Classical Carbonium Ions. Part 10.[1] Selectivity in the Solvolytic Products from 1-Adamantyl Derivatives in Aqueous Ethanol

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The relative proportions of adamantan-1-ol and its ethyl ether obtained when 1-adamantyl bromide, picrate, 2,4-dinitrophenolate, and toluene-*p*-sulphonate undergo solvolysis at 100 °C in aqueous ethanol were measured at four solvent compositions. Differences between the four substrates were observed, implying ion-pair involvement, and variations with solvent composition which are attributed to differences in the ability of the various ion-pairs to select a molecule of water or of ethanol in forming a solvent-separated ion-pair.

SOME time ago[2] we analysed the reaction products obtained when four derivatives of adamantan-1-ol underwent solvolysis at 100 °C in '50%', '80%', '90%', and '95%' aqueous ethanol, in the presence of 0.15M-potassium acetate as a buffer, which was necessary to prevent equilibration. The molar product-ratio, adamantanol/adamantyl ethyl ether, equal to the reaction-rate ratio with water and ethanol, was divided by the molar solvent-ratio, water/ethanol to give a figure expressing the selectivity of the substrate between these two solvents: $S = k_w/k_E$. The quantity S proved to be a function both of solvent composition and leaving group, and the variation with leaving group clearly implicates ion-pairs, rather than free cations, as the species mainly involved in the product-forming step of the reaction. Our results, at the time hard to interpret or relate to other work, have now been provided with a context in papers by Pross *et al.*,[3] whose nomenclature and general theoretical framework we adopt. Coincidentally our work can be compared directly with that of Karton and Pross[3] in the case of 1-bromoadamantane at 100 °C in the three least aqueous systems; only the buffering agents used are different. Our Table and Table 2 of ref. 3 both show a preference for reaction with water by a factor of *ca.* 2, little affected by solvent composition. Both tables show good internal consistency, but the numerical values differ somewhat, by rather more than estimated experimental precision, which is about the same. Probably there are different minor systematic errors in, for example, the making up of solvent mixtures, the measurement of response factors in g.l.c., and the presence of more ethanol than water in the gas phase above the reaction mixture, *etc.*, which imply that each set of figures can be used to compare one substance with another with better accuracy than is available in comparing results from one study with those from the other.

Solvolysis products from 1-adamantyl-X in aqueous ethanol

Solvent			*S* values			
v/v	mol % H_2O	*R*	X = Br	OTs	OPic	ODin
50	76.5	0.625	2.06	1.68	1.49	1.51
80	44.8	1.43	2.10	2.13	1.73	1.85
90	26.2	1.89	2.23	2.61	1.96	1.99
95	14.6	2.16	2.22	2.52	1.96	2.13
		1 (calc)	2.1	1.9	1.6	1.7
slope of *S versus R*			0.1	0.6	0.3	0.4
ρ			0.94	0.97	0.98	0.998

$S = k_w/k_E$. $R = \gamma_{H_2O}/\gamma_{EtOH}$, where γ = activity coefficient at 60 °C; ρ = correlation coefficient.

Karton and Pross examined only two compounds of type 1-adamantyl-X, where X = Cl and Br; no significant difference was observed. We, however, observed considerable differences between X = Br, X = OTs,[4] X = $O{\cdot}C_6H_2(NO_2)_3$,[4] and X = $OC_6H_3(NO_2)_2$.[5] (These compounds reacted at very different rates, the last two, for example, having half-lives of *ca.* 3 min, and 30 h at 100 °C in '80%' ethanol. It was necessary to know whether the observed selectivity values were sensitive to temperature, as the more reactive compounds [X = OTs and $OC_6H_2(NO_2)_3$] would presumably solvolyse mainly at temperatures significantly lower than 100 °C, during the warming-up period. Even a reduction to 20 °C, in the case X = OTs, however, changed S by little more than the experimental precision; and Karton and Pross report a similar insensitivity of S to temperature.) Whereas the bromide (and chloride[3]) gave S values which varied little with solvent composition, the other three substrates showed a marked tendency for selectivity to increase with decreasing water content. There is, indeed, a good linear relationship between S and the activity-coefficient ratio R ($= \gamma_{H_2O}/\gamma_{EtOH}$); we used values reported[6] for 60 °C, but as only the general trend is relevant, some change in R with temperature would not matter. We assume, with Pross and following much modern work on solvolysis generally, that a bridgehead system, unable to react by substitution with inversion at the contract ion-pair stage of ionisation, will probably give products by collapse of a solvent-separated ion-pair. One could roughly interpret the value of S at $R = 1$ as measuring the tendency to prefer a water to an ethanol molecule in the formation of the latter, corrected for the relative probabilities of collapse and of extrusion of solvent and return to starting-material. The slope of the S *versus* R plot could be taken to measure the need, during the formation of the solvent-separated ion-pair, to isolate the interstitial solvent molecule from the rest of the solvent. For X = Br this is slight (*i.e.* the interstitial molecule remains associated, through the pre-existing hydrogen-bond network, with other solvent molecules); for X = OTs it is considerable, for X = $OC_6H_2(NO_2)_3$ or $OC_6H_3(NO_2)_2$ it has intermediate values. This order accords well with the steric effects of the groups concerned, and the interpretation proposed is therefore reasonable. Other correlations with, *e.g.*

