unimolecular reaction data to low temperature is not simple; a general theoretical formula is presented, which can be used approximately to extrapolate these data to stratospheric conditions.

Introduction

At sunset in the stratosphere, essentially all nitric oxide is rapidly converted to nitrogen dioxide

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (1)$$

and during the night approximately 25 percent of the nitrogen dioxide is converted to di-nitrogen pentoxide

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad (2)$$

$$NO_2 + NO_3 + M \rightarrow N_2O_5 + M \quad . \qquad (3)$$

After sunrise the N_2O_5 is slowly broken down, by photolysis primarily, and to some extent by thermal decomposition

$$N_2O_5 + M \rightarrow NO_2 + NO_3 + M \quad . \qquad (4)$$

Recent direct observations of NO_3 by Noxon et al. [1978], who detected visible absorption by NO_3 at 6620 Å in the night sky, have afforded the possibility of testing diurnal atmospheric models for proper treatment of this portion of NO_x chemistry.

Previous experimental work on this reaction includes measurements made over a wide pressure range at 300 K by Mills and Johnston [1951], measurements made between 300 and 343 K in the low pressure region [Johnston and Perrine, 1951; Johnston, 1953], the relative efficiencies for activation of N_2O_5 decomposition of several buffer gases [Johnston, 1953; Wilson and Johnston, 1953], values obtained by Hisatsune et al. [1957] near 300 K at two intermediate pressures, and values obtained at 450 - 550 K in a shock tube by Schott and Davidson [1958].

The rate of the forward reaction (4) can be found by observing the rate of N_2O_5 decomposition in the presence of nitric oxide

$$\begin{array}{lll} N_2O_5 + M \rightarrow NO_2 + NO_3 + M & \text{slow} & (5) \\ NO + NO_3 \rightarrow 2\ NO_2 & \text{fast} & \\ \hline \text{net:}\quad N_2O_5 + NO \rightarrow 3\ NO_2 & & \end{array}$$

The equilibrium constant K for the reaction $N_2O_5 = NO_2 + NO_3$ has been obtained by Graham and Johnston [1978]. The rate constant of the reverse reaction (3) can then be calculated from the measured thermal decomposition rate constants $k_3 = k_4/K$.

We report here measurements made on the rate of reaction (4) by observation of N_2O_5 decomposition in the presence of NO, using infrared absorption by N_2O_5 as the monitoring technique. The experiments covered a set of conditions between temperatures of 262 and 307 K and total gas concentrations of 4×10^{14} molecules/cm^3 to 2.8×10^{19} molecules/cm^3.

Experimental

The reaction was studied in a 63 liter quartz cell equipped with internally mounted gold-surface mirrors in a multi-reflection White-cell arrangement. The optical pathlength was adjusted from 8 to 24 meters to suit conditions. The entire cell was surrounded on five sides with eight inches of rigid closed-cell polyurethane foam and two inches of aluminum-backed fiberglass and on the bottom with two inches of insulating neoprene rubber. A radiator coil, through which circulated cooled methanol, was mounted above the cell. A circulator fan and proportional temperature controller operating a resistive heater element produced

temperature stability of 0.5 K, measured by thermocouples in contact with the quartz cell.

A beam of 8.028 μm IR radiation passed through the cell and through a McPherson one-meter monochromator set at a resolution of 0.013 μm, and its intensity was measured by a Cu-doped Ge detector operated at 4.2 K. The background intensity, I_o, through the evacuated cell was recorded before and after a kinetic run. The cell was charged with reactants and buffer gas through a disperser tube designed to promote mixing throughout the cell. Pressures were measured either before or after expansion into the cell by a quartz spiral manometer. The IR intensity as a function of time after the cell was filled was recorded at intervals appropriate to the reaction rate by a multichannel instrument-computer equipped with a 12 bit A/D.

