

REACTIVITY OF COMPOUNDS OF DIPHENYLMETHANE SERIES. II.*
 PROTONATION OF MONO- AND POLYSUBSTITUTED
 BENZHYDROL DERIVATIVES

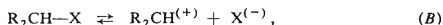
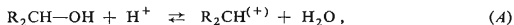
J. MINDL and M. VEČEŘA

*Department of Organic Chemistry,
 Institute of Chemical Technology, Pardubice*

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The values pK_{R^+} of a series of eleven mono- and six polysubstituted benzhydrols have been determined in concentrated sulphuric acid medium. These values have been determined on the basis of a H_R scale constructed by us for benzhydrols in the medium mentioned, based on the pK_{R^+} value of *p*-methoxytriphenylcarbinol (-3.40) given by Deno. The pK_{R^+} values have been correlated with the Brown σ^+ constants. Deviations of 4-alkoxy derivatives are discussed.

Diphenylmethane derivatives represent a suitable model for both the study of the equilibrium reactions (Eq. (A)) and the study of solvolysis kinetics (Eqs (B)–(C)).



R = aryl, SH = solvent.

These reactions can serve for a study of the substituent effects during electrophilic aromatic substitution of compounds with a side chain, the underlying principle being the similarity of the carbonium ions in reactions (A), (B) and the transition state of an aromatic electrophilic substitution. The substituent influence on the course of electrophilic aromatic substitution was studied intensively (using the empirical Eq. (I)) in the previous papers with the use of a number of models¹⁻¹³ besides diphenylmethane derivatives¹⁴⁻¹⁹.

$$\log(k/k_0) = \rho\sigma^+. \quad (I)$$

The question is often discussed whether the principle of linear free energy relationships can be used for electrophilic aromatic substitution in spite of the fact that it is not very likely that the

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resonance stabilization of the transition state by substituents on substrate will depend on the reaction type. There seems to be no simple answer to this question, and the validity of the Hammetts rule²⁰ for electrophilic aromatic substitution must be, first of all, proved experimentally especially with highly activated substrates. Yukawa and Tsuno^{1,3} proposed equations which took into account the variability of the resonance contribution of substituents to stabilization of the transition state according to the reaction type (Eqs (2) and (3)).

$$\log(k/k_0) = \rho[\sigma + R(\sigma^+ - \sigma)], \quad (2)$$

$$\log(k/k_0) = \rho[\sigma^\circ + R(\sigma^+ - \sigma^\circ)]. \quad (3)$$

The value R is a measure of conjugation of the reaction centre with the substituent. So far there are not enough experimental data for judging whether the Brown² two-parameter equation (1) represents a sufficiently appropriate approximation for reactivity estimates in special cases or whether the Yukawa-Tsuno equation (2) and (3) is more advantageous.

The aim of the present work was to follow the substituents effects during the reactions of benzhydrol derivatives. We want to judge the suitability of this model which makes it possible to determine the reactivity in strongly polar media (equilibrium studies of benzhydrols) as well as in slightly polar ones (kinetic studies), and hence, to derive the substituent constants. As it is known that the values of some σ^+ constants depend on the substrate structure (*e.g.* the calculated σ^+ constants of 4-methyl group increase in the series $\text{tert-C-X} < \text{sec-CH-X} < \text{CH}_2\text{X}$ (ref.²¹)), we want to judge the suitability of the model chosen from the point of view of the similarity of the transition states (resp. intermediates) of electrophilic aromatic substitution and those of reactions of α -carbon atom in a side chain.

In the present work we have followed the dependence of the acid-base equilibrium (A) on the substituent effects using benzhydrol derivatives 1–17. We have chosen the substituents covering as broad range of the Brown σ^+ scale² in the given medium as possible. For the sake of comparison we have included methoxy, ethoxy and phenoxy substituents the values of which are subjected to frequent discussions^{3,6,22}.

Deno and coworkers^{14–16} determined informatively the apparent dissociation constants of seven monosubstituted benzhydrols in aqueous sulphuric acid medium. The determination of the correct values $\text{p}K_{\text{R}^+}$ is difficult in this medium because of the slight solubility of the unprotonated indicators and because of decomposition and precipitation of those benzhydrols especially whose $\text{p}K_{\text{R}^+}$ is in the concentration range of 75% aqueous sulphuric acid and above.

