Role of Hydrogen Bonding in the Mechanism of Hydrogen Atom Abstraction from Alkyl-substituted Phenols by Polyvinyl Acetate Radicals

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Application of a novel dilution technique to the kinetic study of the inhibited radical polymerisation of vinyl acetate provided experimental evidence for the following conclusions. (i) The title reaction proceeds *via* simultaneous pathways owing to hydrogen bonding between phenols and vinyl acetate. (ii) The influence of hydrogen bonding on the reactivity at 50 °C depends on the type of substitution. The free phenol is more reactive than the bonded form if at least one of the *ortho*-positions is unsubstituted. The hydrogen bonded species is more reactive than the free form for 2,6-dialkylphenols. (iii) The individual reaction paths are associated with significantly differing Arrhenius parameters.

THERE is almost unanimous agreement among observers that hydrogen bond formation decreases the radical reactivity of O–H reaction centres.[1-3] At the extreme, hydrogen-bonded species are sometimes regarded as being unreactive.[4,5] Recent reports[6] indicated that

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[1] J. A. Howard and K. U. Ingold, *Canad. J. Chem.*, 1964, **42**, 1044.

[2] M. Simonyi and F. Tüdős, *Adv. Phys. Org. Chem.*, 1971, **9**, 127.

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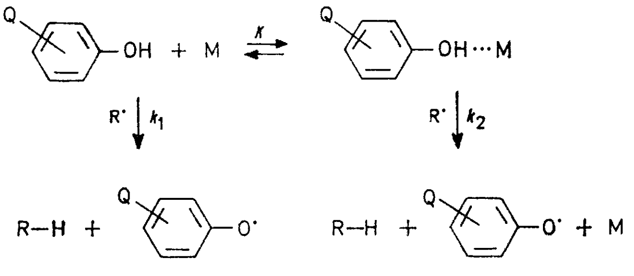
this view could not be applied to phenols reacting with polyvinyl acetate radicals. Instead, simultaneous pathways for free and hydrogen-bonded phenols were established according to the Scheme, where M denotes



SCHEME

vinyl acetate molecules, K is the equilibrium constant of hydrogen bonding, and k_1 and k_2 are characteristic to individual hydrogen atom abstraction reaction (HAA)-paths starting from free and bonded phenols, respectively. The overall rate constant (k) of HAA is given by equation (1). The expression $(K[M] + 1)^{-1}$

$$k = \frac{k_1 + k_2K[M]}{K[M] + 1} = k_2 + \frac{k_1 - k_2}{K[M] + 1} \qquad (1)$$

gives the fraction of phenols existing in the free state when the concentration of vinyl acetate is [M]. Experimental values for k_1 and k_2 can be obtained by direct determination of K [7] and by applying a dilution method which allows the measurement of k in media of varying composition.

EXPERIMENTAL

Materials.—Commercially available phenols of analytical grade were used after sublimation. The purity of 2,2-bis-*p*-hydroxyphenylpropane (BHPP) and its derivatives was checked by t.l.c. and high resolution gel chromatography.[8] The techniques for purification of purum grade vinyl acetate (Fluka) and azobisisobutyronitrile (AIBN; Fluka) have been described elsewhere.[9]

Procedure.—The method of inhibiting the radical polymerisation of vinyl acetate with phenols [10] has been modified by using carbon tetrachloride as diluent. Vinyl acetate–CCl_4 mixtures containing <50 p.p.m. oxygen were prepared under argon in a specially designed vacuum funnel by mixing prepolymerised and distilled vinyl acetate with CCl_4 distilled from AIBN. Oxygen-free dilatometers containing AIBN (5—10×10^{-3}M) and the phenol investigated (10^{-4}—10^{-2}M) were filled with solvent mixture from the vacuum funnel. The concentration and density of mixtures were determined by refractometry. Concentration of vinyl acetate in the mixtures varied from 5 to 100 mol %. The rate of polymerisation was measured dilatometrically. The value of the dilatometric coefficient determined in vinyl acetate–CCl_4 mixtures agrees well with that measured in pure vinyl acetate.

