465. *The Ionisation of Triarylcarbinols in Strong Acids and the Definition of a New Acidity Function.*

By V. Gold and B. W. V. Hawes.

Expressions have been derived and experimentally tested for the dependence of the degree of ionisation of a triarylcarbinol according to

$$R{\cdot}OH + 2H_2SO_4 \rightleftharpoons R^+ + H_3O^+ + 2HSO_4^-$$

or

$$R{\cdot}OH + H_2SO_4 \rightleftharpoons R^+ + H_2O + HSO_4^-$$

upon the composition of the medium, in the case of strong aqueous acids and acid solvent mixtures of low water content. An acidity function (J_0) has been defined (and tabulated for H_2SO_4–H_2O mixtures) which plays for the triphenylcarbinol type of ionisation a rôle analogous to that of Hammett's H_0 function for the ionisation of electrically neutral Brønsted bases. Some applications of this acidity function to compounds other than triarylcarbinols are briefly considered.

Many organic substances behave as simple monoacid bases when dissolved in strong acids (Hammett, "Physical Organic Chemistry," New York, 1940, Chap. IX). In concentrated sulphuric acid as solvent they give rise to two particles, as can be shown by cryoscopy (see Gillespie, Hughes, and Ingold, *J.*, 1950, 2473, where a literature summary is also given). The dependence of the degree of ionisation on the composition of the medium may be satisfactorily expressed in terms of Hammett's acidity function (Hammett and Deyrup, *J. Amer. Chem. Soc.*, 1932, **54**, 2721).

Triphenylcarbinol typifies a different kind of reversible ionisation in strong acid. The freezing-point depression in sulphuric acid is in this case four times that produced by an ideal inert solute (Hantzsch, *Z. physikal. Chem.*, 1907, **61**, 257; Hammett and Deyrup, *J. Amer. Chem. Soc.*, 1933, **55**, 1900) and the light absorption of the solution is identical with that of triphenylmethyl chloride in sulphur dioxide and other non-aqueous ionising solvents (Hantzsch, *Ber.*, 1921, **54**, 2573). The ionisation has plausibly been represented in the form

$$Ph_3C{\cdot}OH + 2H_2SO_4 \rightleftharpoons Ph_3C^+ + H_3O^+ + 2HSO_4^-$$

Baeyer suggested as early as 1905 (*Ber.*, **38**, 569) that in this case a triphenylcarbonium hydrogen sulphate, with an abnormal "carbonium valency" between the two groups, is formed. The dependence of the degree of ionisation on the composition of the medium would be expected to be different from that for the monoacid bases, and this has been shown to be so for certain substituted derivatives of triphenylcarbinol by Westheimer and Kharasch (*J. Amer. Chem. Soc.*, 1946, **68**, 1871) and by Murray and Williams (*J.*, 1950, 3322).

The present study was undertaken to examine the nature of this dependence more precisely. The experimental data considered in this connection are (i) published colorimetric indicator measurements on trinitrotriphenylcarbinol in sulphuric acid–water mixtures, carried out by Murray and Williams (*loc. cit.*) in a simultaneous investigation, and (ii) new spectrophotometric measurements of the degree of ionisation of triphenylcarbinol and of a simple monoacid base (4-chloro-2-nitroaniline) over certain ranges of composition in the ternary solvent system sulphuric acid–acetic acid–water.

The interest in this type of ionisation is not exhausted by the consideration of the typical example triphenylcarbinol. We may recall that an ionisation

$$\mathrm{XOH} + 2\mathrm{H_2SO_4} \rightleftharpoons \mathrm{X^+} + \mathrm{H_3O^+} + 2\mathrm{HSO_4^-}$$

is required to produce species such as NO_2^+, Br^+, Cl^+, HSO_3^+, (acyl)$^+$, OH^+—all of which have recently received attention as probable reaction intermediates—from nitric acid (reviewed by Gillespie and Millen, *Quart. Reviews*, 1948, **2**, 277), hypobromous acid (Derbyshire and Waters, *J.*, 1950, 564), hypochlorous acid (de la Mare, Hughes, and Vernon, *Research*, 1950, **3**, 192, 242; Derbyshire and Waters, *J.*, 1951, 73), sulphuric acid (Stubbs, Williams, and Hinshelwood, *J.*, 1948, 1065; Brand, *J.*, 1950, 1004), carboxylic acids (Treffers and Hammett, *J. Amer. Chem. Soc.*, 1937, **59**, 1708; Newman *et al.*, *ibid.*, 1941, **63**, 2431; 1942, **64**, 2324; 1945, **67**, 704; Kuhn and Corwin, *ibid.*, 1948, **70**, 3370; Kuhn, *ibid.*, 1949, **71**, 1575), and hydrogen peroxide (Derbyshire and Waters, *Nature*, 1950, **165**, 401), respectively.

It is noteworthy that the type of ionisation considered for triphenylcarbinol is not basic behaviour in the sense of the Brønsted–Lowry definition. One may fit these examples into the Brønsted–Lowry scheme by assuming that the course of the ionisation is proton transfer to the carbinol and subsequent dehydration of the conjugate acid, or by assuming other, less plausible, mechanisms. We have found no evidence for the existence of the undehydrated conjugate acid $[\mathrm{Ph_3C{\cdot}OH_2}]^+$, although there may be cases where the analogous compound may exist (cf. the results of Treffers and Hammett, *loc. cit.*, for 2 : 6-dimethylbenzoic acid and 3 : 5-dibromo-2 : 4 : 6-trimethylbenzoic acid; $\mathrm{Br\overset{+}{O}H_2}$, Derbyshire and Waters, *J.*, 1950, 564; $\mathrm{NO_2{\cdot}\overset{+}{O}H_2}$, Halberstadt, Hughes, and Ingold, *J.*, 1950, 2441). It is, however, unsatisfactory that the behaviour of triphenylcarbinol, as expressed in a thermodynamic equation, may only be described as basic if a hypothetical reaction mechanism is assumed for it. In the absence of a clearer term * we would propose the name " secondary base " for triphenylcarbinol and other compounds ionising in this way, the conjugate acid being the water molecule formed. It is interesting that this extended definition is necessary to reconcile basicity in hydroxyl-containing bases (the *real* bases according to older views) with the Brønsted–Lowry definition, whereas the concept of secondary acids is necessary to fit the hydrogen acids into Lewis's scheme of acids and bases (cf. Bell, *Quart. Reviews*, 1947, **1**, 113).

