560. *Aromatic Arylalkylation. Part I. The Triphenylmethylation of* o-*Cresol in Sulphuric Acid–Acetic Acid.*

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The reaction between triphenylmethanol and *o*-cresol to form 4-hydroxy-3-methylphenyltriphenylmethane in sulphuric–acetic acid has been studied. Rates of reaction and the extent of ionisation of the alcohol over a wide range of media indicate reaction through the electrophilic attack by the Ph_3C^+ ion: $Ph_3C^+ + C_6H_4Me{\cdot}OH \longrightarrow Ph_3C{\cdot}C_6H_3Me{\cdot}OH + H^+$. The constants of the Arrhenius equation have been evaluated.

The nature of the coloured compound which is immediately formed on mixing of the reactants is discussed.

STUDIES of absorption spectra, conductivity, freezing-point depression, and salt formation have shown that triphenylmethanol is readily converted into the triphenylmethyl ion in strong acids.[1] The possibility arises that in such media this ion might be an effective electrophilic substituting reagent and this appears to be the case in the reaction between triphenylmethanol and phenols in sulphuric–acetic acid (1 : 6 v/v) first reported by Baeyer and Villiger.[2] They found that phenol formed *p*-hydroxyphenyltriphenylmethane, and anisole formed *p*-methoxyphenyltriphenylmethane. Baeyer[3] also found that tetra-arylmethanes were obtained, with hydrogen chloride, from solutions of triphenylmethyl chloride in various phenols, heat sometimes being needed for reaction; if potassium phenoxide was used substitution in the nucleus did not occur and a triphenylmethylphenyl ether was formed, but it was later shown by Gomberg and Kamm[4] that in the presence of acid the sole product was *p*-hydroxyphenyltriphenylmethane. These workers also found that the action of sulphuric acid in the Baeyer–Villiger reaction was purely catalytic and that it could be reduced to a very small concentration or replaced by hydrochloric acid.

Boyd and Hardy[5] studied the reaction of many phenols with triphenylmethanol in acetic acid containing 10—20% of sulphuric acid. The phenols fell into three groups, (i) those giving a tetraphenylmethane derivative, (ii) those reducing triphenylmethanol to triphenylmethane, and (iii) those which did not react. Phenols of groups (i) and (ii) produced a deep brown colour when added to the yellow solution of triphenylmethanol in the sulphuric–acetic acid, and Hardy[5] proposed that for these the first step was 1 : 4 addition of the ions of triphenylmethyl hydrogen sulphate followed by breakdown of the resulting quinonoid complex to a hydroxyphenyltriphenylmethane (group i) or triphenyl methane (group ii).

Hart and Cassis[6] recently found reaction of triphenylmethyl chloride and phenol in dilute *o*-dichlorobenzene solution to be autocatalytic, the hydrochloric acid liberated acting as a catalyst. They concluded that the acid facilitated the ionisation of the chloride to the triphenylmethyl ion and represented the reaction as direct triphenylmethylation of the aromatic nucleus by the ion. Since there could be little doubt that the same ion is present in a solution of triphenylmethanol in sulphuric–acetic acid and that the extent of its formation varies with the acidity, it was decided to find whether the rate of triphenylmethylation in this medium could be directly correlated with the degree of ionisation of the alcohol.

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[1] Gomberg, *Ber.*, 1902, **35**, 1837; Walden, *ibid.*, p. 2018; Hantzsch, *Ber.*, 1921, **54**, 2573; Hammett and Deyrup, *J. Amer. Chem. Soc.*, 1933, **55**, 1900; Gillespie and Wasif, *J.*, 1953, 221.

[2] Baeyer and Villiger, *Ber.*, 1902, **35**, 3013.

[3] Baeyer, *Ber.*, 1909, **42**, 2624.

[4] Gomberg and Kamm, *J. Amer. Chem. Soc.*, 1917, **39**, 2009.

[5] Boyd and Hardy, *J.*, 1928, 630; Hardy, *J.*, 1929, 1000.

[6] Hart and Cassis, *J. Amer. Chem. Soc.*, 1954, **76**, 1634.

