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Deuterium Isotope Effects in the Solvolysis of Benzal Chlorides. 4. Salt Effects and α-Deuterium Isotope Effects

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Abstract: The effect of $LiClO_4$, Bu_4NClO_4, LiCl, Bu_4NCl, and mixtures of these salts on the rate and α-deuterium isotope effects are reported for the solvolysis of *p*-methoxybenzal chloride in 75% and 85% (v/v) dioxane–water mixtures at 25 °C. In the less polar of these solvents (85D), k_{ext}^0 values from the Winstein equation for the two salts $LiClO_4$ and Bu_4NClO_4 are the same, and very little common-ion rate depression is observed although induced common-ion rate depression is observed. In the more polar solvent (75D), extensive common-ion rate depression is observed for both LiCl and Bu_4NCl. k_{ext}^0 values for Bu_4NClO_4 and $LiClO_4$ are not the same in this more polar solvent. These results are interpreted by using Winstein's ion-pair mechanism for this solvolysis.

Introduction

At the present time, positive, noncommon-ion salt effects (i.e., $k_{salt} > k_0$) are expected for ion producing reactions as suggested by Ingold.[1] Operationally Winstein has shown[2] that in solvolysis reactions in nonpolar solvents k_{obsd} can be expressed as a linear function of added salt (eq 1).

$$k_{obsd} = k^0(1 + b[\text{salt}]) \qquad (1)$$

In certain systems[3-6] it has been known for quite a long time that common-ion salts depress the rate at which solvolysis product is produced. Much of this earlier, oft-cited work has been summarized.[6,7]

For these systems it was suggested that the kinetically free carbonium ion intermediate would be prevented from reacting with solvent by this simple "mass law" effect (Scheme I). Subsequent to this, Winstein showed that ion pairs as well as free carbonium ions are involved in many solvolyses[6-8] (Scheme II). Indeed, Shiner has used Winsteins scheme in the interpretation of α-deuterium (α-D) isotope effects in solvolysis mechanisms.[9] It seems appropriate here to summarize some of Shiner's conclusions. (1) α-Deuterium isotope effects are primarily a measure of the net change between initial and transition states of the bending force constant of the α-CH bond. (2) For solvolyses involving rate-determining dissociation of ion pairs (k_2 or k_3, Scheme II), maximum α-D effects characteristic of the leaving group but reasonably independent of carbonium structure are expected. (3) For solvolyses involving rate-determining formation of ion pairs or rate-determining attack of solvent on carbonium ions or ion-pair intermediates, the expected α-D effect is 60–80% of this characteristic maximum value. (4) For solvolyses which are of the S_N2 type, α-D effects nearer to unity are expected.

Scheme I

$$RX \underset{-1}{\overset{1}{\rightleftharpoons}} R^+ + X^- \xrightarrow{2} ROH + H^+ + X^-$$

Scheme II

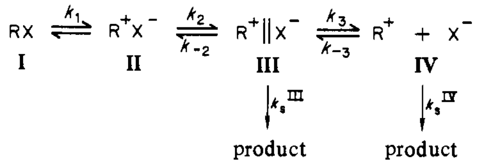

Table I. Hydrolysis of *p*-Methoxybenzal Chloride in the Presence of Common-Ion Salts, Rates, and α-Deuterium Effects in 85% Dioxane–15% H_2O (v/v) at 25 °C

salt (concn, M)	10^5k_{obsd}, s^{-1}	k_H/k_D[a]
none	8.96 ± 0.18	1.127 (2)
LiCl (0.10)	8.17 ± 0.04	
LiCl (0.15)	7.80 ± 0.06	1.114 (1)
Bu_4NCl (0.05)	8.79 ± 0.07	1.131
Bu_4NCl (0.10)	8.77 ± 0.10	1.130
Bu_4NCl (0.20)	8.54 ± 0.02	1.125
Bu_4NCl (0.30)	8.48 ± 0.07	1.127
Bu_4NCl (0.40)	8.26 ± 0.07	1.127

[a] Average isotope effect for all Bu_4NCl runs: k_H/k_D = 1.128 (6).

