

FLUORONITRENE¹

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Rate measurements of reactions in solutions under high pressure have been employed to study the nature of reactive intermediates in numerous instances.² Such measurements allow an estimate to be made of ΔV^* , the activation volume, by means of the expression $\Delta V^* = -RT \delta \ln k/\delta p$. In most instances, the mutual approach of the reagent molecules and/or the formation of charges with its concomitant electrostriction of the solvent produce negative values of ΔV^* ; the molar volume of the transition state is then less than that of the initial state. In those reactions in which either the reactant molecule or ion - or a species in equilibrium with it - undergoes simple bond cleavage to form a reactive intermediate such as those mentioned below, ΔV^* is positive. This latter type of reaction has an alternative mode, namely the displacement reaction, which can usually not be distinguished from it by means of the kinetics and the products; however, the activation volume for that pathway has the opposite sign, and the effect of pressure is therefore a simple criterion for judging the freeness of the intermediate. Reactions believed to generate carbonium ions from molecules containing a protonated ether linkage,³ carbenes⁴ or benzyne⁵ from carbanions, and free radicals from neutral molecules⁶ all have been studied by means of this technique. Although valuable information was thus obtained, the question of the existence of these various intermediates had already been extensively explored and was therefore not in very serious doubt. We now wish to report an example of the use of high pressure rate measurements in the

demonstration of a new intermediate, viz., fluoronitrene (NF).

Fluoronitrene has been detected in a low temperature argon matrix upon photolysis of either FN_3 ⁷ or NF_2 ⁸, and its emission spectrum has been observed from a sample of NF_3 through which a discharge had been passed;⁹ its nature has also been explored from a theoretical point of view.¹⁰ Although its presence in several reactions in the liquid phase has been invoked to account for products,¹¹ there appears to be no direct evidence for this species as an intermediate in reactions in solution.

Ward and Wright¹² have demonstrated that difluoramine reacts with aqueous base to give primarily difluorodiazine (N_2F_2), and Stevens and Freeman^{11-c} have shown that difluoramine can give rise to the NF_2^- anion. The hydrolysis is a process first order in difluoramine and first order in hydroxide.^{13,14} A polarographic procedure¹⁵ was used to monitor difluoramine in these experiments. We have used the same method to measure the rate constants, and those determined under comparable conditions are in good agreement. We find that the rate is retarded by the application of hydrostatic pressure in a remarkable way; at $15.0 \pm 0.2^\circ$, ΔV_0^* , the activation volume at zero pressure, is $+14.2 \pm 0.3 \text{ cm}^3/\text{mole}$. If an attempt is made to take the effect of pressure on the pH of the phosphate buffer into account by use of the known¹⁶ ionization volumes of water ($-21.3 \text{ cm}^3/\text{mole}$) and of monophosphate anion ($-28.1 \text{ cm}^3/\text{mole}$), then ΔV_0^* is still substantially positive: $+7 \text{ cm}^3/\text{mole}$. This value is not quite as large as the activation volume found for the base promoted hydrolysis of chloroform⁴ ($+16 \text{ cm}^3/\text{mole}$) - another well-known case of a B_1 -reaction; this large value may be due to charge delocalisation into the chlorine d-orbitals.^{4,17}

By contrast, the data in Table I show that the reaction of difluoramine with acetate at a pH of 5.5 has an activation volume of $-17.6 \text{ cm}^3/\text{mole}$. Craig, who has studied both the hydroxide and acetate reactions as well as those with a number of additional anions,^{13,14} has pointed out that hydroxide ion is situated far off the line correlating the rate constants with the nucleophilicity constants based on methyl bromide; the other anions are clearly involved in displacement reactions. In this connection, it is of interest to recall that a similar rate anomaly led Hine to postulate dichlorocarbene as

an intermediate in the hydrolysis of chloroform.¹⁸

TABLE I

Rate Constants for Several Reactions of Difluoramine			
Pressure, kbar	Temperature, °C	Anion	k_2 , l/mole, sec.
0.001	30.0	OH ^{-a}	1780
0.001	25.0	OH ⁻	960 ^b
0.001	20.0	OH ⁻	440
0.001	15.0	OH ⁻	198
1.03	15.0	OH ⁻	117
2.07	15.0	OH ⁻	79
3.10	15.0	OH ⁻	62
4.14	15.0	OH ⁻	59
0.001	30.0	OAc ⁻	4.08×10^{-5}
0.001	25.0	OAc ⁻	2.43×10^{-5c}
0.001	20.0	OAc ⁻	1.03×10^{-5}
1.03	20.0	OAc ⁻	2.18×10^{-5}
2.07	20.0	OAc ⁻	2.70×10^{-5}
3.19	20.0	OAc ⁻	3.53×10^{-5}

(a) The reactions with hydroxide were carried out with a potassium phosphate buffer of pH 7.420 and a total phosphate concentration of 0.5 M. The water contained 7% methanol and 0.002% of Triton X-100, which served as the maximum suppressor. (b) Craig's value for this constant is 690 ± 30 l/mole, sec.¹⁴ (c) Craig's value for this constant is $(2.5 \pm 0.3) \times 10^{-5}$ l/mole, sec.¹⁴

Additional evidence for the formation of fluoronitrene is the large and positive entropy of activation in the hydroxide reaction: + 24.8 e.u. By contrast, we find that quantity to be - 1.4 e.u. in the acetate reaction. It has been pointed out many times^{2b} that the factors giving rise to either positive or negative volumes of activation affect the corresponding entropy changes in a similar manner.

It is noteworthy that the product is derived from two molecules of difluoramine: evidently the NF intermediate survives many collisions with the solvent and the species making up the buffer, finally to react with a molecule of HNF₂. This suggests that there must be other compounds that can be used to trap the intermediate; indeed, it seems likely that this reaction may have synthetic possibilities, and that a number of the earlier speculations¹¹ are indeed correct. Proof of capture of the intermediate is made difficult by the requirement that the trap must ignore other species such as the starting material, the product and the precursor anion. We are now exploring this aspect of the reaction, and hope to be able to report the results at a later date.

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