= 0 to infinity (eq A51–A58), where T, P, and R are given by eq 9, A33, and A44.

$$I(\mathrm{P}) = \int_0^\infty \mathrm{P}\,\mathrm{d}X \qquad \text{(A51)}$$

$$I(R) = \int_0^\infty \mathrm{R}\,\mathrm{d}X \qquad \text{(A52)}$$

$$I(\mathrm{TT}) = \int_0^\infty \mathrm{T}^2\,\mathrm{d}X \qquad \text{(A53)}$$

$$I(\mathrm{PT}) = \int_0^\infty \mathrm{PT}\,\mathrm{d}X \qquad \text{(A54)}$$

$$I(\mathrm{RT}) = \int_0^\infty \mathrm{RT}\,\mathrm{d}X \qquad \text{(A55)}$$

$$I(\mathrm{PP}) = \int_0^\infty \mathrm{P}^2\,\mathrm{d}X \qquad \text{(A56)}$$

$$I(\mathrm{RP}) = \int_0^\infty \mathrm{RP}\,\mathrm{d}X \qquad \text{(A57)}$$

$$I(\mathrm{RR}) = \int_0^\infty \mathrm{R}^2\,\mathrm{d}X \qquad \text{(A58)}$$

For the integrations of eq A51–A58, we have used both numeric (trapezoid rule and Gauss quadrature from X = 0–20 with analytic integrations of the remaining tails, which have very small magnitudes, to infinity) and analytic methods, with agreement among them. Equations A59–A66 give the results of analytic integrations.

$$I(\mathrm{P}) = B[(3/C)E_2(C) + 3E_1(C) + e^{-c}] \qquad \text{(A59)}$$

$$I(\mathrm{R}) = (A/G)[(3/GC)E_2(GC) + 3E_1(GC) + e^{-GC}] \qquad \text{(A60)}$$

$$I(\mathrm{T}^2) = 16/3C^3 \qquad \text{(A61)}$$

$$I(\mathrm{PT}) = (4B/C)[(3/C^2)E_4(C) + (3/C)E_3(C) + E_2(C)] \qquad \text{(A62)}$$

$$I(\mathrm{RT}) = (4A/C)[(3/G^2C^2)E_4(GC) + (3/GC)E_3(GC) + E_2(GC)] \qquad \text{(A63)}$$

$$I(\mathrm{P}^2) = \mathrm{B}^2[(9/C^3)E_4(2C) + (18/C^2)E_3(2C) + (15/C)E_2(2C) + 6E_1(2C) + e^{-2C}/2] \qquad \text{(A64)}$$

$$I(\mathrm{RP}) = AB[(9/G^2C^3)E_4[(G+1)C] + [9(G+1)/G^2C^2]E_3[(G+1)C] + [3(G^2+3G+1)/G^2C]E_2[(G+1)C] + [3(G+1)/G]E_1[(G+1)C] + e^{-(G+1)C}/(G+1)] \qquad \text{(A65)}$$

$$I(\mathrm{R}^2) = (A^2/G)[(9/G^3C^3)E_4(2GC) + (18/G^2C^2)E_3(2GC) + (15/GC)E_2(2GC) + 6E_1(2GC) + e^{-2GC}/2] \qquad \text{(A66)}$$

$$\int_a^\infty e^{-by}\,\mathrm{d}y/y^n = a^{-(n-1)}\int_1^\infty e^{-abt}dt/t^n = a^{-(n-1)}E_n(ab) \qquad \text{(A67)}$$

Here the $E_n(z)$ are exponential integrals (A67) that are described, for example, by Abramowitz and Stegun, who also tabulate their values and give accurate numerical approximations.[8] Except for a multiplicative constant, each term of each integrand of eq A51–A58 (when expressed as a function of U) is of the form of eq A67.

The fluxes of formation of solution products, corresponding to the mass-action terms for product formation in eq A9–A11, are given by combinations of these integrals, taking into account the relationships among T, P, R, Q, and S. The yield of each product is the formation flux divided by V, the flux of formation of R (eq A68–A75).

$$Y_{\mathrm{PH}} = I(\mathrm{P})/V \qquad \text{(A68)}$$

$$Y_{\mathrm{RH}} = I(\mathrm{R})/V \qquad \text{(A69)}$$

$$Y_{\mathrm{QH}} = [I(\mathrm{P}) - I(\mathrm{R})]/V \qquad \text{(A70)}$$

$$Y_{\mathrm{TT}} = (3/2)I(\mathrm{T}^2)/V = 8/C^3V \qquad \text{(compare eq 12)} \qquad \text{(A71)}$$

$$Y_{\mathrm{PP}} = (3/2)I(\mathrm{P}^2)/V \qquad \text{(A72)}$$

$$Y_{\mathrm{PS}} = 3[I(\mathrm{PT}) - I(\mathrm{P}^2)]/V \qquad \text{(A73)}$$

$$Y_{\mathrm{SS}} = (3/2)[I(\mathrm{T}^2) + I(\mathrm{P}^2) - 2I(\mathrm{PT})]/V \qquad \text{(A74)}$$

$$Y_{\mathrm{RR}} = (3/2)I(\mathrm{R}^2)/V \qquad \text{(A75)}$$

$$Y_{\mathrm{RQ}} = 3[I(\mathrm{RP}) - I(\mathrm{R}^2)]/V \qquad \text{(A76)}$$

$$Y_{\mathrm{QQ}} = (3/2)[I(\mathrm{P}^2) + I(\mathrm{R}^2) - 2I(\mathrm{RP})]/V \qquad \text{(A77)}$$

$$Y_{\mathrm{RS}} = 3[I(\mathrm{RT}) - I(\mathrm{RP})]/V \qquad \text{(A78)}$$

$$Y_{\mathrm{QS}} = 3[I(\mathrm{PT}) + I(\mathrm{RP}) - I(\mathrm{P}^2) - I(\mathrm{RT})]/V \qquad \text{(A79)}$$

Registry No. Mg, 7439-95-4.

Supplementary Material Available: A listing of a computer program for calculating product yields and concentration profiles [in interpreted BASIC, a double-precision (16 decimal digits) calculation takes ~3 s on an Amiga 1000] (14 pages). Ordering information is given on any current masthead page.

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[8] Exponential integral: Reference 7; Chapter 5, pp 227–251.

Mechanism of Grignard Reagent Formation. Comparisons of D-Model Calculations with Experimental Product Yields[1]

John F. Garst* and Brian L. Swift

Contribution from the Department of Chemistry, School of Chemical Sciences, The University of Georgia, Athens, Georgia 30602. *Received April 12, 1988*

Abstract: For the reaction of 5-hexenyl bromide in diethyl ether with magnesium at 40 °C, calculations based on a mechanism (the D model) in which intermediate alkyl radicals diffuse freely agree in detail and within probable experimental error with the product distribution reported by Bodewitz, Blomberg, and Bickelhaupt (*Tetrahedron* **1975**, *31*, 1053). All parameters of the calculation are taken or estimated from independent experiments. When the net rate and the reactivities of alkyl radicals at the magnesium surface are adjusted for best fit, the agreement is also excellent for solvent THF and good to excellent for solvents and solvent mixtures involving di-*n*-butyl and di-*n*-pentyl ethers and benzene, as well as diethyl ether, THF, and benzene.

According to Kharasch and Reinmuth,[2] "it might be said that he who knows and understands the Grignard reactions has a fair grasp of organic chemistry, for most fundamental processes have prototypes or analogs in phenomena observable in Grignard

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systems". It has not proved easy to know and understand all of the phenomena observable in Grignard systems. Nearly 90 years after the initial reports,[3] there remain important unsettled questions about the mechanism of Grignard reagent formation from magnesium metal and an alkyl halide.

Kinetic studies might answer some of these questions. However, quantitative treatments of the kinetics of the competitive reactions involved in Grignard reagent formation have been discouraged by the heterogeneous nature of the reactions.

