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KINETIC STUDY OF THE PHOTOCHEMICAL SIDE-CHAIN CHLORINATION OF P-XYLENE

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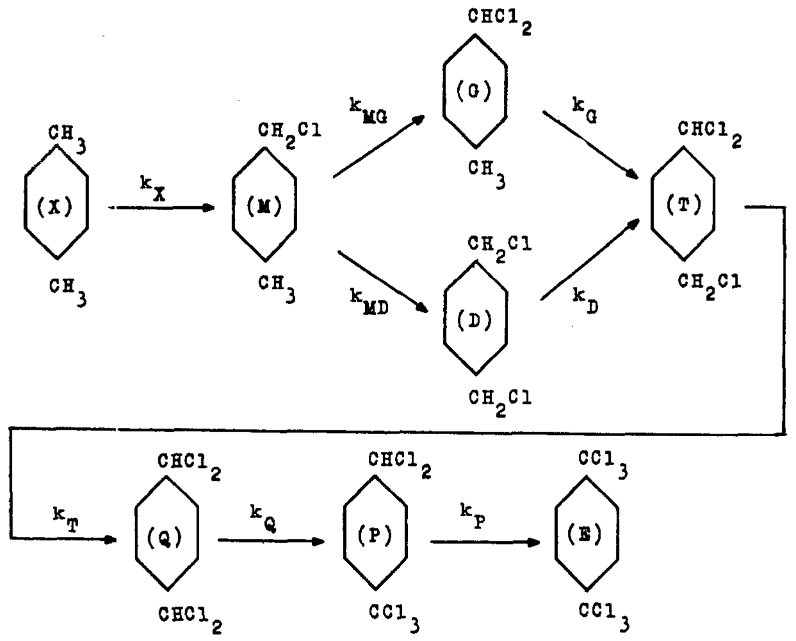
The side-chain chlorination of p-xylene was carried out in a 0.5 M CCl_4 solution, under irradiation of 3600 Å UV source. The chlorine was introduced as a continuous constant flow in a stirred glass reactor kept at 30° or 50° by circulating thermostated water into its jacket. Samples were taken and analyzed using vapor phase chromatography (Apiezon L grease on Chromosorb W at 135°).

The analytical results fitted a system of competitive, consecutive irreversible reactions according to the scheme:



Compounds M , D , Q and E were isolated as reaction products in a pure state ; G was prepared from p-tolualdehyde and PCl_5. Using these pure samples the corresponding peaks were individuated on the gas chromatograms of the reaction mixtures. Two other peaks , coming out with reasonable values of the retention time in the gas chromatographic sequence , were attributed to T and P as the only possible choice. Other products , for instance ring chlorinated compounds , did not appear in appreciable amount.

k_X , k_{MG} , k_{MD} , ... are meant as rate constants of reactions first order respect both to chlorine and to the organic substrate , for a set of kinetic equations as follows :

$$\frac{dC_X}{dt} = - k_X C_C C_X \qquad \text{(Ia)}$$

$$\frac{dC_M}{dt} = k_X C_C C_X - (k_{MG} + k_{MD}) C_C C_M \qquad \text{(Ib)}$$

$$\frac{dC_G}{dt} = k_{MG} C_C C_M - k_G C_C C_G \qquad \text{(Ic)}$$

. . . .

where C_C is the chlorine concentration; C_X , C_M , ... are the substrates concentrations. For each chlorinated compound, except E, the concentration vs. time curve goes through a maximum. This corresponds to equations of the type :

$$\frac{k_{MG} + k_{MD}}{k_X} = \frac{C_X}{C_M} \quad \text{at the maximum of M} \qquad \text{(IIa)}$$

$$\frac{k_G}{k_{MG}} = \frac{C_M}{C_G} \quad \text{at the maximum of G} \qquad \text{(IIb)}$$

. . . .

Furthermore the (k_{MG}/k_{MD}) ratio is equal to the limit value of the distribution ratio (C_G/C_D) at the initial time of reaction, that is :

$$\frac{k_{MG}}{k_{MD}} = \lim_{C_D \to 0} \left(\frac{C_G}{C_D} \right) \qquad \text{(III)}$$

Plots were made reporting C_M vs. C_X , C_G vs. C_M , ... and (C_G/C_D) vs. C_D in order to get the maximum or limit values required from equations (II a,b,....) and (III). Relative rate constants (referred to the arbitrary value $k_X = 1$) were so obtained. Four runs have been performed at 50° , some mainly covering the low degrees of chlorination , some the high ones. They gave the following average values :

k_X	k_{MG}	k_{MD}	k_G	k_D	k_T	k_Q	k_P
1	0.085	0.234	0.396	0.0793	0.0333	0.00843	0.00346

One run at 30° gave the values:

1	0.075	0.235	0.353	0.0749	0.0277	0.00694	-

The relative rate constants at 50° reported above were tested calculating with them the concentrations C_X , C_M , C_G , ... as functions of the degree of chlorination y. The mathematical treatment employed will be reported elsewhere. Continuous curves in Fig.1 represent the results of the calculation; the experimental points refer to only one run, the other runs being equally satisfactory.

