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THE CONSTITUTION OF THE GRIGNARD REAGENT

X *. COMPLEXES OF SOME ORGANOMAGNESIUM COMPOUNDS WITH AN ELECTRON DONOR IN BENZENE

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Summary

Measurements of association of RMgBr (R = Me, Et, i-Bu) with one (or slightly more than one) equivalent of an electron donor E (E = Et_3N, Et_2O or THF) revealed that the complexes formed were partly dimeric. Further addition of E causes a decrease in the degree of association.

Equilibrium constants were calculated, assuming that the conversion from dimer to monomer (and vice versa) proceeds via two equilibria: a dimer containing two molecules of E (dim(2)) gives a dimer containing three molecules of E (dim(3)) which gives a monomer with two ligands E (mon(2)). Dim(3) probably exists in appreciable amounts only if most of the ligands are relatively small (R = Me, Et and E = THF).

The Et_2Mg/Et_2O complex in benzene, studied in the same way, was found to be partly tetrameric at low Et_2O/Et_2Mg ratios. At higher Et_2O concentrations dimeric and monomeric species are present and the relevant equilibrium constants are calculated. The most probable equilibria involve a tetramer with two molecules of E (tetra(2)) in equilibrium with dim(2) which is in equilibrium with mon(2).

Introduction

Ever since the discovery of Grignard reagents attempts have been made to prepare Grignard reagents in hydrocarbon solvents [1—6]. In spite of the many studies on the use of non-basic solvents in Grignard chemistry, relatively little is known about the structure of organomagnesium compounds in such solvents.

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[*] Part IX, see ref. 18.

It was found [5,7] that "Grignard compounds" could be made in good yields in pure hydrocarbons from an alkyl halide and magnesium. In all cases, a precipitate is formed, and the species in solution always contains far more alkyl groups R than halide X, indicating that the predominating species in solution are $(R_2Mg)_n$ and/or $(R_2Mg)_n \cdot RMgX$.

Most of the physicochemical studies have been performed with pure dialkylmagnesium compounds (R_2Mg). Thus di-n-pentylmagnesium [8] and di-sec-butylmagnesium in cyclopentane [9] are dimeric in benzene, and dicyclopentadienylmagnesium is monomeric in benzene [10].

More work has been performed on solutions of organomagnesium species in hydrocarbons containing equivalent amounts (or more) of electron-donating compounds as complexing agents. R_2Mg complexes appear to exist as monomers, or dimers, or an equilibrium mixture of both, depending on the basicity and concentration of the electron donor [11—15].

Ducom calculated equilibrium constants from NMR data for dimer—monomer equilibria of diethylmagnesium (Et_2Mg) in benzene with dimethoxyethane (DME), tetrahydrofuran (THF) and diethyl ether (Et_2O) [12]. In the last case (Et_2O) especially the assumption of only a dimer—monomer equilibrium may be in error; we have found (vide infra) that Et_2Mg eith Et_2O in benzene is partly tetrameric at low Et_2O concentrations.

Only two studies have been published dealing with the structure of organomagnesium halides (RMgX) in hydrocarbons in the presence of electron donors (in pure hydrocarbons a precipitate of MgX_2 is always formed). Coates and Heslop crystallized $(t\text{-}BuMgCl \cdot Et_2O)_2$ from hexane, and found that it dissolves in benzene as a dimer [11]. Vink et al. studied EtMgBr with (+)(*S*)-1-ethoxy-2-methylbutane (S) in benzene [12]. The following equilibria were thought to exist:

$$(EtMgBr \cdot S)_2 + S \overset{K_I}{\rightleftharpoons} (EtMgBr \cdot S)_2S$$

$$(EtMgBr \cdot S)_2S + S \overset{K_{II}}{\rightleftharpoons} 2\ EtMgBr \cdot 2S$$

However, as an incorrect relation between the equilibrium constants was used in the calculations, their conclusion that $(EtMgBr \cdot S)_2S$ was the predominant species was not justified. On the basis of the hypothesis presented in this work it seems likely that $(EtMgBr \cdot S)_2S$ is present only in minor amounts.

