The Mechanism of Hydrogen Atom Abstraction from Phenols involved in Hydrogen Bonding with Ester Carbonyl Groups

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Rate constants have been determined in different solvents for hydrogen atom abstraction from alkyl-substituted phenols and deuteriated analogues by polyvinyl acetate radical ($R^{\cdot}$). The following solvents were used: ethyl acetate, ethyl [$^2H_3$]acetate, ethyl pivalate, ethyl trifluoroacetate, acetone, [$^2H_6$]acetone, dimethyl sulphoxide. The reactivity of the phenols and the primary kinetic deuterium isotope effect (p.k.i.e.) demonstrate a strong solvent dependence exhibiting the highest values in ethyl trifluoroacetate (p.k.i.e. 57 ± 23 for 2,4,6-trimethylphenol at 50 °C). Incorporation of $CH_3{}^{14}COOCH_2CH_3$ and $(CH_3)_3C^{14}COOCH_2CH_3$ into polyvinyl acetate increases in the presence of phenols. These facts conclusively prove that hydrogen atom abstraction proceeds within the hydrogen bond to the radical formed by addition of $R^{\cdot}$ to the ester carbonyl hydrogen bonded to phenol.

IT has been proved that hydrogen atom abstraction from the hydroxy-group of phenols in media containing polar molecules [*e.g.* vinyl acetate (VA)] proceeds along two simultaneous pathways starting from free and hydrogen bonded species.[1] For 2,6-dialkylphenols at 50 °C, the hydrogen bonded species is more reactive than the free form, thus indicating the role of the solvent (VA) molecule attached to the phenol in increasing reactivity. At the same time the primary kinetic deuterium effect (p.k.i.e.) for these phenols is >10 (*i.e.* greater than the largest p.k.i.e. value which could be accounted for by the total loss of zero-point energy differences of all three vibrational modes of the phenolic OH and OD bonds), thus indicating tunnelling.[2] In order to rationalise these facts we have supposed that hydrogen atom abstraction proceeds within the hydrogen bond.[2b] This paper reports evidence for the mechanism.

EXPERIMENTAL

Materials and Techniques.—Commercially available (Merck, Uvasol) solvents, ethyl acetate (EA), acetone (A), [$^2H_6$]acetone ([$^2H_6$]A), and dimethyl sulphoxide (DMSO) were used. Synthetic grade (Merck) ethyl pivalate (EP) was used after distillation according to ref. 3. Synthetic grade (Fluka) ethyl trifluoroacetate (EFA) was purified according to ref. 4. Ethyl [$^2H_3$]acetate ([$^2H_3$]EA) was prepared by direct esterification of CD_3COOD formed by heating deuteriated malonic acid. The isotopic purity was found to be 95% by mass spectrometry. $CH_3{}^{14}COOCH_2CH_3$ (3.5 μCi g^{-1}) was prepared from $CH_3{}^{14}COOK$ with triethyl phosphate; the labelled potassium acetate [5] was formed by carbonyl exchange with $^{14}CO_2$. $(CH_3)_3C^{14}COOCH_2CH_3$ (20 μCi g^{-1}) was prepared from the acid [6] *via* $(CH_3)_3C^{14}COCl$, treating the latter with ethanol.

The techniques for purification of purum grade (*Fluka*) VA and azobisisobutyronitrile (AIBN) have been described elsewhere.[7] Oleic and trifluoroacetic acid (Fluka, synthetic

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grade) used in control experiments were used after distillation. Commercially available (Fluka) 2,4,6-trimethylphenol (TMP) of analytical grade was used after sublimation. The purity of bisphenols: 2,2-bis-*p*-hydroxyphenylpropane (BHPP) and its tetra-*o*-alkyl derivatives, and the tetra-*o*-methyl derivative of 6,6′-dihydroxy-1,1,1′,1′-tetramethyl-3,3′-spirobisindane (5,5′,7,7′-Me_4-HSBI) was checked by t.l.c. and high resolution gel chromatography.[8] Deuteriation of phenols was carried out using D_2O (99.5% by n.m.r.) in previously dried sample tubes (TMP) or by repeated deuteriation in D_2O–A mixtures based upon the fast exchange of phenolic OH with OD.[9a] To eliminate exchange with traces of moisture [9b,c] the inner surface of the evacuated glass apparatus was dried with P_2O_5 and the dried VA–solvent was saturated with D_2O.

Polyvinyl acetate samples were prepared from polymer solutions polymerised to equal conversion. The solvent mixtures (VA–radioactive EA and VA–radioactive EP) were removed *in vacuo* at room temperature. To remove BHPP, TMP, and AIBN from the samples [10] the impure polymer was dissolved in benzene (1% polymer solution) and precipitated six times in hexane (hexane–benzene 20 : 1 v/v). Each precipitation was followed by centrifugation at 3 000 r.p.m. After washing with hexane, the polymer samples were dried *in vacuo* for a day.

