[Contribution from the College of Chemistry and Physics, Pennsylvania State University]

Carbonium Ions. I. An Acidity Function (C_0) Derived from Arylcarbonium Ion Equilibria[1]

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From a study of the position of alcohol–carbonium ion equilibria as a function of sulfuric acid concentration, an empirical acidity function (C_0) has been evaluated for the water–sulfuric acid system. Eighteen arylmethanols were used to evaluate this function. Data for an additional ten arylmethanols support the general applicability of the C_0 function to equilibria of the type: arylmethanol + H^+ = arylmethyl cation + H_2O. For three chemical reactions, C_0 correlates the change in rate with change in sulfuric acid concentration. Since one of these reactions involves the equilibrium, $HNO_2 + H^+ = NO^+ + H_2O$, the C_0 function may be applicable to a wider variety of equilibria of the type $ROH + H^+ = R^+ + H_2O$, than only those involving arylmethanols.

Two problems have concerned us: (1) the application of Hammett's concept of acidity functions[3] to the equilibria between alcohols and carbonium ions and (2) the effect of substituents on the stability of arylcarbonium ions. In regard to the first problem, Gold and Hawes[4] proposed an ingenious solution. They defined an acidity function (J_0) by eq. 1. If the equilibrium constant expression (eq. 3) for reaction 2 and the definition of H_0 (eq. 4) are introduced, eq. 5 can be derived. The standard state is dilute solution in water. The notation used is a_A, the activity of A; c_A, the concentration of A in moles/liter; and f_A, the activity coefficient of A ($a = fc$).

$$J_0 = H_0 + \log a_{H_2O} \qquad (1)$$

$$R^+ + H_2O = ROH + H^+ \qquad (2)$$

$$K_{R^+} = (a_{ROH}a_{H^+})/(a_{H_2O}a_{R^+});\ pK_{R^+} = -\log K_{R^+} \qquad (3)$$

$$H_0 = -\log a_{H^+} - \log (f_B/f_{BH^+}) \qquad (4)$$

$$J_0 = pK_{R^+} - \log (c_{R^+}/c_{ROH}) + \log (f_{ROH}f_{BH^+}/f_Bf_{R^+}) \qquad (5)$$

Gold and Hawes[4] suggested that the last term in eq. 5 would be negligible and thus J_0 would be an acidity function relating alcohol–carbonium ion equilibria to sulfuric acid concentration analogous to the way that Hammett's H_0 function relates equilibria between base and protonated base to the sulfuric acid concentration by eq. 6.

$$H_0 = pK_{BH^+} - \log (c_{BH^+}/c_B) \qquad (6)$$

The essence of their argument was as follows. Since ROH is a typical uncharged base, f_{BH^+}/f_B may be expected to equal $f_{ROH_2^+}/f_{ROH}$. The last term in eq. 5 can then be reduced to log ($f_{ROH_2^+}/f_{R^+}$). Since this is a ratio of two positively charged ions, Gold and Hawes suggested that it would be approximately equal to unity and thus the last term of eq. 5 would reduce to zero.

There was little experimental evidence for this conclusion, but it looked plausible and we initially accepted it.[5] Some of our early work seemed to support the conclusions of Gold and Hawes, but it is now apparent that their conclusion and eq. 7, which results, are not generally valid throughout the entire range of sulfuric acid concentrations.

$$J_0 = pK_{R^+} - \log (c_{R^+}/c_{ROH}) \text{ for } 80\text{–}95\%\ H_2SO_4 \qquad (7)$$

We were initially misled for two reasons. First, eq. 7 is experimentally valid for the region 80–95% sulfuric acid and approximately true for 60–80% acid, although in both regions the values of pK_{R^+} become based on 80–95% sulfuric acid as the standard state instead of dilute water solution. Secondly, some of our early work with *p*-alkyl substituted triarylmethanols was conducted at concentrations of triarylmethanol which were greater than the region of concentrations in which the experimental ratios of c_{R^+}/c_{ROH} are independent of stoichiometric alcohol concentration and were thus in serious error.

The equilibrium between 18 arylmethanols and their respective carbonium ions now has been investigated quantitatively as a function of sulfuric acid concentration. In each case a number of concentrations of the arylmethanol were used. From this work a new acidity function, defined by eq. 8, was evaluated. To be a useful acidity function, the value of C_0 will have to be independent of the structure of ROH for at least certain variations. An investigation of this question will be the principal concern of this paper.

$$C_0 = pK_{R^+} - \log (c_{R^+}/c_{ROH}) = -\log a_{H^+} + \log a_{H_2O} + \log (f_{R^+}/f_{ROH}) \qquad (8)$$

The difference between C_0 and Gold and Hawes' J_0 function is expressed in eq. 9, which was obtained by subtracting eq. 5 from eq. 8.

$$C_0 - J_0 = \log (f_{R^+}/f_{ROH_2^+}) \qquad (9)$$

Experimental

Triarylmethanols.—Most of the triarylmethanols[6] were prepared by methods previously described.[5]

4,4′,4″-Trimethoxytriphenylmethanol was prepared by treating ethyl anisate with 4-methoxyphenylmagnesium bromide. After the reaction had progressed in ether for 12 hr., the ether was replaced with benzene and the benzene solution was refluxed for 20 min. The reaction product was isolated by the usual method.[5] The crude product was purified by formation of the picrate. The yield of pure white crystals of the alcohol, m.p. 81–82° (reported 83.5–84°[7]), was 25%. This method of preparation appears to be inferior to that used by Baeyer and Villiger.[7]

4,4′-Dimethoxytriphenylmethanol was prepared from 4-methoxyphenylmagnesium bromide and benzoyl chloride. Although pure white crystals were obtained eventually by

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[2] Recipient of the Shell Fellowship at the Pennsylvania State University, 1954.

[3] L. P. Hammett, "Physical Organic Chemistry," McGraw–Hill Book Co., Inc., New York, N. Y., 1940, Chapter IX.

[4] V. Gold and B. W. V. Hawes, *J. Chem. Soc.*, 2102 (1951).

[5] N. C. Deno, J. J. Jaruzelski and A. Schriesheim, *J. Org. Chem.*, **19**, 155 (1954).

