Relative Reactivities of Substituted Phenyl Radicals in Elementary Reactions

By **Toshihiko Migita,* Kiyoshige Takayama, Yoichi Abe,** and **Masanori Kosugi,** Department of Chemistry, Faculty of Technology, Gunma University, Kiryu, Gunma 376, Japan

The relative reactivities of phenyl, *p*-chlorophenyl, and *p*-nitrophenyl radicals, derived from arylazotriphenylmethane, towards chlorine abstraction from carbon tetrachloride were estimated from the results of the competitive reaction of the radicals with carbon tetrachloride and iodine, assuming that the rate of scavenging of the radicals by iodine is almost invariant, irrespective of the substituent on the radical. On the basis of the results, the relative reactivities of these radicals in other elementary reactions such as hydrogen abstraction, bromine abstraction, addition to benzene or allyl sulphide, and S_H2 displacement on disulphide were estimated. These data show that *p*-chloro- and *p*-nitro-phenyl radicals are more reactive than phenyl towards electron-donating substrates and less reactive towards electron-accepting substrates.

MANY free radical reactions have been investigated from the point of view of structure–reactivity relationships.[1] In all these studies, the relative reactivity of a series of substrates towards a radical were determined by a competitive method, and the chemical behaviour of the radical has been characterized by the selectivity thus observed. The relative rates for hydrogen abstraction by aryl radicals from various hydrogen donors have been estimated from the competitive reaction of the hydrogen donor and carbon tetrachloride with the radical.[2-5] The

$$\mathrm{Ar}\cdot + \mathrm{CCl_4} \xrightarrow{k_{\mathrm{Cl}}} \mathrm{AeCl} + \cdot\mathrm{CCl_3} \qquad (1)$$

$$\mathrm{Ar}\cdot + \mathrm{RH} \xrightarrow{k_{\mathrm{H}}} \mathrm{ArH} + \mathrm{R}\cdot \qquad (2)$$

k_H/k_{Cl} values for an individual radical show that the rate of hydrogen abstraction is influenced by the dissociation energy of the C–H bond being attacked as well as the polar nature of the radical. Thus, phenyl radical has little polar nature, while *p*-nitrophenyl radical showed electron-seeking selectivity by comparison.

On the basis of a series of k_H/k_{Cl} values, however, an unequivocal diagnosis cannot always be made about relative reactivities of various aryl radicals towards a particular hydrogen donor. For example, with cyclohexane as donor the k_H/k_{Cl} value for *p*-nitrophenyl radical is larger than that for phenyl. From this fact, however, we cannot immediately draw conclusions about the relative reactivities of the two radicals towards cyclohexane, unless the ratio of k_{Cl} between *p*-nitrophenyl and phenyl radical is known.

Similar situations arise for other reactions, *e.g.* S_H2 displacement on disulphide,[6] bromine abstraction,[7] and aromatic substitution by aryl radical.[8]

$$\mathrm{Ar}\cdot + \mathrm{RSSR} \xrightarrow{k_s} \mathrm{ArSR} + \mathrm{RS}\cdot \qquad (3)$$

$$\mathrm{Ar}\cdot + \mathrm{RBr} \xrightarrow{k_{\mathrm{Br}}} \mathrm{ArBr} + \mathrm{R}\cdot \qquad (4)$$

$$\mathrm{Ar}\cdot + \mathrm{C_6H_6} \xrightarrow{k_{\mathrm{PhH}}} \mathrm{ArC_6H_6}\cdot \qquad (5)$$

The rates of reactions (3) and (4) have been measured by comparison with the rate of chlorine abstraction from carbon tetrachloride. The orientation of the aromatic arylation and reactivities of the aromatic substrates have been extensively studied. These data give much information about factors influencing the rates of the reactions and the selectivities of the attacking aryl radicals. However, again, the relative reactivities of aryl radicals towards a particular substrate, *e.g.* a disulphide, benzyl bromide, or benzene are still unknown. The present work aims to obtain at least semi-quantitative information about the relative reactivities of aryl radicals towards chlorine abstraction from carbon tetrachloride and, in turn, other elementary reactions.

