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Addition–Elimination Reactions in Heterolytic Chlorinations of *p*-Xylene

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Chlorinations of *p*-xylene and chloro-*p*-xylene with molecular chlorine at 20—21 °C in the dark and in acetic acid and, second, of *p*-xylene in nitrobenzene and neat with or without weak catalysts, have been carried out. The results are compared with those obtained for the $FeCl_3$-catalysed chlorinations of *p*-xylene and chloro-*p*-xylene and reveal that dichloro derivatives (especially 2,3-dichloro-*p*-xylene) are obtained directly from *p*-xylene, probably by an addition–elimination mechanism which occurs in all the media used except for the $FeCl_3$-catalysed chlorination. The direct formation of dichloro derivatives from *p*-xylene, as well as that of trichloro-*p*-xylene from chloro-*p*-xylene, is shown by chlorination of an equimolar mixture of [$^2H_{10}$]-*p*-xylene and chloro-*p*-xylene. The separation and evaluation of deuteriated and non-deuteriated chloro derivatives are carried out by g.l.c. on capillary columns.

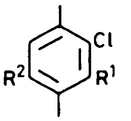
Addition–elimination may be a general mechanism for electrophilic substitution in aromatic systems. Nevertheless, the higher stability of aromatic products in comparison with that of non-aromatic adducts has made it customary to consider aromatic substitution essentially as a reaction in which carbocations are involved. However, addition–elimination routes ought to receive more attention in view of the many examples in the literature in which addition accompanies (or precedes) substitution in reactions of quite simple aromatic hydrocarbons under conditions leading to heterolytic processes. Thus, in the chlorination of biphenyl derivatives in acetic acid,[1] products of substitution are obtained as the main components, accompanied by products of addition such as tetrachloro and acetoxytrichloro derivatives. Products of addition are also obtained in the chlorination of naphthalene,[2] phenanthrene,[3] and some benzene derivatives.[4,5] Even side-chain substitution can be a consequence of addition–elimination reactions occurring under heterolytic conditions.[6]

If addition–elimination occurs in the chlorination of alkylbenzenes, it should lead to dichloro rather than monochloro derivatives because the olefinic system produced by the addition of one molecule of chlorine is very reactive and it is able to take up a further molecule of chlorine giving rise to unstable tetrachloro adducts which are transformed into aromatic dichloro derivatives by elimination of two molecules of HCl.

Although this reaction has not been observed in the chlorination of benzene and its alkyl derivatives by molecular chlorine under heterolytic conditions, when industrial xylene is chlorinated in acetic acid or in nitrobenzene greater quantities of dichloro-*m*-xylenes are obtained than when the same xylene is chlorinated with $FeCl_3$ catalyst. Moreover, the rate of formation of dichloro-*m*-xylenes in the chlorination of industrial xylene in acetic acid or nitrobenzene is greater than that of chloro-*p*-xylene.[7] On the other hand, the quantity of dichloro-*m*-xylenes obtained by chlorination of industrial xylene using dichloroacetic acid (DCA) as a catalyst decreases with the increasing concentration of DCA.[8]

These results are in opposition to those expected for an electrophilic chlorination, and suggest the formation of dichloro derivatives by an addition–elimination route.

In this paper we report the results obtained in the chlorination of *p*-xylene and chloro-*p*-xylene by molecular chlorine in several media and with different catalysts, focused on the formation of 2,5-dichloro-*p*-xylene (**1**) and 2,3-dichloro-*p*-xylene (**2**). The evidence for the formation of (**2**) directly from *p*-xylene is corroborated by chlorination of an equimolar mixture of [$^2H_{10}$]-*p*-xylene and normal chloro-*p*-xylene.



(**1**) $R^1 = H$, $R^2 = Cl$
(**2**) $R^1 = Cl$, $R^2 = H$

Results and Discussion

Dichloro derivatives (**1**) and (**2**) are obtained in the electrophilic chlorination of *p*-xylene by consecutive chlorination of chloro-*p*-xylene. But they might also derive directly from *p*-xylene if addition–elimination occurs. If chlorination only proceeds through an S_E2 mechanism, the concentration of chloro derivatives should fit the kinetic equations for a consecutive reaction of the second order, from which the equation $d[Clpx]/d[Cl_2px] = \{(K_1/K_2)([px]/[Clpx])\} - 1$ can be deduced, where [px], [Clpx], and [Cl_2px] are the respective concentrations of *p*-xylene, chloro-*p*-xylene, and the sum of the two dichloro-*p*-xylenes.