We apply a kinetic analysis of a simplified mechanism to reactions between magnesium and 5-hexenyl bromide in several ethers, allowing for the possible formation of 11 products, 5-hexenylmagnesium bromide, cyclopentylmethylmagnesium bromide, a solvent-derived "alkylmagnesium bromide", 1-hexene, methylcyclopentane, three isomeric hexenyl and cyclopentylmethyl dimers $C_{12}H_{22}$, 5-hexenyl-S, cyclopentylmethyl-S, and S–S, where S is derived from the solvent. An earlier kinetic analysis of the product distribution in Grignard reagent formation was based on an abbreviated form of the same mechanism in which all side reactions were neglected.[4]

The mechanism of Grignard reagent formation has been and is a topic of active interest.[2,4-11] In 1954 it was already believed that alkyl radicals are intermediates (eq 1).[2] Subsequent work

$$RX + Mg \rightarrow\rightarrow R^{\bullet} \rightarrow\rightarrow RMgX \qquad (1)$$

is consistent with eq 1,[4-11] although it could be argued plausibly that there might be a competing "direct" pathway (without an $R^{\bullet}$ intermediate) or one involving geminate recombination of a very short-lived radical pair such as $[R^{\bullet}\ {}^{\bullet}MgX]$, which could emulate a direct reaction. However, Lawrence and Whitesides were able to trap intermediate cyclopentyl radicals (from cyclopentyl bromide) with >80% efficiency with an added nitroxyl radical.[6e] Our working hypothesis is that there is no direct pathway

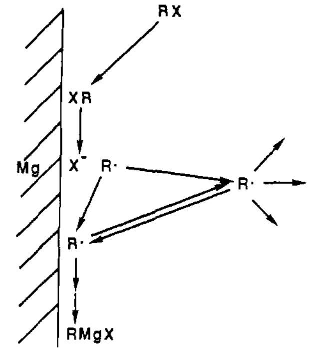
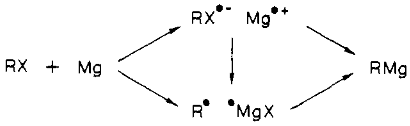


Figure 1. Basic D model for Grignard reagent formation. RX is converted to $R^{\bullet}$ and X^- at the magnesium surface. $R^{\bullet}$ diffuses freely but must return to the surface to be converted there to Grignard reagent. While in solution, $R^{\bullet}$ reacts with solvent, isomerizes, couples, etc.

for simple alkyl bromides; eq 1 describes 100% of the reaction.

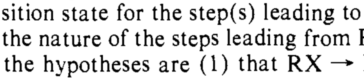
We apply this hypothesis to typical "simple" alkyl halides, that is, saturated, unstrained compounds like hexyl and cyclopentyl halides. Strained small-ring or unsaturated compounds such as 1-methyl-2,2-diphenylcyclopropyl, benzonorbornadienyl, and benzonorbornenyl halides may behave differently.[5,9] In particular, their reactions are more likely to involve intermediate alkyl halide anion radicals $RX^{\bullet-}$ that undergo reactions other than decomposition to $R^{\bullet}$ and X^- (eq 2). Intermediate alkyl halide anion



(2)

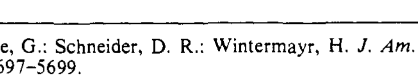
radicals have been invoked to explain the partial retention of configuration that is found when optically active 1-methyl-2,2-diphenylcyclopropyl halides react heterogeneously with magnesium and homogeneously with alkali naphthalenes.[5,12,13] Adamantyl halides also exhibit atypical behavior in reactions with magnesium.[11]

Remote, isolated carbon–carbon double bonds do not appear to influence the mechanisms of Grignard reagent preparations. Thus, similar Grignard reagent yields, product distributions, and CIDNP have been reported from reactions of both 5-hexenyl and saturated alkyl halides.[7c,d] We assume that the only role of the carbon–carbon double bond in reactions of 5-hexenyl halides in ethers with magnesium is to participate in the cyclization of intermediate 5-hexenyl radicals (eq 3).[14] Cyclization of the



(3)

Grignard reagent is also possible (eq 4),[15] but the evidence in-



(4)

dicates that it is negligible under the ordinary conditions of Grignard reagent formation.[7d]

Some of the important remaining questions concern the nature of the transition state for the step(s) leading to $R^{\bullet}$, the mobility of $R^{\bullet}$, and the nature of the steps leading from $R^{\bullet}$ to RMgX. In this work, the hypotheses are (1) that $RX \rightarrow R^{\bullet}$ occurs at the magnesium surface, (2) that $R^{\bullet}$ is not adsorbed at the surface but

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instead diffuses freely in solution, where it can isomerize and react with solvent and with other radicals, and (3) that $R^\bullet \rightarrow RMgX$ (through several undefined steps) is initiated at the magnesium surface and has a rate that is proportional to the concentration of $R^\bullet$ at the surface. This basic "D (for "diffusion") model" is outlined in Figure 1.

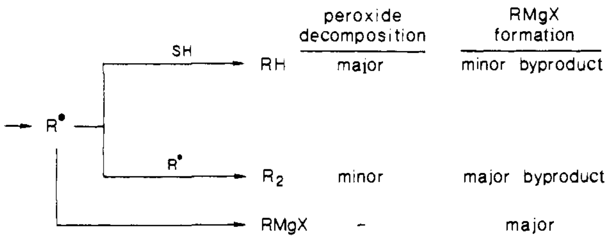
Hypothesis 2, that $R^\bullet$ intermediates diffuse freely in solution, is controversial. Some data have been interpreted in terms of "adsorption models", in which intermediate alkyl radicals remain adsorbed at the magnesium surface.[2,5,9] Other data suggest that the radicals do not remain adsorbed, implying that "diffusion models" are appropriate.[4,6e,11]

While the arguments for surface-bound intermediates presented by Walborsky et al. and by Buske and Ford are based on data from strained or unsaturated substrates,[5,9] the argument of Kharasch and Reinmuth concerns typical alkyl halides.[2] Therefore we address it in detail.

Then we compare calculations based on the D model with experimental data from the work of Bodewitz, Blomberg, and Bickelhaupt.[7] D-model calculations agree remarkably well with these data. For reactions of 5-hexenyl bromide in diethyl ether (DEE), the entire product distribution is calculated within the reported experimental precision by using only parameters derived from experiments on other systems.

Fallacy of the Kharasch–Reinmuth Argument against Freely Diffusing Intermediate Alkyl Radicals. Kharasch and Reinmuth state: "There would appear to be no compelling reason to regard these (intermediate) radicals as "free" in the sense that they occur in significant numbers in the body of the solution. The processes described might very well take place at the solid–liquid interface ... In the cases of such highly reactive free radicals as the phenyl, or even the methyl, the notion that they could survive long enough in the presence of any of the usual Grignard solvents to undergo the reaction $2R^\bullet \rightarrow R_2$ to an appreciable extent is absurd. Surface-attached radicals, however, probably have a considerable degree of surface mobility ... and it seems altogether probable that two adjacent radicals might form a dimer....".[16]

When simple alkyl radicals are created in homogeneous solutions in ethers by such processes as peroxide decompositions, the dominant products are RH and other solvent-derived products; very little R_2 is formed. On the other hand, R_2, not RH, is the dominant byproduct in Grignard reagent formation. These are the kinds of facts on which the Kharasch–Reinmuth argument is based.



The flaw in the argument is the statement that it is absurd that radicals in solution could dimerize instead of react with solvent.[17]

Since reaction with solvent is first-order while coupling is second-order, the competition is concentration dependent and eq 5 (where subscript C denotes coupling and disproportionation,

$$\mathrm{rate}_C/\mathrm{rate}_S = 2k_C[R^\bullet]^2/k_S[R^\bullet] = (2k_C/k_S)[R^\bullet] \qquad (5)$$

while S denotes solvent reaction) gives the relative rates of radical consumption in the two processes. Let $2k_C$ have a typical value of 3×10^9 M^{-1} s^{-1}.[18] For THF, k_S is about 6×10^3 s^{-1},[19] so that $2k_C/k_S$ is about 5×10^5 M^{-1}. (In diethyl ether, k_S is a little smaller.)[19] If the steady-state concentration of $R^\bullet$ in THF is 2×10^{-6} M, then the yields of coupling and solvent cleavage are the same. Steady-state concentrations in typical peroxide decompositions are usually less than this, or the reactions are carried out at higher temperatures so that k_S is larger, or both, so that most of the radicals are consumed in reactions with the solvent.

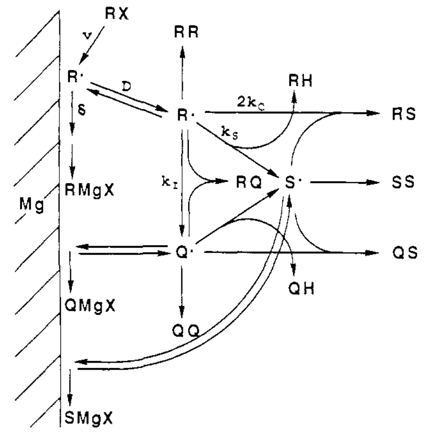


Figure 2. D model for Grignard reagent formation, including side reactions occurring in solution. Not all bimolecular reaction partners are shown. The reactivity parameters are defined in more detail in the text. In the idealized model considered here, the same parameter applies to each member of each set of parallel processes of radicals $R^\bullet$, $Q^\bullet$, and $S^\bullet$.

On the other hand, when the radicals are formed at a solid surface, they tend to "pile up" near it, even if they are freely diffusing in solution. This can result, during Grignard reagent formation, in a steady-state concentration near the surface that approaches or exceeds 10^{-4} M,[17] at which concentration the rate of coupling is about 50 times that of reaction with the solvent.

Thus, what Kharasch and Reinmuth consider to be "absurd" is quite possible.

Diffusion and Solvent Reaction. During Grignard reagent formation, there is very little RH formation by reaction of $R^\bullet$ with the solvent. This raises the question, "How far from the magnesium surface must a radical be in order to escape reaction at the surface and react instead with solvent?"

