clohexane of $<10^{-9}$ s for $CH_3Br^{-}\cdot$ and 3×10^{-8} s for $CH_3Cl^{-}\cdot$ (P. P. Infelta and R. H. Schuler, *J. Phys. Chem.*, **76**, 987 (1972)). If these data are correct, alkyl bromides and alkyl chlorides might react by different initial steps.

(14) Radical chain reactions are usually detected by rate inhibitions resulting from addition of free-radical scavengers. Any reactions involving free-radical chains in this system must be fast to be compatible with the observation that the overall reaction is mass transport limited. Although it is possible to find a limited number of radical scavengers which are compatible with a reacting mixture of alkyl halide and magnesium, and although these scavengers produce no obvious effect on the reaction rate, it is difficult to guarantee that these scavengers would be effective in trapping the very short-lived radicals implied by the high rates observed.

(15) Clear derivations of equations relating current density to stirring rate and kinematic viscosity for a rotating disk electrode are given by J. Albery, "Electrode Kinetics", Clarendon Press, Oxford, 1975, p 49 ff; R. N. Adams, "Electrochemistry at Solid Electrodes", Marcel Dekker, New York, 1969, Section 4-4. For this electrode, the rate of consumption of reactant under transport-limited conditions depends on (diffusion constant)$^{2/3}$, (disk rotation frequency)$^{1/2}$, and (solution kinematic viscosity)$^{-1/6}$.

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Mechanism of Formation of Grignard Reagents. Kinetics of Reaction of Substituted Aryl Bromides with Magnesium and with Tri-*n*-butyltin Hydride in Ethereal Solvents[1]

Harold R. Rogers,[2] Randall J. Rogers, H. Lee Mitchell,[3] and George M. Whitesides*

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.

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Abstract: Hammett constants for reaction of substituted aryl bromides with magnesium in several solvents follow: diethyl ether ($\rho = 1.1$); di-*n*-butyl ether ($\rho = 1.9$); 3:1 v:v di-*n*-butyl ether-cyclohexane ($\rho = 2.0$); tetrahydrofuran ($\rho \simeq 0$); 3:1 v:v tetrahydrofuran-hexamethylphosphoramide ($\rho \simeq 0$); diethyl ether containing 0.8 M cyclopentylmagnesium bromide ($\rho \simeq 0$). In the polar solvents, reaction appears to be mass transport limited. The rate of reaction of aryl iodides with magnesium in diethyl ether is probably also mass transport limited ($\rho = 0$). The rate of reaction of chlorobenzene with magnesium ($\rho \simeq 2.0$) is ca. 10^4 slower than that of bromobenzene in diethyl ether, and is not mass transport limited. The reaction of aryl bromides with tri-*n*-butyltin hydride (AIBN, hν) has $\rho = 1.3$. Analysis of these values of ρ narrows the choice for the rate-determining step in the reaction of bromobenzene with magnesium in diethyl ether to one of three limiting possibilities: electron transfer from the metal to the aryl bromide (**3**), aryl radical formation by bromine abstraction from the aryl bromide by the metal (**6**), or, less probably, insertion of a magnesium atom into the carbon-bromine bond (**7**).

Introduction

This paper summarizes the results of a study of the influence of substituents and solvent on the relative rates of reaction of aryl halides with magnesium and with tri-*n*-butyltin hydride. These studies differentiate between solvents in which reactions with magnesium are mass transport limited and those in which reaction is slower than mass transport, but do not distinguish between the two most plausible limiting mechanisms for the initial reaction of organic halides with magnesium: electron transfer (eq 1) and halogen atom (or halide ion) abstraction (eq 2) (in these equations, Mg_s represents a surface magnesium atom).[4,5]

$$RX + Mg_s \rightarrow [RX^{-}\cdot] + Mg_s^{+}\cdot \rightarrow R\cdot + X^{-} + Mg_s^{+}\cdot \quad (1)$$

$$RX + Mg_s \rightarrow R\cdot + X^{-}Mg_s^{+}\cdot \quad (2)$$

Analogous studies involving alkyl halides are detailed in accompanying papers.[4,5] Aromatic bromides are reduced electrochemically at approximately the same potential as alkyl bromides,[6] but sp^2 carbon-bromine bonds are stronger than sp^3 carbon-bromine bonds, and a hypothetical aryl bromide radical anion might be longer lived than an alkyl bromide radical anion.[6-11] Further, stereochemical evidence suggests that reactions of vinylic (and, by analogy, aromatic) bromides with magnesium differ from analogous reactions of aliphatic bromides: the reaction of several stereoisomeric vinylic halides with magnesium proceeds with significant retention of stereochemistry,[12] while aliphatic organic halides appear to react with magnesium with loss of stereochemistry in all but a few cases.[13-15] Aliphatic radicals are effectively planar; unstabilized vinylic radicals are bent but invert with rate constants of ca. 10^{10} s^{-1} at room temperature.[16] Loss of stereochemistry of vinylic radicals might thus be expected to compete even with the very fast reaction of free radicals with (at) a magnesium surface inferred from studies of the kinetics and products of reaction of alkyl halides with magnesium.[4,5,14,17,18]

Results

Hammett ρ values are similar for reaction of aryl halides with magnesium and tri-n-butyltin hydride in diethyl ether solutions, but differ in THF solutions. Relative rates of reaction were determined using competitive kinetics techniques.[4] These rates were not sensitive to small variations in most experimental parameters (cf. Experimental Section). We did not vary the stirring rate over a wide range, and we caution that the experimental rate ratios are expected to show some sensitivity to this parameter when the component rates are influenced to different extents by mass transport:[4] competitive rate measurements involving rates close to transport limited must be interpreted with care. Figure 1 gives representative experimental data for reactions of pairs of aryl bromides with magnesium; Figure 2 shows similar data for reductions of aryl bromides by tri-*n*-butyltin hydride (hν, AIBN).

