Halogen Abstraction Studies. IV. Abstraction of Iodine by Phenyl Radicals from 2-Substituted Iodobenzenes and Iodoferrocene[1,2]

Wayne C. Danen,* Donald G. Saunders,[3] and Kenneth A. Rose

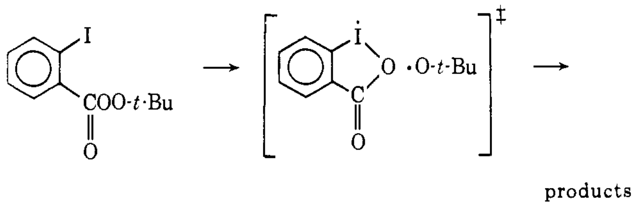
Contribution from the Department of Chemistry,
Kansas State University, Manhattan, Kansas 66506. *Received March 14, 1972*

Abstract: The rate of abstraction of iodine by phenyl radicals from a variety of 2-substituted iodobenzenes relative to the rate of abstraction of chlorine from carbon tetrachloride is reported. Qualitatively, it is found that electron-donating substituents retard and electron-withdrawing groups enhance the rate of homolytic C–I bond cleavage. Attempts are made to correlate the observed rates with various ortho-substituent parameters as well as the extended Hammett relationship (eq 6). It is concluded that steric interactions are important in determining the rate of iodine abstraction from 2-substituted iodobenzenes but that there is no need to invoke anchimeric assistance by a neighboring bromo or iodo group. The rates of iodine abstraction from 2-iodobiphenyl and 2-iodo-2′-methylthiobiphenyl are comparable, indicating no participation by the sulfide group in the abstraction process. Iodoferrocene is shown to be slightly more reactive to the phenyl radical than iodobenzene indicating a possible weak interaction of the iron atom in the abstraction process.

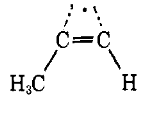
There is currently much interest in determining the influence of substituents on the course and kinetics of free radical reactions. We have demonstrated that the rates abstraction of iodine by the phenyl radical from a series of meta- and para-substituted iodobenzenes can be adequately correlated with Hammett substituent constants.[4] The positive ρ value obtained from such a correlation contrasts analogous hydrogen abstraction processes, all of which exhibit negative ρ values, indicating that there is a substantial difference in charge distribution in the transition state for homolytic cleavage of a C–I bond as compared with a C–H bond. A similar study on the rate of abstraction of iodine from a series of aliphatic iodides showed that the influence of inductive effects could be correlated by Taft polar substituent constants with a positive ρ value.[5]

In addition to exerting a usually rather minor polar effect, certain substituents, particularly bromine, iodine, and sulfur-containing groups, profoundly affect the rate and/or stereochemistry of a given homolytic process. Anchimeric assistance by neighboring halogens in homolytic reactions has been postulated in many instances, both in aliphatic[5,6] and aromatic[7] systems. In addition to the classical studies of Skell and coworkers on bridged free radicals,[6] our studies of the phenyl radical abstraction of iodine from aliphatic iodides provided evidence for anchimeric assistance by neighboring halogen substituents in appropriate aliphatic iodides.[5] The β bromine substituent in 2-bromoiodoethane produced a rate enhancement of *ca.* 90% over that anticipated from inductive effects alone. It is not possible, however, to ascertain whether the stabilization derived from the neighboring bromine is a result of greatly enhanced hyperconjugation,[8] an unsymmetrically bridged radical with incipient 1,3 bonding between the unfilled d orbital of the bromine and the p orbital of the carbon radical center,[9] or a symmetrically bridged species.[6]

In an aromatic system, Bentrude and Martin[7] have observed large accelerations in the first-order thermal decomposition rates of *tert*-butyl perbenzoates substituted in the ortho position with either an iodide or sulfide group. The enhancements observed were ascribed to neighboring-group participation in the homolytic decomposition, the O–O bond cleavage being accompanied by simultaneous O–S or O–I bond formation, probably involving an expansion of the sulfur or iodine valence octet.



