Some Observations Relating to Substituent Effects in Halogenation. Part III.[1] The Kinetics of the Reaction of Diphenylmethane with Chlorine Acetate in Aqueous Acetic Acid at 25°

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The reaction of diphenylmethane with chlorine acetate has been examined in acetic acid–water mixtures in the presence of varying amounts of perchloric acid at 25°. In 98% acetic acid and in the presence of perchloric acid the reactive species are considered to be molecular chlorine acetate and its protonated form. Under these conditions diphenylmethane reacts 21·8 times faster than benzene and gives 40·0% of the 4- and 59·3% of the 2-chlorodiphenylmethane. The reaction in 75% acetic acid in the presence of catalytic amounts of perchloric acid involves protonated forms of hypochlorous acid as chlorinating species, is 29·6 times faster than the reaction with benzene, and gives 63·0% of the 2- and 37·0% of the 4-chlorodiphenylmethane. The relative rates and product compositions determine the partial rate factors for the chlorination reactions. Comparison with the results for other electrophilic reagents indicates that the reactions of chlorine acetate result in a higher proportion of *ortho*-substitution. No addition or side-chain chlorination accompanies these reactions.

Not many quantitative studies are available of the substitution reactions of diphenylmethane, but its reactivity relative to benzene[2] and other aromatic compounds has been recorded for bromination by molecular bromine, nitration by cold fuming nitric acid,[3] and chlorination by molecular chlorine.[4]

Nitration by cold fuming nitric acid gave 2,4′- and 4,4′-dinitrodiphenylmethanes. Mononitration in excess of hydrocarbon gave mainly a mixture of mononitro-derivatives from which, together with the relative rate, partial rate factors for the nitration reaction were calculated.[3]

The chlorination of diphenylmethane in acetic acid as studied by de la Mare, Johnson, and Lomas[4] gave 53·5% of the 2-, 0·5% of the 3-, and 46·0% of the 4-chlorodiphenylmethane. The reactivities of the 2- and 4-positions of the same compound in detritiation were found by Bancroft, Bott, and Eaborn[5] to be about four times smaller than the corresponding positions in toluene.

The results of these investigations clearly show that the benzyl group activates the *ortho*- and *para*-positions. The results also show that the activation of these positions is less than of those in toluene and the difference in reactivity has been reasonably attributed to the electron-withdrawing inductive effect of the phenyl group.

In the present investigation the reaction of diphenylmethane with chlorine acetate in aqueous acetic acid in the presence of added perchloric acid has been investigated. The results obtained are discussed in terms of the electronic effect of the benzyl group and the nature of reagents concerned in the chlorination reactions.

EXPERIMENTAL

Preparation and Purification of Materials.—Acetic acid, m.p. 16·6°, and solutions of chlorine acetate were obtained using standard procedures.[6] *p*-Chlorodiphenylmethane was prepared by the reduction of *p*-chlorobenzophenone by the Huang-Minlon modification of the Wolff–Kischner reduction,[7] b.p. 117—118°/1·7 mm., n_D^{25} 1·5837 (lit.,[8] b.p. 298°/742·5 mm.) (Found: C, 76·95; H, 5·55; Cl, 17·45. Calc. for $C_{13}H_{11}Cl$: C, 77·05; H, 5·45; Cl, 17·5%). The *p*-chlorobenzophenone was a commercial specimen (Eastman Kodak) purified by crystallisation from ethanol, m.p. 77° (lit.,[8,9] 75°, 77—78°). *o*-Chlorodiphenylmethane was prepared by a similar procedure from *o*-chlorobenzophenone. The latter compound was prepared by the Friedel–Crafts reaction of *o*-chlorobenzoyl chloride and benzene.[9] o-*Chlorodiphenylmethane* had b.p. 95°/0·6 mm., n_D^{25} 1·5869 (Found: C, 76·95; H, 5·6; Cl, 17·35%). Diphenylmethane (Light & Co.) was purified by repeated fractional distillation. The middle fraction, b.p. 117—118°/6 mm., n_D^{20} 1·5771, was used for the kinetic runs. The purity of the compound was checked by t.l.c. and i.r. spectroscopy. Toluene and benzene (AnalaR) were purified as described elsewhere.[6]

Kinetic Measurements.—The reaction was followed by the conventional procedure. Silver perchlorate was added to ensure that there was no reaction with molecular chlorine. All data given below are derived from reactions of the aromatic compound with solutions of chlorine acetate in aqueous acetic acid at 25°. The reactions were followed over 50% of the reaction range. Blank determinations were carried out accompanying each run.