This is treated quantitatively in the Appendix. It would be naive to assume that a radical at some distance such as 10 or 100 Å has "escaped" from the surface and behaves as would an ordinary radical in a homogeneous solution It is shown in the Appendix that 5-hexenyl radicals at distances of thousands of Ångstrom units from a planar surface (of infinite extent) have high probabilities of diffusing to the surface before reacting with solvent.

D-Model Kinetic Analysis. In the preceding paper the mathematical treatment of a simplified version of the D model was described in detail.[17] The model treated may apply to Grignard reagent formation from 5-hexenyl bromide, which gives an intermediate alkyl radical that can isomerize. The D model and the reactions that are considered here in the case of an isomerizing intermediate radical (rate constant k_I) are illustrated in Figure 2.

The model is simplified by using the same diffusion coefficient D for each of the intermediate radicals $R^\bullet$, $Q^\bullet$, and $S^\bullet$, where $R^\bullet$ isomerizes to $Q^\bullet$ and $S^\bullet$ results when either $R^\bullet$ or $Q^\bullet$ reacts with the solvent. Also, the same rate constant k_S is used to describe the reaction of each radical, $R^\bullet$ and $Q^\bullet$, with the solvent; the same rate constant $2k_C$ (for unlike radicals; k_C for like radicals) is used to describe the coupling of radicals in each possible combination; and the same parameter δ is used to describe the reactivity of each radical, $R^\bullet$, $Q^\bullet$, and $S^\bullet$, at the surface, where they form RMgX, QMgX, and "SMgX". Here "coupling" is used as a brief term for "radical–radical reaction" (including the possibility of disproportionation instead of literal "coupling") and "SMgX" is whatever results from the reaction of $S^\bullet$ at the surface.

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These are all reasonable approximations when R$^\bullet$ and Q$^\bullet$ are similar, for example, both primary alkyl radicals. Since S$^\bullet$ is formed only to a minor extent, it is of little consequence what assumptions are made about its reactivity. S$^\bullet$ is included in the analysis in order to allow in principle for reactions of R$^\bullet$ and Q$^\bullet$ with the solvent; once this is allowed for, completeness requires that the possible reactions of S$^\bullet$ be included also.

Below, "P" is a collective symbol for R and Q. Thus, "PMgX" includes both RMgX and QMgX. Similarly, "PP" includes RR, RQ, and QQ.

The kinetic treatment is a steady-state analysis for a constant initial step flux v (mol area^{-1} s^{-1}). "Flux" is used here instead of "velocity" in order to distinguish an area-based rate from the usual volume-based rate (mol volume^{-1} s^{-1}) used for homogeneous reactions.

The mathematical solution, although rather complex, is in closed form.[17] The product distribution depends on only three parameters, the scaled radical isomerization rate constant $G^2 - 1$, the scaled initial-step flux V, and the scaled reactivity Δ of the surface toward radical (eq 6–8). When reactions of radicals with the solvent are negligible, which are conveniently chosen as an alternatively scaled flux V_I and surface reactivity Δ_I (eq 9 and 10).

$$G^2 - 1 = k_I/k_S \tag{6}$$

$$V = [4k_C/3(k_S{}^3D)^{1/2}]v \tag{7}$$

$$\Delta = (D/k_S)^{1/2}\delta \tag{8}$$

$$V_I = [4k_c/3(k_I{}^3D)^{1/2}]v \tag{9}$$

$$\Delta_I = (D/k_I)^{1/2}\delta \tag{10}$$

The dependencies of the product distributions on these parameters were detailed in the preceding paper.[17]

Effect on Variation of Concentration of RX during Grignard Reagent Formation—the Constant-V_I Approximation. The kinetic analysis outlined above and given in detail in the preceding paper assumes a constant flux v or R$^\bullet$ formation. The system then has a true steady state. In experiments, however, the concentration of RX decreases during the reaction. Since v is proportional to [RX],[6a] v decreases constantly and the system has no true, nontrivial steady state.

It does have a pseudo-steady state. Relaxation of the concentrations of very reactive transient intermediates to pseudo-steady-state values is much faster than the overall reaction. Pseudo-steady-state concentrations are not truly steady; they vary slowly. Here we deal with pseudo-steady-state concentration profiles, in which concentrations vary not only with time (slowly) but also with distance from the magnesium surface.

The variations of the pseudo-steady-state concentration profiles, due to decreasing [RX], should be calculated, and the net product yields should be obtained by appropriate integrations over the reaction time. However, in the calculations reported below, we have used a constant effective V_I, which gives an effective true steady state.

Numerical tests show that this is an excellent approximation. In a "pseudo-exponential-decay" calculation, the net product distribution is obtained by summing the products formed in a succession of steady-state reactions with velocities V_I that decay exponentially in time. For a corresponding "constant-V_I" calculation, the V_I value is found that (with the Δ_I value used in the pseudo-exponential-decay calculation) reproduces in a single true-steady-state calculation the yields of RMgX and QMgX that were found in the pseudo-exponential-decay calculation; this is the effective value of V_I. Then we compare the yields of other products calculated with a constant V_I with those from the corresponding pseudo-exponential-decay calculation.

There is excellent agreement over the parameter ranges that are relevant here (V_I from 10^{-1} to 10^3, Δ_I from 1 to 10^2, with $G^2 - 1 = 100$). The worst agreement between the two calculations occurs with $V_I = 10$ and $\Delta_I = 1$, where the pseudo-exponential-decay calculation gives 31.2% isomerization I_D in the alkyl dimer PP and the constant-V_I calculation gives 33.8%. This variation is insignificant.

D-Model Calculations vs Experimental Data for the Grignard Reagent Formation from 5-Hexenyl Bromide in Diethyl Ether. We compare D model calculations with data reported by Bodewitz, Blomberg, and Bickelhaupt on the reaction of 5-hexenyl bromide in DEE with magnesium at 40 °C.[7d] The necessary parameters for this calculation (v, δ, D, k_I, k_C, and k_S) can all be obtained or estimated from data that are independent of this reaction.

The diffusion coefficient D and the coupling rate constant $2k_C$ are assigned typical values, 3×10^{-5} cm^2 s^{-1} and 3×10^9 M^{-1} s^{-1}, respectively.[18,21] The radical isomerization rate constant k_I is very well known; it is 4.4×10^5 s^{-1} at 40 °C.[14] While the rate constant k_S for hydrogen abstraction from the solvent is not precisely known for DEE at 40 °C, it is reported as 1×10^3 s^{-1} for DEE at 22 °C and as 6×10^3 s^{-1} for THF at 50 °C.[19] Since very little solvent reaction is calculated (or reported) for any value of k_S near this, we have chosen k_S for convenience as 4.4×10^3 s^{-1}, so that k_I/k_S (or $G^2 - 1$) is 100.

The effective flux v is estimated as approximately 2×10^{-5} mol cm^{-2} s^{-1} from data of Rogers et al. and Bodewitz et al.[6a,7d] Rogers et al. found that all alkyl bromides react at nearly the same (diffusion-control) rate.[6a,b] For cyclopentyl bromide, they found first-order kinetics with a half-life of 8 min ($k_{obsd} = 1.4 \times 10^{-3}$ s^{-1}) at 0 °C and an activation energy of 2.3 kcal mol^{-1} (giving $k_{obsd} = 2.4 \times 10^{-3}$ s^{-1} at 40 °C) for the reaction of 0.053 mol of alkyl halide in 400 mL of DEE with magnesium rods of (macroscopic) constant surface area 66.5 cm^2. They also found the rate to be proportional to the surface area A (eq 11).

$$-\mathrm{d}[RX]/\mathrm{d}t = k_{obsd}[RX] \tag{11}$$

$$v = -(U/A)\mathrm{d}[RX]/\mathrm{d}t = (U/A)k_{obsd}[RX] = a[RX]$$
$$a = (U/A)k_{obsd} \tag{12}$$

Equation 12 relates the flux v to [RX]; here U is the volume of the solution and a is a proportionality constant. From the data of Rogers et al., a is determined to be 1.4×10^{-2} cm s^{-1} at 40 °C. Since Bodewitz et al. used a 2.1 M solution of 5-hexenyl bromide, the initial value of v in their experiment is estimated to be $(1.4 \times 10^{-2})(2.1)(10^{-3})$ or 2.9×10^{-5} mol cm^{-2} s^{-1}. Since Mg was limited so as to consume about half of the RX in their experiments, the average value of v during the run would be $\sim 2 \times 10^{-5}$ mol cm^{-2} s^{-1}. We neglect differences in stirring between the experiments of Rogers et al. and those of Bodewitz et al.

We take δ as 0.01 Å^{-1} from Garst, Deutch, and Whitesides,[4] who presented a treatment of a D model that neglects byproduct formation and extracted a V value from data on three alkyl bromide, including 5-hexenyl bromide. If 5-hexenyl bromide is dropped from the analysis, the same value of δ, 0.01 Å^{-1}, still results. Thus, this value can be obtained from data on Grignard reagent formaton from primary alkyl bromides *other than* 5-hexenyl bromide.

