

# Mechanism of Formation of Grignard Reagents. Rate of Reaction of Cyclopentyl Bromide with a Rotating Disk of Magnesium<sup>1</sup>

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**Abstract:** Careful studies of the dependence of the rate of reaction ( $k$ ) of cyclopentyl bromide in diethyl ether with the surface of a rotating magnesium disk as a function of the angular velocity ( $\omega$ ) of the disk confirm the relation  $k \propto \omega^{1/2}$  expected for a mass-transfer limited reaction. More limited studies also indicate that the variations in this rate with other parameters are compatible with those expected for a mass-transfer limited reaction:  $k \propto (\eta)^{-5/6}(\rho)^{1/6}$  ( $\eta$  is the shear viscosity of the solution and  $\rho$  is its density);  $k \propto D^{2/3}$  ( $D$  is the diffusion coefficient of the alkyl halide).

## Introduction

We have suggested that the rate of reaction of cyclopentyl bromide with magnesium in diethyl ether is mass-transfer limited under conditions representative of those used in preparing Grignard reagents.<sup>3-9</sup> The experiments on which this suggestion was based were carried out using a geometry for the magnesium sufficiently complicated that exact analysis of the rate of mass transfer to the magnesium surface as a function of agitation and solution viscosity was impossible.<sup>3,4</sup> Here we describe a parallel but more easily analyzed study of the reaction of cyclopentyl bromide in ethereal solutions at a rotating magnesium disk. The mass transfer characteristics of this system are, in principle, well defined.<sup>10-13</sup> The rate of reaction of a mass-transfer limited process is inversely proportional to the thickness  $X_D$  of a diffusional boundary layer whose dependence on disk angular velocity  $\omega$  ( $s^{-1}$ ), medium

kinematic viscosity  $\eta/\rho$  ( $cm^2 s^{-1}$ ), and reactant diffusion coefficient  $D$  ( $cm^2 s^{-1}$ ) is described by eq 1.<sup>10,12</sup> For a diffusion-controlled

$$X_D = 1.61D^{1/3}\omega^{-1/2}(\eta/\rho)^{1/6} \quad (1)$$

process the rate is equal to the flux  $j$  ( $mol\ cm^{-2}\ s^{-1}$ ) of the reacting material at the disk surface, as described by Fick's first law of diffusion (eq 2). The heterogeneous rate constant  $k_s$  is, therefore,

$$j = -DX_D^{-1}[RBr]_l \quad (2)$$

given by eq 3. Experimentally, the reaction of alkyl halides with

$$k_s = DX_D^{-1} = 0.62D^{2/3}\omega^{1/2}(\eta/\rho)^{-1/6} \quad (3)$$

magnesium in ethereal solutions is pseudo first order in alkyl halide and pseudo zero order in magnesium (eq 4). Inspection of eq

$$-d[RBr]/dt = k^{obsd}[RBr]_l \quad (4)$$

2-4 reveals that  $k_s$  can be calculated from  $k^{obsd}$  according to eq 5, where  $V$  is the solution volume and  $A$  is the apparent area of the magnesium disk.

$$k_s = k^{obsd}VA^{-1} \quad (5)$$

## Results

**Apparatus-Procedure-Products.** Experiments were carried out using the apparatus illustrated in Figure 1. The magnesium disks used for most experiments had radii of 0.79 cm. Only the bottom surface of each disk was exposed; the top and sides were covered with phenolic enamel. The steel brush (C in the diagram) was used to scratch the surface to initiate reaction:<sup>14</sup> the disk was raised

(14) Scratching the magnesium surface in the assembled apparatus provided an effective method of initiating reaction across the entire surface of the disk; the metallurgical factors underlying this initiation are discussed elsewhere.<sup>6</sup> Traces of transition metals have no influence on the rate of formation of Grignard reagents,<sup>3</sup> although they may, in principle, catalyze reaction of preformed Grignard reagent with unreacted alkyl halide (Kochi, J. K. *ACS Symp. Ser.* 1977, 55, 167-185, and references cited). We have found no evidence for this type of reaction in the present work.

(1) Supported by the National Science Foundation, Grants CHE-80-12722, DMR 7824185, and CHE-75-03472.