EXPERIMENTAL.

Materials.—Acetic acid was purified and dried by Orton and Bradfield's method (*J.*, 1927, 983). The purity was checked by freezing-point determinations and only samples having f. p. > 16·40° (*i.e.*, containing less than 0·1% of water) were used. The purified acid was transparent to wave-lengths greater than 2400 A., although no exact measurements were attempted with it below λ 2500 A.

Sulphuric acid (100%) was prepared by dilution of sulphur dioxide-free oleum with 98% AnalaR sulphuric acid to the cessation of fuming at a low temperature (Brand, *J.*, 1946, 585). The composition was checked by freezing-point determinations, only acids of f. p. within 0·08° of the maximum corresponding to the composition H_2SO_4 being used. The oleum for this preparation was obtained by addition of potassium persulphate to a dilute commercial oleum and distillation of sulphur trioxide from it into 98% AnalaR sulphuric acid in an all-Pyrex apparatus (cf. Brand, *J.*, 1950, 997). Sulphuric acid prepared in this way was transparent to light above λ 2300 A. and did not show appreciable absorption due to sulphur dioxide (cf. Gold and Tye, *J.*, 1950, 2932).

Solvent mixtures were made up by weight, and compositions are stated as weight percentages of the solution. Attention was paid to avoiding the complications of the ageing effect of mixtures of acetic acid and sulphuric acid reported by Tolbert and Branch (*J. Amer. Chem. Soc.*, 1947, **69**, 1083).

Triphenylcarbinol and 4-chloro-2-nitroaniline were purified by repeated crystallisations from benzene

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* The term pseudo-base advocated by Hammett (*Chem. Reviews*, 1937, **13**, 63) is also in use with a different meaning and is therefore undesirable.

and water, respectively, and the progress of the purification checked by absorption-spectrum measurements (Figs. 1, 2, and 5).

Measurements.—Extinction coefficients in the near ultra-violet and visible spectral regions were measured by means of a Hilger " Uvispek " Photoelectric Spectrophotometer, fused quartz cells of the design shown in Fig. 3 being used. The matching of the cells was checked by comparison of the internal lengths and of their transmission over the whole spectral region investigated. Minor mechanical alterations were made to the instrument in order to adapt it for use with these cells. No accurate temperature control was maintained during the measurements, the results given referring for the most part to a temperature of 20° ±3°. Extinction coefficients (ε) are defined by the usual relation $\log_{10} I_0/I = \varepsilon cl$ (l = thickness of absorbing layer in cm., c = stoicheiometric concentration of solute, in moles/l.). None of the spectra of the solutions examined changed measurably with time.

FIG. 1.

Absorption spectra of 4-*chloro*-2-*nitroaniline*: (A) *in acetic acid*, (B) *in sulphuric acid* (100%).

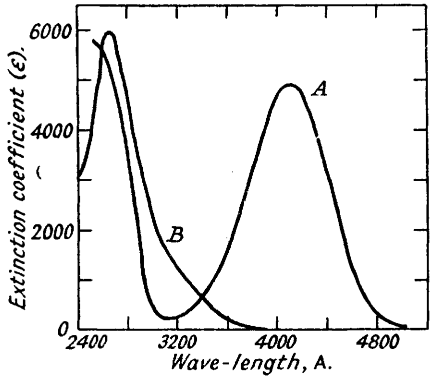


FIG. 2.

Absorption spectrum of triphenylcarbinol in acetic acid.

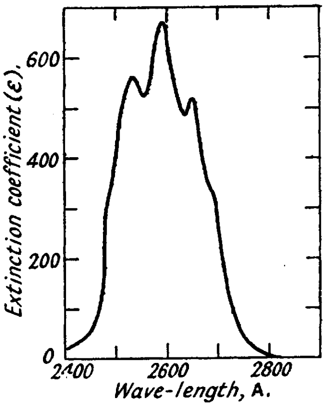


FIG. 3.

Spectrophotometer absorption cell.

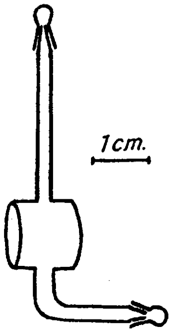
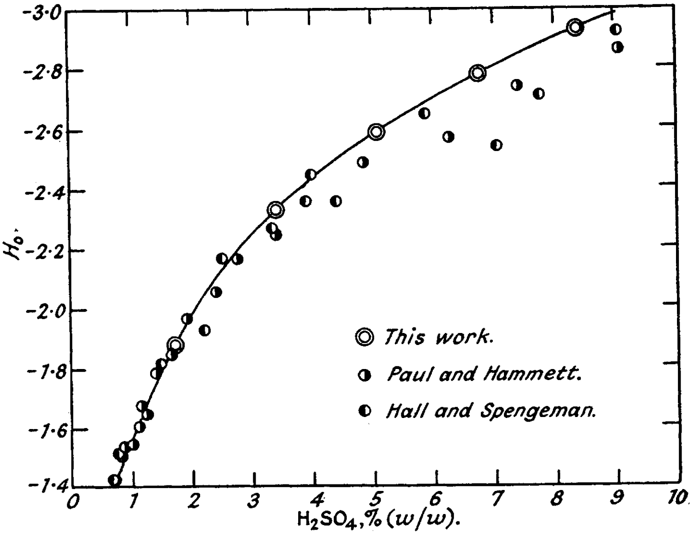


FIG. 4.

