648. *The Ionisation of Triarylcarbinol Indicators in Sulphuric Acid–Water Mixtures.*

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The extent of ionisation of triarylcarbinol indicators in 90—65% sulphuric acid has been measured with a photoelectric absorptiometer, by using indicators carrying fully ionised trimethylammonium groups as nuclear substituents. Westheimer and Kharasch's measurements on the ionisation of trinitrotriphenylcarbinol in 95—80% sulphuric acid have been confirmed.

The ionisation of triarylmethyl halides and of the corresponding carbinols (*e.g.*, under the influence of Friedel–Crafts catalysts and of strong acids, respectively) is well established (compare, for example, Hantzsch, *Ber.*, 1921, **54**, 2573; Hammett, "Physical Organic Chemistry," New York, 1940, p. 53). Cryoscopic evidence (Hantzsch, *Z. physikal. Chem.*, 1907, **61**, 257; Hammett and Deyrup, *J. Amer. Chem. Soc.*, 1933, **55**, 1900; Treffers and Hammett, *ibid.*, 1937, **59**, 1708) shows that in nearly anhydrous sulphuric acid, the ionisation of a triarylcarbinol has the form:

$$Ar_3C{\cdot}OH + 2H_2SO_4 \rightleftharpoons Ar_3C^+ + OH_3^+ + 2HSO_4^- \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The carbinol and the carbonium ion are characterised by differences in absorption spectra; and the variation of the extent of ionisation in sulphuric acid–water mixtures, as a function of medium composition, has been measured colorimetrically by Westheimer and Kharasch (*J. Amer. Chem. Soc.*, 1946, **68**, 1871) for a single example, trinitrotriphenylcarbinol, in 80—95% sulphuric acid. At the aqueous end of the range, this indicator ionises only very slightly. To determine the behaviour in still more aqueous media more strongly basic triarylcarbinol indicators are needed. The required basic strength, coupled with adequate solubility in the relevant media, may be secured by using triarylcarbinols carrying ionised trimethylammonium substituents in the aromatic nuclei. The indicators employed are formulated in Table I of the preceding paper.

TABLE I.