The present investigation is intended to extend knowledge of the structure of organomagnesium compounds in the presence of electron donors in benzene.

Results and discussion

Organomagnesium halides (RMgX) in the presence of an electron donor (E) in benzene

To a solution of ethylmagnesium bromide (EtMgBr) in benzene containing approximately one equivalent of a basic solvent E (E = diisopropyl ether ($i\text{-}Pr_2O$), triethylamine (Et_3N), diethyl ether (Et_2O) or tetrahydrofuran (THF) known amounts of E were added in small portions, and the degree of association i (= formal concentration/osmotic concentration = $[Mg]_f/[\text{particles}]$) was determined as a function of E (the method used is described in the experimental part). The results are shown in Fig. 1 (Tables 7, 8 and 9).

Similarly the degree of association of isobutylmagnesium bromide (i-BuMgBr) and of methylmagnesium bromide (MeMgBr) in benzene were determined as a function of the concentration of THF. The results are given in Tables 11 and 12.

The measurements with E = i-Pr_2O could not be performed because upon dilution of a 0.3 M solution of $(EtMgBr \cdot i\text{-}Pr_2O)_n$ in benzene to about 0.03 M a white flocculent precipitate was formed, apparently because the weakly bound i-Pr_2O was removed from the complex to give a less solvated oligomeric "EtMgBr" which is insoluble. However, it is very likely that $(EtMgBr \cdot i\text{-}Pr_2O)_n$ is dimeric in benzene in view of the results with other bases E and the fact that EtMgBr is a dimer in pure i-Pr_2O [17].

EtMgBr with one equivalent of Et_2O and Et_3N is a dimer in benzene; since it is very difficult to control the exact ratio of the components, we did not actually obtain a solution of EtMgBr with one equivalent of THF, but extrapolation to EtMgBr/THF = 1 makes it probable that the same is true in this case. Upon addition of an excess of E the degree of association decreased, indicating the existence of a monomer—dimer equilibrium. This can be represented either by eq. 1 and 2 or by eq. 3, where dim(2) and dim(3) are dimers containing two or

$$\text{dim}(2) + \text{E} \overset{K_{I}}{\rightleftharpoons} \text{dim}(3) \qquad (1)$$

$$\text{dim}(3) + \text{E} \overset{K_{II}}{\rightleftharpoons} 2\,\text{mon}(2) \qquad (2)$$

$$\text{dim}(2) + 2\text{E} \overset{K}{\rightleftharpoons} 2\,\text{mon}(2) \qquad (3)$$

three molecules of E ($(EtMgBr \cdot E)_2$ and $(EtMgBr \cdot E)_2E$, respectively) and mon(2) is the monomer containing 2 E ($EtMgBr \cdot 2\,E$).

