that exchange is faster in ethyllithium than in methyllithium.

The results obtained on the $LiCH_3$–$LiM(CH_3)_4$ systems provide an accurate and reliable value for the rate and activation energy of the process

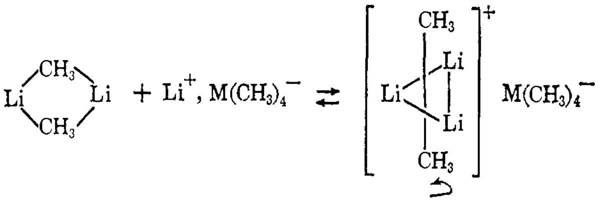
$$(LiCH_3)_4 \longrightarrow 2(LiCH_3)_2$$

It is rather striking that the activation energy for tetramer dissociation should be as high as 11 kcal/mole in ether. Under these same conditions the trimethylaluminum dimer is completely dissociated, and dimethylmagnesium is probably largely in monomeric form.[17] On the basis of what is now known, homolytic dissociation of tetramers is apparently much faster than ionization,[4] which might be envisaged as occurring from either the tetramer or dimer

$$Li_4R_4 \rightleftarrows Li_4R_3^+ + R^-$$

$$Li_2R_2 \rightleftarrows Li_2R^+ + R^-$$

^7Li exchange *via* the mechanism proposed involves a rapid exchange between Li_2R_2 and Li^+, $M(CH_3)_4^-$. We suggest that this proceeds through intermediate formation of $Li_3R_2^+$, $M(CH_3)_4^-$. Ions of the form $Li_nR_{n-1}^+$ are abundant in the mass spectrum of organolithium compounds.[18,19] The detailed form of the exchange, excluding consideration of the solvent, is then probably



Acknowledgments. The authors are indebted to O. W. Norton for assistance in obtaining the nmr data, to L. M. Seitz for helpful discussions, and to J. A. Ladd for writing the two-site exchange program.

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(17) A. D. Vreugdenhil and C. Blomberg, *Rec. Trav. Chim.*, **82**, 453 (1963).

(18) D. A. Bafus, J. Berkowitz, and T. L. Brown, *J. Phys. Chem.*, **65**, 1380 (1961).

(19) G. E. Hartwell and T. L. Brown, *Inorg. Chem.*, **5**, 1257 (1966).

Organometallic Exchange Reactions. III. Lithium-7 and Proton Nuclear Magnetic Resonance Spectra of Methyllithium–Dimethylmagnesium and Methyllithium–Dimethylzinc in Ether[1]

Larry M. Seitz and Theodore L. Brown[2]

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Abstract: Proton and ^7Li nuclear magnetic resonance spectra of ether solutions of methyllithium with dimethylmagnesium and dimethylzinc have been examined over a range of temperatures. The spectra show that complex species of the form $Li_2M(CH_3)_4$ and $Li_3M(CH_3)_5$ (M = Zn or Mg) are formed. No 1:1 complex is observed. Exchange of ^7Li between $LiCH_3$ and complex appears to occur at about the same rate, and with the same activation energy, as methyl-group exchange. The exchange processes are faster in the zinc than in the magnesium system. It appears that in the zinc system the rate-determining process is dissociation of methyllithium tetramer to dimers. Exchange of methyl groups between $Mg(CH_3)_2$ and $Li_2Mg(CH_3)_4$ is quite rapid, despite a comparatively high activation energy, 15 kcal/mole. The analogous exchange is rapid in the zinc system at −107°, the lowest temperature studied.

It is well known that alkyl- and aryllithium compounds react with other organometallic compounds to form mixed organometallic complexes.[3] Wittig and co-workers studied the phenyllithium–diphenylmagnesium and phenyllithium–diphenylzinc systems and isolated solid mixed complexes of 1:1 stoichiometry, *e.g.*, $LiMg(C_6H_5)_3$.[4] Hurd succeeded in isolating a 2:1 complex, $Li_2Zn(CH_3)_4$, by adding methyllithium to dimethylzinc in ether.[5] Aside from this work, no other investigation of the reaction of methyllithium with dimethylmagnesium or dimethylzinc has been reported.

In view of the 1:1 complexes reported by Wittig, *et al.*, for the phenyl compounds and the 2:1 complex reported by Hurd, it was of interest to determine the stoichiometry of the complexes in solution. We report here the results of a ^7Li and ^1H magnetic resonance study of the reaction of methyllithium with dimethylmagnesium and dimethylzinc in ether, which reveal the presence of two complexes in solution under certain conditions. The data relate to the stoichiometry of each complex and provide information on the rates of various exchange processes involved. The results of a similar study of the corresponding phenyl compounds will be reported in another paper.

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(1) The research was sponsored by a grant from the National Science Foundation.

(2) Alfred P. Sloan Research Fellow.

(3) G. E. Coates, "Organometallic Compounds," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1960.

