Alkoxide Solutions: ^{1}H Nuclear Magnetic Resonance Chemical Shifts, Deuterium Fractionation Factors, and the Solvation of Alkoxide Ions

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The effect of added sodium alkoxides on the position of the hydroxy proton resonance of the respective alcohols has been measured for ethanol, isopropyl alcohol, and t-butyl alcohol. Corresponding measurements have also been performed for solutions in hydroxy-deuteriated alcohols containing only a small fraction of the hydroxy-protiated alcohol. Analysis of the data leads to the conclusions (1) that for all three alcohols the deuterium fractionation factor (measuring the isotopic discrimination between bulk solvent molecules and solvent molecules hydrogen-bonded to alkoxide ions) has a value (*ca.* 0.75) close to that in the previously studied sodium methoxide–methanol system, (2) that the average number of solvent molecules hydrogen-bonded to alkoxide ions decreases down the series, from 3 for methanol to *ca.* 1.6 for t-butyl alcohol, which is consistent with the parallel increase in basicity of the solutions, (3) that the effect of sodium perchlorate, unlike that of sodium alkoxides, on the position of the hydroxy-proton resonance is essentially the same in all solvents, and (4) that hydroxy-deuteriation of the solvent appears to lead in all cases to a small upfield shift of the resonance of the residual hydroxylic protium.

The proton resonance of hydroxylic protons in the n.m.r. spectrum of liquid methanol is shifted downfield in the presence of sodium methoxide.[1,2] The position of the displaced signal is interpreted as the concentration-weighted average [3] of the absorptions of unbound (or mutually hydrogen-bonded) solvent molecules and of solvent molecules attached by solvation forces to the solute particles. The largest contribution to the downfield displacement of the signal is ascribed to the deshielding of hydroxylic protons in hydrogen-bonded alkoxide–alcohol solvates $RO^- \cdots (HOR)_v$. Provided the concentrations are not too high, the effect is proportional to concentration. Corresponding shifts have also been noted in related hydroxylic solvents, water [4] and ethanol.[5]

Analogous measurements of the position of proton resonances in hydroxy-deuteriated alcohol media show the same effect in a more pronounced manner. At low concentrations the observed chemical shift Δ, measured relative to a fixed standard signal, is expressed by equation (1) (where Δ° is the

$$\Delta = \Delta^\circ + x\bar{\delta} \qquad (1)$$

shift in the absence of alkoxide and x the mole fraction of alkoxide in solution) (see Figure 1). The coefficient $\bar{\delta}$ (or slope) measures the sensitivity of the position of the hydroxy signal to the presence of alkali metal alkoxide. The ratio of the coefficient $\bar{\delta}$ in a light solvent ($\bar{\delta}_0$) relative to that in a partly deuteriated solvent ($\bar{\delta}_n$, where n represents the atom fraction of deuterium in hydroxylic positions) depends on the deuterium fractionation factor φ, according to equation (2).[6]

$$\bar{\delta}_0/\bar{\delta}_n = 1 - n + n\varphi \qquad (2)$$

Provided the effect expressed by φ is entirely ascribable to the presence of alkoxide ions, the factor φ represents the fractionation of deuterium between alkoxide-bonded and ' free ' (or mutually solvent-bonded) hydroxy groups. Measurements of $\bar{\delta}_0$ and $\bar{\delta}_n$ (usually when n is close to unity) thus allow an

$$\varphi = (D/H)_{\text{alkoxide-bound}}/(D/H)_{\text{bulk alcohol}} \qquad (3)$$

evaluation of φ. The method was originally developed to study fractionation in aqueous hydrogen ions,[7] but it has successfully been applied to sodium methoxide in methanol [1,2] and sodium ethoxide in ethanol.[5] Since $\bar{\delta}$ contains a contribution from the metal cation, the value of φ obtained in this manner should be corrected for the effect of the metal cation. This has been attempted in the case of sodium methoxide where the correction was shown to be small;[2] for other alcohols the requisite information is not directly available, but there is evidence that a similar correction may be more generally valid.