[6] The name triarylmethanol has been used to conform with *C. A.* Cations of the type Ar_3C^+ are termed "triarylmethyl cations."

[7] A. Baeyer and V. Villiger, *Ber.*, **35**, 1198 (1902).

repeated recrystallizations, the yield was only 5%. The m.p. was 75–76°, reported 76–77°.[8]

4-Methoxytriphenylmethanol was prepared from ethyl anisate and phenylmagnesium bromide.[9] The yield was 23%, m.p. 56–58° (reported 58–61°[9]).

4,4′-Dinitrotriphenylchloromethane was prepared by the method of Ziegler and Mathes.[10]

4-*t*-Butyltriphenylchloromethane was prepared by the method of Marvel, *et al.*[11] A 55% yield, m.p. 133–134° (reported 133–134°[11]) was obtained based on diphenyl ketone.

4,4′-Di-*t*-butyltriphenylchloromethane was prepared by the method of Marvel, *et al.*,[12] except that benzoyl chloride was used in place of ethyl benzoate. A 33% yield, m.p. 164–166°, was obtained based on the benzoyl chloride compared with the m.p. of 162–163° and reported[12] yield of 25%.

Diarylmethanols.—The preparation of several of the diarylmethanols has been reported previously.[5]

4,4′-Dimethoxydiphenylmethanol was prepared in 92% yield by reduction of 4,4′-dimethoxydiphenyl ketone by the method reported.[13]

4,4′-Dimethyldiphenylmethanol was prepared by reduction of 4,4′-dimethyldiphenyl ketone.[14]

2,2′-Dimethyldiphenylmethanol was prepared from 2-methylphenylmagnesium bromide and ethyl formate in ether. The yield of white crystals, m.p. 116–117° (reported 119.5°[15]), was 56% after five recrystallizations from benzene–pentane.

The preparation of 4,4′-di-*t*-butyldiphenylmethanol has not been recorded previously. Ethyl formate was treated with an excess of 4-*t*-butylphenylmagnesium bromide in ether. After treating the reaction mixture with excess aqueous ammonium chloride, the ether extract was steam distilled and the residue recrystallized from 1:1 benzene–pentane. The yield of white crystals of 4,4′-di-*t*-butyldiphenylmethanol, m.p. 220.5–221.2°, was 59% after five recrystallizations.

Anal. Calcd. for $C_{21}H_{28}O$: C, 85.08; H, 9.53. Found: C, 85.00; H, 9.44.

The preparation of 3,3′-dichlorodiphenylmethanol has not been reported previously. It was prepared in a manner similar to that used in the above preparation of 4,4′-di-*t*-butyldiphenylmethanol. The 3-chlorophenylmagnesium bromide was prepared from 3-chloro-1-bromobenzene. The yield of viscous yellow oil, b.p. 170–180° (2 mm.), was 13% based on the 3-chloro-1-bromobenzene.

Anal. Calcd. for $C_{13}H_{10}OCl$: C, 61.68; H, 3.98. Found: C, 61.14; H, 3.76.

9-Methyl-9-fluorenol was prepared by the method reported.[16]

Monoarylmethanols.—The synthesis of 2,4,6-trimethylbenzyl alcohol has been reported.[17]

An optically active form of 2-phenylborneol has been reported as the product of the reaction of *d*-camphor and phenylmagnesium bromide.[18] The yield was reported to be 20–30%, m.p. 41°, and b.p. 173–174° (16 mm.).

We have now repeated this synthesis using *dl*-camphor. Phenylmagnesium bromide was prepared from 15 g. (0.625 mole) of magnesium turnings and 94 g. (0.6 mole) of bromobenzene in 400 ml. of ether. The *dl*-camphor (75 g., 0.5 mole) was dissolved in 100 ml. of ether and added to the Grignard reagent over ten min. After 12 hr., aqueous ammonium chloride was added to the reaction mixture, and the ether solution washed with water and 5% aqueous potassium hydroxide. The ether solution was steam distilled through a wide-bore condenser to remove the camphor. The residue was extracted with ether, dried and distilled. The water-white distillate, b.p. 170–172° (16 mm.), weighed 28.6 g. (25%). It completely crystallized on standing to give white crystals, m.p. 40°, sintered at 45°, resolidified at 50–56°. Recrystallization from pentane gave 26.0 g. (23%) of massive prisms, m.p. 54–58°. The compound is soluble in pentane so that the solvent must be used sparingly in washing the crystals. The highest m.p. obtained was 57.6–58.5°.

Anal. Calcd. for $C_{16}H_{22}O$: C, 83.42; H, 9.62. Found: C, 82.98; H, 9.58.

It is not known whether this compound is the *exo-* or *endo-*2-phenylborneol. However, it is doubtful if any distinction would remain after conversion to the carbonium ion.

Spectroscopic Measurements.—When each arylmethanol was dissolved in sufficiently concentrated sulfuric acid, a new spectroscopic species appeared which absorbed strongly in the visible region of the spectrum. This species was identified as the carbonium ion for reasons given in the Discussion section. The alcohol that was not converted to carbonium ion was assumed to exist as the free alcohol. An extensive discussion of the reasons for this assumption is given later. The absorption of the free alcohol was negligible at λ_{max} for the carbonium ion so that the concentration of carbonium ion was directly proportional to the optical density at λ_{max}. The optical densities were measured with a Beckman model DU spectrophotometer. The cell chamber was thermostated with Thermospacers.

It was convenient to define the quantity "Q" by eq. 10.

$$Q = \frac{\text{concn. of colored species}}{\text{concn. of colorless species}} = \frac{\text{concn. of } R^+}{\text{concn. of ROH}} \quad (10)$$

Three methods were used for measuring Q. Method A used a square 1-cm. cell of Corex glass or quartz to which was sealed a Pyrex glass bulb of about 200-ml. capacity. The bulb contained a ground glass joint and stopper. The Pyrex bulb can be sealed directly to the Corex glass, but with the quartz cell a graded Pyrex to quartz seal was necessary. A known weight of sulfuric acid of known concentration was added to the bulb. A small amount of the arylmethanol was introduced by dissolving the arylmethanol in acetic acid and adding one drop of the acetic acid solution to the bulb containing the acid.

