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Two Familiar Gas Reactions at Suprahigh Pressure

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We studied the pyrolysis of NO_2Cl and of N_2O_5, with up to 300 atm of added N_2, in an apparatus permitting optical measurement of NO_2 concentration. NO_2Cl appears to be a well-behaved RRKM molecule over the whole range of accessible pressures. There is some evidence for a rise in the N_2O_5 disappearance rate at very high pressure. The possible implications of this are discussed.

Introduction

"Suprahigh" is a description coined by Rabinovitch, *et al.*,[1] to describe the range of pressures from somewhat above 1 atm to that corresponding to about 10^{-13} sec between collisions. These pressures are obtainable from commercial gas cylinders. For simple gases, this is also the range in which collisions are mostly binary. There are several reasons for wanting to study simple gas reactions with suprahigh inert diluent pressures.

It has been proposed on theoretical grounds that a high rate of binary collisions might diagnose departures of unimolecular reactions from conventional RRKM kinetics. Baetzold and Wilson[2] pointed to the possibility of a transient appearing in the distribution of natural lifetimes of energized molecules, caused by nonrandomness in the way collisions produce short-lived states. The most prominent effect of this would probably be a deficiency of very short-lived molecules, leading to a decline of the unimolecular rate constant at high enough pressures. A phenomenon having the

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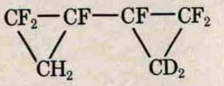
[1] I. Oref, D. Schuetzle, and B. S. Rabinovitch, *J. Chem. Phys.*, **54,** 575 (1971).

[2] R. C. Baetzold and D. J. Wilson, *J. Phys. Chem.*, **68,** 3141 (1964); J. *Chem. Phys.*, **43,** 4299 (1965). "RRKM" is Rice, Ramsperger, Kassel, Marcus.

opposite sense was suggested by one of the present authors as a result of early trajectory studies.[3] The main assumption of RRKM theory, that of rapid intramolecular vibrational relaxation, was found to fail for certain model triatomic molecules. For these, transition from relaxation-controlled to true RRKM behavior occurs at a collision rate high enough to require nearly all reactive states to be formed on the favorable side of the intramolecular energy bottleneck. Acceleration of decomposition at suprahigh pressures would be expected.

Several experiments have been done, and as a result some of the unimolecular kineticist's favorite molecules have come under suspicion of non-RRKM behavior. Rate decline at high pressure[4] and temperature[5] for cyclopropane, and at high pressure for ethylcyclobutane,[6] has been tentatively reported. Methyl isocyanide seems to be a badly behaved molecule in preliminary trajectory studies,[7] and there is a suggestion that a free-radical mechanism contributes to its high-pressure isomerization.[8] (Some of these results have been challenged.[9]) On the other hand, the *sec*-butyl radical shows no anomalous behavior[1] up to 203 atm of added H_2. Our measurements are on NO_2Cl, which has had a prior, unpublished high-pressure study[10] not directed at the effects under discussion here. We wanted a simpler molecule because it was thought at one time that this would favor the second type of deviation mentioned above.[3] It turned out that NO_2Cl is free of non-RRKM behavior up to 310 atm of added N_2 and is now perhaps the best characterized molecule that conforms to the standard theory. (Meanwhile, this type of non-RRKM behavior has been rather conclusively shown at lower pressures by Rynbrandt and Rabinovitch[11] for



and convincing photochemical demonstrations of nonrandom energy partitioning in the decomposition of ground-state molecules have begun to appear.[12])

The relationship between gaseous first-order unimolecular behavior and that in inert solvents is also of interest, although we have not attacked the question in this paper. For example, NO_2Cl decomposition in a halocarbon solvent is appreciably slower[13] than we find. What is the relationship between rates measured under these two sets of conditions? Variation of the ideality of the pressurizing gas might help show this.

A problem to which little attention has been given is that of the possible high-pressure dependence of bimolecular reaction rates. Sufficiently frequent collisions should produce relaxed intermediates for which the description used in transition state theory is an actuality, rather than an approximation requiring separability or adiabaticity of nonreactive motions. Reaction rates might be expected to change when the time between collisions approaches the lifetime of the activated complex. One possible way of exploring this, for one of the bimolecular steps in the N_2O_5 decomposition, is described in this paper. The results are faintly positive.