Table II. Rates of Hydrolysis at 25 °C and α-Deuterium Isotope Effects for *p*-Methoxybenzal Chloride in 85% (v/v) Dioxane-H_2O, $LiClO_4$

[$LiClO_4$], M	10^5k_{obsd}, s^{-1}	k_H/k_D[a]
0.00	8.96 ± 0.18	1.127 (2)[
0.01	24.6 ± 0.8	1.182 (2)
0.03	56.0 ± 0.2	
0.05	90.9 ± 0.5	1.195 (4)
0.075	116 ± 0.4	
0.100	142 ± 1	1.195 (5)
0.150	194 ± 1	

[a] Average isotope effect for greater than 0.05 M $LiClO_4$, k_H/k_D = 1.195 (5).

This paper presents results a portion of which were published in preliminary form earlier.[10] In this work, we include data for two solvents [85% (v/v) dioxane–15% H_2O (85D) and 75% (v/v) dioxane–25% H_2O (75D)] with several salts: $LiClO_4$, LiCl, Bu_4NClO_4, and Bu_4NCl.

Results

Addition of common-ion salts such as LiCl and Bu_4NCl only slightly reduces the solvolysis rate of *p*-methoxybenzal chloride

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Table III. Rates of Hydrolysis at 25 °C and α-Deuterium Isotope Effects for *p*-Methoxybenzal Chloride in 85% (v/v) Dioxane-H_2O, Bu_4NClO_4

$[Bu_4NClO_4]$, M	10^5k_{obsd}, s^{-1}	k_H/k_D[a]
0	8.96 ± 0.18	1.127 (2)
0.01	13.1 ± 0.2	1.154 (5)
0.025	18.4 ± 0.2	1.168 (6)
0.050	25.1 ± 0.2	1.179 (2)
0.100	35.3 ± 0.3	1.191 (3)
0.180	47.9 ± 0.7	1.199 (4)
0.250	54.9 ± 0.4	1.204 (7)
0.320	60.7 ± 0.3	1.209 (3)
0.400	65.6 ± 0.7	1.209 (2)
0.500	72.2 ± 0.3	1.207 (6)

[a] Average isotope effect for greater than 0.18 M Bu_4NClO_4: $k_H/k_D = 1.206$ (4).

Table IV. Special Salt Effect Parameter for *p*-Methoxybenzal Chloride in 85% (v/v) Dioxane-Water at 25 °C

salt	$10^3 \times [salt]_{1/2}$, M	b_s	$10^5k_{ext}^0$, s^{-1}	k_{ext}^0/k_0
$LiClO_4$	9.4	27.1	38.3 ± 0.2	4.27
Bu_4NClO_4	46	1.78	38 ± 1	4.3

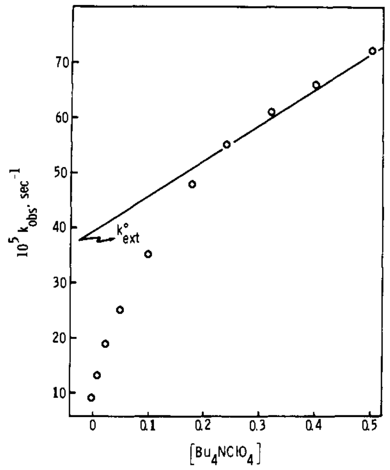


Figure 1. k_{obsd} vs. $[Bu_4NClO_4]$ in 85% (v/v) dioxane-15% H_2O; k_{ext}^0 is obtained from the linear portion of the figure.

(I) in 85D (Table I). The α-D isotope effect is virtually unchanged from its value in 85D with no added salt suggesting a commonality of mechanism. Since these α-D isotope effects are some 60% of the maximum expected for benzal chlorides (vide supra), we suggest that attack of solvent on III (Scheme II) is nearly wholly rate determining in 85D with or without chloride salts (Shiner's case 3 in ref 9).

Addition of $LiClO_4$ or Bu_4NClO_4 to 85D results in substantial increases in solvolysis rate for I (Tables II and III). A plot of k_{obsd} vs. $[LiClO_4]$ was given earlier.[10] A similar plot for Bu_4NClO_4 is given here (Figure 1). A summary of the special salt effect[6,7] parameters for **1** in 85D for $LiClO_4$ and Bu_4NClO_4 is given in Table IV. Here $[salt]_{1/2}$ is the salt concentration required to produce half of the special salt effect (i.e., the salt concentration which would furnish the rate numerically equal to the average of k_0 and k_{ext}^0), and b_s is the normal salt effect from the Winstein equation (eq 1) obtained from the linear portion of Figure 1 extrapolated to zero salt concentration.

