

REACTIVITY OF COMPOUNDS OF DIPHENYLMETHANE SERIES. III.\*  
 PROTONATION OF MONO- AND POLYSUBSTITUTED BENZHYDROL  
 DERIVATIVES; ACIDITY SCALE  $H_R$  FOR SYSTEMS SULPHURIC  
 ACID-WATER-ACETIC ACID

J. MINDL

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

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The influence of varying acetic acid content in the system sulphuric acid-water-acetic acid on the  $pK_{R+}$  values and the shape of acidity function has been studied in the series of 10 mono-substituted and 7 polysubstituted benzhydrols. The  $pK_{R+}$  value of 4-methoxytriphenylcarbinol ( $-3.40$ ) has been chosen as the basis of acidity functions  $H_R^+$ . It has been found that the  $pK_{R+}$  value of most benzhydrols is independent of the acetic acid amount in the media with constant amounts of acetic acid 10% (I), 20% (II), 50% (III) and continuously varying content 0–80% (IV). With decreasing acetic acid content, however, the slope of the respective acidity function decreases proportionally as compared to its shape in the binary system sulphuric acid-water. The shapes of individual  $H_R^+$  functions for media I–IV and the dependences of indicator ratio on sulphuric acid content are given.

The readiness for formation of carbonium ion from an arylcarbinol generally depends on the acidity properties of medium<sup>1–8</sup> and on the type of the arylcarbinol, and it is represented by the corresponding  $H_R$  acidity function. Former studies of the equilibrium reactions arylcarbinol-carbonium ion, first of all, dealt with the influence of medium *viz.* the concentration of mineral or organic acid in binary systems with water<sup>7,9,10</sup> as well as in ternary mixtures water-organic solvent-mineral acid<sup>6,8</sup>.

The influence of composition of protogeneous media on the protonation of four benzhydrols was studied by White and Stout<sup>6</sup> in the systems sulphuric acid–80% by wt. aqueous acetic acid. In this study, however, a further necessary condition was not respected *viz.* a sufficiently extensive and homogeneous series of indicators fulfilling the relation (I).

$$\Delta H_{R+} = pK_{R_1+} - pK_{R_2+} = \log \frac{[R_1^+]}{[R_1OH]} - \log \frac{[R_2^+]}{[R_2OH]} - \log \frac{f_{R_1OH} \cdot f_{R_2+}}{f_{R_1+} \cdot f_{R_2OH}} \quad (I)$$

The aim of the present paper which represents a continuation of our former work<sup>5</sup> was to extend the indicator series by benzhydrols carrying electronegative substituents. Their low solubility is fundamentally improved by addition of acetic acid.

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This method was used by Deno and coworkers<sup>1</sup>, too. It is not yet known, however, what amount of the acetic acid added for the sake of improving the solubility of only some member of the indicator series will cause a marked error in  $H_R$  construction as a consequence of the fact that the indicator ionizes in a system characterized by a different  $H_R$  function. On the one hand, this method could make it possible to define the reaction constant value  $\rho$  of protonation of these compounds with more precision by using derivatives with electronegative substituents<sup>9</sup> as well as to extend the acidity scale (towards higher sulphuric acid concentrations); on the other hand, in the case of marked deviations, doubt might arise as to the correctness of  $pK_{R+}$  of triphenylcarbinols and the respective  $H_R$  function in the acidity range where Deno<sup>1</sup> introduced acetic acid into the system to improve the solubility.

For these reasons the study of the influence of acetic acid on the individual  $pK_{R+}$  values and the shape of acidity function of benzhydrols<sup>9</sup> in media sulphuric acid–water–acetic acid became the aim of the present work.

If a further (protogeneous) component *viz.* acetic acid is introduced into the system sulphuric acid–water, an acidity decrease of the carbonium ions dissolved can be anticipated. This decrease should be constant for  $pK_{R+}$  value of each indicator of the series (Eq. (2), where  $f^0$  are the respective standard activity coefficients in the given solvent (S) with respect to pure water,  $k$  is the Boltzmann constant,  $e$  charge of the electron,  $\epsilon$  dielectric constant, and  $r$  the radius of the solvated ion.

$$pK_{R+}^{(S)} - pK_{R+}^{(H_2O)} = -\log \frac{f_{H^+}^0 \cdot f_{ROH}^0}{f_{R^+}^0 \cdot f_{H_2O}^0} = -0.87 \frac{e^2}{kT} (r_{(SH^+)}^{-1} - r_{(R^+, H_2O)}^{-1}) \cdot (\epsilon_{(S)}^{-1} - \epsilon_{(H_2O)}^{-1}) = \text{const.} \quad (2)$$