As one approach, we tried to estimate the relative reactivities of substituted phenyl radicals towards chlorine abstraction from carbon tetrachloride by examining the competitive reaction of an aryl radical with CCl_4 and iodine, using arylazotriphenylmethane (ArAT) as the source of aryl radical. Since the reaction of the radical

$$\mathrm{Ar}\cdot + \mathrm{I_2} \xrightarrow{k_{\mathrm{I}}} \mathrm{ArI} + \mathrm{I}\cdot \qquad (6)$$

with a scavenger such as iodine is of very low activation energy, k_I may be assumed to be almost invariant, irrespective of the nature of the substituent on the radical. Then, to a first approximation, k_{Cl}/k_I obtained from the above competitive method is a measure of the relative reactivities of the radicals towards carbon tetrachloride [equation (7)]. Since the relative rate constants

$$\frac{(k_{\mathrm{Cl}})_{\mathrm{Ar}}}{(k_{\mathrm{Cl}})_{\mathrm{Ph}}} = \left(\frac{k_{\mathrm{Cl}}}{k_{\mathrm{I}}}\right)_{\mathrm{Ar}} \Big/ \left(\frac{k_{\mathrm{Cl}}}{k_{\mathrm{I}}}\right)_{\mathrm{Ph}} \qquad (7)$$

of a number of other elementary reactions of aryl radicals have been measured as k/k_{Cl} values, we can estimate the relative reactivities of aryl radicals for these reactions from the values of k/k_{Cl} and $(k_{Cl})_{Ar}/(k_{Cl})_{Ph}$ [equation (9)].

$$\mathrm{Ar}\cdot + \mathrm{S} \xrightarrow{k} \text{products} \qquad (8)$$

$$\frac{(k)_{\mathrm{Ar}}}{(k)_{\mathrm{Ph}}} = \frac{(k_{\mathrm{Cl}})_{\mathrm{Ar}}}{(k_{\mathrm{Cl}})_{\mathrm{Ph}}} \left(\frac{k}{k_{\mathrm{Cl}}}\right)_{\mathrm{Ar}} \Big/ \left(\frac{k}{k_{\mathrm{Cl}}}\right)_{\mathrm{Ph}} \qquad (9)$$

According to Huyser's classification,[9] radicals such as t-butyl and benzyl which on loss of an electron yield comparatively stable carbonium ions are defined as donor radicals; donor substrates are the species that yield

TABLE 1

Decomposition of arylazotriphenylmethane in carbon tetrachloride in the presence of iodine at 60 °C

$10^5[ArAT]_i/M$	$10^2[CCl_4]_i/M$	$10^5[I_2]_i/M$	$10^6[ArCl]_f/M$	$10^5[ArI]_f/M$	Total yield (%)	$10^4k_{Cl}/k_T$
Phenylazotriphenylmethane (PAT)						
4.71	2.05	3.35	9.81	3.26	90.2	1.32
4.88	2.04	4.69	7.18	3.83	93.1	2.09
4.88	2.04	4.69	7.24	3.79	92.4	2.16
4.94	2.04	6.38	5.30	4.02	92.0	2.63
4.65	2.04	6.38	4.93	3.95	95.6	2.51
4.42	2.04	8.02	3.77	3.72	92.7	2.98
4.51	2.04	8.02	3.71	3.61	88.2	3.07
4.72	2.04	8.02	3.99	3.62	84.7	3.29
4.84	2.04	9.60	3.74	3.90	87.7	3.36
4.68	2.04	9.60	3.88	3.84	90.3	3.70
5.06	2.03	10.0	4.02	4.32	93.3	3.61
5.06	2.03	10.0	3.98	4.12	89.3	3.79
p-Chlorophenylazotriphenylmethane (CAT)						
4.23	2.05	3.33	7.17	3.07	89.6	1.39
4.44	2.04	4.55	5.51	3.45	90.1	1.90
4.23	2.04	4.55	5.10	3.33	90.7	1.91
4.52	2.04	6.58	4.02	3.80	93.0	2.28
4.18	2.04	6.68	3.45	3.43	90.4	2.30
6.84	2.03	8.66	4.84	5.65	89.7	2.27
6.84	2.03	8.66	4.99	5.76	89.7	2.26
6.84	2.03	8.66	4.93	5.61	89.2	2.34
3.70	2.04	8.90	2.54	3.13	91.8	2.86
3.70	2.04	8.90	2.42	3.13	91.1	2.76
3.70	2.04	8.90	2.49	3.14	91.6	2.80
p-Nitrophenylazotriphenylmethane (NAT)						
4.52	2.03	3.23	3.31	2.76	68.4	0.84
4.40	2.03	3.23	3.21	2.73	69.3	0.85
4.58	2.04	4.59	2.11	3.03	70.8	0.95
4.45	2.04	4.59	2.07	3.12	74.8	0.89
4.47	2.03	5.12	1.64	2.98	70.4	0.93
4.47	2.03	5.12	1.71	2.99	70.7	0.96
4.83	2.04	6.56	1.62	3.87	83.5	0.89
3.74	2.03	8.77	0.638	2.44	66.9	0.95
3.74	2.03	8.77	0.724	2.23	61.5	1.22
4.85	2.03	8.79	1.09	3.44	73.2	1.08
4.85	2.03	8.79	1.20	3.58	76.3	1.12
4.85	2.03	8.79	1.15	3.36	71.7	1.17