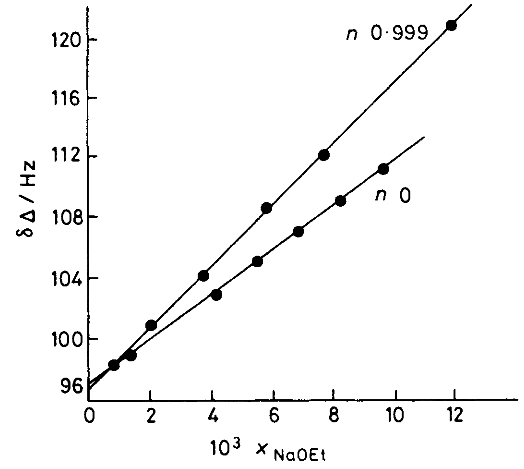


Figure 1. Dependence of ^{1}H n.m.r. signal separation ($CH_3C\mathit{H}_2O\mathit{H}$) on concentration of sodium ethoxide in ethanol (60 MHz)

The present study extends measurements of these effects to other alcohols in order to provide information on the solvation of alkoxide ions through the series CH_3OH, CH_3CH_2OH, $(CH_3)_2CHOH$, $(CH_3)_3COH$. Indicator measurements on alkoxide solutions (in the corresponding alcohols) reveal remarkably large differences in their basicity, as measured by *H*-functions for solutions of equal concentration. On this basis Bowden [8] gave the following values for the relative basicities on the (logarithmic) H_- scale H_2O : MeOH : EtOH : Pr^iOH : Bu^tOH = 14.00 : 13.66 : 15.57 : 17.95 : 20.14 which corresponds to a factor of *ca.* 3 × 10^6 in basicity between MeOH–MeONa and Bu^tOH–Bu^tONa media of equal molarity of alkoxide ions. The present work explores the information on hydrogen bonding that can be deduced from chemical shift

Table 1. N.m.r. observations on alcohol–sodium alkoxide solutions

System	t/°C	n	Maximum value of x	$\bar{\delta}$/p.p.m. x^{-1}	Δ°/p.p.m.	Signal separation observed
MeOH–MeONa [a]	33.5	0		25.41	1.4735	CH_3–OH
MeOD–MeONa [a]	33.5	0.965		35.09	1.456	CH_3–OH
EtOH–EtONa	34.8	0	0.0098	23.22 [b]	1.619	CH_2–OH
EtOD–EtONa	34.8	0.999	0.012	32.18 [c]	1.611	CH_2–OH
Pr^{i}OH–Pr^{i}ONa	34.8	0	0.020	18.03	1.222	CH–OH
Pr^{i}OD–Pr^{i}ONa	34.8	0.994	0.018	24.90	1.177	CH–OH
Bu^{t}OH–Bu^{t}ONa	34.8	0	0.024	12.10	3.329	CH_3–CH
Bu^{t}OD–Bu^{t}ONa	34.8	0.997	0.025	16.90	3.300	CH_3–OH

[a] From ref. 2. [b] Beltrame *et al.*[5] report a value of 24.00 at 42.0 °C. [c] Beltrame *et al.*[5] report a value of 32.50 for n 0.897 at 42.0 °C.

Table 2. N.m.r. observations on alcohol–sodium perchlorate solutions

Alcohol	t/°C	Max. conc. (M) [a]	$\bar{\delta}_{salt}$/p.p.m. x^{-1}	Δ°/p.p.m.	Signal separations observed	Source
MeOH	33.5	0.48	-7.79 ± 0.10 [b]	1.474	CH_3–OH	c
EtOH	20	0.22	-7.11 ± 0.09	4.2128	CH_3–OH	This work
			$+0.22$	2.4322	CH_3–CH_2	This work
Pr^{i}OH	20	0.12	-6.50 ± 0.10	4.1886	CH_3–OH	This work
			$+0.53$	2.7816	CH_3–CH	This work
	30	0.14	-6.79 ± 0.32	4.0646	CH_3–OH	This work
			$+0.24$	2.7823	CH_3–CH	This work
Bu^{t}OH	30	0.021	-7.3 ± 1.6 [d]	3.404	CH_3–OH	This work

[a] M = mol dm^{-3}. [b] Standard deviation. [c] Ref. 2. [d] Results at single concentration (0.0205M) only, limited by low solubility.

and fractionation measurement and its possible bearing on the basicity of the media.

