Effects of Deuterium Substitution on the Rates of Organic Reactions. XI. α- and β-Deuterium Effects on the Solvolysis Rates of a Series of Substituted 1-Phenylethyl Halides[1]

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Abstract: The rates of solvolysis of eight different *meta*- and *para*-substituted 1-phenylethyl chlorides, three 1-phenylethyl bromides, and their α-*d* and β-d_3 analogs have been measured in a series of acetone–water and ethanol–water mixtures with a precision of 0.1% or better using conductance techniques. The fact that 1-phenylethyl chloride and all of its more reactive derivatives, including the *p*-methoxy compound, have closely similar α-deuterium effects ($k_H/k_D = 1.15$) is interpreted in terms of a limiting carbonium ion mechanism applying for all of these compounds. The smaller α effects for the *m*-bromo (1.13) and *p*-nitro (1.11) derivatives are believed to indicate that these solvolyses involve appreciable nucleophilic character. The fact that the three bromides examined show α-*d* effects which are about 3% smaller than those of the corresponding chlorides is believed to be due to the HCBr bending force constant being smaller than the HCCl bending force constant in the initial state. The similarity in the influence of substituents indicates that the solvolytic mechanisms for bromides and chlorides are similar. Increasingly electron-releasing substituents in the ring were found to be associated with increasingly smaller β-*d* effects for all compounds more reactive than 1-phenylethyl chloride. The substituents and approximate $k_H/k_{\beta D_3}$ effects were H (1.22), *m*-CH_3 (1.22), *p*-F (1.21), *p*-CH_3 (1.20), *p*-phenoxy (1.16), and *p*-methoxy (1.11). This trend has been attributed to the electron-releasing substituents raising electron density at the reaction center and reducing the demand for hyperconjugation from the β-CH_3 (or CD_3) group. Thus, this result confirms earlier conclusions that the β-deuterium effect on the rate of carbonium ion forming reactions depends in major part on a hyperconjugative mechanism of interaction between the reaction center and the site of isotopic substitution. The smaller than otherwise expected β-d_3 effects for the *m*-bromo (1.22) and *p*-nitro (1.20) α-phenylethyl chlorides is in accord with the conclusion that these compounds react in part at least by a nucleophilic mechanism. The β-deuterium effects for the α-phenylethyl bromides are very near those for the corresponding chlorides in agreement with the conclusion that chlorides and bromides react by very similar mechanisms and that the difference in α effects is due primarily to the HCX bending force constant difference in the initial state.

The effects of α- and β-deuterium substitution on the rates of solvolysis reactions have been the subject of a number of investigations, the results of which are analyzed in terms of the Bigeleisen[3] or Melander[4] formulations for the effect of isotopic substitution on reaction rate. In this theory, as derived from absolute rate theory and statistical mechanics, the isotope effect is quantitatively related to the molecular vibrational frequencies of the initial and transition states for the protium and deuterium compounds. Thus, the measured isotope effects and vibrational frequencies for the initial states obtained from spectral observation can be used to provide information concerning transition state vibration frequencies and, indirectly, other transition-state structural features.

In a recent important advance, Wolfsberg and Stern[5] have developed machine programs for the calculation of isotope rate effects from atomic weights, molecular dimensions, and assigned force constants for initial and transition states. The capacity of the program is such that isotope effects on reactions of fairly large molecules can be directly related to force constants which, as more localized bond properties, can be conceptually more easily related to structure and mechanism than can normal mode frequencies which are more complex properties of the entire molecular structure. One of the important results of the calculations is the rigorous confirmation of an assumption previously explicitly made in the analysis of α- and β-deuterium effects on solvolysis rates; these isotope effects are caused by force constant changes at the site of isotopic substitution. Of interest to the problem of reaction mechanism is the identification of the particular force constant changes which are responsible for the isotope effects and the rationalization of these changes in terms of the various modes of intra- or intermolecular interaction.

α-Deuterium effects on solvolysis reactions were apparently first observed independently by three different groups.[6–8]

It was suggested that the effect should be a useful criterion of the degree of nucleophilic participation by the solvent in the rate-determining step, since some typical SN2 reactions showed effects near unity[9] while

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[1] (a) Taken in part from the theses of W. E. Buddenbaum and B. L. Murr submitted to the Graduate School of Indiana University in partial fulfillment of the requirements for the Ph.D. degree. (b) Supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund. Also supported in part by Grant G 16831 from the National Science Foundation and Grant AT (11-1)-1008 from the U. S. Atomic Energy Commission (Document No. COO-1008-2).

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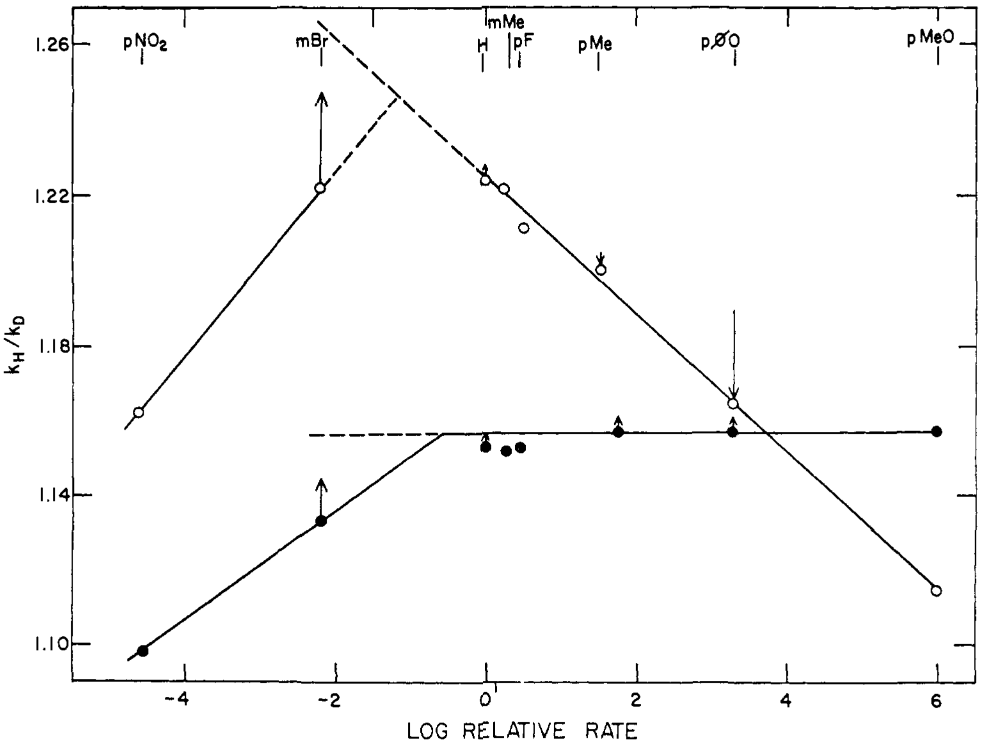