Table I gives the yields of products calculated from the D model by using the parameters above together with those reported by Bodewitz et al.[7d] Since the latter reported yields as mole of product per mol of Mg consumed, the calculated yields are reported on this basis.

In the calculation, it is assumed that dimers are the only products of radical–radical reactions. Since disproportionation amounts to only about 10% of the radical–radical reactions among primary alkyl radicals such as 5-hexenyl and cyclopentylmethyl,[22] and since the dimer yield is atmost only about 9%, disproportionation will account for less than 1% of the products.

The agreement between the calculated and experimental values is astonishing. With no adjusted parameters, the calculation reproduces closely every detail of the experimental product distribution, that is, the absolute yields of five products, two Grignard reagents, and three dimers. The yields of products of solvent

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Table I. Products of the Reaction of 5-Hexenyl Bromide in Ether with Magnesium at 40 °C

	calcd[a]	exptl[b]
RMgBr[c,d]	88%	85.5 (2.0)%
QMgBr[c,d]	3.0%	2.5 (0.5)%
PP[c,d]	8.7%	9.0 (3.0)%
RH (from R$^\bullet$ + SH)[c,d]	0.068%	
QH (from Q$^\bullet$ + SH)[c,d]	0.059%	
(RR)/(PP)[e]	66%	64.5 (5.0)%
(RQ)/(PP)[e]	26%	28.0 (2.5)%
(QQ)/(PP)[e]	8.2%	7.5 (2.0)%
I_G[f]	3.3%	2.8%
I_D[g]	21%	22%
H[h]	1.1	1.3
$[P^\bullet]_0$[i]	5.6×10^{-4}	
$G^2 - 1$[j]	1.00×10^2	
V[k]	2.50×10^4	
Δ[l]	8.26×10^1	

[a] See ref 17 for mathematical details of calculations. See text for parameter values. [b] From ref 7d. Values in parentheses are the reported precisions (±). [c] Absolute yields, mole of product per mole of Mg consumed. [d] R = 5-hexenyl; Q = cyclopentylmethyl. P = R or Q. [e] (...) denotes yield of ... [f] Extent of isomerization in PMgBr; (QMgBr)/(PMgBr). [g] Extent of isomerization in dimer; [(RQ) + 2(QQ)]/(PP). [h] Homogeneity quotient; $(RQ)/[(RR)(QQ)]^{1/2}$. [i] Steady-state concentration at the magnesium surface. The concentration of the solvent-derived radical S$^\bullet$ is calculated as only ~0.04% of that of the others (combined). [j] Scaled value of k_I (eq 6). [k] Scaled value of v (eq 7). [l] Scaled value of δ (eq 8).

cleavage are calculated as negligibly small; experimental values are not available.

In the experimental data, the difference between the extents of isomerization in the Grignard reagent (3%) and the dimer (21%) is important. If both were formed through the same steady-state pool of surface-bound radicals, the extents of isomerization would be the same. This indicates clearly that Grignard reagent and dimer are not derived from the same pool of radicals. It is a very significant success that the D model calculation agrees precisely with experiments.

The value of the "homogeneity quotient" H is also important. Given a homogeneous steady-state pool of intermediates R$^\bullet$ and Q$^\bullet$, the relative rates of formation of RQ, RR, and QQ will be such that the yield ratio H [eq 13, where "(product)" denotes

$$H = (RQ)/[(RR)(QQ)]^{1/2} = 2k_C[R^\bullet][Q^\bullet]/(k_C[R^\bullet]^2 k_C[Q^\bullet]^2)^{1/2} = 2 \quad (13)$$

product yield] has the value 2. The observed value is 1.3 instead. A value 1.1 is calculated; the difference between 1.1 and 1.3 is within the reported precision of the experimental result.

As discussed in the preceding paper, the deviation of calculated H values from 2 is a consequence of concentration heterogeneity. Significant amounts of dimers are formed up to several thousand Ångstrom units from the magnesium surface, over which distance the steady-state concentrations of R$^\bullet$ and Q$^\bullet$ vary widely. In calculating yields, one must integrate over all space. Although an H value of 2 is calculated for dimers formed at any particular distance from the surface, integration over all space leads to H values nearer 1.

At the magnesium surface, the total steady-state radical concentration, consisting almost entirely of R$^\bullet$ and Q$^\bullet$, is calculated as 5.6×10^{-4} M. At the surface, the rate at which radicals are consumed in coupling will be 280 times as fast as the rate at which they are consumed in reactions with solvent, according to eq 5. This illustrates quantitatively the fallacy of the argument of Kharasch and Reinmuth that is discussed above.[2]

Although there are no adjusted parameters in this calculation, the effective flux v of formation of R$^\bullet$ is estimated in such an indirect and approximate way that it could be in considerable error. The sensitivities of the calculations to all parameters are illustrated graphically in the preceding paper. In addition, in Table II we give the results of calculations using v values of 1×10^{-5}, 2×10^{-5}, and 4×10^{-5} mol cm^{-2} s^{-1}. The total dimer yields and the extents of isomerization are especially sensitive to variations in v.

Table II. Sensitivity of Calculated Yields of Products of the 5-Hexenyl Bromide–Magnesium Reaction to Variations in the Effective Reaction Flux v

	v[a]		
	1×10^{-5}	2×10^{-5}	4×10^{-5}
RMgBr	89%	88%	86%
QMgBr	4.0%	3.0%	2.2%
PP	6.4%	8.7%	11.6%
(RR)/(PP)	56%	66%	75%
(RQ)/(PP)	31%	26%	20%
(QQ)/(PP)	14%	8.2%	4.5%
I_G	4.3%	3.3%	2.5%
I_D	29%	21%	15%
H	1.1	1.1	1.1
$[P^\bullet]_0$, M	2.9×10^{-4}	5.6×10^{-4}	1.1×10^{-3}

[a] Reaction flux (in mol cm^{-2} s^{-1}). All other parameters are the same as for the calculations of Table I. See Footnotes to Table I for meanings of other symbols.

Since the calculations are rather sensitive to variations in v, it is simply luck that the estimated v value is very close to that which gives the best agreement with experiment. If the value of v required to calculate the product distributions correctly had differed from our independent estimate by a factor approaching 10, for example, we still would have considered that to be good agreement, given the uncertainties of the independent estimate of v. The impressive fact remains that an experimentally reasonable v value gives calculated results that are in excellent agreement with observed Grignard product distributions.

Solvents THF, Di-*n*-butyl Ether, and Di-*n*-pentyl Ether. Bodewitz et al. investigated Grignard reagent formation from 5-hexenyl bromide in THF, di-*n*-butyl ether (DBE), and di-*n*-pentyl ether (DPE), as well as diethyl ether (DEE).[7d] These solvents differ both in viscosities and in polarities. The dielectric constant of THF is ~7.4, while that of DEE is 4.3; DBE and DPE probably have successively lower dielectric constants. The viscosities increase in the order DEE < THF < DBE < DPE.

As long as reactions of alkyl radicals with solvent are negligible, then product distributions are determined by only two scaled parameters, V_I and Δ_I, as discussed in the preceding paper.[17] It is appropriate then to fix k_I/k_S (or $G^2 - 1$) at some large value (we use 10^2) and vary the scaled reaction flux V (or V_I) and the scaled surface reactivity parameter Δ (or Δ_I) in efforts to fit calculations to experimental data. This is the course we follow.

Table III gives the experimental and calculated results. Two calculations are given for each set of experimental results. In calculation 1, V_I and Δ_I are adjusted for a fit to the experimental total yield of Grignard reagent (PMgBr) and extent of isomerization I_G therein. In calculation 2, the parameters are adjusted for a "best" (subjective) overall fit to the experimental data.

For DEE, the two calculations use nearly the same parameters (calculation 2 is the same as in Table I) and the fit to experimental data is excellent. THF is also excellent; calculation 2 overestimates the PMgBr yield slightly, but the reported value is 88.5 ± 5.0%, so the calculation is almost within the reported experimental precision.

For both DBE and DPE, the fits of calculated to experimental data are reasonable but not as good as for DEE and THF. In each case, calculation 1 overestimates the extent of isomerization in the alkyl dimer while calculation 2 overestimates the yield of dimer and underestimates that of Grignard reagent. All of the observed trends are captured by the calculations and the homogeneity quotient H is correctly calculated, within experimental variation, in every case. If these worst cases had been the best, we still would have been judged the D-model calculations to be very successful.