The determination of the  $pK_{R+}$  difference between two media is often problematic with respect to the existence of suitable indicators of the given series studied necessary for identifying the functions pH and  $H_R$  for non-aqueous or mixed media. The structure of the used series of carbinols chosen as indicators must fulfil the condition of the consecutive relation of their  $pK_{R+}$  values, as it can be expressed by Eq. (1) with an assumption that the  $\log a_{H_2O}$  value does not change

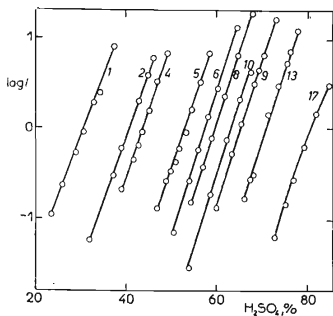


FIG. 1

Dependence of Logarithm of Indicator Ratios ( $\log I$ ) of Benzhydrols in Medium 10% by wt. Acetic Acid–Aqueous Sulphuric Acid on Weight Concentration of Sulphuric Acid  
For numbers see Table I.

in the concentration range of the two carbinols (eventually the respective carbonium ions  $R_1^+$  and  $R_2^+$ ) compared. The last term of this equation must correspond to the Hammett condition (3) of the applicability of the carbinol series chosen for construction of a new acidity scale by the overlap method.

$$(f_{R_1OH} \cdot f_{R_2^+}) / (f_{R_1^+} \cdot f_{R_2OH}) = 1. \quad (3)$$

Of the acidity functions the  $H_R$  scale shows the highest sensitivity to acidity change. It can be presumed that even a slight structural change of basicity centre will affect its behaviour to the protons. *E.g.* according to some of the previous papers dealing with  $H$  functions<sup>10,11</sup> the protonations of dialkylanilines and anilines are quite different in the same media. The slope of the dependence of indicator ratios on the acid content increases in given range with decreasing number of dissociable hydrogen atoms of the conjugate acid in the series  $ArNH_3^+ < ArNRH_2^+ < ArNR_2H^+$ . A similar increase can be expected in the carbonium ion series  $ArCH_2^+ < Ar_2CH^+ < Ar_3C^+$ , too.

## EXPERIMENTAL

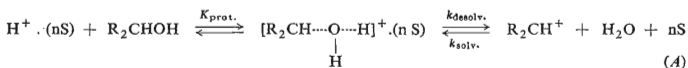
*The chemicals used.* The sulphuric acid was obtained by distillation of p.a. 98% sulphuric acid (Lachema), 100% sulphuric acid was prepared by dissolving the respective amount of sulphur trioxide in distilled 98% sulphuric acid, 100% acetic acid was obtained by drying the p.a. 99% acetic acid with the corresponding amount of diphosphorus pentoxide and distillation.

*Indicators.* The benzhydrol series described in our report<sup>9</sup> was used. The additional 2-methyl-4,4'-dimethoxybenzhydrol was prepared by reaction of 2-methyl-4-anisaldehyde with 4-methoxyphenylmagnesium bromide in dry tetrahydrofuran (yield 27%). The raw product was recrystallized from a mixture light petroleum-2-propanol 5:1 and isolated as a colourless crystalline solid melting at 63–64°C. For  $C_{16}H_{18}O_3$  (258.3) calculated: 74.41% C, 6.97% H; found: 74.24% C, 7.07% H. *Ionization constants* were measured spectrophotometrically<sup>9</sup>.

## RESULTS AND DISCUSSION

The selection of the indicators 1–18 given in the Tables I and II was chosen with respect to the homogeneity of the indicator model according to Eq. (1), as in our previous report. Original intention to choose acetic acid as the third component of the ternary system sulphuric acid–acetic acid–water was due to the fact that we wanted to determine the  $pK_{R^+}$  values of benzhydrols carrying electronegative substituents (3- and 4-nitro-, 3- and 4-cyano-, 3-halogen derivatives). The presence of acetic acid made it possible to get a homogeneous solution, but the condition of reversibility (in the time interval of 15 minutes necessary for the measurement) was not fulfilled. Slight influence of the acetic acid present on the position of the absorption band of carbonium ions in UV region ( $\lambda_{R^+}^{max}$  in Tables I and II) was observed for each medium and indicator (1–18). The  $pK_{R^+}$  values in all the media I–IV were measured at the wavelengths corresponding to the maximum absorption in 98% aqueous sulphuric acid given in Table II. The  $pK_{R^+}$  values of most indicators do not practically change with the acetic acid content in individual media (Tables I and II). As the  $H_R$  function was identified for all the media by the value  $pK_{R^+} - 3.40$  of 4-methyl-

triphenylcarbinol, and if we presume the radii of diphenylcarbonium ions to be the same, then the dependence of  $pK_{R^+}$  values on medium according to Eq. (2) agrees with experiment. Generally, the change of solvent structure and solvation properties affect the equilibrium of the reactions involving the proton. The introduction of acetic acid with a low dielectric constant causes a shift of equilibrium of the system in favour of desolvation and basicity increase of carbinol (Eq. (A)).