Figure 1. Isotope rate effects for solvolysis of 1-phenylethyl-1-*d* (●) and -2,2,2-d_3 (○) chlorides corrected to 50 vol % ethanol-water at 25°. Vertical arrows indicate direction and approximate magnitude of change of effect per unit increase in solvolyzing power.

reactions more nearly limiting in character showed k_H/k_D effects around 1.14. Robertson and coworkers[10,11] have presented additional evidence in support of this hypothesis. Seltzer[12] has argued from such empirical evidence that reactions which involve a rate-controlling unimolecular bond scission should show α-deuterium isotope effects of about 1.12 at 105° (or 1.15 at 25°) per deuterium atom. The treatment of Wolfsberg and Stern, however, suggests that the α isotope effect should depend directly on the difference between the force constants of the HCX bond in the initial and transition states. The near-constancy commented on by Seltzer must result from the similar size of most bending force constants and the fact that in the reactions studied they are all weakened by a similar amount. Thus, the α effect on a limiting solvolysis can be thought of as being due principally to the partial loss of the HCX bending force constant which would be expected to accompany the breaking of the C–X bond. The lower effect in nucleophilic reactions arises from a partially compensating gain of a new bending force constant produced by partial covalent attachment of the nucleophile to carbon. The classification of this effect as being due to changes in steric[13] or electronic interactions would then depend upon whether the bending force constants are considered to be steric or electronic in origin or, as seems more likely in a general case, due to some mixture of both effects.

The β-deuterium effect is also much larger in limiting solvolyses than in typical SN2 processes and should also serve as a convenient criterion of mechanism although it is known to be strongly influenced also by conformational factors.[14] The reduction in β-CH force constant in the activation process for a limiting sovolysis has been associated with a hyperconjugative interaction of this bond with the developing vacant orbital at the reaction center. A contrary suggestion has also been made to the effect that the reduction in force constant might be due to a reduction in steric interactions associated with the geometric reorganization around the reaction center.[13,15] However, the steric explanation suffers a number of serious inadequacies including the following. The estimated steric effect is smaller than the observed by a factor of 2 and is admittedly approximate;[13] the steric postulate allows no explanation of isotope effects transmitted through unsaturated linkages;[16] force constants of the methyl group are insensitive to the coordination number of the adjacent carbon atom;[17] and a sizeable β-isotope effect has been observed in the protonation of acetophenone,[18] a reaction which does not involve an appreciable change in the coordination number or geometry around the reacting carbon. Recent more extensive calculations using the Bartell equations show that steric contributions to the β effects are only a small fraction of the total observed.[19]

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Robertson and co-workers[10,11,20] have provided the most detailed information available on both α- and β-deuterium effects on solvolysis in a related series of compounds. These are summarized in Tables I and II.

Table I. Solvolysis of α-Deuterated Alkyl Esters in Water, k_H/k_D

Leaving group	Methyl-d_3	Ethyl-d_2	Isopropyl-d_1
Tosylate	0.96	1.038	1.134
Methanesulfonate	0.96	1.037	1.143
Iodide	0.87	0.968	1.050
Bromide	0.90	0.983	1.069
Chloride	0.92	...	...
Nitrate	0.92	...	...

Table II. Solvolysis of β-Deuterated Alkyl Esters in Water, k_H/k_D

Leaving group	Ethyl-β-d_3	Isopropyl-β-d_6	t-Butyl-β-d_9
Tosylate	1.018	1.551	...
Methanesulfonate	1.028	1.545	...
Iodide	1.033	1.313	...
Bromide	1.031	1.336	...
Chloride	...	...	2.568

One interpretation of the α effect suggests that the point of "mechanistic change" for the sulfonate esters is between the methyl and ethyl compounds while in the halide series it is between ethyl and isopropyl.[21] The β effects roughly reflect the same changes. The isopropyl sulfonates show β effects only slightly smaller per D than that for *t*-butyl chloride which certainly reacts by the limiting SN1 mechanism. The effect in the isopropyl halides is smaller and in all of the ethyl derivatives it is quite small.

Thus, the expected general trends are borne out but the data do not seem to be subject to quantitative interpretation and several nagging qualitative problems remain. First, the effects do not sort out into two types, one characteristic of each mechanism, but vary more or less continuously. Does this signal a continuous variation in mechanism? If so, how is this variation accomplished? Second, it is impossible to sort out what, if any, effects are due to structural changes independent of mechanistic changes. For example, would the β effect per CD_3 group in a limiting process be independent of the leaving group? Within a given mechanistic type, how much does variation in reactivity influence the isotope effect?[22,23] The structural variations possible in the alkyl series are too limited and too close to the reaction center to allow firm conclusions on these questions to be drawn.

In order to shed some further light on these problems, we undertook a study of α and β effects in the solvolysis of a series of substituted 1-phenylethyl halides. We sought to identify changes in both α and β effects not only due to mechanistic changes but, within a given mechanism, due to variations in substituent, leaving group, solvent, and over-all reactivity.

Results

The solvolysis rates measured by the conductance method published earlier,[24] with some modifications and extensions,[25] are summarized in Table III.