Kinetics.—In vinyl acetate–CCl_4 mixtures, the polymer conversion depends linearly on the time up to high conversion which allows a more accurate determination of the rate [11] than in bulk polymerisation. The rate of polymerisation in vinyl acetate–CCl_4 mixtures was found to be proportional to the concentration of the monomer as well as to the square root of the concentration of initiator. Thus the kinetic requirements of the mechanism of radical polymerisation are satisfied.

The overall rate constant of polymerisation, $k_0 = k_p(2k_if)^{1/2}k_t^{-1/2}$ (where k_p, $2k_if$, and k_t are rate constants of propagation, initiation, and termination, respectively) was found to be constant in the whole dilution range; its value (3.58×10^{-4} dm$^{3/2}$ mol$^{-1/2}$ s^{-1} at 50 °C) is slightly lower than the corresponding value in pure vinyl acetate (4.17×10^{-4} dm$^{3/2}$ mol$^{-1/2}$ s^{-1} according to ref. 9). Similar decreases of the overall rate constant of polymerisation have been observed in vinyl acetate–CCl_4 mixtures at 30 and 70 °C; consequently, the activation energy of vinyl acetate polymerisation [12] was found to be independent of the presence of CCl_4. The decreased value of k_0 in the mixtures is presumably due to a chain transfer reaction [13] between polyvinyl acetate radicals and CCl_4. Carbon tetrachloride is not inhibiting the polymerisation, however, since the effect of CCl_4 on k_0 is constant in the range of 5—95 mol %.

Because of chain transfer, one has to account for the presence of CCl_3 radicals that might attack [14] on inhibitor molecules. To check the effect of CCl_3 radicals on the reactivity of the inhibitor, we have performed kinetic investigations on oleic acid. This compound inhibits the polymerisation of vinyl acetate owing to its allylic C–H bonds.[15] These reaction centres cannot act as proton donors towards vinyl acetate; hence hydrogen bonding to phenols is absent in this case. Experiments proved that the inhibition effect of oleic acid does not depend on the presence of CCl_4. Hence, we concluded that the effect of hydrogen bonding on the radical reactivity is reflected by the dependence of the inhibition activity of phenols on the composition of the medium. Rate constants for the reaction of polyvinyl acetate radicals and phenols were calculated from the inhibited rate of polymerisation [10,16] using the values of elementary rate constants [12] of the polymerisation of vinyl acetate.

RESULTS AND DISCUSSION

The effect of dilution with CCl_4 on the overall rate constant of HAA from BHPP can be seen in Figure 1 plotted according to equation (1).

The experimental data define a straight line the left

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hand side intercept of which equals k_2, while the slope is $k_1 - k_2$. The variable on the horizontal axis has meaning only within 0 and 1, and the intercept on the right hand side gives the value of k_1. The experimental points also correspond to equation (2). Both equations

$$k\{K[\mathrm{M}] + 1\} = k_1 + k_2K[\mathrm{M}] \qquad (2)$$

were used to determine k_1 and k_2; the probable errors are estimated to be within ±10%. Kinetic studies have been performed on ten different derivatives. Similar plots to that shown in Figure 1 were found to give straight lines in each case. The results are collected in Table 1.

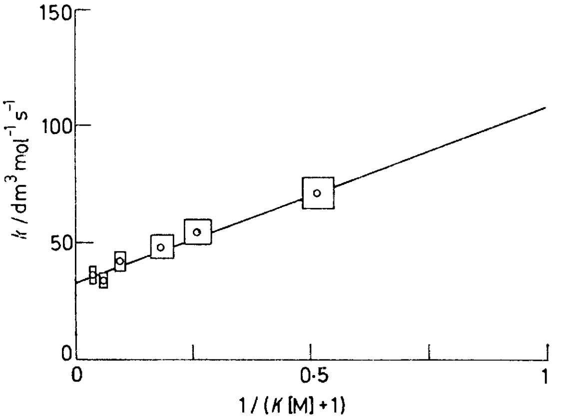

FIGURE 1 The dependence of the rate constant on the composition of the medium for BHPP according to equation (1). Each square represents six kinetic runs