R = aryl, S = solvent

Free or only partially solvated carbonium ion will be probably more sensitive to internal steric requirements decreasing the reverse reaction with solvent. A higher  $pK_{R^+}$

TABLE I  
Dissociation Constants of Benzhydrols in Media Sulphuric Acid-Acetic Acid-Water (I-III)

Com- pound	Substituent(s)	I <sup>a</sup>			II <sup>b</sup>			III <sup>c</sup>		
		$-pK_{R^+}$	$\pm_{5}pK$	$\lambda_{R^+}^{max}$ , nm	$-pK_{R^+}$	$\pm_{5}pK$	$\lambda_{R^+}^{max}$ , nm	$-pK_{R^+}$	$\pm_{5}pK$	$\lambda_{R^+}^{max}$ , nm
1	4-OCH <sub>3</sub> <sup>d</sup>	3.40	0.06	478	3.40	0.02	478	3.40	0.01	476
2	2,2'-(CH <sub>3</sub> ) <sub>2</sub> -4,4'-(OCH <sub>3</sub> ) <sub>2</sub>	5.01	0.02	524	4.98	0.01	526	4.92	0.01	526
3	2-CH <sub>3</sub> -4,4'-(OCH <sub>3</sub> ) <sub>2</sub>	—	—	—	5.21	0.03	514	—	—	—
4	4,4'-(OCH <sub>3</sub> ) <sub>2</sub>	5.47	0.02	507	5.40	0.04	505	5.43	0.01	507
5	4-OCH <sub>3</sub> -4'-CH <sub>3</sub>	7.29	0.07	483	7.24	0.01	481	7.20	0.01	480
6	4-OCH <sub>3</sub>	8.04	0.02	465	7.91	0.01	464	8.07	0.03	464
7	3-OC <sub>2</sub> H <sub>5</sub>	—	—	—	7.83	0.03	466	—	—	—
8	4-OCH <sub>3</sub> -4'-Cl	8.39	0.02	474	8.38	0.03	476	—	—	—
9	4-OC <sub>6</sub> H <sub>5</sub>	9.45	0.02	472	9.37	0.09	472	—	—	—
10	4,4'-(CH <sub>3</sub> ) <sub>2</sub>	9.15	0.07	472	9.51	0.02	469	—	—	—
11	3,4'-(CH <sub>3</sub> ) <sub>2</sub>	—	—	—	10.29	0.04	462	—	—	—
12	4-t-C <sub>4</sub> H <sub>9</sub>	—	—	—	10.74	0.02	462	—	—	—
13	4-CH <sub>3</sub>	10.66	0.02	462	10.60	0.01	459	—	—	—
14	3-CH <sub>3</sub>	—	—	—	11.47	0.01	444	—	—	—
15	H	—	—	—	11.86	0.00	442	—	—	—
16	4-F	—	—	—	11.53	0.01	450	—	—	—
17	4-Cl	12.05	0.02	464	12.06	0.01	462	—	—	—
18	4-Br	—	—	—	12.19	0.03	475	—	—	—

<sup>a</sup> 10% by wt. acetic acid, <sup>b</sup> 20% by wt. acetic acid, <sup>c</sup> 50% by wt. acetic acid, <sup>d</sup> triphenylcarbinol.

value was found for 2,2'-dimethyl-4,4'-dimethoxybenzhydrol in the medium *IV* ( $pK_{R^+}$  4.88) as compared to that measured in the absence of acetic acid ( $pK_{R^+}$  -6.34); we ascribe this fact to the steric effect of two hydrophobic methyl groups. A solvent of a lower dielectric constant has smaller influence on the  $k_{solv}$  value of this indicator than on those of the other members of benzhydrol series.

