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CHEMICAL REACTIONS UNDER HIGH PRESSURE. IX. THE ACTIVATION VOLUMES AND MECHANISM OF THE HYDROLYSIS OF CHLORAMINES

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Much research has been devoted to the mechanism of the base promoted hydrolysis of chloramine and to that of the related Raschig reaction (1). This mechanism is now partly understood. It is clear that hydroxylamine is formed as an intermediate (2), and that this compound goes on to react with chloramine to form diimide (3), which in turn disproportionates to nitrogen and hydrazine, and which can be intercepted with reduceable organic substrates (4). It is less clear how the hydroxylamine is formed.

Two reasonable paths are permitted by the observed rate law, $R = k_2[NH_2Cl][OH^-]$: the S_N2 mechanism (direct displacement of Cl^- by OH^-), and the B1 mechanism (rapid equilibration with base to form $NHCl^-$ followed by rate controlling loss of Cl^-). Anbar and Yagil (2) found that chloramine, methylchloramine and dimethylchloramine all hydrolyze at similar rates and with similar activation energies, and they concluded that the reaction goes by way of an S_N2 path*. They

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* This interpretation is open to question, however. The methyl hydrogen atoms of dimethylchloramine do not rapidly exchange with the solvent during the hydrolysis, so that both β-elimination and the B1 mechanism are ruled for that compound; but the similarity in rates may well be coincidental, and is certainly not expected for S_N2 reactions (these for methyl and i-propyl halides differ by a factor of 10^{3-4}; see A. Streitwieser, Jr., Solvolytic Displacement Reactions, McGraw-Hill Book Co., Inc., New York, 1962; p. 12).

preferred this evidence over other observations that tended to support the alternative mechanism; rapid concurrent hydrogen exchange of the chloramine with the solvent, and a linear correlation of the rate constant with h_- (5). The B1 intermediate, NH (imidogen, also often referred to as nitrene), can be generated photochemically (6) and thus has been shown to react with ammonia to form hydrazine (7) and with water to form hydroxylamine (8). Finally, at least one instance of a solvolytic generation of a substituted nitrene is known (9). Perhaps for these various reasons, many authors continue to regard the evidence on this point as uncertain (10).

It has been shown that these mechanisms are characterized by greatly different activation volumes (11). Thus, the base promoted hydrolysis of chloroform has a large and positive ΔV^* (+16 cm^3/mole); S_N2 substitutions at a carbon atom as a rule have a small and negative ΔV^* (-7 cm^3/mole). Both of these values may be expected to change somewhat when a nitrogen rather than a carbon atom is considered. Because of the greater electronegativity of the former, the N-Cl elongation in a B1 transition state will, according to the Hammond postulate, be greater than that of C-Cl; for the same reason the central nitrogen atom in an S_N2 transition state will have a smaller positive charge than a carbon atom, and hence less electrostriction will be associated with displacement at nitrogen.

This criterion has now been applied to the hydrolysis of NH_2Cl, CH_3NHCl and $(CH_3)_2NCl$. Aqueous stock solutions of these chlorides were prepared by adding cold, dilute solutions of ammonia or the appropriate amine to an equivalent amount of sodium hypochlorite. These solutions were buffered as recommended by Metcalf (12); the analytical procedures were essentially those used by Anbar (2). All three reactions were followed to about 75% completion. The initial chloramine concentrations were about 10^{-3} M; rate constants were calculated from 4-6 determinations, and the usual corrections were made for the initial heat of compression and the compressibility of the solutions. The reproducibility varied from 5-10%; the results are given in Table I.

TABLE I

The Effect of Pressure on the Rate of Basic Hydrolysis of Several Chloramines in 1 M Aqueous NaOH

$10^4 k_2$, 1/mole sec.

Pressure, kbar	NH_2Cl[a]	CH_3NHCl[b]	$(CH_3)_2NCl$[c]
0.001	0.66	0.66	0.63
1.034	0.85	0.68	0.69
2.068	0.88	0.70	0.81
3.102	0.99	0.69	0.87
4.136	1.19	0.72	1.03
5.170	1.14	0.72	1.45
6.204	1.57	----	----

(a) At 25°. (b) At 34°. (c) At 30°.

The rate constants at zero pressure agree well with those reported (2). The activation volumes at zero pressure are -2.6, -0.6 and -1.1 ± 1 cm^3/mole for the hydrolysis of NH_2Cl, CH_3NHCl and $(CH_3)_2NCl$, respectively. We conclude that nitrenes are ruled out as intermediates in these reactions (α-elimination is excluded on the same grounds) and that all three reactions are bimolecular displacements, and confirm the remarkable observation that methyl substitution has virtually no effect on the rate of such displacement at nitrogen (13).

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