We have determined spectrophotometrically the $\text{p}K_{\text{R}^+}$ values of thirteen monosubstituted benzhydrol derivatives for aqueous sulphuric acid as a medium. For this system of indicators a new acidity scale H_{R} has to be constructed. In order to be able to relate this scale to the pH scale, we have also to include polysubstituted benzhydrols and 4-methoxytriphenylcarbinol which was taken as a basis of the new H_{R} scale.

EXPERIMENTAL

Reagents

The *benzhydrols* were prepared by reduction of the respective benzophenones with lithium aluminium hydride in dry ether. The raw products were purified and isolated by crystallization from light petroleum-ethanol mixtures (3 : 1 to 1 : 2). Physical constants were compared with the literature data (Table I). 3-Phenoxybenzophenone was prepared from 3-bromobenzophenone (0.1 mol) and potassium phenolate (0.15 mol) by melting at 200°C for eight hours in the presence of copper powder (0.2 g). The product was isolated by extraction with ether, washed with 10% aqueous potassium hydroxide and distilled *in vacuo* at 215°C/4 Torr to give a colourless viscous liquid, n_D^{20} 1.6188, d_{20}^{20} 1.1431. For $C_{19}H_{14}O_2$ (274.3) calculated: 83.20% C, 5.15% H; found: 83.28% C, 4.91% H. 3-Phenoxybenzhydrol was prepared by reduction of 3-phenoxybenzophenone with lithium aluminium hydride in ether and isolated as a syrupy liquid, b.p. 170–172°C/0.3 Torr, n_D^{20} 1.6082, d_{20}^{20} 1.1389. For $C_{19}H_{16}O_2$ (276.3) calculated: 82.58% C, 5.84% H; found: 82.84% C, 5.85% H. 4-Hydroxybenzhydrol was obtained by four hours boiling of 4-methoxybenzhydrol with 48% hydrobromic acid. The reaction mixture was cooled and neutralized, and the product was isolated as phenolate; therefrom the raw product was obtained by saturation with carbon dioxide and crystallized from water-ethanol mixture 1 : 1 to give colourless crystals melting at 162°C (ref.²³ 162°C). Sulphuric acid 100% was prepared by dissolving the respective amount of sulphur trioxide in p.a. 98% sulphuric acid which was freshly distilled.

Ionization Constants

The solutions of the indicator dissolved in 5% aqueous sulphuric acid and in 100% sulphuric acid were mixed at suitable ratios under good cooling at 20°C (at 0°C for 3-phenoxybenzhydrol) (the benzhydrol concentrations in the both solutions to be mixed were the same). The concentration ratios of the both indicator forms at known sulphuric acid concentrations were measured spectrophotometrically at 20°C (at 0°C for 3-phenoxybenzhydrol) in the range of 440–530 nm using a VSU-1 apparatus (Zeiss, Jena). Spectral course and absorption values were checked at various time intervals using a Unicam SP 800 B spectrophotometer. The sulphuric acid concentration was measured by means of a Mohr-Westphal balance. The indicator concentration for measurements was chosen in the range 10^{-4} – 10^{-5} M.

Those benzhydrols which did not fulfil the condition of reversibility in media of sulphuric acid concentrations higher than 80% as e.g. 3-fluoro-, 3-chloro-, 4-bromo-, 3-cyano-, 4-cyano-, 3-nitro-, 4-nitro-, 4-hydroxy- and 3-methoxybenzhydrols were not included in the series studied by us. The benzhydrols having 2-methoxy group as e.g. 2,4-dimethoxybenzhydrol, 2,4,4'-trimethoxybenzhydrol, 2,2',4,4'-tetramethoxybenzhydrol showed a different character of protonation.

RESULTS AND DISCUSSION

The pK_{R+} values of the benzhydrols 1–17 determined in the aqueous sulphuric acid medium are summarized in Table I. Statistical characteristics of the dependences of the pK_{R+} given in Table I on the substituent constants are presented in Table II, and in Fig. 1, the values pK_{R+} are plotted against resp σ^+ constants. Regression analysis using the Yukawa-Tsuno equation gave the closest bond of the equations (2) and (3) respecting, in our case, the fact that the influence of substituents with +M effect is different from that during cumyl chloride ($R = 1$) hydrolysis which served for

