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BEHAVIOUR OF 1-PHENYLETHYL CHLORIDE IN AQUEOUS ETHANOL: α-DEUTERIUM ISOTOPE EFFECT ON SOLVOLYSIS RATES†

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Abstract—α-Deuterium effects on the voltolysis rates of 1-phenylethyl chloride in ethanol-water mixtures within the 80–100% EtOH range are reported. According to Shiner's investigations,[9] a monotonical decrease of k_H/k_D with decreasing water content was expected. Results show the existence of a minimum for k_H/k_D in approximately 90 vol.% EtOH. This behaviour might be accounted for in the framework of Shiner's mechanistic scheme if (i) H-bonded intermolecular associations, in which ethanol and water should have their reactivity changed (ii) the structure of such clusters should depend upon the solvent composition.

Although nucleophilic substitutions at saturated carbon are among the best studied reactions in organic chemistry, many fundamental mechanistic problems have not been solved. Thus, a large number of examples characterised by properties associated at one and the same time with $S_{N}1$ and $S_{N}2$ mechanisms have been a subject of controversy. Several theories[1-5]—including $S_{N}1$–$S_{N}2$ dual mechanism, variable transition state structure, ion-pair intermediates—have been advanced to account for these "borderline" cases.

Substituent effects are widely used in mechanistic investigations, although modifications in the reactant structure change its electronic potential energy surface. On the other hand, because isotopes of a same atom have identical nuclear charges, the electronic energy of a molecule is independent of isotopic substitution within the limits set by the Born-Oppenheimer approximation.[6,7] Consequently:

(1) Isotope effect is nothing but nuclear mass effect;

(2) vibrational force constants (but not reduced mass dependent vibrational frequencies) are identical for isotopic atoms as well in the reactant as in the transition state, and, because of the difference in vibrational frequencies of isotopic atoms, the zero point energy is different for molecules differing only by isotopic substitution;

(3) isotope effects are more appropriate than ordinary substituent effects to provide information about the nature of the transition state: this property has widely been used.[8]

α-Deuterium effects on the solvolysis rates of 1-phenylethyl chloride and bromide, and some of their substituted derivatives in a series of aqueous organic solvents have been investigated by Shiner *et al.*[9]

The present paper reports kinetic α-deuterium isotope effects (k_H/k_D) on the solvolysis of 1-phenylethyl chloride in ethanol–water mixtures, the alcohol content of which rises from 80 to 100%.

Reaction reates were successively measured at 50 ± 0.05° and at 60 ± 0.05° by classical volumetric methods. In all cases, kinetics were carried out, until *ca.* 80% of the substrate had reacted. Each of them was composed of ten or more points. The pseudo first order rate constant was deduced from the slope of the straight line:

$$\log\frac{V_\infty}{V_\infty - V} = k.t$$

determined by means of the least square method, each k value being the mean of four or more measurements (V and V_∞ being respectively the titrant volume at t and at $t = \infty$). The probable error of the means varied between 0.10% and 0.20% and that of the ratio k_H/k_D between 0.20% and 0.40%, whilst k values were reproducible within 0.3 to 0.9%.

Between 50 and 80 vol % EtOH, 1-phenylethyl chloride has shown a kinetic α-D effect which decreases monotonically from 1.153 to 1.146 (Table 1). It seemed reasonable to predict a similar variation of k_H/k_D between 80 and 100% EtOH. The dielectric constant of H_2O–C_2H_5OH mixtures is known to decrease monotonically, as the water content is lowered.

Contrary to all expectations, the results reported here show the ratio k_H/k_D decreasing from 1.149 in 80 vol % EtOH to 1.097 in pure ethanol by passing through a minimum near 1.055 in approximately 90 vol % EtOH.