In making a typical measurement the cell was placed in the cell holder. The bulb and fittings projected above the instrument and were covered by several thicknesses of black cloth to prevent light from entering the cell chamber. After several readings of the optical density; a measured amount of water was added; the cell, bulb and contents were brought to 25 ± 1°; and readings of the optical density were taken at the new acid concentration. This process was repeated until either the optical density fell to a negligible value or the arylmethanol commenced precipitating. In calculating the optical densities corrected to constant stoichiometric concentration of arylmethanol, the decrease in concentration of arylmethanol due to successive dilutions had to be taken into account. The details of these calculations are presented elsewhere.[19]

The principal advantage of method A is that the arylmethanol was introduced only once. It was not necessary to weigh the amount of arylmethanol added because its concentration could be obtained from the spectroscopic measurements at sulfuric acid concentrations at which it was completely ionized to carbonium ion. Method A also permitted optical densities to be measured rapidly at a large number of acid concentrations because only the weight of water added had to be measured at each new acid concentration in order to obtain the stoichiometric concentration of arylmethanol.

Method B employed a commercial cell of 50-cm. light path obtained by a single reflection through a 25-cm. tube. The method of operation was similar to method A except that a measured amount of solution had to be removed each time the measured amount of water was added. This procedure was necessary in order to maintain the proper liquid level in the cell. It complicated the calculations by introducing a double dilution effect. The details of the calculation are available elsewhere.[19]

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[8] A. Baeyer and V. Villiger, *Ber.*, **36**, 2787 (1903).

[9] A. Baeyer and V. Villiger, *ibid.*, **35**, 3027 (1902).

[10] K. Ziegler and W. Mathes, *Ann.*, **479**, 118 (1930).

[11] C. S. Marvel, M. S. Mueller, C. N. Himel and J. F. Kaplan, THIS JOURNAL, **61**, 2773 (1939).

[12] C. S. Marvel, J. F. Kaplan and C. N. Himel, *ibid.*, **63**, 1895 (1941).

[13] H. Schnackenberg and R. Scholl, *Ber.*, **36**, 655 (1903).

[14] L. C. Bateman, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 974 (1940).

[15] H. H. Hatt, *ibid.*, 1623 (1929).

[16] H. Wieland and E. Krause, *Ann.*, **443**, 129 (1925).

[17] M. S. Newman and N. C. Deno, *ibid.*, **73**, 3645 (1951).

[18] S. S. Nametkin, A. A. Kichkina and D. N. Kursanov, *J. prakt. Chem.*, **124**, 144 (1930).

[19] Ph.D. Thesis of Alan Schriesheim at the Pennsylvania State University, 1954.

The advantages of method B are that due to the longer light path a more dilute solution of the alcohol can be used. This proved to be absolutely necessary for most of the alkyl-substituted triarylmethanols in order to get values of Q independent of the stoichiometric triarylmethanol concentration. As in method A the measurements are independent of the amount of arylmethanol added.

In method C a constant amount of acetic acid solution, measured with micropipet, was added to each concentration of acid. The principal advantage of this method is that for species that decompose at an appreciable rate, this method allows an estimate of the optical density to be made by extrapolation of the data to zero time.

Table I contains values of C_0 obtained from the experimental data and eq. 8. Tables II, III and IV contain experimentally measured values of log Q and the derived values of pK_{R^+}. The pK_{R^+} values reported in these tables differ from those previously reported[5] partially because they are derived from more accurate data but principally because they are based on eq. 8, whereas the previously reported values of pK_{R^+} were based on eq. 7 of Gold and Hawes.[4] This latter equation now has been shown to have only limited validity.

TABLE I

VALUES OF C_0 FOR WATER-SULFURIC ACID

H_2SO_4, %	C_0 [a]	$-d(C_0)/d(\%\ H_2SO_4)$	J_0 [b]	$-d(J_0)/d(\%\ H_2SO_4)$	$-\log (f_{R^+}/f_{ROH_2^+})$ [c]
0.5	1.25				
1.0	0.92		0.97		0.05
2.0	.62				
3.0	.37	0.28			
4.0	.13	.22			
5.0	− .07	.17	.23		.30
6.0	− .23	.15			
7.0	− .36	.13			
8.0	− .48	.12			
10.0	− .72	.12	− .18	0.08	.54
15.0	− 1.32	.12	− .58	.07	.74
20.0	− 1.92	.12	− .95	.07	.97
25.0	− 2.55	.13	− 1.30	.07	1.25
30.0	− 3.22	.14	− 1.66	.08	1.56
35.0	− 4.00	.16	− 2.07	.09	1.93
40.0	− 4.80	.16	− 2.52	.10	2.28
45.0	− 5.65	.18	− 3.05	.12	2.60
50.0	− 6.60	.20	− 3.67	.13	2.93
52.0	− 7.01	.21	− 3.94	.14	3.07
54.0	− 7.44	.22	− 4.24	.14	3.20
56.0	− 7.90	.24	− 4.52	.15	3.38
58.0	− 8.40	.26	− 4.81	.15	3.59
60.0	− 8.92	.26	− 5.11	.16	3.81
70.0	−11.52	.26	− 6.91	.20	4.61
80.0	−14.12	.26	− 9.11	.25	5.01
90.0	−16.72	.26	−11.80	.26	4.92
92.0	−17.24	.26	−12.32	.26	4.92
93.0	−17.51	.26	−12.59	.26	
94.0	−17.78	.28	−12.86	.28	
95.0	−18.08	.33	−13.16	.33	
96.0	−18.45		−13.53		
97.0	−18.94		−14.02		
98.0	−19.64		−14.72		

[a] Values of C_0 from 93–98% sulfuric acid were calculated from the relation $C_0 - J_0 = -4.92$, which is equivalent to assuming that $f_{R^+}/f_{ROH_2^+}$ is constant throughout this region. The basis for such an assumption is presented in ref. 20. [b] Values of J_0 are computed from eq. 1 using the values for log a_{H_2O} listed in ref. 20. [c] This term is equal to $C_0 - J_0$ as shown in eq. 9. Because of the stepwise nature of evaluating both the C_0 and H_0 functions, the values in this column may have a large experimental error at the larger acid concentrations. It is difficult to estimate what the probable error might be.