Medium, H_2SO_4, %.	$10^{-3}S/c$.	Ionisation, %.	$\log \frac{[R^+]}{[ROH]}$.	Medium H_2SO_4 %.	$10^{-3}S/c$.	Ionisation, %.	$\log \frac{[R^+]}{[ROH]}$.
(III) * 4 : 4′-*Bis*(*trimethylammonium*)*triphenylcarbinyl methyl ether diperchlorate.*							
65·04	0·280	0·94	−2·022	73·92	24·1	81·0	+0·634
65·25	0·336	1·13	−1·944	73·96	24·2	81·2	+0·634
66·16	0·530	1·78	−1·742	74·06	24·4	81·8	+0·659
67·16	0·919	3·08	−1·498	75·88	28·1	95	—
67·39	1·04	3·48	−1·443	75·91	28·3		
67·63	1·07	3·54	−1·429	75·93	28·2		
68·57	2·17	7·28	−1·105	77·96	29·5	~100	—
68·73	2·41	8·10	−1·056	78·00	29·5	—	—
68·92	2·70	9·07	−1·002	78·07	29·7	—	—
70·33	5·54	18·6	−0·644	79·65	30·0	—	—
70·36	5·68	19·1	−0·628	80·46	30·0	—	—
70·62	6·07	20·4	−0·594	81·94	30·3	—	—
72·01	13·4	45·1	−0·082	—	29·7	—	—
72·11	13·7	46·1	−0·065	85·74	30·2	—	—
(I) * 4 : 4′ : 4″-*Tris*(*trimethylammonium*)*triphenylcarbinyl methyl ether triperchlorate.*							
75·84	0·0933	0·31	−2·506	83·20	8·73	29·0	−0·386
—	0·0963	0·32	−2·491	—	8·81	29·2	−0·383
77·21	0·158	0·54	−2·269	—	9·03	30·0	−0·366
77·73	0·225	0·75	−2·122	85·30	21·7	72·0	+0·414
78·11	0·279	0·93	−2·027	—	21·5	71·5	+0·402
80·44	1·40	4·64	−1·315	—	21·7	72·2	+0·414
80·63	1·60	5·31	−1·251	87·42	28·9 ± 0·4	96	—
80·65	1·60	5·31	−1·250	89·45	29·9 ± 0·1	~100	—
82·10	4·26	14·15	−0·783	90·95	30·0 ± 0·2	—	—
—	4·40	14·6	−0·767	92·32	30·1 ± 0·2	—	—
—	4·60	15·2	−0·746	94·60	30·1 ± 0·3	—	—
				98·95	30·1 ± 0·4	—	—
(II) * 4 : 4′ : 4″-*Tris*(*trimethylammonium*)*triphenylcarbinol triperchlorate.*							
79·92	0·755	2·62	−1·570	83·93	13·1	45·4	−0·080
80·39	1·17	4·05	−1·375	—	13·4	46·5	−0·062
81·60	3·00	10·4	−0·937	85·02	20·2	70·0	+0·367
81·80	3·63	12·6	−0·842	—	20·3	70·4	+0·375
82·00	3·66	12·7	−0·835	—	20·3	70·4	+0·374
83·93	13·2	45·6	−0·071	92·38	28·9	—	—
(IV) * 4 : 4′ : 4″-*Trinitrotriphenylcarbinol.*							
80·40	0·0798	0·24	−2·625	86·04	4·39	13·05	−0·821
82·19	0·313	0·93	−2·029	86·09	4·58	13·6	−0·803
82·26	0·319	0·95	−2·020	87·54	11·4	34·0	−0·290
82·32	0·335	1·0	−2·010	87·55	11·6	34·4	−0·278
83·37	0·703	2·09	−1·671	87·56	11·6	34·4	−0·280
83·46	0·755	2·24	−1·638	90·70	25·9	77·1	+0·544
85·33	2·72	8·1	−1·056	90·71	25·8	76·9	+0·524
85·34	2·70	8·05	−1·060	90·71	26·5	79·0	+0·573
85·37	2·78	8·3	−1·046	92·32	30·6 ± 0·3	91	—
85·79	3·71	11·0	−0·907	95·47	33·3 ± 0·2	~100	—
85·94	4·11	12·2	−0·859	96·92	33·1 ± 0·3	—	—
86·00	4·35	12·9	−0·826	99·15	33·6 ± 0·4	—	—
				—	33·5 ± 0·4	—	—

* These numerals refer to formulæ numbers of the preceding paper.

The absorption spectrum of the unsubstituted triphenylcarbinyl cation has been fully examined in sulphuric acid and other solvents, and shows a double peak in the violet, with maxima at 4320 and 4050 A. (Anderson, *ibid.*, 1930, **52**, 4567; Fairbrother, *J.*, 1949, 1058). Kehrmann and Sandoz (*Ber.*, 1918, **51**, 918) find the ultra-violet absorption of all the *p*-aminotriphenylcarbinols in strong sulphuric acid (when all the substituents become NH_3^+) to be very similar; and it is therefore to be expected that the visible absorption maximum for the trimethylammonium salts will be at 4000—4300 A.

In the present work, the intensity of colour of the indicator solutions in a range of sulphuric acid–water mixtures has been measured with monochromatic mercury light (4358 A.) by means of a "Spekker" photoelectric absorptiometer. The "Spekker" readings were converted into concentrations of triarylcarbinyl cation by means of a calibration curve obtained in an acid just sufficiently strong to ionise the indicator completely. The fully methylated quaternary salts derived from Malachite-green and Crystal-violet are colourless and water-soluble, and differ from other quaternary salts only in their further ionisation to coloured ions in strong acids.

The question of the anion to be introduced with the indicators for acidity measurements is not very important since the concentrations involved are never more than about 10^{-3} molar (cf. Table II). However, the iodides cannot be used, since iodine is liberated from them by concentrated sulphuric acid; nor can the picrates be used on account of their colour. The perchlorates appeared to be the most suitable. They are readily isolated and purified, since their solubility in water in the presence of excess of perchlorate ion is low; also the perchlorate ion is the one likely to be least affected by strong sulphuric acid. Several perchlorates of this type were prepared by Brand and Modersohn (*J. pr. Chem.*, 1928, [ii], **118**, 97) who used methyl sulphate as methylating agent and then converted the methyl sulphates (often non-crystalline) into perchlorates. They isolated colourless perchlorates both of the carbinyl methyl esters and of the carbinols; but since, with very small concentrations of indicator in sulphuric acid–water media, equilibrium will be rapidly established in favour of the carbinol, there is no objection to using the methyl ethers as indicators, and thus avoiding a further step in their preparation. The extent of ionisation of the carbinol does, in fact, coincide with that of its methyl ether (see Table I of this paper and Fig. 1 of the preceding paper).

