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(9) It is not obvious from examination of molecular models that this specificity reflects a preferential rotational orientation[6] of the acyl side chain. An interesting alternative possibility presently being examined is that it results from a stereoelectronic effect.

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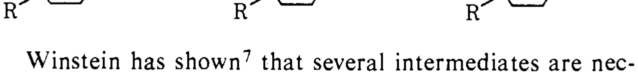
Deuterium Isotope Effects in the Solvolysis of Benzal Chlorides. I. α-Deuterium Isotope Effects and Salt Effects in the Solvolysis of *p*-Methoxybenzal Chloride in Dioxane–Water Mixtures

Sir:

Shiner has proposed that α-deuterium (α-D) isotope effects can be used as a very sensitive guide to transition state structure in solvolysis reactions.[1] He has shown that α-D effects are a function of leaving group (OR ≈ F > Cl > Br > I) and mechanism (*i.e.*, variable and predictable according to which step in the overall solvolysis scheme is rate determining).

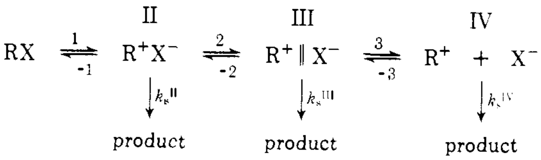
In this communication we show how the variation of the α-D effect with the nature and concentration of added salt can be a powerful tool in the elucidation of the nature of the rate-determining step in solvolysis reactions. To our knowledge this is the first application of α-D isotope effects in conjunction with salt effects to problems in solvolysis.

The kinetics and mechanism of the hydrolysis of benzal chlorides has been the subject of numerous reports.[2-6] All of the available evidence points to a carbonium ion intermediate in these solvolyses. For example, ρ^+ calculated from published data[3] is −5.2 and the rate of hydrolysis is unaffected[4-6] by external nucleophiles thus suggesting that bimolecular SN2 processes are unimportant.



Winstein has shown[7] that several intermediates are necessary to explain certain kinetic observations. For example,[8] the rate at which optically active *threo*-3-*p*-anisyl-2-butylbromobenzene sulfonate racemizes, k_{rac}, exceeds the rate at which solvolysis product is produced, k_t. While addition of certain "special" salts such as $LiClO_4$ can narrow the gap between k_{rac} and k_t, it cannot be eliminated. Presumably, one of these intermediates, the solvent separated ion pair (III, Scheme I), is trapped by anion exchange with perchlorate while II is not. Thus some, but not all, ion pair return can be eliminated. Addition of perchlorate salts has been shown to give rise to this "special" salt effect in several instances.[7-11] Azide ion has also been shown to be an effective scavenger of solvent-separated ion pairs in the solvolysis of α-*p*-anisylethyl-*p*-nitrobenzoate.[12] This system is closely related to that of the present study. Because the perchlorate solvent-separated ion pair cannot return to starting material, the substantial rate increases observed by the addition of small amounts of perchlorate salts have their origin in part in eliminating return from III.

Scheme I



Recently Shiner[1] has used the Winstein scheme in an evaluation of α-D isotope effects in solvolysis. In summary, from a number of different examples he has concluded that maximum α-D effects are expected for reaction whose rate-limiting step is either k_2 or k_3. For reactions whose rate-limiting step is k_1 or any of the capture steps (k_s^{II}, k_s^{III}, or k_s^{IV}) the observed α-D effect is reduced to about 60–80% of its maximum value. This, of course, is due to the higher zero point energy of the transition state for these processes because of the "stiffer" force constants for the α-CH bond if a leaving group or nucleophile is partly bound to the carbonium ion center.

Our results for the α-D effect in *p*-methoxybenzal chloride in various dioxane-water mixtures are given in Table I.

For Cl as the leaving group, Shiner[13,14] has shown that the maximum α-D effect expected is 1.15–1.16. The results reported in Table I show that α-D effects in benzal chlorides can be considerably larger. This is not too surprising since the ground and transition state structures for these hydrolyses are very different than Shiner's system (α-phenylethyl halides). However, there is a marked reduction in the α-D isotope effect in the less aqueous solvents. We interpret this change as signaling the incursion of some rate-limiting attack on III (k_s^{III}) in the less aqueous dioxane-water mixtures. Additional support for this interpretation comes from a study of salt effects and isotope effects in 85% aqueous dioxane.

In both 75 and 85% dioxane, the rate of hydrolysis is increased by addition of $LiClO_4$. Rate *vs.* [$LiClO_4$] plots are

Table I. α-D Isotope Effects for the Hydrolysis of *p*-Methoxybenzal Chloride in Dioxane–Water Mixtures at 25

% dioxane[a]	k_H/k_D[b]
65	1.20 ± 0.02
75	1.178 ± 0.004
80	1.142 ± 0.005
85	1.127 ± 0.002
90	1.132 ± 0.008

[a] Volume per cent (*e.g.*, 65% dioxane = 65 ml dioxane + 35 ml water). [b] Determined spectrophotometrically by monitoring the appearance of *p*-methoxybenzaldehyde at 275 nm. Except for 65% dioxane each result is an average of about four isotope effects determined by running two H's and two D's at the same time in a Cary 16K at 25.0 ± 0.1°. The errors are standard deviations. From the results reported here and other unpublished work, we estimate the standard error of most isotope effects determined in this way is ±0.005. Because of the rapid rate of hydrolysis, the 65% dioxane isotope effect is the average of 11 H runs compared to 11 D runs.