TABLE I
Physical Constants of Benzhydrols I-17 and Triphenylcarbinol 18

Com- pound	Substituent	M.p., °C		ref.	$-\text{p}K_{\text{R}}^+$	$-\text{p}K_{\text{R}}^{\text{a}}$	σ^{b}	$\sigma^{\text{+b}}$	σ^{c}	$\lambda_{\text{R}}^{\text{+max}}$ ^d
		found	ref.							
1	3-OC ₆ H ₅	e	—	—	12.66 ^f	—	0.252	—	—	438
2	4-Br	65.0-66.0	65.0-66.0 ^f	—	12.09	—	0.232	0.150	0.26	474
3	4-Cl	62.0-63.0	62.5-63.0 ^f	—	12.08	12.01	0.227	0.114	0.27	464
4	4-F	48.0-49.0	48.5-49.0 ^f	—	11.55	—	0.062	-0.073	0.17	450
5	H	67.0-67.5	67.0-67.5 ^f	—	11.77	11.68	—	—	—	442
6	3-CH ₃	52.0-53.0	52.0-53.5 ^f	—	11.37	—	-0.069	-0.066	-0.17	443
7	4-C(CH ₃) ₃	81.0-82.0	82 ^h	—	10.81	—	-0.197	-0.256	-0.17	462
8	4-CH ₃	55.5-56.5	56.0-56.5 ^f	—	10.59	10.55	-0.170	-0.311	-0.15	457
9	4-OC ₆ H ₅	69.5-70.5	71 ⁱ	—	9.85	—	-0.320	-0.500	-0.03	473
10	4-OC ₂ H ₅	liq.	39 ^j	—	8.19	—	-0.240	-0.778 ^h	-0.12 ^h	466
11	4-OCH ₃	67.0-68.9	67.0-68.0 ^g	—	8.12	7.50	-0.268	-0.778	-0.12	464
12	3,4'-(CH ₃) ₂	liq.	liq. ^g	—	10.24	—	—	—	—	463
13	4,4'-(CH ₃) ₂	71.0-71.5	71.0 ^g	—	9.53	9.46	—	—	—	472
14	4-OCH ₃ -4'-Cl	63.0-63.5	62 ^k	—	8.31	—	—	—	—	477
15	4-OCH ₃ -4'-CH ₃	60.0-61.0	59.5-60.5 ^l	—	7.36	—	—	—	—	482
16	4,4'-(OCH ₃) ₂	72.0-72.5	72 ^m	—	5.56	5.61	—	—	—	507
17	2,2'-(CH ₃) ₂ -4,4'-(OCH ₃) ₂	89.0-90.0	90.5-91.5 ⁿ	—	6.34	—	—	—	—	526
18	4-OCH ₃	56.0-58.5	56.0-58.0 ^b	—	3.40	3.40	—	—	—	476

^a The $\text{p}K_{\text{R}}^+$ values are recalculated to fit our H_{R} scale (ref.¹); ^b taken from ref.⁹; ^c taken from ref.²⁰; ^d measured in 98% sulphuric acid; ^e see Experimental; ^f measured at 0°C; ^g taken from ref.¹⁸; ^h the values for 4-OC₂H₅ are made identical with those for 4-OCH₃; ⁱ ref.²⁸; ^j ref.²⁹; ^k ref.³⁰; ^l ref.¹⁴; ^m ref.³¹; ⁿ ref.³².

construction of σ^+ scale. The value of the constant $R = 1.25$ points to an increased sensitivity of the reaction centre towards the resonance influence of substituents during acid-base equilibria of benzhydrols as compared to solvolyses of cumyl chlorides (Table III). From Fig. 1 it is obvious that 4-methoxy- and 4-ethoxybenz-

TABLE II

Dependence of Empirical Constant σ^+ of 4-Methoxy Group on the Type of Substrate during Electrophilic Aromatic Substitution