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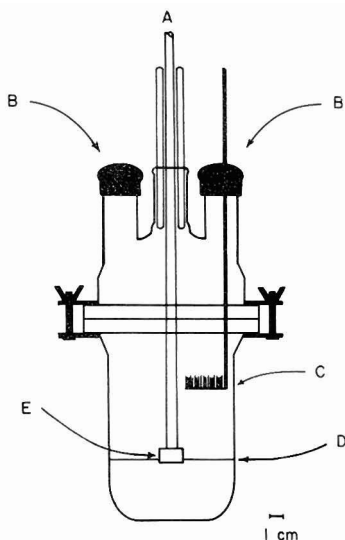
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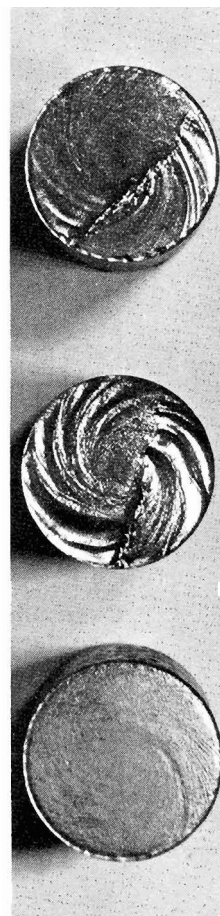
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**Figure 1.** Apparatus for following the reaction of cyclopentyl bromide with a rotating disk of magnesium: (A) adjustable constant-speed stirrer; (B) inlet for argon, reactants, sampling; (C) steel brush for abrasion of the metallic surface; (D) solvent level; (E) magnesium disk 1.59 cm in diameter and 1.27 cm in height, with only the bottom face exposed.

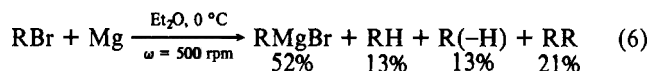
from the solution, scratched with the brush, and then lowered back into the solution. In typical kinetic experiments, the magnesium disks were allowed to react with quantities of alkyl halides totaling 10–20 mmol. Corrosion of the metal was nonuniform across the disk surface (Figure 2). The initially smooth magnesium surface developed a macroscopic pattern of visible irregularities clearly reflecting the pattern of stream lines of liquid flowing across the surface.<sup>15</sup> This pattern did not become pronounced as reaction progressed as long as only very small amounts of cyclopentyl bromide were allowed to react. In practice, as long as each disk was used for the determination of only one relative rate (*vide infra*), increases in surface area or deviations from planarity were sufficiently small to have no significant influence on experimental accuracy. Most of the obvious increase in the magnesium surface area seen in Figure 2 (top) occurred during the treatment of the disk with a concentrated solution of 1,2-dibromoethane, used to activate the entire disk surface before its reaction with cyclopentyl bromide. A fair estimate of the amount of dibromide which reacted in this pretreatment phase is ~10 mmol. This amount of reaction would have consumed ~10 mg-atoms (0.15 cm<sup>3</sup>) of magnesium. In a subsequent kinetic run at that same disk, a total of 2 mmol of cyclopentyl bromide was allowed to react, consuming 2 mg-atoms (0.03 cm<sup>3</sup>) of metal. Together these two reactions would remove a layer of magnesium ~1 mm thick (with approximately 15% of that being due to reaction with cyclopentyl bromide), had the disk corroded uniformly. The extensive pitting which occurred upon reaction of a magnesium disk with substantially larger quantities of alkyl halide (~40 mmol) can be seen in Figure 2 (center).

Most of the disks used in these studies were cut from cold-rolled magnesium rods, each of which had a crack running its length. Pitting was most prominent near these cracks, and the fluid flow in their vicinity was more turbulent (as opposed to laminar) than at other parts of the disk surface. Since  $d(\log k_s)/d(\log \omega)$  is not expected to be 0.5 for any rotating disk system which does not conform to the theoretical requirements for laminar flow,<sup>10,12</sup> we were concerned that local pitting near the crack might make the experimental kinetics difficult to interpret. Control experiments carried out with uncracked disks gave results indistinguishable from those obtained with cracked disks (Figure 2, bottom). Either gave irreproducible results if extensive pitting was allowed to develop, and, as a precaution, only one value for the relative rate of reaction was obtained from each disk.



**Figure 2.** Relief structure on disk surfaces following reaction with cyclopentyl bromide in ether. (Top) Disk used in typical kinetic runs. Data obtained using this disk are included in Figure 5. The heavily etched line across the disk results from preferential etching close to a microscopic crack. The total quantity of alkyl bromide consumed by reaction of this disk (including 1,2-dibromoethane) was 12 mmol. (Center) A disk which had been allowed to react with 35–40 mmol of alkyl bromide. The etching in this disk was sufficient to produce an appreciable change in surface area. (Bottom) Uncracked disk, used to establish that the crack-associated etching obvious in the top disk had not distorted the observed rate constants. This disk was allowed to react with 12 mmol of alkyl bromide.