Figure 1 shows the ratio of the finite increments of chloro-*p*-xylene and dichloro-*p*-xylene *versus* the average value of [px]/[Clpx] in each time interval. It can be seen that only the experimental values from the $FeCl_3$-catalysed chlorination give a straight line. In the chlorination of *p*-xylene in the other media used (see Table) the more inert the reaction medium the greater are the deviations from the straight line.

In the same way the (**2**):(**1**) ratio should remain constant throughout each chlorination. Nevertheless changes of this ratio occur except in the $FeCl_3$-catalysed chlorination (Table), and it does not seem probable that a change of the medium due to the conversion of *p*-xylene can account for them, even working at high concentrations of substrate. The unaltered (**2**):(**1**) ratio in the chlorination of chloro-*p*-xylene in acetic acid supports this opinion. Also, in the chlorination of *m*-xylene in acetic acid or nitrobenzene the ratio 2-chloro-*m*-xylene:4-chloro-*m*-xylene remains constant.[7]

Changes of the (**2**):(**1**) ratio and deviations shown in Figure 1 are produced, in our opinion, by addition–elimination reactions which accompany the main substitution reaction and lead to dichloro derivatives, mainly to derivative (**2**), directly from *p*-xylene. These reactions are also responsible for obtaining greater quantities of dichloro compounds in the uncatalysed or weakly catalysed chlorinations of *p*-xylene. Comparing the results obtained in the two chlorinations of *p*-xylene in acetic acid it is obvious that the addition–elimination reactions

Table. Ratios and quantities of dichloro derivatives in the chlorination of *p*-xylene and chloro-*p*-xylene

Ratio or quantity of Cl_2px	Substrate	Conversion [(%)]	10^3[$FeCl_3$]/ mol l^{-1}	CH_3CO_2H [(1:1) mol]	CH_3CO_2H [(5:1) mol]	$C_6H_5NO_2$ [(1:1) mol]	Neat	[DCA]/ 0.32 mol l^{-1}	[TFA]/ 0.28 mol l^{-1}
(2):**(1)**	*p*-Xylene	40	0.3	6.0	1.5	7.0	12.5	11.0	11.5
		60	0.3	3.5	1.2	5.7	9.0	7.8	8.4
		80	0.3	2.0	0.7	2.9	6.0	5.3	5.9
		100	0.3	0.7	0.4	1.2	2.3	2.0	2.1
[**(2)** + **(1)**][a]	*p*-Xylene	40	1.4	4.5	2.0	5.0	6.9	7.8	8.0
		60	2.8	7.4	3.6	8.5	12.0	12.3	13.2
		80	5.8	12.0	6.8	13.6	17.6	17.6	18.9
		100	20.0	30.5	18.9	30.8	30.4	30.4	31.2
(2):**(1)**	Chloro-*p*-xylene	20	0.3	0.2					
		30	0.3	0.2					
		40	0.3	0.2					
		50	0.3	0.2					

[a] Percentage in reaction mixture.

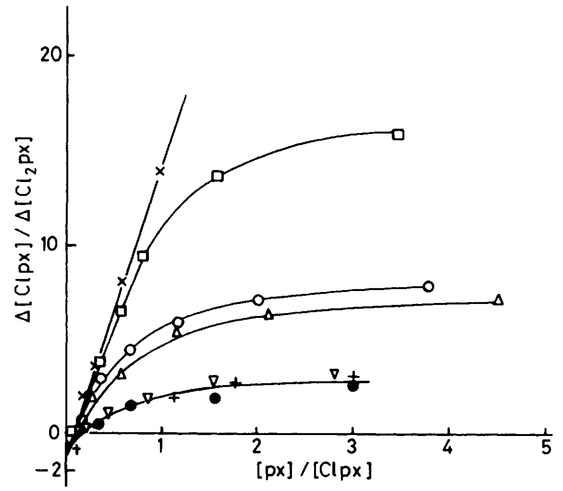


Figure 1. Plot of Δ[Clpx]/Δ[Cl_2px] *versus* [px]/[Clpx] (average value), for the chlorination of *p*-xylene in: ×, $FeCl_3$ (10^{-3} mol l^{-1}); □, CH_3CO_2H (5:1 mol); ○, CH_3CO_2H (1:1 mol); △, $C_6H_5NO_2$ (1:1 mol); ▽, DCA (0.32 mol l^{-1}); +, TFA (0.28 mol l^{-1}); ●, neat

increase with the concentration of the substrate but they obtain even for a solvent–substrate ratio of 5.

