Some Observations relating to Substituent Effects in Halogenation. Part VII.[1] The Kinetics and Reactions of Toluene and *o*- and *p*-Xylene with Chlorine Acetate in Aqueous Acetic Acid and Acetic Acid–Perchloric Acid

By **Osman M. H. El Dusouqui, Abdel Rahman H. El Nadi, Mustapha Hassan,*** and **Ghariballa Yousif,**
Chemistry Department, University of Khartoum, P.O.B. 321, Khartoum, Sudan

The reactions of toluene and *o*- and *p*-xylene with chlorine acetate and its protonated form in aqueous acetic acid have been investigated at 25°. The relative rates and product compositions determined by isotopic dilution and g.l.c. allow calculations of the partial rate factors in the various positions for the chlorinations. The values obtained for *o*- and *p*-xylenes are well correlated by those obtained for the individual positions in toluene on the basis of additivity.

ALKYL substituent effects in electrophilic aromatic substitution reactions are well established. The inductive and hyperconjugative effects determine both the rate and orientation in the reactions of these substrates with electrophiles. The regularity with which these groups influence the course of electrophilic substitution reactions led Condon [2] to correlate successfully the rates of halogenation of methylbenzenes by assuming additivity for the values obtained for the individual positions in toluene. The procedure has been extended to many reactions of the polymethylbenzenes including mercuriation,[3] bromination,[4] molecular chlorination,[5–7] and protodesilylation.[8]

However, few investigations [9,10] have been made to test the applicability of such treatment for systems in which the reacting species are formally positively charged reagents as with protonated forms of chlorine acetate or acidified hypohalogenous acids. The present investigation deals with chlorination of toluene and *o*- and *p*-xylene with neutral and positively charged species, *i.e.* $ClOAc$, $ClOAcH^+$, H_2O^+Cl, and Cl^+. Such an investigation seemed desirable if only to examine the effect of substituents on the selectivity of the reagents and the comparison of their reactivities with known directive influences of these substituents. The investigation was also designed to test the applicability of the additivity principle to systems in which the same substituent is introduced in a given substrate through different reacting species. It is known that conjugative effects are invoked more effectively in reactions involving molecular species, whereas inductive influences should be more important in reactions brought about by positively charged species. Differences between halogenation reactions effected by molecular and ionic species which introduce the same substituent should be accommodated by the theory if it is to be of general applicability.

EXPERIMENTAL

Preparation and Purification of Materials.—The hydrocarbons were purified by standard procedures. Toluene had b.p. 110° (lit.,[11] 110.16°), n_D^{20} 1.4960 (lit.,[11] 1.4961). *o*-Xylene had b.p. 143° (lit.,[12a] 143.59—144.15°), $n_D^{16.6}$ 1.5071 (lit.,[12b] $n_D^{16.5}$ 1.507 12). *p*-Xylene had b.p. 136—137° (lit.,[12c] 137.5—138°), n_D^{21} 1.5003 (lit.,[12c] 1.5004). Acetic acid was purified by methods described in earlier papers.[13] Chlorine acetate was prepared according to standard procedures. The chlorotoluenes utilized in the product analysis were commercial specimens purified by fractionation and their purity was determined by g.l.c. The chloroxylenes were prepared from the corresponding xylidenes by the Sandmeyer reaction. They were purified by washing with small amounts of sulphuric acid, then with water, hydrogen carbonate, and water again. The dried materials were repeatedly distilled and further purified by elution through alumina type H with light petroleum. From 3-amino-*o*-xylene, 3-chloro-*o*-xylene was obtained b.p. 137—138° at 30 mmHg. 4-Chloro-*o*-xylene had b.p. 143—144° at 30 mmHg. 2-Chloro-*p*-xylene had b.p. 184° (lit.,[14] 184—185°).

Kinetic Measurements.—The rates of chlorination of the aromatic compounds were followed iodimetrically by conventional procedures. The results were derived from the reaction of chlorine acetate with the aromatic compounds at 25° in acetic acid and in the presence of 0.0300M-silver perchlorate. The decomposition of the chlorinating agent as shown by a blank was found to be negligible. The reactions were followed over 50% of the reaction range. Aliquot portions (5 ml) were quenched in aqueous potassium iodide and the liberated iodine was titrated against thiosulphate.

Product Analysis.—Analysis of the reaction products was carried out by the method of isotopic dilution using chlorine acetate labelled with chlorine-36. The procedure has been described in previous papers. For the reaction of chlorine acetate with toluene, it was found that the *ortho*-isomer was produced to the extent of 61%, and the *para*-isomer to the extent of 36%.

---

[1] Part VI, O. M. H. El Dusouqui, M. Hassan, and B. Ibrahim, *J. Chem. Soc.* (*B*), 1970, 926.

[2] F. E. Condon, *J. Amer. Chem. Soc.*, 1948, **70**, 1963.

[3] H. C. Brown and C. W. McGary, *J. Amer. Chem. Soc.*, 1955, **77**, 2310.

