The Mechanism of Metal–Ammonia Reduction of Alkyl Halides

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WHILE reduction of organic halides (RX) by alkali metals (M) in ammonia is an old, well known reaction,[1] and one whose mechanism has received some study,[2,3] the kinetics of these reductions have never been examined. In order to study this reaction we devised an apparatus which

$$RX + 2M + NH_3 \rightarrow RH + MX + MNH_2 \qquad (1)$$

would allow the controlled addition of blue metal-in-ammonia solutions from a burette to clear ammonia solutions of a variety of organic halides in a stirred reactor. The apparatus (burette and reactor) was vacuum-jacketed and the solutions were maintained at −33°.

With all halides studied, with one exception, the reductions were stoicheiometric according to equation (1) and were extremely fast, occurring as rapidly as the metal solution was added. The blue metal solution acted as its own coloured indicator. In other words, this colour disappeared in the reactor immediately, until an equivalent of metal solution had been added; with the next drop of metal solution, the solution in the reactor became a persistent blue. Saturated chlorides, bromides, and iodides and unsaturated fluorides, chlorides, bromides, and iodides all were reduced immediately. The one exception to this reduction being extremely fast was with saturated fluorides. Neither alkyl fluorides nor polyfluoroalkanes were reduced by the metal-in-ammonia solutions.

Because the reduction (1) of alkyl halides proved to be too fast to be amenable to kinetic analysis by common techniques, competitive reactions were employed to ascertain approximate rate constants. Liberation of hydrogen from ammonium salts [equation (2)] was found

$$NH_4X + M \rightarrow NH_3 + \tfrac{1}{2}H_2 \qquad (2)$$

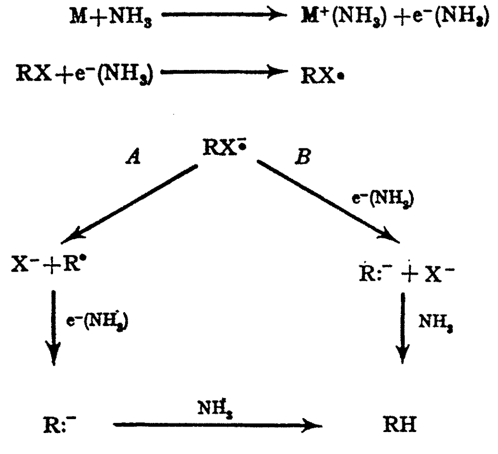
to be of the same order of magnitude in reaction rate as the reduction. Collected in the Table are data obtained for the reduction by lithium of cyclohexyl chloride and bromide in liquid ammonia in the presence of ammonium salts as competitive reactants.

The reaction of $e^-(NH_3)$ with ammonium ion is diffusion-controlled.[4] As can be seen from the data in the Table (experiments 1—4), in competition with ammonium ion the relative rate of the reaction of cyclohexyl chloride is in the range 0·5—1·0, *i.e.* the rate constant is *ca.* $10^9 < k < 10^{10}$, while for cyclohexyl bromide the relative rate is in the range 0·1—0·2, *i.e.* the rate constant is *ca.* 10^9.

Competitive reductions[a]

Experiment number	1	2	3	4	5	6
X in $C_6H_{11}X$	Cl	Cl	Cl	Cl	Br	Br
X in NH_4X	Cl	Br	Cl	Br	Cl	Br
$C_6H_{11}X$	25·3	65·8	22·5	22·8	23·4	29·0
NH_4X	24·9	65·8	44·9	45·7	46·8	58·0
Li	48·7	131·1	45·4	47·3	46·7	60·6
H_2 (produced)	11·7	21·0	18·1	18·0	21·4	25·6
C_6H_{12} (produced) ..	12·2[b]	44·2[b]	4·6[b]	5·5[b]	2·9[c]	4·5[d]

[a] All values in millimoles. [b] Sole organic product except for recovered halide. [c] Product contained 0·2 mmole of cyclohexene plus recovered halide. [d] Product contained 0·25 mmole of cyclohexene plus recovered halide.



SCHEME

A priori, two mechanisms by which the reaction might proceed are a free-radical pathway (*A*) or a carbanionic pathway (*B*) (Scheme). In a series of papers, Wepster *et al.*[3] have considered both pathways and have concluded, mainly on stereochemical grounds, that the reduction proceeds *via* pathway *B*., since "A study of data in the literature which in reason must be assumed to relate to reactions proceeding *via* free radicals leads to the conclusion that free radicals always undergo racemization before any other reaction...can take place."[3a]

Bartlett *et al.* have demonstrated that free radicals can be trapped prior to loss of stereochemical integrity;[5] the 9-decalyl radical has been successfully trapped with oxygen ($k > 3 \times 10^7 \text{M}^{-1}$ sec.$^{-1}$). Garst[6] has shown that the reaction of hex-5-enyl radical with sodium naphthalenide (e^-) has $k > 10^8 \text{M}^{-1}$ sec.$^{-1}$. The reaction of alkyl carbanions with proton donating solvents such as NH_3 should be diffusion controlled.[7] In other words, it is reasonable that the reaction of an intermediate free radical with $e^-(NH_3)$ has a rate constant of the order 10^8—10^{10}M^{-1} sec.$^{-1}$ to form a relatively configurationally stable carbanion and that protonation of the carbanion thus formed is also rapid; hence, the stereochemical results are not contrary to pathway *A*, the free radical pathway. We believe that the data of Wepster *et al.* can be interpreted as the first evidence of an optically active free radical. Experiments currently under investigation will distinguish between pathways *A* and *B*.

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[1] See, for example, the review by H. Smith, "Organic Reactions in Liquid Ammonia" Part 2, Interscience, New York, 1963, pp. 196 ff.

[2] A. Beverloo, M. C. Dielemann, P. E. Verkade, K. S. DeVries, and B. M. Wepster, *Rec. Trav. chim.*, 1962, **81**, 1033.

[3] P. E. Verkade, K. S. DeVries, and B. M. Wepster, *Rec. Trav. chim.*, 1964, **83**, (a) p. 367; (b) p. 1149.

[4] W. L. Jolly and L. Prizant, *Chem. Comm.*, 1968, 1345.

[5] P. D. Bartlett, R. E. Pincock, J. H. Rolston, W. G. Schindel, and L. A. Singer, *J. Amer. Chem. Soc.*, 1965, **87**, 2590.

[6] J. F. Garst, P. W. Ayers, and R. C. Lamb, *J. Amer. Chem. Soc.*, 1966, **88**, 4260.

[7] D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, 1965, p. 14.