Winstein–Grunwald Y values[7] would be possible; the topic is discussed in ref. 2, but a more extensive set of data than our Table contains, of no less precision, would probably be needed. In particular, the work of Harris, Becker, Fagan, and Walden[8] has shown that at a constant solvent composition the ratio S varied considerably with the *para*-substituent in a series of 2-adamantyl arenesulphonates, with sterically constant leaving groups. Here, the problem lies in separating selectivity effects similar to those observed in the 1-adamantyl case from variations in the inversion/retention ratio, since 2-adamantyl compounds react in comparable degree by both processes;[9] in substitution with inversion, S values are <1.

We may compare the low selectivity between water and ethanol of the 1-adamantyl picrate and the 1-adamantyl dinitrophenolate ion-pairs in product formation with the low Winstein–Grunwald m-values[7] observed in the corresponding solvolysis rates. These similarly imply a smaller difference between water and ethanol in the first phase of the reaction, leading to the formation of ion-pairs from covalent starting material, than in the cases where the leaving group is halide or arenesulphonate.

Systems with less than 50% ethanol (v/v) cannot conveniently be used in such experiments because of solubility problems, but if they could, extrapolation allows the hypothesis that the toluenesulphonate, picrate, and dinitrophenolate would show a similar and low selectivity. This is the result predicted for reaction *via* free carbonium ions, and the involvement of free ions, or of ion-pairs so effectively solvated that they approach free cations and anions, is not an absurd suggestion for a tertiary system in a very polar solvent. The results for 1-bromoadamantane, however, do not appear to approach this limit, and firmly require the familiar solvent-separated ion-pair throughout and beyond the solvent range investigated.

EXPERIMENTAL

The 1-adamantyl derivatives (2 mg) were prepared as described,[4,5] the 1-adamantyl toluenesulphonate being largely freed from adamantan-1-ol by rapid chromatography on alumina. A correction was made for the small adamantan-1-ol content by solvolysis in dry ethanol and measurement of the alcohol/ether ratio—typically this was 2%. Solvolysis for periods of *ca.* 10 half-lives (checked by rough g.l.c. measurements) was carried out in mixtures (100 μl) of water and ethanol, 0.15M in potassium acetate, in sealed ampoules at 100 °C. Five 1 μl samples were taken from each ampoule after cooling, and injected directly onto a 1 m stainless-steel column of 12% 'Geo 100' (a glycerol–ethylene oxide condensate similar to Carbowax) on Chromosorb, maintained at 140 °C in a Perkin-Elmer F11 gas chromatograph. With an inlet pressure of 1 atm excess, retention-times were 2 and 4 min. The molar response factor, determined in the same way by heating a weighed mixture of adamantan-1-ol and its picrate in dry ethanol until solvolysis of the latter was complete, was 1.023 (ether) : 1(alcohol), very close to that calculated from carbon content. All peak areas were assumed to be proportional to (height × retention time); replicate measurements were averaged; standard deviations implied a standard error of ± 0.07 for the ratios in the Table.

The buffer was necessary, as in the presence of toluene-*p*-sulphonic acid equilibration of adamantan-1-ol + ethanol with the ethyl ether + water occurred, the equilibrium constant (*ca.* 1.8, favouring alcohol + ethanol) being effectively independent of solvent composition.

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