The determination of the equilibrium constant of hydrogen bonding between phenols and solvents in CCl_4 was carried out according to ref. 11 by i.r. measurements. Radioactive samples were counted with a Packard Tri-Carb model 574 scintillation spectrometer and a type OE 973 carbon–tritium automatic gas-phase analyser (Chinoin Co.).

Kinetics.—The method of inhibiting radical polymerisation of VA with phenols [12] has been modified by using EA, EP, EFA, A, and DMSO as diluents. The diluting technique is described in ref. 1*b*.

The rate of polymerisation in different VA–solvent mixtures was found to be proportional to the concentration of VA monomer as well as that of the initiator (AIBN). Thus the kinetic requirements for radical polymerisation are satisfied. The overall rate constants of polymerisation were found to be constant over the whole dilution range for the above solvents. (Other solvents examined, *e.g.* acetonitrile, dioxan, ethyl acetoacetate, do not fulfil the above requirements and were not applied in dilution experiments.)

Because of chain transfer, [13] radicals formed from the solvent ($S^\bullet$) and which might attack inhibitor molecules must be taken into account. Using oleic acid, an inhibitor with reaction centres other than hydroxy-groups,[14] the effect of $S^\bullet$ radicals on the reactivity could be checked.[1b] Experiments proved that the inhibition effect of oleic acid does not depend (within experimental error) on the presence of EA, EP, EFA, A, and DMSO. Results are summarised in Table 1.

Table 1

Kinetic orders (r), overall rate constants (k_o) and the reactivity of oleic acid (k_{oa}) for different VA–solvent mixtures at 50 °C

	r(VA)	$r(\text{AIBN})^{1/2}$	10^4k_o [a]	k_{oa} [b]	k_{oa}/k_{oa}^{VA}
VA–EA	1.00	1.00	4.92	78.6	1.05
VA–EP	1.01	1.01	8.06	72.0	0.96
VA–EFA	1.00	1.00	5.17	81.2	1.08
VA–A	1.00	1.00	4.84	67.2	0.89
VA–DMSO	1.00	1.00	7.16	73.6	0.98

[a] k_o in $dm^{3/2}\ mol^{-1/2}\ s^{-1}$. [b] k_{oa} In $dm^3\ mol^{-1}\ s^{-1}$, error limit ±10%. [c] According to ref. 14 k_{oa}^{VA} is 75.2.

Rate constants for the reaction of $R^\bullet$ and phenols were calculated from the inhibited rate of polymerisation [12,15] using the elementary rate constants [16] for the polymerisation of VA. The presence of D_2O (0.1%) does not influence the rate of polymerisation. Minute amounts of CF_3COOH present in $CF_3COOCH_2CH_3$ do not change the reactivity of TMP and oleic acid.

RESULTS AND DISCUSSION

The point of diluting VA by another polar solvent is to have a distribution of phenol molecules among different bonded states. A number of studies have indicated 1 : 1 stoicheiometry to be characteristic of hydrogen bond formation between phenols and polar solvents.[11,17] Hence, it may be assumed that one solvent can only affect the association of phenol with another solvent if the polar solvents themselves interact with each other. However, the density of VA–EA, VA–EP, VA–EFA, and VA–A mixtures depends linearly on the composition which indicates a lack of specific interaction between the two components. (The only exception is VA–DMSO in which a slight volume contraction was observed.) Consequently, the concentrations of hydrogen bonded and free phenol in the above mixtures may be obtained from equilibrium constants for hydrogen bonding between the phenol and each solvent separately.

One can thus examine how the reactivity of phenols changes when a certain portion of the VA–hydrogen bonds are replaced by hydrogen bonds formed with the diluent. The experimentally determined rate constant can then be divided into three different contributions of the free and the two bonded states, as given by equation (1) where [VA] and [S] are in mol dm^{-3}. k_{free} and k_{VA}

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values are in ref. 1*b*, while K_{VA} values are available from ref. 11. Applying these together with relevant K_S data

$$k = \frac{k_{free} + k_{VA}K_{VA}[VA] + k_SK_S[S]}{1 + K_{VA}[VA] + K_S[S]} \qquad (1)$$

determined by i.r. spectroscopy, one can calculate k_S, *i.e.* the reactivity of the phenol hydrogen bonded to the polar solvent.

The solvents have been selected in order to elucidate which part of the solvent molecule participates in hydrogen atom abstraction. Rate constants are collected in Table 2. Table 3 summarises rate constants for deuteriated phenols and p.k.i.e. values.