The distributions of products of reaction of cyclopentyl bromide with a rotating magnesium disk in diethyl ether (eq 6,



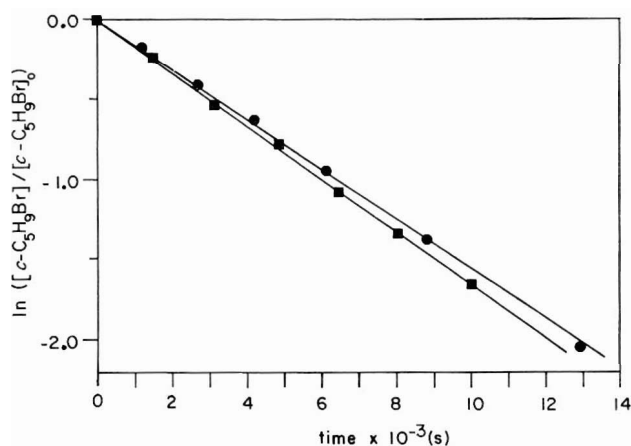
$\text{R} = \text{c-C}_5\text{H}_9$ ) are very similar to those obtained in typical preparative reactions.<sup>16</sup> The yield of Grignard reagent determined by titration<sup>17</sup> (50%) agrees well with that inferred from GLC analysis of the hydrocarbon products of the reaction (52%),<sup>18</sup> and implies that exclusion of water and oxygen during the kinetics runs was adequate. We believe that the byproducts of the reaction (cyclopentane, cyclopentene, bicyclopentyl) originate almost exclusively in radical–radical combination and disproportionation

(16) For example, yields in a carefully controlled preparative reaction are: RMgBr (39%); RH (18%); R(-H) (18%); RR (25%). Cf Lawrence, L. M. M.S. Thesis, Massachusetts Institute of Technology, Cambridge, Mass., 1980, Shih, Y.-S., unpublished results.

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(18) A small amount of cyclopentanol was detected by GLC (5%) and was assumed to have been formed by the oxidation of cyclopentylmagnesium bromide during the quench and not by reaction of the Grignard reagent with dioxygen in the reaction vessel itself. The actual GLC yields of all products follow: cyclopentene, 13%; cyclopentane, 60%; cyclopentanol, 5%; bicyclopentyl, 21%. The inferred yield of cyclopentylmagnesium bromide was, therefore, %RH + %(ROH) – %R(-H), or 52%. A mass balance of 95% was obtained. See also ref 14.

(15) Similar stream lines have been observed in previous corrosion and metal deposition studies carried out using rotating disks.<sup>10,12</sup>

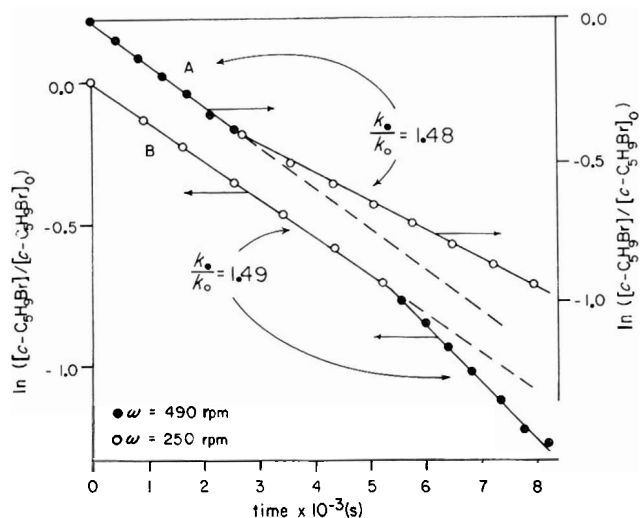


**Figure 3.** Plot of  $\ln ([c-C_5H_9Br]/[c-C_5H_9Br]_0)$  vs.  $t$  for the sequential reaction of two 2-mmol portions of cyclopentyl bromide with a rotating disk of magnesium ( $r = 0.79$  cm; diethyl ether,  $0^\circ\text{C}$ ,  $\omega = 600$  rpm): (●) first run,  $k^{\text{obsd}} = 1.59 \pm 0.03 \times 10^{-4} \text{ s}^{-1}$ ; (■) second run,  $k^{\text{obsd}} = 1.67 \pm 0.03 \times 10^{-4} \text{ s}^{-1}$ . Uncertainties are expressed at the 95% confidence level.

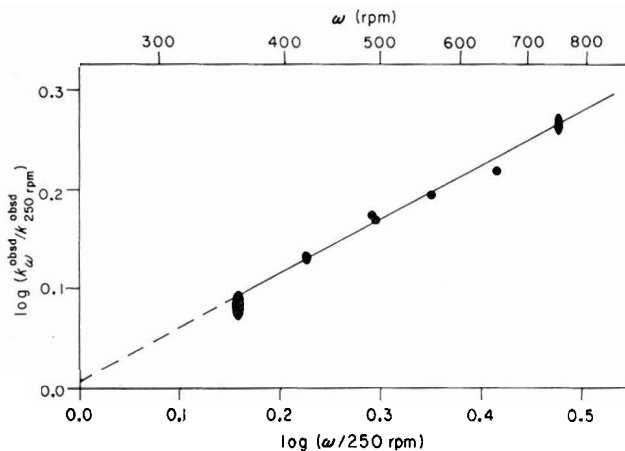
reactions of cyclopentyl free radicals.<sup>7</sup> Calculation of the ratio of rate constants for disproportionation and combination of these radicals from the yields summarized in eq 6 gives a value of  $k_d/k_c = 1.2$ . This value agrees closely with that obtained in preparative syntheses of cyclopentylmagnesium bromide,<sup>16</sup> and with values obtained using authentic cyclopentyl free radicals generated in other ways.<sup>19,20</sup>

