Solvolysis Mechanisms for Benzyl Substrates

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Summary The solvolysis of *p*-methoxybenzyl bromide in 80% v/v dioxan–water involves trappable carbonium ion intermediates as shown by increases in rate and α-D isotope effects with increasing perchlorate ion concentration and reductions in rate and α-D isotope effect with increasing concentrations of common ion salt.

In this paper evidence is presented that *p*-methoxybenzyl bromide solvolyses (in 80% v/v dioxan–water) by a mechanism that involves carbonium ion intermediates. In contrast, nucleophilic reactions of benzyl systems[1–5] and formaldehyde acetals[6,7] have been suggested to involve 'loose' S_N2 transition states where the 'looseness' or 'tightness' depends on the electronic properties of the substituent in the benzene ring.

The most direct method for demonstrating the presence of a reactive intermediate is the trapping of that intermediate as in the hydrolysis of acetophenone acetals,[2] the 'special' salt effect,[8,9] and common ion rate depression in ionization reactions.[9,10] Our earlier results[8,10] suggest that α-deuterium isotope effects coupled with salt effects on reaction rate are powerful tools in evaluating mechanisms.

Shiner[11] has suggested that the *maximum* α-D effect expected in the solvolysis of an alkyl bromide is 1·125 and that this effect is expected if the transition state does not involve partial covalent bonding to the nucleophile or the leaving group.

Both the rate and α-D isotope effect for *p*-methoxybenzyl bromide increase with perchlorate ion concentration in 80% v/v dioxan–water (Figure). This isotope effect reaches a maximum in the region 0·4 and 0·5M $LiClO_4$ (k_H/k_D = 1·123 and 1·120, respectively). Added common ion salt (LiBr) reduces the solvolysis rate and the α-D isotope effect (Figure). Thus, in the presence of LiBr, k_H/k_D = 1·060, which is significantly less than the maximum.

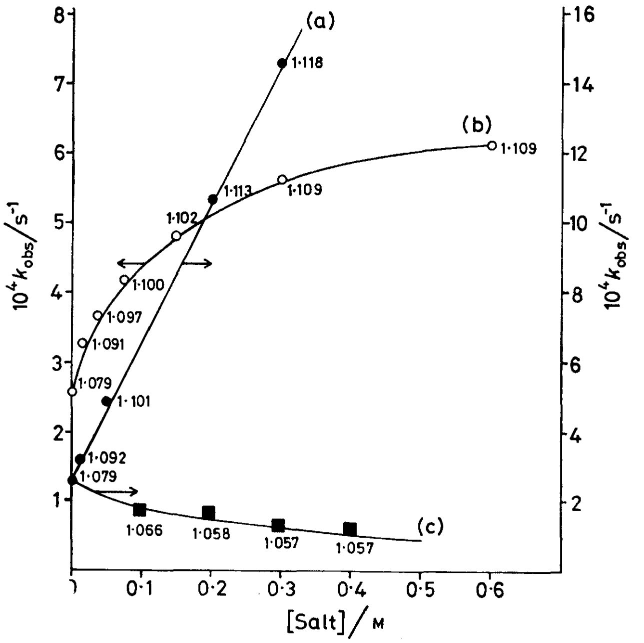

FIGURE. Rates of solvolysis and α-deuterium isotope effects of *p*-methoxybenzyl bromide in 80% v/v dioxan–water as a function of (a) $LiClO_4$, (b) Bu_4NClO_4, and (c) LiBr concentrations at 25 °C.

The solvolysis of benzyl bromide in 0—50% v/v dioxan–water furnishes very low α-deuterium isotope effects (1·018—1·005) and this is consistent with a rather tight S_N2 transition state.[†][12]

The stability of the carbonium ion intermediate dictates the mechanism for solvolysis of these two substrates. The

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[†] Isotope effects are averages of 2—5 determinations and have standard deviations of ± 0·005.

p-methoxybenzyl carbonium is sufficiently stable so that exchange with perchlorate salts of one or more of its ion pairs is rate-determining (perchlorate salt effects). A solvent-equilibrated free carbonium ion is also indicated from the common ion rate depression results.[13]

By contrast, the unsubstituted benzyl carbonium ion is so unstable that an enforced concerted displacement results.

Interestingly, the solvent isotope effects for benzyl bromide in water and *p*-methoxybenzyl bromide in 80% dioxan–water are nearly the same [$k(H_2O)/k(D_2O) = 1{\cdot}38$ and 1·37, respectively] although these substrates hydrolyse by different mechanisms.

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