

windings of Nichrome over asbestos are used to heat the cell. One is controlled to $\pm 1^\circ$ or better from a thermocouple inserted $\frac{3}{8}$ in. into the cell wall. The other is for final rapid destruction of the sample, as described below.

A double-beam spectrophotometer is folded around the cell in such a way as to keep photomultipliers (931-A), filters (Corning 3398 + 5113), and the lamp (W filament) out of the way of possible flying fragments of silica. The lamp is operated by a regulated voltage source. Concentration of NO_2Cl vs. time is recorded by means of an electrometer and strip-chart recorder. Illumination of the sample during the experiment produced no detectable photochemistry.

Gases at the high densities employed here have to be mixed as if they were liquids. We ordinarily use a premixing cylinder that can be detached from the apparatus and shaken (some Teflon beads were put inside). If the volume of the premixing cylinder greatly exceeds that of the cell, the cell can be filled directly with little pressure loss. Subsequently attaining constant temperature requires an appreciable portion of a half-life, so that initial rates are not accessible with this method. Analysis of the data requires knowledge of the initial NO_2Cl concentration, however; this is found at the end of the useful kinetic measurement by rapid pyrolysis of the remaining NO_2Cl to NO_2 .

Nitryl chloride and nitrogen pentoxide were prepared by literature methods,¹⁵ purified by repeated distillation, and checked for purity by ir spectrometry.¹⁶ Matheson dry N_2 of 99.99% purity, from 6000 psi cylinders, was used directly. Rather than trying to remove residual O_2 , we established its unimportance experimentally by adding some more. Auxiliary runs with variable initial reactant concentrations were also made to verify the order of the reaction under our conditions.

Results for NO_2Cl

The experimental results at three temperatures are displayed in Figure 2. The high-pressure values of k are 2.00 , 3.48 , and $7.05 \times 10^{-4} \text{ sec}^{-1}$ at 105 , 115 , and 123° , respectively. The most important feature of these observations is that no appreciable deviation from the high-pressure k limit was found for mean collision intervals as small as $2.8 \times 10^{-13} \text{ sec}$ (calculated using the second virial coefficient of N_2). This is shorter than most of the intramolecular relaxation times found for badly behaved model molecules in the trajectory studies.³ Therefore there is a strong presumption that NO_2Cl is a well behaved RRKM molecule under all conditions. In view of the results cited earlier, it would seem that at least at the moment, NO_2Cl is the molecule of whose compliance with the theory we are most nearly sure.

Our temperature range is not broad enough for an independent determination of the activation energy.

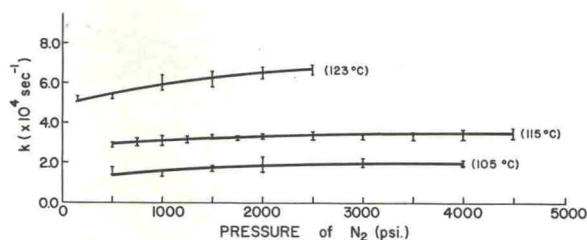


Figure 2. Observed rate constant for NO_2Cl decomposition, vs. pressure of added N_2 .

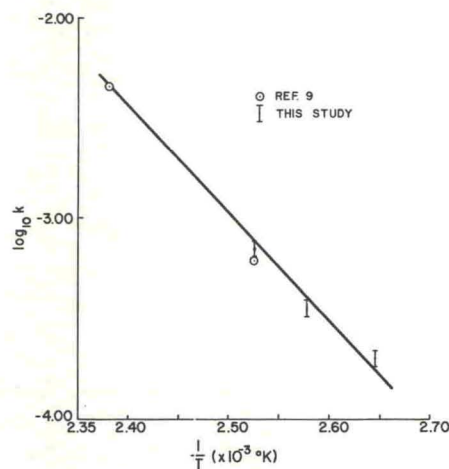


Figure 3. Activation energy determination for NO_2Cl .

In combination with the data of Casaletto,¹⁰ our results lead to $E_{\text{act}} \cong 25 \text{ kcal/mol}$ (see Figure 3), with enough uncertainty not to contradict earlier estimates.^{13,17}

Although our study did not produce many data on the falloff of k with pressure, we are able to make a comparison which clarifies some of the findings in the earlier high-pressure study.¹⁰ In that work, two groups of measurements were made, one at moderate and the other at relatively high pressure. Mismatch of these was attributed to a grease-catalyzed contribution to the reaction rate at moderate pressures. Our system does not have this hazard, and we agree better with the moderate-pressure measurements; our high-pressure data are systematically higher than those of ref 10. In Figure 4 we have displayed (at 123°) our results, both groups of those of ref 10, and data from a low-pressure study (Cordes and Johnston^{17b}). Our view is that the moderate pressure data of ref 10 are the more reliable of the two sets.

(15) NO_2Cl : H. Schechter, F. Conrad, A. L. Daulton, and R. B. Kaplan, *J. Amer. Chem. Soc.*, **74**, 3052 (1951). N_2O_5 : N. S. Gruen-hut, M. Goldfrank, M. L. Cushing, and G. V. Caesar, *Inorg. Syn.*, **3**, 78 (1950).

(16) Spectra: NO_2Cl , R. Ryason and M. K. Wilson, *J. Chem. Phys.*, **22**, 2000 (1954); N_2O_5 , I. Hisatsune, J. Devlin, and Y. Wada, *Spectrochim. Acta*, **18**, 1641 (1962).