When dim(3) is not present to a significant extent, only the overall equilibrium

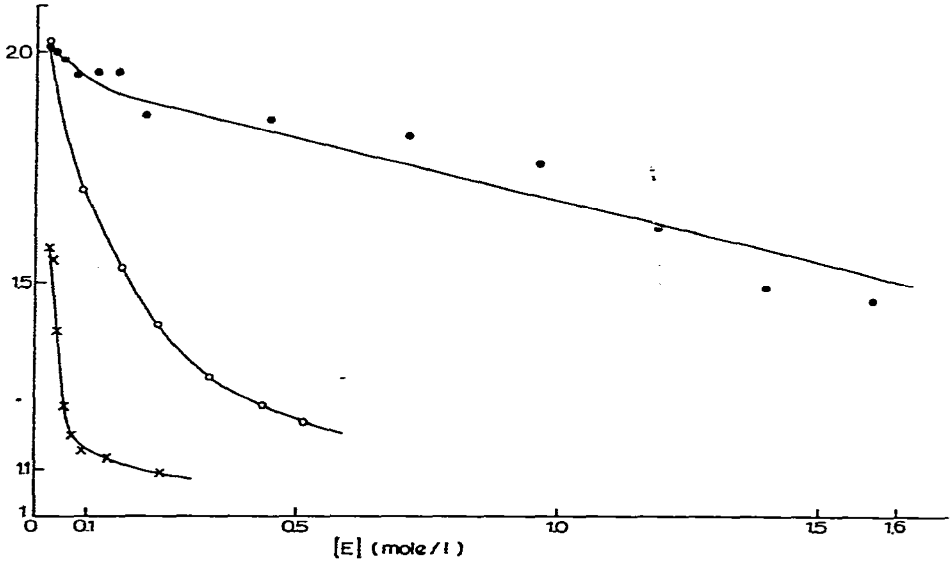


Fig. 1. Degree of association of EtMgBr in benzene at varying concentrations of E. ○ E = Et_2O, [EtMgBr] = 0.0150 M (starting concentration)—0.0143 M (final concentration) × E = THF, [EtMgBr] = 0.0199—0.0196 M; ● E = Et_3N, [EtMgBr] = 0.0235—0.0182 M.

constant $K = [\text{mon}(2)]^2/[\text{dim}(2)][E_{\text{free}}]^2$ is relevant. When dim(3) is the predominant species $K_{II} = [\text{mon}(2)]^2/[\text{dim}(3)][E_{\text{free}}]$ may be found. The results of calculations, based on both assumptions are given in Tables 1 and 2. Because association measurements do not discriminate between the two possible dimers, equilibrium 1 cannot be obtained by this method, and thus the separate calculation of K_I cannot be performed.

The features of the results are:

a. The dimers are relatively stable: several equivalents of electron donor E are required to replace the halogen bridging bonds (bridging via the alkyl group is not very likely in view of the crystal structures of $(EtMgBr \cdot i\text{-}Pr_2O)_2$ [18] and $(EtMgBr \cdot Et_3N)_2$ [19] by the Mg—O or Mg—N coordinating bonds.

b. The errors found in the equilibrium constants calculated are relatively large. This will in part be due to the fact that in the calculations either K or K_{II} is obtained, not both K_I and K_{II}. As it may be expected that both equilibria play a rôle in the transition from the dimer to the monomer, this may cause systematic errors. Furthermore in the case of Et_3N the measurements were relatively inaccurate, as can be seen from the calibration curve for benzene/Et_3N-mixtures (Table 5). With this restriction it can be concluded that when bulky ligands are involved (Et_3N, Et_2O; i-Bu), the standard deviation of the overall equilibrium constant K is smaller than that for K_{II}, indicating that in those cases dim(3) is probably an important component.

To account for these observations requires a detailed knowledge of the structure of the species involved. In Scheme 1 the most probable structures are depicted.

Dim(2) may be a dimer with two halogen bridges, in accord with the crystal structure of $(EtMgBr \cdot i\text{-}Pr_2O)_2$ [18]. The structure of monomer RMgBr. 2E can be inferred from, e.g., the crystal structure of $EtMgBr \cdot 2Et_2O$ [20]. The situation in dim(3) may roughly be the same as in mon(2); the Mg—Br—Mg angle may be expected to be ~130° (cf. calculations of Wild [21] for the H—F—H angle in H_2F^+). It is not very likely that E (even if it is THF) could be in a bridging position as found by Wade [22] for $(Ph_2C{=}NMgBr \cdot THF)_2THF$ in the solid state. In fact, Wade found that one of the THF molecules, presumably that loosely bound in the bridging position, separated from the dimer upon dissolution in benzene.

It can be seen from Scheme 1, that dim(3) may be the less favourable structure from a steric point of view, especially when the ligands E (or R) have large steric requirements. Front strain between groups on the two different Mg atoms and back strain between groups on the same Mg atom (in particular if large

TABLE 1

EQUILIBRIUM CONSTANTS FOR THE DIMER—MONOMER EQUILIBRIUM OF EtMgBr IN BENZENE WITH Et_3N, Et_2O AND THF AT 28°C

E	$K \pm \sigma$ (l/mol) [a]	$\frac{\sigma}{K} \times 100$	$K_{II} \pm \sigma$	$\frac{\sigma}{K_{II}} \times 100$
Et_3N	$(2.5 \pm 1.9) \times 10^{-3}$	76	$(1.8 \pm 1.8) \times 10^{-3}$	100
Et_2O	$(1.7 \pm 0.2) \times 10^{-1}$	12	$(3.3 \pm 2.6) \times 10^{-2}$	79
THF	82 ± 71	86	2.1 ± 0.7	33

[a] σ = standard deviation of the mean.