(4) G. Wittig, F. J. Meyer, and G. Lange, *Ann.*, **57**, 167 (1951).

(5) D. T. Hurd, *J. Org. Chem.*, **13**, 711 (1948).

Experimental Section

All operations, except manipulations involving dimethylmercury, were performed in a glove box under argon atmosphere. Removal of traces of oxygen and water was effected by continuous circulation of the atmosphere through molecular sieve and manganese(II) oxide columns as described previously.[6] The concentrations of methyllithium and dimethylmagnesium were determined by decomposing aliquot samples with water and titrating to a phenolphthalein end point with standard 0.1 *N* hydrochloric acid. Concentrations of dimethylzinc were determined by decomposing aliquot samples with water inside a glove bag filled with nitrogen and titration with standard EDTA solution (NH_4Cl–NH_4OH buffer, pH 10) using erichrome black T as indicator.[7]

Dimethylmercury was obtained from Eastman Organic Chemicals, and sublimed magnesium metal from Dow Chemical Co. Mallinckrodt analytical reagent grade anhydrous ether was dried over sodium wire and used without further purification.

Solutions of methyllithium in ether were prepared by adding dimethylmercury to a cooled lithium metal–ether mixture. Excess lithium was used to ensure complete reaction. The lithium amalgam and excess lithium were removed by filtration to produce a clear methyllithium solution. This method was chosen to eliminate contamination by lithium halides.

Ether solutions of dimethylmagnesium were prepared by two different methods. The first method involved preparation of the Grignard reagent, CH_3MgBr, and then addition of dioxane to precipitate the dioxane complex of $MgBr_2$, leaving dimethylmagnesium in solution. After addition of dioxane the solutions were shaken at room temperature for at least 24 hr. Using a silver nitrate test, the dimethylmagnesium solution was tested to ensure that just enough dioxane was added to completely remove the bromide. In the second method, dimethylmercury was added to a magnesium metal–ether mixture and stirred for several hours. A large excess of magnesium was used; it was added in small amounts until the metal remained bright, indicating the absence of any remaining dimethylmercury. The magnesium–mercury amalgam and excess magnesium were removed by filtration. Proton and ^7Li spectra obtained from solutions containing dimethylmagnesium prepared by either method were exactly the same.

Dimethylzinc was prepared by the addition of the Grignard reagent, CH_3MgI, to anhydrous zinc chloride and removal of dimethylzinc etherate from the reaction mixture by distillation.

After the concentrations (usually about 1 *M* for methyllithium, 0.5 *M* for dimethylmagnesium and dimethylzinc) of the separate solutions were determined, they were mixed in the appropriate volume proportions to form the methyllithium–dimethylmagnesium and methyllithium–dimethylzinc mixtures. The solutions were degassed, sealed under vacuum in standard-size nmr tubes, and stored in Dry Ice.

Nuclear Magnetic Resonance Spectra. Lithium-7 spectra were obtained at 23.3 Mc in a field of 14,092 gauss using a Varian Associates Model DP60 spectrometer. Aqueous lithium bromide solution (7 g of commercial grade LiBr/10 ml of solution) was employed as an external standard for the room temperature ^7Li chemical-shift measurements. Proton spectra were obtained on both a Varian Associates A-60 and DP60 spectrometer at 60 Mc.

The low temperatures were obtained using the standard low-temperature accessories supplied by Varian Associates. After allowing the system to come to equilibrium at each temperatures, a number of spectra were recorded, with temperature measurements before and after.

Results and Discussion

At room temperature the proton chemical shifts of methyllithium, dimethylmagnesium, and dimethylzinc in ether are 3.08, 2.55, and 1.80 ppm, respectively, upfield from the center of the ether triplet. The proton spectrum of a methyllithium–dimethylmagnesium or dimethylzinc mixture consists of a single sharp resonance at room temperature whose chemical shift depends on Li/Mg(Zn),[8] which implies rapid exchange between different species in solution. At low temperatures the exchange is slowed such that a multiplet structure occurs, as shown in Figure 1.

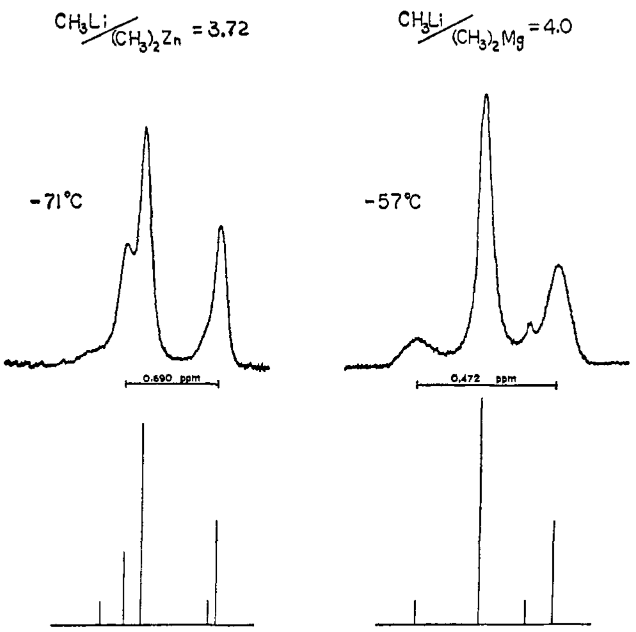

Figure 1. Low-temperature proton spectra of $LiCH_3$–$Mg(CH_3)_2$ and $LiCH_3$–$Zn(CH_3)_2$. The calculated intensities are shown below the experimental spectra.