TABLE II

VALUES OF LOG Q FOR 4,4′,4″-TRIMETHOXYTRIPHENYLMETHANOL

H_2SO_4, %	log Q [a]	log $Q + H_0$ or J_0 [b]	$d(\log Q)/d(\%\ H_2SO_4)$
0.3	−0.613	0.820	
.4	− .515	.818	
.5	− .423	.824	
.6	− .340	.827	
.8	− .206		
1.0	− .100		
1.5	+ .095	.895	
2.0	+ .200		
3.0	+ .450		
4.0	+ .685	1.01	0.22
5.0	+ .885	1.12	.17
6.0	+1.055	1.21	.15
7.0	+1.185	1.25	.13

$pK_{R^+} = +0.82$

[a] Above 1% acid the data are the averages of at least two runs employing at least a twofold difference in alcohol concentration. All data were measured at λ 485 mμ. [b] Up to 7% sulfuric acid, there is little difference between H_0 and J_0. The lack of constancy in this column supports the contention that eq. 7 is not generally valid.

Discussion

Determination of Q.—The experimental quantity Q was defined by eq. 10. If Q is the ratio c_{R^+}/c_{ROH}, it should be independent of the stoichiometric concentration of ROH. With some of the arylmethanols such as the methoxy substituted triphenylmethanols, the experimental values of Q were independent of concentration of alcohol over a thousand-fold range, 10^{-5} to 10^{-8} M. With others such as those with several alkyl substituents, the values of Q were independent of concentration of alcohol only at the most dilute solutions studied, and consistent results were obtained only by the use of experimental method B. However, for every arylmethanol reported in Table III, identical values of Q were obtained for at least the two runs employing the most dilute concentration of arylmethanol and in these two runs the stoichiometric concentration of alcohol differed by at least a factor of two.

These facts indicate that errors due to surface absorption were not important. Independent support of this conclusion was obtained by testing Beer's law for each alcohol at an acid concentration slightly above that at which ionization to the carbonium ion was essentially complete.

Where values of Q were not independent of alcohol concentration, a characteristic behavior was noted. In a plot of log Q *vs.* % H_2SO_4, the curve would follow that for dilute solution data part way (starting from high H_2SO_4 concn.) and then would rather sharply change slope so that values of log Q would be too low. As the stoichiometric concentration of alcohol was increased, the region of coincidence of the curves would become shorter. This behavior corresponds to a threshold in c_{ROH} above which data are erratic, and could be due to the solubility limit for ROH.

It was not possible to see visually any precipitate or cloudiness near the threshold concentration of arylmethanol, but at somewhat higher concentra-

TABLE III

VALUES OF LOG Q FOR ARYLMETHANOLS USED IN EVALUATING THE C_0 FUNCTION

H_2SO_4, %	log Q	C_0 + log Q (pK_{R^+})	d(log Q)/d(% H_2SO_4)
4,4′-Dimethoxytriphenylmethanol (λ 500 mμ; the data are an average of 4 runs in which the stoichiometric concentration of alcohol varied from 10^{-5} to 10^{-8} *M*)			
4.0	−1.30	−1.17	
6.0	−0.99	−1.22	0.14
8.0	− .73	−1.21	.12
10.0	− .51	−1.23	.11
12.0	− .29	−1.25	.11
14.0	− .05	−1.25	.12
16.0	+ .18	−1.26	.12
18.0	+ .41	−1.27	.12
20.0	+ .65	−1.27	.12
22.0	+ .89	−1.27	.12
24.0	+1.16	−1.26	.13
26.0	+1.41	−1.27	.13
		pK_{R^+} = −1.24	
4-Methoxytriphenylmethanol (λ 476 mμ; the data are an average of 4 runs in which the concn. of alcohol varied from 10^{-5} to 10^{-8} *M*)			
24	−0.95	−3.37	0.12
26	− .71	−3.39	.13
28	− .45	−3.39	.13
30	− .18	−3.40	.14
32	+ .11	−3.41	.15
34	+ .42	−3.42	.16
36	+ .73	−3.43	.16
38	+1.05	−3.43	.17
40	+1.39	−3.41	.17
		pK_{R^+} = −3.40	
2,2′,2″-Trimethyltriphenylmethanol (λ 454 mμ; the data are an average of two runs at about 10^{-7} *M*)			
26	−0.56	−3.26	0.12
28	− .33	−3.32	.12
30	− .09	−3.31	.12
32	+ .16	−3.36	.13
34	+ .40	−3.43	.13
36	+ .68	−3.48	.14
38	+ .97	−3.51	.15
		pK_{R^+} = −3.4	
4,4,′,4″-Trimethyltriphenylmethanol (λ 452 mμ; the data are an average of 3 runs at 10^{-7} to 10^{-8} *M*)			
24	−1.16	−3.58	0.14
26	−0.88	−3.56	.14
28	− .59	−3.53	.15
30	− .30	−3.52	.15
32	− .01	−3.54	.15
34	+ .28	−3.56	.15
36	+ .56	−3.60	.15
38	+ .85	−3.63	.15
		pK_{R^+} = −3.56	
4-Methyltriphenylmethanol (λ 450 mμ; the data are an average of runs at 10^{-5} to 10^{-8} *M* using exptl. methods A, B and C)			
38	−0.79	−5.27	0.16
40	− .47	−5.27	.17
42	− .12	−5.24	.18
44	+ .25	−5.22	.18
46	+ .61	−5.22	.19
48	+1.00	−5.21	.20
		pK_{R^+} = −5.24	
4,4′-Dimethoxydiphenylmethanol (λ 507 mμ; a slight instability at 48–52% sulfuric acid necessitated the use of exptl. method C)			
38	−1.28	−5.76	0.16
40	−0.91	−5.71	.16
42	− .60	−5.72	.16
44	− .25	−5.72	.17
46	+ .10	−5.73	.18
48	+ .48	−5.73	.20
50	+ .94	−5.66	.21
52	+1.42	−5.59	.22
		pK_{R^+} = −5.71	
3,3′,3″-Trimethyltriphenylmethanol (λ 414 mμ; the data are an average of 5 runs at 10^{-5} to 10^{-8} *M*)			
44	−0.97	−6.44	0.19
46	− .55	−6.38	.19
48	− .12	−6.33	.20
50	+ .30	−6.30	.20
52	+ .71	−6.30	.20
54	+1.05	−6.39	
		pK_{R^+} = −6.35	
4,4′,4″-Triisopropyltriphenylmethanol (λ 456 mμ; the data are an average of runs at 10^{-5} to 10^{-6} *M* using exptl. methods A and C)			
44	−1.12	−6.59	0.18
46	−0.75	−6.58	.19
48	− .35	−6.56	.20
50	+ .10	−6.50	.20
52	+ .52	−6.49	.21
54	+ .91	−6.53	.22
		pK_{R^+} = −6.54	
Triphenylmethanol (λ 431 mμ; the data are an average of 4 runs at 10^{-5} to 10^{-8} *M*)			
46	−0.81	−6.64	0.20
48	− .41	−6.62	.20
50	− .01	−6.61	.20
52	+ .38	−6.63	.20
54	+ .78	−6.66	.20
		pK_{R^+} = −6.63	
4,4′,4″-Trichlorotriphenylmethanol (λ 465 mμ; the data are an average of 3 runs at 10^{-7} to 10^{-8} *M*)			
52	−0.72	−7.73	0.22
54	− .28	−7.72	.22
56	+ .19	−7.71	.23
58	+ .63	−7.77	.24
59	+ .90	−7.76	.26
		pK_{R^+} = −7.74	
4-Nitrotriphenylmethanol (λ 454 mμ; the data are an average of 2 runs at 10^{-5} *M*)			
57	−0.99	−9.14	0.23
58	− .76	−9.16	.25
60	− .24	−9.16	.26
62	+ .29	−9.15	.26
64	+ .81	−9.15	.26
		pK_{R^+} = −9.15	