donor radicals in radical reactions. On the other hand, acceptor substrates give radicals, *e.g.* trichloro- and acylmethyl, which yield comparatively stable carbanions upon gaining an electron. The relative reactivities of substituted phenyl radicals obtained in the present work showed the expected tendencies. Radicals with electron-withdrawing substituents are more reactive than phenyl towards donor substrates and less reactive towards acceptor substrates.

RESULTS

Decomposition of ArAT *in* I_2–CCl_4.—A solution of 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 h. The chloro- and iodo-benzenes formed were analysed by g.l.c. Results are given in Table 1. The combined yields of the chloro- and iodo-benzenes, *ca.* 90%, are roughly independent of the initial iodine concentration for the reactions of *p*-chlorophenyl and phenyl radicals. About 70% of the *p*-nitrophenyl radicals were accounted for by the corresponding products.

The relative rate constants k_{Cl}/k_I can be derived from the yields of chloro- and iodo-benzenes by equations (10) and (11) where the suffixes i and f represent the initial and final concentrations, respectively. Since the concentration of carbon tetrachloride are much larger than that of ArAT, the values of $[ArCl]_f/[CCl_4]_i$ are so small that we can apply a series expansion to the numerator of equation (11), and neglect the second and higher terms of the series.

$$\frac{k_{Cl}}{k_I} = \log\left(\frac{[CCl_4]_i}{[CCl_4]_i - [ArCl]_f}\right)\Bigg/\log\left(\frac{[I_2]_i}{[I_2]_i - [ArI]_f}\right) \quad (10)$$

$$= \log\left(1 - [ArCl]_f/[CCl_4]_i\right)/\log\left(\frac{[I_2]_i}{[I_2]_i - [ArI]_f}\right) \quad (11)$$

$$\log\left(1 - [ArCl]_f/[CCl_4]_i\right.$$

$$= -\left(\frac{[ArCl]_f}{[CCl_4]_i}\right) - \left(\frac{[ArCl]_f}{[CCl_4]_i}\right)^2 - \ldots \quad (12)$$

$$= -\frac{[ArCl]_f}{[CCl_4]_i} \quad (13)$$

Then, k_{Cl}/k_I can be represented by equation (14).

$$\frac{k_{Cl}}{k_I} = \frac{[ArCl]_f}{[CCl_4]_i}\Bigg/\log\left(\frac{[I_2]_i}{[I_2]_i - [ArI]_f}\right) \quad (14)$$

If reactions (1) and (6) are the only paths to chloro- and iodo-benzenes, the values of k_{Cl}/k_I thus obtained should be constant, irrespective of the initial concentration of ArAT and iodine. As shown in the Figure, the apparent k_{Cl}/k_I values, however, increased linearly with an increase in the initial concentration of iodine relative to that of ArAT. This suggests that there are other paths leading to aryl iodide which become important as iodine is consumed. For example, aryl iodide may be formed by iodine abstraction from trityl iodide formed during the reaction.

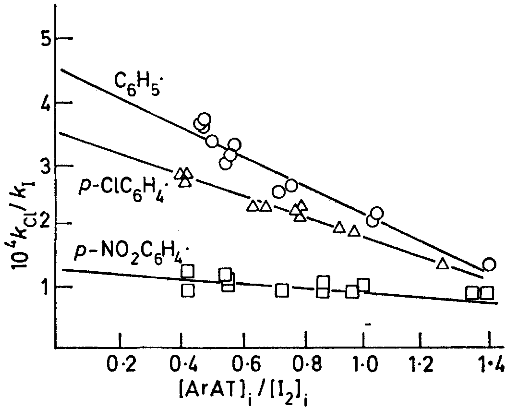
The true k_{Cl}/k_I values, therefore, were estimated by extrapolating the lines to $[ArAT]_i/[I_2]_i = 0$, giving 4.62×10^{-4}, 3.48×10^{-4}, and 1.23×10^{-4} for phenyl, *p*-chlorophenyl, and *p*-nitrophenyl radicals, respectively. If k_I can be assumed to be almost invariant irrespective of the nature of the aryl radical, then, to a first approximation, the relative reactivities of *p*-chloro- and *p*-nitro-phenyl radicals towards carbon tetrachloride are 0.75 and 0.27, respectively, that of phenyl radical being taken as unity. Thus, electron-withdrawing substituents on the radical retard the reactivity towards chlorine abstraction from carbon tetrachloride.