TABLE 1

Reactivities [a] of free (k_1) and hydrogen bonded (k_2) phenols towards polyvinyl acetate radicals at 50 °C

No.	Phenols	K [b]	k_1	k_2	k_1/k_2
1	Phenol	2.92	44	11	4.0
2	BHPP	2.37	109	33	3.3
3	2,2′-$\mathrm{Bu^t{}_2}$-BHPP	2.00	184	68	2.7
4	2,2′-$\mathrm{Me_2}$-BHPP [d]	1.92	208	100	2.1
5	2,4,6-$\mathrm{Me_3}$-phenol [e]	0.72	240	420	0.6
6	2,2′,6,6′-$\mathrm{Me_4}$-BHPP [e]	0.86	225	485	0.5
7	2,2′,6,6′-$\mathrm{Pr^i{}_4}$-BHPP	0.77	205	530	0.4
8	2,2′,6,6′-$\mathrm{Et_4}$-BHPP	0.66	165	510	0.3
9	2,2′-$\mathrm{Bu^t{}_2}$-6,6′-$\mathrm{Me_2}$-BHPP [e]	0.83	80	260	0.3
10	2,2′,6,6′-$\mathrm{Bu^t{}_4}$-BHPP	0.33	7	44	0.2

[a] The rate constants are given in dm^3 mol^{-1} s^{-1} per O–H group assuming additivity in bisphenols. [b] In dm^3 mol^{-1} according to ref. 7 at 45 °C. Error limit is ±10%. [c] Ref. 6*a*. In view of the errors in individual k_1 values, some changes in the sequence of the ratios are possible. [d] Corrected values of ref. 6*b*. [e] Ref. 6*b*.

Experimental data in Table 1 demonstrate that the influence of a given substituent is not the same in the two reaction paths. The effect of individual types of substitution has been calculated as reactivity factors [17] indicating the ratio of reactivities of substituted and unsubstituted compounds. These factors are collected in Table 2. For 2,6-dialkyl substitution, the factors corresponding to additive substituent effects [10,2,17] are given in parentheses.

The reactivity factors indicate that the rate-increasing effect of *o*-alkyl substitution is higher in the second path (for hydrogen bonded phenols) than in the first (for free phenols). A difference of the corresponding factors by about an order of magnitude is characteristic for double *ortho*-substitution.

TABLE 2

Reactivity factors for different types of *o*-alkyl substitution at 50 °C

Type of *ortho*-substitution	Reaction paths	
	1	2
2-Me	1.9	3.1
2,6-$\mathrm{Me_2}$	2.1	14.7
	(3.6)	(9.6)
2,6-$\mathrm{Et_2}$	1.5	15.5
2,6-$\mathrm{Pr^i{}_2}$	1.9	16.1
2-$\mathrm{Bu^t}$	1.7	2.1
2-$\mathrm{Bu^t}$, 6-Me	0.7	7.9
	(3.3)	(6.5)
2,6-$\mathrm{Bu^t{}_2}$	0.06	1.3
	(2.9)	(4.4)

The different influences of the first *ortho*-substituents on the reactivity in the two paths may be represented by Hammett plots given in Figure 2. The significantly different slopes (ρ_1 −1.2; ρ_2 −1.6) indicate that free and hydrogen bonded phenols are not equally sensitive to substituent effects. Hence, the early suggestion that the effect of substitution on the reactivity would be the same in different media [1] may be close to reality when reactions in CCl_4 are compared with those in benzene [18] but does not hold for our case.