The chemical shift of the ^7Li resonance of methyllithium in ether at room temperature appears at -1.32 ppm relative to the aqueous LiBr standard; it exhibits a negligible concentration dependence. When dimethylmagnesium or dimethylzinc is added, the resonance remains a sharp singlet at room temperature, but it is shifted considerably upfield (see Table I). This suggests a rapid exchange between methyllithium and one or more other components with chemical shifts upfield from methyllithium. Just as in the proton spectrum, separate resonances are observed at low temperature when Li/Mg(Zn) > 2. The ^7Li spectra in Figure 2 serve to illustrate the close similarity of the two systems.

Table I. ^7Li Chemical Shift in $LiCH_3$–$Mg(CH_3)_2$ and $LiCH_3$–$Zn(CH_3)_2$ Solutions in Ether at 30°

CH_3Li/ $(CH_3)_2Mg$	^7Li shift, ppm	CH_3Li/ $(CH_3)_2Zn$	^7Li shift, ppm
∞	−1.32	∞	−1.32
4.00	−0.704	3.72	−0.665
3.66	−0.700	0.935	+0.285
2.20	−0.330	0.624	+0.285
2.00	−0.279	0.312	+0.285
1.83	−0.283		
1.10	+0.0815		
0.915	+0.142		
0.800	+0.214		

Stoichiometries and Structures of Complexes. As expected, methyllithium reacts with dimethylmagnesium and dimethylzinc to form mixed complexes. An unexpected result is that both 2:1 and 3:1 complexes, $Li_2M(CH_3)_4$ and $Li_3M(CH_3)_5$, respectively (M = Mg,

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(6) T. L. Brown, D. W. Dickerhoof, D. A. Bafus, and G. L. Morgan, *Rev. Sci. Instr.*, 33, 491 (1962).

(7) F. J. Welcher, "The Analytical Uses of Ethylenediaminetetraacetic Acid," D.Van Nostrand Co., Inc., Princeton, N. J., 1958.

(8) Li/Mg(Zn) will be used to represent the mole ratios methyllithium/dimethylmagnesium and methyllithium/dimethylzinc.

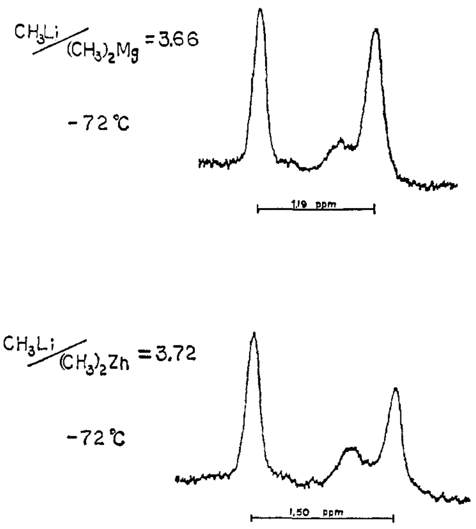

Figure 2. Low-temperature ^{7}Li of $LiCH_3$–$Mg(CH_3)_2$ and $LiCH_3$–$Zn(CH_3)_2$ solutions in ether.

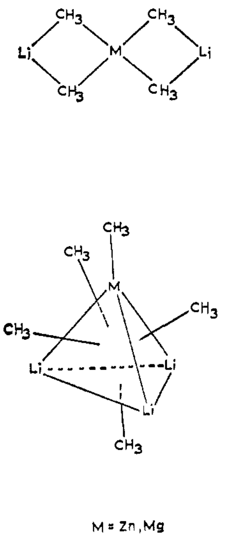

Figure 3. Proposed structures of the 2:1 and 3:1 complexes. Coordinated solvent has been omitted for simplicity.

Zn), exist in solution at low temperature when Li/Mg(Zn) > 2. The 2:1 complex is more readily formed, as suggested by the following observations. When Li/Mg(Zn) = 2, only a single resonance is observed in both the ^{7}Li and proton spectrum at all temperatures. When the ratio is greater than two, an absorption ascribable to free methyllithium is observed at low temperature in both the proton and ^{7}Li spectrum. With Li/Mg(Zn) < 2, a proton resonance line representing excess dimethylmagnesium appears at about −60° (depending on concentration). However, a similar absorption characteristic of dimethylzinc was not observed even at −107°, presumably owing to very rapid methyl group exchange between dimethylzinc and $Li_2Zn(CH_3)_4$. It is therefore concluded that the following reaction proceeds essentially to completion.

$$\frac{1}{2}(CH_3Li)_4 + (CH_3)_2M \longrightarrow Li_2M(CH_3)_4 \ (M = Mg, Zn) \quad (1)$$

The structure of the 2:1 complex is probably as shown in Figure 3.