In a study of the radical-chain addition of hydrogen bromide to propyne, Skell and Allen[10] observed a stereospecific trans addition yielding 100% *cis*-1-bromo-1-propene. This result was interpreted as probably arising from a rather high (≥17 kcal/mol) activation energy for the cis–trans isomerization of the $CH_3\dot{C}{=}CHBr$ radical, although it was noted that the intermediacy of a bromine-bridged radical could not be excluded.



We presently wish to report the relative rates of abstraction of iodine from a series of ortho-substituted

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[2] Part III: W. C. Danen, T. J. Tipton, and D. G. Saunders, *J. Amer. Chem. Soc.*, **93**, 5186 (1971).

[3] National Science Foundation Undergraduate Research Participant, summer 1968.

[4] W. C. Danen and D. G. Saunders, *J. Amer. Chem. Soc.*, **91**, 5924 (1969).

[5] W. C. Danen and R. G. Winter, *ibid.*, **93**, 716 (1971).

[6] P. S. Skell, *Chem. Soc., Spec. Publ.*, No. **19**, 131 (1965).

[7] W. G. Bentrude and J. C. Martin, *J. Amer. Chem. Soc.*, **84**, 1561 (1962).

[8] A. R. Lyons and M. C. R. Symons, *ibid.*, **93**, 7330 (1971); *Chem. Commun.*, 1068 (1971).

[9] P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **93**, 846 (1971).

[10] P. S. Skell and R. G. Allen, *ibid.*, **86**, 1559 (1964).

iodobenzenes. Attempts are made to correlate the rates obtained with various ortho-substituent parameters and the question of anchimeric assistance by an adjacent halogen or sulfur group is considered. The abstraction of iodine from iodoferrocene is shown to occur somewhat more readily than abstraction from iodobenzene possibly indicating participation of the iron atom in the abstraction process.

Results

The relative rates reported in Table I were obtained by the competitive technique employed in our earlier studies[2,4,5] in which the phenyl radical is allowed to react with a large excess of both the aryl iodide and carbon tetrachloride. The phenyl radicals were generated

Table I. Relative Rates of Abstraction of Iodine from 2-Substituted Iodobenzenes by Phenyl Radical at 60°

2-Substituent	k_I/k_{Cl}[a]	2-Substituent	k_I/k_{Cl}[a]
NH_2	7.6	$2'\text{-}CH_3SC_6H_4$	24.9
CH_3O	8.3	Cl	25.9
C_2H_5O	8.5	C_6H_5	34
F	14.5	Br	50
CH_3, CH_3[b]	14.6	I[d]	77
CH_3	16.9	CF_3	103
H[c]	16–18	NO_2	186
C_2H_5	19.7		

[a] Rate of abstraction of iodine relative to the abstraction of chlorine from carbon tetrachloride. [b] 2,6-Dimethyliodobenzene. [c] Estimated from the data in ref 4. [d] Corrected for a statistical factor of 2.

$$ArI + \cdot Ph \xrightarrow{k_I} Ar\cdot + PhI \qquad (1)$$

$$CCl_4 + \cdot Ph \xrightarrow{k_{Cl}} CCl_3\cdot + PhCl \qquad (2)$$

by thermal decomposition of phenylazotriphenylmethane (PAT) at 60.0 ± 0.10° and the k_I/k_{Cl} values calculated from eq 3. The combined yields of iodobenzene and chlorobenzene typically averaged 80–90% based on PAT and the k_I/k_{Cl} values were virtually insensitive to variation of the PAT concentration and ArI/CCl_4 ratio. The estimated reliability of the k_I/k_{Cl} values is ±5% for all except the faster reacting compounds for which the uncertainty is somewhat greater due to the difficulty in precisely determining the small amount of chlorobenzene produced.

