8×10^{-8} s at 25 °C in water (S. P. Mishra and M. C. R. Symons, *J. Chem. Soc., Perkin Trans. 2*, 391 (1973)). The lifetime of $CH_3Br^{-}\cdot$ is less than 10^{-9} s in cyclohexane, and the lifetime of $CH_3Cl^{-}\cdot \simeq 3 \times 10^{-8}$ s in cyclohexane (P. P. Infelta and R. H. Schuler, *J. Phys. Chem.*, **76**, 987 (1972)).

(34) S. Bank and D. A. Jackson, *J. Am. Chem. Soc.*, **98**, 7742 (1976).

(35) J. Barber and G. M. Whitesides, *J. Am. Chem. Soc.*, accompanying paper in this issue.

(36) M. C. R. Symons, *J. Chem. Res. (S)*, 360 (1978).

(37) H. C. Brown, G. W. Kramer, and M. M. Midland, "Organic Synthesis via Boranes", Wiley, New York, 1975.

Mechanism of Formation of Grignard Reagents. The Rate of Reaction of Cyclopentyl Bromide with Magnesium Is Transport Limited in Diethyl Ether[1]

Harold R. Rogers,[2] John Deutch, and George M. Whitesides*

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received September 11, 1978*

Abstract: Three observations indicate that the rate of reaction of cyclopentyl bromide with metallic magnesium in several ethereal solvents is limited by the rate of its encounter with the metal. First, the rate of disappearance of cyclopentyl bromide is dependent on the first power of the organic halide concentration, the magnesium surface area, and rate at which the solution is stirred, and is inversely dependent on the solution viscosity ($-d[RBr]/dt \propto [RBr]^1, A^1, \omega^1, \eta^{-1}$). Second, the activation energy for the reaction in diethyl ether ($E_a \simeq 2.3$ kcal/mol) is consistent with mixing and diffusion as rate limiting. Third, a number of representative alkyl halides react with magnesium in diethyl ether at very similar rates; no organic halides examined react faster than this rate. The dependence of the rate of reaction of neopentyl bromide on solution dielectric constant illustrates transition from transport-limited to non-transport-limited rates, and suggests appreciable charge separation in the chemical step which breaks the carbon–bromine bond.

Introduction

An examination of the relative rates of reaction of organic halides with magnesium in diethyl ether solution established that reaction occurred (at least in major part) at the magnesium-solution interface, and suggested the existence of a well-defined upper limit to the rates:[3] all alkyl iodides examined, many alkyl bromides, and one particularly reactive alkyl chloride (benzyl chloride) reacted in diethyl ether at rates that were experimentally almost indistinguishable; no organic halide tested reacted faster than this rate.[3] This paper rationalizes the observation of an upper limit to these reaction rates by demonstrating that cyclopentyl bromide—a representative alkyl bromide whose rate of reaction falls at this upper limit—reacts with magnesium in a number of solvents (including diethyl ether) at a mass transport limited rate. Comparisons of the rates of reaction of cyclopentyl bromide and neopentyl bromide (one of the alkyl bromides which reacts significantly more slowly in diethyl ether than the observed upper limit) in solvents of a range of polarities indicates that the magnitude of the rate of reaction of the latter bromide is sensitive to dielectric constant, and that an increase in dielectric constant from $\epsilon < 10$ to $\epsilon > 10$ changes its rate from one slower than transport to one limited by transport. An accompanying paper demonstrates that the rate of reaction of aryl bromides with magnesium also changes from non-transport-limited to transport limited as the solvent polarity increases.[4]

Rates and Discussion

The rate of reaction of cyclopentyl bromide with magnesium in several solvents is inversely proportional to viscosity. The rate of a diffusion-limited homogeneous reaction is characterized by an inverse proportionality to the solution viscosity.[5] Identification of an encounter-limited solid–liquid heterogeneous reaction is more complicated, because both mass transport of reactant from bulk solution to the vicinity of the interface (convection) and diffusion of reactants through the stationary fluid boundary layer immediately adjacent to the solid surface contribute to the rate. We have not separated these contributions, and both mass transport and diffusional contributions are evident in certain experiments. For convenience in what follows, we will refer to any reaction whose overall rate is limited by the encounter of soluble reactant with the solid surface as "transport limited", without distinguishing between mass transport and diffusion.