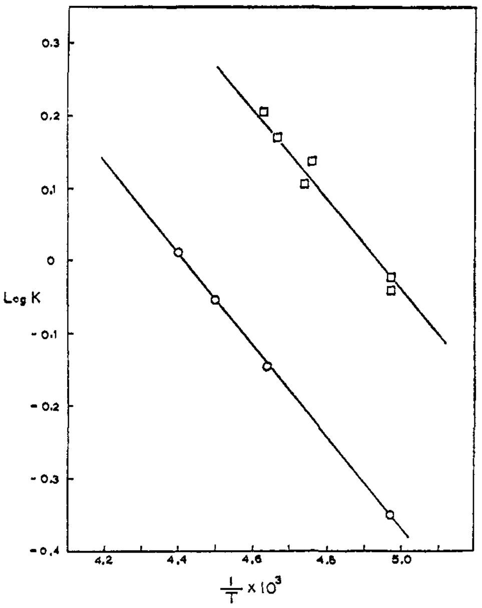

Figure 4. Plot of log K *vs.* $1/T$(°K) based on eq 2: ○, magnesium system; □, zinc system.

The 3:1 complex forms only when the ratio Li/Mg(Zn) > 2, so that an equilibrium of the following type is established.

$$\frac{1}{4}(CH_3Li)_4 + Li_2M(CH_3)_4 \rightleftharpoons Li_3M(CH_3)_5 \quad (2)$$

In order to establish that the stoichiometry of this second complex is indeed 3:1, the areas of all absorptions in the low-temperature ^{7}Li spectra were measured. The middle absorption is assigned to $Li_3M(CH_3)_5$ since its area increases as Li/Mg(Zn) increases. From the relative areas of the absorptions ascribed to the complexes, the mole ratio 2:1/3:1 can be computed. The expected area of the methyllithium peak can then be calculated and compared with the measured value, with good agreement (*i.e.*, to within 10% in relative area).

It is apparent in both ^{7}Li and proton spectra that the amount of the 3:1 complex increases with temperature. Since the concentrations of the original methyllithium, dimethylmagnesium, and dimethylzinc solutions are known, ^{7}Li area data can be employed to calculate equilibrium constants at several temperatures based on eq 2. A plot of log K *vs.* $1/T$(°K) results in a straight line (Figure 4); from the slope of the line, $\Delta H = +2.8 \pm 1.5$ kcal/mole. Data of this kind are more difficult to obtain in the zinc system, since the absorptions coalesce at lower temperatures. It is clear, however, that the equilibrium constants are larger. The value of ΔH is more approximate, but it also is on the order of 2.8 kcal/mole. It appears, therefore, that the entropy change for 3:1 complex formation is relatively more favorable in the zinc system.

Interpretation of the low-temperature proton spectra when Li/Mg(Zn) > 2 is now in order. Before all of the absorptions and their relative intensities can be explained, however, one must assume a reasonable structure for the 3:1 complex. In a previous paper, we have presented evidence that methyllithium is tetrameric in ether.[9] We propose that the 3:1 com-

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[9] L. M. Seitz and T. L. Brown, *J. Am. Chem. Soc.*, **88**, 2174 (1966).

plex results from replacement of one of the lithium atoms in the tetramer with a magnesium or zinc atom (Figure 3). The low-temperature proton spectra exhibited in Figure 1 can be interpreted in terms of this structure. One methyl group is bonded directly to the magnesium or zinc atom; its chemical shift should be near dimethylmagnesium or dimethylzinc. The resonance furthest downfield is assigned to this methyl group. Another methyl group is bonded to three lithium atoms *via* a four-centered bond; its chemical shifts should be similar to methyllithium. The small peak just downfield from methyllithium is assigned to this methyl group. The three remaining methyl groups are bonded to two lithium atoms and one magnesium or zinc atom by a four-center bond, so their chemical shift should be near those of the 2:1 complex, $Li_2M(CH_3)_4$. Using these ideas and the measured areas of the ^7Li spectra at the corresponding temperature, good agreement of the calculated intensities with experimental spectra is obtained (Figure 1). In the magnesium case, the three equivalent methyl groups in the 3:1 complex apparently accidentally have the same chemical shift as the 2:1 complex, whereas in the zinc system they are shifted about 8 cps downfield. It is not unreasonable that this should occur; the methyllithium–dimethylzinc chemical-shift separation is much greater than for methyllithium–dimethylmagnesium.