For the best fits of calculations to data for DBE and DPE, V_I has to be lower by at least a factor of 10 (DBE) to 20 (DPE) than for DEE and THF. Rogers, Deutch, and Whitesides, however, found by direct measurement that the rate of reaction of cyclopentyl bromide with magnesium is 0.44 times that in DEE (at

Table III. Experimental and Calculated Yields from Reactions of 5-Hexenyl Bromide with Magnesium in Ethers at 40 °C[a]

solvent[b]		η/cP[c]	yield, %							
			PMgBr[d]	PP[d]	I_G	I_D	H	V_I[e]	Δ_I[f]	b/b_0[g]
DEE	exptl	0.194	88	9.0	2.8	22	1.3			
	calcd 1[h]		88	11.9	2.8	16	1.1	39.5	7.49	0.91
	calcd 2[i]		91	8.7	3.3	21	1.1	25.0	8.26	1.00
THF	exptl	0.389	88	4.0	2.8	32	1.0			
	calcd 1		88	11.3	2.8	16	1.1	38.8	7.72	0.66
	calcd 2		96	3.9	3.2	31	1.1	15.0	12.7	1.09
DBE	exptl	0.506	92	7.0	20	41	1.4			
	calcd 1		92	7.2	20	63	1.1	0.46	2.35	0.18
	calcd 2		82	17	15	43	1.3	2.15	2.00	0.15
DPE	exptl	0.80	92	4.0	29	46	1.3			
	calcd 1		92	4.8	29	77	1.1	0.091	1.66	0.099
	calcd 2		77	22	22	53	1.3	0.962	1.21	0.072

[a] For symbols not defined here, see notes to Table I. Experimental data are from Bodewitz et al.[6d] For calculations, the scaled reaction flux V_I and the scaled surface reactivity Δ_I are varied. The calculations are insensitive to the value of k_S as long as solvent attack is negligible (as is the case here). [b] THF = tetrahydrofuran; DEE = diethyl ether; DBE = di-*n*-butyl ether; DPE = di-*n*-pentyl ether. [c] Viscosity.[6d] [d] Yield, mol of product per 100 mol of Mg consumed. [e] Scaled effective reaction flux; eq 9. [f] Scaled surface reactivity toward alkyl radicals; eq 10. [g] Relative reactivities (unscaled) of radicals at the surface (see text). [h] Calculation with parameters chosen to fit the experimental yield of PMgBr and I_G. [i] Calculation with parameters giving a "best" overall fit to the experimental data.

0 °C).[6b] Most alkyl bromides react at the diffusion-control limit, which is expected to vary inversely with viscosity. Thus, the effective reaction flux v for the reaction of 5-hexenyl bromide in DBE at 40 °C ought to be 0.194/0.506 (viscosity ratio) or 0.38 times that in DEE. This, however, is not the total effect of viscosity on the *scaled* flux V_I (eq 9); $2k_C$ and D also depend on the viscosity, and they introduce an additional factor of $(0.38)^{1/2}$, or 0.62, assuming Stokes' law behavior. Together with the original factor of 0.38 reduction in v, this accounts for a reduction in V_I by a factor of 0.23. This is within a factor of 2 of the necessary reduction (0.1) for the best fit calculation. Applying the same considerations to DPE, the calculated reduction of V_I from that for DEE is $(0.194/0.80)^{3/2}$, or 0.12, again within a factor of 2 of that required for best fit calculation.

It should be noted that Rogers et al. found that dissolved RMgBr (1.0 M) increases viscosities (at 0 °C) of DEE–hydrocarbon mixtures by factors of ~2.5.[6b] The final concentrations of the solutions of Bodewitz et al. are ~2.1 M. Consequently, the viscosities probably increase by a factor of ~5 during each experiment of Bodewitz et al.

There is a concomitant effect of dissolved RMgBr on the dielectric constant. A 1 M solution of ethylmagnesium bromide in DEE is reported to have a dielectric constant of 35 (pure DEE, 4.3).[23] Thus, the effective polarity of the medium probably increased substantially during each experiment of Bodewitz et al. The surface reactivity parameter δ could vary with the polarity of the medium (see below) and therefore this could vary during each run.

Neither the variations in v due to changes in viscosity nor the possible variation in δ due to changes in the polarity of the medium during the reaction are taken into account in the calculations. Despite this, the agreement of calculations with experiment is good to excellent. It should be noted that to bring any particular aspect of the calculations into agreement with the reported results never requires a very large variation in the parameters of the calculations. In the worst case (DPE), a variation of a factor of ~10 in V is sufficient for this purpose, in other cases the variation is by no more than a factor of ~4.

Turning now to the variations in Δ_I that are required for good fits of calculations to experiments, we see that there is little variation in Table III between Δ_I values for calculations 1 and 2 for any solvent. Omitting THF, the fitted values of Δ_I vary from ~8 for DEE to ~1–2 for DPE and DBE, suggesting the possibility of a medium polarity effect on the reactivities of radicals at the magnesium surface.

For such considerations, Δ_I is "unscaled" to factor out the viscosity dependence. The total viscosity dependence is not clearly given by eq 10, since δ is b/D, where $b[\mathrm{P}^\bullet]_0$ is the flux of reaction of radicals P$^\bullet$ into the surface, $[\mathrm{P}^\bullet]_0$ being the concentration at the surface.[17] Eq 14 describes the scaling in terms of b. Ratios

$$\Delta_I = b/(k_I D)^{1/2} \tag{14}$$

of b values for solvents of different viscosities are given by eq 15,

$$b/b_0 = (\Delta_I/\Delta_{I0})(D/D_0)^{1/2} = (\Delta_I/\Delta_{I0})(\eta_0/\eta)^{1/2} \tag{15}$$

where subscript zeros denote a reference solvent, η is the viscosity, and k_I is assumed to be solvent independent. The last column of Table III gives b/b_0 values (reference solvent DEE), Δ_{I0} is taken to be 8.26 (calculation 2 for DEE, Table III), and ratios of the viscosities of the pure solvents are taken to be the effective viscosity ratios for the reactions.

The "best fit" parameter b decreases by a little more than a factor of 10 from DEE to DPE. If the decrease is interpreted as an effect of the polarity of the medium, then the magnesium surface is less reactive toward alkyl radicals in less polar media. This is plausible, since an alkyl radical is essentially nonpolar, while the product of the reaction step at the surface, whatever it may be in detail, probably produces a more polar species that includes an alkyl anion or anionoid. The transition state should be more polar than the reactants and more polar solvents should promote reaction, matching the direction of solvent effect on b that is found. The observed factor of 10, however, is not very large. This could be a consequence of a polarity-leveling effect of dissolved salts and Grignard reagent; these may enhance the effective polarity of each solvent and thereby attenuate the differences among their effects on b.

Nearly Constant Viscosity Mixtures of THF and Benzene. Bodewitz et al. studied reactions in a series of mixtures of THF and benzene with molar ratios (benzene/THF) of 0/1–6.7/1 and viscosities varying only from 0.389 to 0.480. If the reaction of 5-hexenyl bromide with magnesium is diffusion controlled in all of these solvents, then v should vary only slightly through the series while δ may vary more, due to changes in the polarity of the medium. With added benzene, it was found that the total yield of PMgBr and PP remains constant at 90–95% while the yield of dimer and the extent of isomerization in the Grignard reagent increase. At the same time, the extent of isomerization in the dimer remains nearly constant.

To test our calculations against these data, we sought a value of V_{I0} that (with minor viscosity corrections and with adjusted values of Δ_I) reproduces the observed product distributions. To do this, we took the "best fit" values of V_I for this series of experiments and made viscosity corrections to obtain a series of values of V_{I0} (V_I corrected to the viscosity of THF). The resulting set of V_{I0} values ranged from 15 (100 mol % THF) to 4.2 (13.0 mol % THF), with an average near 8. Then, taking 8.00 as V_{I0} and correcting for (small) viscosity variations, we calculated V_I and sought a "best" value of Δ_I for each solvent mixture. The

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Table IV. Calculated (Constant-V_0) and Experimental Yields from Reactions of 5-Hexenyl Bromide in THF/Benzene Mixtures with Magnesium at 40 °C[a]

X_{THF}[b]	Δ_I	RMgBr[c]	QMgBr[c]	PP[c]	RR[c,d]	RQ[c,d]	QQ[c,d]
1.00	10.0	92 (86)	4.2 (2.5)	4 (4)	47 (54)	33 (29)	20 (17)
0.50	10.0	92 (86)	4.4 (2.0)	4 (3)	44 (50)	33 (34)	23 (16)
0.33	6.0	87 (84)	5.9 (5.5)	7 (4)	48 (44)	34 (36)	19 (19)
0.30	5.5	86 (83)	6.1 (4.5)	8 (4)	48 (45)	34 (36)	18 (18)
0.26	4.0	81 (73)	6.9 (9.5)	12 (9)	50 (48)	34 (38)	16 (14)
0.23	4.0	81 (76)	6.9 (8.5)	12 (8)	50 (50)	34 (37)	16 (13)
0.16	2.0	67 (64)	7.7 (11)	25 (14)	52 (50)	34 (36)	13 (14)
0.13	1.7	63 (54)	7.7 (20)	28 (18)	52 (46)	34 (36)	13 (18)

[a] All entries are percentages. See relevant notes to Table I. V_{I0} = 8.00 for each calculation. V_I, calculated from solvent viscosities, varies from 8.00 (X_{THF} = 1.00) to 5.84 (X_{THF} = 0.13). Slightly better fits to the experimental data can be obtained in some cases by adjusting both V_I and Δ_I (compare pure THF in Table III, for example, with the entry here). [b] Mole fraction THF. [c] First number is the calculated value; number in parentheses is the experimental value. [d] Relative yields of components of PP.