EXPERIMENTAL

Initial Experiments.—The limited solubility of the tetraphenylmethane product from phenol in the media employed led to the choice of *o*-cresol for the kinetic work. This reaction is known [7] to give 4-hydroxy-3-methylphenyltriphenylmethane. At higher acidities, it was found that some interaction occurred between the medium and *o*-cresol. Quantitative bromination of the product, based on Francis and Hill's method,[8] showed that a monosubstituted derivative had been formed, probably 4-hydroxy-3-methylbenzenesulphonic acid. To limit this and extend the range of sulphuric–acetic media, all media were prepared with a water content of 5% w/w. Provided the initial concentrations of the reactants were not greater than 0·1M, no precipitation of the tetraphenylmethane product occurred. The reported reversibility [5] of the reaction was found to be negligible in media containing 5% of water, the extent of breakdown of the product in an anhydrous media containing 30% of sulphuric acid being only 3·4% after 5 hr. at 55°.

Media and Reagents.—Acetic acid was purified by Orton and Bradfield's method; [9] no sample was obtained by this method with a m. p. lower than 16·5°. B.D.H. "AnalaR" sulphuric acid was used as supplied. B.D.H. *o*-cresol was distilled three times at atmospheric pressure before use (b. p. 195°); triphenylmethanol was recrystallised from alcohol (m. p. 160—162°). Media for kinetic experiments were made up by weight and all figures quoted are for % by wt. The water content was maintained in the range 4·9—5·1%.

Triphenylcarbonium-ion Spectrum.—The spectrum of this ion is well-known.[1, 10] In sulphuric–acetic acid it has the usual broad double-peaked band with maxima at 4080 and 4320 Å ($\varepsilon_{max.}$ *ca.* 35,000). Where there is complete ionisation the extinction coefficient at the maxima changes by only 2% between 18° and 55°. At 4320 Å, the extinction coefficients of *o*-cresol (ε 0·26) and of 4-hydroxy-3-methylphenyltriphenylmethane (ε 0·4) are negligible.

Solutions containing triphenylmethanol were analysed with a Hilger Spekker photoelectric absorptiometer, having a mercury-lamp light source and a filter to transmit a narrow band at *ca.* 4350 Å. Samples (1 ml.) of the mixture were always diluted between 625 and 5000 times with a stock solution containing 1 : 3 sulphuric–acetic acid. Complete ionisation of the triphenylmethanol occurred in this solution, in agreement with Gold and Hawes's observation [10] that ionisation is complete in the anhydrous mixture, 16 : 84 sulphuric–acetic acid. The composition of the stock solution was not critical as the same analytical results were obtained, within 1—2%, when the sulphuric acid content was varied over the range 20—30%.

A sample removed from the diluted solution for measurement in the absorptiometer gave a lower reading if the solution had been kept for some time after shaking than if it had been removed immediately. This suggested that moisture had been absorbed at the surface of the solution in the stoppered flask. The error was avoided by pouring away the first few ml. of solution before transference to the absorption cell.

Kinetic Measurements.—These were carried out at 25° and at 55°. The solutions of triphenylmethanol and *o*-cresol were made up separately in the particular medium at the given temperatures. Triphenylmethanol sometimes dissolved rather slowly and had to be heated to 80—100°. High temperatures and prolonged heating were avoided as a slow reaction then occurred. An appropriate sample, usually 20 ml., of the triphenylmethanol solution was pipetted into a 100 ml. flask, and the flask stoppered and returned to the thermostat. To start the reaction the required volume of the *o*-cresol solution was run in from a pipette, zero time corresponding to the end of the free flow of the solution. Six 1 ml. samples were removed at suitable times. In each case the reaction was stopped by running the solution into 20—40 ml. of the 1 : 3 sulphuric–acetic acid stock solution, and the resulting solution made up to 25 ml. or 50 ml. 1 ml. of this solution was diluted 25—100 times and then measured in the absorptiometer, 1 cm. cells and a control of the stock diluent solution being used. Two separate samples of each solution were measured and three readings were taken on each sample. The corresponding value of the triphenylmethanol concentration was read off from the previously prepared standard curve. Rates were measured over the range of media containing from 5% to 40% of H_2SO_4. Excellent second-order rate constants were obtained below 25% sulphuric acid

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[7] Iddles, French, and Minckler, *J. Amer. Chem. Soc.*, 1940, **62**, 2757.