The effect of the second *o*-alkyl substituent on the reactivity causes a marked difference between the two paths. While in the second path, the influence of the

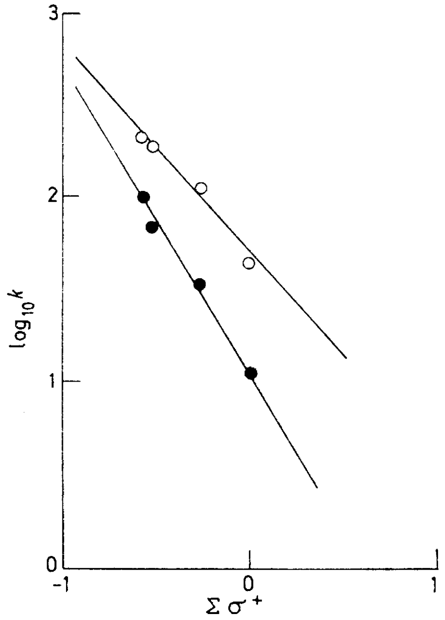

FIGURE 2 Hammett correlations for the two reaction paths for the first four compounds of Table 1: ○, path 1; ●, path 2

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[17] M. Simonyi, J. Kardos, F. Tüdős, and J. Pospišil, *J. Polymer Sci, part C, Polymer Symposia*, 1973, **40**, 163.

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second substituent tends to be even higher than that of the first (with 2,6-Bu^t_2 substitution as the only exception), the reactivity of free 2,6-dialkylphenols is always smaller than that required by simple additivity. Analogously, a decreased effect by the second *ortho*-substituent has been observed for other systems.[19-21]

A comparison with reactivity factors of the second path may be made by considering rate constants relating to both phenol and bisphenol series and determined in pure vinyl acetate.[10,17] The reactivity factors in vinyl acetate were 3.2 and 4.0 for the first and second *o*-methyl substituents, respectively. This deviation from additivity disappeared within the general scatter of the Hammett plot.[2]

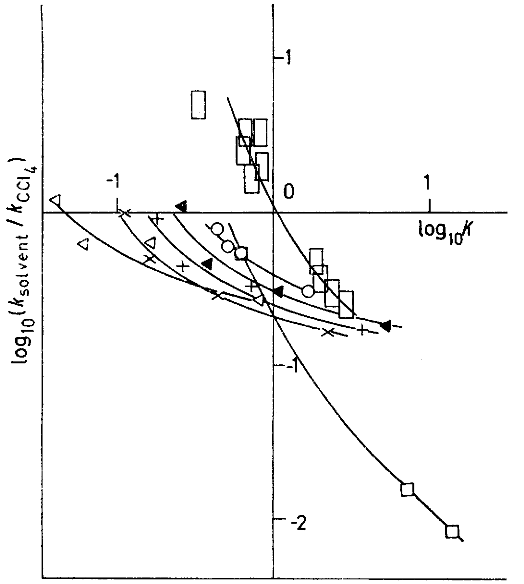

FIGURE 3 Solvent effect on HAA for various systems as a function of hydrogen bonding (error-squares represent data from this work): □, 2,4,6-Bu^t_3-phenoxyl radical and phenol in benzene (B), acetonitrile (AN), and dioxan;[18] ○, 2,4,6-Bu^t_3-phenoxyl radical and substituted phenols in B;[18] ▲, styrylperoxyl radical and 4-Me-C_6H_4OH in chlorobenzene (CB), Styrene (St), nitromethane (NM), and AN;[1] +, styrylperoxyl radical and 4-Me-2-Bu^t-C_6H_3OH in CB, St, MN, and AN;[1] ×, styrylperoxyl radical and 2,4,6-Me_3-C_6H_2OH in CB, St, NM, and AN;[1] △, styrylperoxyl radical and 4-Me-2,6-Bu^t_2-C_6H_2OH in CB, St, NM, and AN;[1]