**Kinetics.** The procedure used in obtaining kinetic information with the apparatus of Figure 1 was essentially that described previously.<sup>3,4</sup> Because the surface area of the magnesium was not known exactly and because the influence of magnesium surface structure on rates of reaction was also undetermined,<sup>6</sup> kinetic experiments were designed to yield relative rates of reaction of RBr with magnesium under different reaction conditions, rather than absolute rates. The heterogeneous rate constant  $k_s$  can be calculated from  $k^{\text{obsd}}$  by the use of eq 5 for a particular run on a particular disk, but the rate constants obtained in runs at different disks cannot be quantitatively compared even when the identical procedure is followed in the two runs. The rate of disappearance of alkyl bromide was followed under a standard set of experimental conditions. A selected experimental parameter (for example, angular velocity of the disk or solution viscosity) was changed, and a parallel experiment using the same magnesium disk was then carried out to follow the rate of disappearance of alkyl bromide under these new conditions. Comparison of these results defined the change in rate due to the change in the experimental parameter which was varied. Thus, these experiments yielded ratios of rate constants ( $k_{\omega}^{\text{obsd}}/k_{\omega'}^{\text{obsd}}$ ;  $k_{(\eta/\rho)}^{\text{obsd}}/k_{(\eta'/\rho')}^{\text{obsd}}$ ). Our previous application of this method was based on the approximation that the surface area and possible other (unknown) surface characteristics of the magnesium which determine the reactivity did not vary from run to run, and that the variation in rates reflected only changes in properties of the solution or the alkyl halide (especially, in this context, changes in the rate of mass transfer to the surface). Figure 3 gives representative data for two successive runs carried out using 2-mmol quantities of cyclopentyl bromide and a disk of 0.79-cm radius. The disappearance of cyclopentyl bromide followed pseudo-first-order kinetics in both runs, with the observed rate constant in the second run being 5% greater than in the first. Thus, the change in rate constant which would result from an increase in surface area of this magnitude is within the experimental uncertainty of a single rate constant.

A further simplification was made in the experimental protocol when measuring the dependence of relative rates on the angular velocity of the disk. A 2-mmol portion of RBr (the smallest amount practical) was introduced into the reaction vessel with



**Figure 4.** Plot of  $\ln \{[c-C_5H_9Br]/[c-C_5H_9Br]_0\}$  vs.  $t$  for two separate experiments in which 2 mmol of cyclopentyl bromide was allowed to react with a rotating magnesium disk ( $r = 0.79$  cm; diethyl ether,  $0^\circ\text{C}$ ): (●)  $\omega = 490$  rpm; (○)  $\omega = 250$  rpm. Experiment A:  $k_s^{\text{obsd}} = 1.50 \pm 0.06 \times 10^{-4} \text{ s}^{-1}$ ,  $k_o^{\text{obsd}} = 1.01 \pm 0.02 \times 10^{-4} \text{ s}^{-1}$ ;  $k_s^{\text{obsd}}/k_o^{\text{obsd}} = 1.48$ . Experiment B:  $k_o^{\text{obsd}} = 1.33 \pm 0.06 \times 10^{-4} \text{ s}^{-1}$ ,  $k_s^{\text{obsd}} = 1.99 \pm 0.03 \times 10^{-4} \text{ s}^{-1}$ ;  $k_s^{\text{obsd}}/k_o^{\text{obsd}} = 1.49$ . Uncertainties are expressed at the 95% confidence level.

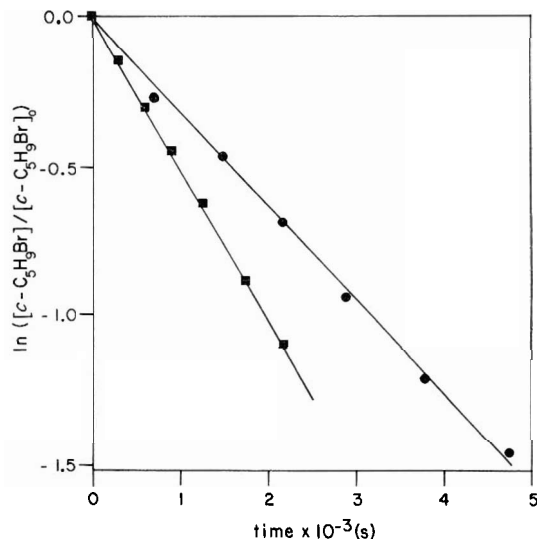


**Figure 5.** Plot of  $\log (k_{\omega}^{\text{obsd}}/k_{250\text{rpm}}^{\text{obsd}})$  vs.  $\log (\omega/250 \text{ rpm})$  for the reaction of cyclopentyl bromide with a rotating magnesium disk ( $r = 0.79$  cm; diethyl ether,  $0^\circ\text{C}$ ). Linear regression gave: slope =  $0.53 \pm 0.07$ ;  $y$  intercept =  $0.007 \pm 0.023$ . The uncertainties are expressed at the 95% confidence level.

