387. *Aromatic Alkylation. Part I.* The Kinetics of the Acid-catalysed Aralkylation by Diarylmethanols in Acetic Acid Solution.*

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The rate of formation of triphenylmethane derivatives by the action of diphenylmethanol on mesitylene and anisole and of 4 : 4′-dichlorodiphenylmethanol on mesitylene has been studied at 25° in a series of sulphuric acid–acetic acid mixtures with and without the deliberate addition of small amounts of water. In parallel with the kinetic measurements, the ionisation of more basic methoxydiphenylmethanols and of 4 : 4′ : 4″-tribromotriphenylmethanol in these media was examined spectrophotometrically. The kinetic orders of the reactions and the close agreement between the influence of the medium on indicator ionisation ratios and reaction velocities indicate that all the reactions studied involve a bimolecular attack of the rapidly formed diphenylcarbonium ion on the aromatic compound. Deuterium labelling at the seat of substitution does not affect the reaction velocity.

The theory of ionisation equilibria of alcohols in this solvent system is given, account being taken of the simultaneous esterification of alcohols by acetic acid. The results suggest that diphenylmethanols are appreciably esterified, whereas triphenylmethanols are not. The esterification equilibrium is established rapidly in the presence of sulphuric acid.

WESTHEIMER and KHARASCH [1] showed that the relationship between the velocity of an aromatic substitution in a series of acid media and the ionisation of primary and secondary bases in the same media could be used to identify the nature of the molecular entity responsible for attack on the aromatic molecule. Westheimer and Kharasch's study of nitration was extended,[2] especially by the late Prof. Gwyn Williams and his pupils, and the principle of the method formulated more precisely [3,4] by the definition of the acidity function J_0.

A similar approach has now been made to aromatic alkylation under acidic conditions. Although investigated kinetically earlier,[5] the mechanism of aromatic alkylation, under the influence of both acid and metal chloride (Friedel–Crafts) catalysts, has been inferred largely from more indirect observations, such as the nature of reaction products.[6] These studies have led to the suggestion [7] that the alkylation step of the mechanism is sometimes a bimolecular displacement reaction by the aromatic compound on an intermediate formed from the alkylating agent and the catalyst. On the other hand, it has been shown and is generally accepted that triphenylmethyl chloride acts as a triphenylmethylating agent by virtue of its ability to give rise to carbonium ions which are the effective substituting species.[8] A distinction between these two alternatives in other cases is possible by the method now reported.

First, we examined diarylmethyl compounds (such as diphenylmethanol) in acetic acid as alkylating agents towards anisole and other reactive aromatic compounds. This choice

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* A preliminary summary of the present group of papers appeared in *Chem. and Ind.*, 1956, 741.

[1] Westheimer and Kharasch, *J. Amer. Chem. Soc.*, 1946, **68**, 1871.

[2] Lowen, Murray, and Williams, *J.*, 1950, 3318; Bonner, Bowyer, and Williams, *J.*, 1952, 3274; Deno and Stein, *J. Amer. Chem. Soc.*, 1956, **78**, 578.

[3] Gold and Hawes, *J.*, 1951, 2102.

[4] Gold, *J.*, 1955, 1263.

[5] *E.g.*, Olivier and Berger, *Rec. Trav. chim.*, 1926, **45**, 710; Brown and Grayson, *J. Amer. Chem. Soc.*, 1953, **75**, 6285; Lebedev, *J. Gen. Chem. U.S.S.R.*, 1954, **24**, 673; Nenitzesco, Tzitzeica, and Ioan, *Bull. Soc. chim. France*, 1955, 1272, 1279; Jungk, Smoot, and Brown, *J. Amer. Chem. Soc.*, 1956, **78**, 2185.

[6] Baddeley, *Quart. Rev.*, 1954, **8**, 355 (review).

[7] Brown and Nelson, *J. Amer. Chem. Soc.*, 1953, **75**, 6292; Brown, Pearsall, Eddy, Wallace, Grayson, and Nelson, *Ind. Eng. Chem.*, 1953, **45**, 1462; Schmerling, *ibid.*, p. 1447.

[8] Hart and Cassis, *J. Amer. Chem. Soc.*, 1954, **76**, 1634; see also Bonner, Clayton, and Williams, *J.*, 1957, 2867.

of compounds and conditions naturally restricts the scope of the conclusions reached concerning the mechanism of the Friedel–Crafts reaction. However, it was known that these conditions were particularly favourable to aralkylation in high yield [9] and without complications from olefin formation or rearrangements. Furthermore, it appears that reaction is essentially limited to attack at the *para*-position in compounds like toluene [9] or anisole.

A complication due to the use of acetic acid as solvent is the possibility of esterification of the alkylating agent by the solvent, *i.e.*,

$$\mathrm{R{\cdot}OH + HOAc \rightleftharpoons R{\cdot}OAc + H_2O} \quad . \; . \; . \; . \; . \quad (1)$$

This reaction appears to occur only to an insignificant extent in the case of solutions of triarylmethanols, as is indicated by measurements of the ionisation of triphenylmethanol, and is to be expected from the known difficulty of esterifying these alcohols. However, some esterification is known to occur with other alcohols, including 4 : 4′-dimethoxydiphenylmethanol,[10] in acetic acid solution, and the analysis of experimental results on diarylmethyl compounds must take this reaction into account.

The present results relate to aralkylations with sulphuric acid as catalyst and the effect of addition of water upon the reaction velocity, and to related indicator measurements in the presence of these substances. In Part II the same method is applied to aralkylation under the influence of metal a halide catalyst (zinc chloride).

EXPERIMENTAL

Materials.—Acetic acid (" AnalaR ") was dried in large batches by addition of benzene and separation of the water–benzene azeotrope and excess of benzene by fractional distillation.[11] The absence of benzene from the anhydrous acetic acid distillate (f. p. $\not<$16·60°) was checked by use of the formalin–sulphuric acid reagent.[12] Anhydrous sulphuric acid was prepared by addition of sulphur dioxide-free oleum to 98% acid until the maximum freezing point was reached.