$$k_I/k_{Cl} = \frac{[C_6H_5I][CCl_4]}{[C_6H_5Cl][ArI]} \qquad (3)$$

Discussion

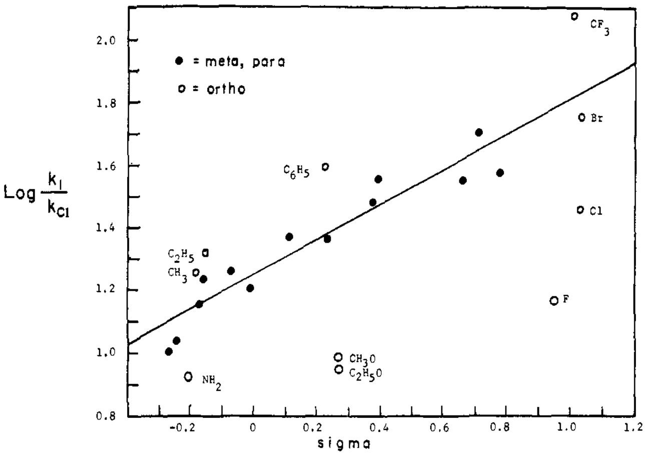

Figure 1. Plot of log (k_I/k_{Cl}) *vs.* Hammett substituent constants for meta- and para-substituted iodobenzenes (●) and ortho substituent constants proposed specifically for ortho-substituted iodobenzenes[13] (○).

2-Substituted Iodobenzenes. It is apparent from the data in Table I that the ortho substituent exerts a rather pronounced effect on iodine abstraction with a greater than 20-fold difference in rate between the slowest and fastest reacting compounds. Although steric effects are undoubtedly affecting the kinetic results to various degrees, in general, electron-donating substituents appear to retard the rate while electron-withdrawing substituents enhance the rate of iodine abstraction. This is in accord with our earlier studies which demonstrated that halogen abstraction processes produce anionic character in the transition state on the carbon from which the halogen is being removed (eq 4).[4,5]

$$\left[\overset{\delta^-}{R}\text{---}\overset{\delta^+}{I}\text{---}Ph\right]^\ddagger \quad \text{or} \quad \left[\overset{\delta^-}{R}\text{---}\overset{\delta^+}{I}\text{—}Ph\right]^\ddagger \qquad (4)$$

It should be emphasized that such a transition state description does not necessarily imply a buildup of excess electron density on the carbon in the transition state, but only that this atom acquires an increased amount of electron density relative to the ground state. It is possible that electron-donating substituents stabilize the ground state and electron-withdrawing groups destabilize the ground state, while neither type strongly perturbs the transition state. Also, it is not possible to deduce from these studies whether the iodine abstraction involves a concerted bond-breaking and bond-forming or if the reaction proceeds through two steps with the formation of a phenylaryliodine species as an intermediate.[4] However, distinction between these various possibilities is unnecessary for the following discussion.

Although the Hammett relationship has enjoyed rather widespread success in correlating rates and equilibria of meta- and para-substituted benzene derivatives, attempted correlations of ortho derivatives have been less successful. This is undoubtedly due to various *proximity effects*, a term commonly applied to the plethora of interactions possible between a reacting site and an adjacent substituent.[11] We have shown in previous studies that the relative rate of abstraction of iodine from a series of meta- and para-substituted iodobenzenes can be successfully correlated with Hammett substituent constants[4] (see Figure 1, blackened circles). Attempts to correlate the relative rates of abstraction of iodine from the ortho-substituted iodobenzenes reported in Table I were much less successful. Wide scatter was obtained when the present results were plotted *vs.* Taft's ortho-substituent constants, σ_o^*.[12] The *o*-haloiodobenzenes were particularly ill-behaved since these species exhibited rather wide differences in reactivity while the polar-substituent constants for the ortho halo groups are virtually identical.

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(11) M. Charton, *Progr. Phys. Org. Chem.*, **8**, 235 (1971), and references cited therein.

(12) R. W. Taft in "Steric Effects in Organic Chemistry," M. S. Newman Ed., Wiley, New York, N. Y., 1956, Chapter 13.