[8] Francis and Hill, *ibid.*, 1924, **46**, 2498; Francis, Hill, and Johnston, *ibid.*, 1925, **47**, 2211; Francis and Hill, *Ind. Eng. Chem. Analyt.*, 1941, **13**, 357.

[9] Orton and Bradfield, *J.*, 1927, 983.

[10] Anderson, *J. Amer. Chem. Soc.*, 1928, **50**, 208; Gold and Hawes, *J.*, 1951, 2102.

(Fig. 1). The rate of reaction was unchanged when the glass surface was increased by means of glass balls.

Interaction of the Medium with o-*Cresol.*—Reaction of sulphuric acid in the medium with *o*-cresol in the absence of the triphenylmethanol was followed by the bromination method.[8] Aliquot parts of the solution, at appropriate intervals, were run into dilute sulphuric acid and treated with a slight excess of standard bromate–bromide solution, and the unconsumed bromine estimated by addition of potassium iodide and titration of the iodine liberated with sodium thiosulphate solution. Analyses of standard *o*-cresol solutions by this method were correct within 1%.

Ionisation of Triphenylmethanol in Sulphuric–Acetic Acid Media.—The extent of ionisation of triphenylmethanol was obtained by plotting the ultraviolet absorption spectrum for each mixture over the range 3600—4600 Å with a Hilger "Uvispek" Spectrophotometer. The "specific colour intensity," *S*, at a given wavelength is defined as (log I_0/I)/(concn. of $Ph_3C{\cdot}OH$). The % ionisation in any particular medium is obtained from the ratio of the specific colour intensity at a selected wavelength to that at the same wavelength in a medium containing 3 : 7 sulphuric–acetic acid in which triphenylmethanol is completely ionised. Values obtained at the two maxima (at 4080 and 4320 Å) gave identical % ionisation. During measurements the absorption cells were kept in a constant-temperature jacket (±1°). Measurements were carried out at 25° and at 55° over the range 5—22% of sulphuric acid.

FIG. 1.

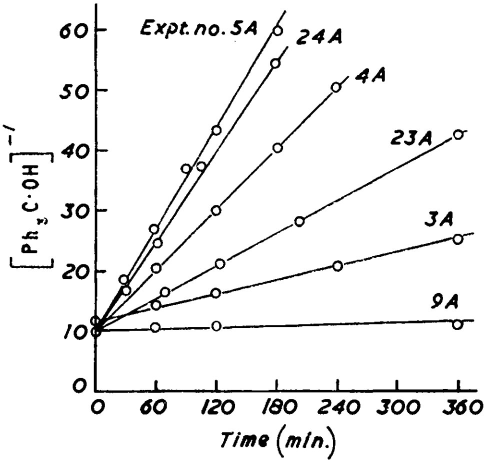
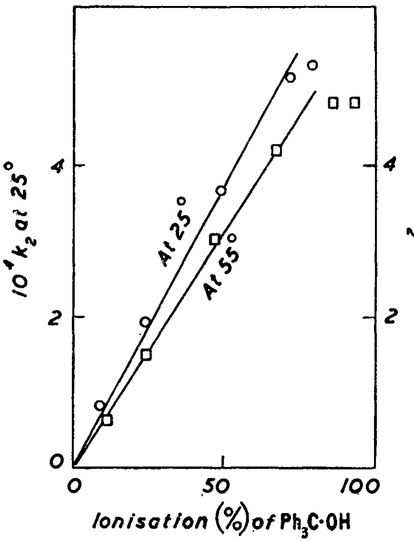


FIG. 2.