The rates summarized in Table I were correlated with substituent effects using Hammett σ parameters (rather than, say, half-wave reduction potentials[19-25]) because Hammett

Table I. Relative Rates (k_R/k_H) for Reactions of Aryl Halides (RC_6H_4X) with Magnesium and with Tri-*n*-butyltin Hydride[a]

	Mg									Bu_3SnH			
solv R = X	Et_2O Cl	C_6H_{12}-Bu_2O Br	Bu_2O Br	Et_2O Br	THP Br	THF Br	HMPA-THF; Br	RMgBr-Et_2O; Br	Et_2O I	Et_2O Br	THF Br	σ_R[b]	$E_{1/2}$[c] Br
4-OCH_3		0.53	0.69	0.78	0.66	0.76	0.82	0.84	0.91	0.62	0.76	−0.27	−1.84
4-CH_3	0.69	0.54	0.54	0.59	0.69	0.86	0.92	0.92	0.87	0.65	0.71	−0.17	−1.84
3-CH_3	0.71	0.64	0.53	0.69	0.73	0.82	0.86	0.92		0.89	0.89	−0.07	−1.85
H	1	1	1	1	1	1	1	1	1	1	1	0.00	−1.81
4-F	4.9	3.0		1.6	0.97	1.1	0.89	0.98	1.2	1.6	1.4	0.06	
3-OCH_3		2.0	1.8	1.6		0.92				1.2	1.3	0.12	−1.76
4-Cl	2.9[d]	6.2	4.1	2.1	1.1	1.0	0.99			2.2	2.3	0.23	−1.61
4-Br				(0.95)[d]		1.3[e]				2.7	2.3	0.23	
3-F		5.1		2.4		1.0			1.3	4.5	5.9	0.34	
3-Cl		7.3		2.3	0.93		1.0			4.2		0.37	−1.53
3-Br				(1.3)[d]		1.2[e]				4.1	5.8	0.39	
3-CF_3		4.8	8.8	2.5		0.96	0.82	0.99	1.1	4.2	4.2	0.42	−1.59
4-CF_3		7.2		3.7	0.83	1.0				5.5	5.5	0.55	−1.52

[a] All reactions were carried out using standard conditions described in the Experimental Section. Rates in different solvents cannot be compared. Reproducibility of ratios of rates in individual competition experiments was ±10%. THP is tetrahydropyran; RMgBr-Et_2O is a 0.8 M solution of cyclopentylmagnesium bromide in diethyl ether; C_6H_{12}-Bu_2O, 1:3, v:v; HMPA-THF, 1:3, v:v. Reactions of ArBr and ArI with Mg were carried out at 0 °C; reactions of ArCl with Mg were carried out at 23 °C. [b] J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, 1963, p 173. [c] Half-wave reduction potentials vs. Ag/AgBr in DMF.[22] [d] Statistically corrected for the presence of two identical carbon-halogen bonds by dividing the observed rate constant by 2.0. [e] Not corrected statistically. See the text for discussion.

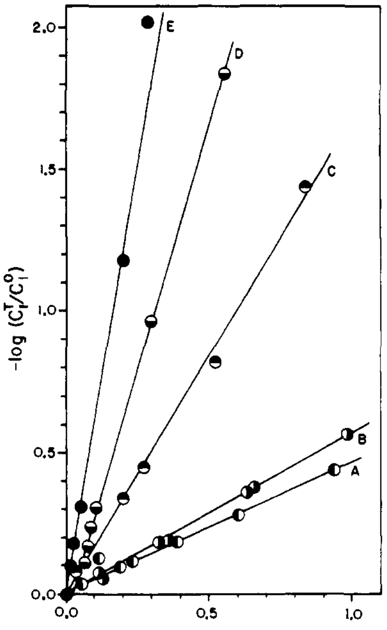


Figure 1. Typical data for the reactions of magnesium with substituted aryl bromides in diethyl ether. The substituents for the curves A–E follow: A_1 = *m,p*-H, A_2 = *p*-Cl, B_1 = *p*-CH_3, B_2 = *m,p*-H, C_1 = *p*-CF_3, C_2 = *p*-Cl, D_1 = *p*-Cl, D_2 = *p*-CH_3, E_1 = *p*-CF_3, and E_2 = *p*-CH_3.

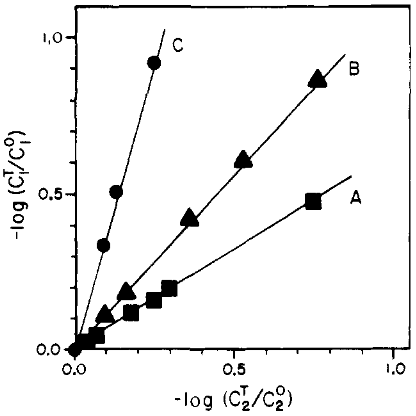


Figure 2. Typical data for the reduction of substituted aryl bromides by tri-*n*-butyltin hydride in ether. Substituents for the curves A–C follow: A_1 = *p*-CH_3, A_2 = *m,p*-H, B_1 = *m,p*-H, B_2 = *m*-CH_3, C_1 = *m*-Br, and C_2 = *p*-Cl.

ρ values are available for a number of other reactions, especially heterogeneous ones. The rates of reaction of aryl bromides with tri-*n*-butyltin hydride have indistinguishable ρ's in diethyl ether and tetrahydrofuran (Figure 3, Table II). It is not clear whether this relatively large magnitude of ρ should be ascribed to charge separation in the transition state or to differences in homolytic carbon-bromine bond energies.[26-28] For comparison, abstraction of iodine atoms from substituted iodobenzenes by phenyl radical[29]—a reaction in which substituent effects have been suggested[27] to originate almost entirely in bond energies—has $\rho = 0.57$.

Hammett plots for the reactions of aryl bromides with magnesium in several solvents are given in Figure 4; values of ρ are listed in Table II. Straight lines with similar scatter were observed in diethyl ether, di-*n*-butyl ether, di-*n*-butyl ether–cyclohexane (3:1), and diethyl ether containing 0.8 M cyclopentylmagnesium bromide. Hammett plots in tetrahydrofuran, tetrahydropyran, and tetrahydrofuran-hexamethylphosphoramide (3:1) appear to be slightly curved. This slight curvature notwithstanding, the rates in polar solvents are clearly much less sensitive to substituents than are rates in diethyl ether and less polar solvents. Thus, the reactions of aryl halides with tri-*n*-butyltin hydride and magnesium respond differently to solvent effects. The former give a single value of ρ, independent of changes in solvent; the latter give values of ρ which depend strongly on solvent.

The rate of reaction of aryl bromides is mass transport limited in THF and more polar solvents, but not in diethyl ether and less polar solvents. The relative rates of reaction of bromobenzene and cyclopentyl bromide with magnesium in diethyl ether differ only by a small factor: $k_{C_6H_5Br}/k_{c\text{-}C_5H_9Br} = 0.48$.[4] The rate of reaction of cyclopentyl bromide is mass transport limited in all solvents listed in Table I.[5] We have established that the small value of ρ characterizing reactions of aryl bromides with magnesium in polar solvents reflects a transport-limited reaction using a procedure analogous to that applied to neopentyl bromide.[5] Relative rates of reaction of cyclopentyl bromide and bromobenzene were measured in two series of solutions of increasing polarity (Figure 5).[30] High