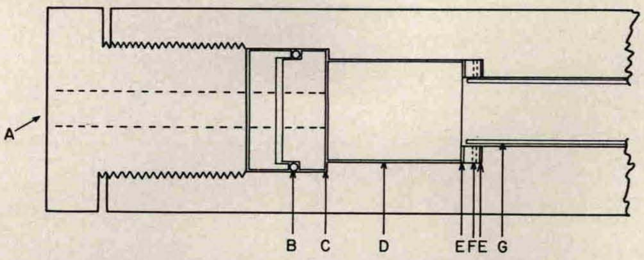


Figure 1. Reaction cell (overall length 14 in., diameter 3 in.). All unlabeled parts are made of Type 316 stainless steel: A, light path; B, silicone O-ring; C, 0.002-in. Teflon spacer; D, 2-in. fused silica window; E, 0.015-in. Teflon rings; F, pressure distribution channel; G, Pyrex liner.

Experimental Section

We use a simple apparatus.[14] Its only novel feature is a reaction cell that permits optical transmission at the pressure of our experiments.

One end of the cell is shown in Figure 1. The materials are Type 316 stainless steel, polished cylindrical fused-silica windows, and a Pyrex liner. The closure is made by compressing a Teflon annulus against the outside face of the window, so that the unloaded surface of the silica cylinder is minimized. This arrangement fails reproducibly by slow leakage at about 320 atm. We did not have any violent accidents.

The cell holds 65 ml and is connected through a side fitting and double Aminco 30,000-psi valves to a conventional vacuum line and to a pressure gauge. Two

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(3) D. L. Bunker, *J. Chem. Phys.*, **40,** 1946 (1964).

(4) H. Yokokawa, L. Dell'Osso, and E. W. Graham, to be published; private communication.

(5) J. N. Bradley and M. A. Frend, *Trans. Faraday Soc.*, **67,** 72 (1971).

(6) J. Aspden, N. A. Khawaja, J. Reardon, and D. J. Wilson, *J. Amer. Chem. Soc.*, **91,** 7580 (1969).

(7) H. H. Harris and D. L. Bunker, *Chem. Phys. Lett.*, **11,** 433 (1971).

(8) C. K. Yip and H. O. Pritchard, *Can. J. Chem.*, **48,** 2942 (1970).

(9) In particular, these are ref 5 and 8 (B. S. Rabinovitch, private communication). The results in ref 6 were interpreted in terms of the volume of activation, which is an empirical construct rather than an alternative physical interpretation to the ones used here. The exact relationship of the trajectory studies to the CH_3NC experiments requires a careful discussion which will appear in a future publication (D. L. Bunker and W. L. Hase).

(10) G. J. Casaletto, Thesis, Stanford University, 1956; University Microfilms, Ann Arbor, Mich.

(11) J. D. Rynbrandt and B. S. Rabinovitch, *J. Phys. Chem.*, **75,** 2164 (1971).

(12) F. H. Dorer and S. N. Johnson, *ibid.*, **75,** 3651 (1971).

(13) D. Beggs, C. Block, and D. J. Wilson, *ibid.*, **68,** 1494 (1964).

(14) For additional details see M. L. Dutton, Thesis, University of California, Irvine, 1972; University Microfilms, Ann Arbor, Mich.

windings of Nichrome over asbestos are used to heat the cell. One is controlled to ±1° or better from a thermocouple inserted $^3/_8$ 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_2 *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 × 10^{-4} 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 × 10^{-13} 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.

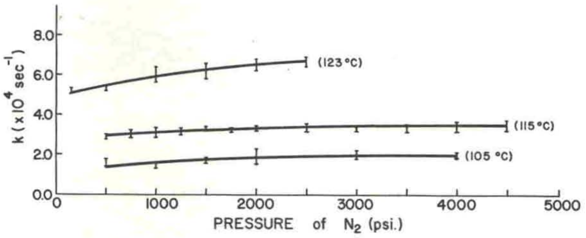

Figure 2. Observed rate constant for NO_2Cl decomposion, *vs.* pressure of added N_2.