The difference in vibrational zero point energy between the ground and transition states, as a result of modifications in molecular vibrational force constants is believed to provide the major contribution to kinetic α-deuterium isotope effects. In the framework of this assumption, the difference in zero point energy between C–H and C–D is greater in the fundamental state than in the transition state, if activation causes the force constants to decrease; hence, $k_H/k_D > 1$, according to the relationship:

$$\frac{k_H}{k_D} = \exp[-\Delta ZPE/kT]$$

where:

$$\Delta ZPE = \sum_{1}^{3n-7}\frac{h}{2}(\nu_H^{\neq} - \nu_D^{\neq}) - \sum_{1}^{3n-6}\frac{h}{2}(\nu_H - \nu_D)$$

represents the difference in zero point energy. If

Table 1. α-D effect in the solvolysis of 1-phenylethyl chloride in 50–80 vol % EtOH[9]

Vol. % EtOH	50	60	70	80
k_H/k_D (25°C)	1.153	1.151	1.149	1.146

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ivation causes the force constants to increase, then $/k_D < 1$. Two other factors have implicitly been eglected in the preceding approximation: the transmission coefficient and the tunnel effect. The transmission coefficient which expresses the fact that not all systems lying above the potential barrier will actually react, should not be affected by isotopic substitution, since it depends upon the geometry of the potential energy surface. As to the tunnel effect, it is usually believed to provide no appreciable contribution to deuterium isotope effect. This assumption has been criticized by Bell.[10] More recently, the problem has been reexamined by Weston.[11]

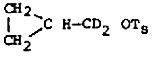
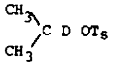
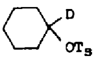
The value of the ratio k_H/k_D in a unimolecular process is a function of not only hydrogen- carbon-leaving group bending force constant changes attendant upon activation ($f_{HCX} \rightarrow f^{\ddagger}_{HCX}$), but also of the transition state geometry. However, although its magnitude depends upon the nature of the leaving group[12] and despite the fact that no information about the geometry of the activated complex is available, it has been suggested from empirical evidence that an α-D effect of *ca.* 1.12 per α-D at 105° (or 1.15 at 25°) should be characteristic of a Sn_1 reaction. On the other hand, the ratio k_H/k_D in a synchronous displacement is a function of the bonding of both the leaving group X and the nucleophile N to the reacting carbon C_α. Its value depends upon the difference ($f_{HCX} - f^{\ddagger}_{HCX}$) and upon the magnitude of $f^{\ddagger}_{HCN}$. Again in spite of the fact that the force constants $f^{\ddagger}_{HCX}$ and $f^{\ddagger}_{HCN}$ are unknown, an α-D effect of *ca.* 1.0 per α-D has been advanced as an evidence in support of the bimolecular process.

In actual fact, α-D effects greater than 1.15 and less than 1.0 have been reported (Table 2). Nevertheless, these postulates are helpful in mechanistic investigations.

The examination of Fig. 1 leads to the conclusion that according to the discussion above, the mechanism involved in the solvolysis of 1-phenylethyl chloride in aqueous ethanol within the 80–100% EtOH composition range is neither pure Sn_1, nor pure Sn_2, but lying between these two extreme types. But the most interesting fact reported in the present paper is the existence of a minimum of *ca.* 1.055 for the α-D effect in approximately 90 vol % EtOH. In that solvent, the Sn_2 character should be predominant.

If we were dealing with a mixture of Sn_1 and Sn_2 mechanisms in 80–100% EtOH, a lowering in solvent polarity would be to favour the bimolecular process. A second possibility is that the transition state structure should be varying with the solvent composition, its nucleophilic character being more and more important, as

Table 2.

Substrate	Reaction	k_H/k_D (per α-D)	Ref.
	EtOH 20° C	1.20	13
	CF_3CO_2H 25° C	1.22	14
	AcOH 50° C	1.22	15
CD_3I	H_2O 70° C	0.95	16
CD_3Br	H_2O 80° C	0.96	16
CD_3Cl	H_2O 90° C	0.97	16