Table 1 shows the results of typical kinetic runs in 98% (v/v) acetic acid. The second-order rate coefficients were calculated by using the formula

$$k_2 = \frac{2\cdot303}{t(a-b)}\log_{10}\frac{b(a-x)}{a(b-x)}$$

Table 2 lists the results obtained in the reaction of the aromatic compound with chlorine acetate in 75% (v/v) acetic acid.

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[2] P. W. Robertson, P. B. D. de la Mare, and B. E. Swedlund, *J. Chem. Soc.*, **1953**, 1821.

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[8] P. J. Montague, *Rec. Trav. chim.*, 1910, **26**, 266.

[9] P. J. Montague and S. A. Koopal, *Rec. Trav. chim.*, 1910, **29**, 128.

TABLE 1

(a) Diphenylmethane (0·0300M); chlorine acetate (0·0089M); perchloric acid (0·00M); silver perchlorate (0·0253M)

Time (min.)	0·00	3·50	6·50	9·50	12·50	15·50	19·50	22·50
Titre (ml.)	16·02	13·21	11·32	9·78	8·45	7·27	6·19	5·41
k_2 (l. mole^{-1} min.$^{-1}$)		1·89	1·87	1·85	1·85	1·88	1·88	1·87

Mean value of $k_2 = 1{\cdot}87 \pm 0{\cdot}01$ l. mole^{-1} min.$^{-1}$. The rate coefficient for benzene under the same conditions is 0·071 l. mole^{-1} min.$^{-1}$ (ref. 6).

(b) Diphenylmethane (0·0300M); chlorine acetate (0·0133M); perchloric acid (0·0300M); silver perchlorate (0·0253M)

Time (min.)	0·00	1·50	2·50	4·00	7·00	8·50	9·50
Titre (ml.)	23·80	15·80	12·40	8·85	4·80	3·64	3·00
k_2 (l. mole^{-1} min.$^{-1}$)		9·90	9·90	9·91	9·95	9·91	9·97

Mean value of $k_2 = 9{\cdot}923 \pm 0{\cdot}025$ l. mole^{-1} min.$^{-1}$.

TABLE 2

(a) Diphenylmethanes (0·0286M); chlorine acetate (0·0090M); perchloric acid (0·00M); silver perchlorate (0·030M)

Time (min.)	0·00	5·0	10	15	20	25	30	40
Titre (ml.)	10·39	8·53	7·03	5·79	4·87	4·13	3·55	2·56
k_2 (l. mole^{-1} min.$^{-1}$) ...		1·43	1·44	1·48	1·47	1·45	1·43	1·44

Mean value of $k_2 = 1{\cdot}45 \pm 0{\cdot}016$ l. mole^{-1} min.$^{-1}$. The rate coefficient for benzene under the same conditions is 0·044 l. mole^{-1} min.$^{-1}$.

(b) Diphenylmethane (0·0286M); chlorine acetate (0·0085M); perchloric acid (0·0301M) silver perchlorate (0·0300M)

Time (min.)	0·00	2·5	4·25	6·50	8·0	10·0
Titre (ml.)	9·76	7·05	5·74	4·43	3·76	3·03
k_2 (l. mole^{-1} min.$^{-1}$) ...		4·75	4·69	4·70	4·67	4·68

Mean value of $k_2 = 4{\cdot}70 \pm 0{\cdot}02$ l. mole^{-1} min.$^{-1}$.

(c) Benzene (0·0303M); chlorine acetate (0·0118M); perchloric acid (0·302M); silver perchlorate (0·0300M)

Time (min.)	0·00	5	20	40	70	90
Titre * (ml.)	9·6	9·44	9·01	8·49	7·77	7·38
k_2 (l. mole^{-1} min.$^{-1}$) ...		0·104	0·105	0·104	0·104	0·101

Mean value of $k_2 = 0{\cdot}104 \pm 0{\cdot}01$.

* Corrected for blank decompositions.

Table 3 shows the variation of the second-order rate coefficient with increase in perchloric acid concentration for reactions in both media.

Table 4 shows the variation of the rate coefficient with change in the solvent composition.

Analysis of Products of the Reaction of Chlorine Acetate and Diphenylmethane in 98% *Acetic Acid*.—The proportion of isomers obtained in the chlorination of diphenylmethane with chlorine acetate was determined by the method of isotopic dilution by using chlorine acetate partially labelled with chlorine—36.