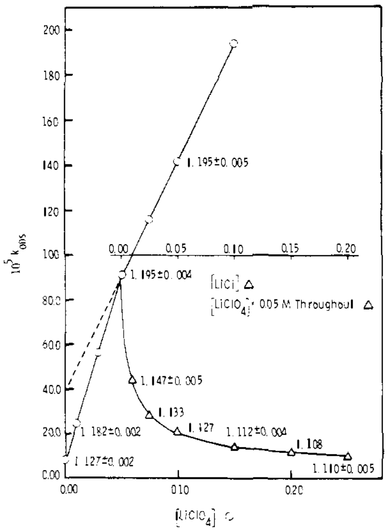


Figure 1. Plot of k *vs.* [LiX] for solvolysis of *p*-methoxybenzal chloride in 85% aqueous dioxane. ○ represents points for $LiClO_4$ in 85% dioxane, while △ represents points for varying LiCl concentration in 85% dioxane containing a constant concentration of $LiClO_4$ [0.05 *M*]. The numbers recorded next to each point refer to the α-D isotope effect determined under those conditions. Analysis of the special salt effect curve using the Winstein equation gives $k^{\circ}_{ext}/k^{\circ} = 4.4$ and $b = 26.5$.

characteristic of systems showing the "special" salt effect, although the separation of normal and "special" salt effects is not as pronounced as other cases.[8-11] (The results in 85% dioxane are displayed in Figure 1.) Since perchlorate has been shown to effectively prevent return (by ion pair exchange) of III, it is very interesting to examine the α-D effect as a function of $[LiClO_4]$. As is evident from Figure 1, addition of 0.01 *M* $LiClO_4$ increases the rate of hydrolysis (2.7-fold) and also increases the α-D effect from 1.127 ± 0.002 to 1.182 ± 0.002. This result suggests that most, but not all, return from III has been eliminated. Addition of 0.05 *M* $LiClO_4$ results in an even greater rate enhancement (8.6-fold) and an even larger α-D effect, 1.195 ± 0.004. However, while 0.10 *M* $LiClO_4$ increases the hydrolysis rate even more, there is no further change in the α-D effect, 1.195 ± 0.005. Thus it would appear that all kinetically significant return from III is eliminated by the addition of 0.05 *M* $LiClO_4$ and k_2 now becomes rate limiting.[15,17]

Similar results are obtained in 90% dioxane. Addition of 0.10 *M* $LiClO_4$ increases solvolysis rate (40-fold) and the α-D effect increases from 1.132 ± 0.008 to 1.204 ± 0.004. Interestingly, the same maximum α-D effect (1.199 ± 0.008) is observed for the hydrolysis of the much less reactive benzal chloride in water.

It should be noted here that addition of 0.15 *M* LiCl to 85% dioxane results in only a 13% rate reduction and therefore return from dissociated ions is relatively unimportant in this solvent.[18] However, the α-D effect is reduced slightly (1.114 ± 0.001) showing that some return from IV does occur.

While addition of LiCl to 85% dioxane does not result in substantial rate depression, addition of LiCl to this solvent containing 0.05 *M* $LiClO_4$ results in substantial *induced* depression.[7] Thus, addition of 0.10, 0.15, and 0.20 *M* LiCl to 0.05 *M* $LiClO_4$ (Figure 1) in 85% dioxane results in rate depressions of 5.3-, 6.4-, and 7.6-fold, respectively. The α-D effect in this range is constant and equal to 1.111 ± 0.004 (Figure 1). This then corresponds to the α-D effects expected for rate-limiting attack of solvent on III (k_s^{III}) to produce solvolysis product.

Because further additions of LiCl were not possible for solubility reasons, the limiting rate at high Cl^- could not be obtained. However, the rate in 0.20 *M* LiCl and 0.05 *M* $LiClO_4$ is only 29% greater than the rate observed in 0.15 *M* LiCl alone. Thus, a substantial part of the rate enhancement observed for $LiClO_4$ can be eliminated with additional LiCl.

We are continuing these and related investigations with a view toward establishing the usefulness of this technique in problems of solvolysis mechanisms.

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(18) This is to be compared to a 2.7-fold rate reduction observed in 75% dioxane containing 0.15 *M* LiCl. Thus, in this solvent return from dissociated ions is quite important.

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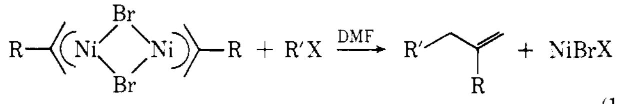
Reaction of π-Allylnickel Bromide Complexes with Organic Halides. Stereochemistry and Mechanism

Sir:

The reaction of π-allylnickel halide complexes with organic halides (eq 1) has been known for several years[1] and



(1)

is finding increased use in organic synthesis.[2] Since this reaction proceeds equally well with alkyl, aryl, and vinyl halides, it is clearly not an S_N2 process. We present herein evidence that this reaction proceeds via a radical chain mechanism.

To examine the stereochemistry[3] of this coupling reac-