Table II. Hammett ρ Values for Reactions of Aryl Halides with Magnesium and with Tri-*n*-butyltin Hydride and ρ Values for Model Reactions Involving Cleavage of Bonds to, or Electron Transfer with, an Aryl Moiety

reaction	solvent	ρ
ArCl + Mg	Et_2O	2.0 + 0.2
ArBr + Mg	$3Bu_2O$–$1C_6H_{12}$	2.0 ± 0.3
	Bu_2O	1.9 ± 0.3
	Et_2O	1.1 ± 0.2
	THP	<0.6–0.0[a]
	THF	<0.5–0.0[a]
	3THF–1HMPA	<0.4–0.0[a]
	Et_2O, RMgBr (0.8 M)	0.1 ± 0.2
ArI + Mg	Et_2O	0.2 ± 0.2
ArBr + Bu_3SnH	Et_2O	1.4 ± 0.2
	THF	1.3 ± 0.2
ArI + Ph·	CCl_4	0.57[29]
ArI + *p*-NO_2Ph·	CCl_4	0.1–0.0[27]
ArI + $2e^-$	H_2O,[21] DMF[22]	0.3,[21] 0.35[22,23]
ArBr + $2e^-$	DMF	0.57[22,b]
ArCl + $2e^-$	DMF	0.81[22,b]
ArR + e^-	H_2O	4.7[c]
$^-O_2CArR + e^-$	H_2O	0.74[c]
$Ar_2Hg + {}^{203}Hg$	benzene	−1.0[24]
ArD + H_2O (Pt catalyst)	H_2O	0.0[25]
ArH + KNH_2	NH_3	[~6][d]
$Ar_2Hg + HgX_2$	dioxane	−5.9[e]
ArR + $SO_4^{-}\cdot$	H_2O	−2.4[f]

[a] Nonlinear Hammett plots; see Figure 4 and the text. [b] These "ρ" values are the slopes of plots of σ_p vs. $E_{1/2}$ from polarographic reduction at a dropping mercury electrode. [c] M. Anbar, *Adv. Phys. Org. Chem.*, **7**, 115 (1969); R = Br, I fall off the correlation lines. [d] An approximate value obtained by plotting partial rate factors from A. I. Shatenstein, *ibid.*, **1**, 155 (1963), vs. σ_p. The plot shows considerable scatter. [e] R. E. Dessy and Y. K. Lee, *J. Am. Chem. Soc.*, **82**, 689 (1960). [f] P. Neta, V. Madhaven, H. Zemel, and R. W. Fessenden, *ibid.*, **99**, 163 (1977).

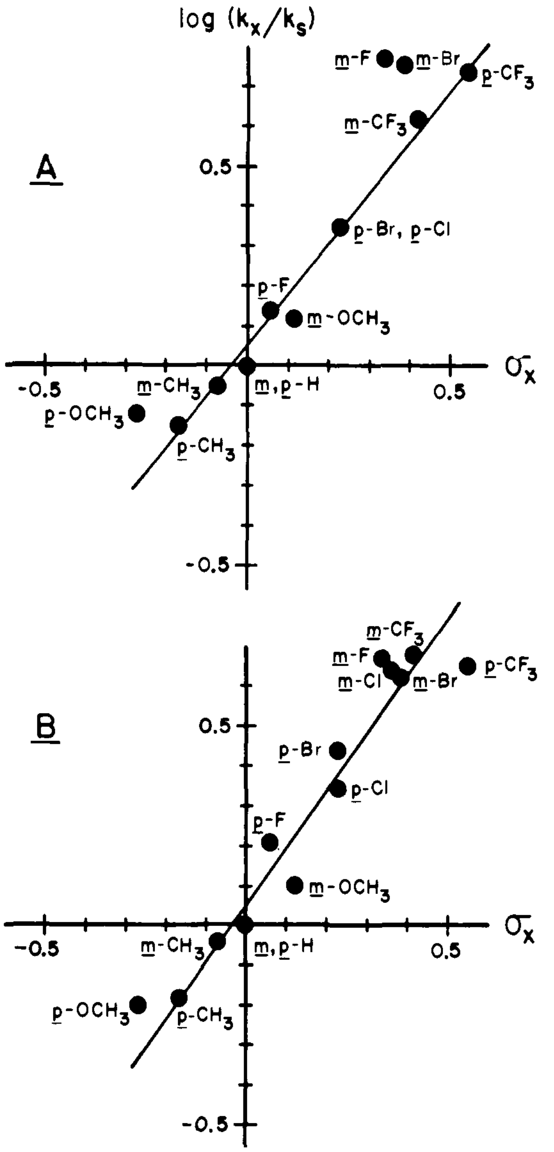


Figure 3. Hammett plots for reactions of substituted bromobenzenes with tri-*n*-butyltin hydride under free-radical conditions (AIBN, $h\nu$): A: THF, $\rho \simeq 1.3$; B: Et_2O, $\rho \simeq 1.4$.

dielectric constants were obtained in one series of experiments (the upper plateau of Figure 5) using mixtures of THF and HMPA. Dielectric constants of mixed solvents were estimated on the assumption that contributions from the two components were additive. In a second series of experiments (the lower plateau of Figure 5), ether containing high concentrations of cyclopentylmagnesium bromide was used to obtain high dielectric constants. Dielectric constants for these solutions were assumed to be the same as those for corresponding concentrations of ethylmagnesium bromide in diethyl ether.[31]

Figure 5 effectively related the rate of reaction of bromobenzene to the rate of diffusion of cyclopentyl bromide. In media of low dielectric constant, bromobenzene appears to react more slowly than it encounters the magnesium. This observation is compatible with large values for ρ in these solvents (Table II). As the solution dielectric constant increases, the rate of reaction of bromobenzene increases toward that of cyclopentyl bromide. Above $\epsilon \sim 7$, the ratio of the rate constants of bromobenzene and cyclopentyl bromide remains constant: $k_{C_6H_5Br}/k_{c\text{-}C_5H_9Br} = 1.1$ in THF and in THF containing HMPA. This ratio was confirmed as the ratio of diffusion constants by measuring the diffusion currents, i_d, for each in dc polarographic reduction: $i_{d,C_6H_5Br}/i_{d,c\text{-}C_5H_9Br} = 1.1$ (DMF, Bu_4NBF_4, 25 °C). Thus for $\epsilon > 7$, the reaction of bromobenzene with magnesium is also mass transport controlled. This behavior closely resembles that observed for neopentyl bromide.[5]

Figure 5 contains one feature not observed for the relative rates of reactions of neopentyl and cyclopentyl bromides:[5] two clearly defined plateaus appear at high dielectric constant, one for THF-HMPA mixtures and one for diethyl ether containing various concentrations of cyclopentylmagnesium bromide. The value of ρ in diethyl ether containing 0.8 M cyclopentylmagnesium bromide (point 15 on this latter plateau) is also approximately zero, and is consistent with transport-limited reaction for the substituted bromobenzenes. Since there is no evidence that the behavior of cyclopentyl bromide differs in THF-HMPA solutions and in diethyl ether containing cyclopentylmagnesium bromide,[5] the most straightforward rationalization of the lower plateau in Figure 5 is that the diffusion constant of bromobenzene is decreased slightly in solutions containing high concentrations of Grignard reagents, perhaps by complex formation.