The acidity function (H_0) *of solutions of sulphuric acid in acetic acid.*



Colorimetric measurements were carried out with a Hilger Visible " Spekker " Absorptiometer in conjunction with filters to limit the transmitted wave-band of light from a filament lamp. Such measurements were used only in cases where it was desired to check the absence of a change in the absorption spectrum over certain regions of solvent composition or to confirm the stability of certain solutions on storage.

Evaluation of Ionisation Ratios.—Ionisation ratios used in the calculation of acidity functions and of ionisation constants were obtained from the spectrophotometric measurements, the relationship $[\text{Ion}]/[\text{Base}] = (\varepsilon - \varepsilon_{\text{Base}})/(\varepsilon_{\text{Ion}} - \varepsilon)$ being used. The reference spectra of the ion and base were obtained from solutions in 98% or 100% sulphuric acid and acetic acid respectively (cf. Flexser, Hammett, and Dingwall, *J. Amer. Chem. Soc.*, 1935, **57**, 2103). The concentration of 4-chloro-2-nitroaniline was usually in the range 10^{-2}—10^{-3}M., that of triphenylcarbinol ~10^{-5}M. It has been reported by these workers that solvent changes not only alter the ionisation ratio but also affect the wave-length of the absorption bands, and various procedures have been adopted to minimise the effect of this complication (see also Brand, *J.*, 1950, 997). Our own procedure, which was simplified by the choice of indicators the two forms of which absorbed strongly in different spectral regions only, is based on the folllowing considerations :

Let ε_λ stand for the extinction coefficient of the indicator in the solution examined, and $\varepsilon_\lambda{}^\circ$ for that of the absorbing form of the indicator at a wave-length λ. If there is no solvent effect on the position of the spectrum, the fraction (a) of indicator in the absorbing form will be given by $a = \varepsilon_\lambda/\varepsilon_\lambda{}^\circ$, but if the spectrum in the solvent examined is displaced by an amount $\Delta\lambda$ relative to the reference spectrum of the absorbing form, then

$$a = \varepsilon_{(\lambda+\Delta\lambda)}/\varepsilon_\lambda{}^\circ$$

where

$$\varepsilon_{(\lambda+\Delta\lambda)} = \varepsilon_\lambda + \int_\lambda^{\lambda+\Delta\lambda} \frac{\partial\varepsilon}{\partial\lambda} \mathrm{d}\lambda \quad = \varepsilon_\lambda + \int_\lambda^{\lambda+\Delta\lambda} \sigma_\lambda \, . \, \mathrm{d}\lambda$$

Assume that the slope (σ_λ) of the curve of extinction coefficient against wave-length is constant over the short range λ to $\lambda + \Delta\lambda$, then

$$\varepsilon_{(\lambda+\Delta\lambda)} = \varepsilon_\lambda + a\int_\lambda^{\lambda+\Delta\lambda} \sigma_\lambda{}^\circ \, . \, \mathrm{d}\lambda \quad = \varepsilon_\lambda + a\sigma_\lambda{}^\circ \, . \, \Delta\lambda$$

where $\sigma_\lambda{}^\circ$ is the corresponding slope of the curve for the pure absorbing form of the indicator. Therefore

$$\varepsilon_\lambda/\varepsilon_\lambda{}^\circ = a(1 - \sigma_\lambda{}^\circ \, . \, \Delta\lambda/\varepsilon_\lambda{}^\circ)$$

If it is possible to choose two wave-lengths, λ_1 and λ_2, at which the slopes $\sigma_{\lambda_1}{}^\circ$ and $\sigma_{\lambda_2}{}^\circ$ do not change rapidly with wave-length, such that

$$\sigma_{\lambda_1}{}^\circ/\varepsilon_{\lambda_1}{}^\circ = -\sigma_{\lambda_2}{}^\circ/\varepsilon_{\lambda_2}{}^\circ$$

then

$$a = (\varepsilon_{\lambda_1}/\varepsilon_{\lambda_1}{}^\circ + \varepsilon_{\lambda_2}/\varepsilon_{\lambda_2}{}^\circ)/2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

and if $a \ll 1$ and $\varepsilon_{\text{“non-absorbing”}} \ll \varepsilon_{\text{absorbing}}$

$$\frac{[\text{absorbing form}]}{[\text{“ non-absorbing ” form}]} = \frac{a}{1-a} \sim \left\{ \left(\frac{\varepsilon - \varepsilon_{\text{“non-abs.”}}}{\varepsilon_{\text{abs.}} - \varepsilon}\right)_{\lambda_1} + \left(\frac{\varepsilon - \varepsilon_{\text{“non-abs.”}}}{\varepsilon_{\text{abs.}} - \varepsilon}\right)_{\lambda_2} \right\} \Big/ 2 \quad . \; . \quad (2)$$

Either equation (1) or (2) could be applied to our indicator measurements, with $\lambda_1 = 4000$ A. and $\lambda_2 = 4200$ A. in the case of 4-chloro-2-nitroaniline, and with $\lambda_1 = 4100$ A. and $\lambda_2 = 4200$ A. for triphenylcarbinol.

We may stress that the particular points chosen should only be subject to small solvent effects (ε° = large; $|\sigma^\circ|$ = small), yet the two members of each pair should be affected in *opposite* senses if, as has been reported, the solvent effect consists in a lateral displacement of the absorption curve. Nevertheless, the values of log [Ion]/[Base] calculated from the individual points of such pairs differed at the most by 0·03 unit only. Our values for the logarithm of the *mean* are therefore unlikely to be seriously in error from this source of complication.

TABLE I.

Some acidity functions of the system acetic acid–sulphuric acid–water, 4-chloro-2-nitroaniline being used as indicator.