There are 24 different compounds (eight halides and their *α-d* and *β-d_3* analogs) measured in nine different aqueous acetone and aqueous alcohol solvents. Since each compound was not studied in every solvent, there are a total of only 58 different reactions. In some cases one to four duplicate rate determinations were done giving a total of 130 rate constant measurements. The solvolysis rate of 1-phenylethyl chloride in 60% aqueous ethanol was measured a number of times by three different experimenters over a period of 4 yr using different conductance cells as well as different sample and solvent preparations. The rate constants were generally reproducible to within better than ±0.1% and standard errors were around 0.01–0.02% except for the solvolyses of the *p*-phenoxy compounds where standard errors were sometimes as large as 0.1% and the reproducibility limit was as much as ±0.5%. Except for the *p*-phenoxy compound, we believe that the isotope effects in Tables IV, V, and VI are accurate to within 0.1%.

It can be seen by comparing the numbers within a given vertical column in Tables IV and V that both the α- and β-deuterium effects are somewhat solvent dependent, although the variations are small except for the *m*-bromo and *p*-phenoxy derivatives. For purposes of comparing *substituent* effects alone, Table VII gives the isotope effects "corrected" to the value expected in 50% ethanol.

The corrected value for the *m*-methyl compound in 50% ethanol was obtained by substracting the difference in isotope effects between the *m*-methyl and unsubstituted compounds in 70% ethanol from the value for the unsubstituted compound in 50% ethanol. Similarly, "corrected" values for *p*-fluoro and *p*-methyl in 50% ethanol were obtained by comparisons with the parent compound in 60 and 80% ethanol, respectively. Values corrected to 50% ethanol were obtained for the *p*-phenoxy compound by comparison with the *p*-methyl compound in 95% ethanol and for the *p*-methoxycompound by comparison with the *p*-phenoxy analog in 93% acetone. The corrections applied for the *p*-nitro compound were taken to be the same as those for the *m*-bromo compound. A different scheme would give slightly different values because the solvent influences on the isotope effects are not the same for all compounds. Nevertheless, the resulting changes would not significantly affect the conclusions about substituent effects to be drawn from the "solvent corrected" values. The solvent influences will be discussed subsequently.

Discussion

α-Deuterium Effects. The solvolysis of α-phenylethyl halides in aqueous organic solvents is thought to proceed predominately if not exclusively through a limiting, SN1, carbonium ion mechanism.[26,27]

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Table III. Solvolysis Rate Constants at 25° (10^{-5} sec^{-1})

Substituent	Solvent[b]	Undeuterated[a]	1-d[a]	2,2,2-d_3[a]	Reproducibility error (±)
		A. Substituted 1-Phenylethyl Chlorides			
p-Nitro	5% acetone	0.1526 (2)	0.1370 (1)	0.1276 (2)	0.0001
m-Bromo	5% acetone	33.94 (1)	...	...	...
m-Bromo	9% acetone	20.12 (2)	17.52 (2)	15.89 (2)	0.02
m-Bromo	50% ethanol	0.2370 (2)	0.2091 (2)	0.1941 (2)	0.0001
None	50% ethanol	36.20 (1)	31.43 (1)	29.58 (3)	0.01
None	60% ethanol	10.865 (5)	9.4401 (1)	8.867 (1)	0.001
None	70% ethanol	3.4403 (2)	2.991 (1)	2.808 (1)	0.001
None	80% ethanol	1.0019 (1)	0.8744 (1)	0.8191 (1)	...
m-Methyl	70% ethanol	7.041 (4)	6.139 (2)	5.759 (3)	0.005
p-Fluoro	60% ethanol	31.66 (2)	27.52 (2)	26.10 (2)	0.02
p-Methyl	80% acetone	3.471 (3)	3.000 (2)	2.865 (2)	0.004
p-Methyl	80% ethanol	58.87 (5)	51.19 (4)	49.10 (5)	0.05
p-Methyl	95% ethanol	3.817 (2)	3.324 (2)	3.1825 (2)	0.001
p-Phenoxy	80% acetone	115.2 (2)	100.4 (2)	99.5 (2)	0.5
p-Phenoxy	93% acetone	1.818 (2)	1.586 (2)	1.535 (2)	0.001
p-Phenoxy	95% ethanol	191.8 (4)	167.0 (3)	164.8 (4)	0.6
p-Methoxy	93% acetone	70.51 (3)	61.46 (2)	62.21 (2)	0.05
		B. Substituted 1-Phenylethyl Bromides			
p-Nitro	5% acetone	2.0 (2)	2.032 (1)	1.829 (1)	0.001
None	80% ethanol	20.203 (2)	18.004 (2)	16.56 (3)	0.01
p-Phenoxy	93% acetone	90.2 (4)	80.1 (3)	75.7 (3)	0.5

[a] The number of determinations is given in parentheses. The values were generally reproducible to within 0.1% or better, except for the reaction of the p-phenoxy derivative in 80% acetone, 93% acetone, and 95% ethanol, where the reproducibilities were 0.5, 0.7, and 0.3%, respectively. Standard errors within a run were generally between 0.01 and 0.1%. [b] In volume per cent.

Table IV. α-Deuterium Effects on Rates of Solvolysis of 1-Phenylethyl Chlorides at 25°

	Substituent							
Solvent	p-MeO	p-C_6H_5O	p-Me	p-F	m-Me	None	m-Br	p-NO_2
5% acetone								1.114
9% acetone							1.149	
80% acetone		1.147	1.157					
93% acetone	1.147	1.147						
95% ethanol		1.149	1.149					
80% ethanol			1.150			1.146		
70% ethanol					1.147	1.149		
60% ethanol				1.150		1.151		
50% ethanol						1.153	1.133	

Table V. β-Deuterium Effects on Rates of Solvolysis of 1-Phenylethyl Chlorides at 25°

	Substituent							
Solvent	p-MeO	p-C_6H_5O	p-Me	p-F	m-Me	None	m-Br	p-NO_2
5% acetone								1.197
9% acetone							1.267	
80% acetone		1.159	1.211					
93% acetone	1.133	1.184						
95% ethanol		1.164	1.200					
80% ethanol			1.199			1.223		
70% ethanol					1.223	1.225		
60% ethanol				1.213		1.226		
50% ethanol						1.224	1.221	

Table VI. α- and β-Deuterium Effects on Rates of Solvolysis of 1-Phenylethyl Bromides at 25°