It seems to be generally accepted that the relative basicities are related to the solvation of the alkoxide ions: they certainly do not find a ready explanation on the basis of simple electronic effects or ion pairing. The electronic effects of methyl substitution on the proton affinity of the proximate oxygen atom of the alkoxide ion appear to be inadequate since in the corresponding series of amines, CH_3NH_2 to $(CH_3)_3CNH_2$, the K_a values do not differ by more than a factor of two.[9] Again, although ion-pairing effects play a role in alcoholic media, studies of ethoxide solutions in ethanol suggest that such effects do not exert a major influence on acidity function values until higher concentrations than those considered by Bowden [8] are reached.[10,11] Ion pairing reduces the basicity of solutions. It is thought to be most marked in the alcoholic media of lowest relative permittivity for which the *highest* basicities are in fact observed; it is therefore not responsible for the relative base strengths of the alcohol–alkoxide systems considered.

Experimental

The purest commercially available alcohols were refluxed over sodium (over potassium in the case of t-butyl alcohol) and fractionally distilled. The corresponding deuteriated alcohols [C_2H_5OD from Fluorochem. Ltd., $(CH_3)_2CHOD$ and $(CH_3)_3COD$ from Aldrich Chemical Co.] were used without purification. Their deuterium content was assayed by n.m.r. (99.5% D). Stock solutions of sodium alkoxides were prepared by dissolving freshly cut sodium metal in the appropriate alcohol whilst passing a stream of nitrogen (oxygen-free). The solutions were standardised by titration against hydrochloric acid.

Because of the very high basicity and reactivity of the solutions of t-butoxide, additional precautions were taken in this case. The specimens of the alcohols used (both normal and deuteriated) were de-gassed by repeated freeze–pump–melt cycles on a vacuum line. Solutions were then prepared and diluted in a nitrogen-flushed glove-box. Before its n.m.r. spectrum was taken, each sample was centrifuged under nitrogen in order to remove any precipitated sodium carbonate. A small amount of the supernatant solution was placed in the n.m.r. tube. Several portions of the remainder were diluted with water and titrated. N.m.r. tubes were sealed with Parafilm before removal from the glove-box and spectra were taken within 10 min of being centrifuged.

For measurements on solutions of sodium perchlorate, ethanol was dried by refluxing with diethyl succinate (2 h) and the other alcohols over previously dried (3 h, 260°) molecular sieve, followed by slow fractional distillation with collection of the middle half of the distillate.

For all alkoxide solutions n.m.r. spectra were recorded at a series of concentrations (Perkin-Elmer R12B spectrometer operating at 60 MHz and sample temperature of 34.8 °C). The position of the hydroxylic peak was measured relative to that of a CH signal of the specimen (centre of the CH_2 group in the case of ethanol, CH group in the case of propan-2-ol, CH_3 group for t-butyl alcohol). These frequency differences (Δ) were fitted (least squares) to the linear equation (1) (see Table 1).

In accordance with current practice downfield chemical shifts are taken as positive. This sign convention differs from that used in our previous papers but we wish to draw attention to the erroneous omission of minus signs in the last two lines of Table 4 of ref. 2.