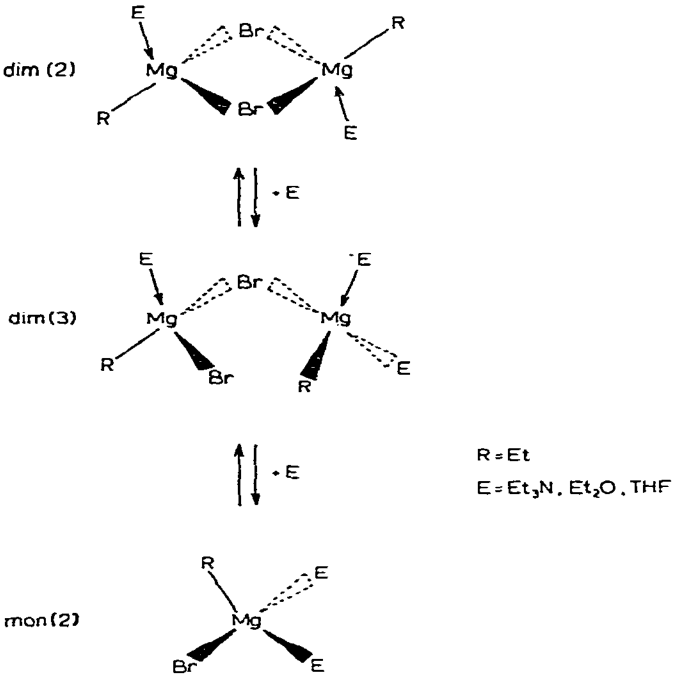
TABLE 2

EQUILIBRIUM CONSTANTS FOR THE DIMER-MONOMER EQUILIBRIUM OF RMgBr IN BENZENE WITH THF at 28°C

R	$K \pm \sigma$ (l/mol) [a]	$\frac{\sigma}{K} \times 100$	$K_{II} \pm \sigma$	$\frac{\sigma}{K_{II}} \times 100$
Me	16 ± 6	38	0.85 ± 0.20	24
Et	82 ± 71	86	2.1 ± 0.7	33
i-Bu	83 ± 37	45	1.9 ± 1.1	58

[a] σ = standard deviation of the mean.

SCHEME 1



ligands interfere with each other) could diminish the stability of dim(3) relative to dim(2).

c. In the series Et_3N, Et_2O, THF, the monomer persists at decreasing ratios [E]/[RMgBr]; as it is well known that a stronger base favours species of lower degree of association, it can be concluded that the order of basicity is THF > Et_2O > Et_3N. This is in agreement with the results of Ducom [23] (who used Et_2Mg as the Lewis acid) but not those of Vink [24], who found the basicity order THF > Et_3N > Et_2O. Thus it is clear that "basicity" is very much dependent upon the reference system and the method of determination. Recent determination of the heat of solution of Et_2Mg in Et_2O and Et_3N indicate that by this measure (which is the only well defined one) the difference of basicity between the two bases is quite small [25].

Diethylmagnesium (Et_2Mg) with Et_2O in benzene

To a solution of Et_2Mg in benzene containing a small amount of Et_2O, more

Et_2O was added in portions and the degree of association (i) determined as a function of the Et_2O concentration. The results are given in Table 10. At low Et_2O concentrations i was greater than two, and diminished at higher Et_2O concentrations.

As for RMgBr in the region $i < 1.9$, either the overall equilibrium constant K, or K_{II} (eq. 1—3) can be calculated (Table 3A). In agreement with the hypothesis presented for RMgBr, K shows the smaller standard deviation, indicating that an appreciable amount of dimeric species with three Et_2O molecules (dim(3)) is not present. The concentration of Et_2O was relatively high in these experiments (see Table 10) and thus the concentration of free Et_2O does not depend significantly on the number of Et_2O molecules bound per Mg-atom. For simplicity this number was taken to be one.