TABLE 2

k_S [a] and K_S [b] values determined for different solvents [c]

		$CH_3COOCH{=}CH_2$		$CH_3COOCH_2CH_3$		$CD_3COOCH_2CH_3$	$(CH_3)_3CCOOCH_2CH_3$	
No	Phenol	k_{VA}	K_{VA}	k_{EA}	K_{EA}	$k_{[^2H_3]EA}$	k_{EP}	K_{EP}
1	BHPP	66	2.37	67 [d]	6.34	37 [d]	78	6.07
2	2,2′-Me_2-BHPP	200	1.92	250	4.30	124	266	4.03
3	TMP	420	0.72				421	1.32
4	5,5′,7,7′-Me_4-HSBI	1 250 [g]		1 126 [h]				
5	2,2′-Me_2-6,6′-Bu^t_2-BHPP	520	0.83	438 [d]	2.01	321 [d]	590	1.52
6	2,2′,6,6′-Bu^t_4-BHPP	88	0.33	92	0.31	64		

		$CF_3COOCH_2CH_3$		CH_3COCH_3		CD_3COCD_3	CH_3SOCH_3
No	Phenol	k_{EFA}	K_{EFA}	k_A	K_A	$k_{[^2H_6]-A}$	k [f]
1	BHPP	606 [e]	0.68	31	7.25	30.0	8.8
2	2,2′-Me_2-BHPP						
3	TMP	2 219	0.32	234	1.89		40.3
4	5,5′,7,7′-Me_4-HSBI						
5	2,2′-Me_2-6,6′-Bu^t_2-BHPP						
6	2,2′,6,6′-Bu^t_4-BHPP						

[a] k_S Values at 50 °C are in $dm^3\ mol^{-1}\ s^{-1}$, probable error within $\pm 20\%$. [b] K_S values at 45 °C in $dm^3\ mol^{-1}$, error limit $\pm 10\%$. [c] Abbreviations are given in the Experimental section. [d] Ref. 2*b*. [e] Because of the unfavourable ratio of the equilibrium constants, K_{VA}/K_{EFA} for BHPP, the error of extrapolation increases. Thus the estimated error limit for this value is $\pm 40\%$. [f] The application of equation (1) for VA–DMSO mixtures is subject to error due to the slight interaction of the two solvents. Hence, the experimental rate constants are given. [g] Overall rate constant [1] determined [2b] in pure VA. [h] Experimental value relating to 80% EA-bonded 5,5′,7,7′-Me_4-HSBI.

TABLE 3

The k,[a] k_S, and p.k.i.e.[b] values determined for different solvents at 50 °C

		$[^2H_2]$BHPP		$[^2H]$TMP		$[^2H_2]$-5,5′,7,7′-Me_4-HSBI	
No.	Solvent	k	P.k.i.e.	k_S[c]	P.k.i.e.	k	P.k.i.e.
1	VA	10.0 [d]	6.6	32.0	13.1	92.0 [e]	13.6
2	EA	10.5	6.4			85.5	13.2
3	EP	11.4	6.9	35.5	11.9		
4	EFA			39.1	56.8 [f]		
5	A	8.9	3.5	28.8	8.1		
6	DMSO	2.5	3.5	6.3	6.4		
7	$[^2H_3]$EA	5.9	6.3			61.6	

[a] k In $dm^3\ mol^{-1}\ s^{-1}$. The values have been determined in the presence of *ca.* 80% solvent bonded species. The only exception is EP. In this case the EP-bonded fraction was 64%. Because the k values in EP and VA do not differ significantly the error in p.k.i.e. covers the error of extrapolation. [b] Neither set of values is corrected for 0.5% light isotope impurity. [c] See footnote *a* in Table 2. The k_{free} and k_{VA} values and the assumption of $K_S^H = K_S^D$ for $[^2H]$ TMP are taken from ref. 18. [d] Ref. 2*a*; see footnote *g* in Table 2. [e] Ref. 2*b*; see footnote *g* in Table 2. [f] The experimental p.k.i.e. value, measured in the presence of 47% EFA-bonded species, is 30.7 (uncorrected for isotopically normal phenol impurity).

From data given in Tables 2 and 3 the following conclusions can be drawn. (i) k_{VA}, k_{EA}, and k_{EP} are equal within experimental error. (ii) EFA increases, A and DMSO decrease the reactivity. (This is the first observation of the reactivity increasing due to hydrogen bonding with a phenol having free *ortho*-positions.[1]) (iii) The reactivity of isotopically normal phenols varies to a far greater extent than that of deuteriated phenols (in agreement with ref. 18), and consequently the p.k.i.e. shows significant solvent dependence (see for example nos. 4 and 6 in Table 3). (iv) The solvent dependences (i)—(iii) do not show a substantial substituent effect, *i.e.* the effects which increase or decrease reactivity are of the same order of magnitude for different types of alkyl-substituted phenols. (v) Solvent kinetic isotope effects (s.k.i.e.) emerge in the case of $[^2H_3]$EA (on average 1.6 per molecule) but are absent for $[^2H_6]$A.