No	Reaction	Medium	σ^+ ^a	n^b
1	solvolysis of cumyl chlorides ²	90% CH ₃ COCH ₃ -H ₂ O, 20°C	-0.778	34
2	mol. chlorination ⁴	60% CH ₃ COOH-H ₂ O, 25°C	-0.766	12
3	mol. bromination ¹³	CH ₃ COOH-CH ₃ NO ₂ , 25°C	-0.982	7
4	pK_{BH^+} - benzoic acids ⁵	H ₂ O-H ₂ SO ₄ , 20°C	-0.578	15
5	pK_{BH^+} - benzophenones ¹⁹	H ₂ O-H ₂ SO ₄ , 20°C	-0.891	15
6	mercuration ⁶	Hg(OCH ₃) ₂ CH ₃ COOH, 20°C	-0.891	14
7	acetylation ⁷	CH ₃ COCl, AlCl ₃ , ClCH ₂ CH ₂ Cl, 25°C	-0.761	11
8	protodesilylation ⁹	HClO ₄ , CH ₃ OH-H ₂ O, 51.2°C	-0.683	12
9	protodesilylation ¹⁰	HClO ₄ , CH ₃ OH-H ₂ O, 51.2°C	-0.852	10
10	protodegermylation ¹¹	HClO ₄ , CH ₃ OH-H ₂ O, 50°C	-0.638	13
11	protodestanylation ¹²	HClO ₄ , C ₂ H ₅ OH-H ₂ O, 50°C	-0.734	13
12	solvolysis of benzhydryl chlorides ¹⁸	C ₂ H ₅ OH, 25°C	-0.899	14
13	pK_R - benzhydrols	H ₂ SO ₄ -H ₂ O, 20°C	-0.905	10

^a Calculated according to $\rho^{-1} \log(k/k_0)$; ^b number of the k values used for calculation of $\sigma^+(4-OCH_3)$.

TABLE III

Correlation of pK_a Values with the Substituent Constants of Empirical Models

Equation ^a	$-\rho$	s_e^b	R	r	ψ^c	n^d
(1)	4.132	0.210	—	0.989	0.153	10
(1) ^e	3.591	0.130	—	0.995	0.180	9
(2)	3.432	0.014	1.537	0.995	0.105	10
(3)	3.711	0.037	1.253	0.989	0.108	9

^a See text; ^b standard deviation; ^c Exner's test²¹; ^d number of the values tested; ^e the value of the 4-methoxy derivative was not included in calculation.

TABLE IV
The log *I* Values of the Benzhydrols Used as Indicators for Construction of H'_R Scale

% H ₂ SO ₄	log <i>I</i>	$\frac{\delta(\log I)}{\delta(\% \text{H}_2\text{SO}_4)}$	$-H'_R$	% H ₂ SO ₄	log <i>I</i>	$\frac{\delta(\log I)}{\delta(\% \text{H}_2\text{SO}_4)}$	$-H'_R$
18				15			
39.7	1.199	—	4.57	62.5	1.402	—	8.77
37.5	0.870	0.15	4.25	60.3	0.958	0.20	8.33
35.0	0.506	0.15	3.85	57.3	0.393	0.19	7.75
31.4	-0.026	0.15	3.35	56.2	0.185	0.19	7.55
29.0	-0.375	0.15	3.04	55.3	0.022	0.18	7.38
26.8	-0.635	0.12	2.76	54.2	-0.164	0.17	7.19
$pK_{R+} = -3.385 \pm 0.012$				53.8	-0.232	0.17	7.13
16				51.4	-0.655	0.18	6.65
53.0	1.410	—	6.98	49.7	-0.988	0.20	6.34
49.0	0.670	0.19	6.25	$pK_{R+} = -7.364 \pm 0.024$			
46.9	0.291	0.18	5.85	11			
44.2	-0.206	0.18	5.35	68.2	1.779	—	9.92
42.4	-0.502	0.16	5.05	63.1	0.787	0.19	8.91
41.6	-0.634	0.16	4.91	61.7	0.504	0.20	8.62
39.1	-1.046	0.16	4.50	59.8	0.130	0.20	8.22
$pK_{R+} = -5.561 \pm 0.021$				56.9	-0.451	0.20	7.68
17				53.5	-1.073	0.18	7.04
55.5	0.978	—	7.42	$pK_{R+} = -8.120 \pm 0.051$			
52.0	0.398	0.17	6.76	13			
49.5	-0.076	0.19	6.35	69.9	0.724	—	10.25
48.5	-0.256	0.18	6.15	67.4	0.223	0.20	9.77
47.6	-0.417	0.18	5.98	66.8	0.100	0.20	9.64
41.6	-1.440	0.17	4.91	62.0	-0.865	0.20	8.67
$pK_{R+} = 6.344 \pm 0.009$				60.8	-1.097	0.19	8.42
9				$pK_{R+} = -9.532 \pm 0.024$			
72.9	1.017	—	10.91	3			
77.8	0.604	0.20	10.45	87.6	1.170	—	13.17
69.2	0.279	0.21	10.10	85.3	0.892	0.12	12.95
67.3	-0.089	0.19	9.76	82.4	0.510	0.13	12.59
65.0	-0.608	0.20	9.25	80.6	0.225	0.16	12.37
$pK_{R+} = -10.849 \pm 0.028$				78.0	-0.229	0.18	11.88
				72.0	-0.404	0.20	10.68
				$pK_{R+} = -12.078 \pm 0.011$			