[Added water], M.	H_2SO_4, %	ε_{4000}	ε_{4200}	log ([BH⁺]/[B])$_{\text{mean}}$	$-H_0$
0	0	4700	4700	—	—
,,	1·73	460·5	456·0	0·97	1·88
,,	3·43	177·9	179·0	1·42	2·33
,,	5·11	100·0	99·8	1·68	2·59
,,	6·76	68·0	65·5	1·87	2·78
,,	8·39	50·0	45·9	2·02	2·93
,,	100	6·06	1·27	—	—
0·111	1·73	485	491	0·94	1·85
,,	3·43	193·0	194·9	1·37	2·28
,,	5·11	108·1	108·9	1·64	2·55
,,	6·76	71·4	69·3	1·84	2·75
,,	8·39	51·5	47·9	2·00	2·91
0·222	1·73	574	586	0·85	1·76
,,	3·43	224	227	1·30$_5$	2·21$_5$
,,	5·11	121·1	121·9	1·59	2·50
,,	6·76	78·0	76·1	1·80	2·71
,,	8·39	55·5	52·3	1·97	2·88
0·555	1·73	975	1009	0·57	1·48
,,	3·43	370	381	1·07	1·98
,,	5·11	139·0	139·9	1·52$_5$	2·43$_5$
,,	6·76	113·0	113·2	1·62	2·53
,,	8·39	76·0	74·1	1·81	2·72

TABLE II.

The ionisation of triphenylcarbinol in some acetic acid–sulphuric acid–water mixtures.

$[H_2O]_{\text{Added}}$	$[H_2O]_{\text{Total}}$*	H_2SO_4, %	H_0	$2H_0$ + log $[H_2O]_{\text{Total}}$*	ε_{4100}	ε_{4200}	log $([R^+]/[ROH])_{\text{mean}}$
0	0·032	0	—	—	0·0	0·0	—
,,	,,	0·78	−1·46	−4·42	1,158	1,121	−1·49
,,	,,	1·00	−1·58	−4·66	2,130	2,060	−1·21
,,	,,	1·49	−1·79	−5·08	5,350	5,200	−0·76
,,	,,	2·26	−2·05	−5·60	11,940	11,550	−0·32
,,	,,	3·00	−2·25	−6·00	17,010	16,650	−0·06
,,	,,	3·16	−2·28	−6·06	18,100	17,550	−0·01
,,	,,	4·16	−2·45	−6·40	28,020	27,350	+0·52
,,	—	100	—	—	36,180	35,840	—
0·111	0·143	1·73	−1·85	−4·54	1,214	1,191	−1·46
,,	,,	3·43	−2·28	−5·40	8,652	8,426	−0·51
,,	,,	5·11	−2·55	−5·94	20,770	20,340	+0·12
,,	,,	6·76	−2·75	−6·34	27,050	26,310	+0·46
,,	,,	8·39	−2·91	−6·66	29,910	29,110	+0·66
0·222	0·254	1·73	−1·76	−4·12	571	550	−1·80
,,	,,	3·43	−2·215	−5·03	4,223	4,109	−0·88
,,	,,	5·11	−2·50	−5·60	13,770	13,430	−0·22
,,	,,	6·76	−2·71	−6·02	23,960	23,150	+0·28
,,	,,	8·39	−2·86	−6·32	29,340	28,880	+0·63
0·555	0·587	1·73	−1·48	−3·19	125	118	−2·47
,,	,,	3·43	−1·98	−4·19	1,021	991	−1·54
,,	,,	5·11	−2·435	−5·10	4,362	4,247	−0·87
,,	,,	6·76	−2·53	−5·29	10,140	9,868	−0·41
,,	,,	8·39	−2·72	−5·67	16,610	16,180	−0·08

* The significance of these columns is given in the Discussion (p. 2110).

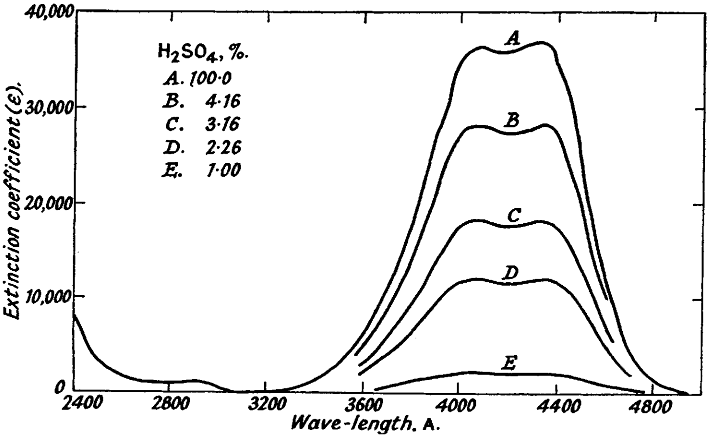
The acidity function H_0 was calculated from the ionisation ratios for 4-chloro-2-nitroaniline by means of Hammett's defining equation

$$H_0 = pK_a + \log [B]/[BH^+]$$

where pK_a, the negative logarithm of the acidity constant of the acid $[NO_2{\cdot}C_6H_3Cl{\cdot}NH_3]^+$, was taken to have the value −0·91 (Paul and Hammett, *J. Amer. Chem. Soc.*, 1936, **58**, 2182). The exact value of this does not affect the argument concerning the mechanism of ionisation of triphenylcarbinol. The results for the H_0 measurements are summarised in Table I, and those for the ionisation of triphenylcarbinol in Table II. In Fig. 4 our values for the H_0 function of some mixtures of acetic and sulphuric acids are plotted against the solvent composition, together with the results of earlier investigations based on colorimetric measurements (Paul and Hammett, *loc. cit.*; Hall and Spengeman, *J. Amer. Chem. Soc.*, 1940, **62**, 2487).

FIG. 5.

Absorption spectra of triphenylcarbinol in acetic acid–sulphuric acid mixtures.



DISCUSSION.