While there is very little common-ion rate depression in 85D, virtually the entire rate enhancing effect of perchlorate salts is eliminated by the addition of common-ion salts. Our results for addition of LiCl or Bu_4NCl to an 85D solution containing a fixed concentration of $LiClO_4$ (0.05 M) or Bu_4NClO_4 (0.10 M) are given in Tables V and VI. The α-D isotope effects are tabulated along with hydrolysis rates for these various salt conditions. For high concentrations of chloride salts the α-D effect appears to be

Table V. Hydrolysis of *p*-Methoxybenzal Chloride in 85% (v/v) Dioxane-Water at 25 °C. Induced Common-Ion Rate Depression (LiCl, 0.05 M $LiClO_4$ throughout)

[LiCl], M	10^4k_{obsd}, s^{-1}	k_H/k_D[a]
0.00	9.09 ± 0.05	1.195 (4)
0.01	4.42 ± 0.04	1.147 (5)
0.025	2.81 ± 0.01	1.133
0.05	2.10 ± 0.01	1.127
0.10	1.45 ± 0.03	1.112 (4)
0.15	1.21 ± 0.01	1.108
0.20	1.01 ± 0.03	1.100 (5)

[a] Average isotope effect for concentrations greater than 0.025 M LiCl: $k_H/k_D = 1.111$ (4).

Table VI. Hydrolysis of *p*-Methoxybenzal Chloride in 85% (v/v) Dioxane-Water at 25 °C. Induced Common-Ion Rate Depression (Bu_4NCl, 0.10 M Bu_4NClO_4 throughtout)

$[Bu_4NCl]$, M	10^5k_{obsd}, s^{-1}	k_H/k_D[a]
0.00	35.3 ± 0.3	1.191 (3)
0.005	26.5 ± 0.5	1.154 (1)
0.020	17.0 ± 0.1	1.129
0.050	12.5 ± 0.1	1.127
0.10	10.4 ± 0.1	1.128
0.20	8.62 ± 0.1	1.133
0.30	7.89 ± 0.1	1.122
0.40	7.00 ± 0.09	1.124

[a] For Bu_4NCl concentrations greater than 0.02 M: $k_H/k_D = 1.127$ (4).

Table VII. Hydrolysis of *p*-Methoxybenzal Chloride in 75% (v/v) Dioxane-H_2O. Common-Ion Rate Depression (LiCl)

[LiCl], M	10^4k_{obsd}, s^{-1}	k_H/k_D[a]
0.00	15.8 ± 0.1	1.178 (4)
0.01	10.1 ± 0.1	1.140 (6)
0.05	7.43 ± 0.03	1.123
0.10	6.31 ± 0.04	1.124
0.15	5.65 ± 0.01	1.120
0.20	5.11 ± 0.09	1.118
0.40	3.55 ± 0.09	1.123

[a] Average isotope effect for greater than 0.05 M LiCl: $k_H/k_D = 1.121$ (4).

Table VIII. Hydrolysis of *p*-Methoxybenzal Chloride in 75% (v/v) Dioxane-H_2O. Common-Ion Rate Depression (Bu_4NCl)

$[Bu_4NCl]$, M	10^4k_{obsd}, s^{-1}	k_H/k_D[a]
0.00	15.8 ± 0.1	1.178 (4)
0.01	9.46 ± 0.05	1.128 (5)
0.05	6.92 ± 0.08	1.120
0.10	6.1 ± 0.1	1.117
0.20	5.05 ± 0.05	1.116
0.30	4.4 ± 0.1	1.118
0.40	3.85 ± 0.03	1.120

[a] Average isotope effect for greater than 0.05 M Bu_4NCl: $k_H/k_D = 1.118$ (4).