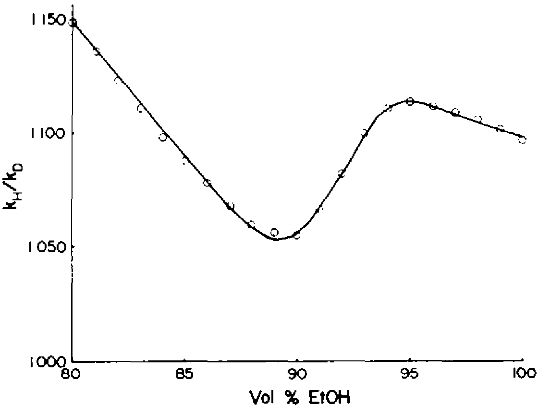
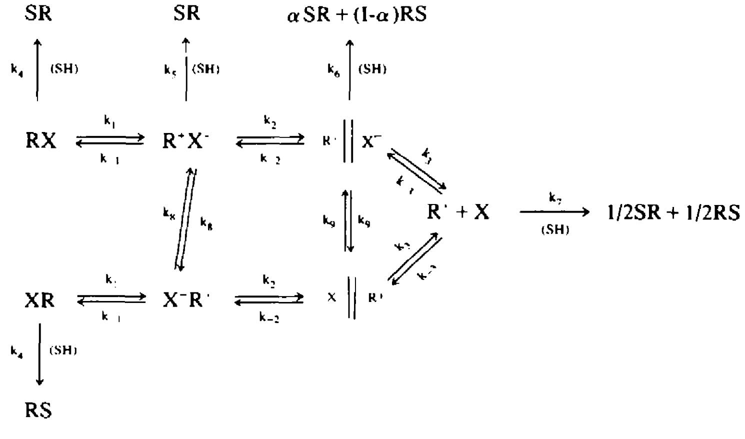


Fig. 1. Solvolysis of 1-phenylethyl chloride in aqueous ethanol.

the dielectric constant is lowered. In other words, the α-D effect in both cases should be to decrease with decreasing water content. In actual fact, k_H/k_D increases, as the ethanol percentage rises from *ca.* 90% to 95%.

Shiner[9] has proposed for solvolytic substitution the following general mechanistic scheme:



in which R^-X^- and $R^+ \| X^-$ are respectively tight and solvent separated ion-pairs, SH the solvent, RX and XR enantiomeric forms of the substrate, RS and SR enantiomeric reaction products. The fact that the solvolysis of 1-phenylethyl chloride and its more reactive derivatives has shown α-D effects of 1.147–1.158 should provide evidence that the formation of $R^+\|X^-$ should be rate determining (k_2) with a transition state having no appreciable covalent attachment of solvent to the reacting carbon C_α. Nucleophilic attack by solvent on $R^+\|X^-$ should not necessarily lead to a racemate, the extent of inversion depending upon the nature of the leaving group. For the less reactive derivatives of 1-phenylethyl chloride ($1.114 < k_H/k_D < 1.146$), nucleophilic attack by solvent on the tight ion-pair should compete with the preceding process. The transition state should have in that case a partial covalent bond between the attacking solvent and C_α, the strength of which should determine the magnitude of k_H/k_D, the leaving group being no longer covalently bound to C_α ($f^{\neq}_{HCX} = 0$).

That strength and therefore the α-D effect should depend upon the substrate ability to ionise and the solvent polarity and nucleophilicity, according to the Hammond postulate. Moreover, if nucleophilic attack by solvent on the substrate were rate determining, the transition state would also have a partial covalent bond between the attacking solvent and C_α and k_H/k_D should also be substrate and solvent dependent, but its magnitude should be much smaller.

Extrapolation to α-D effects of the range 1.055–1.114 is tempting. Indeed, it could be argued that, as k_H/k_D decreases, attack by solvent on the tight ion-pair should be more and more important, although it is presumably competed with by a bimolecular process. In actual fact, it is not easy to decide the frontier between the two mechanisms.

At any rate, an α-D effect of 1.055 should indicate a significant extent of nucleophilic attack by solvent on RX or R^+X^-. The partial covalent bond between the attacking solvent and C_α should have an appreciable strength and, hence, the transition state should be product-like.[17] It is concluded that in the ethanol–water mixture corresponding to the minimum in k_H/k_D, the attacking solvent should be less nucleophilic than water or ethanol.

The temperature dependence of k_H/k_D may be useful in mechanistic discussions. For this purpose, the α-deuterium effect on the solvolysis rate of 1-phenylethyl chloride in ethanol–water mixtures of varying composition was determined successively at 50° and 60°. Results are summarized in Table 3. It is noteworthy that in 90 vol % EtOH, the ratio k_H/k_D is hardly sensitive to temperature change.

Table 3.