Diphenylmethanol. The commercial sample was purified by passage of a benzene solution through an activated alumina column and subsequent crystallisations from light petroleum (b. p. 60—80°); m. p. 67—68°. Its acetate was prepared by means of acetic anhydride in pyridine. After benzene extraction, washing, and drying, the solution of the product in light petroleum (b. p. 60—80°) was passed through an activated alumina column. Colourless crystals were obtained on removal of the solvent from the effluent. Traces of solvent were removed from the crystals of diphenylmethyl acetate (m. p. 41°) by vacuum drying.

4 : 4′-Dimethoxydiphenylmethanol was prepared by two standard methods: (*a*) by zinc-dust reduction of 4 : 4′-dimethoxybenzophenone (Eastman-Kodak Co.), or (*b*) by the reaction between the Grignard reagent of *p*-bromoanisole and anisaldehyde. In either case the product was crystallised from ether–light petroleum (1 : 1), giving silky colourless needles, m. p. 69° (lit.,[13] m. p. 72°). Repeated crystallisations failed to raise the m. p. of the product from either method of preparation.

4-Methoxydiphenylmethanol (m. p. 66—67°) was prepared in 73% yield from anisaldehyde and the Grignard reagent of bromobenzene.

4 : 4′-Dichlorodiphenylmethanol was prepared by zinc-dust reduction of 4 : 4′-dichlorobenzophenone (m. p. 91·5°; lit.,[14] m. p. 91·5°).

A pure sample (m. p. 131°) of 4 : 4′ : 4″-tribromotriphenylmethanol was kindly provided by Dr. G. L. Davies, the specimen of (−)-4-chlorodiphenylmethanol by Dr. A. G. Davies, and the specimen of [4-^{2}H]anisole by Dr. D. P. N. Satchell.

Mesitylene and anisole used in kinetic experiments were fractionally distilled commercial samples.

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[9] Kundiger and Ovist, *J. Amer. Chem. Soc.*, 1954, **76**, 2501.

[10] Balfe, Kenyon, and Thain, *J.*, 1952, 790.

[11] Noyce and Castelfranco, *J. Amer. Chem. Soc.*, 1951, **73**, 4482.

[12] Feigl, " Spot Tests," Vol. II, Elsevier, Amsterdam, 1954, p. 104.

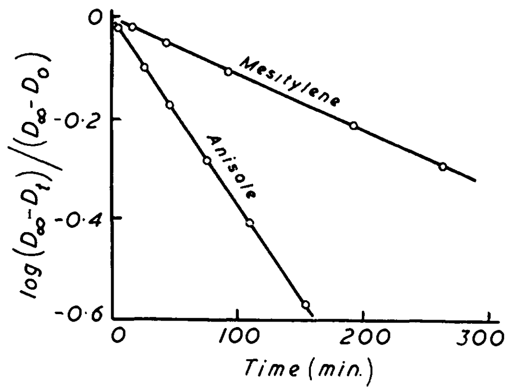
[13] Schnackenberg and Scholl, *Ber.*, 1903, **36**, 655.

[14] Norris and Tibbetts, *J. Amer. Chem. Soc.*, 1920, **42**, 209.

Reaction Products.—Each reaction studied kinetically is known and/or has been found to yield a single product only. Specimens of these products were prepared on a larger scale in almost quantitative yield by use of a method similar to that described by Kundiger and Ovist,[9] the conditions for which closely resemble those of the kinetic experiments. The procedure is exemplified by the preparation of 4 : 4′-dichloro-2″ : 4″ : 6″-trimethyltriphenylmethane.

4 : 4′-Dichloro-2″ : 4″ : 6″-trimethyltriphenylmethane. 4 : 4′-Dichlorodiphenylmethanol (2·0 g.) was added to a solution of mesitylene (12 g., tenfold excess) in a mixture of sulphuric and acetic acid (1 : 5 v/v; 150 ml.). The yellow solution rapidly reddened and was stored at room temperature for 8 days. The mixture was then poured into cold water (*ca.* 1 l.). Sodium carbonate (80 g.) was added, and the excess of mesitylene steam-distilled out of the resulting heterogeneous mixture. The residue was cooled and extracted with ether (2 × 100 ml.). Ether was distilled from the combined ethereal extracts, and some benzene was then added and distilled off the residue to dry it. Removal of this solvent left a brown oil (3·3 g.) which was dissolved in light petroleum (b. p. 80—100°) and passed through an 8 in. column of activated alumina. After removal of the solvent the product was crystallised from ethanol (pale yellow needles, 2·8 g.; 98% yield; m. p. 112—113°). Repeated crystallisations from ethanol gave colourless needles of 4 : *4′-dichloro-2″* : 4″ : *6″-trimethyltriphenylmethane,* m. p. 114—115° (Found: C, 74·4; H, 5·6; Cl, 20·0. $C_{22}H_{20}Cl_2$ requires C, 74·4; H, 5·7; Cl, 20·0%).

FIG. 1.



4-Methoxytriphenylmethane (m. p. 62—63°; lit.,[15] m. p. 61°, 64·5°, 66—67°) and 2 : 4 : 6-trimethyltriphenylmethane (m. p. 119·5—120°, lit.,[9] m. p. 119—119·5°) were similarly prepared in yields of over 90%.

Ultraviolet Absorption Spectra.—Measurements at room temperature on a Beckman Model DU quartz spectrophotometer were used for all reactants and products, for the evaluation of ionisation ratios, and for following the progress of reactions.