We have examined the relative rates of reaction of solutions of cyclopentyl bromide in a number of solvents with metallic magnesium using the "constant-surface" kinetics technique described in detail in an accompanying paper.[3,6] The determination of the relative rates of reaction in two solvents using this technique typically involved four experiments. First, the disappearance of the halide was followed in one solvent, during reaction with a mass of magnesium sufficiently large that its surface area remains effectively constant during the reaction. This reaction was experimentally first order in cyclopentyl bromide and pseudo zero order in magnesium. The initial solvent was then replaced with a second solvent, and the reaction repeated. The ratio of the pseudo-first-order rate constants from these two experiments measured the relative rates of reaction in the two solvents. The procedure was carried through at least twice with each solvent with the same piece of magnesium to check for consistency. This technique provides information about the relative rates of reaction in solvents of different viscosity or polarity, at different temperatures, and under different conditions of agitation. Typical experimental data are given in Figure 1.

Relative Rates as a Function of Solvent Viscosity. Table I summarizes relative rates obtained by applying these techniques of cyclopentyl bromide in several solutions. The essential features of these data are summarized in Figure 2 as a plot of relative rate vs. the inverse of the shear viscosity. These solvent systems cover only a factor of 5 in viscosity, but constitute the widest range we could devise in which the formation of cyclo-

0002-7863/80/1502-0226$01.00/0

Table I. Relative Rates of Reaction of Cyclopentyl Bromide and Cyclopentyl Chloride with Magnesium in Several Solvents

solvent	composition[a]	η,[b] cP	rel rate[c] RBr	rel rate[c] RCl
1	Et_2O	0.33	1	
2	Et_2O-pentane, 80:20	0.33	1.09	
3	THF	0.55	0.64	
4	RMgBr (0.6 M), Et_2O-pentane, 80:20	0.58	0.60	0.05
5	Bu_2O	0.70	0.44	
6	Et_2O-Nujol, 80:20	0.72	0.47	
7	Bu_2O-cyclohexane, 75:25	0.77	0.49	
8	THF-HMPA, 75:25	0.79	0.47	
9	RMgBr (1.0 M), Et_2O-pentane, 70:30	0.80	0.58	
10	RMgBr (1.0 M), Et_2O-pentane, 80:20	0.86	0.47	
11	RMgBr (0.6 M), Et_2O-pentane-Nujol, 80:10:10	0.89	0.36	
12	RMgBr (0.6 M), Et_2O-paraffin oil, 80:20	1.2	0.29	
13	RMgBr (0.6 M), Et_2O-Nujol, 80:20	1.2	0.27	0.05
14	RMgBr (1.0 M), Et_2O-Nujol, 80:20	1.8	0.20	

[a] Abbreviations: Et_2O, diethyl ether; THF, tetrahydrofuran; Bu_2O, di-*n*-butyl ether; RMgBr, cyclopentylmagnesium bromide; HMPA, hexamethylphosphoramide. [b] The Experimental Section describes the procedures used to measure these shear viscosities. [c] Relative to the rate in diethyl ether.

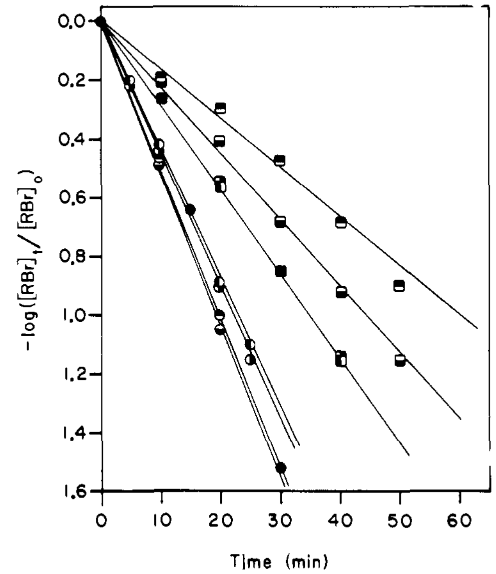

Figure 1. The disappearance of cyclopentyl bromide (RBr) in different solvents is reproducibly pseudo zero order in magnesium and first order in RBr. Two sets of experimental data each involving four kinetics runs with a single piece of magnesium are shown: diethyl ether, 0 °C (◐, first run; ◑, third run) vs. diethyl ether-pentane, 80:20 (⊖, second run; ⊖, fourth run); tetrahydrofuran (◧, first run; ◨, third run) vs. di-*n*-butyl ether (⊟, second run; ⊟, fourth run). The difference between the two runs in di-*n*-butyl ether was representative of the *largest* disagreement accepted; the reproducibility of the data in diethyl ether illustrates typical experiments.