In order to prove the existence of addition–elimination reactions leading to the formation of the compounds **(1)** and **(2)**, the chlorination of an equimolar mixture of [$^2H_{10}$]-*p*-xylene and normal chloro-*p*-xylene was carried out. The deuteriated and non-deuteriated chloro derivatives can be separated by g.l.c. on several phases in capillary columns.[9]

Results of this chlorination are given in Figures 2—4.

The concentration of the non-deuteriated chloro-*p*-xylene is always greater than that of the deuteriated chloro-*p*-xylene (Figure 2); therefore, in a clean electrophilic chlorination, non-deuteriated dichloro derivatives would be present in a greater concentration than deuteriated ones. Nevertheless, the concentration of the deuteriated **(2)** (Figure 3) is 10 times greater than that of the non-deuteriated, showing, as was deduced from the former experiments, that most of the deuteriated **(2)** comes directly from *p*-xylene. On the other hand, the dichloro derivative **(1)** is also obtained from the consecutive electrophilic chlorination of chloro-*p*-xylene.

The rate of formation of **(2)** from [$^2H_{10}$]-*p*-xylene is 30 times greater than that of its formation from chloro-*p*-xylene, under these conditions. The rates of the direct and consecutive formation of **(1)** are similar.

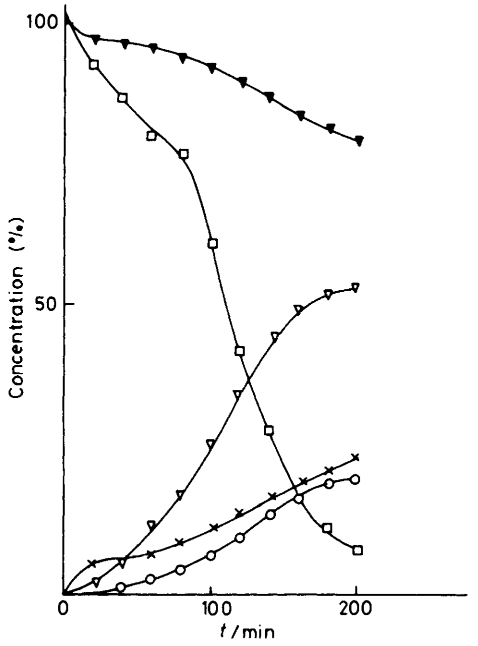


Figure 2. Plot of the chlorination of an equimolecular mixture of [$^2H_{10}$]-*p*-xylene and chloro-*p*-xylene: □, [$^2H_{10}$]-*p*-xylene; ▼, chloro-*p*-xylene; ▽, [$^2H_9$]-chloro-*p*-xylene; ×, α-chloro deuteriated derivatives; ○, deuteriated polychloroxylenes

Figure 4 shows the dichloro and trichloro derivatives obtained from chloro-*p*-xylene. The concentration of trichloro-*p*-xylene is much greater than that expected from electrophilic chlorination of the dichloro derivatives revealing that chloro-*p*-xylene undergoes the same addition–elimination reaction as *p*-xylene. The value of 0.12 obtained for the **(2)**:**(1)** ratio in the chlorination of chloro-*p*-xylene mixed with [$^2H_{10}$]-*p*-xylene remains constant throughout the reaction, confirming that neither compound **(1)** nor **(2)** is essentially monochlorinated, and therefore that trichloro-*p*-xylene comes directly from chloro-*p*-xylene.

Although the extent to which the addition–elimination reaction occurs depends on the nature of the medium, it contributes considerably to the formation of dichloro derivatives in the chlorination of *p*-xylene (except when it is carried out with strong catalysts such as $FeCl_3$) and it ought to be taken into account in interpreting the results.