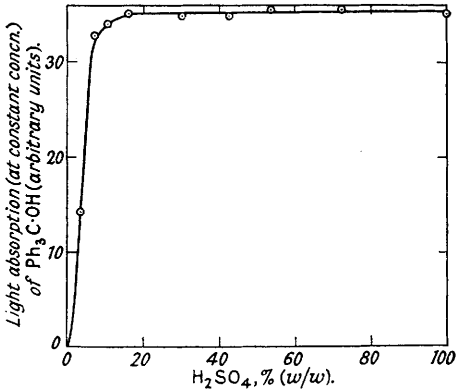
I. *The Identity of the Ion Formed.*—The absorption spectrum of triphenylcarbinol in acetic acid consists of a triple-peaked band centred around λ 2590 A. ($\varepsilon_{\text{max.}}$ = 660) with no detectable absorption above λ 3300 A. It is almost identical with the recorded spectrum of triphenylcarbinol in ethanol (Orndorff, Gibbs, McNulty, and Shapiro, *J. Amer. Chem. Soc.*, 1927, **49**,

1541) and may be attributed to the carbinol molecule. On addition of sulphuric acid to the solvent the absorption is intensified over the whole of the observed ultra-violet and visible region. In particular, a new double-peaked absorption band appears near λ 4200 A. (maxima at λ 4080 and 4310 A.; extinction coefficients 36,400 and 37,360, respectively). The position of this band remains remarkably little altered on changing the composition of the medium (Fig. 5). The absorption intensity remains constant in media containing more than ~16% w/w of sulphuric acid (Fig. 6).

If the light absorption of triphenylcarbinol in sulphuric acid–water mixtures is examined it is found that increasing water content of the medium leaves the absorption intensity unaffected until, in media containing more than ~40% of water, the acidity gets so low that the conversion of the molecule into the triphenylcarbonium ion is no longer complete and, since the un-ionised molecule is insoluble in aqueous sulphuric acid, triphenylcarbinol separates out.

FIG. 6.

Light absorption of solutions of triphenylcarbinol in acetic acid–sulphuric acid mixtures.



These two sets of observations suggest that only two forms of triphenylcarbinol are present in the various solutions in a sufficiently high concentration for their light absorption to matter, *viz.*, the triphenylcarbinol molecule (in the solvents of low acidity) and the coloured species into which the substance is completely converted in the highly acidic solvents. From the cryoscopic measurements it is extremely probable that this species is the triphenylcarbonium ion, and this conclusion is strengthened by the identical absorption spectra obtained with triphenylmethyl halides under ionising conditions. The simple medium dependence of the spectrum makes it very unlikely that the ion $Ph{\cdot}CO_2H_2^+$, a third species, is also present in the acid solutions of weaker dehydrating power to any appreciable extent, even though the light absorption of this ion would be expected to be similar to that of the triphenylcarbonium ion. The ionisation of triphenylcarbinol, also in solutions of lower acidity than that for which the quantitative formation of triphenylcarbonium ion has been established cryoscopically, will therefore be represented by the equations

$$Ph_3C{\cdot}OH + H_2SO_4 \rightleftharpoons Ph_3C^+ + H_2O + HSO_4^- \quad . \; . \; . \; . \; . \quad (I)$$

or

$$Ph_3C{\cdot}OH + 2H_2SO_4 \rightleftharpoons Ph_3C^+ + H_3O^+ + 2HSO_4^- \quad . \; . \; . \; . \; . \quad (II)$$

According to the medium employed the first or the second equation will be found more convenient.

II. *The Ionisation of Triarylcarbinols in Aqueous Media and the Definition of the Acidity Function* J.—It is in this case more convenient to consider the equilibrium (I) in order to obtain a relation between the degree of ionisation and the nature of the medium. This ionisation may, for mathematical convenience, be split into several auxiliary steps. In view of the results quoted in the preceding paragraph we assume that there is no storage of reagent at any intermediate stage and do not wish to imply that there need be any chemical significance in this breaking up of the thermodynamic equilibrium which must, of course, be independent of any assumed intermediate reaction path:

$$\begin{aligned} &(1)\ H_2SO_4 && \rightleftharpoons HSO_4^- + H^+ \\ &(2)\ R{\cdot}OH + H^+ && \rightleftharpoons R{\cdot}OH_2^+ \\ &(3)\ R{\cdot}OH_2^+ && \rightleftharpoons R^+ + H_2O \end{aligned}$$

Let the equilibrium constants of these hypothetical steps be denoted by K_1, K_2, K_3, and the equilibrium constant of the overall equilibrium (I) by K_I. Then

$$K_I = K_1 \, . \, K_2 \, . \, K_3 = (R^+)(HSO_4^-)(H_2O)/(R{\cdot}OH)(H_2SO_4)$$

It follows from the definition of H_0 and of the related function h_0 ($H_0 = -\log_{10} h_0$), that

$$\frac{(HSO_4^-)}{(H_2SO_4)} = \frac{K_1}{h_0} \cdot \frac{f_{R\cdot OH}}{f_{R\cdot OH_2^+}} = \frac{K_1}{(H^+)} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

where parentheses refer to activities and the *f*'s are activity coefficients relative to the standard state of an infinitely dilute aqueous solution (Hammett, *loc. cit.*). Therefore

$$K_{\mathrm{I}} = \frac{(\mathrm{R}^+)\,(\mathrm{H_2O})}{(\mathrm{R{\cdot}OH})} \cdot \frac{K_1}{h_0} \cdot \frac{f_{\mathrm{R{\cdot}OH}}}{f_{\mathrm{R{\cdot}OH_2}^+}}$$

and we may define a thermodynamic constant $K_{\mathrm{R{\cdot}OH}}$ which will be a measure of the secondary basicity of R•OH :

$$K_{\mathrm{R{\cdot}OH}} = K_{\mathrm{I}}/K_1 = K_2{\cdot}K_3 = \frac{[\mathrm{R}^+]}{[\mathrm{R{\cdot}OH}]} \cdot \frac{(\mathrm{H_2O})}{h_0} \cdot \frac{f_{\mathrm{R}^+}}{f_{\mathrm{R{\cdot}OH_2}^+}} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