Reaction of bromobenzene with magnesium thus shows a response to solvents very similar to that observed for neopentyl bromide.[5] In diethyl ether, reaction is slightly slower than transport to the metal surface. As the solution polarity increases, the reaction rate increases, and in solvents having $\epsilon > 7$ the rate becomes mass transport limited. The curvature observed for Hammett plots in tetrahydrofuran and tetrahydropyran may reflect the greater contribution of mass transport limitations for the rates of the slower compounds in each series. Figure 6 plots ρ as a function of solvent dielectric constant. As

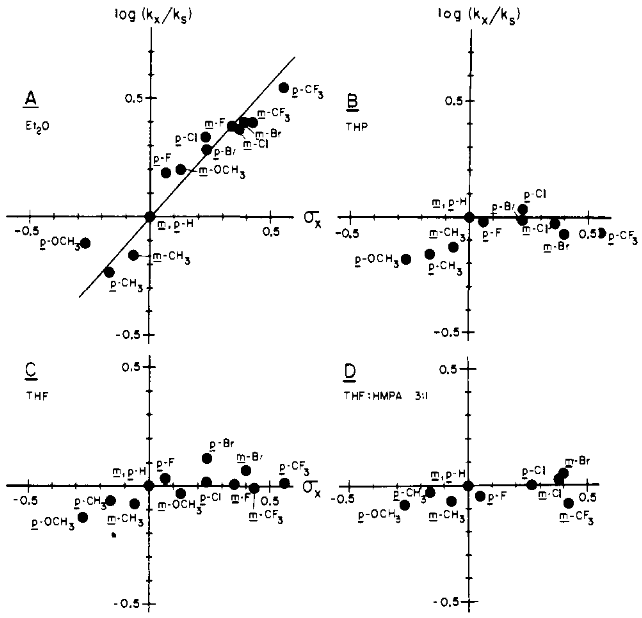


Figure 4. Hammett plots for the reaction of magnesium with substituted bromobenzenes: A, diethyl ether, $\rho \simeq 1.1$; B, tetrahydropyran, $0 \leq \rho \leq 0.6$; C, tetrahydrofuran, $0 \leq \rho \leq 0.4$; D, THF-HMPA (3:1), $\rho \simeq 0$. Points for *m*- and *p*-dibromobenzenes in diethyl ether have been corrected statistically for the presence of two carbon-halogen bonds by dividing the observed relative rates by two; points for these compounds in THF have *not* been corrected (see the text for a discussion).

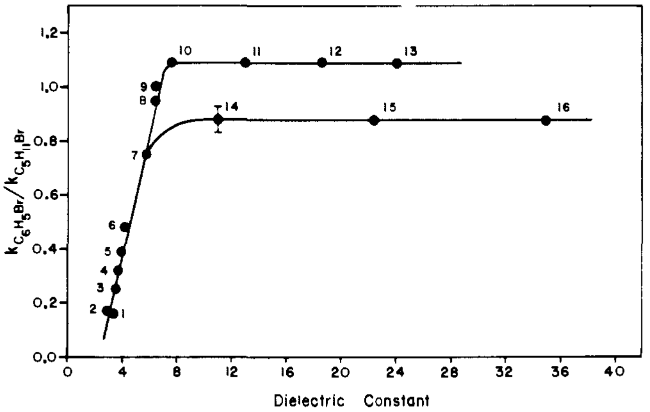


Figure 5. Comparison of the response of the relative rates of reaction of bromobenzene and cyclopentyl bromide to the solution dielectric constant indicates that the former rate becomes transport limited at dielectric constants greater than ~7. The solvents employed in this study included (1) Bu_2O, (2) Bu_2O-C_6H_{12}(3:1), (3) Et_2O-pentane (7:3), (4) Et_2O-pentane (4:1), (5) Et_2O-pentane (9:1), (6) Et_2O, (7) Et_2O-0.2 M RMgBr, (8) THF-Et_2O (2:1), (9) THP, (10) THF, (11) THF-HMPA (3:1), (12) THF-HMPA (1:1), (13) THF-HMPA (1:3), (14) Et_2O-0.4 M RMgBr, (15) Et_2O-0.8 M RMgBr, (16) Et_2O-1.0 M RMgBr. RMgBr denotes cyclopentylmagnesium bromide. Solvent compositions are v:v. The experimental reproducibility, as indicated for the point determined in Et_2O-0.4 M RMgBr (14), is approximately the same for all points.

the dielectric constant increases (and, presumably, as the rates of reaction increase), the value of ρ smoothly decreases. Since the approximately zero values observed for ρ in high dielectric solvents have been identified with transport-controlled reactions, it appears that the decrease in ρ in going from dibutyl ether-cyclohexane to diethyl ether reflects the proximity of the reaction rates to the transport-limited rate.[32]

Figure 7 shows the rate of reaction of bromobenzene with magnesium in several solvents, obtained using the "constant surface" kinetics technique described elsewhere,[4,5] plotted vs. the reciprocal of the viscosity of the solvent. These data provide

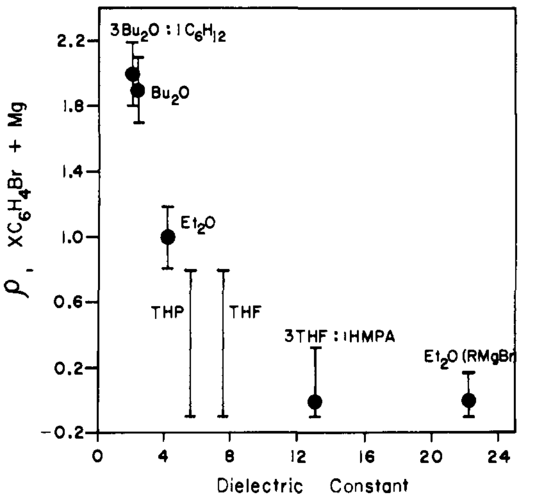


Figure 6. Hammett ρ values for the reaction of magnesium with substituted bromobenzenes in different solvents. The Hammett plot in tetrahydropyran (THP) was nonlinear. Et_2O(RMgBr) denotes diethyl ether containing 0.8 M cyclopentylmagnesium bromide. The error bars are subjective estimates of the relative accuracies of these estimates.