Substituent	Solvent	$k_H/k_{\alpha\text{-}d}$	$k_H/k_{\beta\text{-}d_3}$
p-Phenoxy	93% acetone	1.126 ± 0.01	1.192 ± 0.01
None	80% ethanol	1.122 ± 0.001	1.220 ± 0.001
p-Nitro	5% acetone	1.085 ± 0.001	1.205 ± 0.001

Table VII. Rates and Isotope Effects for 1-Phenylethyl Chlorides Corrected to 50% Ethanol, 25°

Substituent	Relative rate	$k_H/k_{\alpha\text{-}d}$	$k_H/k_{\beta\text{-}d_3}$
p-Methoxy	11.4–7.6 × 10^5	1.157	1.113
p-Phenoxy	3.0–2.0 × 10^3	1.157	1.164
p-Methyl	59.0	1.157	1.200
p-Fluoro	3.0	1.152	1.211
m-Methyl	2.0	1.151	1.222
None	1.0	1.153	1.224
m-Bromo	6.6 × 10^{-3}	1.133	1.221
p-Nitro	2.9 × 10^{-5}	1.098	1.151

Not all the product can, however, be derived from a "free" carbonium ion since solvolysis of the optically active chloride proceeds with about 5–15% net inversion.[28] The faster solvolyzing derivatives should have an even greater tendency to react by the limiting mechanism than the unsubstituted compound because the electron-releasing substituent groups are expected to accelerate carbonium ion formation more than nucleophilic attack. The fact that the α-deuterium effects are large and very nearly the same for 1-phenylethyl chloride and the *m*-methyl, *p*-fluoro, *p*-methyl, *p*-phenoxy, and *p*-methoxy compounds is strong evidence that all proceed by the limiting mechanism (in the sense that nucleophilic attack by solvent is not involved in the rate-determining step). It is interesting that no significant changes show up in this series even though the solvolysis rates cover a range of six powers of 10; both the Hammond and Swain–Thornton postulates suggest causes for variation in such isotope effects with substitution;[22,23a] although the original formulation of the Swain–Thornton rule made, for the present example, a prediction opposite to that of the Hammond postulate, a recent formulation by Thornton[21b] is in agreement with the Hammond postulate. The smaller isotope effects for the *m*-bromo and *p*-nitro compounds are consistent with an incursion of some nucleophilic character into their solvolytic mechanisms; otherwise, if these solvolyses are also limiting, the decrease correlates with the prediction of the Swain–Thornton postulate (but not the Hammond postulate) that electron-attracting substituents would make the reacting bonds shorter, or more like the initial state. The fact that the more electron-releasing substituents do not cause the isotope effect to increase could be reconciled to the Swain–Thornton rule by an *ad hoc* postulate that the C–Cl transition-state length in the solvolysis of 1-phenylethyl chloride itself was already large enough so that the Cl had no effect on the H force constants; thus, the transition states for the more reactive derivatives might have longer C–Cl bonds but the same hydrogen vibration frequencies. That this argument is *not* valid can be demonstrated by including the results of the α-phenylethyl bromides in the comparison. The α effect is lower for the unsubstituted bromide (1.122) than for the chloride (1.153), as expected from the postulate; however, this would indicate an interaction between the α-H and the leaving group that would have to be reduced in the transition state for the solvolysis of the *p*-phenoxy-1-phenylethyl bromide; instead this latter compound shows the same α effect as its unsubstituted relative.

We, therefore, conclude that for the limiting reactions either the degree of progression along the reaction coordinate does not vary appreciably with substrate reactivity (as caused by remote substituents) or, if it does, the α-*d* effect is remarkably insensitive to it. The lower α-*d* effects for the *m*-Br and *p*-NO_2 derivatives signify incursion of nucleophilic attack on carbon in the rate-determining step. The α-*d* effects for all of the bromides are lower than for the corresponding chlorides because in the initial states the HCBr bending force constant is lower than the HCCl bending force constant; if each suffers the same proportional reduction in the transition state, the isotope effect for the bromide would be smaller.

Bending force constants for these halides are not available in the literature to confirm this idea but it seems likely that they would parallel those of the methyl halides.[29,30] The symmetry force constant F_{22} is related to the HCX bending motion and decreases in the order 0.739, 0.656, 0.611, and 0.575 in the series methyl fluoride, chloride, bromide, and iodide. Detailed calculations are in progress to determine quantitatively what effect such force constant changes would be expected to have on a limiting reaction. It seems reasonable that the HCX bending force constant would generally parallel the C–X bond strengths. If this is so one would expect that the limiting reactions involving ionization of a C–O bond might show larger α-deuterium effects than do the chlorides and bromides. There is some preliminary evidence that this is the case since α effects in the solvolysis of alkyl arenesulfonates can be as large as 1.20.[31] Many are smaller than this but the lower values may be due to some nucleophilic character of the solvolysis. We have thus identified two causes for variation in the α effects: (1) differences in HCX initial state bending force constants dependent primarily on the nature of X and (2) the degree of attachment of the incoming group. We expect, but have not yet definitely characterized, a third variable, variation in the HCX bending force constant in the transition state.

β-Deuterium Effect. The solvolysis of 1-phenylethyl chloride has been classified above, on the basis of the α-*d* effects, as limiting; the fact that its β-d_3 effect (1.224) is smaller than that for *t*-butyl chloride (1.30)[32] must then be attributed to internal differences in the alkyl groups themselves, rather than to mechanistic differences in the two solvolyses. The benzene ring should act by conjugation to make the degree of orbital vacancy at the reaction center of the α-phenylethyl chloride transition state less than that for *t*-butyl chloride; the extent of hyperconjugative β-CH bond weakening would be expected to be less and, if this is the main cause of the β-d_3 effect, it should be smaller also, as observed. That this is the correct explanation is confirmed by the observation that electron-releasing *para* substituents all cause the β-d_3 effect to be less; in the *p*-methoxy derivative, it is approximately half (1.113) that of the parent compound (1.224). It should be emphasized that the constancy of the α-*d* effect in this series of reactions indicates the absence of appreciable mechanistic change or any appreciable changes in degree of progression along the reaction coordinate. The smaller β-d_3 effects for the *m*-Br and the *p*-NO_2 derivatives are in accord with the conclusion reached above from comparison of α effects, that the solvolyses of these compounds are partly nucleophilic. The electrons of the nucleophile reduce the degree of vacancy at the reaction center and correspondingly reduce the β-d_3 effect.