Table II. Least-Squares Fit of the Relative Rate of Abstraction of Iodine from a Series of 2-Substituted Iodobenzenes to the Extended Hammett Equation 6

α	β	δ	h	r^a	F	r_v assumed[11]
0.792	0.763	0.934	−0.219	0.960	31.9	$NO_2 = C_6H_5 = 1.77$ Å$^{\circ\ b}$
0.419	0.715	0.736	0.173	0.966	37.3	$NO_2 = 2.59^c$; $C_6H_5 = 1.77$ Å
0.492	0.288	1.427	−0.116	0.984	61.6	Omitting NO_2 and C_6H_5

[a] Multiple correlation coefficient. [b] $r_{v,min}$. [c] $r_{v,max}$. Charton prefers this larger value since the nitro group will attempt to be as nearly coplanar with the ring as possible so as to provide maximum resonance interaction. However, with an adjacent iodine, a coplanar alignment is unrealistic.

An attempt to correlate the present results with a set of σ_o constants derived specifically for ortho-substituted iodobenzenes was also futile. Hussey and Diefenderfer[13] have correlated the polarographic half-wave reduction potentials for 2-substituted bromo- and iodobenzenes with σ_o constants defined by eq 5 where SF is

$$\sigma_o = 2.4\sigma_{I,p} + (1 - SF)\sigma_{R,p} \qquad (5)$$

a steric-hindrance factor defined as the fraction of overlap between the radii of reacting groups, the radii being obtained from data on the resolution of biphenyls. The authors caution that the σ_o values obtained are not universal substituent constants but reflect the case of the phenyl halides. However, our relative rate constants for abstraction of iodine from 2-substituted iodobenzenes should be a good test for the derived σ_o parameters since there is appreciable similarity between the transfer of an electron from an electrode to the iodo group and the attack of a phenyl radical upon the iodo group. Both processes involve the attack of "one-electron species," both result in cleavage of the C–I bond, and both yield a 2-substituted phenyl radical as the initial product of the reaction. One possible difference between the two reactions is that the phenyl radical must attack the iodo group directly to effect reaction, while in the electroreduction the electron could conceivably be placed onto the molecule at a site remote from the iodo group.

A plot of the log k_I/k_{Cl} values obtained in the present work (open circles) *vs.* the set of σ_o constants derived by Hussey and Diefenderfer is shown in Figure 1. The lack of correlation was not surprising to us in view of the manner in which the ortho σ_o constants were derived. The electrochemical reduction of an iodobenzene results in a rapid cleavage of the C–I bond and the half-wave potential is anticipated to shift anodically by 30 mV for every tenfold increase in the rate constant.[14,15] Furthermore, we have demonstrated in previous work[14] that there is a pronounced steric acceleration of decomposition of certain halogenated nitrobenzene radical anions when the leaving halide ion is situated ortho to either the nitro group or another substituent and that the magnitude of the anodic shift can be correlated with the amount of steric interaction experienced by the halogen atom. Thus, the abnormal polarographic behavior of ortho-substituted halobenzenes which has been termed the "positive ortho effect" results primarily from a steric acceleration of cleavage of the carbon–halogen bond.

The futility of defining a single, generally useful set of ortho-substituent constants characteristic of the ortho-electronic effect has been expounded by Charton[11] and the necessity of utilizing an extended Hammett relationship (eq 6) has been emphasized. Here the

$$\log k_I/k_{Cl} = \alpha\sigma_I + \beta\sigma_R + \delta r_{v,min} + h \qquad (6)$$

first two terms reflect inductive and resonance effects, respectively, while $r_{v,min}$ is a steric parameter. Results of various least-squares analyses assuming different values of r_v for the phenyl and nitro groups are given in Table II. Somewhat disconcertingly, it was found that the calculated coefficients were quite dependent upon the choice of r_v and which substituents were included in the correlation. It can be seen that the success of the overall correlation is not seriously affected by these changes, but that the coefficients vary rather significantly although the steric parameter continually predominates both in magnitude and significance of correlation (as determined by individual correlation coefficients for α, β, and δ). These coefficients apparently illustrate that both electronic and steric effects are involved in determining the rate of abstraction of iodine from ortho-substituted iodobenzenes and that the steric interaction is quite significant. This contrasts the great majority of the correlations performed by Charton which were generally independent of steric effects. However, Charton noted that the iodine substituent often showed steric effects; it is not surprising that the present correlation requires a large dependence on r_v since iodine constitutes the reactive site and is common to all the compounds studied.