Ionisation Ratios.—The ratio of ionised to un-ionised form, $I = [R^+]/([ROH]_{stoich} - [R^+])$, was determined in the acid mixtures by using as indicators 4 : 4′ : 4″-tribromotriphenylmethanol (I), 4 : 4′-dimethoxydiphenylmethanol (II), and 4-methoxydiphenylmethanol (III). Measurements were taken at a single wavelength at or near the maximum of the carbonium-ion absorption where absorption by the un-ionised form of the indicator was negligible. The results are summarised in Tables 1, 2, and 7. The last column in Tables 1 and 2 shows that, at constant concentration of water, the measurements are consistent with the result (Ref. 3, eqn.10)

$$\log I = -2H_0 + \text{constant}$$

Kinetic Measurements.—Samples of the reaction mixtures were withdrawn from the thermostatically controlled (25°) reaction vessel at intervals and diluted ten-fold to arrest reaction. The optical densities of the resulting solutions were measured at a suitable wavelength, chosen by reference to the absorption spectra of the pure reactants and products. In order to reduce

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[15] Bistrzycki and Herbst, *Ber.*, 1902, **35**, 3137; Kovache, *Ann. Chim.*, 1918, **10**, 201; Baeyer and Villiger, *Ber.*, 1903, **36**, 2790; Burton and Cheeseman, *J.*, 1953, 832.

the reactions to a first-order course, the aromatic compound alkylated was generally present in large (usually ten-fold) excess over the alkylating agent. The order of the reaction with respect to the aromatic compound was established by variation of this excess. Except for very slow runs, measurements were generally taken over the first 50—80% of reaction. Rate constants were evaluated graphically from plots of log $(D_\infty - D_t)$ against t, where D_∞ and D_t are the optical densities of the diluted samples after completion of the reaction and at a time t after starting the reaction, respectively. Specimen runs are illustrated in Fig. 1. The observed values of D_0 (the extrapolated optical density of the reaction mixture at zero time) and D_∞ agreed closely with values calculated from the previously determined spectra of the reactants and products in acetic acid. The second-order rate coefficients (k_2) tabulated in Tables 3, 4, 5, 8, and 9 were calculated from the first-order rate constants by dividing by the concentration of aromatic compound.

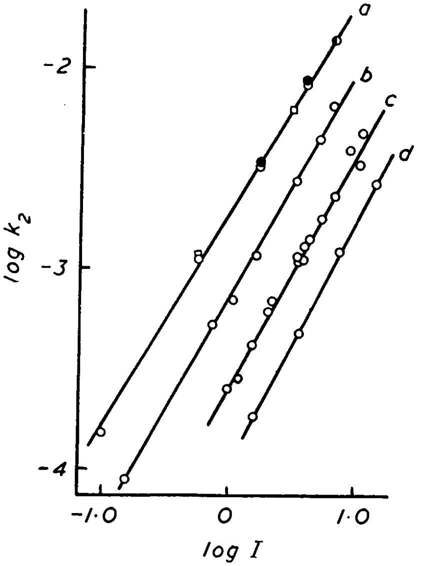

FIG. 2. *Correlation of aralkylation rates with ionisation ratios.*

a Circles: Diphenylmethanol–anisole (no H_2O).
Squares: Diphenylmethyl acetate–anisole (no H_2O).
Dots: Diphenylmethanol–[4-^{2}H]anisole (no H_2O).
b Diphenylmethanol–anisole (0·55M-H_2O).
c Diphenylmethanol–mesitylene (0·55M-H_2O).
d 4 : 4′-Diphenylmethanol–mesitylene (0·55M-H_2O).

TABLE 1. *Ionisation of* 4 : 4′-*dimethoxydiphenylmethanol* * (II) *in* H_2SO_4–AcOH.

No added water. Indicator concentration: $1{\cdot}615 \times 10^{-5}$M. Wavelength of measurements ($\lambda_{\text{max.}}$): 5040 Å. $\varepsilon_{R^+} = 1{\cdot}19_8 \times 10^5$.

H_2SO_4 (M)	ε †	log I	H_0 ‡	log $I + 2H_0$	H_2SO_4 (M)	ε †	log I	H_0 ‡	log $I + 2H_0$
0·317	11,210	−0·986	−2·29	−5·57	1·546	103,300	0·796	−3·30	−5·80
0·711	55,250	−0·068	−2·79	−5·51	1·910	112,600	1·192	−3·46	−5·73
1·143	89,800	0·476	−3·11	−5·74					

* The observed optical densities for this indicator did not change with time (cf. ref. 16).
† ε = extinction coefficient. ‡ Taken from ref. 17.

TABLE 2. *Ionisation of* 4 : 4′ : 4″-*tribromotriphenylmethanol* (I) *in* H_2SO_4–AcOH.

Water concentration low and constant, but unknown. Indicator concentration: 10^{-6}—10^{-4}M. Wavelength of measurements ($\lambda_{\text{max.}}$): 4720 Å. $\varepsilon_{R^+} = 91{,}700$.

H_2SO_4 (M)	ε	log I	H_0	log $I + 2H_0$	H_2SO_4 (M)	ε	log I	H_0	log $I + 2H_0$
0·632	874	−2·017	−2·71	−7·44	1·974	22,250	−0·494	−3·48	−7·45
1·017	3370	−1·419	−3·02	−7·46	2·609	45,500	−0·007	−3·77	−7·55
1·481	9350	−0·945	−3·28	−7·51					

The dependence of reaction rates upon the acidity of the medium was examined from graphs of log k_2 against the logarithm of the ionisation ratio (I) of one of the diphenylmethanol-type indicators (II or III) or against Hammett's acidity function H_0 (in the case of experiments at

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[16] Deno, Jaruzelski, and Schriesheim, *J. Amer. Chem. Soc.*, 1955, **77**, 3044.
[17] Paul and Long, *Chem. Rev.*, 1957, **57**, 1.

constant water concentration). In both cases, rectilinear plots were obtained. In view of the observed relationship between the ionisation ratio and H_0 (Tables 1 and 2) the two tests are not independent. Graphs of the first type are reproduced in Fig. 2 and the slopes obtained are summarised in Table 6.

The ionisation ratios used in some of the comparisons are interpolated values based on the data of Tables 1 and 2. Although the media used for some measurements differ from some of

TABLE 3. *Rate constants for the diphenylmethylation of mesitylene at 25°.*

Concn. of added water = 0·55M. $[Ph_2CH{\cdot}OH]_{initial} = 5 \times 10^{-3}$M. [M] = initial concn. of mesitylene. k_2 in sec.$^{-1}$ mole^{-1} l.