TABLE III (*Continued*)

H_2SO_4, %	log Q	$C_0 + \log Q$ (pK_{R^+})	d(log Q)/d(% H_2SO_4)
2-Phenylbornecol (λ 415 mμ; this compound was unstable, the half-life being of the order of 5 to 10 min. The rate of formation of the carbonium ion from the alcohol was also appreciably slow, the half-life being about 1 to 3 min. Appropriate corrections were made for these effects)			
58	−1.27	−9.67	0.25
60	−0.78	−9.70	.25
62	− .30	−9.74	.25
64	+ .20	−9.76	.25
66	+ .69	−9.79	.25
68	+1.19	−9.81	.25
		$pK_{R^+} = -9.75$	
3,3′,3″-Trichlorotriphenylmethanol (λ 412 mμ; the data are an average of 3 runs at about 10^{-5} *M*)			
64	−1.05	−11.01	0.26
66	−0.54	−11.02	.26
68	− .03	−11.03	.26
70	+ .48	−11.04	.26
72	+ .98	−11.06	.25
		$pK_{R^+} = -11.03$	
4,4′-Dinitrotriphenylchloromethane (λ 449 mμ; the data are an average of 3 runs at about 10^{-5} *M*)			
70	−1.41	−12.93	0.27
72	−0.86	−12.90	.27
74	− .34	−12.90	.27
76	+ .21	−12.87	.27
78	+ .74	−12.86	.26
		$pK_{R^+} = -12.90$	
4,4′,4″-Trinitrotriphenylmethanol (λ 450 mμ; the data are an average of 4 runs at 10^{-5} to 10^{-6} *M*)			
84	−1.12	−16.28	0.26
86	−0.60	−16.28	.26
88	− .07	−16.27	.26
90	+ .46	−16.26	.26
92	+ .99	−16.25	.26
		$pK_{R^+} = -16.27$	
9-Methyl-9-fluorenol (λ 488 mμ; exptl. method C was used)			
88	−0.39	−16.59	0.26
90	+ .13	−16.59	.26
92	+ .64	−16.60	.26
93	+ .89	−16.61	.34
94	+1.32	−16.45	
		$pK_{R^+} = -16.60$	
2,4,6-Trimethylbenzyl alcohol (λ 470 mμ; exptl. method C was used)			
89	−0.93	−17.39	0.26
90	− .67	−17.39	.26
91	− .42	−17.40	.26
92	− .15	−17.39	.29
93	+ .16	−17.34	.31
94	+ .46	−17.31	.32
95	+ .78	−17.29	.34
96	+1.12	−17.32	
		$pK_{R^+} = -17.38$	

tions, about fivefold greater, visible cloudiness was detectable. Triphenylmethanol was studied more extensively than the others, and it was found that above this threshold concentration Beer's law was no longer obeyed.

In several cases the triarylchloromethane was used in place of the triarylmethanol. It was thought that the small amount of chloride ion so introduced would have no effect. This factor was tested in the case of triphenylmethanol. At 53% sulfuric acid, where triphenylmethanol is about 80% ionized, addition of 1% by weight of potassium chloride did not have any effect on the ratio c_{R^+}/c_{ROH}.

The specific absorption spectra of the carbonium ions generally do not change appreciably with changing sulfuric acid concentration. This was tested in two ways. With every alcohol measured by experimental method A or B, an integral part of each run was to measure the optical density at λ_{max} for a range of 10% sulfuric acid above that at which the alcohol was effectively completely ionized to carbonium ion. In all cases no change in the extinction coefficient was observed. A second test was to recheck the wave length of λ_{max} at an acid concentration at which the alcohol was converted only partly to carbonium ion. When this was done, no appreciable shifts were observed. With several of the alcohols, λ_{max} in 40-60% acid was the same as that in 97% sulfuric acid.

Nearly all the work was conducted at 25-27°. This degree of temperature control is necessary since in work to be reported it has been shown that K_{R^+} has an appreciable temperature dependence.

We believe that the largest errors in Q arise from exceeding the solubility limit of certain alcohols.

The C_0 Acidity Function.—There are several ways to test the generality of an acidity function. Hammett[3] used eq. 11

$$\log (c_{BH^+}/c_B) - \log (c_{B'H^+}/c_{B'}) = \text{constant} \quad (11)$$

which should obtain for any pair of indicator bases, in any region of acid concentration, if the acidity function is independent of the structure of the indicator base. The use of eq. 11 requires regions of overlapping data.