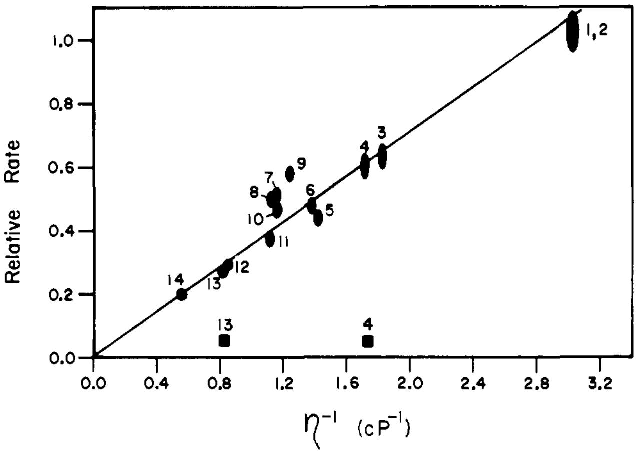

Figure 2. The rate of reaction of cyclopentyl bromide (●) with magnesium is proportional to the inverse of the solvent shear viscosity. The rate of reaction of cyclopentyl chloride (■) with magnesium is insensitive to solvent viscosity.

pentylmagnesium bromide followed useful pseudo-first-order kinetics. The solvents that can be used in these kinetics studies are more restricted than those that can be applied to the preparation of Grignard reagents for synthesis. It is important that the kinetics studies be carried out in solutions that do not contain suspended solids, because these appear to precipitate on the magnesium surface and influence the kinetics; this restriction is less important for synthetic applications. The solvent systems listed in Table I are all based on ethers, for the reason that only these solvents remained free of precipitates during the course of kinetics runs.[7] Rates in diethyl ether, tetrahydrofuran, and di-*n*-butyl ether were measured to try to distinguish solvent effects on rate that could be ascribed to changes in ion-solvating ability or dielectric constant from those due to viscosity. Studies in mixed pentane-ether and Nujol-ether (20:80 v:v) were carried out in an effort to examine systems in which the chemical character of the solutions remained constant, while the solution viscosities changed. THF-HMPA (75:25 v:v) gave a system in which electron-transfer reactions might have been expected to be particularly favorable. Ether containing added cyclopentylmagnesium bromide explored the influence of increased solution dielectric strength on the reaction rate.[7] The relative rates of reaction of cyclopentyl bromide with magnesium in all of these solvents are approximately proportional to the reciprocal of the viscosity, η^{-1} (Table I and the following section); further, a line drawn through these points extrapolates to a rate of zero at $\eta^{-1} = 0$.[8] This observation suggests that the rates of these reactions are transport controlled. In contrast, reaction of cyclopentyl chloride with magnesium is approximately 10^2 slower than that of cyclopentyl bromide and, as shown in Figure 2, is relatively insensitive to solvent viscosity. Cyclopentyl chloride has a slightly larger diffusion coefficient than cyclopentyl bromide, and should react more rapidly in a diffusion-controlled process; hence, cyclopentyl chloride (and most other alkyl chlorides)[3] react with magnesium by a process which is not transport controlled.

Relative Rates as a Function of Agitation. If the hypothesis is correct that the reaction of cyclopentyl bromide with magnesium is transport limited, its rate would qualitatively be expected to increase with increasing stirring rate (ω) in constant-surface kinetics experiments. Improved agitation should decrease the thickness of the boundary layer and increase the

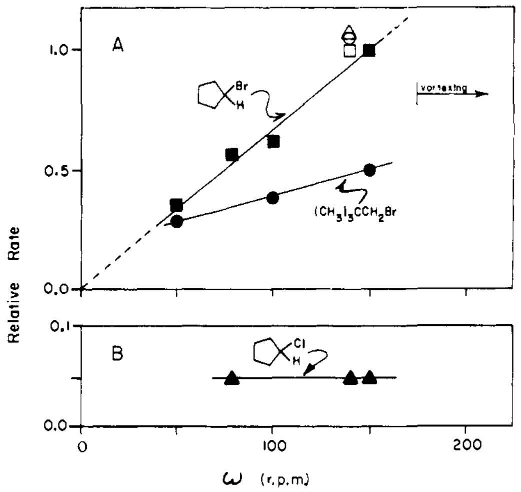

Figure 3. Dependence of the relative rate of reaction of several alkyl halides with magnesium as a function of stirring rate, measured using the apparatus described in ref 3. (A) The lines represent data for cyclopentyl bromide (■), neopentyl bromide (●), and (B) cyclopentyl chloride (▲). Single kinetic results for ethyl iodide (□) and *n*-pentyl bromide (○) and a single point for cyclopentyl bromide derived from an independent set of experiments (△) are also summarized on plot A. All rates are relative to the rate of reaction of cyclopentyl bromide at ω = 150 rpm.