Nitrogen pentoxide was prepared by the method of Schott and Davidson [1958] and was used shortly after its preparation. Nitric oxide was purified by passage through a U-tube filled with silica gel at 196 K to remove residual NO_2 and N_2O_3. Nitrogen was dried by 3A molecular sieve at liquid nitrogen temperature. Despite these precautions, a heterogeneous decay of N_2O_5 was observed in the absence of NO, presumably the result of reaction with water on the surface of the cell, since it was correlated with the appearance of HNO_3 infrared bands. This contribution to the total empirical decay rate was substracted to give the homogeneous rate.

The empirical rate constant was determined by a least squares fit to the slope of the line $\ln[A(t=0)/A(t)] = kt$. The largest recognized source of irreproducibility of the rate constant was the variability of

the heterogeneous rate constant, which was very nearly independent of temperature and pressure and about 2×10^{-5} sec^{-1}. The error from this source varies from about one percent for large rate constants (high T and [M]) to about 80 percent for the smallest (low T and [M]).

Results

The complete set of data is shown in Figure 1. The three substantial sets of data in the second-order region, $[M] < 2 \times 10^{16}$ molecules cm^{-3}, were used to derive an Arrhenius expression for the second-order low-pressure limiting value

$$k_o' = (\lim k/[M])_{M \to 0} \quad . \tag{6}$$

The second-order constants found in this way are entered as circles in Figure 2. Values of k_o', scaled to correspond to N_2 as M [Johnston, 1953], are included as triangles. Other values developed from nonlinear least squares fits to the entire data set in a manner described below are entered as crosses. A least squares fit to the present work gives $k_o'(N_2) = 8.05 \times 10^{-6} \exp[(-9630 \pm 400)/T]$ cm^3 mol^{-1} sec^{-1}, which is in fairly good agreement with the previously determined value [Johnston and Perrine, 1951] of $6.5 \times 10^{-6} \exp[-9640/T]$. A fit to all points gives:

$$k_o'(N_2) = 6.1 \times 10^{-6} \exp[(-9570 \pm 200)/T] \quad . \tag{7}$$

Similarly, the high-pressure limit of the first-order rate constant was derived from

$$k_\infty^{-1} = [\lim_{[M]^{-1}\to 0} k^{-1}/[M]^{-1}] \quad . \tag{8}$$

The data at 272.5, 268, and 262 K at concentrations above 7×10^{18} molecules cm^{-3} (compare Figure 1) were extrapolated to infinite pressure according to (8). The rate constants at 300 K from Mills and Johnston's medium-pressure apparatus over the same concentration range, $7 \times 10^{18} < [M] < 3 \times 10^{19}$, were similarly extrapolated. The data from Mills' high-pressure apparatus appear to be inconsistent with the present results, and these were not used. The combination of the three present results with those from Mills' medium-pressure apparatus gives for the high pressure limit

$$k_\infty = 1.78 \times 10^{17} \exp[(-12540 \pm 130/T) \text{ sec}^{-1} \quad , \tag{9}$$

where the error is the standard deviation of the fit. The high pressure activation energy based on this value is 24.9 kcal/mole, which is somewhat larger than Mills' estimate of 21 ± 2 kcal/mole.

The general formula of Johnston and White [1954] was used in interpolating the first-order rate constants at intermediate pressures between the high and low limits.

$$J = \left(\frac{k_\infty - k}{k}\right)\left(\frac{k_o' - k'}{k'}\right) \quad , \quad k' = k/[M] \quad . \tag{10}$$

The quantity J may be interpreted as the product of the average microscopic rate constants for decomposition from sufficiently excited states and of the average molecular-state lifetime. For a two-state model, such as the simple Lindemann [1922] expression, J is one. For a more realistic model involving many vibration-rotation states above the critical energy, J will be substantially greater than one.

A three-parameter (J, k_∞, k_o') non-linear least-squares fit to all the data at each temperature established that a constant value J = 6.5 gave a reasonable fit to the intermediate pressure data independent of temperature. Although J is expected to vary with pressure and temperature, the sensitivity of the fit to change in J is low. A two-parameter fit (k_o' and k_∞) at each temperature with J fixed at 6.5 then gave the values k_o' plotted as crosses in Figure 2.