There appears to be no reason to invoke anchimeric assistance by a neighboring halogen substituent. The increasing rate of iodine abstraction observed in the series 2-F < 2-Cl < 2-Br < 2-I can probably be attributed largely to a steric acceleration of iodine atom removal which increases with the size of the neighboring halogen. The severe steric interaction between adjacent halogen substituents is evidenced by the distorted geometries observed for 2-diiodobenzene and even 2-dibromobenzene.[16] Additional evidence indicating the absence of halogen bridging in 2-haloaryl radicals has also been obtained[17] by showing that neither the 2-bromo- nor the 2-iodo-4-methylphenyl radical rearranges (eq 7) but instead maintains its configurational identity for a length of time sufficient to abstract a hydrogen atom from an organic solvent. However, stabilization of a radical site by an adjacent halogen by means of a hyperconjugative interaction[8] cannot be ruled out even though the overlap between the necessary orbitals in the aromatic case is not particularly favor-

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(16) L. E. Sutton, *Chem. Soc., Spec. Publ.*, No. 11, M191, M193 (1958); R. G. Strand, *J. Chem. Phys.*, **44**, 1611 (1966).

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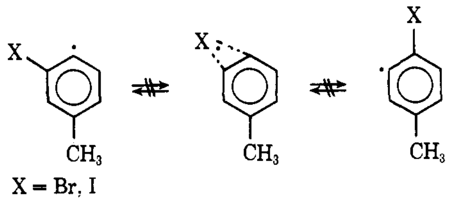
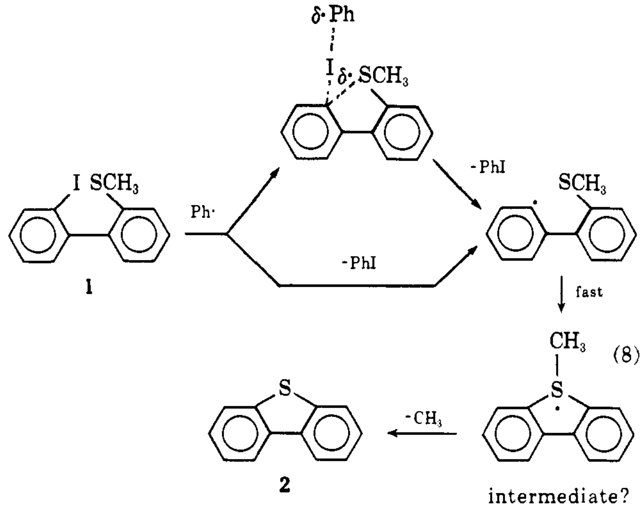


(7)

able. In summary, we have found no evidence to support anchimeric assistance or 1,2-halogen bridging in aromatic radicals but we cannot rigorously exclude such phenomena.

A comparison of the relative rates of abstraction of iodine from 2-iodobiphenyl and 2-iodo-2′-methylthiobiphenyl (**1**) indicates that the methylthiophenyl group likewise is ineffective in lending assistance in the iodine abstraction step (eq 8). Participation by the sulfur substituent in this manner might have been anticipated by analogy to the work of Bentrude and Martin[7] and by the report that **1** is photolytically transformed into dibenzothiophene (**2**), in quantitative yield in benzene solution.[18] It might be noted, however, that the ground state geometry of **1** would undoubtedly have the iodo and methylthio groups quite remote from each other to minimize steric interactions.