TABLE 3

(a) Diphenylmethane (0·0300M); chlorine acetate (0·0089M); silver perchlorate (0·0253M); 98% (v/v) acetic acid as solvent

Perchloric acid (M)	k_2 (l. mole^{-1} min.$^{-1}$)
0·00	1·87
0·009	3·55
0·020	6·24
0·030	9·47
0·040	12·37
0·060	20·55 *

* The rate coefficient for benzene under the same conditions is 0·944 l. mole^{-1} min.$^{-1}$.

(b) Diphenylmethane (0·0268M); chlorine acetate (0·0085—0·0107M); silver perchlorate (0·0300M); 75% (v/v) acetic acid as solvent.

Perchloric acid (M)	k_2 (l. mole^{-1} min.$^{-1}$)
0·00	1·45
0·020	1·48
0·040	1·63
0·060	1·85
0·200	3·08
0·400	4·69
0·500	8·99 *

* Rate coefficient for benzene under the same conditions is 0·304 l. mole^{-1} min.$^{-1}$.

TABLE 4

Diphenylmethane (0·025—0·0286M); chlorine acetate (0·0025M); silver perchlorate (0·025M)

H_2O (% v/v)	2	14	24	34	44
k_2 (l. mmole^{-1} min.$^{-1}$)	6·52	2·00	1·88	1·98	1·13

A litre of a solution of the reactants consisting of diphenylmethane (0·0500M), chlorine acetate partially labelled with chlorine—36 (0·0138M), perchloric acid (0·0600M), and silver perchlorate (0·0300M), all in 98% acetic acid, was allowed to react to completion. A blank determination was carried out to allow for decomposition of chlorine acetate in the solvent. From the molarity of chlorine acetate consumed, the amount of mixed chlorodiphenylmethanes formed in the reaction was determined as 2·7969 g./l. The original chlorine acetate was counted as lithium chloride. This had an activity of 4883 counts/1000 sec. for a 0·0164M-solution in acetone.

para-*Substitution*. To a portion of the reaction mixture (300 ml., containing 0·8391 g. of mixed chloro-diphenylmethanes) was added inactive *p*-chlorodiphenylmethane (11·69 g.). The chloro-diphenylmethanes and unchanged material were recovered, and were then oxidised to the corresponding benzophenones with alkaline permanganate.[10] The product was crystallised several times from aqueous ethanol, and the resulting 4-chlorobenzophenone had m.p. 77°.

A solution in acetone (0·325M) had an activity of 2690, 2692, and 2674 counts/1000 sec. Hence 0·3416 g. (40·0%) of 4-chlorodiphenylmethane had been produced in the reaction.

ortho-*Substitution*. A similar procedure was adopted. The 2-chlorodiphenylmethane was converted into the tetranitro-derivative, which is thought to be 6-chloro-2,2′,4,4′-tetranitrodiphenylmethane, in the following way.

Fuming nitric acid (43 ml.) was added dropwise to a cooled mixture of crude 2-chlorodiphenylmethane (8·5 g.) in concentrated sulphuric acid (43 ml.) with constant stirring. After the addition, the mixture was boiled under reflux for

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[10] A. I. Vogel, ‘Qualitative Organic Analysis,’ Longmans, London, 1956, p. 520.

30 min. and poured into crushed ice. The solid material was filtered off and repeatedly crystallised from acetone–ethanol to give a *product*, m.p. 170° (Found: C, 40·7; H, 1·95; Cl, 9·25; N, 14·6. $C_{13}H_7ClNO_4$ requires C, 40·8; H, 1·85; Cl, 9·25; N, 14·65%).

Comparison of the activity of an acetone solution with that of the original chlorine acetate, converted into lithium chloride for counting, showed that 0·3315 g. (59·3%) of the 2-chloro-isomer was produced in the reaction.

No appreciable amount of the 3-chloro-isomer or products of side-chain chlorination or addition were detected in the reaction mixture. The amounts of the 2- and 4-chloro-diphenylmethanes account, within experimental error, for all the chlorine acetate consumed.

The same procedure was adopted for estimation of the proportion of isomers produced in the reactions of the aromatic compound with chlorine acetate in different media. Table 5 gives a summary of the results.