For $i > 2$, higher oligomers are obviously present. The most likely possibilities are a trimer (tri) or a tetramer (tetra). As the dimer contains two molecules of Et_2O (dim(2)), the tri—dim equilibrium can be represented by eqn. 4, with $n = 2$, 3 or 4 if the two trimers together contain 4, 3 or 2 molecules of Et_2O respectively.

$$2\ \text{tri} + n\ Et_2O \rightleftharpoons 3\ \text{dim}(2) \tag{4}$$

and thus $K_n = [\text{dim}(2)]^3/[\text{tri}]^2\ [Et_2O_{\text{free}}]^n$

For the tetra—dim equilibrium eq. 5 holds, with $n = 1$, 2 or 3 if the tetramer contains 3, 2 or 1 molecule of Et_2O respectively.

$$\text{tetra} + n\ Et_2O \rightleftharpoons 2\ \text{dim}(2) \tag{5}$$

and $K_n = [\text{dim}(2)]^2/[\text{tetra}]\,[Et_2O_{\text{free}}]^n$

The results of these calculations are given in Table 3B. The fit to the experimental data was best for the tetra—dim equilibrium with $n = 2$. This means that the actual equilibrium is probably best represented by eq. 6.

$$\text{tetra}(2) + 2\ Et_2O \rightleftharpoons 2\ \text{dim}(2) \tag{6}$$

Of course, as the standard deviation is large even in this case, no decisive conclu-

TABLE 3

EQUILIBRIUM CONSTANTS AT 28°C FOR DIMER—MONOMER (A) AND OLIGOMER—DIMER (B) EQUILIBRIA OF Et_2Mg WITH Et_2O IN BENZENE

A Dim—mon equilibrium

$K \pm \sigma$ (mol/l)[a]	$\frac{\sigma}{K} \times 100$	$K_{II} \pm \sigma$	$\frac{\sigma}{K_{II}} \times 100$
$(3.3 \pm 0.8) \times 10^{-3}$	26	$(3.4 \pm 2.8) \times 10^{-3}$	82

B Tri—dim equilibrium

n	$K_n \pm \sigma$	$\frac{\sigma}{K_n} \times 100$
2	1.8 ± 2.1	117
3	21 ± 23	109
4	$(3.2 \pm 2.8) \times 10^2$	87

Tetra—dim equilibrium

n	$K_n \pm \sigma$	$\frac{\sigma}{K_n} \times 100$
1	0.15 ± 0.12	80
2	2.7 ± 2.0	74
3	66 ± 75	114

[a] σ = the standard deviation of the mean.

sion can be given. Nevertheless eq. 5 is more probable than eq. 4 because the reaction of two dimers is expected to give at least primarily a tetrameric species; moreover, Voorbergen [17] found a tetramer—dimer equilibrium for Et_2Mg in pure $i\text{-}Pr_2O$.

Finally, the other possible oligomers are either coordinatively unsaturated or contain species in which alkyl bridges have been broken in favour of coordination with Et_2O (except the trimer with two Et_2O molecules; however, in this case ($n = 2$) the standard deviation was the largest found); in view of the predominance of dim(2) over dim(3) this last possibility is not very likely.

The alkyl bridges in the dimer of Et_2Mg in benzene with Et_2O are very stable relative to the Mg—O coordinative bonds; indeed, in benzene the dim—mon equilibrium lies even more on the side of the dimer than for EtMgBr ($K = 3.3 \times 10^{-3}$ and 1.7×10^{-1}, respectively) contrary to the situation in a pure basic solvent such as Et_2O. This apparently contradictory behaviour is not fully understood at the moment. It can be explained, if one assumes that, for both electronic and steric reasons, EtMgBr is less coordinatively saturated in the tetracoordinated state than is Et_2Mg and so EtMgBr needs secondary solvation more than Et_2Mg does. Consequently, EtMgBr is more associated than Et_2Mg in concentrated solutions of Et_2O, where secondary solvation is increasingly impeded; on the other hand benzene can provide secondary solvation to EtMgBr in dilute solutions, thus favouring the monomeric species to a certain extent, while Etg_2Mg is less or not at all susceptible to this effect.

