Rate Constants and Kinetic Deuterium Isotope Effects for Hydrogen Atom Abstraction from Phenols by Polyvinyl Acetate Radical

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Summary The primary kinetic deuterium isotope effect (PKIE) for the hydrogen atom abstraction from substituted phenols by polyvinyl acetate radical shows a large variation, and shows a maximum as a function of the reactivity of the compounds; the high values of PKIE may be attributed to tunnelling.

The primary kinetic deuterium isotope effect (PKIE) in an H-transfer reaction should vary with the symmetry of the transition state and should be a maximum when the hydrogen is symmetrically bonded to the atoms between which it is being transferred.[1] Although maximum functions have been found experimentally[2] the role of the symmetrical transition state has been questioned recently.[3]

Table. Rate constants[a] and PKIE for hydrogen atom abstraction from phenols by polyvinyl acetate radical at 50°C in vinyl acetate

Compound	k_H /l mol^{-1} s^{-1}	k_D /l mol^{-1} s^{-1}	k_H/k_D
Br_5-Phenol	36	5·3	6·8
BHPP[b]	36	5·0	7·2
2,2′-Bu_2^t-BHPP	66	5·6	11·9
2,2′-Me_2-BHPP	100	10·0	10·0
2,6-$(MeO)_2$-Phenol	224	24·8	9·0
2,2′-Bu_2^t,6,6′-Me_2-BHPP	244	28·0	8·7
2,4,6-Me_3-Phenol	400	31·2	12·8
2,2′,6,6′-Me_4-BHPP	460	32·8	14·0
2,2′6,6′-Et_4-BHPP	464	56·0	8·3
2,2′,6,6′-Pr^i_4-BHPP	488	37·6	13·0
2,6-$(MeO)_2$,4-OH-Phenol	3050	371	8·2
2,3,5,6-Me_4,4-OH-Phenol	3320	260	12·8
2,6-$(OH)_2$-Phenol	5414	320	18·0
2,6-$(OH)_2$-4-Oct^t-Phenol[c]	9972	544	18·9
2,6-$(OH)_2$-4-Bu^t-Phenol	15520	1800	8·9
2,4,6-$(OH)_3$-Phenol	34080	4800	7·1

[a] Values for the reactivity of one reaction centre. We believe that the accuracy for k_H and k_D is within $\pm 10\%$. [b] BHPP = 2,2-bis-*p*-hydroxyphenylpropane. [c] $Oc^t = Me_3CCH_2CMe_2$–.

We report results on the PKIE of hydrogen atom abstraction[4] from a number of substituted phenols by the polyvinyl acetate radical at 50 °C. The reactivity was determined by inhibiting the azobisisobutyronitrile-initiated radical polymerisation of vinyl acetate.[5,6] The results for different substituted phenols are in the Table.

The k_H/k_D values in the Table together with eight earlier values[6,7] show a maximum when plotted against the reactivity[2b] of the ^1H compounds. This dependence can be represented by the second-order equation (1).[8] The Table

$$\log (k_H/k_D) = 0{\cdot}769\ (\pm 0{\cdot}130) \log k_H - 0{\cdot}119\ (\pm 0{\cdot}024)\ (\log k_H)^2 - 0{\cdot}111 \quad (1)$$
$$R = 0{\cdot}846$$

contains several k_H/k_D values > 10, *i.e.*, greater than the largest k_H/k_D value which could be accounted for by the loss of all three[9] vibration modes[10] of the phenolic OH and OD bonds. These high values indicate tunnelling. The differences in tunnelling probabilities for the ^1H and ^2H compounds could explain the maximum in the PKIE[3b,11] relative to the reactivity.[3b,11]

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[1] F. H. Westheimer, *Chem. Rev.*, 1961, **61**, 265.
[2] *E.g.*, (a) R. P. Bell and D. M. Goodall, *Proc. Roy. Soc.*, 1966 *A*, **294**, 273; (b) A. J. Kresge, D. S. Sagatys, and H. L. Chen, *J. Amer. Chem. Soc.*, 1968, **90**, 4174; (c) W. A. Pryor and K. G. Kneipp, *ibid.*, 1971, **93**, 5584.
[3] (a) R. F. W. Bader, *Canad. J. Chem.*, 1964, **42**, 1822; (b) R. P. Bell, W. H. Sachs, and R. L. Tranter, *Trans. Faraday Soc.*, 1971, **67**, 1995; (c) J. R. Keefe and N. H. Munderloh, *J.C.S. Chem. Comm.*, 1974, 17; (d) F. G. Bordwell and W. J. Boyle, Jr., *J. Amer. Chem. Soc.*, 1971, **93**, 512; (e) W. McIver, Jr., *Accounts Chem. Res.*, 1974, **7**, 72.
[4] M. Simonyi and F. Tüdős, *Adv. Phys. Org. Chem.*, 1971, **9**, 127.
[5] M. Simonyi, F. Tüdős, and J. Pospišil, *European Polymer J.*, 1967, **3**, 101.
[6] M. Simonyi, F. Tüdős, S. Holly, and J. Pospišil, *European Polymer J.*, 1967, **3**, 559.
[7] R. A. Bird and K. E. Russell, *Canad. J. Chem.*, 1965, **43**, 2123.
[8] U.C.L.A. Scientific Programs: BMDO2R stepwise regression, January 10, 1969.
[9] L. Melander, 'Isotope Effects on Reaction Rates,' Ronald Press, New York, 1960.
[10] P. V. Huong and A. Graja, *Chem. Phys. Letters*, 1972, **13**, 162.
[11] I. Mayer and M. Simonyi, to be published.