We shall take $f_{\mathrm{R}^+}/f_{\mathrm{R{\cdot}OH_2}^+}$ as unity in all solvents considered, a step which is similar to Hammett's suggestion that all ratios of the form $\{f_{\mathrm{AH}^+} \,.\, f_{\mathrm{B}}/f_{\mathrm{BH}^+} \,.\, f_{\mathrm{A}}\}$ are approximately equal to unity, irrespective of the nature of A and B and of the solvent. This assumption is made by Hammett in the derivation of the H_0 function used in our treatment, and it is justified by the fact that the H_0 function has, within the limits of experimental error, a value independent of the indicator used. [It should be mentioned that Conant and Werner (*J. Amer. Chem. Soc.*, 1930, **52**, 4436) also recognised that the activity of water must be involved in this manner in the expression for the equilibrium constant of the ionisation of a triarylcarbinol in " superacid " solutions.] Taking logarithms and rearranging, we get

$$H_0 + \log\,(\mathrm{H_2O}) = -\,\mathrm{p}K_{\mathrm{R{\cdot}OH}} + \log\,[\mathrm{R{\cdot}OH}]/[\mathrm{R}^+]$$

and this may be compared with the relation between the basicity constant K_b^{B} of an electrically neutral Brønsted base and the acidity function of the medium

$$H_0 = -\mathrm{p}K_b^{\mathrm{B}} + \log\,[\mathrm{B}]/[\mathrm{BH}^+] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

It is therefore suggestive to define an acidity function J_0, such that

$$J_0 = H_0 + \log\,(\mathrm{H_2O}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$= -\mathrm{p}K_{\mathrm{R{\cdot}OH}} + \log\,[\mathrm{R{\cdot}OH}]/[\mathrm{R}^+] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

which plays for the triphenylcarbinol type of ionisation (ionisation of an electrically neutral secondary base) a rôle analogous to that of the function H_0 for the ionisation of an electrically neutral Brønsted base. It is possible to define functions J_+, J_-, J_{++}, etc., given by $J_+ = H_+ + \log\,(\mathrm{H_2O})$, etc., to describe the potency of the solvent in inducing the ionisation of electrically charged secondary bases, the subscripts referring to the electrical charge of the base.

From our choice of the standard state [$(\mathrm{H_2O}) \longrightarrow 1$, as solution $\longrightarrow \mathrm{H_2O}$] it follows that as the medium composition tends to pure water, $J_0 \longrightarrow H_0$, which, in turn, under these conditions tends to the pH value.

Since the activity of water in the solvent, as defined above, is given by $(\mathrm{H_2O}) = p/p^0$, where p and p^0 are the vapour pressures of water over the solvent and pure water, respectively, the J_0 scale is completely defined for any acid solution for which the H_0 function and the vapour pressure of water over the acid are known. This is so for nearly the whole of the composition range for $\mathrm{H_2O{-}H_2SO_4}$ mixtures (vapour pressures : Hepburn, *Proc. Physical Soc.*, 1928, **40**, 247; Daudt, *Z. physikal. Chem.*, 1923, **106**, 225; Greenewalt, *Ind. Eng. Chem.*, 1925, **17**, 522; Collins, *J. Physical Chem.*, 1933, **37**, 1191; Shankman and Gordon, *J. Amer. Chem. Soc.*, 1939, **61**, 2370; Stokes, *ibid.*, 1947, **69**, 1291) and for an appreciable range for $\mathrm{H_2O{-}HClO_4}$ mixtures (vapour pressures : Pearce and Nelson, *ibid.*, 1933, **55**, 3075). The J_0 scale calculated in this way for the system $\mathrm{H_2SO_4{-}H_2O}$ is tabulated in Table III, and the course of the function, along with that of the H_0 function, is plotted against the solvent composition in Fig. 7.

TABLE III.

The J_0 *function for sulphuric acid–water mixtures at 25°.*

$\mathrm{H_2SO_4}$, %	H_0	$\log p/p^\circ$	J_0	$\mathrm{H_2SO_4}$, %	H_0	$\log p/p^\circ$	J_0	$\mathrm{H_2SO_4}$, %	H_0	$\log p/p^\circ$	J_0
5	+0·24	−0·01	+0·23	40	−2·28	−0·24	−2·52	70	−5·54	−1·37	−6·91
10	−0·16	−0·02	−0·18	45	−2·72	−0·33	−3·05	75	−6·16	−1·77	−7·93
15	−0·54	−0·04	−0·58	50	−3·23	−0·44	−3·67	80	−6·82	−2·28	−9·10
20	−0·89	−0·06	−0·95	55	−3·79	−0·58	−4·37	85	−7·62	−2·79	−10·41
25	−1·22	−0·08	−1·30	60	−4·32	−0·76	−5·11	90	−8·17	−3·49	−11·66
30	−1·54	−0·12	−1·66	65	−4·89	−1·03	−5·92	95	−8·74	−4·63	−13·37
35	−1·90	−0·17	−2·07								

Alternatively, the J_0 function could be experimentally determined by stepwise colorimetric or spectrophotometric measurements on indicators of the triphenylcarbinol type, analogously to Hammett's determination of the H_0 function by such measurements on Brønsted bases.