the rotation rate set at  $\omega_A$ . Samples were withdrawn for approximately 1 half-life. The rotation rate was changed to  $\omega_B$ , and sampling was continued. With judicious timing of sample withdrawal, all points could be taken before the reactant was 95% consumed. The points taken in each of these regimes were analyzed separately and compared to yield the relative rate of reaction for the ratio of stirring rates,  $\omega_A/\omega_B$ . In these experiments, the slower of the two stirring rates in each run was 250 rpm. Representative data for two separate experiments are shown in Figure 4. In one run, points were first taken at the slower stirring rate while, in the other, the opposite order of stirring rates was used. The reaction rates observed at a particular value of  $\omega$  in the two experiments are different; however,  $k_{\omega=490\text{rpm}}^{\text{obsd}}/k_{\omega=250\text{rpm}}^{\text{obsd}}$  for each of the two runs is nearly the same. Thus, the order of the stirring rates in a single experiment did not affect the measured relative rates. As a further check on the experimental system, the intrinsic rate constant  $k_s$  was calculated for a particular run (eq 5) and compared with the value calculated from eq 1 and 2. For example,  $k_o^{\text{obsd}} = 1.33 \times 10^{-4} \text{ s}^{-1}$  for one run at 250 rpm (Figure 4). Equation 5 gives  $k_s = 9.7 \times 10^{-3} \text{ cm s}^{-1}$ , while the theoretical value of  $k_s$  (eq 1-3) is  $9.2 \times 10^{-3} \text{ cm s}^{-1}$  (using  $D = 4 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  for cyclopentyl bromide<sup>21</sup>). The agreement between the theoretical

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**Figure 6.** Plot of  $\ln([c\text{-C}_5\text{H}_9\text{Br}]/[c\text{-C}_5\text{H}_9\text{Br}]_0)$  vs.  $t$  for the reaction of cyclopentyl bromide (2 mmol) with a rotating magnesium disk ( $r = 1.6$  cm;  $0^\circ\text{C}$ ;  $\omega = 300$  rpm) in two different solvents: (●)  $n\text{-C}_5\text{H}_{11}\text{MgBr}$  in  $\text{Et}_2\text{O}$  (0.7 M, 135 mL;  $\eta = 0.85 \pm 0.02$  cP;  $\rho = 0.850$  g  $\text{cm}^{-3}$ ),  $k_s = 5.36 \pm 0.14 \times 10^{-3}$  cm  $\text{s}^{-1}$ ; (■)  $\text{Et}_2\text{O}$  (155 mL;  $\eta = 0.37 \pm 0.01$  cP;  $\rho = 0.740$  g  $\text{cm}^{-3}$ ),  $k_s = 9.89 \pm 0.15 \times 10^{-3}$  s $^{-1}$ . The relative rate of reaction in the two solvents,  $k_{s,\text{RMgBr}}/k_{s,\text{Et}_2\text{O}} = 0.54 \pm 0.02$ . The uncertainties in the individual rate constants are expressed at the 95% confidence level.

and experimental values of  $k_s$  indicates that the experimental protocol used in these studies satisfies the theoretical requirements for the rotating disk.

Figure 5 establishes that the relative rates obtained in these analyses conform to eq 1; thus, the rate constant for reaction of cyclopentyl bromide with a rotating magnesium disk follows the form expected (eq 2) for a mass-transfer limited reaction:  $k^{\text{obsd}} \propto \omega^{1/2}$ .

An experiment which was performed to establish the influence of solution viscosity on reaction rate followed a similar course. Equations 1 and 2 indicate that the rate of a diffusion-controlled reaction of a species at a rotating disk should be proportional to  $D^{2/3}(\eta/\rho)^{-1/6}$ . Since  $D \propto \eta^{-1}$  (according to the Stokes-Einstein equation), the relative rate of reaction of a particular species at a rotating disk in two solutions (A, B) with different viscosities and densities but equal volumes,  $k_A^{\text{obsd}}/k_B^{\text{obsd}}$ , is given by eq 7.