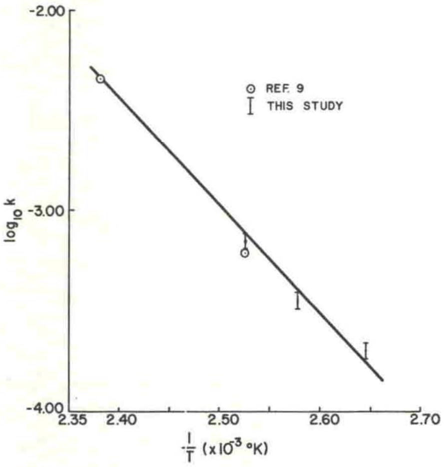

Figure 3. Activation energy determination for NO_2Cl.

Our temperature range is not broad enough for an independent determination of the activation energy. In combination with the data of Casaletto,[10] our results lead to $E_{act} \cong 25$ 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. Gruenhut, 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).

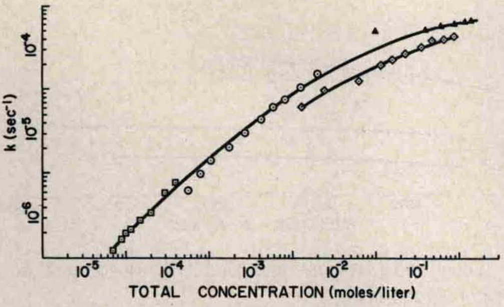

Figure 4. Rate constants for NO_2Cl decomposition, *vs.* pressure; results of Casaletto[10] (⊙, moderate pressure; ◇, high pressure), Cordes and Johnston[17b] (⊡), and this work (▲).

Results for N_2O_5

The textbook mechanism is

$$N_2O_5 \rightleftarrows NO_2 + NO_3 \quad (1)$$

$$NO_3 + NO_2 \longrightarrow NO_2 + O_2 + NO \quad (2)$$

$$NO + NO_3 \longrightarrow 2NO_2 \quad (3)$$

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 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.

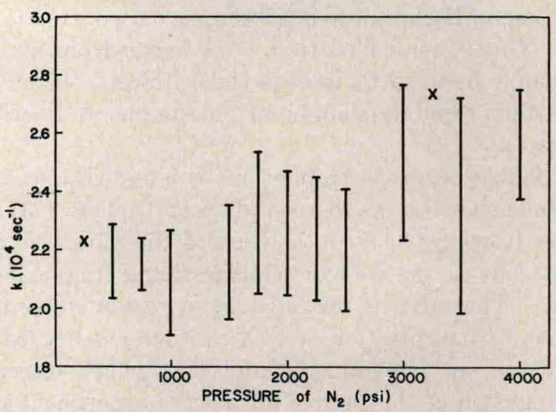

Figure 5. Rate constant for N_2O_5 disappearance, *vs.* pressure of added N_2. The ×'s are single observations and the standard error bars have about six observations per bar.

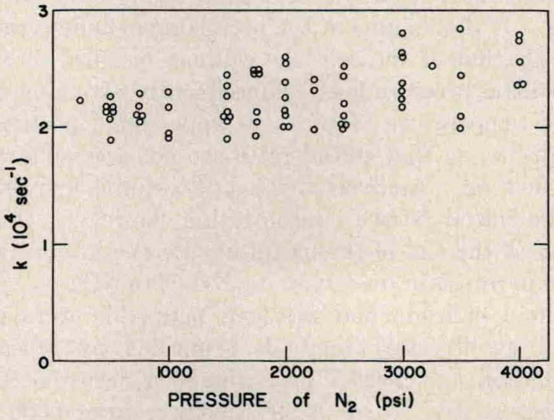

Figure 6. The individual data points corresponding to Figure 5. All measurements were made at multiples of 250 psi; some of the points have been slightly displaced for better visibility.

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 if 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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