Since the different types of methyl groups in the 3:1 complex are distinguishable at low temperature, intramolecular exchange must be slow. Intramolecular exchange in methyllithium should likewise be slow, which is consistent with the proposal put forth earlier that methyllithium is tetrameric in ether.[9]

It is more uncertain which species are present at room temperature, and their relative proportions. One can extrapolate low-temperature data to room temperature. If this is done with the data in Figure 2, it develops that the 3:1 complex becomes predominant. The relative amounts of the complexes would of course depend on the Li/Mg(Zn) ratio. The data in Table I suggest some dissociation of the complex, $Li_2Mg(CH_3)_4$, at room temperature; the ^7Li resonance is shifted upfield as the Li/Mg ratio decreases. Data for the zinc system is less complete, but it appears the tendency of $Li_2Zn(CH_3)_4$ to dissociate is lower, if indeed it dissociates at all.

Formation of a 1:1 complex with a structure similar to the 3:1 complex (*i.e.*, by replacement of a second lithium by a magnesium atom) is unlikely on *a priori* grounds. The dialkylmagnesium compounds show little tendency to associate in ether solutions.[10] Increasing Mg(Zn) content in a complex might therefore be expected to lead to instability. Other structures of a 1:1 complex could be considered, but in any event we have not been able to obtain evidence for a 1:1 complex. If it does exist when Li/Mg(Zn) < 2, its concentration is quite small.[11]

Kinetics and Mechanisms of Exchange Reactions. Examination of the temperature dependences of the ^7Li and proton spectra yields information concerning the mechanisms of exchange processes and their activation energies. The spectra have been analyzed with the aid of a computer program based on a generalized equation which describes the line shape of a two-site exchange system as a function of the mean lifetime, τ, of the group exchanged (in this study, either ^7Li or methyl group). In the program, the transverse relaxation times of the two sites (T_{2A} and T_{2B}), the populations (p_A and p_B), and the separation of the sites in the limit of no exchange are all variables. The complete equation, description of terms therein, and a further description of its use is given in part II of this series.[12]

Allerhand and co-workers[13] have emphasized the importance of certain systematic errors in high-resolution methods, *e.g.*, the peak separation method, of obtaining activation energies. Error can result from temperature dependence of the chemical shifts and T_2 values characteristic of the sites, as well as from error in the chemical shift separation, δ, in the limit of no exchange. In using the computer program, it is possible to account for the T_2 terms by inserting appropriate values for each temperature. The chemical shift dependence on temperature could not be assessed, so it was assumed that δ is insensitive to temperature variation. Also the temperature range over which useful data could be obtained is rather short. From observing the effect on the calculated activation energy when δ and the T_2 values are varied, we estimate that the activation energies we obtain are correct to within ± 3 kcal/mole.

It is possible to distinquish between two general types of exchange systems. One arises when Li/Mg(Zn) < 2 and involves methyl-group exchange between dimethylmagnesium or dimethylzinc and the 2:1 complex. The second arises when Li/Mg(Zn) > 2 and involves methyl *and* lithium exchange between methyllithium and the 2:1 and 3:1 complexes. We shall consider the latter case first. All the Arrhenius plots for activation energy have been placed together in Figure 8 for convenience in making comparisons.

The temperature dependences of the ^7Li spectra when Li/Mg(Zn) > 2 are shown in Figure 5. Their over-all similarity should be noted. The coalescence of the two complex peaks before the methyllithium peak is broadened appreciably indicates a facile exchange between the 2:1 and 3:1 complexes which does not involve free methyllithium. A rapid step such as eq 3 is suggested.

$$Li_2M(CH_3)_4 + Li_3M(CH_3)_5 \rightarrow [Li_2M(CH_3)_4 \cdots \overset{\curvearrowleft}{LiCH_3} \cdots Li_2M(CH_3)_4] \quad (3)$$

It is interesting to note from Figures 5, 6, and 7 that neither the ^7Li nor ^1H resonances due to methyllithium are exchange broadened at temperatures below −50°. This is consistent with the proposal embodied in eq 3, that exchange between the 2:1 and 3:1 complexes occurs *via* a bimolecular reaction in which a methyllithium molecule is transferred.

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(10) A. D. Vreugdenhil and C. Blomberg, *Rec. Trav. Chim.*, **82**, 453 (1963).

(11) The complexes have very little tendency to react with solvent. When an ether solution of methyllithium is allowed to stand at room temperature, a precipitate eventually forms. This is apparently the result of a slow reaction with ether, forming lithium ethoxide (the precipitate might consist of species of type $Li_4(CH_3)_3OC_2H_5$). In solutions of Li/Mg(Zn) about 4, a similar precipitate forms, but when Li/Mg(Zn) < 2, little or no precipitate forms.

(12) Part II: K. C. Williams and T. L. Brown, *J. Am. Chem. Soc.*, **88**, 4134 (1966).