Experimental

All experiments were carried out in a fully closed glass apparatus with rigorous exclusion of oxygen and moisture, using the technique described by Vreugdenhil and Blomberg [26]. The association numbers were determined by measuring the rate of quasi-isothermal distillation of mixtures of benzene with E to a solution of ethylmagnesium compounds in the same solvent mixture, using the apparatus developed by Van Vulpen [27]. A silver wire gauze evaporator, suspended on a thin quartz fibre spiral is wetted with the solvent mixture. Distillation of the solvent from the evaporator to the solution causes loss of weight of the evaporator. The apparent rate of rise of the evaporator, S_a (in mm/h), which is measured with a cathetometer, depends on the number of particles in solution.

The theoretical rate S_{th} (in $\frac{mm/h}{mol/l}$), is obtained by calibrating the apparatus for the solvent mixtures under investigation, with triphenylmethane as the solute, which is assumed to be monomeric in the concentration range studied. The concentration of particles [particles], is obtained by dividing the observed rate of rise of the evaporator (S_a) by the theoretical rate (S_{th}) for this particular solvent mixture. The association number (i) is given by the ratio of the formal concentration of non volatile compound (regarded as monomers) and the particle concentration: $i = [Mg]/[particles]$. To obtain a continuous range of S_{th} values of mixtures of benzene with E, S_{th} was determined at several concentrations of E in benzene (Tables 4—6) and these values were plotted against the concentration of E. S_{th} could thus be found graphically for any concentration of E in benzene.

TABLE 4

CALIBRATION OF BENZENE/Et_2O MIXTURES WITH Ph_3CH AT 28°C

$[Et_2O]$	$[Ph_3CH]$	S_{det} (mm/h)[a]	$S_{th}(\frac{mm/h}{mol/l})$[b]
0	0.0108	0.474	43.7
0.070	0.0108	0.470	43.7
0.147	0.0107	0.461	43.2
0.219	0.0106	0.456	43.0
0.286	0.0105	0.444	42.2
0.360	0.0104	0.439	42.1
0.437	0.0103	0.424	41.0
0.475	0.0072	0.303	42.1
0.555	0.0102	0.410	40.1
0.659	0.0100	0.400	40.0
0.905	0.0069	0.268	39.1
1.297	0.0066	0.255	38.9
1.654	0.0063	0.231	36.8
1.983	0.0060	0.215	35.7
2.285	0.0058	0.208	36.0

[a] The determined rate was compensated for the initial rate which is never exactly zero. [b] S_{th} was obtained by dividing S_{det} by the Ph_3CH concentration.

In the past the "Van Vülpen-apparatus" was only used for solutions in one solvent, but as can be seen (Tables 4—6) the calibration for solvent mixtures gives good results, although they are less accurate than for a single solvent.

It can be seen that the addition of E generally diminishes S_{th}. This can be understood when it is appreciated that a more volatile component E in the apparatus causes a higher vapour pressure, which reduces the rate of vaporization.

The solutions of $(EtMgBr \cdot E)_2$ were prepared in benzene by reaction of EtBr with Mg in the presence of one molar equivalent (or slightly more) of E. This was done at concentrations of approximately 0.3 *M*. Small portions of these solutions were diluted to about 0.02 *M* in the "Van Vulpen-apparatus" and *i* was determined; known amounts of E were added and *i* determined as a function of the concentration of E. The results are given in Tables 7—9.

The solutions of MeMgBr and i-BuMgBr were obtained as follows: MeMgBr (i-BuMgBr) was prepared in THF, the solvent was partly removed under vacuum, and the resulting solid (which still contained ≃2 equivalents THF) was dissolved in benzene.

