Role of Hydrogen Bonding with Medium Molecules in the Radical Reactivity of Phenols

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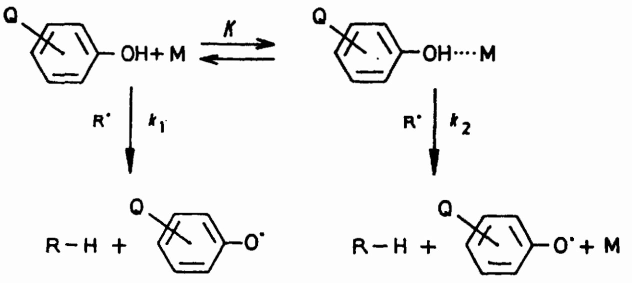
Summary Hydrogen atom abstraction proceeds from free and hydrogen-bonded phenols simultaneously; the influence of hydrogen bonding on the reactivity depends on the type of substitution.

It has been intuitively suggested[1,2] that hydrogen abstraction from the O–H group of phenols in media containing polar molecules proceeds along two simultaneous pathways owing to hydrogen bonding (Scheme), where M denotes polar molecules in the medium, and the rate constants k_1 and k_2 are different for free and bonded O-H groups, respectively. The overall rate constant corresponding to the Scheme is given by equation (1). Thus the



Scheme

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

Scheme predicts a linear dependence of k on $1/(K[\mathrm{M}] + 1)$ from which k_1 and k_2 can be determined by extrapolation of this linear plot. We report now experimental results relating to the reactions in the Scheme.

The reactivity of a series of *ortho*-substituted phenols toward polyvinyl acetate radical (R·) has been determined by inhibiting the radical polymerisation of vinyl acetate.[3] All experiments were carried out in vinyl acetate–CCl_4 at 50 °C using azobisisobutyronitrile as initiator (5—10×10^{-3} mol/l), with concentrations of phenols in the range 10^{-4}—10^{-2} mol/l. The proportion of vinyl acetate (M) in the medium varied from 5 to 100 mol%. The equilibrium constant for hydrogen bonding (K) was determined in the same solvent mixture by using i.r. spetcroscopy. The results gave satisfactory linear plots using equation (1). We believe that the accuracy of the extrapolated values for k_1 and k_2 is within ± 10%. Different derivatives give different intercepts and slopes. The results for different substituted phenols are summarized in the Figure.

The following conclusions can be drawn: (i) k measured in pure vinyl acetate and k_2 are equal within experimental error. (ii) The substituent effect on the radical reactivity of phenols depends on the composition of the medium.

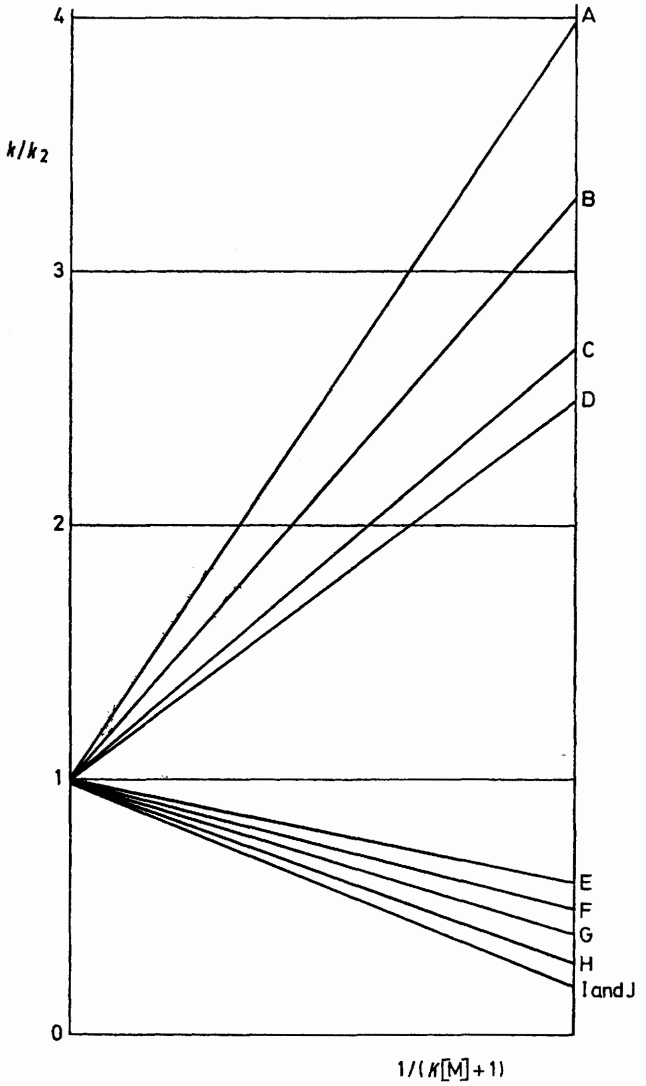


Figure. Normalized plots of k/k_2 *vs.* $1/(K[\mathrm{M}] + 1)$ for substituted phenols. The right hand intercept gives k_1/k_2 values directly. In view of the errors in individual k_1 and k_2 values some changes in the sequence of compounds are possible. A, phenol, B, 2,2-bis-*p*-hydroxyphenylpropane (BHPP); C, 2,2′-$\mathrm{Bu^t_2}$-BHPP; D, 2,2′-$\mathrm{Me_2}$-BHPP; E, 2,4,6-$\mathrm{Me_3}$phenol; F, 2,2′,6,6′-$\mathrm{Me_4}$-BHPP; G, 2,2′,6,6′-$\mathrm{Pr^i_4}$-BHPP; H, 2,2′,6,6′-$\mathrm{Et_4}$BHPP; I, 2,2′-$\mathrm{Bu^t_2}$-6,6′-$\mathrm{Me_2}$-BHPP; J, 2,2′,6,6′-$\mathrm{Bu^t_4}$-BHPP.

This phenomenon agrees well with the different behaviour of 2,6-dimethyl-phenols in styrene[4] and vinyl acetate,[3] but contradicts the supposition of constant Hammett ρ values for different media.[5] (iii) The free phenol is more reactive than the bonded one ($k_1 > k_2$) if the *ortho* positions are unsubstituted or singly substituted. (iv) The hydrogen-bonded phenol is more reactive than the free one ($k_1 < k_2$) if both *ortho* positions of the phenol are substituted.

The last conclusion is highly unexpected in view of the widespread assumption that hydrogen bond formation at O–H reaction centres decreases their radical reactivity.[2,6]

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