rate at which cyclopentyl bromide reaches the metal surface. Figure 3 plots the relative rates of reaction of cyclopentyl bromide as a function of ω. We did not carry these experiments to higher values of ω with the particular experimental geometry used, because vortexing became severe. Low values of ω were not studied, in part because it was difficult to maintain a constant low stirring rate with the apparatus used, and in part because extrapolation of the measured rates to $\omega = 0$ indicated the expected low value.[8] For comparison, Figure 3 also indicates that the rate of reaction of cyclopentyl chloride with magnesium is independent of ω, as would be expected of a process whose rate is not transport limited. Neopentyl bromide shows slightly slower rates than cyclopentyl bromide, and a dependence of rate on viscosity that is lower than that of cyclopentyl bromide. The straight line connecting these points is arbitrary: we have no way of estimating the dependence of rate on ω close to what we believe to be a transport-limited regime. Ethyl iodide, which, as a representative alkyl iodide, might have been expected to be a plausible candidate for a compound which would be *more* reactive than cyclopentyl bromide,[3] shows, within experimental error, the same relative rate as cyclopentyl bromide at the single value of ω examined. Thus, it appears that the plot of the rate of reaction of cyclopentyl bromide with magnesium as a function of ω gives the maximum rates which can be achieved with the experimental protocol used.

The energy of activation for reaction of cyclopentyl bromide in ether with magnesium is low: E_a = *2.3 kcal/mol.* The free energy of activation for diffusion of low molecular weight compounds in solvents of low viscosity is small (ca. 2-5 kcal/mol).[9] Constant-surface kinetics techniques were used to measure this parameter for reaction of cyclopentyl bromide with magnesium. These results are summarized in Figure 4; these data are expressed in terms of the rates of reaction (assumed to be pseudo zero order in magnesium) at a given temperature relative to the rate of reaction at 35 °C. Although data could be obtained only over a narrow temperature range, and are, consequently, not highly accurate, the value derived from Figure 4 (E_a = 2.3 kcal/mol) is compatible with mixing and diffusion as the rate-limiting step.[10]

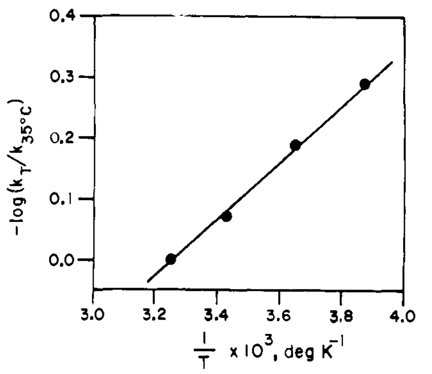

Figure 4. Arrhenius plot ($-\log(k_T/k_{35°C})$) vs. $1/T$ for the reaction of cyclopentyl bromide with magnesium in diethyl ether. The energy of activation estimated from this plot is 2.3 kcal mol^{-1}

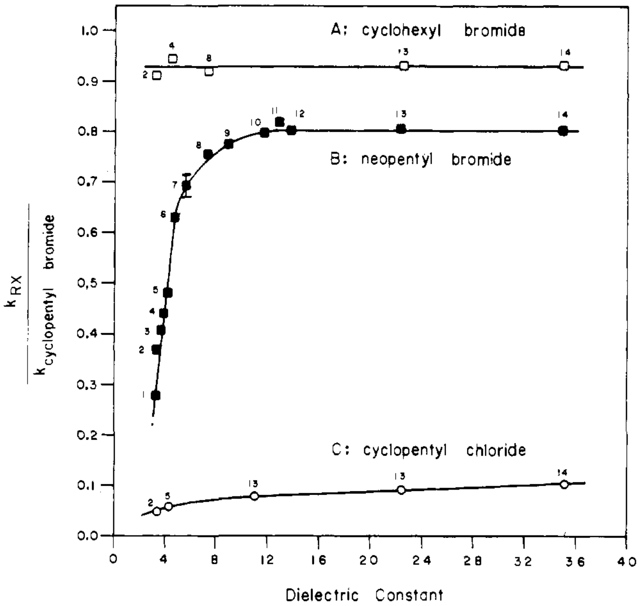

Figure 5. (A) The relative rates of reaction of cyclohexyl bromide and cyclopentyl bromide with magnesium are essentially insensitive to solvent polarity. (B) The relative rates of reaction of neopentyl bromide and cyclopentyl bromide are sensitive to the dielectric strength of the solvent. The rate of reaction of neopentyl bromide becomes diffusion limited at a dielectric strength of approximately 10. (C) The relative rates of reaction of cyclopentyl chloride and cyclopentyl bromide are relatively insensitive to the dielectric strength of the solvent. The solvent systems used in this study (abbreviations are those in Table I) include (1) Bu_2O, (2) Et_2O-pentane, 70:30, (3) Et_2O-pentane, 80:20, (4) Et_2O-pentane, 90:10, (5) Et_2O, (6) RMgBr (0.1 M), Et_2O, (7) RMgBr (0.2 M), Et_2O, (8) THF, (9) RMgBr (0.4 M), Et_2O, (10) Et_2O-sulfolane, 80:20, (11) THF-HMPA, 75:25, (12) RMgBr (0.6 M), Et_2O, (13) RMgBr (0.8 M), Et_2O, (14) RMgBr (1.0 M), Et_2O, and (15) RMgBr (0.5 M), Et_2O.

