Aromatic Substitution: Selectivity and the Rate-determining Step

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THE kinetics of many electrophilic substitution reactions of benzene and alkylbenzenes with strong electrophiles (NO_2^+, Br^+, Cl^+, R^+) have been studied by Olah and his co-workers.[1] The determination of the competitive rate was used to establish the relative reactivities of benzene and alkylbenzenes, which were in line with relative stabilities of complexes of alkylbenzenes with Ag^+, Br^+, I_2, ICl, SO_2, picric acid, HF, and HCl (which are considered as π-complex-forming agents). To explain these results, Olah assumed that the rate-determining step was the formation of a π-complex between the electrophile and the aromatic ring.

Tolgyesi[2] showed however that the competitive nitration of benzene and toluene with nitronium tetrafluoroborate could be influenced by non-kinetic factors (diffusion-control). This has prompted us to investigate the aluminium chloride† catalyzed bromination and chlorination.

We therefore studied (*a*) direct brominations and competitive brominations of benzene and toluene in the solvents, nitromethane and nitrobenzene; (*b*) direct chlorinations and competitive chlorinations of benzene and toluene in nitrobenzene.

All the direct reactions exhibit third-order kinetics: rate = $k_3[X_2][AlCl_3][ArH]$, the results of which are listed and compared with Olah's results (Table 1).

There is too much difference between the rate constants of studied reactions, so that the competitive method of rate determination cannot be applied. To prove this point, we carried out competitive bromination and chlorination of benzene and toluene in nitrobenzene and nitromethane. Table 2 shows that the observed relative rate ratios are different from direct results and change with the initial concentrations of aromatic components; this should not be observed if competitive conditions were experimentally correct.[3]

TABLE 1

Our results obtained by direct kinetics				Olah's results by competitive kinetics	
in $PhNO_2$	$\frac{k_3(\text{Tol})}{k_3(C_6H_6)}$	in $MeNO_2$	$\frac{k_3(\text{Tol})}{k_3(C_6H_6)}$	in $MeNO_2$	$\frac{k(\text{Tol})}{k(C_6H_6)}$
Bromination					
0°	172	0°	470	25°	3·6
30°	52	30°	38		
Chlorination					
0°	247	0°	215	25°	13·5
15°	186				

TABLE 2

Nitrobenzene as solvent $[AlCl_3]$ = 0·8, $[Br_2]$ or $[Cl_2]$ = 0·4 moles l.$^{-1}$						Nitromethane as solvent $[AlCl_3]$ = 1·3, $[Br_2]$ = 0·7 mole l.$^{-1}$		
Bromination 30°			Chlorination 15°			Bromination 30°		
C_6H_6	Toluene	$\frac{k(\text{Tol})}{k(C_6H_6)}$	C_6H_6	Toluene	$\frac{k(\text{Tol})}{k(C_6H_6)}$	C_6H_6	Toluene	$\frac{k(\text{Tol})}{k(C_6H_6)}$
0·4	0·4	31	0·4	0·4	150	0·6	0·6	21
0·5	0·3	30	2·0	0·4	160	0·6	1·3	13
0·8	0·2	29	0·4	2·0	‡	1·3	0·6	16
0·8	0·3	28	1·6	1·6*	‡	2·6	2·6	10*
0·4	2·0	24						
2·0	0·4	24						
1·6	1·6	10*						

* Olah's conditions. ‡ Experimentally nonmeasurable.

Moreover a decrease of the toluene:benzene relative rates occurred with the increase of overall

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† Aluminium chloride is the easiest Friedel–Crafts catalyst to use.

aromatic concentration, whereas Olah had achieved a low substrate selectivity by using from 0·30 to 0·50 mole of aromatic substrate in 1 mole of solvent.

By comparison of these results with those of Olah's, it can be seen that the observed relative reactivities of toluene and benzene cannot be related to the stabilities of the π-complex, and from our experimental results, we suggest that the mechanism of the acidic halide-catalyzed bromination and chlorination involve the formation of a "σ-complex activated state" as the rate-determining step.

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[2] W. S. Tolgyesi, *Canad. J. Chem.*, 1965, **43**, **343**.

[3] J. C. Jungers, "Cinétique chimique appliquée," L'Institut Français du Pétrole, Paris, 1958, p. 151.