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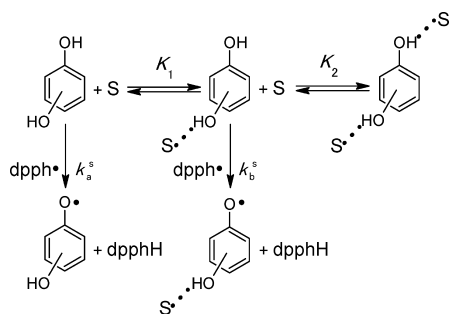
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TABLE 1: Rate Constants ($\text{M}^{-1} \text{s}^{-1}$), $k_{\text{XPhOH/dpph}}^{\text{S}}$, for H Atom Abstraction from XPhOH by dpph• in Various Solvents: Experimental^a and Calculated According to the Kinetic Solvent Effect (KSE)^b

solvent (β_2^{H})	XPhOH (α_2^{H})				
	H (0.59)	2-HO (0.73)	3-HO (0.66) ^f	4-HO (0.61) ^f	4-CH ₃ O (0.57)
heptane/hexane (0.00)	0.19	1800 ^d	0.19 ^e	240 ⁱ	240
methanol (0.41)	0.038	151	1.1	65	18
	0.0037 ^c	300 ^e	0.8 ^h	80 ^h	0.99 ^c
	(0.00090)	(6.1)	(0.0010)	(2.1)	(2.7)
acetonitrile (0.44)	0.019	37.5	0.17	12	5.0
	(0.0013)	(4.0)	(0.00071)	(1.5)	(1.9)
acetone (0.50)		33	0.15	7.0	
	(0.00064)	(1.8)	(0.00033)	(0.72)	(1.0)
tetrahydrofuran (0.51)	0.00061	2.9	0.02	2.2	0.40
	(0.00057)	(1.5)	(0.00029) ^g	(0.64)	(0.90)