The β effects for the three 1-phenylethyl bromides are very close to those for the corresponding chlorides; this is in accord with the conclusion that the chlorides and bromides solvolyze by similar mechanisms and that the difference in α effects, mentioned above, depends

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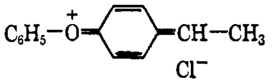
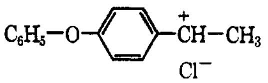
on the difference in HCX bending force constants. This force constant is not expected to have any strong influence on the β effects. On the other hand, if both α and β effects were caused by steric interaction with the halogen[13,15] and the differences in the α effects were due to bromine being effectively smaller than chlorine, then the β effects ought also to be smaller for the bromides, which is not observed.

Solvent Influences. The solvent influences on the α effects are generally very small; indeed, with only two exceptions, discussed below, all α effects measured for the chlorides are within ±0.006 of 1.152. 1-Phenylethyl chloride itself was studied in the widest range of solvent compositions and shows a steady increase in the α effect (from 1.146 to 1.153) as the amount of ethanol in aqueous ethanol solvent is decreased from 80 to 50%. Since this compound is near the mechanistic dividing point in solvolysis in 50% ethanol, it is possible that in 80% ethanol its reaction may be slightly nonlimiting, causing the α effect to be slightly smaller. The α-isotope effect for the *m*-Br derivative changes from 1.133 in 50% ethanol to 1.149 in 9% acetone; this increase of 0.016, to the value characteristic of limiting reaction, concomitant with the increase of solvent polarity, reinforces the conclusion derived above that this reaction is partly nucleophilic in 50% ethanol. Thus, if the α-isotope effects for the *p*-NO_2 compound and the *m*-Br compound in 50% ethanol and the unsubstituted compound in 80% ethanol are accepted as being low because of the nonlimiting character, all of the other α effects are within ±0.003 of 1.150 except for the *p*-Me compound in 80% acetone which shows the value 1.157.

The solvent influences on the β effects show a similar pattern except for the *p*-phenoxy example discussed below. The changes for 1-phenylethyl chloride itself are very small; the effect increases markedly for the *m*-Br derivative when the solvent is changed from 80% ethanol (1.221) to 9% acetone (1.267), consistent with a change from a partly nonlimiting to a limiting reaction. The most unusual solvent influence observed is that on the *p*-phenoxy derivative; in 80% acetone the value is 1.159 but in 93% acetone it is 1.184. This is the only example where an isotope effect is *larger* in the less aqueous solvent. It is argued above that the effect is smaller for the phenoxy derivative because of cross-conjugation, *i.e.*, resonance contributions of the type Ia reduce the degree of orbital vacancy at the reacting carbon in the transition state below that which obtains in the transition state for the unsubstituted compound. This results in lower hyperconjugative demand in the β-CH bonds and a smaller β-isotope effect. Since Ia has a larger charge separation than Ib, it is reasonable to expect it to contribute more importantly to the hybrid structure in a *more polar solvent;* thus, the β effect is *lower* in the more polar solvent. Such a solvent influence on the transition-state electronic distribution appears to offer a simpler alternative explanation for a related set of observations discussed by Swain and Thornton.[23] These authors pointed out that faster solvolyzing derivatives showed *rates which were more sensitive to solvent polarity* than related compounds which solvolyzed more slowly; the faster solvolyzing derivatives are just those with electron-releasing substituents which spread the positive charge, give the transition state a larger dipole moment, and make its stability more sensitive to solvent polarity. This explanation seems more straightforward than the one offered by the Swain–Thornton rule which would attribute the higher dipole moment of the transition state to a longer C–Cl bond.



Ia



Ib

Figure 1 shows the α- and β-deuterium effects "corrected" to 50% ethanol plotted *vs.* the relative solvolytic reactivity of the halides. The right-hand side of the diagram refers to the limiting reactions showing the constant α effect but with the β effect decreasing with more electron-releasing substituents. The left-hand side of the diagram shows the decrease of both α and β effects with the incursion of nonlimiting or nucleophilic character. The α effects for the bromides are lower than for the chlorides but the β effects are nearly the same. The arrows indicate the direction and magnitude of the change of the effect with increasing solvent polarity.

The results reported here are consistent with nonlimiting character involving either the admixture of some SN2 displacement or nucleophilic attack on a tight ion-pair intermediate.[33] However, if the latter obtains it could be a part of the rate-determining step and exert the observed influence on the isotope effects only if the tight ion pair underwent significant internal return; mixed or borderline character might then just involve a competition or partitioning of the tight ion pairs between diffusion apart and nucleophilic attack. Further experiments to check these possibilities and to explore further the problem of the borderline mechanism are under way in these and related reactions.

It is interesting to compare the β- and α-deuterium effects on the rates of unimolecular homolytic and heterolytic cleavage of a bond to the 1-phenylethyl group. Seltzer[12] and Seltzer and Hamilton[34] have shown that the unimolecular homolytic cleavage of a 1-phenylethyl azo compound is slowed by α-deuterium substitution (k_H/k_D = 1.12–1.15) by an amount very close to that observed in this work for the limiting carbonium ion forming reaction. The β-deuterium effect in the radical-forming process is, however, only about one-fourth as large. The drastically lower β effect in the radical reaction would not be expected if all of these effects were predominately due to changes in nonbonded interactions. However, since hyperconjugative demand is expected to be much less at a radical than at a carbonium ion center, the result is expected if the β effect depends on this type of electronic interaction.

Experimental Section

Kinetic Procedure. The rate constants were determined using the conductometric procedure of Murr and Shiner.[24] In the examples of solvolysis in the relatively nonpolar solvents which show nonlimiting conductance behavior the procedure was modified to use a three-parameter equation relating conductance to concentration (see below). The calculations including the use of more complex conductance equations were reprogrammed for an IBM 709 computer and a number of refinements in the output for-

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(34) S. Seltzer and E. J. Hamilton, Jr., *ibid.*, **88**, 3775 (1966).