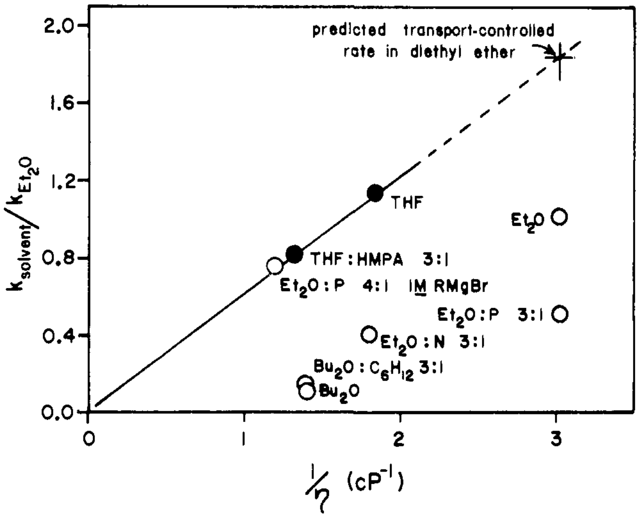


Figure 7. The relative rates of reaction of bromobenzene with magnesium, as a function of the reciprocal of the solvent viscosity. Rates were obtained using "constant surface" techniques[4] at 0 °C, and are arbitrarily normalized to the value in diethyl ether; viscosities were measured at 0 °C. Et_2O-P 4:1 1 M RMgBr is a 4:1 v:v mixture of diethyl ether and pentane containing 1 M cyclopentylmagnesium bromide. The point indicated by "+" is the value of k_{rel} predicted for transport-controlled rate in diethyl ether (see text for a discussion of this point).

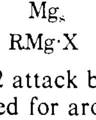
two independent checks on the conclusion that rates are transport limited in solvents of high dielectric constant (THF, THF-HMPA, Et_2O containing 0.8 M c-C_5H_9MgBr). First, rates in the two solvents for which values of $\rho = 0$ have been measured (indicated on the plot by filled circles) fall on a straight line passing through the origin. Second, none of the solvents examined yields rates which fall above this line. Both observations are compatible with the hypothesis that the line represents an upper limit set by the mass transport of bromobenzene. By extrapolating this line to low viscosities, it is possible to predict that the transport-limited rate that would be observed for bromobenzene in a solvent having the viscosity of diethyl ether ($\eta = 0.32$ cP; $\eta^{-1} = 3.1$ cP^{-1})[33] would be faster than the rate actually observed in diethyl ether by a factor of 1.8. This value is in good agreement with estimates of the same number from two separate sources: the factor separating the rate of reaction of bromobenzene in diethyl ether from that of an alkyl halide of approximately the same molecular weight (and thus, diffusion constant) which reacts at a transport-controlled rate in this solvent (e.g., $k_{\text{c-C}_5\text{H}_9\text{Br}}/k_{\text{C}_6\text{H}_5\text{Br}} = 2.1$)[4] and the difference in the ratio of rates in Figure 5 between diethyl ether and solvents in the plateau regions of these plots (for $R = k_{\text{C}_6\text{H}_5\text{Br}}/k_{\text{c-C}_5\text{H}_{11}\text{Br}}$, $R_{\text{THF-HMPA}}/R_{\text{Et}_2\text{O}} = 2.3$ and $R_{\text{Et}_2\text{O-RMgBr}}/R_{\text{Et}_2\text{O}} = 1.7$).

Statistical Corrections to Rates of Reaction of Dibromobenzenes. Table I contains relative rates of reaction of 1,3- and 1,4-dibromobenzene with magnesium in diethyl ether and in tetrahydrofuran. Observed rates in the former solvent were corrected statistically for the presence of two equivalent carbon-bromine bonds by division by two; rates in the latter solvent were not statistically corrected. It was possible to decide if the observed rates should be statistically corrected only after establishing whether the reactions of the aryl dibromides were transport limited. In diethyl ether, evidence summarized above has established that these reactions are not transport limited: the aryl dibromides presumably encounter the magnesium surface many times before they react. In tetrahydrofuran, the rate of disappearance of the aryl mono- and dibromides is determined by transport to the magnesium surface, and is independent of the number of carbon-bromine bonds present. Statistical correction is not appropriate in this solvent. The observation that the statistically uncorrected rates for *m*- and *p*-dibromobenzene in tetrahydrofuran seem to fall slightly above the adjacent points in the Hammett plot of Figure 4 is compatible with the inference drawn from the apparent curvature in this plot, and from the data in Figure 6, that reactions in this solvent straddle the region between transport-limited and non-transport-limited regimes. If the reactions were transport limited, the statistically uncorrected rate should fall on the Hammett plot; if the reaction were not transport limited, a statistical correction of two should be required. In fact, the uncorrected data seem slightly too high, while data corrected by dividing by two would be too low.

Carbon-halogen bond breaking is irreversible. The overall rate-determining step for disappearance of aryl halides in diethyl ether and other solvents of low polarity might, in principle, involve a reaction of a reversibly formed intermediate in which the carbon-halogen bond was broken (e.g., an aryl radical, or a surface arylmagnesium compound). Reaction of a mixture of bromobenzene and *o*-iodotoluene with magnesium to approximately 50% conversion, followed by quenching of the reaction mixture and examination of the residual aryl halides, showed that no iodobenzene or *o*-bromotoluene had been formed (<5% would have been detected). Thus, cleavage of the carbon-halogen bond is probably irreversible.[34]

Discussion

The objective of these kinetics studies was to establish the nature of the rate-determining transition state(s) for disappearance of aryl halides by reaction with metallic magnesium in ethereal solvents. The range of possible limiting structures (**1**–**8**) is similar to that discussed previously for reactions of

1 RBr
2 $(\text{RBr})\cdot\text{Mg}_s$
3 $(\text{RBr})^{\overline{\cdot}}$
4 R^-
5 R^+
6 $\text{R}\cdot$
7 
8 $\text{RMg}\cdot\text{X}$

alkyl halides,[4] although a backside S_N2 attack by a surface magnesium atom on carbon is precluded for aromatic substrates. In polar solvents ($\epsilon > 7$), the rate of reaction of aryl bromides is transport limited. The reaction of iodobenzenes is apparently transport limited even in diethyl ether ($\epsilon \simeq 4$): $\rho = 0$ for this system, and the rate of reaction of iodobenzene itself falls on the line identified with transport-limited rates.[4]

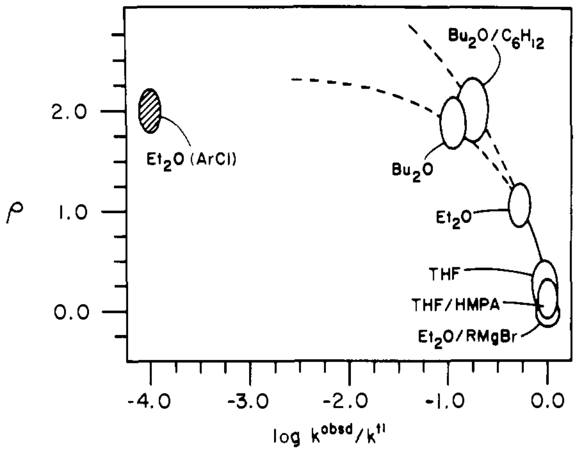


Figure 8. Plot of log ($k^{\text{obsd}}/k^{\text{tl}}$) ($k^{\text{obsd}}$ is the observed rate constant, k^{tl} is the transport-limited rate constant derived from Figure 7) vs. ρ for aryl bromides in several solvents (open symbols) and for aryl chlorides in diethyl ether (filled symbol). The dotted lines represent plausible extremes for ρ at values of $k^{\text{obsd}}/k^{\text{tl}} < 0.1$. Solvent compositions are detailed in Table II.