We have favored the use of eq. 12, obtained by differentiating eq. 8 in respect to % H_2SO_4 after substituting Q for c_{R^+}/c_{ROH}.

$$\frac{-d(C_0)}{d(\%\ H_2SO_4)} = \frac{d(\log Q)}{d(\%\ H_2SO_4)} \qquad (12)$$

A particular advantage of eq. 12 is that the generality of the acidity function can be tested with a minumum amount of overlapping data. For example, the data for 4,4′-dimethoxytriphenylmethanol and 4-methoxytriphenylmethanol overlap only from 24-26% sulfuric acid (Table III). However, the value of d(log Q)/d(% H_2SO_4) is nearly constant, 0.12-0.13, for 4,4′-dimethoxytriphenylmethanol from 14-26% acid. The value for 4-methoxytriphenylmethanol is 0.12–0.13 from 24-28% sulfuric acid and increases to only 0.16 at 36% acid. Thus, despite the small amount of overlap region, it can be assumed with confidence that d(log Q)/d(% H_2SO_4) has the same value for both indicators in the region of 25% sulfuric acid.

The values of d(log Q)/d(% H_2SO_4) in Table III are reasonably independent of the alcohol at each concentration. The less accurate data in Table IV support this conclusion to a lesser degree. It is not possible to conclude at this time whether the discrepancies that exist among the alcohols in Table IV are real or due to errors in the experimental data.

TABLE IV

VALUES OF LOG Q FOR ARYLMETHANOLS THAT WERE NOT USED IN EVALUATING THE C_0 FUNCTION[a]

H_2SO_4, %	log Q	C_0 + log Q	d(log Q)/ d(% H_2SO_4)
4-*t*-Butyltriphenylchloromethane (λ 458 mμ)			
42	−0.92	−6.04	0.16
44	− .60	−6.07	.16
46	− .27	−6.10	.17
48	+ .08	−6.13	.18
50	+ .43	−6.17	.17
52	+ .73	−6.28	.17
$pK_{R^+} = -6.1$			
4,4′-Di-*t*-butyltriphenylchloromethane (λ 465 mμ)			
46	−0.63	−6.46	0.16
48	− .32	−6.53	.16
50	+ .00	−6.60	.16
52	+ .30	−6.71	.16
54	+ .62	−6.82	.16
56	+ .93	−6.97	.16
$pK_{R^+} = -6.6$			
4,4′,4″-Tri-*t*-butyltriphenylmethanol (λ 458 mμ; the data are taken from a single run at 10^{-8} M; runs at 10^{-6} M agree only at log Q values greater than 0.5)			
48	−0.19	−6.40	0.16
50	+ .14	−6.46	.17
52	+ .48	−6.53	.17
54	+ .83	−6.61	.18
56	+1.18	−6.72	.18
$pK_{R^+} = -6.5$			
Dimesitylmethanol (λ 528 mμ; the data are an average of 5 runs at 10^{-5} to 10^{-8} M)			
46	−0.66	−6.49	0.17
48	− .32	−6.54	.17
50	+ .03	−6.57	.18
52	+ .38	−6.63	.18
54	+ .75	−6.69	.18
56	+1.13	−6.77	.19
$pK_{R^+} = -6.6$			
4,4′-Dimethyldiphenylmethanol[b] (λ 472 mμ)			
64	−0.36	−10.32	0.23
66	+ .11	−10.37	.23
68	+ .58	−10.42	.23
69	+ .81	−10.45	.23
$pK_{R^+} = -10.4$			
2,2′-Dimethyldiphenylmethanol[b] (λ 470 mμ)			
70	−0.87	−12.39	0.25
72	− .37	−12.41	.25
74	+ .12	−12.44	.25
76	+ .62	−12.46	.25
78	+1.12	−12.48	.25
$pK_{R^+} = -12.45$			
4,4′-Di-*t*-butyldiphenylmethanol[b] (λ 480 mμ)			
75	−0.54	−13.38	0.23
76	− .21	−13.27	.28
78	+ .45	−13.12	.32
79	+ .77	−13.07	.32
$pK_{R^+} = -13.2$			
Diphenylmethanol[b] (λ 442 mμ)			
74	−0.88	−13.44	0.29
76	− .30	−13.38	.29
78	+ .27	−13.33	.29
80	+ .86	−13.26	.29
$pK_{R^+} = -13.3$			
4,4′-Dichlorodiphenylmethanol[b] (λ 485 mμ)			
77	−0.65	−13.99	0.27
78	− .38	−13.98	.27
80	+ .15	−13.97	.27
82	+ .71	−13.93	.27
83	+ .97	−13.93	.27
$pK_{R^+} = -13.96$			
9-Fluorenol (λ 655 mμ; the log ϵ for this carbonium ion was 3.08, which is much less than the log ϵ values for the other carbonium ions studied. The λ_{max} at 483 mμ had log ϵ 2.856 so that this wave length offered even more difficulties. At the increased concentrations of 9-fluorenol that were necessary, about 10^{-3} to 10^{-4} M, much difficulty was encountered with precipitation which was visibly evident)			
80	+0.19	−13.93	0.21
81	+ .40	−13.98	.22
82	+ .62	−14.02	.22
$pK_{R^+} = -14.0$			

[a] The data in this table are generally less accurate than those in Tables II and III. For the first four compounds in the table, the data were inconsistent in comparable runs. It is suspected that insolubility of the alcohol may be the cause. The data for the second five compounds are less accurate because of the fact that these alcohols were unstable in the region of acid in which they were measured.

[b] The carbonium ions of these diarylmethanols became increasingly unstable at sulfuric acid concentrations below 75–85%.

The fit of the C_0 function with the data for any particular alcohol can best be observed by noting the closeness of the equality between $-d(C_0)/d(\% \, H_2SO_4)$, listed in Table I, and values of d(log Q)/d(% H_2SO_4), which appear in Tables II, III and IV.

The failure of the J_0 acidity function to correlate the data can be observed best by noting the inequality of $-d(J_0)/d(\% H_2SO_4)$, listed in Table I, and values of d(log Q)/d(% H_2SO_4) for any particular alcohol and sulfuric acid concentration.

Above 82% sulfuric acid, C_0 and J_0 have a constant difference. It is in this region that the activity coefficients of ions are constant,[20] and thus in this region the assumption of Gold and Hawes that $f_{R^+}/f_{ROH_2^+} = 1$ is valid providing dilute solution in sulfuric acid is chosen as the standard state.