TABLE IV
(Continued)

% H ₂ SO ₄	log I	$\frac{\delta(\log I)}{\delta(\% \text{H}_2\text{SO}_4)}$	-H _R	% H ₂ SO ₄	log I	$\frac{\delta(\log I)}{\delta(\% \text{H}_2\text{SO}_4)}$	-H _R
8				I			
78.4	1.365	—	11.94	87.6	0.649	—	13.17
76.7	1.007	0.20	11.64	84.4	0.253	0.12	12.83
73.8	0.481	0.20	11.07	82.5	-0.023	0.15	12.58
73.2	0.353	0.21	10.95	79.9	-0.528	0.19	12.25
70.0	-0.312	0.21	10.26	79.0	-0.700	0.19	12.07
68.9	-0.537	0.20	10.05	77.9	-0.916	0.20	11.89
$pK_{R^+} = -10.593 \pm 0.040$				$pK_{R^+} = -12.657 \pm 0.027$			
5							
83.4	0.987	0.14	12.72				
81.5	0.725	0.16	12.47				
80.2	0.522	0.19	12.26				
77.8	0.085	0.20	11.84				
75.7	-0.333	0.20	11.45				
75.0	-0.477	0.20	11.30				
72.5	-0.966	—	10.80				
$pK_{R^+} = -11.768 \pm 0.012$							

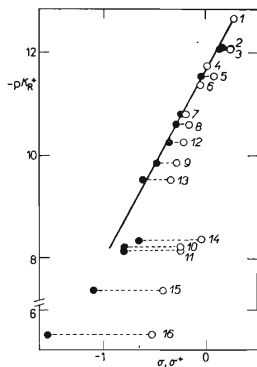
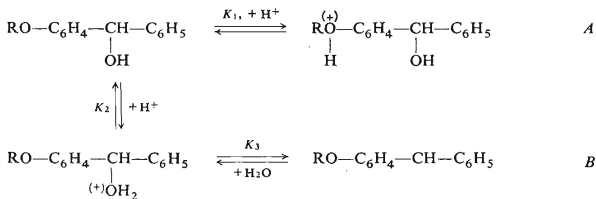


FIG. 1
Dependence of pK_{R^+} of Diphenylcarbonium Ions on the Hammett σ (○) and Brown σ^+ (●) Constants
For numbers see Table I.

hydrols deviate strongly from the linear dependence. From the dependence given it follows that these benzhydrols are apparently more basic. The values pK_{R^+} found for 4-methoxy (-8.12) and 4-ethoxy derivative (-8.19) deviate from those calculated from the relation (1). We give three possible explanations of the deviation found: a) The reaction mechanism differs from that of the other substituted benzhydrol derivatives. We have proved that the protonation equilibrium of the benzhydrols mentioned is strictly reversible within the time of the measurements (*i.e.* maximum 15 minutes) at 20°C . We therefore consider the reason given to be not very likely. b) Besides the alcoholic group the alkoxy group can be protonated too: The reaction of hydrobromic or hydroiodic acid with 4-methoxybenzhydrol or 4-methoxybenzophenone results in demethylation which assumes protonation of alkoxy oxygen (see Experimental). The protonation of alkoxy oxygen would mean that the pK_{R^+} value found is a combined value. From the expression of acid-base equilibria of tautomer mixtures *A* and *B* it can be drawn that $K_{\text{eff}}^{-1} = K_1^{-1} + K_2^{-1}$ (Scheme 1). It was found²⁴⁻²⁶