Table V. Calculated and Experimental Yields from Reactions of 5-Hexenyl Bromide with Magnesium in Ethers and Mixed Ethers at 40 °C[a]

X solvent[b]	η/cP	PMgBr[c]	PP[c]	I_G[c]	I_D[c]	H[c]	V_I	Δ_I
1.00DEE	0.194	91 (88)	9 (9)	3 (3)	21 (22)	1.1 (1.3)	25.0	8.26
0.91DEE/DBE	0.212	90 (88)	9 (10)	4 (3)	23 (22)	1.1 (1.1)	19.6	7.19
0.62DEE/DBE	0.279	88 (92)	12 (6)	7 (7)	30 (30)	1.2 (1.2)	7.90	4.40
0.33DEE/DBE	0.369	89 (91)	11 (7)	8 (10)	35 (34)	1.2 (1.2)	5.54	4.21
0.21DEE/DBE	0.412	80 (92)	19 (6)	13 (15)	38 (35)	1.3 (1.2)	3.32	2.09
1.00DBE	0.506	82 (92)	17 (7)	15 (20)	43 (41)	1.3 (1.4)	2.15	2.00
1.00THF	0.389	96 (88)	4 (4)	3 (3)	31 (32)	1.1 (1.0)	15.0	12.7
0.56THF/DEE	0.286	94 (91)	6 (4)	4 (3)	31 (29)	1.1 (1.1)	11.5	8.63
0.36THF/DBE	0.461	92 (94)	8 (4)	9 (9)	42 (39)	1.1 (1.0)	3.39	4.63
1.00DBE	0.506	82 (92)	17 (7)	15 (20)	43 (41)	1.3 (1.4)	2.15	2.00

[a] See relevant notes to Tables I–III. Calculations are subjective "best" fits. Experimental values are from Bodewitz et al.[6d] [b] Mole fraction of first solvent listed in a mixture with the second. [c] First number is the calculated value; number in parentheses is the experimental value.

"best" values of Δ_I decrease from 10 in 100% THF to 1.7 in 13% THF. The results are given in Table IV.

All of the trends found experimentally are reproduced and the agreement of absolute values is good in most cases, the worst being for the most nonpolar solvent mixtures, where the calculations underestimate QMgBr and overestimate PP. It appears that this type of deviation should be associated with low solvent polarity not necessarily with high viscosity (compare DBE and DPE, Table III, calculation 2). Again, the variation in Δ_I (and therefore b) is not very large, less than a factor of 10.

Other Solvents. Bodewitz et al. also investigated DEE/DBE, THF/DEE, and THF/DBE mixtures. Calculations are compared with experimental data in Table V. Here the calculations are subjective "best fit" calculations (type 2 of Table III) in which more weight is given to fitting the fractions of isomerization (I_G and I_D) than to absolute yields of Grignard reagents and dimers.

The calculated and experimental results both follow the trends that were described earlier. Comparison of reactions in solvent with similar viscosities but differing polarities again reveals that Δ_I is larger in more polar solvents. For example, compare 0.36THF/DBE with 0.21DEE/DBE and 1.00THF with 0.33DEE/DBE.

Other Primary Alkyl Bromides—Variation in k_I. For a D model with an isomerizing radical intermediate but without byproducts, Garst, Deutch, and Whitesides showed that log [(QMX)/(RMgX)] = $^1/_2$ log k_I + constant.[4] This equation applies when solvent reaction is negligible and RX is sufficiently dilute, so that radical coupling is also negligible. The present work allows a treatment for reactions of concentrated alkyl halides, where radical coupling is not negligible.

The D model without byproducts involves three parameters, δ, k_I, and D. When byproducts are included, three additional parameters are introduced, v, k_S, and k_C. The value of v is proportional to the concentration of RBr.[6a] Bodewitz et al. used ~2.1 M 5-hexenyl bromide,[7d] Ashby and Pham used 0.1 M norbornenylethyl bromide,[24] and Patel et al. used ~0.25 M cyclopropylmethyl bromide.[25]

The solid line in Figure 3 is calculated for v = 1.00 × 10^{-5} mol cm^{-2} s^{-1}, corresponding to an initial RBr concentration of ~1 M on the basis of the data of Rogers et al. (eq 12 and a = 1.4 × 10^{-2} cm s^{-1}, and the effective [RBr] taken as 0.7 of the initial value).[6a] The slope approaches $^1/_2$ for large values of k_I. The straight dashed line is the original fitted line of slope $^1/_2$ found by Garst et al.[4]

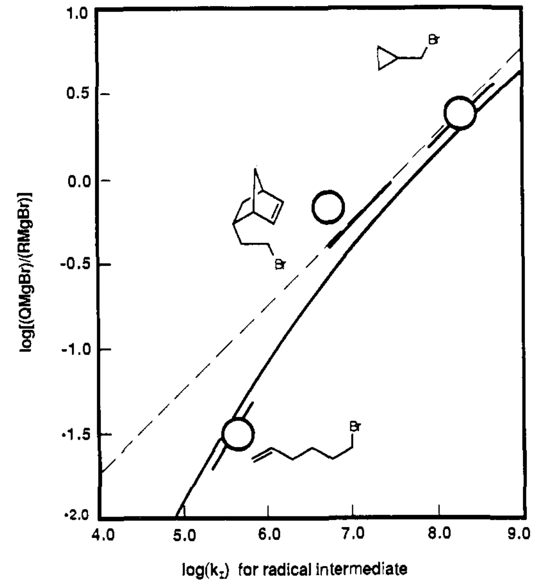

Figure 3. Isomerzation during Grignard reagent preparation from three alkyl bromides. (QMgBr) and (RMgBr) are yields of isomerized and nonisomerized Grignard reagents; k_I is the rate constant for isomerization of the alkyl radical that would be formed by loss of Br• from the alkyl bromide. The long solid curve is calculated for a 1.0 M solution of RBr, as described in the text. Shorter line segments are calculated for the actual initial concentrations of the experiments. Sources of the data and methods of calculation are given in the text. The value of k_I for norbornenylethyl at 40 °C is estimated from that given in ref 24 for 65 °C by assuming a reasonable activation energy (5.2 kcal/mol). Although ref 24 indicates that the Grignard reagent preparation was performed at 65 °C, it is assumed that the actual reaction temperature was near 40 °C (pure DEE bp = 34.5 °C).

Also plotted in Figure 3 are data for the alkyl bromides considered by Garst et al.[4] Values of k_I (40 °C) are taken from Chatgilialoglu, Ingold, and Scaiano (5-hexenyl: 4.4 × 10^5 s^{-1}),[14] Ashby and Pham (norbornenylethyl: 1 × 10^7 at 65 °C, estimated 5 × 10^6 s^{-1} at 40 °C),[24] and Newcomb and Glenn (cyclopropylmethyl: 1.7×10^8 s^{-1}).[26] The short line segments in Figure 3 represent calculations for the RBr concentrations that were used in the experiments; v is adjusted proportionally to [RBr] (eq 12 and paragraph above).

The values of D, δ, k_S, and k_C are the same as for our other calculations for DEE. The only adjusted parameter in these calculations is δ, which is maintained as 1×10^{-2} Å^{-1} for all calculations for DEE in the present work.

The excellent agreement of calculation and experiment for varying k_I adds substantial support to the D model.

Related Data. Ashby and Oswald have recently studied Grignard reagent formation from 5-hexenyl bromide and other alkyl halides mostly in THF at 22 °C with sonication, which was found to have little influence on the product distribution.[27] Their data are similar to those of Bodewitz et al. that we treat above.[7d] In THF at 22 °C, Ashby and Oswald find P_2 distributions with H values (eq 13) between 0.70 and 1.20, similar to predictions of the D model and less than the value of 2.0 predicted for a homogeneous solution or surface reaction. They found that intermediate radicals are trapped by dicyclohexylphosphine (DCPH), but the trapping efficiency is less than that reported for a more reactive trap, a nitroxyl radical.[6e] Ashby and Oswald also find, as expected for either adsorption or diffusion models, that alkyl dimer yields decrease with decreasing concentration of alkyl bromide.

Except for some results suggesting that there is more hydrogen atom abstraction by intermediate radicals than is calculated by assuming that the solvent is the only hydrogen donor, all of the data of Ashby and Oswald appear to be consistent with the D model. Perhaps the solvent is not the only hydrogen donor.

Methyl Bromide. Nuzzo and Dubois have studied the reaction of methyl bromide with magnesium single crystals.[28] CH_3Br is both physisorbed and dissociatively chemisorbed at −150 °C. Although near-monolayer quantities of Br are deposited on the surface, no C is detected there. No evidence of the formation of any product with a stable C–Mg bond was found. The results are not altered by coadsorption with dimethyl ether or by varying the temperature.