Results of measurements are summarised in Tables 1 and 2. The parameters φ derived from the data by use of equation (2) are given in Table 3. These fractionation factors do not take into account the contribution (δ_2) to the value of $\bar{\delta}$ by the sodium ion. If this contribution is explicitly included [2] (and assumed not to depend on the isotopic composition of the solvent) equation (4) results, where φ_{corr} represents a counter-

$$\frac{\bar{\delta}_o - \delta_2}{\bar{\delta}_n - \delta_2} = 1 - n + n\varphi_{corr} \qquad (4)$$

Table 3. Deuterium fractionation factor measurements in NaOR–ROH systems

R	t/°C	n	δ_n	φ [a]	φ_{corr} [b]
Me [c]	33.5	0.965	35.09	0.714	0.736
Et	34.8	0.999	32.18	0.721	0.735
Pr^i	34.8	0.994	24.90	0.723	0.752
Bu^t	34.8	0.997	16.90	0.715	0.758

[a] Equation (2). [b] Equation (4), with δ_2 −2.97 p.p.m. x^{-1}. [c] Ref. 2.

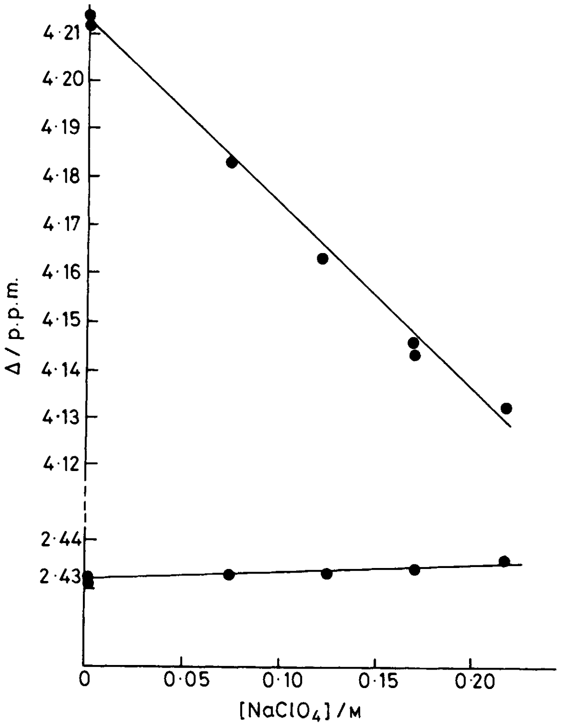


Figure 2. Dependence of ^1H n.m.r. signal separations on concentration of sodium perchlorate in ethanol (250 MHz) (upper line: CH_3CH_2OH; lower line: CH_3CH_2OH)

ion corrected fractionation factor. Values of δ_2, derived from experimental measurements on salt solutions, are available for methanol[2] but not for other alcohols. The role of this first-order correction is considered in the Discussion section in relation to the results for sodium perchlorate solutions.

The spectral results for sodium perchlorate solutions were obtained on Bruker 250 MHz spectrometers, those at 20 °C at King's College and the ones at 30 °C at Imperial College (thanks to the co-operation of Dr. H. Rzepa). For these small solute shifts the signal separations were obtained from the Fourier transform of a single free-induction decay on a sample uncontaminated by an internal standard. The finite channel width of the spectrometer computer sets a limit of between 5×10^{-4} and 7×10^{-4} p.p.m. on the accuracy of the individual signal separations measured. The data were again fitted to a linear equation (1), (see Figure 2) with the slope designated as δ_{salt}.

The most significant source of error in all measurements is probably the temperature of the sample in the probe, since the position of the hydroxy proton resonance changes with temperature. The standard deviations in the measurements on sodium perchlorate in isopropyl alcohol, for example, would correspond to probe temperature fluctuations of ±0.1 K, since $d\delta/dT = -0.016$ p.p.m. K^{-1}.