In less polar solvents—diethyl and dibutyl ether and dibutyl ether-cyclohexane—the observation of linear Hammett plots with significant ρ values establishes that the reactions of aryl bromides with magnesium are not transport limited. Interpretation of these ρ values in terms of charge in the transition state is complicated by the proximity of the rates from which they are derived to the mass-transport-limited regime. Phenyl bromide reacts with magnesium in diethyl ether at approximately the same rate as neopentyl bromide:[4] that is, at approximately one-half the expected mass-transport-limited rate. Since the proximity of these rates to the mass-transport-controlled limit would be expected to decrease the magnitude of ρ, the observed values of ρ should be considered minimum values, when discussing the charge distribution in a hypothetical, non-transport-limited transition state.

It is possible to get a qualitative picture of the behavior of ρ in the regime close to transport-limited rates using a procedure based on Figure 7. For each solvent system in this figure, we estimated the proximity of the observed rate k^{obsd} to the transport-limited rate k^{tl} in that solvent: the latter quantity may be estimated at any value of η^{-1} from the line proposed to represent transport-limited reaction. Thus, for example, $k^{\text{obsd}}/k^{\text{tl}} = 0.11$ for Bu_2O. Figure 8 plots these data. Although it appears that the apparent value of ρ decreases rapidly for values of $k^{\text{obsd}}/k^{\text{tl}} > 0.1$, we do not have the data for $k^{\text{obsd}}/k^{\text{tl}} < 0.1$ which would be required to extrapolate ρ to a reliable value at rates sufficiently slow as to be uninfluenced by their proximity to transport-limited values. Attempts to slow the rates experimentally by adding quantities of hydrocarbons led to precipitates or two-phase liquid mixtures. A value of ρ is available for aryl *chlorides* in diethyl ether which is far removed from $k^{\text{obsd}}/k^{\text{tl}} = 1$, but the relevance of this datum to reactions of aryl bromides is unclear. Fragmentary evidence derived from comparisons of rate-structure profiles for reactions of alkyl bromides and alkyl chlorides suggested that reaction rates for the latter group of compounds were less sensitive to changes in alkyl group structure than the former by approximately a factor of 4:[4] if the same difference in sensitivity holds for aromatic halides, the value of ρ for slowly reacting aryl chlorides might be much smaller than that for a (presently hypothetical) group of slowly reacting aryl bromides.[35]

Even given present uncertainty concerning the significance of ρ for diethyl or dibutyl ether, it is possible to interpret these values to exclude several of the possible transition-state

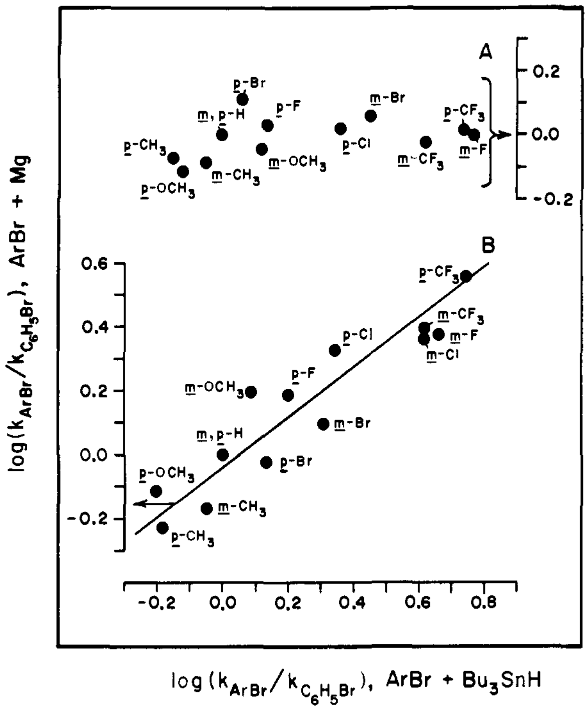


Figure 9. Comparison of the relative rates of reaction of substituted bromobenzenes with magnesium and with tri-*n*-butyltin hydride: A, THF; B, diethyl ether.

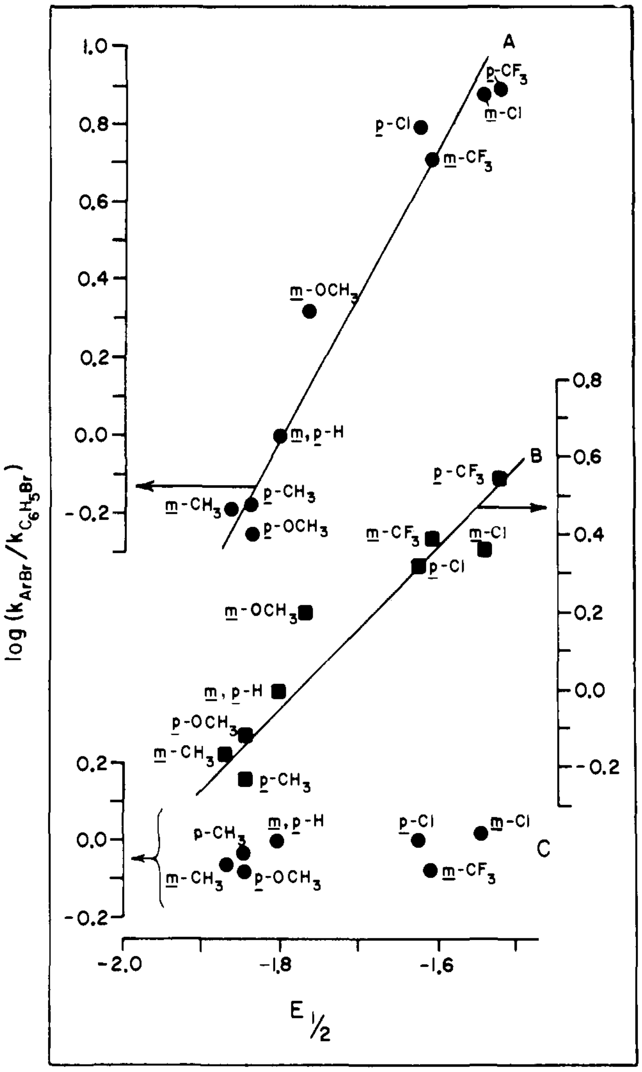


Figure 10. Relative rates of reaction of substituted bromobenzenes as a function of their half-wave reduction potentials (footnote *c*, Table I): A, Bu_2O-C_6H_{12}(3:1); B diethyl ether; C, THF-HMPA (3:1).

structures represented by **1–8.** Since ρ has a significant positive value, the transition state does not resemble the starting material, and **1** can be discarded. The magnitude of ρ seems too large to be compatible with physisorption, **2.** The sign of ρ is incompatible with an intermediate aryl cation, **5.** Without knowing an accurate magnitude for ρ, it is difficult to exclude carbanionic structures (**4**). Nonetheless, since the largest values observed are similar to those for tin hydride reduction, and considerably smaller than that estimated for reactions generating aryl anions ($\rho \simeq 6$, Table II), the magnitude of ρ seems too small for a fully formed aryl carbanion **4.** A rate-determining step involving an intermediate in which the carbon-magnesium bond is partially or fully formed (**8**) is unlikely, both because this transition state bears a large negative charge on carbon and would be expected to show a large value for ρ and because cleavage of the carbon-bromine bond appears to be irreversible.