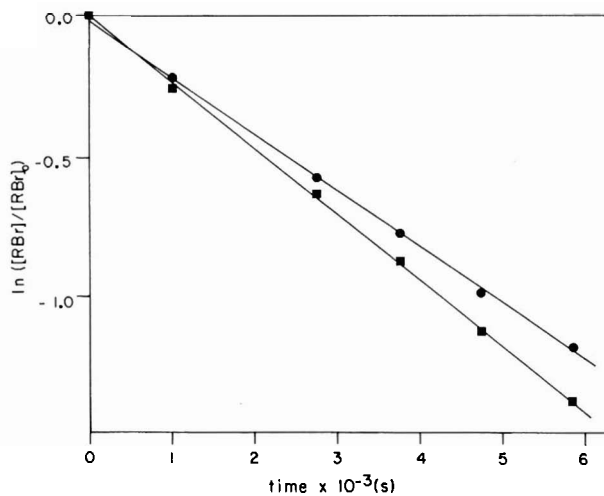
$$k_A^{\text{obsd}}/k_B^{\text{obsd}} = (\eta_B/\eta_A)^{5/6}(\rho_A/\rho_B)^{1/6} \quad (7)$$

The results of an experiment to test the predictions of eq 1, 2, and 7 are given in Figure 6. The value of  $k_s$  in each solvent was calculated from eq 5 and compared:  $k_{s,\text{RMgBr}}/k_{s,\text{Et}_2\text{O}} = 0.54 \pm 0.02$ . This value agrees with the relative rate predicted by eq 7:  $k_{s,\text{RMgBr}}/k_{s,\text{Et}_2\text{O}} = 0.51$ . Previous work had established that changes in solvent polarity have no influence on the rate of reaction of cyclopentyl bromide with magnesium.<sup>4</sup>

An additional prediction of eq 1 and 2 is that the relative rate of reaction of two different alkyl halides at the same rotating magnesium disk ("competitive" kinetics<sup>3,4</sup>) should depend only on the ratio of their diffusion coefficients (eq 8), as long as each

$$k_{\text{RBr}}/k_{\text{R'Br}} = (D_{\text{RBr}}/D_{\text{R'Br}})^{2/3} \quad (8)$$

reacts in a diffusion-controlled process. Figure 7 shows the result of an experiment in which equimolar amounts of cyclopentyl bromide and neopentyl bromide were allowed to react with a rotating magnesium disk in a 0.6 M solution of  $n\text{-C}_5\text{H}_{11}\text{MgBr}$  in  $\text{Et}_2\text{O}$  (a solvent in which neopentyl bromide appears to react at a diffusion-controlled rate<sup>4</sup>). Experimentally,  $k_{(\text{CH}_3)_3\text{CCH}_2\text{Br}}^{\text{obsd}}/k_{\text{c-C}_5\text{H}_9\text{Br}}^{\text{obsd}} = 0.88 \pm 0.03$  ( $D_{(\text{CH}_3)_3\text{CCH}_2\text{Br}}/D_{\text{c-C}_5\text{H}_9\text{Br}} = 0.87 \pm 0.05^4$ ). The value of this ratio of rate constants estimated from the ex-



**Figure 7.** Plot of  $\ln([R\text{Br}]/[R\text{Br}]_0)$  vs.  $t$  for the simultaneous reaction of cyclopentyl bromide and neopentyl bromide (5 mmol of each) with a rotating magnesium disk in an ethereal solution of  $n\text{-C}_5\text{H}_{11}\text{MgBr}$  (0.6 M;  $r = 1.6$  cm;  $0^\circ\text{C}$ ;  $\omega = 300$  rpm): (●)  $(\text{CH}_3)_3\text{CCH}_2\text{Br}$ ,  $k^{\text{obsd}} = 2.03 \pm 0.05 \times 10^{-4}$  s $^{-1}$ ; (■)  $\text{c-C}_5\text{H}_9\text{Br}$ ,  $k^{\text{obsd}} = 2.32 \pm 0.07 \times 10^{-4}$  s $^{-1}$ . Uncertainties in the rate constants are expressed at the 95% confidence level. The relative rate of reaction of the two alkyl bromides is  $k_{(\text{CH}_3)_3\text{CCH}_2\text{Br}}^{\text{obsd}}/k_{\text{c-C}_5\text{H}_9\text{Br}}^{\text{obsd}} = 0.88 \pm 0.03$ .

perimental ratio of diffusion coefficients and eq 8 is  $k_{(\text{CH}_3)_3\text{CCH}_2\text{Br}}/k_{\text{c-C}_5\text{H}_9\text{Br}} = 0.91 \pm 0.03$ .