Discussion

The observed values of $\bar{\delta}$ for light alcohols (*i.e.* the sensitivity of the position of the hydroxy resonance to the presence of sodium alkoxide) are strongly dependent on the nature of the alcohol (Table 1). Using only the strictly comparable values from our laboratory, we find a slight decline in $\bar{\delta}$ from methanol to ethanol and larger ones from ethanol to isopropyl alcohol and from isopropyl to t-butyl alcohol. The value of $\bar{\delta}$ for t-butyl alcohol is just under one-half the value for methanol. These variations immediately suggest that there is a progressive and large change in the interaction between alkoxide ions and alcohol along this series of systems, affecting either the strength of the hydrogen bonding or the number of hydrogen bonds, or possibly both.

However, in spite of these differences, the deuterium fractionation factors, evaluated according to equation (2), stay remarkably constant throughout the series (Table 3). The n.m.r. method employed in these measurements yields values that are independent of any assumptions about the number of sites in the solute that are in isotopic exchange equilibrium with the free (or mutually hydrogen-bonded) solvent.[6]

Fractionation factors are governed solely by the effect of isotopic substitution on molecular properties that are in principle accessible *via* molecular spectra.[12] The most important of these are force constants, especially those of stretching vibrations which have the largest values and accordingly make the most important (though not the only) contribution to the effect. The preferential enrichment of the lighter isotope protium in solvent molecules bonded to the lyate ion is therefore linked to the lowering by strong hydrogen bonding, of the force constant of the O–H bond in the solvate. The near constancy of the isotopic fractionation for different hydroxylic solvents therefore suggests that there is a similar decrease in the mean O–H stretching force constant (and weakening of the O–H bond), irrespective of the nature of the alcohol and of the corresponding number ν. To produce a fractionation effect of the size observed for the sodium alkoxide solutions, the change in hydrogen-bonding in the species concerned in the exchange equilibrium (5) must be more marked than that involved in the change from liquid alcohol to vapour, where the deuterium fractionation is quite small.[13,14] The fractionation observed in the alkoxide solutions is therefore essentially attributable to the hydrogen-bonding in the alkoxide solvates.

$$(\mathrm{RO{-}H}\cdots)_\nu\,\bar{\mathrm{O}}\mathrm{R}$$

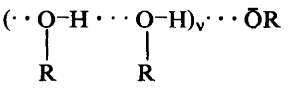
(I)

$$\nu\mathrm{ROD} + (\mathrm{ROH})_\nu\cdot\cdot\bar{\mathrm{O}}\mathrm{R} \rightleftharpoons \nu\mathrm{ROH} + (\mathrm{RO\bar{D}})^\nu\cdot\cdot\mathrm{OR}^- \qquad (5)$$

The similarity of these fractionation factors for different alcohol–alkoxide systems then suggests further that the OH stretching force constants of the alcohol molecules in the alkoxide solvates have very similar values for all these systems. It therefore also implies that the hydrogen bonds involved are of similar strength. If the argument is correct, then the remarkably large differences in the measured values of δ_0 of these alcohols must, in the main, be due to differences in the number of hydrogen bonds to the different alkoxide ions. The decrease along the series CH_3OH, $MeCH_2OH$, Me_2CHOH, Me_3COH can then straightforwardly be interpreted as a sterically induced diminution of the average solvation number ν.

Formula (I) for the solvate is somewhat simplistic in that it represents the ν solvating alcohol species as single molecules.

It is reasonable to suppose that the first ROH molecule would itself be hydrogen bonded to further alcohol molecules,



$$(\cdots \underset{\displaystyle R}{\underset{|}{O}}{-}H\cdots\underset{\displaystyle R}{\underset{|}{O}}{-}H)_{\nu}\cdots\bar{O}R$$

(II)

perhaps in a chain as in formula (II). To the extent that the deshielding effect of $\bar{O}R$ is transmitted beyond the alcohol molecules that are immediately hydrogen bonded to it, there may be a contribution to $\bar{\delta}$ from hydroxy groups involved in these more remote hydrogen bonds. However, their effect cannot be large. Although the fractionation factor was evaluated for methanol–methoxide from equation (2) on the assumption that only three equivalent hydrogen atoms are involved, these fractionation factors seem to be consistent with the solvent isotope effect on a chemical equilibrium constant.[15] The simple model (I), though certainly inadequate in a general sense,[16] thus seems sufficient for describing the alkoxide-induced chemical shift and for the evaluation of solvent isotope effects.