It is more difficult to differentiate between reactions leading to the three remaining limiting structures—electron transfer from magnesium to aryl bromide generating the radical anion **3**, bromine abstraction by magnesium forming an aryl radical **6**, and insertion of magnesium directly into the carbon-bromine bond of an adsorbed aryl bromide **7**—on the basis of the available evidence. The rates of reaction of aryl bromides with magnesium correlate equally well with rates of bromine abstraction by tri-*n*-butyltin radical (Figure 9) and with polarographic reduction potentials (Figure 10). A concerted insertion would presumably share the character of halogen abstraction and electron donation, and would also be expected to correlate. The abstraction of the bromine atom from an aryl bromide by tri-*n*-butyltin radical is probably a good model for atom abstraction by a metal surface. Whether polarographic reduction adequately models single-electron transfer is less clear, since the detailed mechanism of polarographic reduction of organic halides is still not established.

Experimental Section

General. Magnesium powder (Mallinckrodt), triply sublimed magnesium turnings (Dow), and reagent grade magnesium turnings (Eastman or J. T. Baker) were used. Unless otherwise specified, the reactions were run using the Eastman or J. T. Baker magnesium turnings. Reagent grade diethyl ether, di-*n*-butyl ether, tetrahydrofuran, and tetrahydropyran were distilled under argon from lithium aluminum hydride, calcium hydride, or disodium benzophenone dianion. 2-Butanol was distilled from magnesium 2-butoxide. Xylene (a mixture of isomers) and cyclohexane were distilled from sodium. Hexamethylphosphoramide was distilled from sodium under vacuum (bp 65 °C, 0.4 Torr).[36] Manipulation of solutions for Grignard formation or tri-*n*-butyltin hydride reductions followed standard inert atmosphere procedures.[37] Electrochemical measurements were carried out using a Princeton Applied Research Model 174A polarographic analyzer.

Standard Conditions for Competitive Reaction of Substituted Aryl Halides with Magnesium in Ether. Since there are significant variations in the rate of consumption of organic halides in Grignard reactions due to magnesium reactivity, solvent effects, and halide reactivity, it was convenient to vary the amounts of both magnesium and organic halides which were used in the various runs to achieve a tractable rate of reaction. These variations had no effect on the relative rate constants obtained. In all cases a three- to sevenfold excess of magnesium was present at the beginning of the reaction. Typically, to a three-necked, 50-mL, round-bottomed flask containing a magnetic stirring bar was added 0.18–3.0 g (0.008–0.12 g-atom) of magnesium. The amount of magnesium used depended on the solvent, the halide reactivity, and the number of halides competing in each run. In general, for experiments involving aryl halides, 3.0 g (0.12 g-atom) of magnesium was used for 1.0 g (5–6 mmol) of each aryl halide in all solvents. The flask

Table III. Effects of Changes in Relative Amounts of Magnesium,[a] Aryl Halides,[b] and Initial Magnesium Bromide Concentrations[c] on a Representative Ratio of Rate Constants

reaction[d] no.	$Mg/\Sigma ArX$[e]	$MgBr_2/\Sigma ArX$[c]	(k_2/k_1)[6]	comments
1	0.25	0.5	0.55	
2	0.50	0.5	0.56	
3	1.0	0.5	0.57	
4	1.0	0.0	0.58	no surface cleaning
5	1.0	0.0	0.54	no surface cleaning, wet ether[f]
6	3.0	0.5	0.56	
7	3.0	0.5	0.61	
8	3.0	0.5	0.61	magnesium powder
9	3.0	0.5	0.63	triply sublimed magnesium
10	3.0	0.0	0.58	no surface cleaning
11	3.0	0.0	0.54	surface cleaned, salts removed[g]
12	3.0	1.0	0.57	
13	4.0	0.5	0.61	
14	4.0	0.5	0.62	
15	4.0	0.5	0.61	
16	8.6	0.5	0.54	
17	10.0	0.5	0.59	
18	10.0	1.0	0.57	
19	10.0	0.0	0.63	surface cleaned, salts removed[g]

[a] Grignard reagent grade magnesium turnings were used unless otherwise specified. [b] These reactions were run in dried ether using aliquots of a standard solution of *n*-decane and equimolar amounts of *p*-bromotoluene (2) and bromobenzene (1). [c] The ratio ($MgBr_2/\Sigma ArX$) is the amount of $MgBr_2$ in solution at the start of the reaction, relative to total aryl bromides present. Unless the salts were removed, as specified, the value of ($MgBr_2/\Sigma ArX$) is the same as the amount of 1,2-dibromoethane added to "clean" and "activate" the magnesium surface. [d] These numbers correspond to the points plotted in Figure 8. [e] The surface of the magnesium was "cleaned", unless otherwise specified, by the reaction of 0.5 molar equiv of 1,2-dibromoethane with a stoichiometric excess of Mg. The ratio ($Mg/\Sigma ArX$) is the amount of magnesium in the reaction flask *after* the cleaning of the surface, relative to the total quantity of aryl bromides in competition for the magnesium. [f] The ether was water and oxygen saturated in air for this reaction. [g] The ether solution of $MgBr_2$ which resulted from cleaning the magnesium surface was removed by cannula. Fresh ether was added as the solvent used in the reaction.