## Discussion

This work establishes that the dependence of the rate constant for reaction of cyclopentyl bromide with a rotating magnesium disk on the angular velocity of the disk is that expected for a mass-transfer limited reaction (eq 1-4). The dependences of the rate constant on solution viscosity and reactant diffusion coefficient have not been determined accurately, but are also compatible with those expected for mass-transfer limited reaction.<sup>22</sup>

Although the combination of the present work with that reported previously<sup>3-7</sup> leaves little doubt concerning the correctness of the conclusion that the rate of reaction of cyclopentyl bromide with magnesium is mass transfer limited, we note that this rotating disk system only approximates an ideal system. The roughness of the surface, the change in surface area and geometry during reaction, and the inevitable eccentricity of the spinning disk all combine to introduce an unknown degree of inaccuracy into the experimentally determined relative rates. Fortunately, previous practical experience with rotating disks in electrochemistry and corrosion studies suggests that the analysis of rates as a function of angular velocity for the purpose of detecting diffusion-controlled reactions is not seriously affected by small deviations from ideality.<sup>13</sup> Nonideality might also result from the failure to use a range of angular velocities which ensures operation within the laminar flow regime. In this work stirring rates from 250 to 750 rpm were employed, which are well within the recommended range of 10-1200 rpm for a disk of 0.79-cm radius in diethyl ether.<sup>13</sup>

Our previous studies of the dependence of  $k^{\text{obsd}}$  on stirring rate had been carried out using an arrangement in which four magnesium cylinders, attached to the side of a stirring rod, were allowed to react with cyclopentyl bromide.<sup>3,4</sup> These studies had established that  $k^{\text{obsd}} \propto \omega\eta^{-1}$  (approximately) for this geometry. We cannot rationalize this result analytically. We note, however, that the exponent of  $\omega$  is expected to be  $\sim 0.9$  at high Reynolds numbers,<sup>10,12</sup> and that flow in such experiments appeared to be very turbulent.

(22) We have not explicitly determined the dependence of the rate constant on magnesium surface area and on the volume of the reacting solution, but we note that half-lives for the reaction range from 70 to 110 min when disks of 0.79-cm radii are used, while half-lives of 15-30 min are typically observed when larger disks are used ( $r = 1.6$  cm,  $V \approx 150$  mL; cf Figures 3 and 6); the removal of approximately one-half of the volume of the solution resulted in an approximate twofold increase in  $k^{\text{obsd}}$ . The qualitative observation that  $k^{\text{obsd}} \propto AV^{-1}$  is consistent with previous results.<sup>3,4</sup>

## Experimental Section

**General Methods.** Magnesium rods (99.8%, Belmont Metals, Brooklyn, N.Y.) 3.2 or 1.6 cm in diameter were cut into disks 1.27 cm in height and machined to smoothness. Cyclopentyl bromide (Aldrich), neopentyl bromide (Aldrich), 1,2-dibromoethane (Baker), and nonane (Aldrich Gold Label, 99+%) were used without further purification. Reagent grade diethyl ether was distilled under argon from a dark purple solution containing disodium benzophenone dianion, and was distilled directly into a storage flask with a Teflon stopcock, which had been previously flame dried and allowed to cool under a stream of argon. Solvent transfers were made using standard cannulation techniques.<sup>23</sup> The concentration of Grignard reagent was determined by titration,<sup>17</sup> using 2-butanol (0.10 N in xylene) as titrant and 2,2'-biquinoline as indicator. Analytical GLC analyses were performed on a Perkin-Elmer Model 3920B instrument equipped with a flame ionization detector and a Perkin-Elmer Model M-2 calculating integrator, using SE-30 columns (isothermal mode). Solvent shear viscosities were measured at 0 °C with a Cannon-Fenske viscometer (calibrated at 23 °C with methanol and water). Solution densities were determined at 0 °C under argon by weight difference using a 2-mL volumetric flask equipped with a rubber septum.

**Kinetics Methods.** A magnesium cylinder 1.59 cm in diameter and 1.27 cm in height (ca. 4.3 g, 0.18 g-atom) was coated with a phenolic resin (Phenolflex, Bisonite Corp., Tonawanda, N. Y.) on all but one face, such that only that face would be available for reaction. The disk was fixed to a Trubore stirring rod using epoxy cement. Graphite was used as a lubricant for the sleeve for the stirring rod. The reaction vessel consisted of a 500-mL reaction kettle (Lab Glass) with a flat flange grooved to take an O-ring (Figure 1). The kettle cover had a center neck and two side necks 180° apart (all three were 24/40) and a matching grooved flat flange. A precision glass sleeve for the stirring rod was placed in the central neck, and the stirring rod with attached disk was connected to a constant-speed stirring motor (Talboys Model 134-1). One side neck was fitted with a 24/40 rubber septum through which was inserted a length of 12-gauge copper wire with attached soft steel brush. The other 24/40 outlet, also fitted with a rubber septum, contained a 20-gauge syringe needle as vent and later served as the port for introduction and removal of alkyl halides, solvents, and samples from kinetics runs. The reaction kettle was joined to its cover by a McCarter clamp.