The findings summarised in (i)—(v) show that the solvent involved in hydrogen bonding has a marked influence on hydrogen atom abstraction. For the esters a mechanism operates which increases the reactivity and p.k.i.e. The s.k.i.e. for $[^2H_3]$EA may be interpreted as being either a primary or a secondary [19] kinetic isotope effect depending on the mechanism by which $R^{\bullet}$ reacts with EA hydrogen-bonded to phenol. The effect is primary if the reaction involves hydrogen atom abstractions from the acetyl group. If methyl is replaced by t-butyl, however, there is no opportunity for such a pathway. Because the reactivity does not decrease in EP, it can be concluded that the s.k.i.e. cannot be a primary effect.

As shown, increased p.k.i.e. and reactivity are observed in EFA where the carbon atom of the carbonyl group is electron deficient compared with the other

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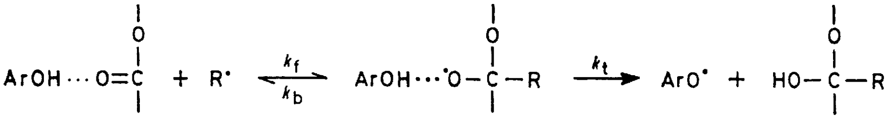
esters. It seems to be a general trend that increased electron donation in the substrate favours hydrogen atom abstraction, while in the case of electron deficiency, alkyl radicals may prefer an addition pathway.[20] In agreement, it has been found that electron-attracting groups (CF_3, halogen, C=O) attached to the carbonyl group of ketones,[21] quinones,[22] and esters[23] facilitates radical addition to the C=O double bond. For benzoyl radical addition to benzaldehyde, a positive Hammett ρ value was reported.[24]



SCHEME

We suppose the first step of hydrogen atom abstraction from phenol hydrogen-bonded to ester to be the addition of R· to the carbon atom of the carbonyl linkage. A further consequence of polyvinyl acetate radical attack on carbonyl is the incorporation of solvent into the polymer. The alteration of electron density brought about by hydrogen bond formation with a carbonyl group was observed by de Jeu;[25] as a consequence of hydrogen bonding the electron density increases on oxygen while decreasing on the carbon of the carbonyl group. It may therefore be suggested that hydrogen bonding between phenols and esters should increase the ability of radicals to add to carbonyl groups, and hence would enhance the incorporation of solvents into the polymer. It is shown by the data in Table 4 that the presence of phenol increase the incorporation of the solvent examined.

TABLE 4

Incorporation of solvent into polyvinyl acetate. Relative radioactivity of polyvinyl acetate prepared from

	VA–$CH_3{}^{14}COOCH_2CH_3$	VA–$(CH_3)_3C^{14}COOCH_3CH_3$
No Phenol	1	1
BHPP	1.8	4.0
TMP	1.4	2.5

In conclusion the mechanism in the Scheme is proposed. The acetal-type radical formed in the forward step (k_f) may react further along two different paths. It may either decompose (k_b) and thus return ' kinetically ' into the initial state without necessarily reversing [21d, 26] exactly the forward step. Alternatively, the acetal-type radical may abstract the hydrogen atom of phenol in the second step implying a significant tunnel contribution (k_t). In the steady state, the overall rate constant for hydrogen atom abstraction from phenols, hydrogen bonded to esters[1] (k_2) is given by equation (2), allowing for the large p.k.i.e. observed.

$$k_2 = \frac{k_f k_t}{k_b + k_t} = \frac{k_f k_t}{k_b} \text{ for } k_b \gg k_t \qquad (2)$$

The appearance of k_t on the right-hand side of equation (2) offers an explanation for the solvent dependence of p.k.i.e. The replacement of the hydrogen acceptor molecule by another may strongly influence the probability of tunnelling within the hydrogen bond. This would be much more reflected by the reactivity of isotopically normal phenols than that of the heavy isotopes. The mechanism proposed also explains the reactivity increasing effect of hydrogen bonding to esters which could not be observed in other solvents.[1b, 20, 27]

The extremely large p.k.i.e. for TMF in EFA (Table 3) is higher than any other published value at 50 °C. Another extremely high value has been reported[28] for intramolecular hydrogen atom abstraction in 2-hydroxyphenoxyl radical at 25 °C ($k_H/k_D \simeq 104$). These high p.k.i.e. values correspond to such a narrow barrier[28, 29] that they can be realised only within a hydrogen bond.[30] This is further evidence for the proposed mechanism.

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