H_2SO_4 (M)	10^2 [M]	10^4k_2	H_2SO_4 (M)	10^2 [M]	10^4k_2	H_2SO_4 (M)	10^2 [M]	10^4k_2	H_2SO_4 (M)	10^2 [M]	10^4k_2
0·729	3·04	2·59	0·981	6·03	6·45	1·162	7·20	11·3	1·497	3·04	23·6
0·758	,,	2·92	0·981	7·53	6·36	1·233	3·04	11·3	1·660	,,	40·3
0·871	,,	4·26	1·008	3·01	7·08	1·238	,,	13·3	1·721	,,	33·8
0·981	3·01	6·20	1·160	,,	11·3	1·256	,,	14·5	1·760	,,	49·1
0·981	4·52	6·17	1·162	,,	11·2	1·358	,,	18·3			

TABLE 4. *Rate constants for the diphenylmethylation of anisole at 25°.*

$[Ph_2CH{\cdot}OH]_{initial} = 3 \times 10^{-3}$M; $[Anisole]_{initial} = 3 \times 10^{-2}$M. k_2 in sec.$^{-1}$ mole^{-1} l.

(*a*) No added water				(*b*) Concentration of added water = 0·55M			
H_2SO_4 (M)	10^4k_2	H_2SO_4 (M)	10^4k_2	H_2SO_4 (M)	10^4k_2	H_2SO_4 (M)	10^4k_2
0·306	1·53	1·225	82·7	0·377	0·90	1·149	28·0
0·612	11·2	1·478	140·7	0·671	5·33	1·349	45·2
0·919	32·7			0·772	7·10	1·470	65·8
				0·909	11·8		

TABLE 5. *Rate constants for the* 4 : 4′-*dichlorodiphenylmethylation of mesitylene at* 25°.

Concn. of added water = 0·55M. $[Diarylmethanol]_{initial}$ = 0·01M; $[mesitylene]_{initial}$ = 0·1M.

H_2SO_4 (M)	0·886	1·190	1·580	1·914
10^4k_2 (sec.$^{-1}$ mole^{-1} l.)	1·87	4·87	12·53	27·25

TABLE 6. *Dependence of reaction velocity upon acidity.*

ROH	ArH	[Added water] (M)	Table of results used	Slope (λ) of plot of log k_2 vs. log I *	Slope (λ) of plot of log k_2 vs. $-2H_0$	log k_2 at $H_0 = -3$
Diphenylmethanol	Mesitylene	0·55	3	1·18	1·06	−3·23
,,	Anisole	—	4 (*a*)	1·05	0·97	−2·36
,,	,,	0·55	4 (*b*)	1·11	1·07	−2·77
4 : 4′-Dichlorodiphenylmethanol	Mesitylene	0·55	5	1·24	1·14	−3·60

* For 4 : 4′-dimethoxydiphenylmethanol as indicator.

TABLE 7. *Influence of added water on the ionisation of* 4 : 4′ : 4″-*tribromotriphenylmethanol* (I) *and* 4-*methoxydiphenylmethanol* (III).

$[H_2SO_4]_{stoich.}$ = 1·428M. Indicator concentrations: ~10^{-5}M.

Added water (M)	0·0	0·28	0·55	1·11	2·78
log I for I	−0·07	−0·82	−1·22	−1·83	−3·17
log I for III	−2·53	−2·64	−2·75	−2·99	−3·67

TABLE 8. *Influence of added water on the diphenylmethylation of anisole at 25°.*

$[H_2SO_4]_{stoich.}$ = 1·428M. $[Ph_2CH{\cdot}OH]_{initial} = 3 \times 10^{-3}$M. $[Anisole]_{initial} = 3 \times 10^{-2}$M

Added water (M)	0·0	0·28	0·55	1·11	2·78
3 + log k_2	1·096	1·010	0·903	0·681	0·054
3 + log k_2 − log I * for I	1·17	1·83	2·12	2·51	3·22
3 + log k_2 − log I * for II	3·63	3·65	3·65	3·67	3·72

* Indicator results from Table 7.

TABLE 9. *Rate constants for diphenylmethylation of anisole by diphenylmethyl acetate.*

No added water. Temp.: 25°. $[Ph_2CH{\cdot}OAc]_{initial} = 3 \times 10^{-3}$M. $[Anisole]_{initial} = 3 \times 10^{-2}$M. k_2 in sec.$^{-1}$ mole^{-1} l.

H_2SO_4 (M)	10^4k_2	log I *	H_2SO_4 (M)	10^4k_2	log I *
0·612	11·6	−0·265	1·122	63·0	0·475

* Indicator ratios interpolated from results on 4 : 4′-dimethoxydiphenylmethanol (Table 1).

TABLE 10. *Diphenylmethylation of anisole and* [4-²H]*anisole at* 25°.

No added water. $[Ph_2CH{\cdot}OH]_{initial} = 3 \times 10^{-3}$M. $[Anisole]_{initial} = 3 \times 10^{-2}$M.

H_2SO_4 (M)		0·919	1·225	1·478
10^4k_2 for	anisole	33	83	141
	[4-²H]anisole	34	87	141

those used in the kinetic experiments in the (constant) amount of water present, this comparison is considered to be valid in view of the result [3] that, at different constant and low water concentrations, ionisation ratios depend upon the concentration of sulphuric acid in a fairly parallel way.

