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THE EFFECT OF ION PAIRING ON THE STEREOCHEMISTRY OF ELIMINATION FROM QUATERNARY AMMONIUM SALTS

J. K. Borchardt and W. H. Saunders Jr.

Department of Chemistry, University of Rochester, Rochester, New York 14627

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Recent reports have called attention to the importance of ion pairing in determining the stereochemistry of elimination from cycloalkyl tosylates and bromides.[1,2] It was suggested some time ago that syn elimination from quaternary ammonium salts might be favored by electrostatic interaction of the attacking negatively-charged base with the positively-charged leaving group.[3] We wish to report evidence bearing on this prediction.

Data on the reaction of erythro-3-hexyl-4-d-trimethylammonium iodide with various phenoxides, PhO^-M^+, in t-butyl alcohol containing 20 mole percent of dimethyl sulfoxide are recorded in the Table. It is evident that the positive ion has a marked effect on stereochemistry, but the effect is not a simple one. The strength of ion pairing in the metal phenoxides is expected to run $Li > Na > K$, which makes it appear that ion-paired phenoxide is more effective than free phenoxide in promoting syn elimination. The attraction between base and leaving group,[3] however, should clearly be more effective with free phenoxide ion.

A plausible resolution of this paradox is to be found in an ion-pair equilibrium which we suggested earlier (Equation 1) to account for unusual kinetic

$$RO^-M^+ + RNMe_3^+ + X^- \rightleftharpoons M^+X^- + RNMe_3^+ + RO^- \qquad (1)$$

Table. The Effect of Cation on Stereochemistry of Elimination from *erythro*-3-Hexyl-4-d-trimethylammonium Iodide with PhO^-M^+ in 20 mole % Dimethyl Sulfoxide in *t*-Butyl Alcohol[a]

M in PhO^-M^+	trans/cis 3-ene	trans/cis 2-ene	2-ene/ 3-ene	% syn → trans[b]
K	0.51 ± 0.03	0.47 ± 0.03	3.0 ± 0.1	34 ± 1
Na	0.48 ± 0.03	0.55 ± 0.03	3.2 ± 0.1	55 ± 2
Li	0.44 ± 0.04	0.78 ± 0.02	4.1 ± 0.1	74 ± 2
NMe_4^+ + K[c]	0.48 ± 0.04	0.50 ± 0.02	3.2 ± 0.1	67 ± 3

[a] Reaction was carried out for 24 hr at 135° C, substrate concentration 0.005 M, base concentration 0.25 M. [b] Calculated as before (ref. 5) from mass spectrometric deuterium analysis on the *trans*-3-hexene + *trans*-2-hexene fraction. Separation of the product isomers was done by glpc on a 20-ft column of 20% adiponitrile on Chromosorb P-AW followed by a 12-ft column of 20% silver nitrate in ethylene glycol on Chromosorb P-AW. Each calculation uses the average of two or more independent determinations of olefin composition and deuterium content. $(k_H/k_D)_{anti}$ was assumed to be 3.0. [c] Made by adding a 10% excess of tetramethylammonium iodide to 0.25 M potassium phenoxide.

features of eliminations from quaternary ammonium salts with sodium *t*-butoxide in *t*-butyl alcohol.[4] Conductivity data provided independent support for the assumption that the sodium *t*-butoxide was largely ion paired while the quaternary ammonium salt was largely dissociated.

The effect of the cation on the equilibrium of Equation 1 depends on the relative stabilities of the two ion pairs RO^-M^+ and M^+X^-. The addition of tetramethylammonium iodide to the reaction mixture, however, should clearly shift the equilibrium to the right, and comparison of lines 1 and 4 in the Table shows a substantial *increase* in *syn* elimination. This result is in agreement with the expectation that RO^- should more effectively promote *syn* elimination than RO^-M^+.[3] We thus conclude that the stabilities of M^+X^- must control the position of equilibrium for the three metal phenoxides, and that the concentration of free phenoxide increases in the order K < Na < Li.

Though the ion-pairing effect can clearly produce a substantial change in the extent of *syn* elimination, it is interesting that the results do not follow the previously-noted trend of increasing *trans*-ene with increasing *syn* elimination.[6] The changes in the *trans*/*cis* ratios in the Table are barely beyond experimental error, with one exception. This would suggest that ion-pairing effects are not the primary cause of the concomitant increases in *syn* elimination and *trans* olefin that result from such variations as the change from an *n*-alkoxide in an *n*-alcohol to a *t*-alkoxide in a *t*-alcohol.[5]

The present results are in striking contrast to those reported on eliminations from 5-decyl tosylate, where changes in ion pairing markedly change *trans*/*cis* ratios, but have little effect on the propensity for *syn* elimination.[7] The reasons for the relative insensitivity of our *trans*/*cis* ratios to changes in ion pairing are not immediately obvious, but the phenomenon does provide a potential tool for distinguishing changes in stereochemistry of ammonium-salt eliminations due to base strength or solvation effects from those due primarily to ion pairing. The changes in stereochemistry with the nature of the alkoxide and alcohol are probably caused mainly by base-strength effects[8] rather than ion pairing for the relationship between increasing *syn* elimination and increasing *trans*/*cis* ratio is followed.[6]

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