Vol.% EtOH	k_H/k_D (50°C)	k_H/k_D (60°C)
80	1.149	1.133
85	1.088	1.080
90	1.055	1.052
95	1.114	1.104
100	1.097	1.089

Now, the kinetic α-D isotope effect may be expressed approximately by:

where M_H = (= 140.5) and M_D (= 141.5) are the molecular weights of $C_6H_5CHClCH_3$ and $C_6H_5CDClCH_3$, I_{H_1}, I_{H_2}, I_{H_3}, the principal moments of inertia relative to the hydrogenated reactant, and n the number of nuclei in the isotopic molecules. The ratio k_H/k_D appears to be the product of three factors:

$$\frac{k_H}{k_D} = \text{MMI} \cdot \text{EXC} \cdot \text{ZPE}.$$

The MMI (mass, moment of inertia) term involves the translational and rotational partition functions, whilst the EXC (excitation) and ZPE (zero point energy) terms represent the vibrational partition function. The relative mass variation by replacing PhCHClMe by PhCDClMe is less than 0.8%. Hence, MMI is very close to one. On the other hand, the vibration involved in deuterium isotope effects are usually of high frequency, so that e^{-u_i} is near zero and the term EXC approximately equals one. The α-D effect is then given by:

$$\frac{k_H}{k_D} = \frac{\exp\left[\sum_{1}^{3n-6} (u_{H_i} - u_{D_i})/2\right]}{\exp\left[\sum_{1}^{3n-7} (u^{\neq}_{H_i} - u^{\neq}_{D_i})/2\right]} = \exp\left[-\Delta ZPE/kT\right]. \quad (2)$$

ΔZPE is the difference in zero point energy of the hydrogenated and deuterated molecules between the transition and ground states. $\Delta ZPE < 0$, when $k_H/k_D > 1$, so that in the solvolytic reactions under investigation, k_H/k_D must decrease, as the temperature rises. The temperature dependence of k_H/k_D is determined by the magnitude of $|\Delta ZPE|$. The greater the latter is, hence the greater k_H/k_D is, the more sensitive to temperature k_H/k_D is. On the other hand, α-D effects near unity ($\Delta ZPE \simeq 0$) depend little on temperature.

Thus, a unimolecular process is characterised by a ratio $k_H/k_D > 1$ very sensitive to temperature and a bimolecular mechanism by a ratio $k_H/k_D \simeq 1$ depending very little on temperature.

The validity of the preceding conclusion depends upon that of the successive approximations leading to the eqn (2). Indeed, it might be objected that, when the sensitivity of k_H/k_D to temperature is very low, the contribution to the α-D effect of the translational and rotational partition functions would be predominating. In that case, the MMI term in eqn (1) could no longer be set to one.

The behaviour of the α-D effect in the solvolysis of 1-phenylethyl chloride in $EtOH–H_2O$ mixtures, especially the minimum in k_H/k_D might be characteristic of these binaries. The replacement of ethanol by another alcohol appears to be of great interest.

Thus, 1-phenylethyl chloride was allowed to solvolyse in methanol-water mixtures at 50 ± 0.05°. The composition dependence of k_H/k_D is shown in Fig. 2.

The values taken by the ratio k_H/k_D in 80–100 vol % MeOH indicate that 1-phenylethyl chloride should solvolyse in these solvents through a "borderline" mechanism. Such a process might involve as rate-determining step the formation of a solvent separated ion-pair and/or nucleophilic attack by solvent on the tight ion-pair coming

$$\frac{k_H}{k_D} = \frac{\left(\frac{M_D}{M_H}\right)^{3/2}}{\left(\frac{M^{\neq}_D}{M^{\neq}_H}\right)^{3/2}} \cdot \frac{\frac{I_{D_1}I_{D_2}I_{D_3}}{I_{H_1}I_{H_2}I_{H_3}}}{\frac{I^{\neq}_{D_1}I^{\neq}_{D_2}I^{\neq}_{D_3}}{I^{\neq}_{H_1}I^{\neq}_{H_2}I^{\neq}_{H_3}}} \cdot \frac{\prod_{1}^{3n-6} \frac{1-e^{-u_{H_i}}}{1-e^{-u_{D_i}}}}{\prod_{1}^{3n-7} \frac{1-e^{-u^{\neq}_{H_i}}}{1-e^{-u^{\neq}_{D_i}}}} \cdot \frac{\exp\left[\sum_{1}^{3n-6} (u_{H_i} - u_{D_i})/2\right]}{\exp\left[\sum_{1}^{3n-7} (u^{\neq}_{H_i} - u_{D_i})/2\right]} \quad (1)$$