Table VIII. Conductance Parameters Used for HCl

Solvent	Equation	Λ_0	S_a	E	J	K_A	$\mathring{a}$
5% acetone	1[a]	...	...	...	...	...	...
9% acetone	1[a]	...	...	...	...	...	...
80% acetone	3	109.38	215.7	299.8	1551.0	31	3.56
93% acetone	3	117.30	400.1	804.3	4491.1	1133	4.04
50% ethanol	1	140.40	85.8	...	...	...	...
60% ethanol	1[b]	113.57	87.0	...	...	...	...
70% ethanol	1[b]	91.03	99.0	...	...	...	...
80% ethanol	1[b]	71.64	112.0	...	...	...	...
95% ethanol	2	48.48	127.7	236.6	1169.0	...	3.48

[a] It was found that the kinetic results for this solvent were very insensitive to reasonable choices for Λ_0 and S_a and for simplicity $S_a = 0$ was used. [b] Data from ref 24.

mat were adopted. In particular a plot of the percentage resistance residuals *vs.* time proved very useful in assessing the quality of fit of the data to the first-order rate law. Synthetic first-order rate data were used to check the performance of the program; the influence of bad data points, errors in the conductance parameters, salt effects, and mass law effects were examined; random errors in both time and resistance were entered to check the validity of the weighting procedure. A Computer Measurements Corp. crystal controlled electronic digital clock with an accuracy of one unit or one part in 10^6 was used to reduce errors in time; it could be set to count up to seven digits of 0.001-, 0.01-, 0.1-, or 1-sec units; the clock reading could be instantaneously stopped on manual or electrical command while the time base continued the count; a reset command caused the reading to resume the correct time count. The purification of ethanol was improved by first passing the commercial absolute ethanol through a 2 × 60 cm column of fresh analytical grade Amberlite MB-1 ion-exchange resin. When this effluent was dried and purified by the procedure used before, the ethanol showed a specific conductance of about 1×10^{-9} mho, an improvement by a factor of 4.

Conductance Results. The conductance of HCl in 50, 90, and 95 vol % ethanol and in 80 and 93 vol % acetone was measured in the concentration ranges from 1×10^{-4} to 2×10^{-3} mole/l. The results for 50% ethanol were fit by a least-squares code to the limiting Onsager conductance equation as before.[24] However, the

$$\Lambda = \Lambda_0 - S_a\sqrt{c} \qquad (1)$$

results for the other solvents had to be fit to a modification of the Fuoss–Onsager conductance equation for an unassociated electrolyte

$$\Lambda = \Lambda_0 - S^0\sqrt{c} + Ec\ln(c) + Jc \qquad (2)$$

or an associated electrolyte[35]

$$\Lambda = \beta(\Lambda_0 - S^0\sqrt{\beta c} + E\beta c\ln(\beta c) + J\beta c) \qquad (3)$$

because the solvent polarity was too low for the limiting behavior to obtain. In these expressions the constants S^0, E, and J are known functions of the solvent, the temperature, Λ_0, the association constant (K_A), and $\mathring{a}$ (the ion-size parameter of the electrolyte).[35] The degree of association, β, is related to these quantities *via* the equations

$$K_A = \frac{(1-\beta)c}{\beta^2c^2(f\pm)^2} \qquad (4)$$

and

$$\ln(f\pm) = \frac{A\sqrt{\beta c}}{1 + \mathring{a}B\sqrt{\beta c}} \qquad (5)$$

where A and B are functions of the solvent and the temperature.[36]

A similar least-squares treatment of conductance data has been made by Kay[37] using a different weighting method.[25]

The constants used in the kinetic determinations are given in Tables VIII and IX. These constants reproduced the conductance data to within 0.01%.

Table IX. Conductance Parameters Used for HBr

Solvent	Equation	Λ_0	S_a
5% acetone	1[a]	...	...
93% acetone	1	118.4[b]	1020[b]
80% ethanol[c]	1	73.34	113.4

[a] The conductance parameters for HCl were used in this solvent. [b] Estimated from the difference in conductance of HCl and HBr in other aqueous solvents. [c] Measured values of P. Haffley, personal communication, 1964.

Preparation of Halides. A. All of the substituted 1-phenylethyl chlorides and bromides except the *m*-bromo and *p*-nitro derivatives were prepared by treatment of the corresponding alcohol with hydrogen halide according to the following procedure. Commercial tank hydrogen halide was bubbled through a concentrated sulfuric acid trap and then into a 1–2-g sample of the alcohol in a 5-ml centrifuge tube cooled in an ice bath. After about 10 min the water layer ceased to separate and the sample was allowed to warm to room temperature. The halide was separated after centrifugation and dried over 40-mesh CP anhydrous calcium chloride. The dried alkyl halide was placed in a vacuum line and two transfers were made; the middle third was kept for kinetic studies and stored at Dry Ice temperature until used.

B. The *p*-nitro- and *m*-bromo-1-phenylethyl chlorides were made according to the following procedure. To a solution of 2.6 g (0.026 mole) of zinc chloride in 10 ml of concentrated hydrochloric acid was added about 2 g (0.01 mole) of substituted 1-phenylethanol in a 15-ml test tube. Anhydrous hydrogen chloride was bubbled into this homogeneous solution for about 1.5 hr until the chloride separated. The chloride layer was removed and dried with anhydrous calcium chloride. The dried chloride was placed in a vacuum line and two transfers were made. The middle third was stored at Dry Ice temperature until use.

The *p*-nitro-1-phenylethyl bromides were made by an entirely analogous procedure using zinc bromide and hydrogen bromide.

The β-deuterated halides all showed deuterium content in the range of 2.95–2.97 atoms/molecule while the α-deuterated halides showed 0.990–0.994 atom of D/molecule. The ranges covered in each case represent approximately the accuracy of the determination.