Although the measurements of C_0 have not been extended beyond 92% sulfuric acid, it is probable the C_0 can be estimated from 92–99% acid from the relation: $C_0 - J_0 = -4.92$. Values of C_0 estimated on this basis appear in Table I. Since a_{H_2O} has not been measured above 97% sulfuric acid, the values of J_0 from 97–99% acid must be estimated.[20]

Identification of Spectroscopic Species.—In the treatment of the data, the colored species were considered to be the carbonium ions. The only direct evidence is the fact that the spectra of several di- and triarylcarbonium ions were measured in

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(20) N. C. Deno and R. W. Taft, Jr., THIS JOURNAL, **76**, 244 (1954).

100% sulfuric acid where the alcohols were known to be ionized to the carbonium ions from *i*-factor data.[21] As the sulfuric acid concentration was decreased with each of these carbonium ions, the characteristic absorption spectrum remained unchanged and undiminished in intensity until a region was reached where the spectrum smoothly graded into that of the alcohol without the appearance of any new spectroscopic species.

It was assumed also, in the treatment of the data, that any arylmethanol that was not converted to the carbonium ion, remained as the free unprotonated alcohol. The absence of ether or other species formed from two or more molecules of arylmethanol was indicated by the fact that the values of log Q were independent of stoichiometric alcohol concentrations.

We do not have any decisive evidence that the amount of protonated arylmethanol was negligible in every case. However, the following arguments support this contention. If only the carbonium ion and *free* arylmethanol are present, eq. 13 can be derived. In the region 82–99% sulfuric acid, activity coefficients of polar species are constant[20] so that eq. 13 reduces to eq. 14. Differentiation in respect to % H_2SO_4 gives eq. 15. The data for 4,4′,4″-trinitrotriphenylmethanol in Table V show that eq. 15 is followed with good precision.

TABLE V

DEMONSTRATION OF THE VALIDITY OF EQ. 15

H_2SO_4, %	d(log Q)/ d(% H_2SO_4)	$-$d(H_0 + log a_{H_2O})/ d(% H_2SO_4)	$-$d(log a_{H_2O})/ d(% H_2SO_4)
4,4′,4″-Trinitrotriphenylmethanol			
84	0.26	0.26	0.13
86	.26	.26	.13
88	.26	.26	.13
90	.26	.26	.14
92	.26	.26	.15
4,4′-Dinitrotriphenylmethanol			
70	0.27	0.20	0.07
72	.26	.21	.08
74	.26	.22	.09
76	.27	.24	.09
78	.27	.25	.10

In contrast, if only the carbonium ion and *protonated* triarylmethanol were present, Q would actually be the ratio of $c_{R^+}/c_{ROH_2^-}$, and eq. 16 can be derived. In a manner similar to above, eq. 17 was derived from eq. 16. The data in Table V demonstrate that eq. 17 is not valid and so it can be concluded that for the trinitrotriphenylmethanol, $Q = c_{R^+}/c_{ROH}$.

A choice between eqs. 15 and 17 also can be made from the data for 4,4′-dinitrotriphenylmethanol. Although activity coefficients of polar species are not exactly constant in 70–78% sulfuric acid, they approach constancy so that eq. 15 or 17 will be approximately correct if the basis of their derivation is valid. The data again follow eq. 15 and reject eq. 17 indicating that free alcohol and not protonated alcohol was present.

$$\log (c_{R^+}/c_{ROH}) = pK_{R^+} - H_0 - \log a_{H_2O} - \log (f_{R^+}/f_{ROH_2^+}) \tag{13}$$

$$\log (c_{R^+}/c_{ROH}) = -H_0 - \log a_{H_2O} + \text{constant} \tag{14}$$

$$\frac{d(\log c_{R^+}/c_{ROH})}{d(\%\ H_2SO_4)} = \frac{-d(H_0 + \log a_{H_2O})}{d(\%\ H_2SO_4)} \tag{15}$$

$$\log (c_{R^+}/c_{ROH_2^+}) = \text{constant} - \log a_{H_2O} - \log (f_{R^+}/f_{ROH_2^+}) \tag{16}$$

$$\frac{d(\log c_{R^+}/c_{ROH_2^+})}{d(\%\ H_2SO_4)} = \frac{-d(\log a_{H_2O})}{d(\%\ H_2SO_4)} \tag{17}$$

Since the dinitro- and trinitrotriphenylmethanols are not protonated appreciably in 70–78% and 82–92% sulfuric acids, respectively, it would be surprising if alcohols such as triphenylmethanol were protonated in 50% acid. A more convincing argument is the fact that the values of d(log Q)/d(% H_2SO_4) were nearly independent of alcohol at any particular sulfuric acid concentration. If no protonated alcohols were present, the above result will obtain if f_{R^-}/f_{ROH} is independent of R since all the terms in the alternate definition of C_0 (second part of eq. 8) then become independent of R. This is analogous to the discovery by Hammett that ratios of the type f_{BH^+}/f_B were independent of B in polar media. In contrast, if protonated alcohol is partially or completely present, no such simple justification for the above result can be derived.

In the case of monoarylmethanols and aliphatic alcohols, ROH_2^+ will be in greater proportion and may become a serious factor.

Application of C_0 to Kinetics.—For any reaction in which a positively charged transition state is formed from neutral reactants by loss of hydroxide ion (OH^-), the plot of the log of the rate constant against $-C_0$ will be linear with unit slope, providing that $f_{R_*^+}/f_{ROH}$ (ROH is the reactant and R_*^+ is the transition state) has the same value as f_{R^+}/f_{ROH} for the arylmethanols used to evaluate the C_0 function. The derivation of this principle is given in detail elsewhere[19] and is exactly analogous to a similar relation derived by Hammett[3] for the H_0 function.