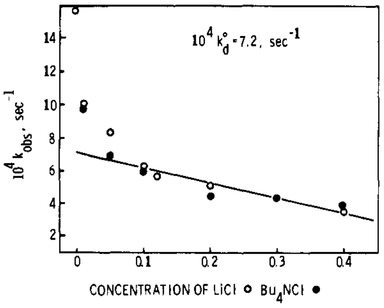


Figure 2. Common-ion rate depression for solvolysis of *p*-methoxybenzal chloride in 75% (v/v) dioxane–25% H_2O at 25 °C: ○, LiCl; Bu_4NCl, ●.

Table IX. Rates of Hydrolysis of *p*-Methoxybenzal Chloride and α-Deuterium Isotope Effects in 75% (v/v) Dioxane–Water at 25 °C ($LiClO_4$)

$[LiClO_4]$, M	$10^3 k_{obsd}$, s^{-1}	k_H/k_D
0.00	1.58 ± 0.01	1.178 (4)
0.01	3.12 ± 0.01	1.188 (7)
0.02	3.94 ± 0.06	
0.03	4.71 ± 0.04	
0.04	5.48 ± 0.03	
0.05	6.01 ± 0.12	
0.075	7.54 ± 0.05	
0.100	8.95 ± 0.11	

Table X. Rates of Hydrolysis of *p*-Methoxybenzal Chloride and α-Deuterium Isotope Effects in 75% (v/v) Dioxane–Water at 25 °C (Bu_4NClO_4)

$[Bu_4NClO_4]$, M	$10^3 k_{obsd}$, s^{-1}	k_D/k_H
0.00	1.58 ± 0.01	1.178 (4)
0.01	2.23 ± 0.04	1.182 (5)
0.025	2.71 ± 0.03	
0.050	3.34 ± 0.06	
0.10	4.34 ± 0.04	
0.20	5.11 ± 0.03	
0.30	5.39 ± 0.12	
0.40	5.70 ± 0.06	

Table XI. Special Salt Effect Parameters for *p*-Methoxybenzal Chloride in 75% (v/v) Dioxane–Water at 25 °C

salt	$10^3 \times [salt]_{1/2}$, M	b_s	$10^3 k_{ext}$, s^{-1}	k_{ext}/k_0
$LiClO_4$	4.7	19.7	3.0 ± 0.1	1.9
Bu_4NClO_4	37	0.65	4.52 ± 0.03	2.9

1.11–1.12, again some 60% of the maximum expected for benzal chlorides.

The situation in the more polar solvent, 75% (v/v) dioxane–25% H_2O, is quite a bit different. For example, significant rate depressions are obtained with LiCl and Bu_4NCl in this solvent. These data along with the attendant α-D isotope effects are given in Tables VII and VIII and Figure 2. These salts fit the Winstein equation (eq 2), where $k_d^0 = 7.4 \times 10^{-4}\ s^{-1}$ and $b_s = -1.3 \pm 0.1$. Once again the α-D isotope effect for the chloride-ion-depressed rate is substantially less than the maximum.

$$k_{obsd} = k_d^0(1 + b_s[\text{salt}]) \qquad (2)$$

Our results for the effect of $LiClO_4$ and Bu_4NClO_4 as well as some selected isotope effects are given in Tables IX and X, respectively. While these results appear at first glance to resemble the special salt effect there are significant differences. As the summary in Table XI indicates, the rate constant extrapolated to zero salt concentration is dependent on the nature of the salt. It seems clear that the effect of added perchlorate salts is different in the two solvents (75D and 85D).

Discussion

Addition of certain salts to some solvolyzing systems results in a two-stage salt effect: an initial substantial rate acceleration followed by a more modest normal salt effect.[8] In investigations of neighboring-group participation many other examples of this so called "special salt effect" have been reported.[12-16] It now seems clear that nonrearranging systems can give rise to this special salt effect as well.[6,7] Ion pair return from the solvent-separated ion pair (III) is prevented by ion-pair exchange with perchlorate salts (Scheme III).[17]

Scheme III. Ion-Pair Exchange

$$R^+\|X^- + M^+Y^- \underset{k_{ey}^{III(MX)}}{\overset{k_{ex}^{III(M^+Y^-)}}{\rightleftarrows}} R^+\|Y^- + M^+X^-$$

Thus, addition of perchlorate salts prevents return from III but not II, and k_2 (Scheme II) becomes more nearly rate limiting. In addition, extrapolation of the linear portion of eq 1 to zero salt concentration furnishes the rate at which solvent-separated ion pair is formed corrected for normal salt effects which might be quite different for $LiClO_4$ and Bu_4NClO_4.