The correctness of these considerations may be tested in a limited way by plotting log ($[R^+]/[R\cdot OH]$) against J_0 [which according to equation (7) should give a straight line of *unit* slope] for a neutral indicator of the triphenylcarbinol type (4 : 4′ : 4″-trinitrotriphenylcarbinol) in sulphuric acid–water mixtures (Murray and Williams, *loc. cit.*; cf. Westheimer and Kharasch, *loc. cit.*). It is found (Fig. 8) that the points lie on a straight line of slope ~1·16. Although this agreement is not perfect, we believe that it is satisfactory, bearing in mind the not very high accuracy to which the H_0 scale is known. Any inaccuracy in this will, by our method of computing J_0, be imported into the J_0 scale. That such a degree of uncertainty in the H_0 scale is quite likely may be seen on plotting the logarithms of the ionisation ratios of several of Hammett and Deyrup's indicators covering the same range against one another. Lines of exactly unit slope are not always obtained, the discrepancies being considerably greater than ours in some cases. A plot of the logarithm of the indicator ratio for anthraquinone against that for 6-bromo-2 : 4-dinitroaniline (these being the only two indicators in Hammett and Deyrup's work which cover the composition range to which the measurements on 4 : 4′ : 4″-trinitrotriphenylcarbinol relate) leads to a straight line of slope 1·08. The curious course of the H_0 function near 85% acid also suggests that the values in this region may require a slight revision. Therefore, while the behaviour of solutes in sulphuric acid still requires more detailed study, we would claim that the ionisation of triarylcarbinols is now as satisfactorily explained as the simpler basic ionisations in sulphuric acid.

FIG. 7.

Acidity functions of H_2SO_4–H_2O *mixtures.*

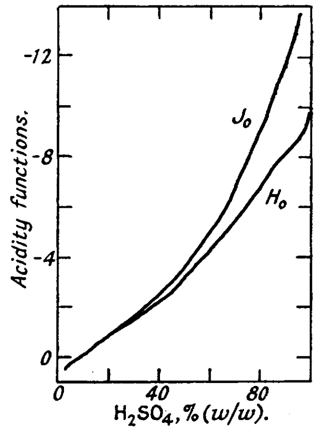
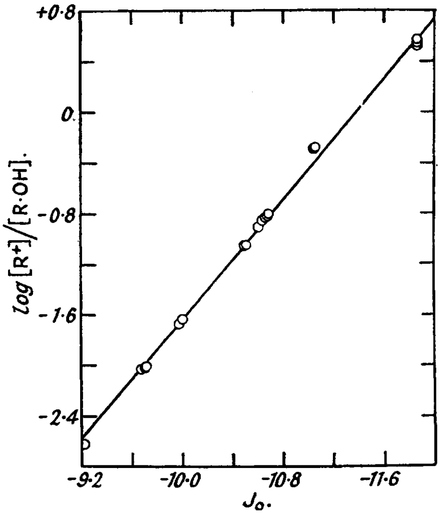


FIG. 8.

The dependence of the ionisation ratio for 4 : 4′ : 4″-*trinitrophenylcarbinol upon the* J_0 *function.*



From Fig. 8 it can also be deduced that $pK_{R\cdot OH}$ for 4 : 4′ : 4″-trinitrotriphenylcarbinol is ~11·4.* There have been earlier attempts to assess quantitatively the basicities of triarylcarbinols, particularly that of Baeyer and Villiger (*Ber.*, 1902, **35**, 3020). However, this work and most of the later investigations were based on an experimental method of doubtful value (cf. Ziegler and Boye, *Annalen*, 1927, **458**, 229) and lacked the understanding that halochromism in ketones and triphenylcarbinol was a manifestation of different kinds of basicity (see, however, Kolthoff, *J. Amer. Chem. Soc.*, 1927, **49**, 1218; Lund, *ibid.*, p. 1346).

The usefulness of the J_0 scale and of the basic dissociation constants obtainable with its aid may be illustrated with reference to the kinetics of aromatic substitution reactions. The

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* Hammett prefers to record the strengths of weak bases in terms of the acidity constants of the conjugate acids, *i.e.*, the reciprocals of the basicity constants (or $pK_b^B = -pK_a^{HB^+}$). Since no such *simple* physical interpretation attaches to the reciprocal of the ionisation constant $K_{R\cdot OH}$ of a secondary base, it is not proposed to follow this practice.

second-order rate constant (k) for nitration by dilute solutions of nitric acid in aqueous sulphuric acid is related to the J_0 function by the equation

$$\log k = \log k_0 - J_0 - \mathrm{p}K_{\mathrm{NO_2\cdot OH}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where k_0 is a constant independent of the medium, and $K_{\mathrm{NO_2\cdot OH}}$ is the ionisation constant of nitric acid as a secondary base, as defined by equation (4), provided that $[\mathrm{HNO_3}] \gg [\mathrm{NO_2^+}]$. From the intensities of Raman spectra of nitric acid in sulphuric acid (Chédin, *Ann. Chim.*, 1937, **8**, 295) it may be inferred that nitric acid (in low concentration) is half-ionised as a secondary base in ~88% sulphuric acid, and therefore that $\mathrm{p}K_{\mathrm{NO_2\cdot OH}}$ is ~11·2. Equation (8) is a slightly more exact statement of the treatment of aromatic nitration in aqueous sulphuric acid by Westheimer and Kharasch (*loc. cit.*) and, more particularly, by Lowen, Murray, and Williams (*J.*, 1950, 3318) where these considerations are elaborated. It is clear that with a more precise knowledge of the constant $K_{\mathrm{NO_2\cdot OH}}$ it will be possible to obtain in a quantitative form the law for the diminution of nitration velocity in mixed acids containing more than ~90% of H_2SO_4, about which there has been considerable speculation (cf. Gillespie and Millen, *loc. cit.*). By studying acid-catalysed halogenations over a range of solvent composition for which the courses of H_0 and J_0 differ appreciably, it should be possible to decide whether halogenation is brought about by a halogen cation or the conjugate acid of the halogen hydroxide (cf. Derbyshire and Waters, *locc. citt.*).