(13) A. Allerhand and H. S. Gutowsky, *J. Chem. Phys.*, **41**, 2115 (1964); A. Allerhand, H. S. Gutowsky, J. Jonas, and R. A. Meinzer, *J. Am. Chem. Soc.*, **88**, 3185 (1966).

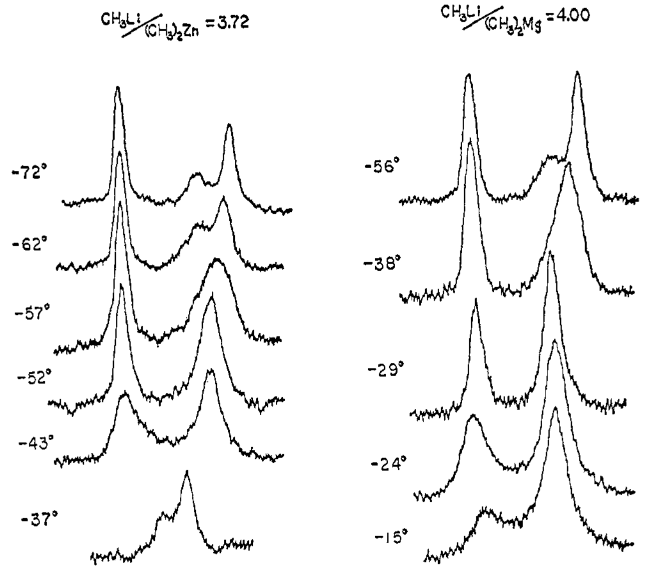

Figure 5. Temperature dependence of the ^7Li spectra (sweep rates are not exactly the same for each temperature).

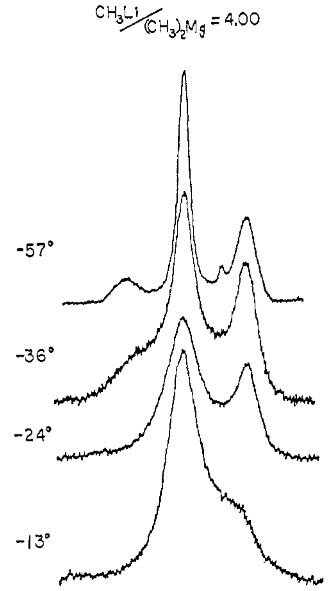

Figure 6. Temperature dependence of the proton spectra in the $LiCH_3$–$Mg(CH_3)_2$ system.

As the temperature is raised, methyllithium becomes involved in exchange with the 2:1 and/or 3:1 complex, and the spectrum eventually coalesces to one resonance. This is potentially a three-site exchange problem, but it can be considered to reduce to a two-site problem at temperatures above the coalescence point of the complex peaks. This is a reasonable approximation if neither complex is involved in the rate-determining step. Therefore, we have employed the two-site exchange program to estimate the activation energies. We consider first the ^7Li spectra, as in Figure 5.

The chemical shift of the second site is taken to be a weighted average of the values for the 2:1 and 3:1 complexes. The separation of the two sites in the limit of no exchange at any given temperature can be estimated from the equation $p_B\omega_B + p_C\omega_C = \delta$. The populations, p_B and p_C, are obtained from extrapolation of data in Figure 4; ω_B and ω_C are the chemical shifts from methyllithium of the 3:1 and 2:1 complexes, respectively (Figure 2). $1/T_2$ for methyllithium is assumed to be the value derived from the half-intensity width of methyllithium alone in ether at each temperature.[14] $1/T_2$ for the complex absorption is not directly measurable. This quantity was varied over a range of values at each temperature and the line shape calculated as a function of exchange rate for each value. The value ($1/T_2$) for the complex which gave the best over-all fit to the total line shape was chosen. Fortunately, the choice of this quantity did not prove to be critical. The value calculated for peak separation was weighted quite heavily in choosing the correct value for τ in each case. Proceeding in this manner, activation energies of 10.3 and 10.9 kcal/mole were obtained for ^7Li exchange in the magnesium and zinc systems, respectively (Figure 8), with an uncertainty of about 3 kcal/mole in each case.

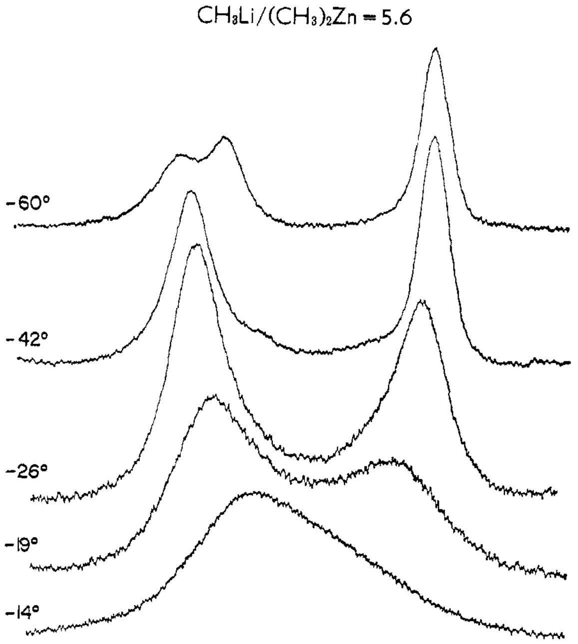

Figure 7. Temperature dependence of the proton spectra in the $LiCH_3$–$Zn(CH_3)_2$ system.