In the evaluation of the H_0 values of the media an allowance was made for the effect of water in reducing the acidity.[3, 11]

DISCUSSION

The acid-catalysed formation of a triarylmethane (ArX) by reaction between diphenylmethanol (XOH) and aromatic compound (ArH) is found to be of first order with respect to both (stoicheiometric) diphenylmethanol (Fig. 1) and aromatic compound (Table 3), *i.e.*,*

$$v = -\frac{d[XOH]_{stoich.}}{dt} = k_2[XOH]_{stoich.}[ArH] \quad . \quad . \quad . \quad . \quad . \quad (2)$$

It is further found that the catalytic effect of added sulphuric acid has the same form as the effect of the acid in promoting the ionisation of an indicator (ROH) of similar structure to that of the alkylating agent XOH. For the measurements now considered ROH differed from XOH only by the presence of one or two methoxy-groups in the 4 : 4′-positions of diphenylmethanol. If the coloured form of the indicator corresponds to the cation R^+, the parallelism between the kinetic and indicator measurements can be expressed in the form (see Fig. 2)

$$\log k_2 = \lambda \log I + \text{constant} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where the constant λ has a value close to unity (see Table 6). Inasmuch as the ionisation ratios I follow a solvent property (or " acidity function ") S in this medium, according to a defining relationship

$$S = \text{constant} - \log I \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

equation (3) can be stated as

$$\log k_2 = \text{constant} - \lambda S \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Hence, we conclude that the active form of the alkylating agent XOH is produced by an ionisation analogous to that of the indicator, that this active form is produced in a rapid pre-equilibrium, and that its equilibrium concentration is always low relative to that of the un-ionised form of the alkylating agent in solution.

In the absence of any esterification of the solutes ROH and XOH, the solvent property S is clearly identical with the acidity function J_0. However, the absence of esterification cannot be assumed, and it must be left open for the present to what extent the alcohol is converted into the acetate. It may, however, be assumed that the interconversion of alcohol and acetate is rapidly established. This conclusion follows from the reproducibility and stability of the indicator spectra, from the exactness of the rate law (2) (see Fig. 1),

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* Square brackets represent concentrations, and parentheses activities of the species mentioned.

and—most convincingly—from comparative alkylation measurements using diphenylmethanol and its acetate [Tables 4(*a*) and 9, and Fig. 2]. The agreement between the rates indicates that the alkylating agent is present in the same form in the two cases.

Interconversion of alcohol and acetate is rapid only when an acid catalyst is present. In the absence of catalyst the reaction is probably slow in most cases. Thus, we find that diphenylmethanol can be recovered unchanged from its solution in glacial acetic acid, and diphenylmethyl acetate can likewise be recovered from its solution. This is presumably due to the slowness of the production of diphenylcarbonium ions when the solution contains no catalyst. This result also agrees with our observation that the optical rotation of a solution of (—)-4-chlorodiphenylmethanol in glacial acetic acid remained unchanged for 43 hr. The same compound, at the same concentration (12·6 g./l.) in a 0·8M-solution of sulphuric acid in acetic acid, was completely racemised before the solution could be examined (*ca.* 10 min.).

The deductions from the kinetic and indicator measurements may be summarised in the reaction scheme

$$\left.\begin{matrix}\mathrm{XOH}\\ \mathrm{XOAc}\end{matrix}\right\} + \mathrm{H}^+ \rightleftharpoons \mathrm{X}^+ + \left.\begin{matrix}\mathrm{H_2O}\\ \mathrm{AcOH}\end{matrix}\right\} \text{(rapid pre-equilibrium)} \quad . \; . \; . \quad (6)$$

$$\mathrm{X}^+ + \mathrm{ArH} \longrightarrow \mathrm{ArX} + \mathrm{H}^+ \text{ (rate-controlling)} \quad . \; . \; . \; . \; . \quad (7)$$

The velocity of a reaction following this mechanism is given by

$$v = k[\mathrm{X}^+][\mathrm{ArH}]f_{\mathrm{X}^+}f_{\mathrm{ArH}}/f_{\ddagger} \quad . \; . \; . \; . \; . \; . \; . \quad (8)$$

where the f's are activity coefficients and $f_{\ddagger}$ relates to the transition state. Combining this with the empirical rate law (2), we obtain in logarithmic notation,

$$\log k_2 = \log k - \log\frac{[\mathrm{XOH}]_{\text{stoich.}}}{[\mathrm{X}^+]} + \log\frac{f_{\mathrm{X}^+}f_{\mathrm{ArH}}}{f_{\ddagger}} \quad . \; . \; . \; . \quad (9)$$

According to a suggestion by Hammett, activity-coefficient ratios, in which the substances which appear in the numerator contain the same chemical fragments as the (one) substance which appears in the denominator, may reasonably be expected to be constant.[18,19] The success of applications of the Zucker–Hammett hypothesis in studies of reaction mechanism can be rationalised in terms of this principle, the limitations of which are, however, not yet known with certainty. The ratio $f_{\mathrm{ArH}}.f_{\mathrm{X}^+}/f_{\ddagger}$ is of the required form since, according to the mechanism considered, the transition state is formed from ArH and X^+. We may therefore write

$$\log k_2 = \log k - \log\left([\mathrm{XOH}_{\text{stoich.}}]/[\mathrm{X}^+]\right) \quad . \; . \; . \; . \quad (10)$$

If the extent of the conversion into carbonium ions X^+ is small, the stoicheiometric concentration of XOH can be set equal to the sum of the actual concentrations of XOH and XOAc. The ratio $[\mathrm{X}^+]/[\mathrm{XOH}]_{\text{stoich.}}$ can now be related to the ionisation ratio of the indicator by considering the hypothetical equilibria

$$\mathrm{ROH} + \mathrm{X}^+ \rightleftharpoons \mathrm{R}^+ + \mathrm{XOH} \text{ (equilibrium constant } K_1) \quad . \; . \; . \quad (11)$$

$$\mathrm{ROAc} + \mathrm{X}^+ \rightleftharpoons \mathrm{R}^+ + \mathrm{XOAc} \text{ (equilibrium constant } K_2) \quad . \; . \quad (12)$$

$$\mathrm{ROH} + \mathrm{XOAc} \rightleftharpoons \mathrm{XOH} + \mathrm{ROAc} \text{ (equilibrium constant } K_1/K_2) \quad . \quad (13)$$

Accordingly,

$$\frac{[\mathrm{XOH}]_{\text{stoich.}}}{[\mathrm{X}^+]} = \frac{1}{[\mathrm{R}^+]}\frac{f_{\mathrm{X}^+}}{f_{\mathrm{R}^+}}\left\{K_1[\mathrm{ROH}]\frac{f_{\mathrm{ROH}}}{f_{\mathrm{XOH}}} + K_2[\mathrm{ROAc}]\frac{f_{\mathrm{ROAc}}}{f_{\mathrm{XOAc}}}\right\} \quad . \; . \quad (14)$$

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[18] Hammett, " Physical Organic Chemistry," McGraw-Hill, New York, 1940, p. 276.