In making comparisons between different alcohols there is the further question whether the hydrogen-bonding in the pure alcohols is sufficiently similar to us to discount the possibility that differences in $\bar{\delta}$ values reflect major differences in the pure alcohols. However, the similarity of the hydrogen bonds in pure alcohols, at least as far as the shielding of the hydroxy-groups is concerned, is demonstrated by the observation that, at the same temperature, the chemical shifts of the four pure liquid alcohols considered in this study all lie within *ca.* ±0.3 p.p.m.

To test this point further we have measured the salt-induced shifts ($\bar{\delta}_{salt}$) of sodium perchlorate in the different alcohols. This salt causes an upfield shift in the hydroxy proton resonance which we take to imply that the effect of the ions in breaking solvent–solvent hydrogen bonds (which is known to result in an upfield shift) must outweigh the effect of forming solvent–perchlorate hydrogen bonds. Sodium perchlorate also has a relatively high solubility and is expected to be free from steric effects of its own. In spite of minor numerical discrepancies (which would not preclude the existence of a small systematic trend), the results (Table 2) demonstrate clearly that the δ_{salt} values are almost the same. (It may also be noted that a very similar value of 7.8 p.p.m. x^{-1} is obtainable from Hindman's tabulation of results for aqueous solutions.[17]) This again strongly suggests that in all the alcohols of the series studied the rupture of solvent–solvent hydrogen bonds has substantially the same effect on the position of the hydroxy proton resonance. Accordingly we also conclude that the inherent hydrogen-bonding ability of hydroxy groups is very similar in all cases, and that the use of the same value of δ_2 in equation (4) is justified.

$$\bar{\delta} = \sum_j \nu_j \delta_j \qquad (6)$$

To express this effect quantitatively, we write equation (6)[3,18] on the supposition that each unit of NaOR dissolved creates *j* sets of new sites for exchangeable hydrogen nuclei in solution, with each set containing ν_j members and characterised by its individual shift δ_j (measured from the resonance position in pure solvent). Let us give the symbol δ_2 to the term in this sum that is attributable to sites created by the introduction of the sodium ion. Let us further assume that only one type of new site (ν_b in number and characterised by the shift δ_b) is due to the introduction of one alkoxide ion into the solution. Equation (6) then takes the more explicit form (7). The ν_b

$$\bar{\delta}_0 = \delta_2 + \nu_b\delta_b \text{ or } \delta_b = (\bar{\delta}_0 - \delta_2)/\nu_b \qquad (7)$$

sites with individual shift δ_b are identifiable with the hydrogen-bonded hydroxy-groups of the alkoxide solvate. We have previously concluded[2] that for the methanol–sodium methoxide system δ_2 has the value −2.97 p.p.m. x^{-1}, opposite in sign to the value of $\bar{\delta}_0$ and that $\nu_b = 3$ {x = [alkoxide]/([alkoxide] + [alcohol])}. Combined with the value[2] $\bar{\delta}_0$ 25.41 p.p.m. x^{-1}, this gives the result δ_b 9.46 p.p.m. x^{-1}. If the same (relatively small) value of δ_2 applies to the sodium ion in all the alcohols studied, the measured values of $\bar{\delta}_0$ for these different media may now be used to calculate the respective values of ν_b, *i.e.* the number ν of directly hydrogen-bonded alcohol molecules per alkoxide ion [equation (8)]. According

$$\nu_b = (\bar{\delta}_0 + 2.97)/9.46 \qquad (8)$$

to this model the results express a progressive fall in the average number of alcohol molecules hydrogen-bonded to the alkoxide ion as we pass down the series from methanol to t-butyl alcohol (Table 4). Correspondingly, there should be a decreasing thermodynamic stabilisation of the alkoxide ions and accordingly a higher basicity of the media, as is indeed observed.

