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Abstract

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AN ATTEMPT TO APPLY CORRELATION EQUATIONS TO KETO-ENOL EQUILIBRIUM

The effect of a solvent on keto-enol equilibrium obeys Meyer' s well-known relation (^{1}) $K_T = EL$, where K_T is the constant of tautomeric equilibrium, E is the enolization constant, and L is the enolizing ability of the solvent. This relation is obeyed by ketoenols whose enol form has the cis configuration and is stabilized by an intramolecular hydrogen bond (^{2}).

It has been shown that Meyer' s formula follows from general considerations of the theory of acid-base tautomeric equilibrium (^{3}) and thus is a consequence of applying the Brønsted equation (^{4}) to tautomeric acids. Since the latter is closely connected with the principle of linear free energies, one could hope for the possibility of applying correlation equations to keto-enol equilibrium.

Campbell and Gilow (^{5}) applied the Hammett equation to the equilibrium constants of 2-aroylcyclohexanones and showed a linear relationship between the σ-constants of substituents in the benzene ring and the equilibrium constants, as well as with the vibration frequencies of the conjugated carbonyl in IR spectra and the absorption maxima of benzoyl and cinnamoyl chromophores in UV spectra. The system studied by these authors belongs to the type

where y is the keto-enol reaction center, i.e., to the class of ordinary objects for application of the Hammett equation.

Table 1

No. of points	R	R′	$\Sigma(\sigma_p - \sigma_I)$	$\log K_T$, water	$\log K_T$, methyl alcohol	$\log K_T$, ethyl alcohol	$\log K_T$, chloroform	$\log K_T$, benzene
1	CH_3	OC_2H_5 (^{1})	−0.61	−2.40	−1.13	−0.89	−1.06	−0.48

Figure 1: correlations of log KT with substituent constants

Figure 2: Figure 1: correlations of log KT with substituent constants

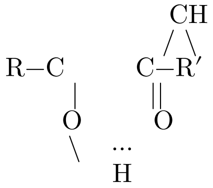
No. of points	R	R′	$\Sigma(\sigma_p-\sigma_I)$	$\log K_T$, water	$\log K_T$, methyl alcohol	$\log K_T$, ethyl alcohol	$\log K_T$, chloroform	$\log K_T$, benzene
2	CH_3	OC_6H_5	−0.53	–	−1.20	−0.97	–	–
3	CH_2Cl	OC_2H_5 (7)	−0.48	–	−1.17	−0.82	–	–
4	C_6H_5	OCH_3 (1)	−0.61	−2.10	−0.80	−0.46	−0.74	−0.35
5	C_6H_5	OC_2H_5 (1)	−0.58	−2.00	−0.77	−0.49	–	−0.29
6	CH_3	CH_3 (1)	−0.24	−0.63	0.45	0.72	0.58	0.76
7	C_6H_5	CH_3 (1)	−0.21	−0.42	0.95	1.14	1.11	–
8	C_6H_5	C_6H_5 (1)	−0.18	–	1.34	1.60	–	–
9	CH_3OOC	OCH_3 (1)	−0.51	–	−1.33	−0.54	–	–
10	C_2H_5OOC	OC_2H_5 (1)	−0.34	–	−0.17	0.18	–	–
11	CH_3	C_2H_5 (8)	−0.22	−0.72	–	–	–	–
12	CH_3	CF_3 (9)	+0.01	–	–	–	–	1.56

We applied a different approach and used, as a kind of "transmitting" system, not the benzene ring of the substituent, but the system of conjugated bonds of the enol form (including the pseudoaromatic six-membered ring with a hydrogen bond) or of the ketone form (hyperconjugation). In other words, the links $-COCH_2CO-$and $-(HO)C=$

Fig. 1. **A** –dependence of $\log K_T$ on $\sum(\sigma_p-\sigma_I)$ in water (**I**), chloroform (**IV**) and benzene (**V**); **B** –the same in ethyl (**II**) (open circles) and methyl (**III**) (black circles) alcohols

$=CH-CO-$are considered as "nuclei," and the radicals R and R′ as substituents:

$$R-C(=O)-CH_2-C(=O)-R' \rightleftharpoons R-C(\;CH\;)-C(=O)-R'$$



These systems contain, as substituents, alkyls, alkoxyls, aroxyls, haloalkyls, and carboxyls. We also assumed that the substituents R and R′ act on the nuclei similarly to ortho- and para-substituents of the benzene ring.

Since the Hammett σ values characterize the combined influence of the induction effect and polar conjugation, while the induction effects of substituents R and R' in the ketone and enol forms should be, if not equal, then very close, the resonance polar effect of the substituent, characterized by the difference $\sigma_p - \sigma_I$ (where σ_I is the inductive component [6]), should largely determine the position of tautomeric equilibrium. To test this assumption, we treated the available literature data on the constants of tautomeric equilibrium of certain ketoenols in various solvents and compared them with the values $\sigma_p - \sigma_I$ for both substituents R and R' according to the formula:

$$\log K_\mathrm{T} = \log K_\mathrm{T}^0 + \rho \Sigma(\sigma_p - \sigma_I).$$

The results are given in Table 1 and in Fig. 1.

The parameters of the linear relationships obtained are given in Table 2.

Table 2

Solvent	n	$\log K_\mathrm{T}^0$	ρ	r	S
Water	6	0,35	4,27	0,99	0,13
Methyl alcohol	10	1,86	5,22	0,92	0,21
Ethyl alcohol	10	2,08	4,98	0,93	0,36
Chloroform	4	1,88	4,57	0,98	0,25
Benzene	5	1,53	3,17	0,99	0,06

The results obtained indicate that the influence of substituents on the position of the tautomeric equilibrium of β-dicarbonyl compounds with a normal chain is determined mainly by their influence on the mesomeric stabilization of the forms.

It is of interest that by means of extrapolation one can calculate the values of the tautomeric equilibrium constants for cases in which they are difficult to determine experimentally, for example, for malonic ester ($\Sigma(\sigma_p - \sigma_I) = -0,98$) and for malonic dialdehyde ($\Sigma(\sigma_p - \sigma_I) = 0$). The following values of the equilibrium constants K_T were obtained:

	Water	Methyl alcohol	Ethyl alcohol	Chloroform	Benzene
Malonic ester	$1,5 \cdot 10^{-4}$	$5,5 \cdot 10^{-4}$	$1,6 \cdot 10^{-3}$	$2,5 \cdot 10^{-3}$	$2,7 \cdot 10^{-2}$
Malonic dialdehyde	2	72	120	76	34

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Note: Figure translations are in progress. See original paper for figures.