Rate constants read from the interpolation curves at constant $[N_2]$, as well as older data at higher temperatures are plotted in Figure 3. The corresponding Arrhenius parameters for total gas concentrations between 3×10^{16} and 3×10^{19} molecules cm^{-3} are tabulated in Table I. Rate constants for the reverse reaction are included as calculated from k_4 and the equilibrium constant.

Extrapolation to Stratospheric Temperature

Hampson and Garvin [1978] report the low pressure limit for this reaction as $2.2 \times 10^{-5} \exp(-9700/T)$ cm^3 $molecule^{-1}$ s^{-1}. This expression is for the low pressure limit ($[M] < 2 \times 10^{16}$) for equimolar NO and N_2O_5 as M gas [Johnston and Perrine, 1951]. Nitrogen is less efficient than NO + N_2O_5 by a factor of 2.8, and thus this expression is not valid for tropospheric or stratospheric conditions. Hampson and Garvin also quote a high-pressure rate expression, k_∞ taken from Mills and Johnston [1951]. Sometimes the simple two-level Lindemann [1922] expression is used to connect low and high pressure limits

$$k = \frac{k_\infty k_o'[M]}{k + k_o'[M]} \quad . \tag{11}$$

However, this expression is a poor approximation [Mills and Johnston, 1951] and one at least as complex as (10) should be used, which when solved for the rate constant is

$$k = \frac{-(k_\infty + k_o'[M]) + \left[(k_\infty + k_o'[M])^2 + 4\, k_\infty k_o'[M](J-1)\right]^{1/2}}{2\,(J-1)} \quad . \tag{12}$$

Although this expression is more nearly realistic than (11), its limitations must be pointed out. The temperature dependence of a unimolecular reaction in its "fall off" region is not given by the Arrhenius equation $k_o' = A \exp(-E/T)$ but by a more complex expression for which the simplest form is $k_o' = B\, T^{-n} \exp(-E'/T)$. The difficulty is that J slowly changes with [M] and T [Johnston, 1966], and the experimental data are not detailed enough to provide good values for n and E'. If one wishes to extrapolate these data to stratospheric temperatures, the recommended procedure at present is to use (7), (9), and (12) with J = 6.5. We estimate a factor of two uncertainty at 220 K due to this extrapolation procedure, whereas use of some of the simpler methods can easily lead to a factor of ten error in the extrapolation.

Acknowledgment

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Table I. Arrhenius parameters for forward and reverse reactions in the decomposition of N_2O_5 at concentrations of nitrogen between 3×10^{16} and 3×10^{19} molecules cm^{-3}.