The rate of reaction of neopentyl bromide with magnesium is transport limited in solutions of high dielectric strength, but slower than transport limited in solvents of low dielectric strength. We have examined the influence of solvent dielectric constant on the rate of reaction of neopentyl bromide (one of the more slowly reacting of the alkyl bromides) with magnesium, by comparing its rate with that of cyclopentyl bromide using competitive kinetics techniques (Figure 5).[3] Since the rate of reaction of cyclopentyl bromide is transport limited in all of the solvents listed in Table I, and thus in all of those included in Figure 6, this study provides a measure of the factor separating the rate of *reaction* of neopentyl bromide with magnesium from the rate of *encounter* of cyclopentyl bromide with magnesium in the solutions examined. Figure 5 also includes similar studies of the much slower reaction of cyclopentyl chloride, and of the reaction of cyclohexyl bromide (an alkyl halide which reacts with approximately the same rate as cyclopentyl bromide in diethyl ether). Two methods were used to vary the dielectric constant. First, several ethers (diethyl ether, tetrahydrofuran, di-*n*-butyl ether) and mixtures of diethyl ether with pentane were examined. The dielectric constants of the mixed solvents were estimated on the assumption that contributions from the individual components were additive. Second, a series of diethyl ether solutions containing increasing concentrations of cyclopentylmagnesium bromide were examined. Concentrated solutions of alkyl Grignard reagents in diethyl ether have surprisingly high dielectric constants: 1 M ethylmagnesium bromide, for example, is reported to have a dielectric constant of 35.[11] The dielectric constants of the cyclopentylmagnesium bromide solutions included as solvents in Figure 5 were estimated assuming that these dielectric constants were the same as those for solutions containing the same concentrations of ethylmagnesium bromide.[11]

Several interesting observations can be based on these plots, and on the conclusion from Figure 2 that cyclopentyl bromide reacts at a transport-limited rate in all of the solvents studied. First, the shape of the plot of $k_{(CH_3)_3CCH_2Br}/k_{C_5H_9Br}$ vs. dielectric constant demonstrates that the rate of reaction of neopentyl bromide with magnesium increases sharply with solution dielectric constant up to a value of $\epsilon \simeq 10$, but stays constant beyond that. We interpret the observed plateau $k_{(CH_3)_3CCH_2Br}/k_{C_5H_9Br} = 0.80 \pm 0.05$ as evidence that neopentyl bromide reacts with magnesium at transport-limited rates at high dielectric constants. This interpretation is supported by an independent estimation of the relative diffusion constants of these alkyl bromides from polarographic diffusion currents (i_d): $i_{d,(CH_3)_3CCH_2Br}/i_{d,C_5H_9Br} = 0.87 \pm 0.05$ (DMF, Bu_4NBF_4, 25 °C). Second, Figure 5 suggests that transport and chemical reaction are competitive for neopentyl bromide in diethyl ether: this solvent falls close to the curved portion of the plot connecting the rising segment characteristic of a chemical reaction influenced by solution dielectric constant and the plateau characteristic of transport control. In agreement with this conclusion, the rate of reaction of neopentyl bromide appears to be slower than a strictly transport-limited process, but still shows a significant increase with increased agitation (Figure 3). Third, although the rate of reaction of neopentyl bromide with magnesium is strongly influenced by solution dielectric constant, the rate of the (faster) reaction of cyclohexyl bromide is unaffected by dielectric constant, and that of the (slower) reaction of cyclopentyl chloride shows only a very small increase with dielectric constant. The first of these observations is consistent with the proposal that the upper limit observed for the rates of reaction of alkyl halides in diethyl ether with magnesium depends on transport. The structures of cyclopentyl bromide and cyclohexyl bromide are similar, and their rates would be expected to respond very similarly to changes in medium: since cyclopentyl bromide reacts as a transport-limited rate in all the solvents examined, so should cyclohexyl bromide. The ratio of their rates in competitive kinetics experiments should thus be a constant, and equal to the ratio of their diffusion constants. The ratio of their rates of reaction with magnesium ($k_{C_6H_{11}Br}/k_{C_5H_9Br} = 0.93 \pm 0.05$) derived from Figure 5 is in satisfactory agreement with the ratio of their polarographic diffusion currents ($i_{d,C_6H_{11}Br}/i_{d,C_5H_9Br} = 0.96 \pm 0.05$, DMF, Bu_4NBF_4, 25 °C). The insensitivity of the rate of reaction of cyclopentyl chloride to solvent polarity (Figure 5) is surprising. The relative rates of reaction of alkyl chlorides with magnesium are, however, significantly less sensitive to changes in alkyl group structure than are the rates of the corresponding, nontransport, reactions of alkyl bromides (cf. Figure 8 of ref 3). The difference in sensitivity to solvent dielectric strength may reflect the same (presently unidentified) cause, or a difference in the nature of the processes that break the carbon–chlorine and carbon–bromine bonds.