As the rates of photochemical chlorinations are governed by the attack of Cl° radicals on C-H bonds (1), relative rate factors per C-H bond (f_r) were obtained taking into account the number of hydrogens available for each reaction. They are reported in **Table 1.**

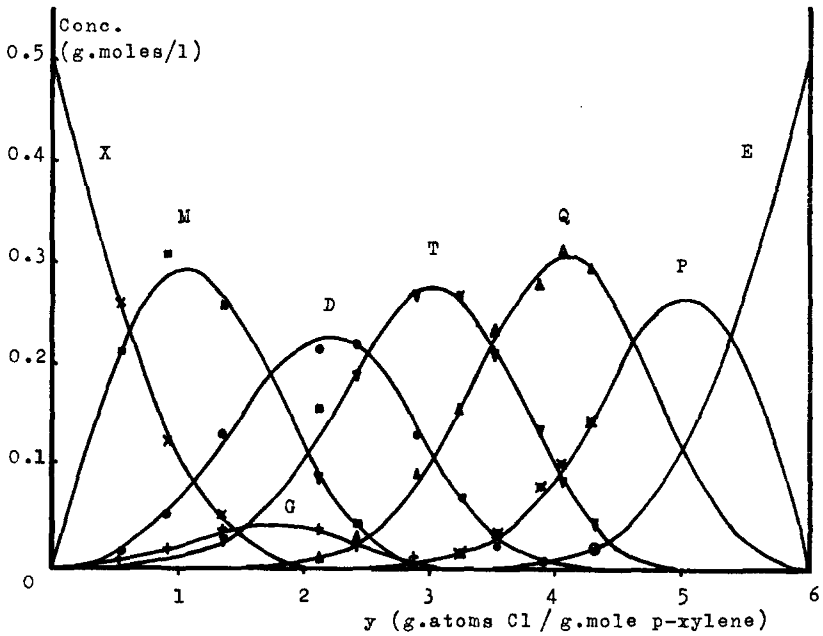


FIG. 1

Molar concentrations of reagent and products vs. degree of chlorination (50°). Solid lines: calculated curves. Points:

× xylene (X)
■ α-chloro-xylene (M)
+ α,α-dichloro-xylene (G)
● α,α'-dichloro-xylene (D)
▼ α,α,α'-trichloro-xylene (T)
▲ α,α,α',α'-tetrachloro-xylene (Q)
✖ α,α,α,α',α'-pentachloro-xylene (P)
○ α,α,α,α',α',α'-hexachloro-xylene (E)

TABLE 1

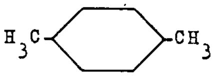
Relative rate factors per C-H bond (f_r) (at 50°).

the bond belongs to the group :	group present in the para position: CH_3	CH_2Cl	$CHCl_2$	CCl_3
CH_3	1	0.47	0.79	-
CH_2Cl	0.26	0.12	0.10	-
$CHCl_2$	-	-	0.025	0.021

As the data in Table 1 show , both chlorine atoms in α- and chlorinated groups in para- lower the reactivity of the C-H bond towards the electrophilic Cl• radicals ; however the former effect is larger than the latter. The relative reactivities in CH_3 and $CHCl_2$ differ by factors in the range 4-8; between CH_2Cl and $CHCl_2$ the factor is around 4. On the other hand the substitution of a Cl atom for hydrogen on the para group gives a reduction of rate between 1.2 and 2.1 , except when going from α-chloro- (M) to α,α-dichloro-p-xylene (G). However it should be pointed out that the f_r factor referring to G is less accurate than the others, that compound being always present in small amounts.

On the whole it appears that the inductive effect of chlorine is governing the rates of the reactions. This has been found also by H.G.Haring and H.W.Knol on toluene (2) , their f_r values being : 1 , 0.18 , 0.042 (at 40°) for C-H bonds included in CH_3 , CH_2Cl and $CHCl_2$ respectively. Similarly G.Benoy and J.C.Jungers (3) have found that side-chain C-H bonds in benzyl chloride react more slowly than in toluene by a factor 1 : 7 . In contrast to this there are cases in which the inductive effect of chlorine is overcome by opposite influences , as for instance in the chlorination of trimethylacetic acid (4).

Our experience at 30° indicates a lowering of almost all the relative rate constants respect to the 50° case. The same fact has been reported for toluene side-chain chlorination (2) in the range 40 - 100°. Clearly successive chlorinations after the first tend to have a higher activation energy. The increments $\Delta\Delta E^{\ddagger}$ are of the order of 1 Kcal/mole going from C-H in CH_3 to C-H in CH_2Cl , and of 2 Kcal/mole going from



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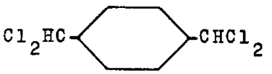

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