TABLE 5

Solvent composition Acetic acid, % v/v	Perchloric acid (M)	% Chloro-diphenyl-methane	
98	0·00	2-	66·2
		3-	
		4-	33·8
	0·06	2-	59·3
		4-	40·0
75	0·00	2-	62·0
		4-	38·0
	0·50	2-	63·0
		4-	37·0

DISCUSSION

The kinetics of chlorination of diphenylmethane in 98% acetic acid are similar to those found for toluene and biphenyl with the same reagent under the same conditions.[6,11] The chlorinating species is concluded to be molecular chlorine acetate. The effect of the solvent composition on the rate is shown in Table 4. The rate of chlorination of the aromatic compound must decrease as the concentration of chlorine acetate decreases. This decrease, however, must be offset by the intrinsic increase in the rate as the polarity of the medium increases. The rate of reaction of aromatic compounds with molecular halogens in acetic acid has been found to be sensitive to the presence of small amounts of water, *e.g.*, the rates of chlorination of toluene and naphthalene.[11,12]

The effect of added perchloric acid on the rate is shown in Table 3. The results are in agreement with those previously recorded for reactions of other aromatic compounds with the same reagent under similar conditions. They confirm the view that in the presence of catalytic amounts of perchloric acid a positively charged species may be involved. In 75% acetic acid the major source of active chlorine must be hypochlorous acid but molecular chlorine acetate, formed from the reaction of hypochlorous and acetic acid, is probably the chlorinating species. Its concentration, however, is expected to be small because of rapid hydrolysis.

The reaction in 75% acetic acid in the presence of sufficient perchloric acid involves protonated species derived from hypochlorous acid. Chlorination by hypochlorous acid in aqueous solvents requires rather high acidities for effective catalysis, when compared with the reaction of chlorine acetate in 98% acetic acid in the presence of perchloric acid. The requirement of higher acidities reflects, presumably, the participation of species such as H_2OCl^+ and/or Cl^+. Thus it is concluded that, in aqueous acetic acid in the presence of perchloric acid, acidified hypochlorous acid may be the dominant component in the chlorination reaction.

Polar Effects of the Benzyl Group.—The relative rates, together with the proportions of isomers formed, determine the partial rate factors for the diphenylmethane system which are given in Table 6. Included are partial rate factors for nitration, detritiation, and molecular chlorination.

TABLE 6

	Partial rate factors			
Reaction conditions	f_o	f_m	f_p	Ref.
Nitration, $AcO{\cdot}NO_2$, Ac_2O, 25°	13		32	3
Detritiation, $CF_3{\cdot}CO_2H$, AcOH, 25°	47	(3·8)	120	5
Chlorination, Cl_2, AcOH, 25° ...	128	(1)	220	4
Chlorination, ClOAc, 75% HOAC, 25°	30·7		37·6	This work
Chlorination, $ClOAcH^+$, Cl^+, H_2OCl^+, 75% HOAc, 25°	28		33	This work
Chlorination, ClOAc, 98% HOAc, 25°	26·15		26·70	This work
Chlorination, ClOAc, $ClOAcH^+$, HOAc, 25°	19·36		26·10	This work

para-*Substitution.* The benzyl group is classified as possessing a $(-I + T)$ effect and would thus be expected to be electron-releasing and to activate the 4- and 2-positions. The phenyl group is expected to reduce the activating power of the alkyl group by virtue of its electron-withdrawing inductive effect. This is in contrast to the effect of the phenyl group in the diphenyl system where it has been shown that the $+T$ effect associated with the group is dominant and dedetermines the orientation. In diphenylmethane the $+T$ effect is rendered ineffective by the intervening methylene group and by the lack of coplanarity of the two rings. Partial rate factors for the 4-position (Table 6) show that this position is activated by the group but to a lesser extent than the corresponding position in toluene by a factor of about four,[13] a result which is similar to that found for detritiation and molecular chlorination of the two compounds.

The partial rate factor for chlorination by neutral reagents in the *para*-position is greater than that for chlorination by positive chlorine. This result in our view accords with the fact that the inductive effect

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[11] P. B. D. de la Mare, I. C. Hilton, and C. A. Vernon, *J. Chem. Soc.*, 1960, 4044.

[12] P. B. D. de la Mare and R. W. Robertson, *J. Chem. Soc.*, 1943, 279.

[13] M. Hassan and G. Yousif, unpublished results.

plays an important part in reactions where the attacking species bears a full positive charge. It is expected in this reaction that the negative inductive effect of the phenyl substituent reduces considerably the activation by the alkyl side chain.