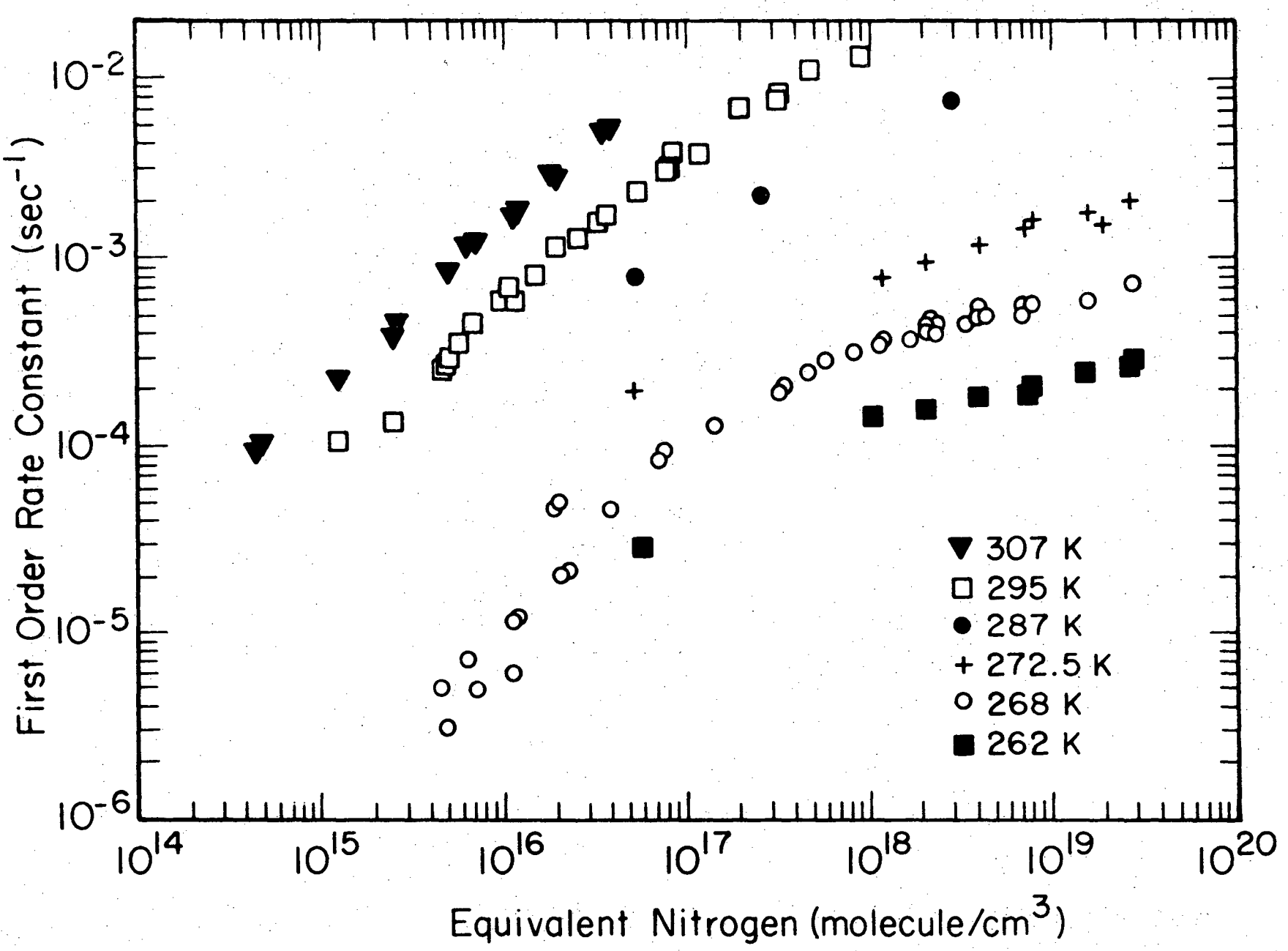
$[N_2]$	A_f, s^{-1}	E_f, K^{-1}	A_r, $cm^3\ s^{-1}$	E_r, K^{-1}
3 E16	4.9 E11	9940	5.9 E-16	-1240
1 E17	3.6 E12	10230	4.3 E-15	-950
3 E17	1.78 E13	10480	2.13 E-14	-700
1 E18	1.64 E14	10920	1.96 E-13	-260
3 E18	1.24 E15	11360	1.48 E-12	180
1 E19	1.53 E16	11960	1.83 E-11	780
3 E19	9.7 E16	12410	1.16 E-10	1230