Three reactions have been found to follow this principle. The rate of nitration of benzene[4] and the rate of decarbonylation of triphenylacetic acid[20] have been discussed previously in terms of the J_0 function. Both of these cases were studied within the 82–99% sulfuric acid region so that there is no distinction between C_0 and J_0. In addition, they do not really test whether f_{R^+}/f_{ROH} was independent of R since the activities of all the species probably were constant in this region.[20]

The third reaction is the oxidation of formic acid by nitrous acid in aqueous sulfuric acid.[22] Although there are only three experimental points that can be used in a plot of C_0 *vs.* log k, this is a particularly good test for the C_0 function. First, the authors propose on other grounds that there is a reversible equilibrium to form NO^+ from HNO_2 and that the NO^+ reacts with formic acid in the rate-determining step. Secondly, the data are in the region of acid concentration (20–32% H_2SO_4) in which d(C_0)/d(% H_2SO_4) and d(J_0)/d(% H_2SO_4) have much different values (Table I).

The slope of a plot of $-C_0$ *vs.* log k is between 0.93 and 1.12 depending on the degree of correction

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[21] M. S. Newman and N. C. Deno, THIS JOURNAL, **73**, 3644 (1951).

[22] J. V. L. Longstaff and K. Singer, *J. Chem. Soc.*, 2604 (1954).

for the non-acid-catalyzed rate. The slope is in good agreement with the ideal value of unity. This correlation implies that the amount of protonated nitrous acid is small. In contrast, a plot of $-J_0$ *vs.* log *k* gives a slope between 1.86 and 2.28, which is in disagreement with the ideal value of unity.

Absorption Spectra.—As an incidental outgrowth of this work, a number of absorption spectra of arylmethyl cations were measured. These are presented in detail elsewhere.[19,23]

The two most remarkable facts about the spectra are the close similarity between the spectra of similarly substituted di- and triarylmethyl cations (summarized in Table VI); and the close similarity between the absorption spectrum of the triphenylmethyl cation (Table VI) and that of the 2-phenylbornyl cation, λ_{max} 415 mμ and log *e* 4.68, although the latter ion contains but a single phenyl ring.

TABLE VI

COMPARISON OF SPECTRA FOR DIARYL- AND TRIARYLMETHYL CATIONS IN WHICH ALL RINGS ARE IDENTICALLY SUBSTITUTED

Substituent	λ_{max}, mμ		log *e*	
	Ar_3C^+	Ar_2CH^+	Ar_3C^+	Ar_2CH^+
4-Dimethylamino	590	610	4.95	
4-Methoxy	483	507	5.02[a]	5.04
2-Methyl	454	470	4.46	4.30
4-Methyl	452	472	5.03	4.87
4-*t*-Butyl	458	480	4.92	4.81
Unsubstituted	404	440	4.60	4.64
	431		4.60	
4-Chloro	465	485	5.01	5.14
3-Chloro	412	434	4.47	4.17

[a] H. Lund (THIS JOURNAL, **49**, 1346 (1927)) reported a lower value but, as previously suspected,[5] Lund's measurements were made at acid concentrations at which the triarylmethanol was not completely converted to the carbonium ion.

A few additional values of λ_{max} and log *e* which have not been reported previously appear in Table VII.

TABLE VII

VALUES OF LOG *e* AND λ_{max} FOR SEVERAL TRIARYLMETHYL CATIONS

Substituted triphenylmethyl cation	λmax	log e
4,4′-Dimethoxy	500	5.47
4-Methoxy	476	4.75
4-Methyl	450	4.66
4,4′,4″-Triisopropyl	456	4.88
4-*t*-Butyl	458	4.67
4,4′-Di-*t*-butyl	458	

Acknowledgment.—We wish to give recognition to the work of two groups of investigators whose investigations have not been discussed directly. Westheimer and Kharasch[24] first used the concept of acidity functions of the type of C_0 in their studies on the mechanism of aromatic nitration. Williams and co-workers[25] defined an acidity function, H_R, similar to C_0 except that no distinction was made between indicator charge types (R^+,R^{++},R^{+++}, etc.). Within the limited region of their investigations, the data indicate that it may not be necessary to distinguish between charge types. However, it is doubtful whether this simplification will hold throughout the water–sulfuric acid system.

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(23) Ph.D. Thesis of J. J. Jaruzelski at the Pennsylvania State University, 1954.

(24) F. Westheimer and M. S. Kharasch, THIS JOURNAL, **68**, 1871 (1946).

(25) A. M. Lowen, M. A. Murray and G. Williams, *J. Chem. Soc.*, 3318 (1950).

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[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS, PENNSYLVANIA STATE UNIVERSITY]

Carbonium Ions. II. Linear Free Energy Relationships in Arylcarbonium Ion Equilibria[1]

BY N. C. DENO AND ALAN SCHRIESHEIM

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The establishment of the C_0 acidity function has provided a basis for determining $pK_R{}^+$ values for the equilibrium $R^+ + H_2O = ROH + H^+$ which are all based on the same standard state. The Hammett σ–ρ treatment is applied to the data and its successes and failures are interpreted. The often suspected parallelism between rates of S_N1 reactions and stability of carbonium ions has been demonstrated quantitatively for a series of diarylmethyl cations.

For the equilibria between alcohols and carbonium ions, eq. 1, an acidity function, C_0, has been evaluated in the water–sulfuric acid system which relates the concentration of acid to the position of equilibrium through eq. 2.[2] By virtue of the definition of C_0, values of pK_{R^+} calculated from eq. 2

$$R^+ + H_2O = ROH + H^+ \quad (1)$$

$$C_0 = pK_{R^+} - \log (c_{R^+}/c_{ROH}) \quad (2)$$

are all based on dilute aqueous solution as the standard state. The subject of this paper will be to compare these pK_{R^+} values with the polar parameters, σ-constants, for the substituent groups to see whether linear free energy relationships exist.

Experimental

Determination of pK_{R^+} Values.—Most of the values of pK_{R^+} have been determined previously.[2] However, the monosubstituted diphenylmethanols and 3,3′-dichlorodiphenylmethanol were so unstable that only a visual estimate of pK_{R^+} could be obtained. This was done by adding a drop of acetic acid solution of the diarylmethanol to a series of sulfuric acids of varying acid concentration. The concentrations were chosen so that the diarylmethanol would

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(1) Grateful acknowledgment is made of the partial support of this research by a grant from the National Science Foundation (G468). This report was taken from the Doctoral Dissertation of A. Schriesheim at the Pennsylvania State University, 1954.

(2) N. Deno, J. Jaruzelski and A. Schriesheim, THIS JOURNAL, **77**, 3044 (1955).