[4] H. C. Brown and L. M. Stock, *J. Amer. Chem. Soc.*, 1957, **79**, 1421.

[5] H. C. Brown and L. M. Stock, *J. Amer. Chem. Soc.*, 1955, **77**, 2300.

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

[7] E. Bacciochi and G. Illuminati, *Chem. and Ind.*, 1958, 917.

[8] C. Eaborn and R. C. Moore, *J. Chem. Soc.*, 1959, 3640.

[9] G. A. Olah, S. J. Kuhn, and S. M. Flood, *J. Amer. Chem. Soc.*, 1961, **83**, 4571; 1962, **84**, 3687.

[10] W. M. Lauer and G. Stedman, *J. Amer. Chem. Soc.*, 1958, **80**, 6439.

[11] J. Turkevich, *J. Amer. Chem. Soc.*, 1949, **71**, 4045.

[12] (*a*) I. G. Farbenind, (*Chem. Abs.*, 1929, **23**, 611); (*b*) E. Tschunkev and F. Eicher, (*Chem. Abs.*, 1929, **23**, 5169); (*c*) I. G. Farbenind, (*Chem. Abs.*, 1933, **27**, 1366).

[13] M. Hassan and S. A. Osman, *J. Chem. Soc.*, 1965, 2194.

[14] Willgrodt and Wolfein, *J. prakt. Chem.*, 1899, **39**, 402.

For *o*- and *p*-xylene, the analysis of products was carried out by g.l.c., as described below.

The reaction mixtures were prepared under the same conditions chosen for the kinetic measurements and the reactions were allowed to proceed to completion by following them kinetically. The reaction mixtures were neutralised by sodium hydroxide and then extracted with ether. The solvent was then removed and the reaction products were utilized for g.l.c. analysis without further purification. Authentic samples of the expected chloro-isomers were prepared and their retention times recorded. The following g.l.c. systems were employed: (i) a panchromatograph, equipped with an argon detector, with a column of trichlorofluororecene (10%) and Carbowax (10%) on Celite (100–120 mesh) with argon as a carrier gas; (ii) a Griffin mark IV unit equipped with a kaltrometer using a 5 ft Apizeon L column on Celite (100–120 mesh) using nitrogen as carrier gas; and (iii) a Pye 104 unit with a flame ionization detector utilizing a 7 ft Bentone column (8%) on siliconized Celite (100–120 mesh) with nitrogen as carrier gas. The isomers were estimated by triangulation. No side-chain chlorinations were observed. The results are shown in Table 1.

TABLE 1

		Isomer distribution	
ArH	Reaction conditions	3-Chloro	4-Chloro
o-Xylene	ClOAc, 99% HOAc, 25°	45.6	54.4
o-Xylene	ClOAc, 75% HOAc, $HClO_4$, 25°	53.4	46.5
o-Xylene	ClOAc, 75% HOAc, 25°	40.2	59.8

DISCUSSION

The reactions of chlorine acetate with aromatic compounds were found to be first order in aromatic compound and first order in chlorine acetate. Biphenyl,[13] toluene,[15] diphenylmethane,[16] and t-butylbenzene [17] show similar kinetics under similar conditions. Similar conclusions have been drawn concerning the reactions of bromine acetate with aromatic compounds.[14] As shown in Table 2, the spread of rates is smaller than that found for the reaction of the same substrates with molecular chlorine. This establishes that chlorine acetate is the chlorinating agent and further that it is more reactive than molecular chlorine.

In the presence of catalytic amounts of perchloric acid, the electrophilic species are largely protonated forms of chlorine acetate, $\mathrm{ClOA\overset{+}{c}H}$, $\mathrm{H_2\overset{+}{O}Cl}$, and $\mathrm{Cl^+}$, and for the range of acidities employed, it was found that the rate rises linearly with increase in acid concentration. For the chlorination of benzene, the xylenes, 4-chloroanisole, t-butylbenzene, mesitylene, and *p*-anisic acid with chlorine acetate in aqueous acetic acid, it was found that small amounts of perchloric acid had only a slight effect on the rate of reaction; at higher concentrations the rate rises linearly with increase in acid concentration and more rapidly beyond concentrations of 0.4M.[15]

Partial Rate Factors and Structural Effects.—The relative rates and product compositions determine the following partial rate factors. The data for toluene also, allow the calculation of partial rate factors for xylenes by assumption of the additive effects of substituents. These are shown in Table 2.

TABLE 2

	Partial rate factors					
	2		3		4	
ArH	Obs.	Calc.	Obs.	Calc.	Obs.	Calc
Toluene in 99% HOAc, 25°	101		3 [a]	2.9	119	
Toluene in 75% HOAc $HClO_4$, 25°	198 [b]		4 [c]		132 [b]	
o-Xylene, 99% HOAc, ClOAc, 25°			253	303	302	357
o-Xylene, 75% HOAc, $HClO_4$, 25°			617	792	537	528
o-Xylene, 75% HOAc, 25°			354		473	
p-Xylene, 99% HOAc, ClOAc, 25°	296	303				
p-Xylene, 75% HOAc, $HClO_4$, ClOAc, 25°	632	792				

[a] Ref. 15. [b] M. Hassan and B. Mudawi, unpublished results. [c] Ref. 12*a*.