$$Ar{-}N{=}N{-}CPh_3 \longrightarrow Ar\cdot + N_2 + \cdot CPh_3 \qquad (15)$$

$$Ar\cdot + I_2 \longrightarrow ArI + I\cdot \qquad (16)$$

$$I\cdot + \cdot CPh_3 \longrightarrow Ph_3CI \qquad (17)$$

$$Ar\cdot + Ph_3CI \longrightarrow ArI + \cdot CPh_3 \qquad (18)$$



Relative rate constant *versus* molar ratio of $[ArAT]_i/[I_2]_i$

Decomposition of ArAT *in* $RBr{-}CCl_4$.—In order to estimate the relative reactivities of aryl radicals in reaction (4), benzyl bromide and bromotrichloromethane were chosen as electron donor and acceptor substrates, respectively.

TABLE 2

Competitive reaction of aryl radical with CCl_4 and RBr

ArAT	$[ArAT]/_i$ M	$[CCl_4]_i/[RBr]_i$	Product ArBr (%)	Product ArCl (%)	k_{PhH}/k_{Cl}
		From bromotrichloromethane			
PAT	0.38	35.8	76.0	10.0	265
	0.32	18.0	73.5	5.0	265
	0.35	21.4	74.0	6.0	265
CAT	0.44	22.6	88.0	7.0	292
	0.30	18.3	90.0	8.6	289
	0.38	26.9	74.0	7.0	284
NAT	0.35	21.4	52.0	3.3	338
	0.25	26.6	70.4	5.7	330
	0.22	22.4	69.0	4.8	319
		From benzyl bromide			
PAT	0.29	2.41	38.0	26.5	3.45
	0.22	1.25	37.4	12.5	3.73
	0.17	2.41	38.8	26.8	3.49
CAT	0.42	2.44	49.7	15.3	7.97
	0.42	2.44	47.8	15.0	7.75
	0.34	2.44	46.8	13.2	8.67
NAT	0.28	2.22	58.3	5.2	25.0
	0.30	1.42	60.1	3.7	22.8
	0.24	3.76	54.0	7.7	26.8

A degassed solution of ArAT in a binary mixture of the bromide and carbon tetrachloride was kept at 60 °C for 4 h. The amounts of ArCl and ArBr produced were determined by g.l.c. (Table 2).

Since the reactions of aryl radicals with bromotrichloromethane have been known to afford the bromine abstraction product almost exclusively,[4] the relative rate constant k_{Br}/k_{Cl} can be estimated from the relative amounts of ArBr and ArCl. Again, the total yield of halogen abstraction products was nearly quantitative (*ca.* 90%) for the reaction of phenyl and *p*-chlorophenyl, and 70% for *p*-nitrophenyl radical. Bromine abstraction from bromotrichloromethane by aryl radicals was much faster than chlorine abstraction from carbon tetrachloride as expected from the difference in bond energy between C–Cl and C–Br. Taking into account the difference in reaction temperature, the observed values of k_{Br}/k_{Cl} coincide tolerably with those estimated by Rüchardt *et al.*[7] from similar competitive experiments using t-butyl perbenzoates as sources of aryl radicals.

Competitive reactions with benzyl bromide and carbon tetrachloride gave aryl halides in combined yields of 60—70%. The residual aryl radical is thought to be consumed by hydrogen abstraction and aromatic arylation. A precise characterization of these products, however, was not achieved.

For both bromide substrates studied, the more electron-withdrawing the substituent, the larger the value of k_{Br}/k_{Cl} obtained: for bromotrichloromethane, 265, 288, and 330, and for benzyl bromide, 3.57, 8.13, and 25.6, towards phenyl, *p*-chlorophenyl, and *p*-nitrophenyl radicals, respectively. However, taking into account the relative reactivities of these radicals towards carbon tetrachloride, the relative reactivities of *p*-chloro- and *p*-nitro-phenyl towards electron-accepting bromotrichloromethane are 0.81 and 0.35, respectively, and, towards electron-donating benzyl bromide, 1.7 and 1.9, respectively, the reactivity of phenyl radical being taken as unity in each case.

Thus, the electron-withdrawing substituent on the radical was found to diminish the reactivity for bromine abstraction from bromotrichloromethane, but to accelerate bromine abstraction from benzyl bromide.