[19] Zucker and Hammett, *J. Amer. Chem. Soc.*, 1939, **61**, 2791.

To simplify the problem, we shall now assume that ratios of the form

$$\frac{f_{X^+}f_{ROH}}{f_{R^+}f_{XOH}} \quad \text{and} \quad \frac{f_{X^+}f_{ROAc}}{f_{R^+}f_{XOAc}}$$

are invariant with solvent composition, and shall set them equal to unity. The first of these assumptions is, in fact, the same as the condition for the existence of a unique acidity function J_0 in the particular medium.[2] It has been shown that a reasonably consistent acidity function H_0 exists in acetic acid–sulphuric acid mixtures,[17] at any rate at low concentrations of sulphuric acid. Accordingly, we expect the function J_0 to be a similarly definite solvent property over the same composition range and hence consider the first assumption justified. The second ratio is of similar form and may reasonably be expected to behave analogously. It will be shown below that the constancy of $f_{X^+}f_{ROAc}/f_{R^+}f_{XOAc}$ may also formally be regarded as the condition for the existence of a related acidity function. The resultant equation can be simplified if

$$K_1 = K_2 = K_{12} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

so that

$$\frac{[\mathrm{XOH}]_{\mathrm{stoich.}}}{[\mathrm{X}^+]} = K_{12}\frac{[\mathrm{ROH}]_{\mathrm{stoich.}} - [\mathrm{R}^+]}{[\mathrm{R}^+]} \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

This assumption requires that the position of the esterification equilibrium be the same for the reagent XOH and the indicator ROH. It leads to a result of the form of (16) and thence, on substitution in (10), to

$$\log k_2 = \text{const.} + \log\frac{[\mathrm{R}^+]}{[\mathrm{ROH}]_{\mathrm{stoich.}} - [\mathrm{R}^+]} \quad . \quad . \quad . \quad . \quad (17)$$

which is identical in form with the experimental result obtained [equation (3) and Table 6]. Simplified equations of the same form are obtained on assuming either complete or, alternatively, negligible esterification of ROH.

Assumption (15) may be regarded as reasonable when the alcohols considered are as closely related in structure as are diphenylmethanol and its *p*-chloro- and *p*-methoxy-derivatives. The esterification equilibrium is not of a kind which would be expected to be strongly dependent on polar effects of substituent groups, and steric influences are identical in the series of compounds considered.

The correlation between the kinetic and indicator measurements is shown by the agreement between the empirical constant λ and the required value of unity (see Table 6), and this is considered to establish the proposed carbonium-ion mechanism in the present instance. This mechanism need not, however, be applicable to all types of acid-catalysed alkylations. Thus, under appropriate conditions, the initial ionisation to give X^+ may not be rapid relative to the speed of interaction of X^+ and ArH. This would lead to kinetic behaviour analogous to the "zeroth-order" reactions observed in aromatic nitration[20] or to the acid-catalysed oxygen-isotope exchange of alcohols.[21] By analogy with the suggestions of H. C. Brown and his co-workers,[7] the possible function of XOH_2^+ as an alkylating agent may also have to be considered. Such a mechanism would require the rate to be related to Hammett's acidity function H_0 according to

$$\log k_2 = \text{constant} - H_0$$

In addition to the experiments in which the acidity of the medium was varied by addition of sulphuric acid, the concentration of water in the medium being kept constant, we have examined the dependence of reaction velocity and indicator ionisation on the concentration of small amounts of added water. Gold and Hawes[3] studied the influence

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[20] Benford and Ingold, *J.*, 1938, 929; Hughes, Ingold, and Reed, *J.*, 1950, 2400.

[21] Dostrovsky and Klein, *J.*, 1955, 791, 4401; Grunwald, Heller, and Klein, *J.*, 1957, 2604; Bunton, Konasiewicz, and Llewellyn, *J.*, 1955, 604.

of addition of water upon the ionisation of triphenylmethanol in mixtures of sulphuric acid and acetic acid. It was found that water represses the ionisation of triphenylmethanol more strongly than that of a Brønsted base. The effect was discussed in terms of a mass-law effect on the equilibrium

$$\mathrm{Ph_3C{\cdot}OH} + 2\mathrm{H_2SO_4} \rightleftharpoons \mathrm{Ph_3C^+} + \mathrm{H_3O^+} + 2\mathrm{HSO_4^-} \quad . \quad . \quad . \quad . \quad (18)$$

which was shown to give a reasonably successful quantitative explanation of the phenomena. Esterification of the alcohol was implicitly assumed to be negligible, as may reasonably be assumed for this particular compound. For the ionisation of a diarylmethanol, esterification must, however, be taken into account, and accordingly we observed the effect of addition of water to be markedly different for a diarylmethanol from that for a triarylmethanol indicator (Table 7). As before, the velocity of diphenylmethylation was found to parallel closely the ionisation of the diarylmethanol (Table 8).