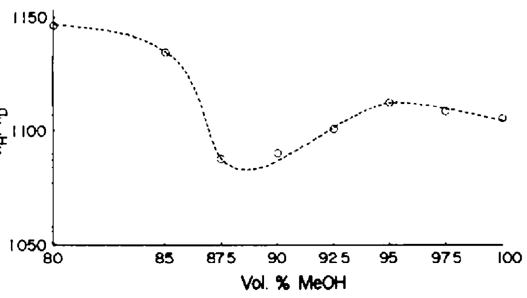


Fig. 2. Solvolysis of 1-phenylethyl chloride in aqueous methanol.

from the substrate. But, again, the most interesting fact is beyond all doubt the minimum in k_H/k_D near 1.088 observed in approximately 87 vol % MeOH, even though it is not as deep as that relative to aqueous ethanol.

The linear free energy rellationship expressed through the Hammett equation implies that changes in ring substituent in the substrate molecule do not cause the nature of the transition state, particularly its charge to change. This constitutes a helpful tool for the present discussion. Thus, the ρ constant relative to a few H_2O-EtOH mixtures has been determined from p-methyl- and m-bromophenylethyl chlorides ($\sigma_{p\text{-}CH_3} = -0.311$ and $\sigma_{m\text{-}Br} = +0.391$).

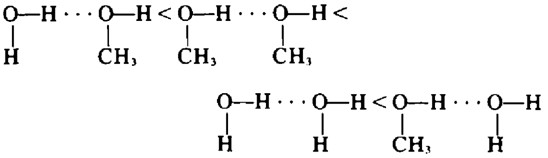
The consideration of Table 4 leads to the following conclusions. The negative values of $\rho(p\text{-Me})$ and $\rho(m\text{-Br})$ seem to indicate that the solvolysis of 1-phenylethyl chloride in ethanol–water mixtures proceeds through a S_N1 type mechanism. But the fact that for a given binary the absolute value of ρ_{60° (m-Br) is less than that of ρ_{60°(p-Me) might be accounted for, if an actual participation of the solvent in the formation of the transition state were assumed. Indeed, nucleophilic assistance of the solvent should stabilize the positive charge of the activated complex, so that the latter should have little sensitivity to electron-withdrawing substituent effects.

The change in rate constant with the solvent composition is related to modifications of $\Delta H^{\neq}$ and $\Delta S^{\neq}$, which partly compensate each other. On the other hand, a structure change in the transition state modifies activation parameters. Compensating changes in $\Delta H^{\neq}$ and $\Delta S^{\neq}$ (Table 5) as the binary solvent composition is varied, are believed to be characteristic of solvation modifications.[18] The minimum in $\Delta H^{\neq}$ and $\Delta S^{\neq}$ in approximately 90 vol % EtOH may be related to the maximum order in the structure of the solvent mixture, according to Arnett's investigations.[19,20] Moreover, negative entropies of activation might be in connection with two factors: (i) important solvation of the transition state (s) with regard to that of the starting material (ii) nucleophilic assistance of the solvent in relation with the bimolecular mechanism. Since the ethanol content is the only parameter, it is concluded that the structure of actual reagents in these solvolytic reactions should depend upon the solvent composition.

The stereochemical aspect has been examined by Okamoto *et al.*,[21] whose results are summarized in Table 6.

These authors reported the inversion extent of the reaction products obtained in the solvolysis of optically active 1-phenylethyl chloride in aqueous ethanol. Up to 90 vol % EtOH, the net inversion of of PhCHOHMe is less than that of PhCH(OEt)Me, but from that alcohol concentration upwards, the reverse result is observed. It is noteworthy, that the minimum in α-D effect occurs also in about 90 vol % EtOH. The changes in α_{ROH} and α_{ROEt} vs the ethanol content seem to indicate that complex phenomena of intermolecular association occur in ethanol-water mixtures, giving rise to aggregates, in which the components have their reactivity changed.

The hydrogen bond energy has been shown to increase in the sequence:[22]



$$\underset{\text{H}}{\text{O}}\text{—H}\cdots\underset{\text{CH}_3}{\text{O}}\text{—H} < \underset{\text{CH}_3}{\text{O}}\text{—H}\cdots\underset{\text{CH}_3}{\text{O}}\text{—H} <$$

$$\underset{\text{H}}{\text{O}}\text{—H}\cdots\underset{\text{H}}{\text{O}}\text{—H} < \underset{\text{CH}_3}{\text{O}}\text{—H}\cdots\underset{\text{H}}{\text{O}}\text{—H}$$

Table 4.