The ^7Li spectrum of the zinc system, where Li/Zn = 5.6, was considered in another way. The line width at half-height, $\Delta_{1/2}$, of the methyllithium resonance was determined a a function of temperature (−57 to −42°). By subtracting the line width of methyllithium not undergoing exchange, $\Delta_{1/2}{}^{\circ}$, one obtains $1/\tau_{CH_3Li} = \pi(\Delta_{1/2} - \Delta_{1/2}{}^{\circ})$. The result of this analysis is shown by the solid black points in Figure 8. From the slope of the line, the activation energy is 12 ± 3 kcal/mole, which is, within experimental error, the same as that obtained by the method described above.

The temperature dependence of the proton and ^7Li spectra are quite similar (compare Figures 5–7). Proton resonances representing the two complexes coalesce first, again suggesting a more facile exchange

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(14) This assumption might lead to a slight error, inasmuch as there is some broadening of the ^7Li line in methyllithium at lower temperature due to ^7Li–CH_3 coupling. Exchange with the complex, if it were more rapid than dissociation of the methyllithium tetramer, could lead to some decoupling, so that a small value of $1/T_2$ would be appropriate. However, the kinetics of exchange with the complex seems to be rate determined by methyllithium dissociation, so the effect on $1/T_2$ should be negligible.

between the two complexes than between methyllithium and the complexes. A comparison of the temperature dependence of the ^{7}Li and proton spectra reveals that the rates of methyl group and lithium exchange in each case (Mg or Zn) are about the same, as would be required by eq 3. The complicated manner in which the spectrum changes with temperature in the magnesium system precludes a detailed analysis, similar to that done with the ^{7}Li spectra, to determine the activation energy required for methyl group exchange between methyllithium and the complexes. A few points were estimated, however, using the computer program; these are shown in Figure 8. It does seem that the activation energy is the same for lithium and proton exchange; furthermore, when statistical factors are considered the rate of exchange is the same. In the zinc system the temperature dependence (Figure 7) is simple enough to permit carrying out a more complete analysis of the ^{1}H spectra. The activation energy obtained in this manner is 8.5 ± 3 kcal/mole (Figure 8).

It is useful to make a few observations about these results which provide a basis for discussion of mechanism. (a) ^{7}Li exchange in the $LiCH_3$–$Zn(CH_3)_2$ system is faster than in the magnesium system. (b) The rate of ^{7}Li exchange in the zinc system is slightly slower than ^{7}Li exchange in the $LiCH_3$–$Al(CH_3)_3$ or $LiCH_3$–$B(CH_3)_3$ system;[12] the Arrhenius activation energy is the same, within experimental uncertainty. (c) Methyl-group exchange in the zinc system occurs at a comparable rate with ^{7}Li exchange.

The results for the zinc system can be explained in terms of the following mechanism.

$$\underset{\mathrm{T}}{(\mp CH_3Li^*)_4} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\mathrm{D}}{2(\mp CH_3Li^*)_2}$$

$$(\mp CH_3Li^*)_2 + Li_2Zn(CH_3)_4 \xrightarrow{k_2} Li^*LiZn(CH_3)_3(\mp CH_3) + (LiCH_3)_2 \quad (4)$$

$$\begin{array}{l} (\mp CH_3Li^*)_2 + Li_3Zn(CH_3)_5 \xrightarrow{k_2'} Li^*Li_2Zn(CH_3)_4(\mp CH_3) + (LiCH_3)_2 \\ \quad \mathrm{D} \quad + \quad \mathrm{C} \quad \longrightarrow \quad \mathrm{C}^* \quad + \quad \mathrm{D} \end{array} \quad (5)$$

It is not possible to determine directly whether both (4) and (5) are operative. It seems reasonable that k_2 for ^{7}Li exchange should be smaller than for the analogous step in the $LiM(CH_3)_4$ systems, since the group II complexes should be less ionic. We have already mentioned that there is a rapid, concurrent exchange of ^{7}Li and methyl groups between the 2:1 and 3:1 complexes. It also appears that ^{7}Li and methyl group exchanges between methyllithium and the complexes proceed at comparable rates.[15] These results seem to be best accommodated by the hypothesis that exchange of $LiCH_3$ occurs between the dimer and 3:1 complex in a concerted process, *i.e.*, that $k_2' \gg k_2$. This assumption is employed in deriving the kinetic expressions which follow. The alternate hypotheses, $k_2 \approx k_2'$ or $k_2 \gg k_2'$, are not ruled out by the data; only relatively small changes in statistical factors would result if the latter extreme alternative were adopted.