SCHEME 1

that protonation of anisol takes place only at sulphuric acid concentrations higher than 75%. As the 4-methoxybenzhydrol protonation takes place already in 50% aqueous sulphuric acid, this reason does not seem likely either. (It is obvious that a very slight concentration of the form protonated at methoxyl is sufficient for demethylation of 4-methoxybenzophenone, or 4-methoxybenzhydrol *e.g.* in the medium of azeotropic hydroiodic acid the ratio of the unprotonated and protonated forms is $1 : 10^{-6}$.) c) The σ^+ value of 4-methoxy group (-0.78) cannot be used for the reaction under investigation. It is known that the Taft σ° constant of this group depend on the medium; a value -0.12 is reported for aqueous solutions and -0.16 for less polar media^{22,24}. It can be expected that the change of σ^+ with the change of polarity of the medium will be still greater. The σ^+ values of 4-methoxy group calculated from the dependences found for the rate constants and acid-base equilibria, resp., in various cases are given in Table II. From the table it is obvious that the values calculated are within the limits -0.578 to -0.982 . From the data published so far it cannot, however, be ascertained whether the deviations are caused by the change of the polarity of medium or by changing sensitivity of the reaction centre towards polar effects of substituents.

TABLE V

The log *I* Values of the Benzhydrols Not Used for Construction of *H*_R⁺ Scale

% H ₂ SO ₄	log <i>I</i>	$\frac{\delta(\log I)}{\delta(\% \text{H}_2\text{SO}_4)}$	- <i>H</i> _R ⁺	% H ₂ SO ₄	log <i>I</i>	$\frac{\delta(\log I)}{\delta(\% \text{H}_2\text{SO}_4)}$	- <i>H</i> _R ⁺
10				7			
67.6	1.629		9.80	77.9	1.124		11.86
65.2	1.143	0.20	9.33	74.9	0.525	0.20	11.25
62.7	0.639	0.20	8.83	72.3	0.014	0.20	10.76
59.9	0.064	0.20	8.25	69.6	-0.547	0.21	10.22
57.1	-0.509	0.20	7.71	68.1	-0.854	0.21	9.86
53.7	-1.162	0.17	7.09	65.5	-1.398	0.21	9.36
$pK_{R^+} = -8.19 \pm 0.02$				$pK_{R^+} = -10.81 \pm 0.03$			
14				4			
66.7	1.220		9.63	82.1	1.057		12.56
64.5	0.768	0.20	9.18	78.9	0.552	0.15	12.07
62.9	0.450	0.20	8.85	76.5	0.091	0.19	11.60
60.0	-0.154	0.21	8.26	73.0	-0.615	0.20	10.90
57.5	-0.625	0.19	7.80	71.1	-0.995	0.20	10.53
55.5	-1.010	0.19	7.42	70.4	-1.131	0.20	10.36
$pK_{R^+} = -8.31 \pm 0.01$				$pK_{R^+} = -11.55 \pm 0.03$			
12				6			
76.7	1.379		11.62	83.8	1.247		12.79
75.0	1.061	0.20	11.29	81.5	0.942	0.13	12.47
73.2	0.692	0.20	10.94	78.7	0.477	0.20	12.02
72.1	0.465	0.20	10.72	75.3	-0.189	0.20	11.35
68.7	-0.223	0.20	10.03	72.8	-0.679	0.20	10.87
64.3	-1.098	0.20	9.13	70.0	-1.247	0.20	10.26
$pK_{R^+} = -10.24 \pm 0.04$				$pK_{R^+} = -11.37 \pm 0.09$			
2							
87.1	1.048		13.15				
84.0	0.717	0.11	12.79				
81.3	0.370	0.13	12.44				
80.0	0.197	0.14	12.24				
77.5	-0.259	0.18	11.80				
72.7	-1.204	0.20	10.73				
$pK_{R^+} = -12.09 \pm 0.02$							

TABLE VI
Course of H_R Function Depending on Concentration of Aqueous Sulphuric Acid Found for Benzhydrols

% H_2SO_4	28.0	30.0	32.0	34.0	36.0	38.0	40.0	42.0	44.0
H_R	2.91	3.15	3.44	3.73	4.03	4.39	4.64	4.98	5.31
% H_2SO_4	46.0	48.0	50.0	52.0	54.0	56.0	58.0	60.0	62.0
H_R	5.67	6.06	6.44	6.79	7.14	7.52	7.86	8.24	8.64
% H_2SO_4	64.0	66.0	68.0	70.0	72.0	74.0	76.0	78.0	80.0
H_R	9.06	9.46	9.87	10.26	10.68	11.10	11.50	11.88	12.24
% H_2SO_4	82.0	84.0	86.0						
H_R	12.54	12.79	13.02						