The solutions of Et_2Mg were hard to obtain because of the low solubility of

TABLE 5

CALIBRATION OF BENZENE/Et_3N MIXTURES WITH Ph_3CH AT 28°C

$[Et_3N]$	$[Ph_3CH]$	S_{det} (mm/h)	$S_{th}(\frac{mm/h}{mol/l})$
0.358	0.0115	0.481	41.8
0.682	0.0110	0.454	41.4
0.977	0.0105	0.424	40.5
1.246	0.0100	0.369	36.8
1.493	0.0096	0.326	32.7
1.719	0.0092	0.281	30.5

TABLE 6

CALIBRATION OF BENZENE/THF MIXTURES WITH Ph_3CH AT 28°C

[THF]	[Ph_3CH]	S_{det} (mm/h)	$S_{th}(\frac{mm/h}{mol/l})$
0.0433	0.00568	0.250	44.0
0.0881	0.00568	0.245	43.1
0.1254	0.00563	0.247	43.9
0.1618	0.00562	0.246	43.8
0.1903	0.00561	0.247	44.0
0.2323	0.00559	0.245	43.8

TABLE 7

ASSOCIATION MEASUREMENTS FOR THE SYSTEM EtMgBr WITH Et_2O IN BENZENE (without excess Et_2Mg) AT 28°C

[Et_2O]	[EtMgBr]	S_a (mm/h)	$S_{th}(\frac{mm/h}{mol/l})$	[particles]	i
0.028	0.0150	0.323	43.70	0.00739	2.03
0.096	0.0149	0.380	43.59	0.00872	1.71
0.167	0.0148	0.419	43.31	0.00967	1.53
0.238	0.0147	0.448	42.98	0.01042	1.41
0.341	0.0146	0.473	42.11	0.01123	1.30
0.442	0.0144	0.480	41.26	0.01163	1.24
0.522	0.0143	0.484	40.73	0.01188	1.20

TABLE 8

ASSOCIATION MEASUREMENTS FOR THE SYSTEM EtMgBr WITH Et_3N IN BENZENE AT 28°C (12% excess $MgBr_2$ was present)

[Et_3N]	[Mg] ^{a}	S_a (mm/h)	$S_{th}(\frac{mm/h}{mol/l})$	[particles]	i
0.025	0.0236	0.510	43.56	0.0117	2.02
0.037	0.0236	0.511	43.56	0.0118	2.01
0.054	0.0235	0.512	43.35	0.0121	1.99
0.082	0.0234	0.521	43.25	0.0119	1.95
0.117	0.0233	0.513	43.05	0.0119	1.96
0.158	0.0232	0.510	43.00	0.0123	1.96
0.212	0.0230	0.527	42.80	0.0118	1.87
0.451	0.0220	0.496	41.90	0.0116	1.86
0.721	0.0212	0.476	40.95	0.0115	1.82
0.971	0.0203	0.456	39.55	0.0120	1.76
1.201	0.0196	0.449	37.20	0.0127	1.62
1.416	0.0189	0.440	34.70	0.0127	1.49
1.615	0.0182	0.402	32.40	0.0124	1.47

^{a} [Mg] = [EtMgBr] + [$MgBr_2$].

TABLE 9

ASSOCIATION MEASUREMENTS FOR THE SYSTEM EtMgBr WITH THF IN BENZENE AT 28°C (8.3% excess Et_2Mg was present)

[THF]	[Mg] ^{a}	S_a (mm/h)	$S_{th}(\frac{mm/h}{mol/l})$	[particles]	i
0.0280	0.0162	0.461	44.85	0.0103	1.57
0.0345	0.0199	0.575	44.85	0.0128	1.55
0.0418	0.0199	0.644	44.85	0.0144	1.39
0.0546	0.0199	0.726	44.85	0.0162	1.23
0.0669	0.0199	0.764	44.85	0.0170	1.17
0.0899	0.0198	0.780	44.85	0.0174	1.14
0.1338	0.0198	0.790	44.85	0.0176	1.12
0.2420	0.0196	0.800	44.85	0.0178	1.09

^{a} [Mg] = [EtMgBr] + [Et_2Mg].