^a Experimental kinetic data for PhOH and 4-CH₃OPhOH (from ref 6a) are at ambient temperatures; other experimental kinetic data for 2-HO, 3-HO, and 4-HOPhOH are from ref 2 (representing average values between 20 and 25 °C), unless stated otherwise. ^b The (apparent) rate constants in hydrogen-bond-accepting solvents, $k_{\text{XPhOH/dpph}}^{\text{S}}$, are calculated using the KSE equation, $\log k_{\text{XPhOH/dpph}}^{\text{S}} = \log k_{\text{XPhOH/dpph}}^0 - 8.3\alpha_2^{\text{H}}\beta_2^{\text{H}}$ (ref 1), and they are presented in parentheses in this table. The α_2^{H} (ref 7a) is the descriptor for the acidity (hydrogen-bond-donating, HBD, ability) of XPhOH, and β_2^{H} (ref 7b) is the descriptor for the basicity (hydrogen-bond-accepting, HBA, ability) of the solvent; $k_{\text{XPhOH/dpph}}^0$ refers to the rate constant in a non-HBA solvent such as heptane with $\beta_2^{\text{H}} = 0.00$. Linear correlations between α_2^{H} and the pK_{a} for meta- or para-substituted phenols (ref 7a) have yielded the α_2^{H} values for 3-HOPhOH (0.66) and 4-HOPhOH (0.61). The α_2^{H} for 2-HOPhOH is taken from ref 3k. ^c In the presence of 100 mM acetic acid (ref 6a) to suppress the ionization of XPhOH. ^d From ref 3k in hexane. Only one OH group is available for H atom abstraction; the second OH (donor) is intramolecularly hydrogen-bonded with the adjacent OH (acceptor); see ref 8. ^e From ref 3m. ^f The hydrogen bond equilibrium constants, K , for $\text{HOPhOH} + \text{S} \rightleftharpoons \text{HOPhOH} \cdots \text{S}$ (K_1) and $\text{HOPhOH} \cdots \text{S} + \text{S} \rightleftharpoons \text{S} \cdots \text{HOPhOH} \cdots \text{S}$ (K_2) (see also Scheme 2) can be calculated from $\log K = 7.354\alpha_2^{\text{H}}\beta_2^{\text{H}} - 1.094$ (ref 7b). The α_2^{H} values for the two OH groups in 3-HOPhOH or 4-HOPhOH are assumed to be identical. Hence, it can be calculated that in the HBA solvents listed in this table, the concentrations of non-hydrogen-bonded 3-HOPhOH and 4-HOPhOH are negligible. Consequently, 3-HOPhOH and 4-HOPhOH behave kinetically as monosubstituted phenols, that is, XPhOH. ^g It has been demonstrated that the rate constants for hydrogen atom abstraction from phenolic compounds by dpph•, $k_{\text{XPhOH/dpph}}^{\text{S}}$, are proportional to the rate constants for hydrogen atom abstraction by peroxy radicals, $k_{\text{XPhOH/ROO}}^0$ (see ref 3i). From $k_{\text{3-CH}_3\text{OPhOH/ROO}}^0 \cong k_{\text{PhOH/ROO}}^0$ (ref 3i, Table S1), it follows that $k_{\text{3-HOPhOH/dpph}}^0 = k_{\text{PhOH/dpph}}^0$ and should be $0.19 \text{ M}^{-1} \text{s}^{-1}$ (per OH) (ref 6a). The rate constants for 3-HOPhOH in 1,4-dioxane ($\beta_2^{\text{H}} = 0.41$) and in ethyl acetate ($\beta_2^{\text{H}} = 0.45$) are determined to be 0.053 and 0.018 $\text{M}^{-1} \text{s}^{-1}$, respectively (see footnote h). According to the KSE equation, $k_{\text{3-HOPhOH/dpph}}^{\text{S}}$ is calculated to be 9.3 or 5.3 $\text{M}^{-1} \text{s}^{-1}$ (per OH), an average of 7.3 $\text{M}^{-1} \text{s}^{-1}$. We note a large discrepancy with the estimated $k_{\text{3-HOPhOH/dpph}}^0$ of $0.19 \text{ M}^{-1} \text{s}^{-1}$ based on the reactivity of peroxy radicals. When $k_{\text{3-HOPhOH/dpph}}^0 = 7.3 \text{ M}^{-1} \text{s}^{-1}$ is used for the calculations, $k_{\text{3-HOPhOH/dpph}}^{\text{THF}} = 0.01 \text{ M}^{-1} \text{s}^{-1}$, which compares quite well with the experimental value of $0.02 \text{ M}^{-1} \text{s}^{-1}$. ^h Measured in this work. The experimental details have been described elsewhere (refs 6a–c). ⁱ See also footnote g. With $k_{\text{4-HOPhOH/ROO}}^0 \cong k_{\text{4-CH}_3\text{OPhOH/ROO}}^0$ (per OH) (ref 3i, Table S1), it follows that $k_{\text{4-HOPhOH/dpph}}^0 = k_{\text{4-CH}_3\text{OPhOH/dpph}}^0 = 240 \text{ M}^{-1} \text{s}^{-1}$ (per OH). Recently, we have determined preliminary values (see footnote h) of $k_{\text{4-HOPhOH/dpph}}^0$ in benzene ($\beta_2^{\text{H}} = 0.14$) and in 1,4-dioxane ($\beta_2^{\text{H}} = 0.47$) of 140 and 3.6 $\text{M}^{-1} \text{s}^{-1}$, respectively. With the KSE equation, see footnote b, this leads to $k_{\text{4-HOPhOH/dpph}}^{\text{S}} = 360$ or 72 $\text{M}^{-1} \text{s}^{-1}$ (per OH), an average of 216 $\text{M}^{-1} \text{s}^{-1}$, in reasonable agreement with the predicted 240 $\text{M}^{-1} \text{s}^{-1}$.

SCHEME 2



f of Table 1), and the reactivity of the free OH is governed by a $\text{OH} \cdots \text{S}$ substituent rather than a OH substituent (Scheme 2). This is illustrated by the fact that $k_{\text{2,5-R}_2\text{-4-HOPhOH/dpph}}^{\text{S}}$ [$\text{R} = (\text{CH}_3)_2\text{CHCH}_2\text{CH}_2$] for 2,5-di-*tert*-amylhydroquinone first increases, that is, $k_b^{\text{S}} > k_a^{\text{S}}$, with the HBA solvent concentration (acetonitrile or DMSO in CCl_4). Subsequently, the rate constant decreases due to further hydrogen bonding of the second OH group with the solvent (see Scheme 2).⁵¹

In conclusion, the radical scavenging ability of, for example, phenolic compounds and the influence imposed by the solvent medium is nowadays quite well-understood. New experimental results should be meticulously interpreted and confronted with the accessible literature on the structure–activity relationship as well as on the kinetic solvent effect in free radical chemistry.

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