For comparing solvent effects in different systems, ratios of reactivities determined in a given solvent and in CCl_4 may be correlated with equilibrium constants of hydrogen bonding between phenols and the given media. One can thus compare correlations relating to various phenols, several solvents, and a number of attacking radicals. If only the phenol or the solvent is varied regular correlations can be given between log ($k_{solvent}/k_{CCl_4}$) data and hydrogen bonding equilibrium constants, as shown in Figure 3. The relevant equilibrium constants cannot always be found; $\Delta\nu$(OH) spectral data are available, however.[22,23] The respective values of K were estimated according to equation (3).[7]

$$\log K = 0.009\,1\ \Delta\nu(\mathrm{OH}) - 0.76 \qquad (3)$$

Figure 3 demonstrates that the only correlation with experimental realization in the positive semi-plane relates to vinyl acetate. Hence, this kind of solvent effect ($k_2 > k_1$ for 2,6-dialkylphenols) seems characteristic of polyvinyl acetate radical attack in vinyl acetate solvent.

The two reaction paths in polyvinyl acetate radical attack may be contrasted by assuming a higher sensitivity to steric protection by 2,6-dialkyl substituents for free phenols while in the second path only 2,6-Bu^t_2-substitution causes a significant steric effect. This can also be seen in Figure 3, where the single square representing 2,2′,6,6′-Bu^t_4-BHPP (no. 10 in Table 1) falls outside the curve which correlates the other nine compounds.

TABLE 3

Influence of temperature on the reactivity of free (k_1) and bonded (k_2) phenols in polyvinyl acetate radical attack

Compound	t/°C	K [a]/ dm³ mol⁻¹	k_1 dm³ mol⁻¹ s⁻¹	k_2 dm³ mol⁻¹ s⁻¹
BHPP	30	2.97	39 ± 8	17.5 ± 2
	70	1.70	262 ± 50	56 ± 6
6,6′-Me_2-2,2′-Bu^t_2-BHPP	30	1.04	27 ± 5	166 ± 16
	70	0.65	210 ± 30	550 ± 60

[a] Calculated from hydrogen bond formation enthalpies.[24]

In two cases (nos. 2 and 9 in Table 1), k_1 and k_2 values have also been determined at 30 and 70 °C. Experimental values are given in Table 3. The error limits are considerable and these allow the determination of Arrhenius parameters (Table 4) with rather poor accuracy. Nevertheless, it may be concluded that the activation energy for hydrogen bonded phenols is significantly lower than the activation energy for free phenols. The difference of the two values ($E_1 - E_2$) is *ca.* 4 kcal mol⁻¹ resulting in a ratio of the corresponding Boltzmann factors of 500 at 50 °C. The fact that

TABLE 4

Arrhenius parameters [a] for the competing reaction paths

Compound	log A_1	E_1	log A_2	E_2
BHPP	8.7 ±1·0	9.8 ±1.5	5.6 ±0.5	6.0 ±0.8
6,6′-Me_2-2,2′-Bu^t_2-BHPP	9.1 ±1.0	10.6 ±1.5	6.6 ±0.8	6.2 ±1.2

[a] Activation energies in kcal mol⁻¹ and pre-exponential factors in dm³ mol⁻¹ s⁻¹ units.

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$k_2 : k_1$ ratios are far from being that large is reflected by the fact that the pre-exponential factors compensate for the difference in activation energies. It may also be noted that for bonded phenols, the increase in reactivity (from BHPP to 2,2′-Bu^t_2-6,6′-Me_2-BHPP) goes parallel with increasing pre-exponential factor. These observations are in accord with earlier results on the compensating nature of Arrhenius parameters for HAA in vinyl acetate medium.[2, 25] The simultaneously decreased values of the activation energy and A factor in the second reaction path compared with those in the first may indicate the importance of tunnelling.

In conclusion, radical attack on phenols bonded to vinyl acetate may be considered as a *kinetically* different reaction path from radical attack on free phenols. The two paths are subject to different substituent effects and characterized by different Arrhenius parameters. The general view that hydrogen bond formation decreases the radical reactivity of phenols may hold only for certain temperature intervals.

[6/539 *Received*, 22*nd March*, 1976]

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