The thin multilayer ice of chemisorbed Br, methyl bromide, dimethyl ether, and reaction products desorbs at −130 °C. Nuzzo and Dubois suggest that the barrier to Grignard reagent formation from chemi- or physisorbed $^\bullet CH_3$ is greater than that for desorption of the multilayer.[28]

These results are consistent with the D model. Methyl radicals formed in the initial step get trapped in the multilayer ice or escape into the gas phase. In either event, they reach the surface only a few times for possible reaction to form Grignard reagent. Grignard reagent formation may be inhibited as well by the low temperature required for multilayer adsorption.

Analogous results (no direct formation of C–Mg) have been reported for matrix isolation reactions of magnesium atoms and clusters with methyl bromide.[29,30]

Bromoadamantanes. Reactions of bromoadamantanes, which are atypical, offer evidence that intermediate radicals diffuse in solution instead of remaining adsorbed at the magnesium surface. Stirred reactions of 1- and 2-bromoadamantanes fail to give Grignard reagents. Dubois and co-workers found that under "static" conditions (no stirring, very slow boil) Grignard reagents form in ~60% yields.[11] If the intermediates remained adsorbed, stirring could have no effect, since stirring does not disturb the layer of medium in contact with the surface.[31]

CIDNP and "$R^\bullet$ $^\bullet$MgX". One mechanistic detail that is not explicit in the D model concerns the initial step. What, other than $R^\bullet$, is formed?

Stoichiometry demands that $R^\bullet$ and "$^\bullet$MgX" be formed together from RX and Mg. One may think of "$^\bullet$MgX" as an ordinary species. However, no CIDNP resulting from [$R^\bullet$ $^\bullet$MgX] pairs is found; CIDNP results only from [$R^\bullet$ $R^\bullet$] pairs.[7b–e,g,h] Why?

Although Bickelhaupt and co-workers offered several other possible explanations,[7h] the simplest is that the initial step does not produce a literal $^\bullet$MgX species or any other that can generate CIDNP. A gross view of this step may be more realistic than the hypothesis of [$R^\bullet$ $^\bullet$MgX] formation. In the gross view, the metal is simply a source of electrons. Some metallic electrons are relatively loosely bound and highly delocalized. Some are unpaired at thermal equilibrium. Electron loss from the metal results in charge but not in any notable change in electronic spin character of the magnesium. Any additional unpaired electrons that might result from electron transfer may be as delocalized as before and they may pair with unpaired electrons that were already present. Similar remarks would apply if the initial reaction were described as covalent bond formation between Mg and X (of RX).

In any event, it is unlikely that the electronic spin state of the metal (even with adsorbed X^- or bound X) is a barrier to its reaction with a free radical $R^\bullet$, since there will always be unpaired electrons in the metal that can be made available for reaction. In the absence of an electronic spin barrier, there can be no nuclear spin selection and no CIDNP.

Other Mechanistic Details. As given here, the D model is skeletal. Possible intermediates between RX and $R^\bullet$ and possible parallel pathways are omitted deliberately in order to test the simplest theory. At present, there appears to be no indication that anything else is required for simple alkyl halides.

Also omitted are details of the steps through which $R^\bullet$ is converted to RMgX. We assume that they have no bearing on the kinetics that we treat.

The simplest picture is that there is bond formation (ionic, partially ionic, or covalent) between $R^\bullet$ and magnesium surface. Surface "X" and "R" can come to adjacent positions, associate with a particular Mg atom, and depart (probably with the assistance of specific solvation by ether molecules) into solution. There are many other possible scenarios.

Predictive Competence of Diffusion and Adsorption Models. The D model has sufficient predictive competence to allow it to be tested against experimental results. If calculation and experiment had disagreed, the present form of the D model would have been disproved (falsified).

A theory that lacks sufficient predictive competence to be falsifiable also lacks sufficient predictive competence to be useful. A useless theory has no value to science, regardless of how plausible or esthetically pleasing it may be.

Adsorption models are weak in predictive competence, and therefore in falsifiability and usefulness, because the properties of adsorbed alkyl radicals and other possible transient intermediates are unknown. One can invoke whatever may be needed in order to mold an adsorption model into consistency with experimental data. For example, this allowed Molle et al. to invoke adsorbed radical-pair intermediates that must have very long lifetimes.[11c]

The predictive incompetence of adsorption models diminishes the usefulness of a correct theory and makes it hard to disprove an incorrect one. In principle, the situation could change as more information is developed.

However, the greater predictive competence of diffusion models at present implies that we should hope for their success. The present study is very encouraging.

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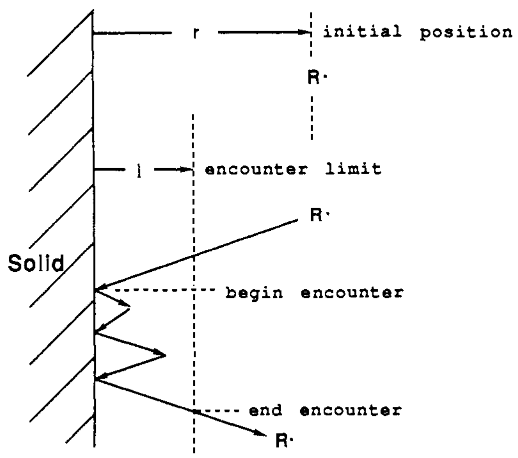

Figure 4. Molecular pair treatment of radical–surface reaction. The radical R• is initially at a distance *r* from the surface. An encounter begins when the radical crosses the plane at the encounter distance *l* and strikes the surface for the first time subsequent to that crossing. The encounter ends when the radical reacts at the surface or diffuses to the plane *l* for the first time after the encounter began.

It should be noted that a D model in which intermediate alkyl radicals linger for a short time in an adsorbed state at the magnesium cannot be distinguished kinetically from the D model described and treated here, provided that the adsorbed radicals do nothing significant other than react to form Grignard reagent or desorb. Nothing in the present work militates against this possible role of adsorption.

Idealizations and Uncertainties in the Present D-Model Calculations. There are several limitations and possible sources of error in the D-model calculations.

First, our treatment is limited to cases in which parallel processes of different intermediate radicals are described by the same parameters. This will require modification when reactivities of intermediate radicals differ. In the present application, 5-hexenyl and cyclopentylmethyl are so similar, both being primary alkyl radicals, that the assumption is reasonable.

Second, we neglect the effects of stirring and boiling. This may be adequate for systems involving such reactive intermediates as primary alkyl radicals, a very high fraction of which suffer reactions within a few thousand Ångstrom units of the magnesium surface. The relevant time and space scales may then be small enough that stirring has negligible impact. For less reactive radicals, the effects of stirring may be more pronounced.

Third, events at and very near the surface on very short time and space scales may not be well described by diffusion equations, which neglect the granularity (molecularity) of matter.

Fourth, we have treated the magnesium surface as if it were uniform. However, reactions may occur preferably at certain places on the surface where there are special features such as adsorbed or bonded halogen atoms, or other species, or crystal or surface imperfections of various types. If the reactive spots on the surface are dense, then the assumption of uniformity is probably better than it would be if they were sparse.

The success of the idealized D model suggests that these potential flaws are less significant than they might have been.

Summary. The excellent agreement between D-model calculations and experimental data on Grignard reagent formation strongly supports the D model and shows that quantitative kinetic treatments of heterogeneous organic reactions are possible.

The following points are especially noteworthy.

(1) The extent of isomerization in the Grignard reagent is always less than that in the alkyl dimer. If both PMgBr and P_2 were drawn from the same steady-state pool of radicals P• adsorbed at the surface, then the extents of isomerization in the two products would have been the same. The D-model calculations reproduce the observed trend and in some solvents, notably in DEE and THF, the observed extents of isomerzation in both products.

(2) The value of homogeneity quotient *H* would be 2.0 if radicals R• and Q• were coupling at steady-state concentrations that were homogeneous in either two or three dimensions. Experiments give values nearer to 1.0. D-model calculations reproduce the experimental values closely in every case.

(3) Decreasing solvent polarity at nearly constant viscosity (THF/benzene mixtures) is found experimentally to give (a) decreasing yields of PMgBr, (b) increasing yields of QMgBr, (c) increasing yields of PP, and (d) nearly constant distributions of PP among RR, RQ, and QQ. Each of these trends is reproduced by correcting the effective reaction flux V_{I0} for (slight) viscosity changes and invoking a decreasing reactivity of the magnesium surface toward alkyl radicals (Table IV).

(4) When both solvent viscosity and polarity are changed, the data are best fit by calculations with scaled reaction fluxes V_I that decrease with increased viscosity and scaled surface reactivities Δ_I that decrease with decreasing polarity. These are rational and consistent effects.

(5) For parameters that are all taken or estimated from independent experiments, D-model calculations fit all of the experimental data within the reported experimental precision for solvent DEE. Similar parameters give a similar fit for THF.

