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KINETIC DEUTERIUM ISOTOPE EFFECT AND HYDROGEN BONDING

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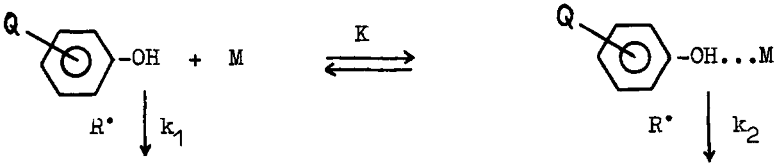
Polyvinyl acetate radicals (R$^\bullet$) abstract hydrogen atom from the O-H group of phenols. The kinetic deuterium effects associated with the process in vinyl acetate solvent[1] can be attributed to O-H groups hydrogen-bonded to medium molecules (M). The hydrogen atom abstraction has been proved to follow simultaneous pathways[2,3] due to hydrogen bonding:



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The first reaction channel involving free phenol molecules can be made dominant over the second by diluting the solvent with carbon tetrachloride. The method allows the individual k_1 and k_2 values to be determined[3]. Kinetic measurements were performed[4] on the above system in vinyl acetate-CCl_4 mixtures with concentration of the polar component ranging from 4 to 100 mol %. The equilibrium constant of hydrogen bonding was measured in the same solvent mixture using infrared spectroscopy. Results are collected in Table 1.

Table 1.

Equilibrium and kinetic* parameters for reaction scheme /1/ at 50 °C

	Phenol			
	2,2'-Me$_2$-dian**	2,4,6-Me$_3$-phenol	2,2',6,6'-Me$_4$-dian**	2,2'-tBu$_2$-6,6'-Me$_2$-dian**
K_H in l mol^{-1} unit	1,92±0,19	0,72±0,07	0,86±0,09	0,83±0,10
K_D in l mol^{-1} unit	1,87±0,37	0,74±0,15	0,68±0,15	0,53±0,15
k_1^H in l mol^{-1}s^{-1} unit	460±25	240±40	225±30	80±8
k_2^H in l mol^{-1}s^{-1} unit	186±10	420±60	485±50	260±26
k_1^D in l mol^{-1}s^{-1} unit	27,8±2	26,0±4	36,0±5	31,0±4
k_2^D in l mol^{-1}s^{-1} unit	19,5±1	32,0±4	33,0±4	27,0±4
$\frac{k_1^H}{k_2^H}$	2,47±0,2	0,57±0,15	0,46±0,1	0,31±0,05
$\frac{k_1^D}{k_2^D}$	1,43±0,2	0,81±0,2	1,09±0,2	1,15±0,2

* Values are per O-H group; ** dian = 4,4'-isopropylidene bisphenol

The following conclusions can be drawn:

1. If one ortho position is free, hydrogen bonding decreases the reactivity of both O-H and O-D reaction centres.
2. If both ortho positions are substituted, hydrogen bonding increases the reactivity of light phenols while it does not seem to influence the reactivity of deuterated phenols.
3. The effect of hydrogen bonding is more pronounced in all cases on O-H than on O-D reaction centres.

The isotopic ratios are given in Table 2.

Table 2.

Kinetic* and equilibrium isotope effects at 50 °C

Phenol	$\frac{K_H}{K_D}$	$\frac{k_1^H}{k_1^D}$	$\frac{k_2^H}{k_2^D}$
2,2'-Me_2-dian	1,03±0,2	17,9±2,5	10,5±1,0
2,4,6-Me_3-phenol	0,97±0,2	9,6±2,0	13,9±2,6
2,2',6,6'-Me_4-dian	1,26±0,25	6,5±1,3	16,0±2,5
2,2'-tBu_2-6,6'-Me_2-dian	1,57±0,5	2,6±0,5	10,0±2,0

* Corrected for 0,5 % light content in the deuterated analogues

Note that the influences of solvent and substitution are superimposed on the kinetic isotope effect. In the first reaction path, the influence of ortho substitution on the kinetic isotope effect is apparent. Such an obvious trend cannot be detected for hydrogen bonded reaction centres. If one of the ortho positions is free, the kinetic isotope effect is considerably larger in non-polar solvent in agreement with recent observations concerning proton transfer reactions[5]. On the other hand, if both ortho positions are blocked the kinetic isotope effects are larger in polar solvent. Between kinetic isotope effects and k_H values, one may find correlations characteristic to the particular reaction paths.

Solvent dependent isotope effects result from the fact that reactivities of light and heavy phenols are subjected to different influences of the solvent. This phenomenon cannot be connected with zeropointenergy differences in the initial state. Most probably, it may be regarded as a new manifestation of the tunnel effect.

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