The partial rate factor for the *para*-position for the reaction in the absence of perchloric acid is considerably higher than that when the substitution is effected by protonated species. This is due, in part, to the deactivating influence of the phenyl group and also to the greater importance of the expected electron release from the methylene group due to hyperconjugation when molecular reagents are involved. Conjugative effects are involved much more effectively by neutral than by positively charged species.

ortho-*Substitution.* The partial rate factors for substitution in the 2-position in diphenylmethane are generally lower than those for alkyl benzenes. This is most reasonably interpreted as owing to the electron-withdrawing effect of the phenyl group as shown by data in Table 7.

TABLE 7

Partial rate factors for *ortho*-substitution in alkyl and substituted alkyl benzenes

Compound	Chlorination by molecular chlorine in acetic acid f_p	Nitration in acetic anhydride f_o	Ref.
$PhCH_2Ph$	128	13	3
PhMe	617	46·5	14
PhEt	450	31·4	15
$PhCMe_3$	56·6	3·8	14
Ph–Ph	190	41	16

Consideration of the $\frac{1}{2}\,o:p$ ratios for nitration of diphenylmethane[3] (0·41) and t-butylbenzene (0·071)[14] and for chlorination of the same compounds by molecular chlorine[4] (0·581) and (0·141)[14] respectively, allow the conclusion to be made that in a series of substituted alkylbenzenes steric hindrance is greater for the t-butyl group than for the benzyl group.

This conclusion is supported by our present findings for the value of the $\frac{1}{2}\,o:p$ ratio for the acid-catalysed chlorination of diphenylmethane by chlorine acetate in 75% acetic acid (0·85) as compared with 0·39 for the reaction of t-butyl benzene with the same reagent under the same conditions.[13]

Comparison of the data for chlorination of diphenylmethane with those of other diphenylalkanes support the view[4] that, for substitution in the 2-position in diphenylmethane, the phenyl group might assume a confirmation more favourable for substitution at this position.

Table 8 shows the values for the $\frac{1}{2}\,o:p$ ratio obtained in reactions of diphenylmethane with different reagents. It is noted that the reaction of molecular chlorine acetate results in a higher $\frac{1}{2}\,o:p$ ratio than the reaction of the protonated form of the same reagent.

TABLE 8

Reagent	$\frac{1}{2}\,o:p$ ratio
$AcO{\cdot}NO_2$, Ac_2O, 25°	0·46
Cl_2, HOAc, 25°	0·58
$ClOAcH^+$, 98% HOAc, 25°	0·98
$ClOAcH^+$, 98% HOAc, 25°	0·74
ClOAc, HOCl, 75%, 25°	0·82
$ClOAcH^+$,H_2OCl^+, Cl^+, 75% HOAc, 25°	0·85

The results obtained from the reactions in the more aqueous solvents are generally in agreement with those of other electrophilic reactions. The $\frac{1}{2}\,o:p$ ratio is higher for the reaction catalysed by perchloric acid but not significantly higher when compared with those of aromatic compounds with molecular and positive halogens. However, the small but significant difference in the $\frac{1}{2}\,o:p$ ratio between the reactions of the aromatic compound in the two different media may be attributed to the greater participation of protonated species in the reaction catalysed by perchloric acid.

The difference in the $\frac{1}{2}\,o:p$ ratio in the reaction of molecular chlorine acetate in 98% and 75% acetic acid as solvent may be reasonably attributed to the change in solvent composition, since the main chlorinating species in either solvent is expected to be the same. It is interesting to note that Stock and Himoe[17] in examining the distribution of isomers in the chlorination of toluene and t-butylbenzene in anhydrous and aqueous acetic acid found that an increase in the rate was followed by a small but significant change in the $\frac{1}{2}\,o:p$ ratio. For each hydrocarbon the increase in the water content of the reaction medium leads to a small but significant increase in amount of *ortho*-substitution, particularly for t-butylbenzene.

Our present results do not confirm this view. Increase in the water content of the media is accompanied by decrease in the amount of *ortho*-substitution. However, whether the decrease in the rate is generally accompanied by a decrease in the $\frac{1}{2}\,o:p$ ratio in the more aqueous solvent or whether it is due to a more effective electron withdrawal by the substituent in a medium of more polar character is still open to question. It would be expected that the *ortho*-position would be more selectively deactivated by the negative inductive effect of the phenyl substituent presumably operating directly through the medium.[18]

We thank Professor P. B. D. de la Mare and Dr. T. G. Bonner for their interest and much valued discussions.

[7/1096 *Received, August 21st*, 1967]

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