Preparation of Alcohols. Procedure A. All of the alcohols except *p*-nitro-1-phenylethanol were prepared by reduction of the corresponding ketone by lithium aluminum hydride according to the following sample procedure. A solution of 15 g (0.100 mole) of redistilled commercial *p*-methoxyacetophenone, bp 82–84° (1.0 mm) (lit.[38] bp 139° (15 mm), dissolved in 150 ml of absolute ether was added dropwise to 10% excess of lithium aluminum hydride suspended in 200 ml of absolute ether in a 1-l. three-necked flask fitted with a mechnical stirrer, a condenser, and a dropping funnel. The solution was allowed to stir overnight under reflux. The excess hydride was destroyed with crushed ice and the precipitated aluminum salts were dissolved by the addition of 20% aqueous

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(38) C. R. Noller and R. Adams, *J. Am. Chem. Soc.*, **46**, 1889 (1924).

Table X. 1-Phenylethyl Alcohols

Substituent	Yield, %	Bp (mm), °C	Lit. bp (mm), °C	Ref	Atoms of D/molecule	Position
p-Methoxy	85	108–109 (3)	109–110 (2.5)	39	0	
p-Methoxy	87	107–108 (3)			2.98	2
p-Methoxy	73	100–101 (1)			0.993	1
p-Phenoxy	86	138–140 (0.7)	160–162 (2)	*a*		
p-Phenoxy	85	139–140 (0.8)			2.97	2
p-Phenoxy	61	137–139 (0.7)			0.993	1
p-Methyl	87	110–111 (15)	120 (19)	*b*		
p-Methyl	87	111–113 (15)			2.97	2
p-Methyl	73	109–111 (12)			0.994	1
m-Methyl	77	58–59 (0.5)	103–105 (6)	*c*		
m-Methyl	80	60–61 (0.8)			2.96	2
m-Methyl	65	62–64 (1)			0.993	1
p-Fluoro	68	57–58 (0.7)	90.5 (10)	*d*		
p-Fluoro	90	112–113 (31)			2.95	2
p-Fluoro	76	53–54 (0.1)			0.993	1
None	78	70–71 (2)	203.5 (760)	*e*		
None	82	71–72 (2)			2.95	2
None	85	83–84 (6)			0.993	1
m-Bromo	57	108–110 (2)	129 (11)	*f*		
m-Bromo	88	106–108 (2.5)			2.96	2
m-Bromo	88	130–132 (6)			0.991	1
p-Nitro	89	117–118 (0.8)	137–138 (2)	39		
p-Nitro	66	118–119 (0.8)			2.97	2
p-Nitro	63	117–118 (0.7)			0.991	1

[a] A. McCoubrey and D. M. Zausmer, *Brit. J. Pharmacol.*, **9**, 289 (1954). [b] M. Sulzbacher and E. Bergmann, *J. Org. Chem.*, **13**, 303 (1948). [c] C. G. Overberger, J. H. Saunders, R. E. Allen, and R. Gander, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 201. [d] M. W. Renoll, *J. Am. Chem. Soc.*, **68**, 1159 (1946). [e] R. R. Dresibach and R. A. Martin, *Ind. Eng. Chem.*, **41**, 2875 (1949). [f] K. B. Wiberg and T. M. Shryne, *J. Am. Chem. Soc.*, **77**, 2774 (1955).

sodium hydroxide. After separating the ether layer, the aqueous layer was extracted twice with 50-ml portions of ether and the combined ether extracts were dried first with magnesium sulfate and then overnight with anhydrous calcium sulfate. The ether was removed by distillation and the alcohol fractionally distilled using an 18 × 400 mm Nestor spinning-band column to give 12.9 g (85%) of product, bp 108–109° (3 mm) (lit.[39] bp 109–110° (2.5 mm). The α-deuterio alcohols were prepared in the same manner from the ketone and lithium aluminum deuteride.

Procedure B was used for *p*-nitro-1-phenylethanol and the 2,2,2-d_3 analog. To a solution of 41.5 g (0.215 mole) of recrystallized *p*-nitroacetophenone, mp 81–82° (lit.[40] mp 80–81°), in 300 ml of methanol, made basic to litmus with sodium hydroxide, in a 500-ml round-bottom flask fitted with a condenser, was added 30 g (0.070 mole) of sodium borohydride. The solution was allowed to stand overnight. It was then diluted with 400 ml of water and made acidic to litmus with dilute hydrochloric acid and the methanol removed by distillation. The organic layer was separated, dried with Drierite, and distilled in a Nestor spinning-band column yielding 37 g (89%) of alcohol, bp 117–118° (0.8 mm) (lit.[39] bp 137–138° 2 mm).

Procedure C was used for *p*-nitro-1-phenylethanol-1-*d*. A solution of 12 g (0.073 mole) of *p*-nitroacetophenone, 3 g (0.03 mole) of aluminum *t*-butoxide, and 8.5 g (0.140 mole) of 2-propanol-2-*d* in 80 ml of dry toluene was refluxed for 5 hr. The acetone and most of the toluene were removed by distillation and the alcohol distilled using the spinning-band column; bp 117–118° (0.7 mm); yield, 7.7 g (63%). Nmr analysis showed 0.991 atom of D per molecule in position 1.

The data for all the 1-phenylethanols are summarized in Table X.

Deuteration of Ketones. The acetophenone-β-d_3 compounds were made according to the following sample procedure. A 25-g (0.167 mole, 1.0 g-atom of exchangeable H) sample of *p*-methoxyacetophenone was dissolved in 60 ml of purified dioxane containing 10 g (0.5 mole, 1.0 g-atom of exchangeable H) of deuterium oxide, and 1 ml of dry redistilled triethylamine. The solution was gently refluxed overnight. The water was removed as the dioxane azeotrope (bp 87–88°) and an additional 5 ml of dioxane was collected, bp 101°. A new mixture of dioxane, deuterium oxide, and triethylamine was added to the residue. The exchange was repeated six more times and then the residue was distilled in the spinning-band column to give 23 g (0.15 mole), bp 86–87° (2 mm), of the ketone-d_3. Deuterium analysis by nmr showed 2.98 atoms of deuterium per molecule in the 2 position. All ketones deuterated by this procedure showed deuterium content in the 2 position in the range 2.95–2.97 atoms per molecule.