Provided the concentration of $\mathrm{R^+}$ is low, the effect of addition of water may be quantitatively expressed by

$$\frac{[\mathrm{R^+}]}{[\mathrm{ROH}]_{\mathrm{stoich.}}} = K\frac{h_0 f_{\mathrm{ROH}} f_{\mathrm{HB^+}}}{(\mathrm{H_2O}) f_{\mathrm{R^+}} f_{\mathrm{B}}}\left[1 + K_{\mathrm{E}}\frac{(\mathrm{AcOH}) f_{\mathrm{ROH}}}{(\mathrm{H_2O}) f_{\mathrm{ROAc}}}\right]^{-1} \quad . \quad . \quad . \quad (19)$$

where K is the equilibrium constant for the hypothetical equilibrium $\mathrm{H^+} + \mathrm{ROH} \rightleftharpoons \mathrm{H_2O} + \mathrm{R^+}$, and K_{E} that for reaction (1).

For the case of negligible esterification equation (19) simplifies to

$$\frac{[\mathrm{R^+}]}{[\mathrm{ROH}]_{\mathrm{stoich.}}} = K\frac{h_0 f_{\mathrm{ROH}} f_{\mathrm{HB^+}}}{(\mathrm{H_2O}) f_{\mathrm{R^+}} f_{\mathrm{B}}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

and can be rearranged to give the equations previously obtained [equation (4) of ref. **3** or equation (12) of ref. **4**]. This result corresponds to the behaviour of triarylmethanols.

If there is complete esterification

$$\frac{[\mathrm{R^+}]}{[\mathrm{ROH}]_{\mathrm{stoich.}}} = \frac{K}{K_{\mathrm{E}}}\frac{h_0 f_{\mathrm{ROAc}} f_{\mathrm{HB^+}}}{(\mathrm{AcOH}) f_{\mathrm{R^+}} f_{\mathrm{B}}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

The significant difference between equations (20) and (21) is that the activity of water does not enter explicitly into the expression (21), so that for the case of extensive esterificaction, water exerts an effect only by virtue of its influence on h_0, the activity of acetic acid being virtually constant at low water concentrations. The change in the ratio $f_{\mathrm{ROAc}}/f_{\mathrm{ROH}}$ on addition of water is unknown but is expected to be of relatively minor importance.

The above analysis fits the observed behaviour of the diarylmethanol (III) at least qualitatively. At low water concentrations, addition of water produces a much smaller change on the ionisation ratio of (III) than it does on that of the triarylmethanol (I) (Table 7). This accords with the hypothesis that diarylmethanols are appreciably converted into the acetates, whereas triarylmethanols are not. However, as the water concentration (and activity) in the solution rises, the relative importance of the two terms in the last factor of equation (19) changes and, at the higher water concentrations, the effect of addition of water on the two indicators becomes gradually less different (Table 7). Thus we conclude that diarylmethanols are extensively converted into the acetates in anhydrous acetic acid but that progressively more hydrolysis takes place as water is added.

It was found (Tables 1 and 2) that for experiments at varying acidities but constant water concentration the ionisation ratios of the diarylmethanol indicator (II) and the triarylmethanol (I) changed in the same manner, the logarithms of the ionisation ratios varying as $-2H_0$. According to the discussion presented, the ionisation of the two indicators should follow equations (20) and (21) respectively. The parallel behaviour of the two indicators seems to indicate approximate constancy of the ratio $(\mathrm{AcOH})f_{\mathrm{ROH}}/(\mathrm{H_2O})f_{\mathrm{ROAc}}$ for these particular changes in the medium.

The strength of a secondary base in an aqueous acid is characterised by the constant K, whereas for acetic acid solutions it is the ratio K/K_{E} which determines the ionisation tendency if there is esterification. Consequently, a direct comparison between individual differences in indicator strengths obtained in the two solvent systems is not possible.

However, according to the discussion presented, K_{E} should have nearly the same value for different diarylmethanols. This assumption allows us to make an approximate comparison of the reactivities of the diphenylcarbonium ion and of the 4 : 4′-dichlorodiphenylcarbonium ion for reaction with mesitylene. The second-order rate constants for the alkylation of mesitylene by the two corresponding alcohols have been measured (Table 6), and $\log k_2{}^{\mathrm{u}}/k_2{}^{\mathrm{s}}$ varies from 0·40 to 0·32 over the range of acid concentrations studied. (The letters u and s refer to unsubstituted and substituted diphenylmethanol respectively.) According to equation (10), this logarithmic rate ratio represents

$$\log\frac{k_2{}^{\mathrm{u}}}{k_2{}^{\mathrm{s}}} = \log\frac{k^{\mathrm{u}}}{k^{\mathrm{s}}} + \log\frac{[\mathrm{X^+{}_u}]}{[\mathrm{X_uOH}]_{\mathrm{stoich.}}} - \log\frac{[\mathrm{X^+{}_s}]}{[\mathrm{X_sOH}]_{\mathrm{stoich.}}} \quad . \quad . \quad . \quad (22)$$

Each one of the ionisation ratios is now given by expression (21), and on making the previously mentioned assumptions we obtain

$$\log\frac{k_2{}^{\mathrm{u}}}{k_2{}^{\mathrm{s}}} = \log\frac{k^{\mathrm{u}}}{k^{\mathrm{s}}} + \log\frac{K^{\mathrm{u}}}{K^{\mathrm{s}}} = 0{\cdot}36 \text{ (mean experimental value)}$$

The value 0·62 can be derived for the second term on the right-hand side from reported measurements of the strengths of secondary bases,[16] so that $\log(k^{\mathrm{u}}/k^{\mathrm{s}}) = -0{\cdot}26$. Hence, the chloro-substituents cause a decrease in the ionisation of the alkylating agent and a slight increase in the reactivity of the intermediate carbonium ion. It is the difference in basic strengths of the alcohols which appears to govern the direction of the substituent effect in the alkylation.