The data for the hydrolysis of I for both $LiClO_4$ and Bu_4NClO_4 are tabulated in Tables II and III, and the special salt effect parameters are summarized in Table IV.

Thus, while $LiClO_4$ and Bu_4NClO_4 have different b_s and $[\text{salt}]_{1/2}$ values, the intercepts (k_{ext}^0) are identical for the two salts in this solvent, 85% (v/v) dioxane–water.

Shiner has laid the ground work for understanding the dependence of the α-D isotope effects on mechanism.[9]

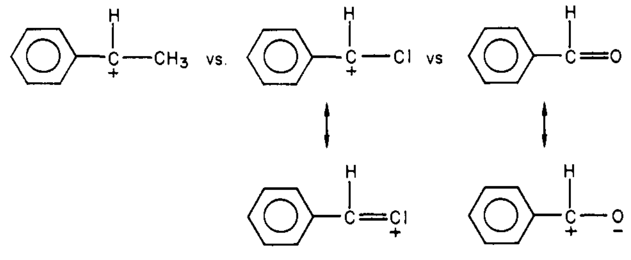
The change in zero-point vibrational energy at the α-carbon is greatest when k_2 or k_3 is rate determining. This is so because the transition states for these two steps involve diffusional steps of the fully formed carbonium ion. With the addition of sufficient perchlorate return, form III will be suppressed, and k_2 becomes more nearly rate determining. As more return is prevented, the α-D isotope effect should rise to a maximum characteristic of the leaving group. Our isotope effects increase with the concentration of perchlorate salts until a maximum value of 1.20 is reached. It should be noted here that our maximum value is significantly larger than the 1.15 expected by Shiner for chlorine as the leaving group.

Both the ground state and transition states are different for benzal chloride and α-phenethyl chloride solvolyses, and both factors may contribute to the difference in α-D effects. In his discussion of the origin of α-D isotope effect, Streitweiser et al.[18] point out that aldehydes might be good models for the carbonium ion in S_N1 reactions (Scheme IV). We would like to suggest that the increase in the α-D effect for benzal chlorides has its origin in part in a further weakening of the α-CH bending force constant as indicated in Scheme IV.

While there is very little common-ion rate depression for the solvolysis of I in 85D, we find substantial *induced*[17] common-ion rate depression for LiCl and Bu_4NCl in this solvent. Addition of incremental amounts of LiCl to a solution containing 0.05 M $LiClO_4$ results in a reduction of the solvolysis rate *and*, importantly, a reduction in the α-D isotope effect. Similar results are observed at fixed Bu_4NClO_4 concentration (0.1 M) with incremental additions of Bu_4NCl (Tables V and VI).

Thus, in 85D the mechanistic interpretation of the solvolysis of I appears straightforward. Addition of perchlorate salts to 85D results in an initial rate acceleration due to prevention of ion-pair return. An increase in the α-D effect, as observed, parallels this rate increase. At high concentrations of perchlorate salt a maximum α-D effect (1.20) is reached when all significant return from III is prevented. This mechanism implies that this "special"

Scheme IV. Structure of Carbonium Ion Intermediates



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salt effect would be reduced or eliminated by the addition of common-ion salts to a solution containing perchlorate ion (induced common-ion rate depression). In addition, a reduction in the α-D effect induced by increasing amounts of ion-pair return with increasing common-ion concentration should obtain. Both of these have been realized.

Thus, in 85D return from solvent-separated ion-pair III is important while free carbonium ions IV are not.

In the more polar solvent (75D) the α-D effect is quite close to the limiting value (1.178 vs. 1.200).

Unlike the less polar solvent (85D), common-ion rate depression with LiCl and Bu_4NCl is extensive (Tables VII and VIII and Figure 2). These results suggest that return from fully dissociated carbonium ions is quite important in this solvent (k_{-3}, Scheme II). The reduction in the α-D effect with increasing amounts of common ion signals a change in rate-limiting step from predominantly k_3 being rate limiting to k_s^{III} being rate limiting.