Preparation of 3 : 5-*Dideutero*-o-*cresol.*—Deuteration of *o*-toluidine to 3 : 5-dideutero-*o*-toluidine was carried out by repeated treatment of the amine hydrochloride with heavy water at 100°, as in the method used for aniline.[11] Dideuterocresol was obtained from the product by diazotisation and separated by steam-distillation. We are greatly indebted to Dr. D. H. Whiffen of the University of Birmingham for infrared analyses of samples of the deuterocresol which indicated its purity and the rapidity of its exchange reaction in sulphuric–acetic acid.

RESULTS AND DISCUSSION

Kinetics of Triphenylmethylation of o-*Cresol.*—The reaction of triphenylmethanol with *o*-cresol was followed over a range of media containing 0—40% w/w of sulphuric acid in acetic acid, all media containing 5% of water. Over the range 0—22·5% sulphuric acid, the kinetic results fitted the equation :

$$-d[Ph_3C{\cdot}OH]/dt = k_2[Ph_3C{\cdot}OH][o\text{-cresol}] \quad . \quad . \quad . \quad . \quad . \quad (1)$$

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[11] Best and Wilson, *J.*, 1946, 239.

the reaction always being followed up to 70—90% conversion of the triphenylmethanol. The results for 55° and 25° are shown in Tables 1 and 3. The rate equation is obeyed for a ten-fold change in the initial concentration of either reactant as shown in Table 2. In media containing 25% or more of sulphuric acid the rate equation applies only to the initial stages, a strong deceleration setting in. Triphenylmethanol was stable in media containing up to 40% of sulphuric acid but interaction of the medium with *o*-cresol was marked in media containing more than 25% of sulphuric acid. The attack on the *o*-cresol was followed by a parallel investigation of its rate of disappearance in each medium in the absence of triphenylmethanol. Comparison with the rate of triphenylmethylation was made by calculation of the time of half-change for both reactions, the results of which

TABLE 1. *Variation of k_2 with medium composition for the triphenylmethylation of* o-*cresol at* 55°.

Initial [$Ph_3C{\cdot}OH$] = [*o*-cresol] = 0·1M.

Expt. no.	Medium (% by wt.) H_2SO_4	H_2O	AcOH	$10^4 k_2$ (l. mole^{-1} sec.$^{-1}$)	$t_{\frac{1}{2}}$ for triphenylmethylation (min.)	t for attack of medium on cresol (min.)
8*A*	0·0	5·1	95·0	0	—	—
8*B*	0·0	5·1	95·0	0	—	—
9*A*	4·9	5·2	89·9	0·521	3400	—
9*B*	4·9	5·2	89·9	0·516	3400	—
3*A*	10·0	5·1	84·9	6·47	275	—
3*B*	10·0	5·1	84·9	6·53	275	—
23*A*	12·4	5·0	82·7	15·1	112	—
23*B*	12·4	5·0	82·7	15·2	112	—
4*A*	15·0	5·1	80·0	29·5	60	>1500
4*B*	15·0	5·1	80·0	30·1	60	>1500
24*A*	17·2	4·9	77·9	41·8	40	—
24*B*	17·2	4·9	77·9	41·1	40	—
5*A*	20·1	5·1	74·9	47·6	36	1056
5*B*	20·1	5·1	74·9	48·6	36	1056
11*A*	22·4	5·3	72·4	48·3	35	—
11*B*	22·4	5·3	72·4	48·1	35	—
6*A*	25·0	5·1	70·0	46·4	36	496
6*B*	25·0	5·1	70·0	46·6	36	496
7*B*	29·7	5·1	65·3	35·6	42	271
7*B*	29·7	5·1	65·3	36·4	45	271
10*A*	34·5	5·0	60·5	25·0	120	123
10*B*	34·5	5·0	60·5	23·6	130	123
12*A*	39·8	5·2	55·0	17·2	180	68
12*B*	39·8	5·2	55·0	17·2	180	68

In media containing more than 25% of H_2SO_4 only the results for the initial 20% reaction could be considered for the calculation of k_2. The reaction in 39·8% H_2SO_4 appeared to stop at about 62% conversion.

TABLE 2. *Effect on k_2 of change of initial concentrations of the reactants.*

Temp. 55°. 21% H_2SO_4, 5·2% H_2O, 73·8% AcOH.