Vol. % EtOH	80	85	90	95	100
ρ (p-CH$_3$) 60°	-5.09	-5.07	-5.05	-5.03	-5.02
ρ (m-Br) 60°	-4.19	-4.01	-3.73	-3.65	-3.59

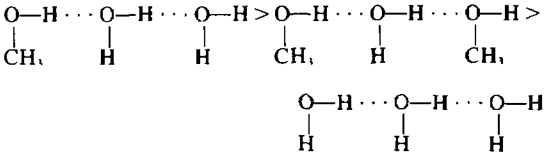
Table 5. Solvolysis of 1-phenylethyl chloride in aqueous ethanol at 50°

Vol.% EtOH	ΔH$^{\neq}$(kcal)	ΔS$^{\neq}$(cal/)	ΔG$^{\neq}$(kcal)
80	20.99	- 9.0	23.90
85	20.97	-10.0	24.31
90	20.35	-13.9	24.85
95	23.21	- 7.1	25.49
100	23.41	- 8.6	26.18

Table 6.

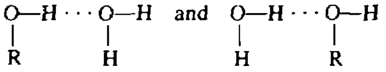
Vol.% EtOH	0	20	30	40	50	60	70	80	90	95
α_{ROH}(%)	23.8	23.6	23.3	24.2	25.6	26.5	27.5	31.5	45.4	61
α_{ROEt}(%)	-	31.0	33.3	-	34.4	32.2	41.1	41.9	46.7	47

On the other hand, the stability of linear trimers should follow the order:



$$\underset{CH_3}{O}\text{—H}\cdots\underset{H}{O}\text{—H}\cdots\underset{H}{O}\text{—H} > \underset{CH_3}{O}\text{—H}\cdots\underset{H}{O}\text{—H}\cdots\underset{CH_3}{O}\text{—H} > \underset{H}{O}\text{—H}\cdots\underset{H}{O}\text{—H}\cdots\underset{H}{O}\text{—H}$$

Accordingly, H-bond formation between methanol and water should be energetically favoured and in the resulting associations, the MeOH molecule should preferentially behave as proton donor. In actual fact, NMR chemical shift and relaxation time measurements have been reported in support of the existence of both H-bond types:[23]



$$\underset{R}{O}\text{—H}\cdots\underset{H}{O}\text{—H} \quad \text{and} \quad \underset{H}{O}\text{—H}\cdots\underset{R}{O}\text{—H}$$

Unfortunately, little is known about ethanol–water associations and their reactivity with regard to nucleophilic substitution.

The variation of k_H/k_D within the 80–100% EtOH concentration range in the solvolysis of 1-phenylethyl chloride in C_2H_5OH-H_2O mixtures was expected to be monotonically decreasing. If such was the case, the behavior of the α-D effect might be explained by the only consideration of the mechanistic scheme proposed by Shiner.[9] In other words, from 50 to *ca.* 80 vol % EtOH, the formation of a solvent separated ion-pair coming from the substrate should be rate-determining. But, from that alcohol content upwards, the preceding process should be competed with by the nucleophilic attack by solvent on the tight ion-pair and/or on the reactant itself. The results reported in this paper are more complex. However, the ratios k_H/k_D observed between 80 and 100% EtOH, especially the presence of the minimum might be accounted for if, in addition to Shiner's mechanistic scheme, H-bonded intermolecular associations, the structure of which should depend upon the solvent composition, were assumed present in the hydroxylic mixed solvents above. In these clusters, which should be the actual reagents in solvolytic reactions, the reactivity of water should be much more attenuated than that of ethanol. The formation of PhCHOHMe should involve a transition state, in which a partial covalent bond of appreciable strength should be established between water and the reacting carbon, providing thus a small α-D effect (near unity). The formation of PhCH(OEt)Me should result from the attack either by an ethanol molecule belonging to a H_2O-EtOH aggregate or by alcohol molecules more or less associated. At any rate, the reactivity of ethanol with regard to nucleophilic substitution should be little affected. The observed ratio k_H/k_D is in actual fact the mean of two α-D effects corresponding to hydrolysis and ethanolysis.

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