The present work involves an attempt to apply the concept of acidity functions to reactions of the type

$$\mathrm{ROAc} + \mathrm{H^+} \rightleftharpoons \mathrm{R^+} + \mathrm{HOAc} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

or, more generally,

$$\mathrm{RX} + \mathrm{H^+} \rightleftharpoons \mathrm{R^+} + \mathrm{HX} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

The case of the ionisation of diphenylmethyl acetate was complicated by the necessity to include a general consideration of the incursion of equilibrium (1), but this should not be allowed to obscure the fact that the analysis presented implies that there is a solvent property (or " acidity function ") which governs ionisation reactions of acetates according to equation (23). By analogy with the definitions of H_0 and J_0 this can be expressed in the form

$$L^{\mathrm{OAc}} = -\mathrm{p}K_{\mathrm{ROAc}} - \log[\mathrm{R^+}]/[\mathrm{ROAc}] \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

and the existence of the function is governed by the condition that activity-coefficient ratios of the form $f_{\mathrm{R^+}}/f_{\mathrm{ROAc}}$ should be independent of the nature of R in the solvent system concerned. The extension to the more general case (24) is obvious. There would not appear to be any reason to suspect that the ratio $f_{\mathrm{R^+}}/f_{\mathrm{ROAc}}$ should be markedly more sensitive to structure than the ratios $f_{\mathrm{R^+}}/f_{\mathrm{ROH}}$ and $f_{\mathrm{BH^+}}/f_{\mathrm{B}}$ although, in the general case, one might hazard the guess that the constancy of $f_{\mathrm{R^+}}/f_{\mathrm{RX}}$ would become a worse approximation with increasing size of X.

It is obvious that functions like L^{OAc} defined above are less interesting and useful than H_0 and J_0, inasmuch as they apply to less general ionisation equilibria. However, the concept may be useful in specific cases to establish the importance of an ionisation pre-equilibrium in a particular reaction mechanism.

The relationship between L^{OAc} and H_0 in acetic acid is evident from equation (21), and is formally analogous to that [4] between J_0 and H_0; L_{OAc} and H_0 are clearly not very different in the dilute range considered, but this is not expected to be generally true.

The discussion in this paper has been presented without explicit consideration of ion association which is known to play an important rôle in this solvent system.[22] The simpler approach appears justified in the present case since only one anion ($\mathrm{HSO_4^-}$) is thought to be present in the system in sufficient concentration to associate with the positively charged form of indicator and reagent. In writing $\mathrm{R^+}$ we implicitly consider that ion to be present in association with $\mathrm{HSO_4^-}$ ions into pairs and higher aggregates, and the activity coefficient $f_{\mathrm{R^+}}$ to refer to a complex entity. Ultraviolet spectra [22b] do not appear to distinguish between free ions and ion pairs. The spectroscopically determined concentrations $[\mathrm{R^+}]$ refer to gross concentrations of $\mathrm{R^+}$ ions, *i.e.* to free ions (if any) and ions in association.

All the equations in the present paper are readily modified to conform to the notation required for a treatment in which ion-pair formation is explicitly included.[22, 23] For instance, equation (19) becomes

$$\frac{[\mathrm{R^+HSO_4^-}]}{[\mathrm{ROH}]_{\mathrm{stoich.}}} = \frac{K'(\mathrm{H_2SO_4})f_{\mathrm{ROH}}}{(\mathrm{H_2O})f_{\mathrm{R^+HSO_4^-}}}\left[1 + K_{\mathrm{E}}\frac{(\mathrm{AcOH})f_{\mathrm{ROH}}}{(\mathrm{H_2O})f_{\mathrm{ROAc}}}\right]^{-1} \quad . \quad . \quad (26)$$

where K' is now the equilibrium constant for the formation of the ion-pair $\mathrm{R^+HSO_4^-}$ according to

$$\mathrm{H_2SO_4 + ROH \rightleftharpoons R^+HSO_4^- + H_2O}$$

If more than one neutral acid is involved in proton donation, equation (26) is generalised to

$$\frac{\sum\limits_{\mathrm{i}}[\mathrm{R^+A_i^-}]}{[\mathrm{ROH}]_{\mathrm{stoich.}}} = \sum_{\mathrm{i}}\left(\frac{K'_{\mathrm{i}}(\mathrm{HA_i})}{f_{\mathrm{R^+A_i^-}}}\right)\cdot\frac{f_{\mathrm{ROH}}}{(\mathrm{H_2O})}\left[1 + K_{\mathrm{E}}\frac{(\mathrm{AcOH})f_{\mathrm{ROH}}}{(\mathrm{H_2O})f_{\mathrm{ROAc}}}\right]^{-1} \quad . \quad (27)$$

where the summation is over all acids $\mathrm{HA_i}$ involved in equilibria $\mathrm{HA_i + ROH \rightleftharpoons R^+A_i^- + H_2O}$.

It has been found that aromatic substitutions fall into two classes according to whether isotopic replacement of hydrogen at the seat of substitution has an influence upon the rate of reaction or not. The experimental study of the isotope effect in the reaction

$$\mathrm{Ph_2CH{\cdot}OAc + C_6H_5{\cdot}OMe \longrightarrow \textit{p}\text{-}MeO{\cdot}C_6H_4{\cdot}CHPh_2 + AcOH}$$

was straightforward since substitution is confined to the *para*-position in anisole, and a sample of [4-^{2}H]anisole was available from work in this laboratory on hydrogen-isotope exchange in anisole.[24] Moreover, this work had established that for the media employed deuterium replacement was a much slower reaction than aralkylation. At the concentrations of sulphuric acid used the rate of alkylation was 16—25 times greater than the rate of exchange.

The results (Table 10) indicate that the rate constants for replacement of protium and deuterium are equal within experimental error, and show that the rate-determining step of the reaction is the process $\mathrm{R^+ + ArH \longrightarrow RArH^+}$ and that the subsequent loss of proton is kinetically insignificant. Diphenylmethylation of anisole is thus analogous to aromatic nitration, both in the mode of generation of the reactive entity in a pre-equilibrium and in the nature of the substitution step proper.

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[22] (*a*) Kolthoff and Bruckenstein, *J. Amer. Chem. Soc.*, 1956, **78**, 1; (*b*) Evans, Price, and Thomas, *Trans. Faraday Soc.*, 1955, **51**, 481.

[23] Satchell, following paper; Bethell, Gold, and Satchell, *J.*, 1958, 1918.

[24] Satchell, *J.*, 1956, 3911.