Decomposition of ArAT *in* $C_6H_6{-}CCl_4$.—Several sources of aryl radicals have been known to arylate aromatic solvents homolytically. Among them, ArAT gives particularly good yields. The mechanism of aromatic arylation has been established to involve addition of an aryl radical derived from ArAT to an aromatic solvent followed by effective hydrogen transfer between the adduct, arylcyclohexadienyl radical, and triphenylmethyl radical derived from ArAT.

Here, in order to obtain information about rates of addition of various aryl radicals to benzene [reaction (5)], relative to those for reaction (1), ArAT was decomposed in a binary mixture of benzene and carbon tetrachloride at 60 °C for 4 h, and k_{PhH}/k_{Cl} was calculated from the relative yields of ArPh and ArCl. Experimental results are shown in Table 3.

The values of k_{PhH}/k_{Cl} show that addition of phenyl and *p*-chlorophenyl radicals to benzene are slower than chlorine abstraction from carbon tetrachloride, while *p*-nitrophenyl radical undergoes addition to benzene in preference to chlorine abstraction.

Quite similar tendencies were observed in experiments using diaroyl peroxide as the aryl radical source (Table 4).

TABLE 3

Decomposition of ArAT in C_6H_6–CCl_4 at 60 °C

ArAT	[ArAT]/ M	$[CCl_4]_i$/ $[PhH]_i$	Product ArCl (%)	Product ArPh (%)	k_{PhH}/k_{Cl}
PAT	0.107	0.334	50.7	32.7	0.22
	0.113	0.334	45.2	24.8	0.18
	0.102	0.334	51.4	34.5	0.22
	0.103	0.248	43.0	27.0	0.16
	0.101	0.248	45.9	33.7	0.18
	0.105	0.248	44.7	30.6	0.17
CAT	0.098	1.006	40.3	31.2	0.78
	0.112	1.006	35.8	26.6	0.95
	0.097	0.339	20.3	43.0	0.72
	0.108	0.339	21.4	47.6	0.75
	0.107	0.454	25.7	40.3	0.71
	0.106	0.454	25.1	37.6	0.68
NAT	0.106	0.980	16.5	71.4	4.24
	0.091	0.980	15.0	62.0	4.04
	0.096	0.329	7.24	84.6	3.96
	0.103	0.338	5.73	72.3	4.26

TABLE 4

Decomposition of aroyl peroxide in C_6H_6–CCl_4 at 80 °C

$(ArCOO)_2$ Ar	$[C_6H_6]_i$/ $[CCl_4]_i$	Product ArPh (%)	Product ArCl (%)	k_{PhH}/k_{Cl}
C_6H_5	3.65	24.0	32.3	0.21
p-ClC_6H_4	3.14	36.0	21.1	0.53
p-$O_2NC_6H_4$	1.02	27.2	7.0	3.79

The reactions of benzoyl and *p*-chlorobenzoyl peroxide were carried out in the presence of a small amount of nitrosobenzene in order to convert the arylcyclohexadienyl radicals into biaryls effectively.[7] However, combined yields of biaryls and aryl chlorides were poorer than for the reaction of ArAT.

On the basis of the k_{PhH}/k_{Cl} values in Table 3 and the relative reactivities of the three aryl radicals towards carbon tetrachloride, we obtain the reactivity ratio for phenyl, *p*-chlorophenyl, and *p*-nitrophenyl towards benzene as 1 : 2.7 : 5.6.

Decomposition of p-*Nitrophenylazotriphenylmethane in Allyl Sulphide*–CCl_4.—To estimate the relative reactivities of aryl radicals towards a double bond, we need relative rate constants (k_{ad}/k_{Cl}) for addition of the respective radicals to a double bond, compared with reaction (1). Since the reaction of aryl radicals with an ordinary olefin does not give simple products, estimation of k_{ad}/k_{Cl} must be done only by indirect methods, for example by measuring the decrease of the chlorine abstraction product caused by addition of an olefin in carbon tetrachloride.[10]

However, we have found that aryl radicals add to the terminal methylene of allyl sulphide, and the adduct loses thiyl radical almost quantitatively, giving 3-arylpropene which can be determined easily by g.l.c.[10] Thus, allyl sulphides are more convenient substrates for our purpose than ordinary olefins.

$$Ar\cdot + CH_2{=}CHCH_2SR \xrightarrow{k_{ad}} ArCH_2CH{=}CH_2 + \cdot SR \quad (19)$$

The values of k_{ad}/k_{Cl} for phenyl and *p*-chlorophenyl radicals are 3.0 and 7.0 for allyl methyl sulphide and 3.7 and 14.3 for allyl phenyl sulphide.[10] The results for the reactions of *p*-nitrophenyl radical, from *p*-nitrophenylazotriphenylmethane, in allyl sulphide–carbon tetrachloride mixtures are presented in Table 5.