Expt. no.	Initial concn. (g. mole l.$^{-1}$) $Ph_3C{\cdot}OH$	$C_6H_4Me{\cdot}OH$	10^4k_2 (l. mole^{-1} sec.$^{-1}$)	Expt. no.	Initial concn. (g. mole l.$^{-1}$) $Ph_3C{\cdot}OH$	$C_6H_4Me{\cdot}OH$	10^4k_2 (l. mole^{-1} sec.$^{-1}$)
13*A*	0·0807	0·0795	48·6	15*B*	0·0202	0·0793	47·8
13*B*	0·0807	0·0798	47·2	16*A*	0·0803	0·2006	47·8
14*B*	0·0799	0·0197	47·2	16*B*	0·0802	0·2006	46·9
14*C*	0·0793	0·0191	47·2	17*A*	0·2002	0·0304	47·8
15*A*	0·0200	0·0815	48·3	17*B*	0·2002	0·0301	47·2

TABLE 3. *Variation of k_2 with medium composition at* 25°.

Initial [$Ph_3C{\cdot}OH$] = 0·025M, [*o*-cresol] = 0·1M.

Expt. no.	Medium (% by wt.) H_2SO_4	H_2O	AcOH	10^4k_2 (l. mole^{-1} sec.$^{-1}$)	Expt. no.	Medium (% by wt.) H_2SO_4	H_2O	AcOH	10^4k_2 (l. mole^{-1} sec.$^{-1}$)
25*A*	21·0	5·2	73·9	5·33	26*B*	17·2	4·9	77·9	3·66
25*B*	21·0	5·2	73·9	5·33	28	14·7	5·0	80·3	1·93
27	19·6	5·1	75·3	5·17	29	12·4	5·0	82·7	0·81
26*A*	17·2	4·9	77·9	3·66	30	0·0	5·1	95·0	0·00

are shown in Table 1. It can be seen that this side reaction is negligible in media containing less than 25% of sulphuric acid.

Correlation of Rate Constant and the Ionisation of Triphenylmethanol.—No reaction was observed in a medium which did not contain sulphuric acid, indicating complete lack of reactivity. If the reaction is bimolecular between the triphenylmethyl ion and *o*-cresol the rate of reaction will be given by:

$$\text{Rate} = k_0[\text{Ph}_3\text{C}^+][o\text{-cresol}] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where k_0, the theoretical rate constant, is independent of the medium. It follows from (1) and (2) that

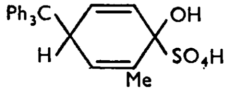
$$k_2 = k_0[\text{Ph}_3\text{C}^+]/[\text{Ph}_3\text{C·OH}] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

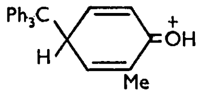
Some values of the % ionisation of triphenylmethanol were directly determined for media in which k_2 had been measured; where they were not directly obtained, the values were read from a plot of the ionisation results given in Table 4 against composition of the medium. The test of equation (3) at 25° and at 55° is shown in Fig. 2. A straight-line relation between k_2 and % ionisation is evident at both temperatures up to 70% ionisation. The failure of the rate constant to continue to rise with increasing formation of the triphenylmethyl ion above this point corresponds to the more strongly acid media containing 20—25% of sulphuric acid. Ionisation of triphenylmethanol is virtually complete in 25% sulphuric acid and its variation with medium strength is normal. The lack of correlation in this range appears therefore to be associated with the *o*-cresol, but it cannot be attributed to chemical attack of the medium on the *o*-cresol as the results in Table 1 show that this is negligible in media having less than 25% of sulphuric acid. A significant fact is that in both the 20% and the 22·4% sulphuric acid the rate equation is followed normally over 80—90% of the triphenylmethylation, as in media of lower acidity, whereas in media above 25% sulphuric acid the rate equation is only followed for about 20% of the reaction. The explanation may be appreciable formation of the conjugate acid of *o*-cresol in the range 20—25% sulphuric acid. The cation $CH_3{\cdot}C_6H_4{\cdot}OH_2^+$ would probably not react with the triphenylmethyl ion, and consequently the experimental rate constant k_2 would be reduced in direct proportion to the extent of formation of this ion.