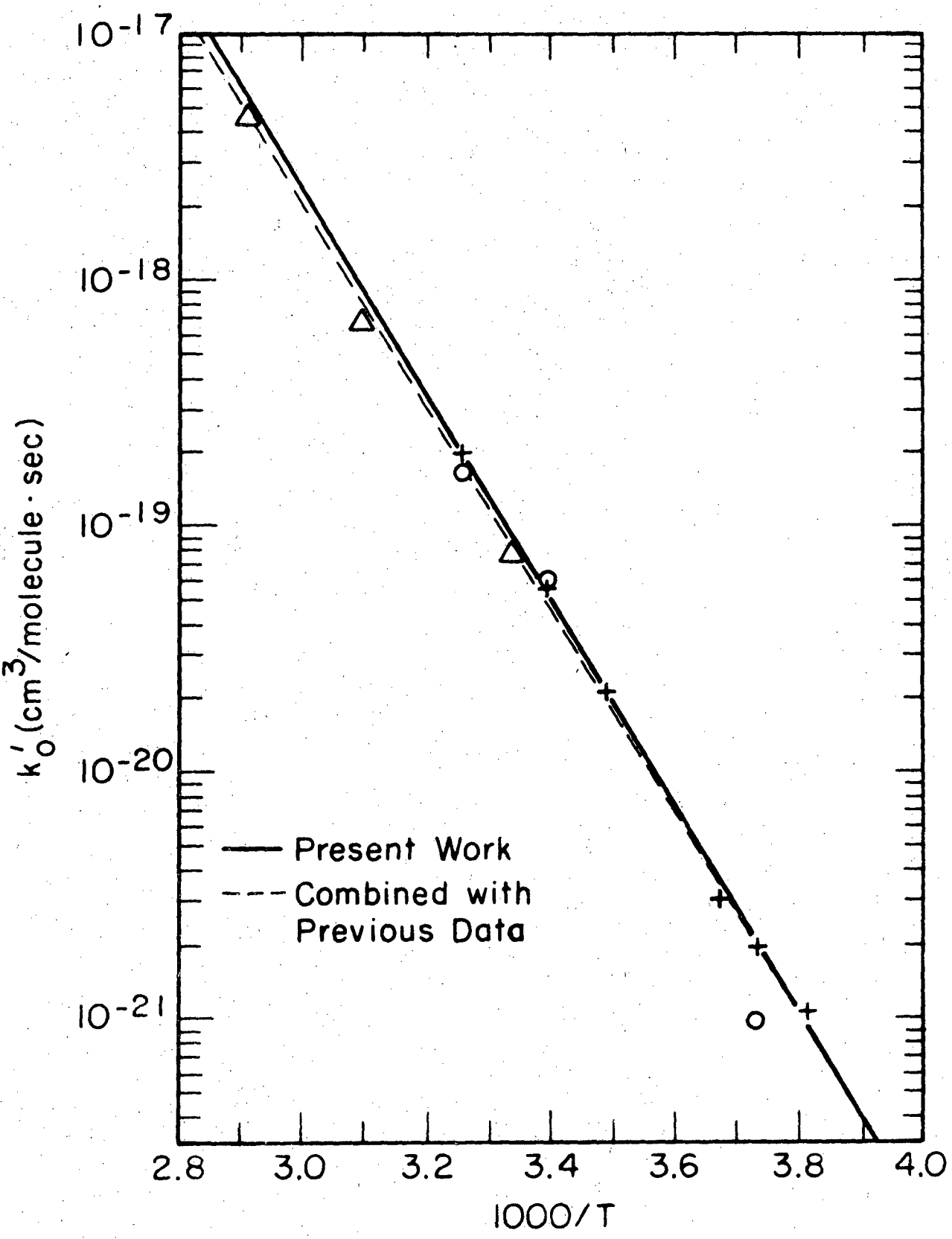
Figure Captions

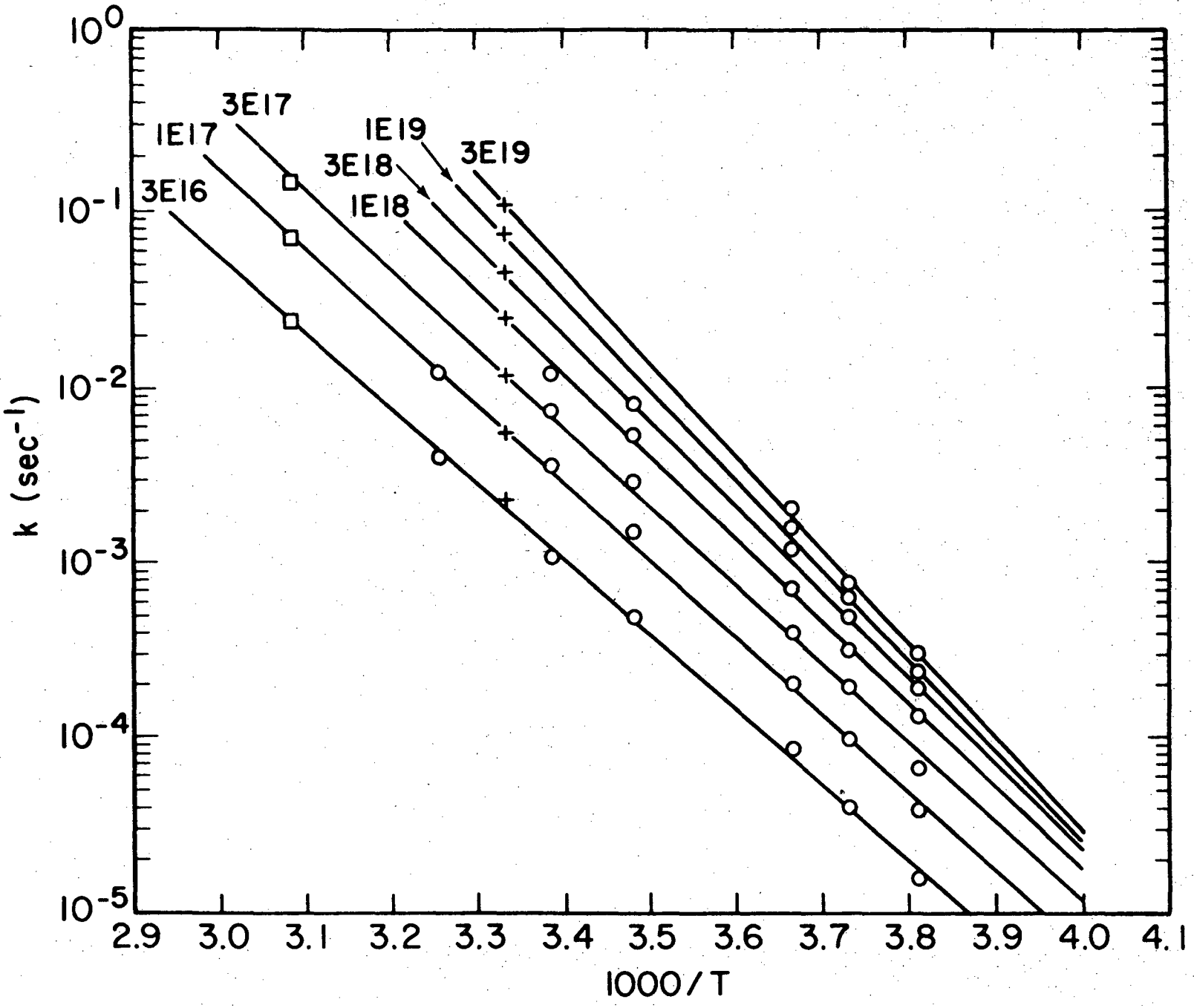
Figure 1. Empirical first order rate constants k for the decomposition of di-nitrogen pentoxide as found in this study.

Figure 2. Arrhenius plot for the low-pressure second-order rate constant $k/[N_2]$. ○, direct observations in this study; +, points fitted to all the data in this study using Eq. (13) as interpolating formula; △, Perrine and Johnston [1951], corrected for relative efficiency of N_2 and $NO + N_2O_5$.

Figure 3. Arrhenius plots for first-order rate constants at various intermediate gas concentrations. ○, based on this study; +, Mills and Johnston's intermediate pressure reactor; □, Johnston [1953]. The numbers refer to equivalent concentration of nitrogen, molecules cm^{-3}.


First Order Rate Constant (sec^{-1})
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{14}
10^{15}
10^{16}
10^{17}
10^{18}
10^{19}
10^{20}
Equivalent Nitrogen (molecule/cm^3)
307 K
295 K
287 K
272.5 K
268 K
262 K


10-17
10-18
10-19
10-20
10-21
k'o(cm3/molecule·sec)
Present Work
Combined with
Previous Data
2.8
3.0
3.2
3.4
3.6
3.8
4.0
1000/T


10^0
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
k (sec^{-1})
3E17
1E17
3E16
1E19
3E18
1E18
3E19
2.9
3.0
3.1
3.2
3.3
3.4
3.5
3.6
3.7
3.8
3.9
4.0
4.1
1000/T

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