Addition of incremental amounts of perchlorate salts again results in what appears to be the "special" salt effect. However, plots of k_{obsd} vs. [perchlorate] give very different intercepts extrapolated from the linear portion of the special salt effect plot for $LiClO_4$ and Bu_4NClO_4 (Tables IX–XI). This suggests to us that, perhaps, ion-pair exchange (Scheme III) is rate limiting.

While the rate for this ion-pair exchange is expected to be dependent on the nature of the salt a maximum α-D effect is expected as neither solvent nor leaving group is bound covalently to the α-carbon. There is a small, but perceptible, increase in the α-D effect as $LiClO_4$ or Bu_4NClO_4 is added in accord with this expectation.

Experimental Section

***p*-Methoxybenzaldehyde-*d*$_1$.** This procedure followed that of Schowen.[18]

In a 100 mL, round-bottomed flask was placed 6.0 g (0.022 mol) of anisil in 25 mL of dry dioxane. Seven milliliters of D_2O was added followed by 2.0 g of KCN (previously dried at 125 °C). The mixture was stirred overnight. After dilution with 75 mL of H_2O, the reaction mixture was extracted with portions of ether (2 × 75 mL). The combined ether extracts were combined and washed with 150 mL of 5% Na_2CO_3, 100 mL of H_2O, and 75 mL of saturated NaCl. The ether extracts were dried ($CaSO_4$) and concentrated. Distillation afforded 2.13 g (70%) of anisaldehyde-*d*$_1$: bp 68–70 °C (0.35 mm); NMR (CCl_4) δ 3.66 (3 H, s), 6.60 (2 H, d), 7.40 (2 H, d). The signal for the aldehydic proton (δ 9.45) was absent.

***p*-Methoxybenzal-*d*$_1$ Chloride.** In a 50-mL, round-bottomed flask were placed 1.00 g of deuterated anisaldehyde-*d*$_1$ and 7.5 g of PCl_5 (with cooling). The contents of the flask were refluxed for 1 h, during which time the solution became homogeneous. The flask was cooled in an ice bath. The liquid content of the flask was decanted from the unreacted PCl_5 into 100 mL of cold water. The aqueous solution was then extracted with portions of ether (2 × 75 mL). The combined ethereal solutions were washed with 100 mL of cold, saturated $NaHSO_3$ and 50 mL of cold, saturating NaCl solution and dried over $CaSO_4$. Distillation afforded 0.53 g (38%) of *p*-methoxybenzal-*d*$_1$ chloride: bp 71–74 °C (0.3 mm); NMR (CCl_4) δ 3.65 (3 H, s), 6.56 (2 H, d), 7.15 (2 H, d). The signal for the benzal proton (δ 6.35) was absent. The unlabeled material was prepared by using unlabeled anisaldehyde in an identical procedure.

Inorganic Salts. All salts used were samples of the highest purity commercially available.

Kinetics. The rate of appearance of *p*-methoxybenzaldehyde at 275 nm was monitored spectrophotometrically in the thermostated cell of a Gilford or Cary 16 K spectrophotometer at 25.0 ± 0.2 °C. In general, the isotope effects reported throughout this paper were the average of three to five isotope effects determined in the following way. The average rate constant from one (two) H runs was compared to one (two) D runs monitored at the same time in the spectrophotometer. This constituted one "run". An average of three to five "runs" were used to determine the isotope effect. The rate constant for each individual run was obtained by a nonlinear least-squares regression analysis of the absorbance–time data. The standard deviation of each individual rate constant was <0.5%. The standard deviation for each isotope effect is given by the number in parentheses following the isotope effect in the tables, i.e., 1.206 (4) = 1.206 ± 0.004. In general, the standard deviation of most isotope effects with this procedure is ±0.005.

The rate constants reported in the tables are the average (standard deviation) for H runs used to determine the isotope effect.

Reaction rates were initiated by adding ~1–2 μL of a dioxane stock solution of IH or ID (~0.07 M) to a solution of a given salt in 75% or 85% dioxane–H_2O, made by addition of 25 (15) mL of H_2O to 75 (85) mL of purified dioxane.

After several days, it was necessary to prepare fresh stock solutions.

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