Analysis of the data for isomeric proportions found for *o*-xylene in the different media reveal some general trends. First, for the reaction of the substrate effected mainly through participation of molecular chlorine acetate, in 99 and 75% acetic acid, the isomers produced differ only slightly indicating that the effective species are the same in both media, and also are of the same magnitude as those found for bromination by hypobromous acid in acetic acid.[18] The difference in the extent of substitution in the 3- and 4-positions is explained on the basis of steric and polar effects. It is known that molecular reagents invoke conjugative effects to a greater extent than do formally charged species. Hence substitution at the 4-position predominates. This is also consistent with the view that for reactants of low reactivity the $o:p$ ratio is determined by the effect of substituents on the distribution of charge in the Wheland intermediate, for which it was found that the amount of charge in the *para*-position is greater than the *ortho*-position.[8] Secondly, the difference in isomer distribution observed for the same positions in 99 and 75% acetic acid may be due, in part, to differences in ionic strength between the two media; a similar but slight decrease in the $o:p$ ratio has been observed in the chlorination of diphenylmethane by the same reagent in the same solvents where it was found that increase in the water content of the medium is accompanied by a small but significant decrease in the $o:p$ ratio. It is significant that bromination of *o*-xylene by bromine in glacial acetic acid and aqueous acetic acid show the same trend. There is also an increase in the $o:p$ ratio between these and bromination by acidified hypobromous acid in aqueous acetic acid.[19] Thirdly, in presence of perchloric acid the $o:p$ ratio is greater than in the previous two cases. This result is consistent with the fact

---

[15] P. B. D. de la Mare, I. C. Hilton, and S. Varma, *J. Chem. Soc.*, 1960, 4044.

[16] M. Hassan and G. Yousif, *J. Chem. Soc.* (*B*), 1968, 458.

[17] M. Hassan and G. Yousif, *J. Chem. Soc.* (*B*), 1969, 591.

[18] P. B. D de la Mare and J. Maxwell, *J. Chem. Soc.*, 1962, 4829.

[19] J. Vaughan, G. J. Welch, and G. J. Wright, *Tetrahedron*, 1965, **21**, 1665.

that the species involved are protonated forms of chlorine acetate. With such reagents the relative reactivities of the *ortho*- and *para*-positions are determined by relative electron densities at these positions and the *ortho*-position would be expected to be of higher reactivity because of its activation by a methyl group *ortho* to it. It is concluded from this that inductive electron displacements are more important than conjugative displacements for positively charged reagents.[20,21]

The *o* : *p* ratio is greater for toluene than for *o*-xylene in the reactions of the substrates with molecular and protonated forms of chlorine acetate. This is, presumably, due to buttressing effects of the methyl groups in *o*-xylene.[22] The difference is, however, greater for the reaction with the more reactive electrophile. It is significant that in the hydrogen exchange reactions of polymethylbenzenes in 83 mole-% aqueous trifluoroacetic acid (a medium which provides a highly reactive electrophile) the *o* : *p* ratio in toluene is greater than in *o*-xylene.[10,22]

The reactivity of the 3-position in *o*-xylene is lower than the 4-position for chlorination by molecular chlorine acetate in 99% ($f_3^{o\text{-xylene}} = 253$, $f_4^{o\text{-xylene}} = 302$,) and in 75% aqueous acetic acid ($f_3^{o\text{-xylene}} = 354$, $f_4^{o\text{-xylene}} = 473$), whereas the reverse order holds for protodesilylation.[7] This confirms the view that for the latter reaction the enhancement of reactivity of the 3- over the 4-position must be due to steric acceleration.

The agreement between observed and calculated values for the partial rate factors for the chlorination of xylenes by chlorine acetate and also by its protonated forms is satisfactory, and thus precludes any appreciable steric effect of the methyl group in *o*-xylene. An indirect estimate of f_3^{Me} can be made from the values established for the 2-position in toluene and the 2-position in *p*-xylene. The value calculated on this basis (2.9) accords well with that quoted by de la Mare *et al.*[15] Our results confirm their finding that for the reactions of the xylenes with chlorine acetate the rates are in reasonable accord with those predicted for the additivity principle. Similar conclusions have been drawn by Lauer *et al.* for the hydrogen exchange reactions of polymethylbenzenes.[10]

We thank Mr. O. T. El Bedawi for help with the g.l.c. analysis.

[4/2234 *Received*, 29*th October*, 1974]

---

[20] R. Baker, C. Eaborn, and R. Taylor, *J. Chem. Soc.*, 1961, 4927.

[21] R. Taylor, G. J. Wright, and A. J. Holmes, *J. Chem. Soc.* (*B*), 1967, 780.

[22] P. B. D. de la Mare and J. H. Ridd, 'Aromatic Substitution, Nitration and Halogenation,' Butterworths, London, 1959, pp. 145—146.