Results for the indicators are shown in Table I, in which S is the "Spekker" reading, and c is the total concentration of indicator in moles/l. In this Table, the carbinol $Ar_3C{\cdot}OH$ of equation (1) is written ROH, and the carbonium ion is written R^+.

Form of Ionisation.—The representation of the ionisation of triarylcarbinol indicators by equation (1) is experimentally established only for nearly anhydrous sulphuric acid media. The equilibrium constant of (1) may be related to a constant given by equation (2):

$$K = a_{R^+}\,a_{H_2O}/a_{ROH}\,a_{H^+} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

The constant K of (2) may be connected with the acidity function H_0. There is evidence for the validity of this equation (Dr. V. Gold, private communication). Its application to the results of Table I will be discussed in a later paper.

The argument of the preceding paper, connecting the extent of ionisation of carbinol indicators with rates of nitration, is, of course, independent of the form of ionisation, provided that nitric acid, $NO_2{\cdot}OH$, ionises similarly to the carbinols, ROH.

EXPERIMENTAL.

Preparation of Carbinol Indicators.—4 : 4′ : 4″-Trinitrotriphenylcarbinol, prepared from triphenylmethane by nitration and subsequent oxidation (Fischer, *Ber.*, 1904, **37**, 3357; Hantzsch, *ibid.*, 1919, **52**, 495), was recrystallised repeatedly from glacial acetic acid or benzene. It furnished small, well-formed rhombs from either solvent, m. p. 190—191°. The crystals always had a very faint yellow tinge, as noticed by Westheimer and Kharasch.

For the preparation of the indicators with NMe_3^+ substituents, modifications of the method of Brand and Modersohn (*loc. cit.*) were adopted, after preliminary experiments, as preferable to methylation of the leuco-bases, followed by oxidation (cf., however, Tadros and Latif, *J.*, 1949, 337).

4 : 4′-*Bis(trimethylammonium)triphenylcarbinyl salts.* Malachite-green (commercial sample) was converted into the methyl ether by dissolving the dye salt (5 g.) in methyl alcohol (50 c.c.) in which excess of sodium (2 g.) had been dissolved, and refluxing the mixture till all the colour was discharged (30 minutes). The solid which separated was filtered off and washed thoroughly with water, then recrystallised from methyl alcohol containing a pellet of sodium hydroxide, and had m. p. 147—148°.

The methyl ether dimethiodide, $(^+NMe_3{\cdot}C_6H_4)_2CPh{\cdot}OMe\}I_2^{--}$, was prepared by treating the methyl ether (0·96 g.) at room temperature with a mixture of methyl iodide (5 c.c.) and methyl alcohol (5 c.c.) and a pellet of sodium hydroxide. After 24 hours, the crystals which had separated were filtered off, washed with a little mixed methyl iodide–methyl alcohol, and recrystallised from methyl alcohol, forming colourless platelets (1·0 g.). The compound started to darken when heated to about 160°

and melted with decomposition at 190°. When " bench " concentrated sulphuric acid was added, some iodine was liberated.

The diperchlorate, $\{^+NMe_3{\cdot}C_6H_4)_2CPh{\cdot}OMe\}(ClO_4^-)_2$, was prepared by dissolving the methiodide in the minimum volume of hot water and adding a concentrated solution of sodium perchlorate. The indicator perchlorate separated immediately, and was washed with dilute sodium perchlorate and then with a very little water, since it is rather soluble in pure water. It could be recrystallised from a small volume of methyl alcohol, forming feathery platelets, m. p. 276° (decomp.). In concentrated sulphuric acid it gave a golden-yellow solution.