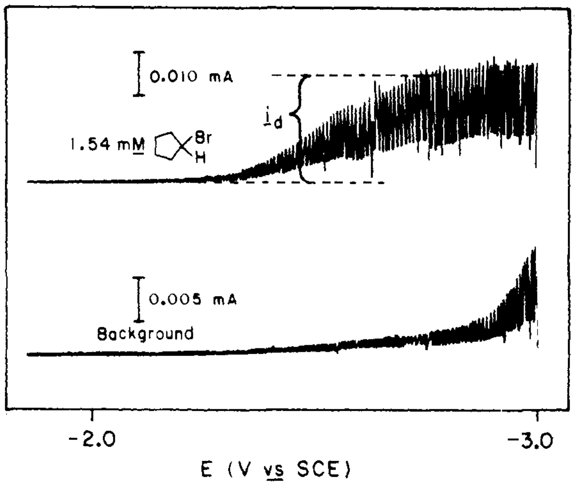

Figure 6. Dc polarogram of cyclopentyl bromide in 0.01 M tetra-*n*-butylammonium tetrafluoroborate in *N,N*-dimethylformamide at 25 °C, indicating the diffusion current (i_d). Also shown is the background current obtained at twice the current sensitivity.

The conclusion that the rate of reaction of cyclopentyl bromide with magnesium correlates with transport rates in the reaction system could, in principle, be interpreted either in terms of the transport of cyclopentyl bromide itself or of diffusion of some product derived from this alkyl halide (most plausibly cyclopentylmagnesium bromide or cyclopentyl radical[3]). Any primary product derived from cyclopentyl bromide should have cleaved the carbon–bromine bond. If a subsequent step in the reaction is overall rate limiting, then the step breaking the carbon–halogen bond must be reversible. To check for reversible carbon–halogen bond breaking, a mixture of cyclopentyl bromide and *n*-pentyl iodide was allowed to react to ca. 50% completion, the reaction mixture was quenched, and the remaining alkyl halides were examined for halogen interchange: no *n*-pentyl bromide or cyclopentyl iodide was detected (0.5% would have been detectable under the GLC analysis conditions employed). Thus, transport of the alkyl halide itself can be identified as the rate-limiting step.

Conclusions

Three groups of observations indicate that the rates of reaction of cyclopentyl bromide with magnesium are limited by mass transport and diffusion in all the solutions examined. First, rates show the qualitative kinetic characteristics expected of a transport-limited heterogeneous reaction: they are proportional to the concentration of cyclopentyl bromide, the surface area of the magnesium, and the degree of agitation of the solution, and inversely proportional to the solution viscosity.

$$-d[RBr]/dt \propto [RBr]A_{Mg}\omega\eta^{-1}$$

Second, the energy of activation for the reaction in diethyl ether is low. Third, cyclopentyl bromide and a number of other organic halides of widely differing structures have approximately the same rate of reaction; no organic halide of the considerable number so far examined reacts more rapidly. Careful measurements of several of these relative rates using competitive techniques under conditions in which our analysis would suggest the individual rates to be transport limited gives ratios equal to the ratios of the corresponding diffusion constants. In addition, Vogler et al. have established that there is no observable heavy atom kinetic isotope effect on the rate of reaction of methyl iodide with magnesium in THF ($k_{^{12}C}/k_{^{13}C}$

= 0.9992).[12] This observation suggests no carbon-iodine bond breaking in the transition state.

The reactions of a few of the organic bromides (neopentyl, phenyl, cyclopropyl, cyclobutyl), and most organic chlorides, are slower than the transport-limited rate.[13] The rate of reaction of neopentyl bromide with magnesium is sensitive to solution dielectric constant: a change from $\epsilon \sim 3$ to $\epsilon \sim 6$ increases the rate by a factor of ca. 2; above $\epsilon \sim 10$ this reaction also become transport limited. The rate of reaction of cyclopentyl chloride increases only slightly with increasing solution dielectric constant. The rate increases observed for neopentyl bromide on increasing solution dielectric strength are compatible with modest charge separation in the transition state. The reaction of neopentyl bromide and bromobenzene,[4] and presumably of the other organic bromides which react in diethyl ether at a rate less than transport controlled,[3] are remarkable in that they provide examples of reactions whose rate can be adjusted from transport limited to non-transport- limited by small changes in medium. These reactions should provide useful processes with which to explore the transition region between these two rate regimes.