***p*-Methoxyacetophenone.** The commercial product was fractionally distilled through a Nestor spinning-band column before use. A center cut was retained, bp 82–84° (1 mm) (lit.[38] bp 139° (15 mm).

***p*-Phenoxyacetophenone** was prepared from 170 g (1.0 mole) of diphenyl ether and 100 ml (1.06 moles) of acetic anhydride as described by Frank, *et al.*[41] The yield of ketone was 140 g (66%). After recrystallization from ethanol-water it showed mp 51–52° (lit.[42] mp 50°).

***p*-Methylacetophenone.** The commercial product was purified by five successive recrystallizations of the semicarbazone. After acid hydrolysis and extraction the ketone was carefully fractionated through a Nestor spinning-band column. A center cut was retained for use, bp 96–97° (10 mm) (lit.[38] bp 93.5° (7 mm)).

***m*-Methylacetophenone** was prepared by the action of dimethylcadmium on *m*-methylbenzoyl chloride.[43]

***p*-Fluoracetophenone.** The commercial product was purified as described above for *p*-methylacetophone.

Acetophenone. The commercial product was carefully fractionated through the Nestor spinning-band column, bp 59–60° (3 mm) (lit.[38] bp 88.5 (16 mm)).

***m*-Bromoacetophenone** was prepared by the procedure described in ref 44. The product was fractionated through the Nestor spinning-band column, bp 97–98° (2.4 mm) (lit.[44] bp 75–76° (0.5 mm)).

***p*-Nitroacetophenone.** The commercial product was recrystallized from ethanol–water, mp 81–82° (lit.[40] mp 80–81°).

2-Propanol-2-*d* was prepared as described by Shiner.[9]

Solvolysis Product Studies. The ultraviolet spectra of aliquots of kinetic reaction mixtures of the substituted 1-phenylethyl halides

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in ethanol–water mixtures that had stood for 13 half-lives or longer were recorded on a Cary 14 spectrophotometer. The concentrations of the styrenes were calculated using published extinction coefficients and $\lambda_{\max}$ values.[45–47] In all cases styrene yields were less than 0.5%. No attempt was made to determine styrene yields in the acetone–water solvolyses.

Deuterium analyses were done with a Varian A-60 magnetic resonance spectrometer. Mixtures of about 1, 2, 3, and 4 mole % of the hydrogen compound in the deuterium components were prepared by weight. The nmr spectrum of each mixture was obtained in carbon tetrachloride. The ratio of the signal of the peaks in question to that of a nearby peak was determined by integration. A plot of these ratios *vs.* the apparent mole per cent yielded the true mole per cent of hydrogen with a precision of about 0.5%.

Acknowledgments. The electronic computations were performed with the facilities of the Indiana University Research Computing Center.

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Rates of Proton Exchange and Epimerization for *dl*- and *meso*-α-Methylbenzyl Sulfones

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Abstract: The ratio of the rate of deuterium exchange to the rate of epimerization for *dl*- and *meso*-α-methylbenzyl sulfones in methanol has been found to be 90:1 at 25°. This result confirms the relative insensitivity of the $k_e/k_{\alpha'}$ ratio to substitution of Ph for R in $MeCHRSO_2C_6H_5$. It is concluded that $[PhCMeSO_2R]^-$ carbanions are rapidly inverting (effectively planar).

The striking observation that the rate of base-catalyzed deuterium exchange for optically active *n*-$HexCH(CH_3)SO_2C_6H_5$ is much faster than the rate of racemization,[3–5] which was made independently in three laboratories, has been rationalized by assuming the formation of asymmetric α-sulfonyl carbanion intermediates. Asymmetric α-sulfonyl carbanions having either a pyramidal or effectively planar structure will satisfy the experimental data, provided the proper assumptions are made.[3] A number of sulfone systems have been examined in a series of ingenious experiments designed to allow a choice between a rapidly inverting or "effectively planar" α-sulfonyl carbanion intermediate with a barrier to rotation and a pyramidal α-sulfonyl carbanion intermediate with a barrier to inversion.[6] The evidence obtained has been interpreted as favoring an effectively planar structure with racemization by rotation,[6] but this interpretation has been challenged.[7] In the course of another investigation we observed that the methyl groups in *dl*- and *meso*-$C_6H_5CH(CH_3)SO_2CH(CH_3)C_6H_5$ (**1** and **2**, respectively) exhibited different nmr chemical shifts. This offered a convenient method for measurement of the rate of base-catalyzed epimerization. It appeared to be of interest to compare this rate with that of deuterium exchange, since we thought that the presence of the α-phenyl group would ensure near-planarity of the carbanion in this instance and that the change in k_e/k_α ratio might provide information concerning the structure of α-sulfonyl carbanions. While this work was in progress Corey and Lowry[6c] reported that k_e/k_α did not change appreciably for $C_6H_5{*}CH(CH_3)SO_2C_6H_5$ as compared to *n*-$Hex{*}CH(CH_3)SO_2C_6H_5$. It seemed worthwhile, however, to check their result by an independent method. We, therefore, completed our study and present the results herein.

A mixture of **1** and **2** when treated successively with butyllithium and deuterium oxide gave the α,α′-dideuterated isomers,[8] which were cleanly separated by column chromatography on silica gel into two diastereomeric forms melting at 89 and 140°. Unequivocal structures cannot be assigned to these on the basis of the information presently available. Examination of molecular models suggests that the *dl* isomer is more symmetrical and less sterically hindered. On this basis the higher melting isomer, which is also more strongly absorbed on the silica gel column, is tentatively assigned the *dl* structure. Equilibration with 0.5 *M* sodium methoxide in methanol at 25° for 7 days gave a mixture consisting of 55.6% of the 140° isomer and 44.4% of the 89° isomer (this corresponds to a 130-cal/mole difference in ground-state energy). Since structure assignment was not vital to the present work, resolution was not attempted.

Most of the rate measurements were made using the isomer melting at 89° since its greater solubility al-

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(1) National Science Foundation Undergraduate Research Participant, summer 1965.

(2) National Institutes of Health Predoctoral Fellow, 1964–1966.

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