**Measurements of Rates as a Function of Disk Angular Velocity.** A typical procedure follows for measurements of rates as a function of  $\omega$ . After assembly of the reaction apparatus, the flask was flushed with argon, flame dried, and allowed to cool under a steady argon stream. Diethyl ether (10–25 mL) and 4 mL of 1,2-dibromoethane (45 mmol) were added to the flask. The magnesium disk was lowered into the solution and briefly rotated (1–2 min), then raised from the solution and thoroughly scratched with the steel brush. Upon immersion of the disk to a depth of ca. 5 mm, vigorous evolution of ethylene began immediately over the entire disk surface. Reaction was allowed to continue, with slow rotation of the disk (50–200 rpm), for only 3–5 min, at which time the metallic surface had the appearance of a mirror and the etched pattern

became evident. The disk was lowered to the bottom of the flask (to keep it beneath the liquid level), and all but 5–10 mL of the solution was removed by cannula. Enough ether was added to bring the solution volume to ca. 50 mL, the solution was mixed well, and all but ca. 5 mL was removed. Ether was added to bring the solution volume to 150 mL, followed by the addition of 0.20 mL of cyclopentyl bromide (2 mmol) and 0.10 mL of nonane (as internal GLC standard). An ice bath was placed beneath the flask, and the stirring rate was adjusted to the desired value (as measured with a General Radio Model 1531-A Strobotac). Sampling was begun after ca. 15 min. Seven or eight samples (each  $\leq 0.15$  mL) were removed at  $\omega_A$  by cannula under a slight positive pressure of argon (2–3 psi) and were quenched by addition to small tubes containing ca. 0.5 mL of a cold, saturated sodium chloride solution. The tubes were vortexed, the phases were separated, and the ethereal layer of each was subjected to GLC analysis. The stirring rate was changed to  $\omega_B$  and the same procedure followed. The volume of solution removed in a single run was  $\leq 2\%$  of the total volume of the reacting solution. Pseudo-first-order rate constants were obtained by plotting  $\ln ([RBr]/[RBr]_0)$  vs.  $t$  and evaluating the slope of each appropriate line segment by linear regression analysis.

**Measurement of Rate as a Function of Solvent Kinematic Viscosity.** After preparation of a magnesium disk ( $r = 1.6$  cm) as described above, a solution of ethereal  $n$ -C<sub>5</sub>H<sub>11</sub>MgBr (0.7 M, ca. 135 mL;  $\eta = 0.85 \pm 0.02$  cP;  $\rho = 0.850$  g cm<sup>-3</sup>) was added to the reaction flask at 0 °C, followed by nonane (0.10 mL) and cyclopentyl bromide (0.20 mL, 2 mmol). The rate of rotation of the disk was adjusted to 300 rpm. Sampling was begun after 5 min. The volume of each sample was  $\leq 0.5$  mL so that the total volume of solution removed was  $\leq 2.5\%$  of the total volume of the reacting solution. Quenching, extraction, and GLC analysis of the aliquots were performed. The solvent was replaced with Et<sub>2</sub>O (ca. 155 mL;  $\eta = 0.37 \pm 0.01$  cP;  $\rho = 0.740$  g cm<sup>-3</sup>) and the procedure repeated. The pseudo-first-order rate constant for each reaction was evaluated by linear regression analysis of the plot of  $\ln ([c\text{-C}_5\text{H}_9\text{Br}]/[c\text{-C}_5\text{H}_9\text{Br}]_0)$  vs.  $t$ . The heterogeneous rate constant for each reaction was calculated from eq 5.

**Measurement of Rate as a Function of Reactant Diffusion Coefficient.** After preparation of a magnesium disk ( $r = 1.6$  cm) as described above, a solution of ethereal  $n$ -C<sub>5</sub>H<sub>11</sub>MgBr (0.6 M, ca. 220 mL) was added to the reaction flask at 0 °C, followed by nonane (0.50 mL) and an equimolar solution of neopentyl bromide and cyclopentyl bromide (1.0 mL, 5 mmol of each). The rate of rotation of the disk was adjusted to 300 rpm. Sampling was begun after 10 min. The volume of each sample was  $\leq 0.6$  mL, so that the total volume of solution removed was  $\leq 2\%$  of the total volume of the reacting solution. Following the quenching and extraction of each sample, the ethereal layer was passed through anhydrous alumina and analyzed by GLC. The pseudo-first-order rate constant for the reaction of each alkyl bromide was evaluated by linear regression analysis of the plot of  $\ln ([RBr]/[RBr]_0)$  vs.  $t$ .

**Product Analysis.** A 30-mmol portion of cyclopentyl bromide was allowed to react with a rotating magnesium disk in 200 mL of diethyl ether (0 °C;  $\omega = 500$  rpm). The yield of Grignard reagent was determined by titration.<sup>17</sup> Cyclopentane, cyclopentene, cyclopentanol, and bicyclopentyl were estimated by GLC following hydrolysis: a response factor of 1.0 was assumed for all hydrocarbons; a response factor of 1.51 was determined for cyclopentanol.

(23) Brown, H. C. "Organic Synthesis via Boranes"; Wiley: New York, 1975; Chapter 9.