Table 4. Solvation numbers of alkoxide ions and maximum solvent isotope effects

Alcohol	Solvation number (ν_b)[a]	Maximum solvent isotope effect ($\varphi_{corr}^{-\nu_b}$)	Solvation number (ν_b)[b]	Maximum solvent isotope effect ($\varphi^{-\nu_b}$)[c]
MeOH	(3)	2.51	(3)	2.75
EtOH	2.77	2.35	2.74	2.45
Pr^{i}OH	2.22	1.88	2.13	2.00
Bu^{t}OH	1.59	1.55	1.43	1.62

[a] Equation (8). [b] From equation (7) with $\delta_2 = 0$. [c] Using values of ν_b from preceding column.

These conclusions also have an application to solvent deuterium isotope effects in alkoxide solutions. It has previously been shown[2] that the thermodynamic solvent isotope effect of an equilibrium constant for a reaction leading to disappearance of a methoxide ion[15] (*e.g.*, a proton transfer or the formation of an alkoxide adduct) is given by $K_D/K_H = \varphi^{-3} = 0.74^{-3} = 2.5$ where the exponent 3 is the value of ν for the methanol–methoxide system. The same factor may be considered also to represent the maximum kinetic solvent isotope on such reactions. Corresponding calculations lead to the thermodynamic (and maximum kinetic) solvent isotope effects in other alcohol–alkoxide systems. These values of $\varphi_{corr}^{-\nu}$ are included in Table 4.

Levin[19] has reported experimental studies directed at measuring solvent isotope effects in proton (deuteron) transfers from carbon acids to the alcohol–alkoxide media considered here. Whilst the results obtained for methanol, ethanol, and isopropyl alcohol are compatible with our calculated maximum isotope effects, with k_D/k_H values decreasing along the series, there is a discrepancy in the case of t-butyl alcohol. The solvent isotope effect (k_D/k_H) in this solvent is stated to be generally larger than for the other alcohols. Its numerical values (up to 2.4 and 25 °C) exceed the maximum effect in Table 4. (Some earlier reports[20] of solvent isotope effects of less simple reactions give values in the range 1.7—2.2.)

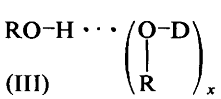
We do not regard Levin's results as disproof of our analysis but believe that they point to a number of relevant experimental and theoretical considerations. Levin's measurements with t-butyl alcohol were performed at a single concentration of base which, because of the high reactivity of t-butoxide, was very much lower than that used for the other alcohols. The preparation of very dilute solutions of exact concentration of bases in alcohols, and especially in t-butyl alcohol, is known to require special care.[21] Such solutions cannot reliably be prepared by ordinary dilution of a more concentrated stock solution, the procedure apparently followed by Levin.

If Levin's results are nevertheless accepted at face value, then the possible role of ion-pairing in all experiments should be considered. In the case of methanolic solutions of hydrogen chloride the n.m.r. measurements from which the deuterium fractionation factor for the hydrogen ion were derived, covered a concentration range in which the degree of ion-pair dissociation changed from 0.8 to 0.4.[2] Nevertheless the observed chemical shifts showed an accurately linear dependence on the stoicheiometric concentration. As was pointed out before, this result implies indistinguishable chemical shifts for ' free ' and ' paired ' hydrogen ions. In the case of the alkoxides the fractionation factor measurements mostly relate to a concentration range in which association is important, according to published values of ion-pair dissociation constants.[22] If, as in the case of t-butoxide, the kinetic measurements relate to a much lower concentration, it could be argued that chemical shifts and fractionation factors, measured at relatively high concentrations, consistently relate to ion pairs, whereas the kinetic measurements at low concentrations possibly refer to a mixture of ' free ' and paired alkoxide ions. Furthermore, it cannot be excluded that ' free ' ions and solvent-separated and solvent-shared ion pairs [23] all play a role at different concentrations, nor can the intervention of higher ionic aggregates be ruled out. If such complications apply, and there is indeed isotopic fractionation between differently associated ions, then fractionation factors may be applied to a kinetic analysis only if comparable alkoxide concentrations are used.