(17) (a) H. Hiraoka and R. Hardwick, *J. Chem. Phys.*, **36**, 2164 (1962); (b) H. F. Cordes and H. S. Johnston, *J. Amer. Chem. Soc.*, **76**, 4264 (1954); (c) H.-J. Schumacher and G. Sprenger, *Z. Anorg. Allg. Chem.*, **182**, 139 (1929).

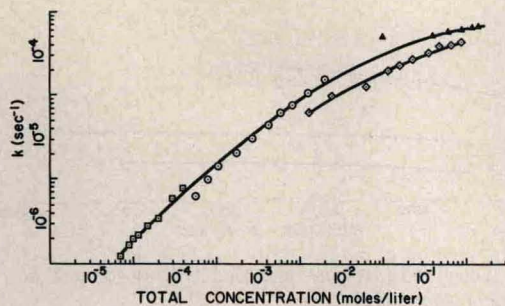
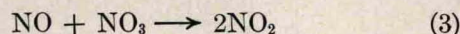
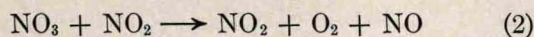
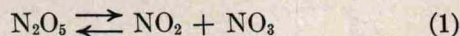


Figure 4. Rate constants for NO_2Cl decomposition, vs. pressure; results of Casaletto¹⁰ (\circ , moderate pressure; \diamond , high pressure), Cordes and Johnston^{17b} (\square), and this work (\triangle).

Results for N_2O_5

The textbook mechanism is



with (1) maintained rapidly and (2) rate determining. At high pressure the overall rate constant is twice that for (2) multiplied by the equilibrium constant for (1). We are thus testing (2) for possible high-pressure effects due to the collisional relaxation of an intermediate aggregate (N_2O_5)*.

This would be an important effect if definitely established, and our results are only marginally positive, so they must be stated with some care. All the data were taken at 35° . Figure 5 shows the results on an expanded ordinate so that the visual level of uncertainty can be assessed. The least-squares slope and its standard deviation—using 67 observations individually, not the centers of the error bars—is $1.11 \times 10^{-4} \pm 0.21 \times 10^{-4}$ in the units of the figure. The individual observations are shown with a zero base line in Figure 6. For comparison, the 115° data in Figure 2 have a slope of $1.28 \times 10^{-4} \pm 0.21 \times 10^{-4}$ with 62 observations; the 28 points with $p > 2000$ psi have a slope of $0.83 \times 10^{-4} \pm 0.45 \times 10^{-4}$. This suggests that we see an effect in Figure 5 with about the same reliability that we can discern a high-pressure limit and a portion of the falloff region with NO_2Cl . Note that exactly the same kind of concentration measurement was made in each case and that any minor heterogeneous effects should be least important at high pressure.

The confidence level of this finding is roughly 90%—not very high, but high enough to suggest that further experiments would be desirable. If the effect is real, it represents a partial thermalization of one or more of the nonreactive degrees of freedom of (N_2O_5)* and a

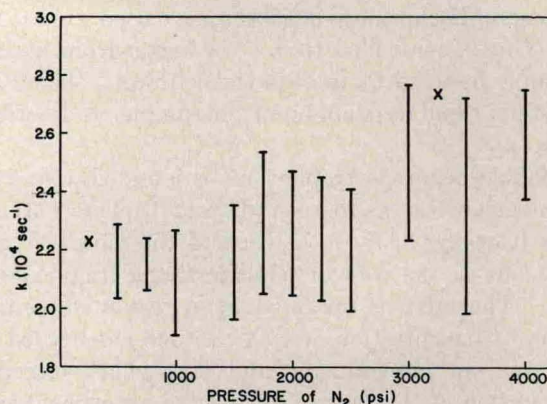


Figure 5. Rate constant for N_2O_5 disappearance, vs. pressure of added N_2 . The \times 's are single observations and the standard error bars have about six observations per bar.

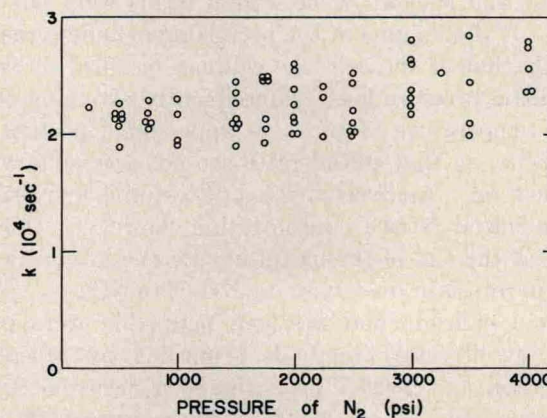


Figure 6. The individual data points corresponding to Figure 5. All measurements were made at multiples of 250 psi; some of the points have been slightly displaced for better visibility.

resulting change in the splitting between the two reactive channels—(2) and the reverse of (1). The potential surface must be rather complicated, and there is no way to decide whether an increase or decrease of rate at high pressure would be the more probable.

Comments

Although the method does not have high precision, it is simple and inexpensive and can yield information worth having at this stage of our understanding. We chose reactions in this study mainly for their feasibility as a test of the apparatus and for the ease with which they lent themselves to spectrophotometry. More reactions of both types need to be studied in this pressure range.

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