TABLE 4. *Ionisation of triphenylmethanol in sulphuric–acetic acid.*

$[\text{Ph}_3\text{C·OH}] \sim 10^{-5}\text{M}$.

Medium (% by wt.)			Ionisation (%)		Medium (% by wt.)			Ionisation (%)	
H_2SO_4	H_2O	AcOH	at 55°	at 25°	H_2SO_4	H_2O	AcOH	at 55°	at 25°
5·0	5·0	90·0	0·718	0·117	17·2	4·9	77·9	66·9	49·5
9·9	5·0	85·1	9·02	2·41	19·6	5·1	75·3	83·6	71·4
12·4	5·0	82·7	23·2	9·07	22·2	5·0	72·7	92·2	85·0
14·7	5·0	80·3	44·9	23·9					

(I)




(II)

Formation of the Coloured Intermediate.—The immediate development of a deep brown colour on the addition of certain phenols, including *o*-cresol, to a solution of triphenylmethanol in sulphuric–acetic acid was discussed by Hardy.[5] Since the colour change appeared only with those phenols which either yield tetraphenylmethane derivatives or reduce the alcohol to triphenylmethane and not for completely unreactive phenols, Hardy suggested that it indicated the formation of a quinonoid intermediate which for *o*-cresol would be (I), this later losing a molecule of sulphuric acid to give 4-hydroxy-3-methylphenyltriphenylmethane. Baeyer[3] had previously observed that triphenylmethyl chloride gave an intense brown colour in phenol, *m*-cresol, and *p*-cresol, a less intense colour in *o*-cresol, but none in guaiacol, thymol, trichlorophenol, or some other deactivated phenols unless stannic chloride was added. All solutions in which a colour was obtained gave off hydrogen chloride when kept or heated. As the above reactions can now be regarded as taking place through electrophilic attack by the triphenylmethyl ion formed from either the alcohol or the chloride, a more correct representation of the intermediate would be (II). However it is unlikely that structure (II) would be the deep brown intermediate since if the triphenylmethyl ion formed a sp^3-hybridised bond with a carbon atom of the ring as shown, with the predominating resonance structure of the product having the positive charge on the oxygen atom, the electrons should be less mobile. Further, this structure is similar to the usual representation of the transition complex for electrophilic aromatic substitution which is momentarily formed by the relatively small fraction of molecules of high energy content and would be expected to lose a proton to form the product or break down to the reactant molecules almost instantaneously. The fact that the intense brown colour changes on dilution into the yellow colour of the triphenylmethyl ion strongly suggests that it is a π-bonded molecular complex between the triphenylmethyl ion and *o*-cresol. This complex could proceed through (II) and proton-elimination to the product. A study of this complex and others similarly formed is being undertaken.

An attempt was made to discover whether there was a hydrogen isotope effect in the reaction by studying the triphenylation of 3 : 5-dideutero-2-cresol under the same conditions. This however could not be achieved as the deuterocresol compound exchanged its deuterium atoms for hydrogen very rapidly in the acid media used.

The Constants of the Arrhenius Equation.—The true rate constants for the triphenylation reaction at 25° and 55° represented by k_0 in equation (3), evaluated from the slopes of Fig. 2, are $7{\cdot}35 \times 10^{-4}$ and $6{\cdot}16 \times 10^{-3}$ l. mole^{-1} sec.$^{-1}$ respectively which lead to the Arrhenius equation $k = 1{\cdot}04 \times 10^7 \exp(-13{,}480/\boldsymbol{R}T)$ (l. mole^{-1} sec.$^{-1}$). The low value of the energy of activation (13·480 kcal. mole^{-1}) is in accordance with the reactive character expected of the triphenylmethyl ion, while the steric limitations imposed by the attachment of three phenyl groups to the central carbon atom would be expected to reduce the non-exponential term appreciably from the theoretical value of *ca.* 10^{11}.

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