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REACTIVITIES OF SUBSTITUTED PHENYL RADICALS

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Relative reactivities of substituted phenyl radicals in chlorine abstraction from carbon tetrachloride were estimated by carrying out competitive reactions of the radicals with carbon tetrachloride and iodine. Negative substituents on the radicals were found to retard the reactivities of chlorine abstraction.

Relative reactivities of many sorts of substrates towards a given radical have been determined and discussed extensively,$^{1)}$ but relative reactivities of several radicals toward a given substrate have not yet been determined, because of experimental difficulties in the estimation. As one of approximate approaches, we tried to estimate relative reactivities of substituted phenyl radicals in chlorine abstraction from carbon tetrachloride by carrying out competitive reactions of aryl radicals between carbon tetrachloride and iodine.

$$\mathrm{Ar}\cdot + \mathrm{CCl_4} \xrightarrow{k_{Cl}} \mathrm{ArCl} + \cdot\mathrm{CCl_3}$$
$$\mathrm{Ar}\cdot + \mathrm{I_2} \xrightarrow{k_{I}} \mathrm{ArI} + \cdot\mathrm{I}$$

Since the reaction of the radical with a scavenger such as iodine is of very low activation energy, k_I may be assumed to be almost unvariable irrespective of the nature of the aryl radical. Then, to a first approximation, k_{Cl}/k_I obtained from the above competitive method will be a measure of the relative reactivities of the radicals towards carbon tetrachloride.

A solution of arylazotriphenylmethane (ArAT) (0.018-0.034M) in carbon tetrachloride containing iodine (0.015-0.05M) was placed in a reaction tube, degassed, sealed in vacuo and heated at 60°C for 4 hours. Chlorobenzenes and iodobenzenes thus produced were analyzed with VPC. Hydrogen abstraction products were not formed and total yields of chlorobenzenes and iodobenzenes, being about 90%, are roughly independent of the initial iodine concentration in the reactions of p-chlorophenyl and phenyl radicals. On the other hand, about 70% of p-nitrophenyl radicals were accounted for as these products. Pryor et al$^{2)}$ obtained similar total yields in decomposing phenylazotriphenylmethane in iodine-containing carbon tetrachloride.

Relative rate constants k_{Cl}/k_I were calculated from the yields of chlorobenzenes and iodobenzenes according to the following equation;

$$\frac{k_{Cl}}{k_I} = \frac{[ArCl]_f}{[CCl_4]_i} \Bigg/ \ln \frac{[I_2]_i}{[I_2]_i - [ArI]_f}$$