Thus, k_{ad}/k_{Cl} for *p*-nitrophenyl radical is 32 and 57 using allyl methyl sulphide and allyl phenyl sulphide, respectively. On the basis of the relative reactivities of aryl radicals towards carbon tetrachloride, we can estimate the reactivity ratio for phenyl, *p*-chlorophenyl, and *p*-nitrophenyl as 1.0 : 1.7 : 2.9 towards allyl methyl sulphide and 1.0 : 2.9 : 4.2 towards allyl phenyl sulphide.

DISCUSSION

Validity of the Assumption.—The method used in this work to estimate relative reactivities of aryl radicals towards carbon tetrachloride is based on the assumption that aryl radicals react with iodine at almost the diffusion-controlled rate which is invariant irrespective of the substituent on the radical. For alkyl radicals in the gas phase, there have been few examples with an activation energy of almost zero for the reaction with iodine.[11] To our knowledge there is no kinetic information on the reactions of aryl radical with iodine in solution. However, our method is thought not to be unreasonable from the following considerations. From a study of the pulse radiolysis of aromatic compounds, McLachlan and McCarthy estimated the rate constant of addition of phenyl radical to chlorobenzene at 25 °C to be 4.8 × 10^4 l mol^{-1} s^{-1}.[12] Thus, the rate constant of addition to benzene is 3—4 × 10^4 l mol^{-1} s^{-1} (the molecular rate factor for phenylation of chlorobenzene being 1—1.5).[8] Since our results give k_{PhH}/k_{Cl} 0.2 and k_{Cl}/k_I 4.6 × 10^{-4} for phenyl radical (60 °C), k_I should be *ca.* 10^8—10^9 l mol^{-1} s^{-1}, which seems near the rate constant for a bimolecular reaction essentially controlled by diffusion in a solvent of fairly low viscosity such as carbon tetrachloride.[13] Thus, our assumption seems valid to a first approximation. For the sake of caution, the point might be added that even if k_I does vary somewhat with the nature of the aryl radical, it will vary much less than k_{Cl}. If the measured k_{Cl}/k_I values reflect the relative reactivities of the radicals slightly less than fully, the observed variations should, however, be in the right order, and the qualitative conclusion would still be valid.

TABLE 5

Competitive reactions of *p*-nitrophenyl radicals from NAT with allylic compounds and carbon tetrachloride at 60 °C

$CH_2{=}CHCH_2X$ X	$\frac{[CCl_4]_i}{[CH_2{=}CHCH_2X]_i}$	Product p-$NO_2C_5H_4Cl$ (%)	Product p-$NO_2C_6H_4CH_2CH{=}CH_2$ (%)	k_{ad}/k_{Cl}
SCH_3	3.14	3.6	38.9	33.9
	3.14	3.8	41.5	34.0
	8.70	9.3	32.4	30.3
SPh	4.24	3.8	51.2	57.2
	4.24	3.7	47.5	54.8
	9.28	6.3	39.3	58.2

Instead of iodine, reactions in the presence of other radical scavengers such as di-t-butyl nitroxide or galvinoxyl were also carried out. In these cases, however, owing to experimental difficulties, particularly in determining the exact concentration of the scavenger and the amount of radical scavenged, the relative rate constants were obtained with poor reproducibility. Nevertheless, the qualitative tendencies observed were essentially the same to those presented here. At present, to obtain numerical values for the relative reactivities of the aryl radicals towards carbon tetrachloride we chose those obtained from the reactions in the I_2–CCl_4 system.

Relative reactivities of aryl radicals in other elementary reactions estimated from relative rate constants are summarized in Table 6.

Hydrogen Abstraction.—Among the data for k_H/k_{Cl} reported so far, those for electron-donating (cyclohexane and toluene) and electron-accepting (acetone and chloroform) substrates, and the relative reactivities of aryl radicals toward the respective substrates calculated from the k_H/k_{Cl} values are listed in Table 6. Towards electron-donating substrates, *p*-nitrophenyl radical reacts slightly faster than phenyl. On the other hand, towards electron-accepting substrates such as chloroform or acetone, the reactivity is reduced by the electron-withdrawing substituent.