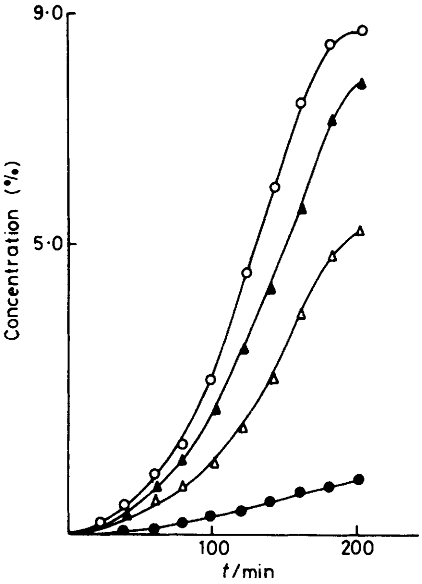


Figure 3. Formation of dichloro derivatives: ○, [$^2H_8$]-2,3-dichloro-*p*-xylene; ▲, 2,5-dichloro-*p*-xylene; △, [$^2H_8$]-2,5-dichloro-*p*-xylene; ●, 2,3-dichloro-*p*-xylene

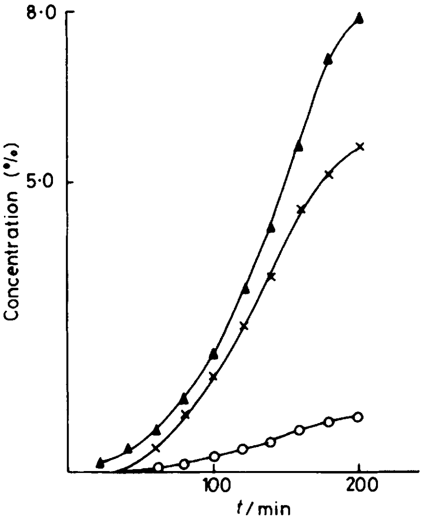


Figure 4. Products obtained in the chlorination of chloro-*p*-xylene: ▲, 2,5-dichloro-*p*-xylene; ×, trichloro-*p*-xylene; ○, 2,3-dichloro-*p*-xylene

Experimental

Materials.—Reagents used were as follows: *p*-xylene (99% pure, by g.l.c.; Scharlau-Ferosa), $FeCl_3$ (99%; Merck), acetic acid (99.7%; Probus), nitrobenzene (99.5%; Scharlau-Ferosa), chloro-*p*-xylene (99%; obtained and purified in our laboratory), chlorine (Solvay) and [$^2H_{10}$]-*p*-xylene (99% ^{2}H; Aldrich).

Chlorination Experiments.—Chlorinations were done in a glass vessel (0.8 l) provided with a refrigeration jacket and four necks, one for the chlorine stream, one for temperature measurement, one for mixing, and one as a gas outlet. Through the outlet, which was also used for sampling, a refrigerated reflux device was fitted to avoid loss of those components which could be removed by the release of hydrogen chloride. One mol of substrate was used in all reactions.

Chlorine was introduced into the medium (for medium composition, see the Table) at a constant flow rate of 3 ml s^{-1}. Purification and drying of chlorine and flow rate regulation were controlled by means of a device composed of three washing-flasks containing sulphuric acid, a flow meter, and a gas burette, as described in ref. 7. The mixing rate was 450 r.p.m. in all experiments. The temperature was maintained at 20—21 °C by refrigeration of the reactor vessel, which was protected from light.

Samples (1 ml) were taken at regular intervals, and chlorine and hydrogen chloride were removed by mixing them with a small quantity of powdered sodium hydroxide, avoiding heating of the sample. The samples were stored in flame-sealed topaz-glass ampoules until the time of analysis.

Chlorination of the equimolar mixture of [$^2H_{10}$]-*p*-xylene and normal chloro-*p*-xylene was carried out using 0.043 moles of each substrate in a small conical flask (50 ml) with a flow rate of chlorine of 0.48 ml^{-1} s^{-1}. Samples were taken by means of a micropipette and put into a glass capillary tube which contained a small quantity of powdered sodium hydroxide near the end through which the sample entered. Both ends were sealed until the time of analysis.

Samples were analysed using a Hewlett-Packard 5830 A gas chromatograph equipped with a flame-ionization detector and stainless-steel capillary columns loaded with 2,4-trixylenyl phosphate. Separation of all components was achieved at a column temperature of 100 °C; injector temperature, 250 °C; detector temperature, 250 °C; and nitrogen flow rate, 1.6 ml min^{-1}.

The products were identified by comparing them with the mixtures resulting from the chlorination of [$^2H_{10}$]-*p*-xylene and normal *p*-xylene. The calibration factors of the deuteriated compounds were calculated with the aid of these mixtures, and it was found that the results obtained from corrected areas are similar to those obtained from uncorrected areas when the percentages are independently calculated for deuteriated and normal products.

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