TABLE 10

ASSOCIATION MEASUREMENTS FOR THE SYSTEM Et_2Mg WITH Et_2O IN BENZENE AT 28°C

$[Et_2O]$	$[Et_2Mg]$	S_a (mm/h)[a]	$S_{th}(\frac{mm/h}{mol/l})$	[particles]	i
0.037	0.00941	0.152	43.70	0.00348	2.70
0.039	0.00907	0.143	43.70	0.00327	2.77
0.064	0.00938	0.157	43.65	0.00360	2.61
0.065	0.00905	0.164	43.65	0.00376	2.41
0.090	0.00902	0.176	43.60	0.00404	2.23
0.117	0.00900	0.186	43.50	0.00428	2.10
0.144	0.00898	0.191	43.38	0.00440	2.04
0.147	0.00930	0.184	43.33	0.00425	2.18
0.242	0.00921	0.201	42.87	0.00469	1.96
0.328	0.00912	0.211	42.08	0.00501	1.82
0.434	0.00902	0.216	41.23	0.00524	1.72
0.549	0.00890	0.215	40.53	0.00530	1.68
1.020	0.00844	0.255	38.80	0.00580	1.46
1.413	0.00803	0.226	37.70	0.00599	1.34
1.829	0.00765	0.224	36.55	0.00613	1.25

[a] S_a was derived from the determined rate by subtracting 0.05 mm/h, which was considered to be a reasonable value for the initial rate, because the Et_2Mg could not be added in portions, the solubility being too low.

Et_2Mg in hydrocarbons in the presence of several equivalents of Et_2O (as reported by Strohmeier [28]). They were prepared by precipitating $MgBr_2$ from EtMgBr in Et_2O with 1,4-dioxane. The clear solution was decanted and heated in vacuum at 125°C overnight to remove Et_2O and 1,4-dioxane. To the solid Et_2Mg, Et_2O in benzene was added, and i determined for the resulting solution; known amounts of Et_2O were added and i determined as a function of the concentration of Et_2O (Table 10).

The initial concentration of E was determined, with an accuracy of better than 5% either by PMR spectroscopy of the original solution when the concentration was high enough, or by gas-chromatographic analysis of the distillate which was obtained by heating the magnesium compound at 125°C in vacuum overnight.

The value of S_{det} (for the calibration measurements) and of S_a (for the actual association measurements) were always corrected for the initial rate (the distilla-

TABLE 11

ASSOCIATION MEASUREMENTS FOR THE SYSTEM i-BuMgBr WITH THF IN BENZENE AT 28°C

[THF]	[i-BuMgBr]	S_a (mm/h)[a]	$S_{th}(\frac{mm/h}{mol/l})$	[particles]	i
0.0123	0.0068	0.185	43.7	0.0042	1.62
0.0179	0.0100	0.284	43.7	0.0065	1.54
0.0234	0.0130	0.380	43.7	0.0087	1.50
0.0285	0.0159	0.498	43.7	0.0106	1.49
0.0335	0.0186	0.555	43.7	0.0127	1.46
0.0452	0.0186	0.620	43.7	0.0142	1.31
0.0571	0.0186	0.678	43.7	0.0155	1.20
0.0689	0.0186	0.698	43.7	0.0160	1.16
0.0807	0.0186	0.702	43.7	0.0161	1.16

[a] S_a was derived from the determined rate by subtracting 0.05 mm/h, which was considered as a reasonable value for the initial rate, because i changed upon addition of new portions i-BuMgBr with THF in benzene.

TABLE 12

ASSOCIATION MEASUREMENTS FOR THE SYSTEM MeMgBr WITH THF IN BENZENE AT 28°C

[THF]	[MeMgBr]	S_a(mm/h)[a]	$S_{th}(\frac{mm/h}{mol/l})$	[particles]	i
0.0609	0.0258	0.769	43.7	0.0176	1.47
0.0660	0.0258	0.801	43.7	0.0183	1.41
0.0704	0.0258	0.831	43.7	0.0190	1.36
0.0759	0.0258	0.862	43.7	0.0197	1.31
0.0923	0.0257	0.896	43.7	0.0205	1.25
0.1078	0.0257	0.940	43.7	0.0215	1.20
0.1407	0.0256	0.959	43.7	0.0219	1.17
0.1886	0.0255	0.961	43.7	0.0220	1.16

[a] As footnote to Table 11 with MeMgBr instead of i-BuMgBr.

tion rate which observed if no solute is added; this may stem from impurities in solvent or apparatus) which is never exactly zero. This initial rate was determined by adding the Ph_3CH- or Mg-containing species in 4—6 portions; the initial rate can then be calculated by the least squares method. When this procedure was not possible, this is mentioned in the table. For all the measurements the total volume was about 200 ml.

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