TABLE 6

Relative reactivities of aryl radicals in various elementary reactions (60 °C)

		Rate constant relative to k_{Cl}			Relative reactivity		
Reaction	Substrate	$C_6H_5\cdot$	p-$ClC_6H_4\cdot$	p-$O_2NC_6H_4\cdot$	$C_5H_5\cdot$	p-$ClC_6H_4\cdot$	p-$O_2NC_6H_4\cdot$
Cl Abstraction	CCl_4	1.0	1.0	1.0	1.0	0.75	0.27
Br Abstraction	CCl_3Br	265	288	340	1.0	0.81	0.35
	$C_6H_5CH_2Br$	3.57	8.13	25.6	1.0	1.7	1.9
H Abstraction	cyclo-C_6H_{12}	1.08 [a]		9.3 [a]	1.0		2.3
	$C_6H_5CH_2H$	0.36 [b]		1.67 [b]	1.0		1.3
	CCl_3H	3.4 [a]	3.5 [c]	2.9 [c]	1.0	0.77	0.23
	CH_3COCH_3	0.17 [b]		0.607 [b]	1.0		0.96
Addition	Allyl–SMe	3.0 [e]	7.0 [c]	32	1.0	1.7	2.9
	Allyl–SPh	3.7 [e]	14.3 [c]	57	1.0	2.9	4.2
	C_6H_6	0.20	0.73	4.12	1.0	2.7	5.6
Metathesis	$(CH_3S)_2$	17.6 [d]		204 [d]	1.0		3.1
	$(Pr^iS)_2$	3.54 [d]		69 [d]	1.0		5.2
	$(Bu^tS)_2$	0.18 [d]		6 [d]	1.0		9.0

[a] Ref. 5. [b] Refs. 2 and 3. [c] Ref. 4. [d] Ref. 6. [e] Ref. 10.

There are many data showing Hammett correlations for hydrogen abstraction by various radicals, and these polar effects have been explained by contributions by polar structures to the transition state. Zavitsas and Pinto [14] proposed that this concept of charge separation in the transition state is not necessary, and the negative ρ values for hydrogen abstractions were ascribed to differences in the C–H bond dissociation energy. Henderson, Pryor, and their co-workers [15] presented evidence against this proposal, showing positive ρ values for hydrogen abstraction by alkyl radicals.

Our estimation of the reactivities of aryl radicals towards electron donor or acceptor substrate also supports the concept of charge separation in the transition state, because if the bond dissociation energies of the breaking and forming C–H bonds were the only factor, the relative reactivities of aryl radicals should be essentially invariant irrespective of the nature of the hydrogen donor. The relative importance of the two

$$[\mathrm{R{\cdot}H{\cdot}\ {\cdot}Ar} \longleftrightarrow \underset{\text{(I)}}{\mathrm{R^{+}H{\cdot}\ {:}Ar^{-}}} \longleftrightarrow \underset{\text{(II)}}{\mathrm{R{:}^{-}\ {\cdot}H\ Ar^{+}}}]$$

kinds of polar structure (I) and (II) in contributing to the transition state is influenced by the polar nature of the substrates and radicals. Thus in abstraction from an electron-donating substrate, the relative importance of a contribution from (I) increases, and as a result, aryl radicals bearing electron-withdrawing substituents become relatively reactive. But for electron acceptor substrates, the importance of (II) increases relatively and aryl radicals bearing electron-withdrawing substituents are less reactive.

Halogen Abstraction.—The reactivities of aryl radicals towards a halogen donor substrate showed similar tendencies to those observed for hydrogen abstraction. Thus, chlorine abstraction from carbon tetrachloride and bromine abstraction from bromotrichloromethane are less favourable for *p*-chloro- and *p*-nitro-phenyl radicals, while towards benzyl bromide *p*-chloro- and *p*-nitro-phenyl radicals are slightly more reactive than phenyl radical.