III. *The Ionisation in Acid Media of Low Water Content.*—For solutions of triphenylcarbinol in mixtures of sulphuric and acetic acids with a very low concentration of water the ionisation is best considered in terms of equation (II), since the activity of water in this system is not so readily accessible. This ionisation may again be split up into several auxiliary steps, and the equilibrium constant K_{II} is then given by $K_{\mathrm{II}} = K_1K_2K_3K_4$, the constants K_1, K_2, K_3 being those defined before, and K_4 the equilibrium constant for $H_2O + H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^-$; *i.e.*,

$$K_{\mathrm{II}} = \frac{(\mathrm{H_3O^+})\,(\mathrm{HSO_4^-})^2}{(\mathrm{H_2SO_4})^2} \cdot \frac{[\mathrm{R^+}]}{[\mathrm{R\cdot OH}]} \cdot \frac{f_{\mathrm{R^+}}}{f_{\mathrm{R\cdot OH}}}$$

the activity coefficients again referring to the standard state of an infinitely dilute aqueous solution. Combining this equation with equation (3), we obtain

$$\frac{K_{\mathrm{II}}}{K_1{}^2} = \frac{[\mathrm{R^+}]}{[\mathrm{R\cdot OH}]} \cdot \frac{[\mathrm{H_3O^+}]}{h_0{}^2} \cdot \left(\frac{f_{\mathrm{H_3O^+}} f_{\mathrm{R^+}} f_{\mathrm{R\cdot OH}}}{f^2{}_{\mathrm{R\cdot OH_2^+}}}\right)$$

or, on taking logarithms,

$$\log \frac{[\mathrm{R^+}]}{[\mathrm{R\cdot OH}]} = \log \frac{K_{\mathrm{II}}}{K_1{}^2} - 2H_0 - \log\,[\mathrm{H_3O^+}] - \log\left(\frac{f_{\mathrm{H_3O^+}} f_{\mathrm{R^+}} f_{\mathrm{R\cdot OH}}}{f^2{}_{\mathrm{R\cdot OH_2^+}}}\right) \quad . \quad . \quad . \quad (9)$$

We have found that this equation assumes a useful form when the last term is taken to have a constant value ϕ independent of the medium—which is probably not introducing a serious error since it is symmetrical relative to the electrical charges and probably has a value close to zero—and $[H_3O]^+$ is replaced by the stoicheiometric concentration of water in the medium ($[H_2O]_{\mathrm{st.}}$), which seems reasonable for very low concentrations of water. Therefore

$$\log\,[\mathrm{R^+}]/[\mathrm{R\cdot OH}] = \log K_{\mathrm{II}}/K_1{}^2 - 2H_0 - \log\,[\mathrm{H_2O}]_{\mathrm{st.}} - \phi \quad . \quad . \quad . \quad . \quad (10)$$

Equation (10) has been tested by studying the variation of the ionisation ratio of triphenylcarbinol with changes of the H_0 function and the water concentration of the medium. It was found that, in sets of experiments in which the water content of the medium was kept constant and the acidity changed, the dependence of the ionisation ratio upon H_0 was twice as great as for a simple base. The dependence of the ionisation ratio upon the water concentration according to equation (10) is confirmed by the observation that all four sets of experiments, relating to different concentrations of added water, can fairly satisfactorily be represented on a single graph of log $[\mathrm{R^+}]/[\mathrm{R\cdot OH}]$ against ($2H_0$ + log $[H_2O]_{\mathrm{st.}}$). This is shown in Fig. 9, where the straight line is drawn with a *theoretical slope* of -1. It must, however, be remarked that in order to bring the points of the set without deliberately added water into coincidence with the other sets it is necessary to assume a value for the residual moisture of the batch of acetic acid used in these experiments. (The water content of the sulphuric acid may be neglected in comparison.) In this way the value 0·032M. (0·055%) for the concentration of water in our " dry " acetic acid was found to give fair agreement, and this value is of the order of magnitude to be expected from our purification method and criteria (cf. Experimental). All stoicheiometric water concentrations were therefore calculated by adding 0·032M. to the concentrations of deliberately added water.

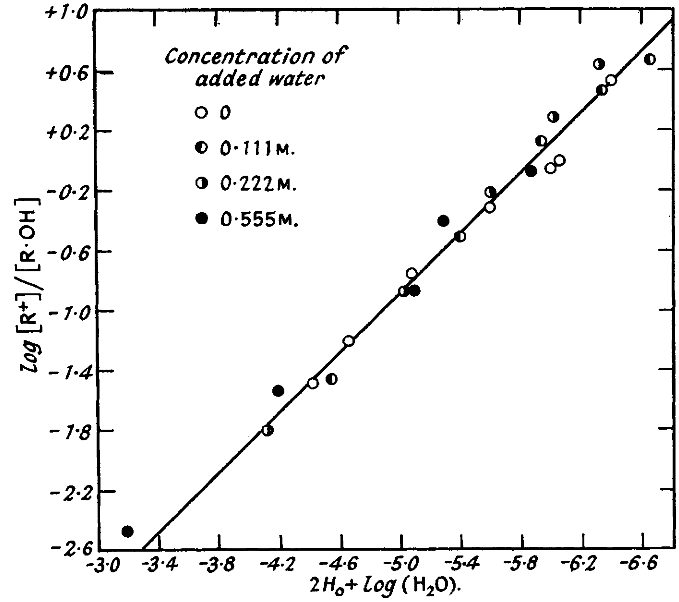
A more exact form of equation (10) must be used for media containing comparable amounts of added water and R·OH. In that case an appreciable second source of hydroxonium ions in the medium would be the ionisation of the triphenylcarbinol itself, and therefore, by modifying equation (10) we obtain

$$\log [R^+]/[R{\cdot}OH] = \log K_{II}/K_I^2 - 2H_0 - \log \{[H_2O]_{st.} + [R^+]\} - \phi \quad . \quad . \quad . \quad (11)$$

It is doubtful if the region of validity of this equation can be investigated by using our technique and triphenylcarbinol as indicator, since the concentration of adventitious water in the hygroscopic medium is probably unavoidably large compared with the low concentration ($<10^{-4}$M.) of the indicator.

FIG. 9.

Test of equation (10).



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