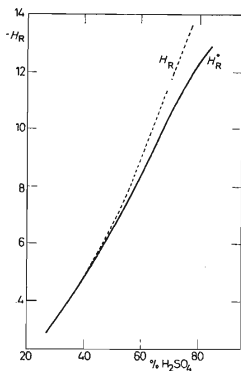


FIG. 2

Dependence of the H_R Function on Sulphuric Acid Concentration as Compared with the H_R Function for Triphenylcarbinols

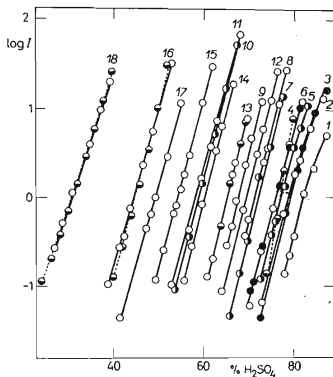


FIG. 3

Dependence of Indicator Ratio $\log I$ of Diphenylcarbonium Ions on Sulphuric Acid Concentration (by wt.)

The values marked with \odot and linked with dotted line are those found by Deno for 4-methoxytriphenylcarbinol, 4,4'-dimethoxybenzhydrol, 4,4'-dimethylbenzhydrol and benzhydrol. For numbers see Table I.

Therefore we suppose that the reason of the deviations found by us in the case of *p*-alkoxy derivatives is either an incorrect value of $\sigma(4\text{-OCH}_3)$ or the fact that the σ^+ value of this group depends on the kind resp. polarity of the reaction medium. This is supported also by our finding that the σ^+ value found by us (-0.905) is practically identical with that calculated from the experimental values of solvolyses of benzhydryl chlorides¹⁸ (-0.896) (assuming that the both bonds, C—OH and C—Cl, participate to the same extent in the intermediate formation).

If we use the value calculated for disubstituted benzhydrols²⁷ containing 4-methoxy group, the deviations from the regression line are minimum in all the cases, as it is shown to some extent by the four indicators used in the present work. If the protonation of methoxyl oxygen were the reason of the deviations, 4,4'-dimethoxybenzhydrol would differ (with respect to the large distance between the both methoxyl groups) practically only by the statistical factor (0.3), mutual influence of the methoxyl groups being not taken into account in the first approximation. The data of the regression analysis of the $\text{p}K_{\text{R}^+}$ values of monosubstituted benzhydrols with the substituent constants are summarized in Table III, Eqs (1), (2) and (3) were used for calculation. From a comparison of the statistical data it follows that the Yukawa-Tsuno equations give a more tight bond. This is caused by the introduction of the third parameter (*R*) in Eq. (2) resp. (3). Even though several objections were taken to the introduction of further parameters into the Hammett equation, we consider the values *R* found to be significant, because they give some information about the topology and stability of the activated complex of the reaction under investigation.

H_{R} Function. The acidity function H_{R} for aqueous sulphuric acid was constructed in the usual way¹⁴⁻¹⁶. The $\text{p}K_{\text{R}^+}$ value of 4-methoxytriphenylcarbinol (-3.40) (ref.¹⁴) was chosen as the basis of our scale. The indicators used for the construction of the scale are given, together with $\log I$, in Table IV. (The $\log I$ values of the benzhydrols not used for the construction of the scale are summarized in Table V). Fig. 2 and Table VI represent the course of the H_{R} function constructed with the use of the indicators given in Table IV. The difference between the both functions increases progressively in the direction to higher sulphuric acid concentrations, so that e.g. the $\text{p}K_{\text{R}^+}$ value of benzhydrol given by Deno (-13.3) and that found by us (-11.77) differ by almost two units. Deno used triphenylmethane derivatives for the construction of this function, ours is constructed with the use of diphenylmethane derivatives.

It seems that the two series cannot be included into one group of indicators. For the sake of completeness it must be added that we have failed in reproducing the $\log I$ values given by Deno for benzhydrol¹⁴ (Table IV, Fig. 3). To make ourselves sure that in the solution measured there are not present any molecules formed from two or more benzhydrols, we compared the measurements at the indicator concentrations $1.1 \cdot 10^{-4}$ and $1.4 \cdot 10^{-6} \text{M}$ ($1:80$). The $\log I$ value was independent of the stoichiometric benzhydrol concentration.

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