Danen and his co-workers [16] have shown that Hammett ρ constants for iodine abstraction from aliphatic and aromatic iodides are positive. We have found that the relative reactivities of *m*-substituted benzyl bromides toward the phenyl radical obey the Hammett relation, and reveal slightly nucleophilic selectivity for bromine abstraction by phenyl radical. Towards *p*-nitrophenyl radical, the reactivities of *m*- as well as *p*-substituted substrates correlate with σ^+ constants.[7]

These findings together with the present results suggest that the transition state for bromine abstraction by aryl radical from benzylic bromide may be expressed by the resonance formulae (III)—(V) and the relative contribution from each polar canonical structure depends on the nature of the substituents on both the substrate and radical. The reaction site of the benzylic substrate seems to have little carbanion character, since no correlation was observed between the relative reactivities of substituted benzyl bromides and the σ-constants of the substituents.[17] On the other hand,

$$[\mathrm{ArCH_2{\cdot}\ {:}Br^-\ Ar^+} \longleftrightarrow \mathrm{ArCH_2^+\ Br{:}^-\ {\cdot}At} \longleftrightarrow \mathrm{ArCH_2{\cdot}\ Br{\cdot}\ {\cdot}Ar}]$$

$$\mathrm{(III)} \qquad \mathrm{(IV)} \qquad \mathrm{(V)}$$

abstraction from good acceptor substrates such as CCl_4 and $CBrCl_3$ may take place through transition states bearing considerable negative charge on the substrate carbon atom, which would disfavour reaction of substrates with electron-withdrawing substituents.

$$[\mathrm{Cl_3C{:}^-\ X{\cdot}\ Ar^+} \longleftrightarrow \mathrm{Cl_3C{\cdot}\ X{:}^-\ Ar^+} \longleftrightarrow \mathrm{Cl_3C{\cdot}\ X{\cdot}\ {\cdot}Ar}]$$

$$\mathrm{(VI)} \qquad \mathrm{(VII)} \qquad \mathrm{(VIII)}$$

Addition to Unsaturated Systems.—Table 6 shows that *p*-chloro- and *p*-nitro-phenyl radical add several times faster to benzene or to the terminal methylene of allyl sulphides than phenyl radical. This implies that addition of a radical to an unsaturated system takes place through a π-electron-donating interaction of the unsaturated bond with the radical. On the basis of partial rate factors for homolytic aromatic arylation[8] and the present results, it can be noted that even with nitrobenzene, which may be electron accepting, the electron-accepting nitrophenyl radical reacts slightly faster (*e.g.* 1.7—2.8 times for the *m*-position) than phenyl. This indicates that interaction involving electron transfer from the radical to an unsaturated bond is not important, as suggested by MO calculations.[17]

S_H2 *Reactions on Disulphides*.—Reactions are known in which radicals attack a sulphur or phosphorus atom in the substrate molecule. For S_H2 reactions on disulphide, the reactivities of disulphides have been measured toward both phenyl and *p*-nitrophenyl radical [reaction (20)].[9] From the k_S/K_{Cl} values which can vary

$$\mathrm{RSSR + Ar{\cdot}} \xrightarrow{k_S} \mathrm{ArSR + RS{\cdot}} \qquad (20)$$

drastically with structural change of disulphide, we can obtain the relative reactivities of the aryl radicals towards each disulphide. The value for *p*-nitrophenyl radical relative to phenyl is larger than unity and increases with increasing electron-donating nature of the substituent on disulphide. This suggests attack of aryl radical on a sulphur atom proceeds *via* electron-donating interaction of a sulphur atom with the radical.

EXPERIMENTAL

Phenyl- (PAT),[18] *p*-chlorophenyl- (CAT),[4] and *p*-nitrophenyl-azotriphenylmethane (NAT),[19] prepared by oxidation of the corresponding hydrazo-compounds with bromine solution, were recrystallized from benzene–ethanol: PAT, m.p. 110—120 °C, $\lambda_{max.}$ 417 nm; CAT, m.p. 108 °C, $\lambda_{max.}$ 422 nm; NAT, m.p. 119 °C, $\lambda_{max.}$ 438 nm. Iodine was purified by repeated sublimation. Allyl sulphides were prepared and purified by the method previously described.[10] Other substrates (carbon tetrachloride, bromotrichloromethane, benzyl bromide, and benzene) and products (aryl iodide, bromide, and chloride, arylbenzenes, and arylpropenes) were commercially available.

Competition Experiments.—The reaction of ArAT in CCl_4–I_2 is described for a typical example. A solution of known concentrations of ArAT and iodine in carbon tetrachloride was placed in a reaction tube which was degassed by three freeze–thaw cycles, sealed under vacuum, and immersed in a thermostat at 60 °C for 4 h. Then, an internal standard for g.l.c. analysis was added [Ohkura model 710 gas chromatograph (15% Carbowax 20M; 2 m column; flame ionization detection)]. A calibration graph of peak area *versus* molarity was prepared. Iodo-, *p*-chloroiodo-, and *p*-nitroiodo-benzene were little affected by passing through the column under the conditions employed.

Other competitive experiments were performed by similar procedures. The results are summarized in Tables 1—5.

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