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CORRELATION BETWEEN RADICAL REACTIVITY AND QUANTUM CHEMICAL INDICES OF SUBSTITUTED PHENOLS

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Polyvinyl acetate radicals abstract hydrogen atom from the O-H group of phenols[1]:

$$R^{\bullet} + Y\text{-}OH \xrightarrow{k} R\text{-}H + Y\text{-}O^{\bullet}$$

The reactivities, k, relative to that of unsubstituted phenol, k_o, can be correlated with electrophilic substituent constants[2b,3]. For 18 phenol derivatives (Table 1) the equation is (Fig.1.a):

$$\log k/k_o = \underset{(\pm 0,044)}{-1,276} \sum \sigma^{+} + 0,228 \qquad (1)$$

significantly differing from the earlier Hammett equation[2b] ($\rho = -1,52$; Fig.1.b). The correlation coefficient, R, for Eq.(1) is 0,991. We have tried to find correlation between reactivities and quantum chemical indices too. The all-valence electron Extended Hückel method[4,5] has been applied for the computations. The computed atomic indices are : the net population[6], n, the free valence[7], F, the frontier orbital density[8], f, the charge density[6], q, the nucleophilic- and radical delocalizability[7], S^N and S^R, the frontier orbital density in the first excited state and the squares of coefficients of the lowest unoccupied molecular orbital. The computer program[9] first selected the charge density, q_{C_1}, of the ring atom C_1. The regression equation is:

$$\log k/k_o = \underset{(\pm 1,693)}{-14,339}\, q_{C_1} + 9,485 \qquad (2)$$

The correlation coefficient, R, for Eq.(2) is 0,904. Next variable to enter the regression equation was the total energy of the molecule divided by the number of valence electrons, E_n:

$$\log k/k_o = \underset{(\pm 1,208)}{-13,638}\, q_{C_1} \underset{(\pm 0,057)}{-0,233}\, E_n + 4,627 \qquad (3)$$

The correlation coefficient, R, for Eq.(3) is 0,956. The measured and estimated values of log k/k_o for 18 substituted phenols are summarized in Table 1.

Table 1

Measured and Estimated Reactivities of 18 substituted Phenols Towards Polyvinyl Acetate Radical

No.	Molecule	Ref.	log k/k_o	Estimated values of log k/k_o		
				Eq.(1)	Eq.(2)	Eq.(3)
1	Phenol	2a	0,0	0,228	0,355	0,231
2	2-methylphenol	2b	0,447	0,625	1,080	0,851
3	2,6-dimethylphenol	2b	1,183	1,022	1,801	1,486
4	2,4,6-trimethylphenol	2a	1,447	1,419	2,223	1,848
5	4-methylphenol	2b	0,549	0,625	0,791	0,577
6	2,4-dimethylphenol	2b	1,106	1,022	1,509	1,208
7	3-methylphenol	2b	0,449	0,312	0,298	0,108
8	3,5-dimethylphenol	2b	0,315	0,397	0,239	0,001
9	2,3,5-trimethylphenol	2b	0,727	0,793	0,957	0,644
10	Hydroquinone (HQ)	2b	1,415	1,402	0,900	1,107
11	HQ monoethyl ether	2b	1,302	1,221	0,914	0,928
12	p-hydroxybenzaldehyde	2b	-0,477	-0,387	-0,796	-0,576
13	Pyrocatechol	2b	1,660	1,402	1,267	1,455
14	Resorcinol	2b	0,195	0,168	0,234	0,473
15	Phloroglucinol	2b	0,125	0,108	0,098	0,634
16	Pyrogallol	2a	2,682	2,576	2,222	2,652
17	Durohydroquinone	2a	2,444	2,364	2,173	1,999
18	5-hydroxypyrogallol	11	3,478	3,750	2,780	3,422
			R:	0,991	0,904	0,956

From these significant correlations[10] the following conclusions can be drawn:

-the hydrogen atom donating ability of phenols decreases as the positive charge on atom C_1 increases;

- it seems reasonable to assume correlation between the sum of electrophilic substituent constants and charge density on ring atom C_1;
- in spite of the high correlation coefficient of Eq.(1) the estimated value of log k/k_o for the molecule 5-hydroxypyrogallol exceeds significantly the experimental value[12]. The set of rate constants covers a broad range of 4 orders of magnitude and log k/k_o is a definitely curved function of electrophilic substituent constants (Fig.1.). The earlier Hammett equation [2b] covered a narrower range, hence the value of ϱ differed from that of Eq.(1).

We emphasize that even the high correlation coefficients (e.g., 0,991) cannot guarantee the linearity of experimentally found correlations.

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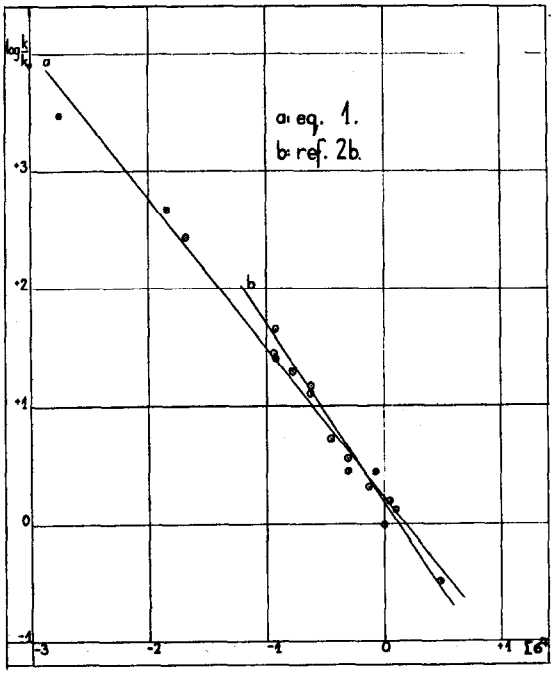

Fig. 1. Correlation according to Eq.1.