(6) D-model calculations agree satisfactorily with experimental results on the extents of isomerization in Grignard reagents derived from three primary alkyl bromides that result in isomerizing alkyl radical intermediates. The k_I values span nearly 3 orders of magnitude (4.4×10^5–1.7×10^8 s^{-1}).

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Appendix

Diffusion and Reaction with Solvent. During a typical Grignard reagent preparation, there is very little reaction of intermediate alkyl radicals with the solvent. We consider the competition between reactions of intermediate radicals at the surface (forming Grignard reagent) and with the solvent (forming RH), neglecting radical coupling (which is insignificant in reactions of dilute solutions of RX).

First, we address the question, "What is the probability ϕ_r that a radical at a distance *r* from a perfectly reactive surface will diffuse to the surface instead of reacting with the solvent?" We treat diffusion as a one-dimensional random walk; only movement perpendicular to the surface (planar, infinite extent) is of consequence.

If a radical starts at a distance *r* from a perfectly absorbing barrier (perfectly reactive surface), the probability $p(r,t)$ of arrival at the barrier between times *t* and $t + dt$ is given by eq A1, where

$$p(r,t)dt = [r/(4\pi D)^{1/2}]t^{-3/2} \exp(-r^2/4Dt)dt \qquad (A1)$$

D is the diffusion coefficient.[32] Since the probability that the radical has survived to time *t* is $\exp(-k_S t)$ (first-order rate law for solvent reaction), the joint probability of survival and arrival at the barrier is $p(r,t) \exp(-k_S t)dt$; ϕ_r results from integrating this over all time. Since $\int_0^\infty \exp(-a/t) \exp(-bt)t^{-3/2}dt$ is $(\pi/a)^{1/2} \exp[-2(ab)^{1/2}]$, ϕ_r is given by eq A2. By analogy with "time constant", σ may be called the "space constant".

$$\phi_r = e^{-r/\sigma} \qquad \sigma = (D/k_S)^{1/2} \qquad (A2)$$

All we need to calculate ϕ_r for a particular initial distance *r* is the appropriate space constant σ, which in turn requires values of *D* and k_S. Newcomb and Kaplan recently obtained a k_S value of 1×10^3 s^{-1} for the reaction of the octyl radical with solvent DEE at 22 °C.[19] Diffusion coefficients do not vary much for small molecules in fluid solvents; we choose a typical value of *D*, 3×10^{-5} cm^2 s^{-1} (3×10^{11} Å^2 s^{-1}). By using these values of k_S and *D*, the space constant σ is ~17,000 Å.

Consequently, if an octyl radical is at a distance *r* of 17 000 Å from a planar surface, the probability ϕ_r that it will diffuse to that surface before reacting with solvent is e^{-1}, or 0.4. The escape

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probability is only 0.6. If the reactivity at the surface were infinite, then the yields surface and solvent reaction products would be 40% and 60%, respectively. Stated another way, an octyl radical in DEE at a distance 17 000 Å from a perfectly reactive surface has only a 60% "escape" probability.

Actually, no surface can be perfectly reactive. We now derive the probability A_r that a radical at a distance r from a less than perfectly reactive surface will react at the surface instead of reacting with the solvent. We use a modified version of Noyes' molecular-pair method.[33]

Let an "encounter" with the reactive surface begin when a radical diffuses to the surface. Let it end when the radical thereafter first reaches an arbitrarily chosen distance l from the surface (Figure 4) or when the radical reacts, either at the surface or with the solvent, before reaching the distance l. Let α and ϵ, respectively, be the probabilities of surface and solvent reactions during an encounter. Then the probability that a radical will escape intact from an encounter is $1 - (\alpha + \epsilon)$.

Since radicals at distances r and l from the surface have probabilities ϕ_r and ϕ_l of surviving until they reach the surface for the first time, the total probability A_r of the surface reaction is given by eq A3 and A4. If ϵ is much smaller than $1 - \alpha$, which

$$A_r = \phi_r\alpha + \phi_r(1 - \alpha - \epsilon)\phi_l\alpha + \phi_r(1 - \alpha - \epsilon)\phi_l(1 - \alpha - \epsilon)\phi_l\alpha + ... \quad (A3)$$

$$A_r = \alpha\phi_r/[1 - (1 - \alpha - \epsilon)\phi_l] \quad (A4)$$

will be the case for all except the largest possible k_S and α values, then it can be neglected. Since l is arbitrary, we can let it be small. As l becomes small, so does α, but the ratio α/l may approach a finite limiting value. At the same time, ϕ_l approaches $1 - l/\sigma$. Then A_r is given by eq A5, where δ is the limit of α/l as $l \rightarrow 0$.

$$A_r = \delta\sigma\phi_r/(1 + \delta\sigma) \qquad (\text{if } \alpha \rightarrow 0 \text{ and } \alpha/l \rightarrow \delta \text{ as } l \rightarrow 0) \quad (A5)$$

The same equation can be derived through a diffusion-equation treatment in which δ is the proportionality constant of the radiation boundary condition (see Appendix of the preceding paper, eq A5–A7 there).[1,4,17]

For Grignard reagent formation from primary alkyl halides in solvents such as DEE and THF, δ appears to be $\sim 10^{-2}$ Å^{-1} (see above). If σ is 17 000 Å, then $\delta\sigma$ is 170 and $1 + \delta\sigma$ is 171, so that A_r is $(170/171)\phi_r$. Thus, a radical in DEE that is initially 17 000 Å from the surface has very nearly the same probability, 0.4, of reacting at the surface instead of with the solvent whether the surface approaches perfect reactivity (δ approaching infinity) or considerably less ($\delta = 10^{-2}$ Å^{-1}).

On reflection, the reason is clear: a δ value of 10^{-2} Å^{-1} is large enough to guarantee that nearly every radical that reaches the surface reacts there instead of with the solvent. In eq A5, the factor $\delta\sigma/(1 + \delta\sigma)$ is the probability A_0 that a freely diffusing radical that is initially at the surface will react with the surface instead of the solvent. As long as δ and σ are such that A_0 is near unity, then A_r will be nearly the same for all values of δ, namely, ϕ_r.

For a radical that is initially at the surface to have a 50% probability of escaping surface reaction, $\delta\sigma$ must be unity. If δ is 10^{-2} Å^{-1}, then k_S has to be 3×10^7 s^{-1}, ~30 000 times the actual values of k_S for primary alkyl radicals in DEE at 22 °C. Alternatively, if k_S is 1×10^3 s^{-1}, then δ has to be $1/\sigma$ or 6×10^{-5} Å^{-1}, ~1/170th of that found.

Thus, freely diffusing radicals formed at a sufficiently reactive surface will undergo surface reaction instead of reaction with solvent, even though their diffusive excursions may take them many, even thousands of, Ångstrom units away from the surface.

Registry No. Mg, 7439-95-4; 5-hexenyl bromide, 2695-47-8.

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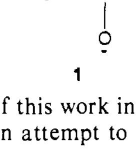
Organoiodinane Reagents for Phosphate Cleavage: Experimental and Computational Studies[†]

Robert A. Moss,* Bogusława Wilk, Karsten Krogh-Jespersen,* John T. Blair, and John D. Westbrook

Contribution from the Wright and Rieman Laboratories, Department of Chemistry, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903. *Received June 3, 1988*

Abstract: Several analogues of 1-oxido-1,2-benziodoxol-3(1*H*)-one, **1** (the valence tautomer of *o*-iodosobenzoate), were examined for their ability to cleave *p*-nitrophenyl diphenyl phosphate in aqueous micellar cetyltrimethylammonium chloride at pH 8. These included the 5,5-dimethyl (**7**) and 5,5-bis(trifluoromethyl) (**8**) analogues, as well as the parent 1-oxidoiodoxol-(3*H*)-ones **9** and **10**. The kinetic reactivity order was **1** > **9** > **10** > **8** ≫ **7**. The results are discussed in terms of the relative acidities shown by the I–OH forms of the catalysts and the nucleophilicities of their I–O$^-$ conjugate bases. Ab initio molecular orbital calculations were performed on **10**, its conjugate acid (**10**-OH), the desoxo analogues (**11**, **11**-OH), and their dimethyl (**12**, **12**-OH) and bis(trifluoromethyl) (**13**, **13**-OH) derivatives to aid this analysis. The electronic structures of these species are discussed in detail.

o-Iodosobenzoate, in its preferred, valence tautomeric, 1-oxido-1,2-benziodoxol-3(1*H*)-one form (**1**), is a potent α-effect O-nucleophile.[1] When solubilized in cationic micellar solution, **1** and its simple derivatives prove to be excellent catalysts for the cleavage of reactive, toxic phosphates.[2-4] More recently, the catalytic properties of **1** have been studied in microemulsions[5] and in nematic lyotropic liquid crystals.[6]



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A natural extension of this work involves the examination of close relatives of **1**, in an attempt to find an even more potent

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[†] Dedicated to the memory of Professor Emil Thomas Kaiser.