4 : 4′ : 4″-*Tris*(*trimethylammonium*)*triphenylcarbinyl salts.* Crystal-violet (B.D.H. stain quality) (4 g.) was refluxed with a solution of sodium (2 g.) in methyl alcohol (50 c.c.) till the solution was only faintly coloured (1½ hours). The solution was cooled and the methyl ether filtered off, washed with water, and dried. Recrystallisation from equal volumes of benzene and light petroleum gave pale violet crystals, m. p. 157—158° (2·6 g.). This material was treated with methyl iodide (10 c.c.) and methyl alcohol (5 c.c.) containing a pellet of sodium hydroxide. The solution, which was violet at first but gradually decolorised, slowly deposited the quaternary tri-iodide in short, stout needles, which were filtered off after 2 days at room temperature, and washed with methyl alcohol–iodide (yield, 5·1 g., 95%). The compound, which was faintly violet, was recrystallised several times from methyl alcohol (10 c.c.), forming colourless prisms, m. p. 195° after gradual decomp. from 150°. The purified material (3·3 g.) was dissolved in water (10 c.c.) and treated with excess of a saturated solution of sodium perchlorate. The thick precipitate was filtered off, dried, and extracted twice with hot methyl alcohol (5 c.c.) (in which it is sparingly soluble) to remove coloured impurities. The yield was 2·7 g. (90%). Two recrystallisations from water (10 c.c.) gave long, colourless needles of the triperchlorate, $(^+NMe_3{\cdot}C_6H_4)_3C{\cdot}OMe\}(ClO_4^-)_3$, m.p. 303° (decomp.).

The corresponding carbinol, $(^+NMe_3{\cdot}C_6H_4)_3C{\cdot}OH\}(ClO_4^-)_3$, was prepared by heating the methyl ether (1·9 g.) with a 1 : 1 mixture of concentrated hydrochloric acid and water (5 c.c.) for 10 minutes. The orange solution was just decolorised with sodium hydroxide, and a saturated solution of sodium perchlorate (2 g.) was added. The product (1·3 g.) crystallised from the cooled solution, and was recrystallised from water (5 c.c.), then from equal volumes of water and methyl alcohol; it had m. p. 296° (decomp.).

Standardisation of Sulphuric Acid Media.—Sulphuric acid–water mixtures were made up from pure concentrated sulphuric acid and were standardised against N-hydrochloric acid, kept as a subsidiary standard, through titration with approx. N-sodium hydroxide, using screened methyl-orange. The hydrochloric acid was standardised against potassium iodate solution, two determinations based on different primary standards agreeing to 0·02%. The reproducibility of the medium composition was better than 0·1% sulphuric acid; and re-standardisations of media which had been kept for some time agreed to within this figure.

Method of Measurement.—The intensity of absorption of the indicator solutions was measured with a " Spekker " photoelectric absorptiometer, by using a mercury lamp and appropriate filters to isolate the 4358 A. line. Three parallel determinations were made with the same medium and slightly different quantities of a stock indicator solution. Four successive readings were taken on each solution, and the cells were then emptied and refilled with fresh solution twice, three or four further readings being taken on each sample, so that the final figures were the mean of 10—12 readings. The liquid used in the comparison cell was the same medium as that used in making up the indicator solutions, although the sulphuric acid media only occasionally showed slight absorption.

The uniformity of the (normally 1 cm.) " Spekker " cells was checked occasionally, by carrying out a series of measurements with the same arbitrary solution of potassium dichromate in all the cells, and only those which gave results closest to the mean value were used regularly; but the deviations were almost always well within the experimental error.

No difficulty was caused through absorption of atmospheric moisture by even the most concentrated acid media. The temperature of observation was about 20°. The readings showed no variations owing to lack of close temperature control, even though the temperature of the solutions in the cells might rise by 1—2° during measurement.