The construction of  $H_R$  values in dependence of acetic acid content in media *I-IV* was based on the constant value  $pK_{R^+} = -3.40$  of 4-methoxytriphenylcarbinol in aqueous sulphuric acid. The series chosen showed an excellent parallelism of the dependence of logarithms of indicator ratios in different media, as it is seen in Fig. 1 (the system sulphuric acid-10% by wt. acetic acid-water). The points of intersection of the acidity functions experimentally constructed coincide practically with the presumed ones as to the content of individual components and confirm the additive influence of acetic acid on the shape of acidity function. The individual dependences

TABLE II

Dissociation Constants of Benzhydrols in Sulphuric Acid -80% Aqueous Acetic Acid (*IV*)

Compound	$-pK_{R^+}$	$\pm s_{pK}$	$\lambda_{R^+}^{max}$ , nm	$-pK_{R^+}^a$	$\lambda_{R^+}^{max}$ , nm <sup>a</sup>
1	3.40	0.08	478	3.40	476
2	4.88	0.01	526	6.34	526
3	5.17	0.01	516	—	—
4	5.49	0.04	508	5.56	507
5	7.20 <sup>b</sup>	0.02	482	7.36	482
6	8.00	0.01	464	8.12	464
7	7.85	0.04	464	8.19	466
8	8.36	0.04	478	8.31	477
9	9.27	0.01	472	9.85	472
10	9.40	0.01	470	9.53	472
11	—	—	—	10.24	463
12	10.71	0.02	462	10.81	463
13	10.60 <sup>b</sup>	0.02	463	10.59	462
14	11.49	0.01	443	11.37	442
15	11.74 <sup>b</sup>	0.01	442	11.77	442
16	—	—	—	11.55	450
17	—	—	—	12.08	464
18	12.14	0.01	474	12.09	474

<sup>a</sup> Ref.<sup>9</sup>, <sup>b</sup> White and Stout<sup>6</sup> give the value -3.12 for 4-methoxytriphenylcarbinol, -7.17 for 4-methoxy-4'-methylbenzhydrol, -10.60 for 4-methylbenzhydrol (transformed to our acidity scale of medium *IV*).

of acidity functions  $H_R^+$  on the by wt. concentration of sulphuric acid (20–90%) in aqueous sulphuric acid are seen in Table III. We have reproduced the results of White and Stout<sup>6</sup> in medium IV (100% sulphuric acid diluted with 80% by wt. aqueous acetic acid) using our benzhydrol series. The difference between our and their  $pK_{R^+}$  values and acidity functions  $H_R^+$  for the medium mentioned can be explained by the fact that the carbinols used for the  $H_R^+$  construction, their number necessary for covering the whole scale at a given acidity range, and the way of linking to the pH scale were different. It can be summed up: even though the  $pK_{R^+}$  values of most indicators remain independent of the acetic acid content in the medium, the slope of  $H_R^+$  function is proportional to this content. The increasing acetic acid amount increases the protogeneous properties of the medium (at a constant sulphuric acid content), but it lowers the increase of the indicator ratio and hence the increase of  $H_R^+$  acidity function as compared to the shape of the function in aqueous sulphuric acid.

TABLE III  
The Course of  $H_R^+$  Acidity Function for Benzhydrols in Sulphuric Acid–Water–Acetic Acid

$H_2SO_4$ %	$CH_3CO_2H$ , %				$H_2SO_4$ %	$CH_3CO_2H$ , %			
	10	20	50	80		10	20	50	80
10	—	—	—	2.97	50	6.65	7.45	9.35	8.72
12	—	—	—	3.31	52	7.03	7.80	—	8.99
14	—	—	2.52	3.62	54	7.40	8.17	—	9.25
16	—	—	2.87	3.94	56	7.78	8.55	—	9.51
18	—	—	3.25	4.25	58	8.17	8.90	—	9.77
20	—	—	3.64	4.57	60	8.53	9.27	—	10.04
22	—	—	4.04	4.88	62	8.91	9.68	—	10.32
24	2.49	2.62	4.43	5.19	64	9.29	10.08	—	10.61
26	2.75	2.98	4.82	5.48	66	9.69	10.45	—	10.86
28	3.03	3.35	5.20	5.72	68	10.06	10.81	—	11.10
30	3.33	3.71	5.59	6.05	70	10.43	11.16	—	11.34
32	3.63	4.07	5.99	6.33	72	10.76	11.48	—	11.56
34	3.93	4.43	6.38	6.62	74	11.10	11.76	—	11.78
36	4.24	4.81	6.75	6.88	76	11.40	12.05	—	11.98
38	4.54	5.20	7.17	7.15	78	11.67	12.30	—	12.19
40	4.85	5.60	7.53	7.41	80	11.94	12.50	—	12.37
42	5.18	5.99	7.92	7.68	82	12.19	—	—	12.55
44	5.55	6.35	8.30	7.95	84	12.43	—	—	12.71
46	5.92	6.72	8.65	8.20	86	12.62	—	—	12.87
48	6.29	7.08	9.01	8.47	88	—	—	—	13.02
					90	—	—	—	13.19

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