Levin's results with 1,3-dimethylindene indicate that, for all the alcohols, the potassium alkoxide is more reactive than the sodium alkoxide. An exact comparison between the different alcohols is not possible because different concentrations of all the alkoxides were used. Nevertheless, the results appear qualitatively to bear out the expectation, derived from earlier studies on these solvents of low relative permittivity,[22,24] that ion pairs are somehow involved.

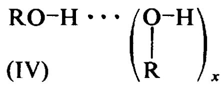
It might appear that the argument leading up to equation (8) relies to a large extent on the assumption regarding the value of the correction δ_2. To put this matter in perspective we have performed parallel calculations in which δ_2 is taken to be completely negligible. Columns 4 and 5 of Table 4 therefore also list solvation numbers and maximum solvent isotope effects calculated on this extreme assumption. It is evident that the detailed assumption about the values of δ_2 affects the main conclusions drawn from the model only to a minor extent.

It was previously noted [2] that the Δ^0 values [evaluated as the intercept from equation (1)] indicate that there is a smaller separation (by *ca.* 0.015 p.p.m.) between the proton resonances of methyl and hydroxy groups in largely hydroxy-deuteriated methanol than in ordinary methanol. Such a small difference, always in the same direction, is observed for all the alcohol systems of the present study. It is noteworthy that the effect is found both in t-butyl alcohol (where the reference signal is a β-methyl group) and in the other alcohols where an adjacent CH signals as used as reference. This adds support to our interpretation that in methanol the phenomenon is due to an upfield isotope effect on the position of the hydroxy resonance, rather than a downfield shift of the C–H resonance. A qualitative deduction from this result would be that the proton in a hydrogen-bonded and mainly deuteriated alcohol, represented by formula (III), is less deshielded relative to the protiated system (IV) or that the hydrogen bonding to the deuteriated



(III)

$$\mathrm{RO{-}H\cdots\left(\begin{array}{c}\mathrm{O{-}D}\\ |\\ \mathrm{R}\end{array}\right)_x}$$



(IV)

$$\mathrm{RO{-}H\cdots\left(\begin{array}{c}\mathrm{O{-}H}\\ |\\ \mathrm{R}\end{array}\right)_x}$$

alcohols is less extensive, *i.e.*, the deuteriated alcohol is a less good hydrogen bond acceptor than the light alcohol. This effect is not in the direction expected by analogy with secondary isotope effects on the strength of bases.

Alternatively, if the position of the hydroxy-resonance is considered to be a weighted mean of signals due to free and hydrogen-bonded hydroxy groups, the isotope shift of the resonance may be looked on as primarily reflecting an isotope effect on the hydrogen-bonding equilibrium (9). The slight

$$-\mathrm{OH}_{\text{non-bonded}} \rightleftharpoons -\mathrm{OH}\cdots\mathrm{O} \qquad (9)$$

upfield displacement of the proton resonance in the predominantly deuteriated system could then also be taken to imply an enrichment of protium in the non-bonded hydroxy-groups, *i.e.* that the equilibrium constant of the isotopic exchange equilibrium (10) is slightly less than unity. This conclusion is

$$-\mathrm{OH}_{\text{non-bonded}} + -\mathrm{OD}\cdots\mathrm{O} \rightleftharpoons -\mathrm{OD}_{\text{non-bonded}} + -\mathrm{OH}\cdots\mathrm{O} \qquad (10)$$

at variance with the experience that the heavy hydrogen isotope is as a rule concentrated in the position with the largest stretching force constant to hydrogen.

We are unable to say whether the difficulties with either interpretation of the very small isotope effect are a reflection on the tenuous state of our detailed knowledge of the structure of alcohols or are indicative of some unrecognised experimental artifact.

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