1

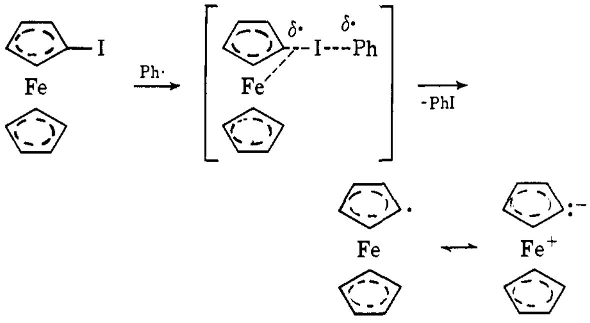
(8)

2

intermediate?

Iodoferrocene. Although the effect of a ferrocenyl group on the kinetics and stereochemistry of carbonium ion processes has received considerable attention in recent years, relatively little is known concerning the influence of this group on free radical reactions. The effect of the iron atom on the rate of formation of the ferrocenyl radical is, of course, of primary interest.

The k_I/k_{Cl} value for the abstraction of iodine from iodoferrocene was found to be 33 indicating that this compound is about twice as reactive as iodobenzene (k_I/k_{Cl} = *ca.* 16–18).[4] It has been suggested[19] that the ferrocenyl group is best considered as a somewhat complexed cyclopentadienide anion and, although its ability to supply electrons by resonance is dampened by this complexing,[20] it appears likely that ferrocene probably possesses more electron density per carbon atom than does benzene. The enhanced k_I/k_{Cl} value observed for iodoferrocene then is exactly opposite that anticipated from a consideration of polar effects and suggests possible involvement of the iron atom in some manner in the homolytic abstraction process (eq 9). The participation by the iron atom as depicted in the abstraction process and in the possible contributing resonance form **3** is, of course, purely speculative.



(9)

3

Nonetheless, the present results do indicate that the (presumably σ) ferrocenyl radical can be formed somewhat more readily by iodine abstraction than the phenyl radical. Since aryl radicals are commonly postulated as intermediates in the Ullmann reaction, it is not surprising that iodoferrocene was found to undergo this coupling reaction readily at relatively mild temperatures (60°) to produce biferrocenyl in nearly quantitative yield.[21] Interestingly, 2-iodonitrobenzene is also quite reactive in the Ullmann reaction and is likewise especially prone to abstraction of iodine by the phenyl radical as compared with other substituted iodobenzenes (Table I and ref 4).

Experimental Section

Most of the compounds used in this study were commercially available and purified in all cases by vacuum distillation.

2-Iodo-2′-methylthiobiphenyl was synthesized according to the procedure given by Kampmeir and Evans.[18] To a 20-fold excess of dimethyl disulfide in benzene cooled in an ice bath was added 1.60 g of dibenziodolium *tert*-butyl mercaptide and the solution was refluxed for 12 hr. Removal of the benzene left impure 2-iodo-2′-methylthiobiphenyl which was recrystallized twice from benzene–ethanol to yield 32% of pure product, mp 88–89°.

The dibenziodolium *tert*-butyl mercaptide was prepared essentially according to the procedure described by Greidanus, *et al.*[22] To 1.44 g of diphenyleneiodonium chloride in 100 ml of H_2O cooled in ice water was rapidly added slightly less than the stoichiometric amount of *tert*-butyl mercaptan in 10% NaOH solution. All solutions had been purged with nitrogen prior to reaction. Shortly after mixing, a fluffy yellow precipitate formed which was immediately filtered with a Büchner funnel and air-dried. No attempt was made to recrystallize the product, mp 126°.

Iodoferrocene was prepared by the reaction of chloromercuriferrocene and iodine in xylene solution,[21] mp 48–49°.

The kinetic analyses were performed as described previously[5] with the exception that carbon tetrachloride was utilized as the solvent in the present study.

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(18) J. A. Kampmeier and T. R. Evans, *J. Amer. Chem. Soc.*, **88**, 4096 (1966).

(19) J. C. Ware and T. G. Traylor, *Tetrahedron Lett.*, 1295 (1965).

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(22) J. N. Greidanus, W. J. Rebel, and R. B. Sandin, *J. Amer. Chem. Soc.*, **84**, 1504 (1962).