Calculation.—One example is given, for indicator (I). For the completely ionised indicator, $S/c = S/[R^+] = (3{\cdot}01 \pm 0{\cdot}03) \times 10^4$ (mean of 14 values in 94·6% sulphuric acid, corrected for calibration). The un-ionised molecule is assumed to be colourless. For observations in other media, a known weight (0·3—2·0 g.) of a stock solution of indicator (0·0718 g. in 20·51 g. of 98·95% sulphuric acid) was made up to a known volume (about 50 c.c.) in the medium concerned and mixed very thoroughly. (Erratic results were most often traced to incomplete mixing of the solutions.) The acid added in the stock indicator solution was allowed for in the final calculation of medium composition. The observed mean value of S' (the " Spekker " reading) for the solution is corrected for non-linear calibration (see below), giving the new value S. (The correction is almost negligible for $S' = 0{\cdot}2$—$0{\cdot}6$.) Then $[R^+] = 10^{-4}S/3{\cdot}01$. The quantity S/c is the specific colour intensity for the medium as a whole (as opposed to that for the cation), and should be a constant for a given medium, being proportional to the degree of ionisation of the indicator. Some specimen results are shown in Table II.

Medium Effect.—With simple basic indicators, ionising by proton uptake, a " medium effect " has sometimes been observed (Flexser, Hammett, and Dingwall, *J. Amer. Chem. Soc.*, 1935, **57**, 2103), because the wave-length of the absorption band of the coloured form of the indicator shifts with changing medium composition; this causes an apparent change of specific absorption with medium, if a fixed wave-length is used for all media. For the wave-length employed, the medium effect is negligible for the triarylcarbinol indicators. Table I shows that S/c is reasonably constant over a range of medium compositions in which ionisation is complete.

TABLE II.

Medium, H_2SO_4, %.	Indicator, 10^{-5} M.	S' (mean).	S.	$[R^+]$, 10^{-5} M.	[ROH], 10^{-5} M.	$\log \frac{[R^+]}{[ROH]}$.	$10^{-4}S/c$.
85·30	1·93	0·418 ± 0·02	0·418	1·39	0·54	0·414	2·16
	2·08	0·447 ± 0·04	0·448	1·49	0·59	0·402	2·15
	2·45	0·530 ± 0·01	0·534	1·77	0·68	0·414	2·17
83·20	3·26	0·287 ± 0·02	0·285	0·949	2·31	−0·386	0·874
	4·54	0·400 ± 0·01	0·400	1·33	3·21	−0·383	0·880
	5·33	0·481 ± 0·02	0·482	1·605	3·72	−0·366	0·903

Calibration.—Since the "Spekker" readings (S') are not necessarily directly proportional to the concentration of the absorbing material, calibration is effected by measuring values of S' for a series of different indicator concentrations (c) in a medium in which ionisation is complete. S'/c is plotted against S'. For indicator (I) the smoothed curve passes through the following points :

S'	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9
$10^{-4}S'/c$	3·02	3·02	3·01	2·99	2·98	2·96	2·93	2·87

This curve was used to correct the "Spekker" readings for indicator (I) in all media.

Instead of correcting the observed values to correspond to an extrapolated value at $S' = 0$, the value at $S' = 0{\cdot}4$ is taken as standard, since this is the region in which measurements are most accurate. The true value S/c for this medium is therefore taken as $3{\cdot}01 \times 10^4$; and the corrections necessary to convert the other smoothed values of S'/c to this figure can be calculated. From $S' = 0{\cdot}2$ to $S' = 0{\cdot}6$ they are less than 1%. After correction, all values of $10^{-4}S'/c$ used to construct the calibration curve lie between 2·98 and 3·04, with a mean of 3·01.

The calibration curve for indicator (III) was very similar to that for (I). For trinitrotriphenylcarbinol (IV) the calibration curve for 99·0% sulphuric acid passed through the points :

S'	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9
$10^{-4}S'/c$	3·21	3·26	3·31	3·35	3·36	3·36	3·36	3·36

The standard value for this medium was taken to be $S/c = 3{\cdot}36 \times 10^4$.

Stability of Indicators.—Anomalous light absorption caused by chemical instability of the stock indicator solutions is negligible for indicators (I) and (III) over one day [there was a 7% error in S/c after the stock solution of (I) had been kept for 7 days at 25°]. Indicator (IV) is less stable, as was found by Westheimer and Kharasch; but stock solutions in 99% sulphuric acid are stable for 8 hours, if kept at 0°. For all indicators stability is greater in 99% than in 91% sulphuric acid. The diluted solutions used for the measurements always appeared to be quite stable over the period of observation. For measurements at small ionisation of (IV), the "Spekker" readings were taken on solutions prepared directly, without an intervening stock solution.

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