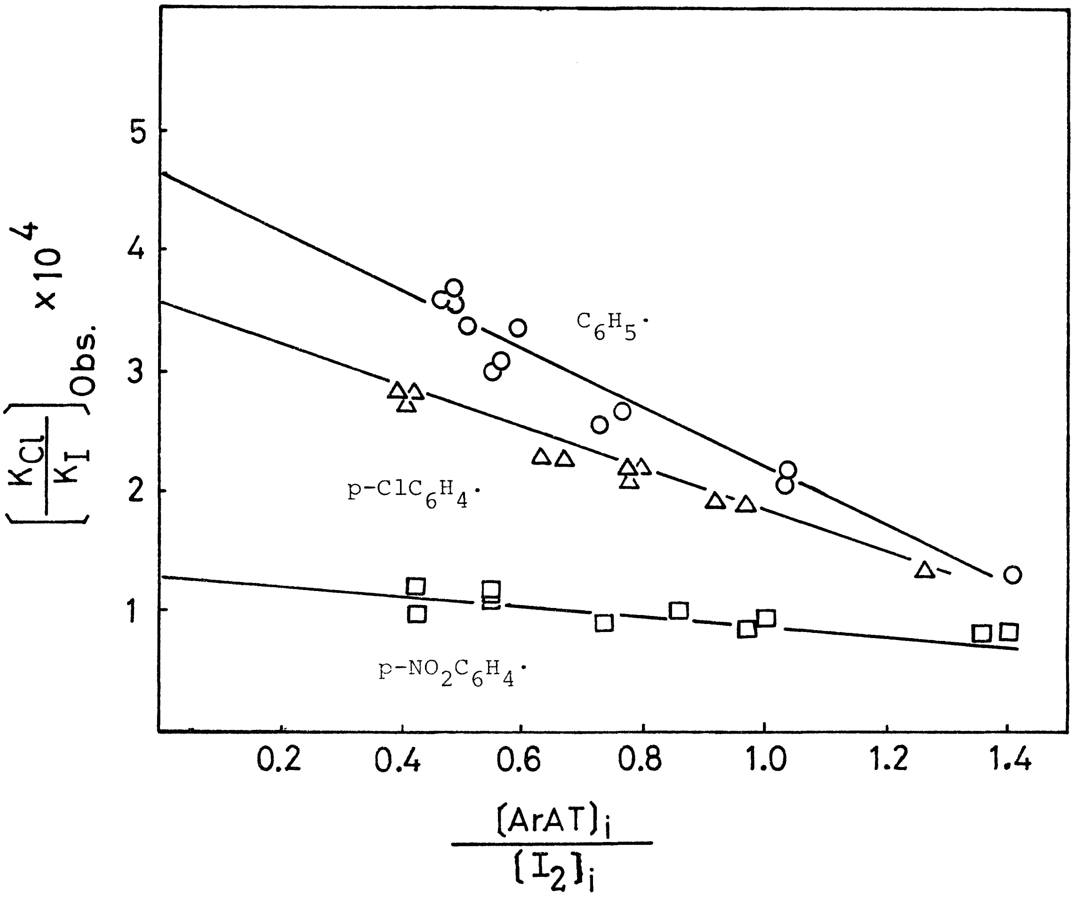
where suffix i and f note initial and final concentrations, respectively. As shown in Fig. 1, the apparent k_{Cl}/k_I values thus obtained, however, were linearly related to the relative initial concentration of iodine to aryl radical generator This indicates that there are other paths forming aryl iodide which become important as iodine is consumed. For example, aryl iodide may be formed through iodine abstraction from trityl iodide which would be formed during the reaction. The true k_{Cl}/k_I values, then, were estimated by extrapolation to $[ArAT]_i/[I_2]_i=0$ to be 4.62×10^{-4}, 3.48×10^{-4} and 1.23×10^{-4} for phenyl, p-chlorophenyl and p-nitrophenyl radicals, respectively. Thus, electronegative substituents on the radicals were demonstrated to retard the reactivities in chlorine abstraction from carbon tetrachloride, as shown in Table 1.

On the other hand, relative rates between hydrogen abstraction from cyclohexane and chlorine abstraction from carbon tetrachloride or between addition tc double bonds of allylic compounds and chlorine abstraction from carbon tetrachloride have been determined.$^{3,4)}$ Combining these data with the present result, relative reactivities of substituted phenyl radicals in hydrogen abstraction and addition can be calculated. These are also shown in Table 1, reactivity of phenyl radical being taken as unity. Contrasting to chlorine abstraction, reactivities in hydrogen abstraction from hydrocarbon and in addition to a double bond are shown to be enhanced by electronegative substituents on radicals.

Table 1 Reactivities of Aryl Radicals

	Substrate	$C_6H_5\cdot$	$p\text{-}ClC_6H_4\cdot$	$p\text{-}NO_2C_6H_4\cdot$
Chlorine Abstraction	CCl_4	1.0	0.75	0.27
Hydrogen Abstraction	Cyclo-C_6H_{12}	1.0	-	2.3
Addition	$CH_2=CHCH_2Br$	1.0	2.0	2.2

Figure 1 Relative Rate Constants vs. Initial Concentration Ratio of $[ArAT]_i/[I_2]_i$



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