The observations reported here are compatible with, but do not require, a mechanism for reaction of cyclopentyl bromide with magnesium in which cleavage of the carbon-bromine bond and formation of the carbon-magnesium bond occur exclusively at the magnesium-solution interface. Some contribution to these reactions might, for example, occur by generation and consumption of a reactive, soluble, magnesium(I) species, or from a radical chain reaction involving soluble species.[14] It should, in principle, be possible to explore alternate mechanisms using the kinetic techniques outlined here by a detailed analysis of the dependence of rate on the diffusion constant of the organic bromide, the viscosity of the solution, and the stirring rate. The particular experimental configuration used here for the magnesium is too complex to be analyzed exactly, and it will be necessary to remeasure these dependences using a rotating magnesium disk to obtain mechanistically useful information.[15] We will describe studies on a system of this sort in the future.

Experimental Section

General. Magnesium turnings (J. T. Baker purified) were used for the competitive kinetics studies; magnesium rod (Fisher A.S.T.M.) was used for the constant surface kinetics studies. Organic halides (Aldrich) except neopentyl bromide (vide infra) were purified by passage through a short (10 cm × 18 mm o.d.) column of dry alumina, activity grade I. Solvents were dried and distilled under argon from purple solutions containing sodium benzophenone ketyl and disodium benzophenone dianion. Manipulations involving Grignard reagents and solvents were performed under argon using standard inert-atmosphere techniques.[16] Polarographic diffusion currents were obtained using a Princeton Applied Research Model 174 polarographic analyzer with a dropping mercury electrode (DME) operating in the dc mode.

Kinetic Methods. Relative rate data were obtained using the competitive kinetics techniques previously described.[3] The rates of disappearance of cyclopentyl bromide and cyclopentyl chloride as a function of solvent were determined using the constant-surface method previously described.[3]

Dielectric constants of Grignard reagent solutions were estimated graphically using a plot prepared from literature data.[11]

Neopentyl bromide, prepared by reaction of neopentyl tosylate with lithium bromide in hexamethylphosphoramide using a modification of the procedure of Stephenson, Solladie, and Mosher,[17] had bp 105-106 °C (lit.[18] bp 104.8 °C).

Preparation of Solutions of Grignard Reagents Used as Solvents. Typical Procedure. To a 500-mL round-bottomed flask were added 12 g (0.5 g-atom) of magnesium metal turnings and a magnetic stirring bar. The flask was fitted with a No-air stopper, purged with argon for 20 min, flame dried and cooled to room temperature in an argon stream, and placed under a slight positive pressure of argon. The flask was placed in a cool (ca. 10 °C) water bath and 300 mL of the appropriate solvent was added by forced siphon through a stainless-steel cannula. With vigorous stirring, 44.7 g (0.3 mol) of cyclopentyl bromide was added in 2-mL portions during 3 h. The solution was stirred for an additional 2 h at room temperature; the dark solution was filtered under argon through a medium-porosity glass frit into a flame-dried Schlenk storage tube. The solutions thus prepared were clear and colorless. The concentration of Grignard reagent was determined by titrating a 1-mL sample to a persistent yellow end point with 1 N 2-butanol in xylenes using 1,10-phenanthroline as indicator.[19] The yields of Grignard reagent were typically 90%; the major byproducts were bicyclopentyl, cyclopentane, and cyclopentene (approximately 3:1:1, respectively).

Determination of Polarographic Diffusion Currents, i_d. Typical Procedure. The oven-dried (120 °C) polarographic cell (Princeton Applied Research) was assembled for three-electrode operation using a platinum wire counter electrode, saturated calomel reference electrode (contact was made via a KCl/agar bridge), and a timed dropping mercury electrode (Princeton Applied Research Model 174/70). A solution of tetra-*n*-butylammonium fluoroborate (Southwestern Analytical Chemicals) in freshly distilled *N,N*-dimethylformamide (25.0 mL, 0.01 M) was introduced and degassed with nitrogen for 15 min. The cell was then placed under a slight pressure of nitrogen and the background current recorded as the potential on the DME was varied from 0.0 to −3.0 V (SCE) at a scan rate of 10 mV/s. In all polarograms recorded, a drop time of 0.5 s was used. To the cell was then added 1.00 mL of 0.040 M organic halide in the stock electrolyte solution. The solution was degassed for 15 min, and the dc polarogram was recorded at the same or lower current sensitivity as was used to record the background. A typical dc polarogram, showing the diffusion current i_d, and background are shown in Figure 6. All polarograms were recorded at room temperature (ca. 22 °C) for identical concentrations (1.54 mM) or organic halide using identical scan rates, drop times, mercury column heights, and electrolyte solution. During each determination the low pass filter (part of the PAR 174A polarographic analyzer) was left in the off position.

