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REACTIVITIES OF ARYL RADICALS IN HYDROGEN ABSTRACTION AND ADDITION

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Relative reactivities of aryl radicals in hydrogen abstraction from negatively substituted aliphatic hydrocarbons and addition reaction to the double bonds of allyl compounds were estimated.

Relative reactivities of aryl radicals in hydrogen abstraction from a number of hydrocarbons, compared with those in chlorine abstraction from carbon tetrachloride, have been determined by Pryor et al.$^{1)}$ Some additional data were obtained by carrying out competitive reactions of aryl radicals derived by decomposition of aroyl peroxides in mixtures of carbon tetrachloride and negatively substituted aliphatic hydrocarbons. Reactivities of hydrogen donors per C-H bond relative to that of one of the four C-Cl bonds in carbon tetrachloride are summarized in Table 1.

On the other hand, reactivities of the radicals in addition reaction to an ethylenic bond have not yet been estimated, perhaps because reactions which are simple and clear enough to estimate the reactivities have not been available.

Recently we found that aryl radical from arylazotriphenylmethane with allyl compounds such as allyl sulfides and allyl bromide gave 3-arylpropenes.$^{2)}$ Since the intermediate radical resulted from addition of an aryl radical to the terminal methylene of an allylic substrate gives rise to 3-arylpropene by liberating a thiyl radical or a bromine atom almost quantitatively, the reaction may be quite suitable for estimation of addition reactivities of aryl radicals.

$$\mathrm{Ar\cdot} \quad + \quad \mathrm{CH_2{=}CHCH_2X} \xrightarrow{k_{ad}} \mathrm{ArCH_2CH{=}CH_2} \quad + \quad \mathrm{X\cdot}$$

$$\mathrm{Ar\cdot} \quad + \quad \mathrm{CCl_4} \xrightarrow{k_{Cl}} \mathrm{ArCl} \quad + \quad \mathrm{\cdot CCl_3}$$

-X: -SR, -Br

Thus relative reactivities of addition reaction of aryl radical to the double bond in comparison with chlorine abstraction from carbon tetrachloride were easily calculated from relative yields of 3-arylpropenes and chlorobenzenes by the following equation;

$$\frac{k_{ad}}{k_{Cl}} = \frac{[ArCH_2CH{=}CH_2]_f}{[ArCl]_f} \times \frac{[CCl_4]_i}{[CH_2{=}CHCH_2X]_i}$$

where suffix f and i represent final and initial concentrations.

A solution of arylazotriphenylmethane (~0.1 M) in a mixture of allylic substrate and carbon tetrachloride was placed in a reaction tube, degassed, sealed in vacuo and heated at 60°C for 4 hours. Products were analyzed with vpc. In all cases more than 80% of aryl radicals were accounted for by hydrogen abstraction from allylic substrates, halogen abstraction and formation of 3-arylpropenes. The relative rate constants k_{ad}/k_{Cl}, average values of three or four runs, are shown in Table 2.

Table 1. Rates of hydrogen abstraction by aryl radicals generated from aroyl peroxides relative to chlorine abstraction from carbon tetrachloride. (80°C)

Substrate	$p\text{-}CH_3C_6H_4\cdot$	$C_6H_5\cdot$	$p\text{-}ClC_6H_4\cdot$	$p\text{-}NO_2C_6H_4\cdot$
CH_3CCl_3	0.033	0.064	0.084	0.137
$(CH_3)_2CCl_2$	0.037	0.056	0.080	0.154
$(CH_3)_3CCl$	0.037	0.044	0.058	0.185
$(CH_3)_3CCN$	0.023	0.030	0.044	0.098
Cyclohexane[‡]	0.37	0.36	1.17*	3.1

* p-bromophenyl radical

‡ aryl radicals generated from arylazotriphenylmethanes

Table 2. k_{ad}/k_{Cl} values* obtained by the competitive reactions of aryl radicals with allyl compounds and carbon tetrachloride. (60°C)

$CH_2=CHCH_2X$	$p-CH_3OC_6H_4\cdot$	$C_6H_5\cdot$	$p-ClC_6H_4\cdot$	$p-NO_2C_6H_4\cdot$
$-SCH_3$	11.2	12.0	28.0	128
-Br	20.0	24.8	67.2	200

*reactivities of terminal methylene compared with those of a C-Cl bond of carbon tetrachloride

The results show that both of k_{ad}/k_{Cl} and k_H/k_{Cl} values increase in introducing electronegative substituents on the radical. At least two factors, perhaps both of them, are responsible to the tendencies, these are effects of polar natures of the attacking radicals on the rate of hydrogen abstraction or addition and on the rate of chlorine abstraction from carbon tetrachloride. We can hardly predict which factor more important is, unless some quantitative informations on relative reactivities of aryl radicals toward carbon tetrachloride are available.

Comparing the values of k_H/k_{Cl} with k_{ad}/k_{Cl} for each attacking radical, it is notable that the radicals add to the double bond much faster than abstract a hydrogen atom. And the preference in addition is almost irrespective of the substituent in radical. Thus for each aryl radical, k_{ad}/k_{Cl} for allyl methyl sulfide is about forty times larger than k_H/k_{Cl} for cyclohexane. This may indicate that the nature and the magnitude of polar influences of the substituents on radicals are almost the same between hydrogen abstraction and addition.

References

1) W. A. Pryor, J. T. Echols, Jr., and K. Smith, J. Amer. Chem. Soc., 88, 1189 (1966).

2) T. Migita, M. Kosugi, K. Takayama, and Y. Nakagawa, Tetrahedron, in press.

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