# 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

(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

$$CF_2-CF-CF-CF_2$$
$$\quad\ \backslash CH_2 \qquad CD_2 /$$
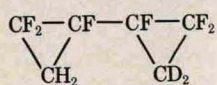
and convincing photochemical demonstrations of nonrandom energy partitioning in the decomposition of ground-state molecules have begun to appear.[12])

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.
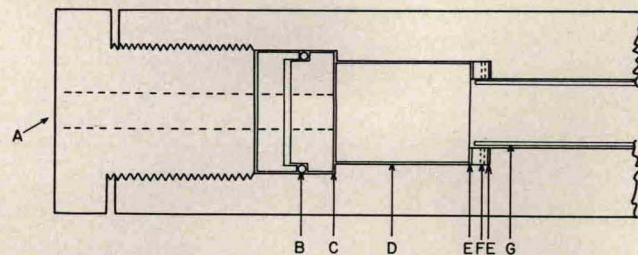


Figure 1. Reaction cell (overall length 14 in., diameter 3 in.). All unlabeled parts are made of Type 316 stainless steel: A, light path; B, silicone O-ring; C, 0.002-in. Teflon spacer; D, 2-in. fused silica window; E, 0.015-in. Teflon rings; F, pressure distribution channel; G, Pyrex liner.

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.

## 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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(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).

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