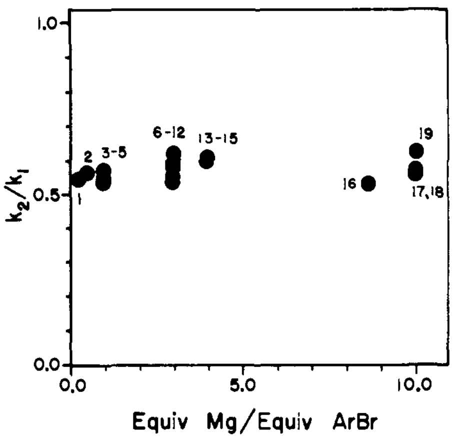


Figure 11. Effects of changes in relative amounts of magnesium to aryl bromides in solution (equiv Mg/equiv ArBr) on the relative rates of reaction (k_2/k_1) of *p*-bromotoluene(2) and bromobenzene(1) in ether. The points in the graph are numbered to correspond to the reactions listed in Table II.

was capped with serum stoppers and was flame dried under a flow of argon provided through a syringe needle. Nitrogen was not used as an inert gas because it reacts with magnesium at high temperature. After the flask had cooled, approximately 25 mL of purified solvent was added to the flask by cannula. To clean the surface of the magnesium, 0.2 mL (0.29 g, 1.7 mmol) of ethyl bromide or an equivalent amount of 1,2-dibromoethane was added to the reaction mixture. The mixture was stirred until reaction between the magnesium and the organic halide had begun. In the case of reactions in di-*n*-butyl ether, it was usually necessary to heat the flask gently to initiate this reaction; in all other cases, the reaction initiated spontaneously. After this initial reaction, intended to remove unreactive surface films from the magnesium, had ceased (2–3 min in ethyl ether), the flask was placed in an ice-water bath and stirred for 45 min. A precooled mixture of the aryl halides whose kinetics was to be examined (typically 1.7 g of each aryl halide, yielding starting aryl halide concentrations of ~0.5 M in solution) and internal standard (0.2–0.5 g depending on the initial halide concentrations) was added to the reaction mixture by cannula. In all cases the reaction began immediately and proceeded to completion. Control experiments were carried out in which the ethylmagnesium bromide or magnesium dibromide generated in cleaning the magnesium surface was removed and replaced with fresh solvent before initiating the kinetic run. This step had no influence on the values for the ratios of rate constants ultimately derived, and was normally omitted. Aliquots were taken at appropriate times by transferring approximately 0.5 mL of the reaction mixture by cannula into a vial, capped with a rubber septum stopper, containing a quenching solution of 1 N hydrochloric acid and ice. If the reaction solvent was water soluble (THF or HMPA), pentane (0.5 mL) was added to extract the unreacted halides; extraction of unreacted halides and internal standards was found to be essentially quantitative. The organic layer was separated and analyzed by GLC. A least-squares plot of ln (C_1'/C_1^0) vs. ln (C_2'/C_2^0) yielded k_1/k_2. Since only the relative amounts of the components were required, it was not necessary to determine the response factor of a given halide, relative to the internal standard. In many cases the plots were linear to greater than 90% reaction of one halide; all were reasonably linear to greater than 65%. Nonlinearity could normally be rationalized on the basis of changes in solution dielectric constant.

Standard Conditions for Competitive Reactions of Aryl Halides with Tri-*n*-butyltin Hydride. The reaction conditions used for these reductions were similar to those for the Grignard reactions. A 50-mL, three-necked, round-bottomed flask was flame dried under a flow of argon. After cooling, 0.1 g of AIBN was added to the flask. The flask was capped with septum stoppers and the argon flow was resumed. After 5 min, the solvent (25 mL) was added by cannula. The flask was placed in an ice bath and stirred for 45 min. The halides (0.5 g each) and the internal standard (0.3 g) were added by syringe, and an initial aliquot was taken by syringe. The cooled tri-*n*-butyltin hydride (1.1 equiv based on total number of moles of halides used) was added by syringe. The reaction was started by irradiating the reaction mixture with a long-wavelength, low-intensity ultraviolet light (Mineralite, UVSL 25). Aliquots (1 mL) were removed every 2 min for 30 min, and the unreacted tin hydride in each aliquot was quenched with carbon tetrachloride (0.5 mL, 0.75 g, 5 mmol) or 1,2-dibromoethane (0.5 mL, 1 g, 5 mmol), placed in the vials into which the reaction mixture was transferred by cannula. The use of 1,2-dibromoethane was sometimes necessary because carbon tetrachloride occasionally interfered with the GLC analysis of a particular set of organic bromides.

Control Experiments to Test the Sensitivity of the Rate Ratio k_x/k_s to Materials and Experimental Conditions. A number of experiments were carried out using modifications of the "standard" kinetics experiments to test the sensitivity of the measured ratios of rate constants to several experimental parameters. These experiments are summarized in Table III and presented in graphic form in Figure 11. The relative rates of reaction of bromobenzene and *p*-bromotoluene with magnesium are insensitive to the amount (and thus the surface area) and type of magnesium present. Wet, oxygen-saturated ether, activation of the magnesium surface by reaction with 1,2-dibromoethane, and low concentrations of magnesium dibromide in solution at the beginning of the reaction also had no effect on the relative rates obtained. Reactivity of tri-*n*-butyltin hydride toward *p*-bromotoluene and bromobenzene was examined under the standard conditions, but omitting AIBN, light, or AIBN and light; no reaction occurred.

Constant-surface kinetics were carried out essentially as described previously.[4]

Diffusion currents (i_d) were measured using a dropping mercury electrode (DME), recording the dc polarogram as described previously.[5]

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References and Notes

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(2) Texaco Fellow, 1975–1976.

(3) National Institutes of Health Predoctoral Fellow, 1966–1969.

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(5) H. R. Rogers, J. Deutch, and G. M. Whitesides, *J. Am. Chem. Soc.*, preceding paper in this issue.

(6) Representative values of pertinent reduction potentials follow: PhBr, −2.32; PhI, −1.62; *n*-BuBr, −2.27 (SCE, 75% dioxane, Et_4NBr);[7] PhCl, −2.56; PhBr, −2.07; PhI, −1.59; *n*-$C_5H_{11}Br$, −2.09; *sec*-$C_5H_{11}Br$, −2.12; *t*-BuBr, −1.91, vs. SCE in Me_2SO (Me_4NPF_6).[8] Further examples are discussed by M. R. Rifi in "Organic Electrochemistry", M. M. Baizer, Ed., Marcel Dekker, New York, 1973, p 283; F. L. Lambert and K. Kobayashi, *J. Am. Chem. Soc.*, **82**, 5324 (1960).

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(34) Cleavage which would not lead to halogen interchange might, in principle, take place. It would, however, seem improbable a priori, and would be exceedingly difficult to test for experimentally.

(35) A recent study of the reaction of aryl halides with nickel(0) complexes has generated these values of ρ: $\rho(ArI) = +2.0$; $\rho(ArBr) = +4.4$; $\rho(ArCl) = +5.4$ (T. T. Tsou and J. K. Kochi, *J. Am. Chem. Soc.*, in press). This reaction has been interpreted as involving an electron-transfer step. The fact that we observe a significantly smaller value for $\rho(ArCl)$ for reaction with magnesium still does not distinguish between inner-sphere electron transfer (halogen abstraction) and outer-sphere electron transfer, because rate-structure profiles for the two types of reactions are probably linearly related. Cf. J. J. Barber and G. M. Whitesides *J. Am. Chem. Soc.*, following paper in this issue; B. Durham, J. F. Endicott, C.-L. Wong, and D. P. Rillema, *ibid.*, **101**, 847 (1979).

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