References and Notes

(1) Supported by the National Science Foundation, Grants MPS 74-20946 and 7711282 CHE to G.M.W. and Grant CHE 75 03472 to J.D.

(2) Texaco Fellow, 1975–1976.

(3) H. R. Rogers, C. L. Hill, Y. Fujiwara, R. J. Rogers, H. L. Mitchell, and G. M. Whitesides, *J. Am. Chem. Soc.*, preceding paper in this issue.

(4) H. R. Rogers, R. J. Rogers, H. L. Mitchell, and G. M. Whitesides, *J. Am. Chem. Soc.*, following paper in this issue.

(5) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism", 2nd ed., Wiley, New York, 1961, p 270; H. L. Fisch and H. G. Kuivila, *J. Am. Chem. Soc.*, **99**, 7200 (1977), and references cited therein.

(6) C. L. Hill, J. B. Van der Sande, and G. M. Whitesides, *J. Org. Chem.*, in press.

(7) A number of other solvent systems were explored and found to be unsuitable for these studies because the Grignard reagent product precipitated as a solid from the reaction, or because the Grignard reagent induced separation into two liquid phases. Solutions of tetrahydrofuran containing hydrocarbons or Grignard reagent, and 1,2-dimethoxyethane (glyme), fell into the former category; solutions of diethyl ether containing greater than 30% hydrocarbon fell into the latter category. Solutions of diethyl ether containing hydrocarbons more viscous than Nujol, viz., petroleum jelly or paraffin waxes, separated into two phases below 35 °C.

(8) Even at $\omega = 0$ the reaction should occur at a finite rate owing to pure diffusion of organic halide to the surface. In practice it would be difficult to measure a nonconvective, diffusional rate since the reaction is exothermic, and mass transport due to thermal convection efficiently mixes the solution even in the absence of external stirring.

(9) S. W. Benson, "The Foundations of Chemical Kinetics", McGraw-Hill, New York, 1960, p 499; D. Shooter in "Comprehensive Chemical Kinetics", Vol. 1, C. H. Bamford and C. F. H. Tipper, Eds., Elsevier, Amsterdam, 1969, p 253. The activation energy for the self-diffusion of alkyl bromides and iodides is approximately 2 kcal/mol: L. H. Stein and P. C. Carman, *J. S. Afr. Chem. Inst.*, **9**, 55 (1956).

(10) Values of E_a for reactions of organic halides with magnesium have not been measured previously. Reported values (kcal/mol) for reaction of organic halides with lithium vary widely and are of untested accuracy: phenyl bromide (0.82, THF; 9.0, Et_2O); *n*-butyl bromide (5.7, Et_2O); neopentyl bromide (13.8, Et_2O). The value in THF was obtained by G. G. Cameron and A. J. S. Milton, *J. Chem. Soc., Perkin Trans. 2*, 378 (1976); others are reported by C. Yao, Ph.D. Thesis, The Ohio State University, Columbus, Ohio, 1963.

(11) R. E. Dessy and R. M. Jones, *J. Org. Chem.*, **24**, 1685 (1959).

(12) E. A. Vogler, R. L. Stein, and J. M. Hayes, *J. Am. Chem. Soc.*, **100**, 3163 (1978). The conclusions reached in this paper concerning the relative importance of halogen abstraction and single-electron transfer in reaction of methyl iodide with magnesium were based on the assumption that the reaction is not diffusion limited. We believe that this assumption is incorrect.

(13) Pulse radiolysis studies have been interpreted to indicate lifetimes in cy-

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)$^{-1/6}$.

(16) H. C. Brown, "Organic Syntheses via Boranes", Wiley, New York, 1975, Chapter 9.

(17) B. Stephenson, G. Solladie, and H. S. Mosher, *J. Am. Chem. Soc.*, **94**, 4184 (1972).

(18) F. C. Whitmore, E. L. Whittle, and B. R. Harriman, *J. Am. Chem. Soc.*, **61**, 1585 (1939).

(19) S. C. Watson and J. F. Eastham, *J. Organomet. Chem.*, **9**, 165 (1967).

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. *Received September 11, 1978*

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

0002-7863/80/1502-0231$01.00/0