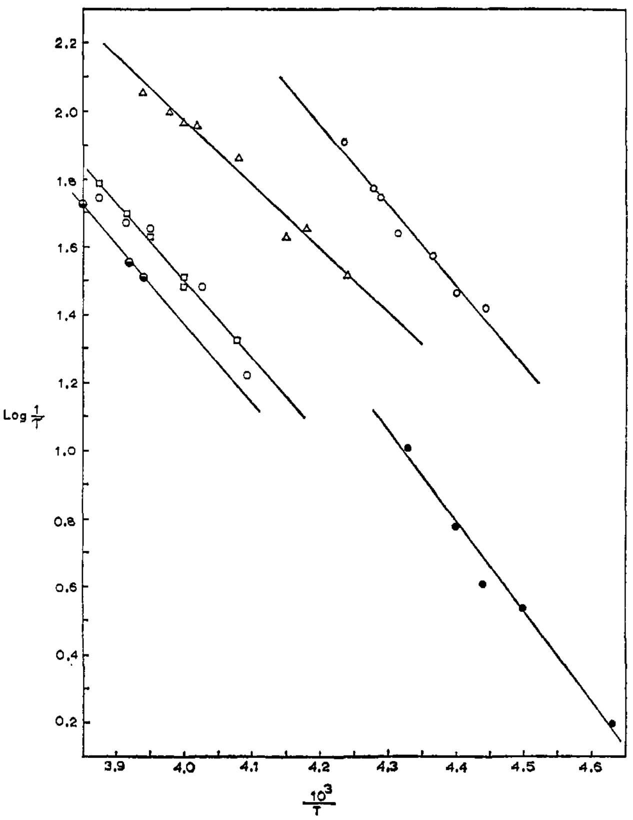


Figure 8. $1/\tau$ as a function of temperature for solution with Li/Mg(Zn) > 2: ○, ^{7}Li data; △, ^{1}H data; ●, ^{7}Li data from CH_3Li line width for Li/Zn = 5.6; for Li/Mg = 4.0: □, ^{7}Li data; ◒, ^{1}H data. The approximate concentrations of species for Li/Zn = 5.6 are: $(CH_3Li)_4$ = 0.1 *M*, $Li_2Zn(CH_3)_4$ = 0.07 *M*, $Li_3Zn(CH_3)_5$ = 0.06 *M*; for Li/Mg = 4.0: $(CH_3Li)_4$ = 0.06 *M*, $Li_2Mg(CH_3)_4$ = 0.1 *M*, $Li_3Zn(CH_3)_5$ = 0.08 *M*.

Employing the usual approach, *i.e.*, adopting a steady-state assumption for (D), the following equations are applicable to ^{7}Li exchange.

$$\frac{d(\mathrm{D})}{dt} = 2k_1(\mathrm{T}) - 2k_{-1}(\mathrm{D})^2 - k_2'(\mathrm{D})(\mathrm{C}) = 0$$

$$(\mathrm{D}) = \frac{2k_1(\mathrm{T})}{2k_{-1}(\mathrm{D}) + k_2'(\mathrm{C})}$$

$$\frac{d(\mathrm{C}^*)}{dt} = k_2'(\mathrm{D})(\mathrm{C}) = \frac{2k_1k_2'(\mathrm{T})(\mathrm{C})}{2k_{-1}(\mathrm{D}) + k_2'(\mathrm{C})}$$

If $k_{-1} \ll k_2'(\mathrm{C})$

$$\frac{d(\mathrm{C}^*)}{dt} = 2k_1(\mathrm{T})$$

$$1/\tau_{\mathrm{C}} = \frac{1}{3}\frac{1}{(\mathrm{C})}\frac{d(\mathrm{C}^*)}{dt} = \frac{2}{3}k_1\frac{(\mathrm{T})}{(\mathrm{C})}$$

$$1\tau/_{\mathrm{T}} = \frac{1}{4}\frac{1}{(\mathrm{T})}\frac{d(\mathrm{C}^*)}{dt} = \frac{k_1}{2} \quad (6)$$

$$1/\tau_{\mathrm{Li}} = 1/\tau_{\mathrm{T}} + 1/\tau_{\mathrm{C}} = \frac{k_1}{2}\left(\frac{4(\mathrm{T})}{3(\mathrm{C})} + 1\right) \quad (7)$$

---

[15] Preliminary data have been obtained on the $Cd(CH_3)_2$–$LiCH_3$ system. Methyl group and ^{7}Li exchange occur at comparable rates; both are more rapid than in the Zn system. A detailed comparison of the exchanges in all three group II systems will be made in a later publication.

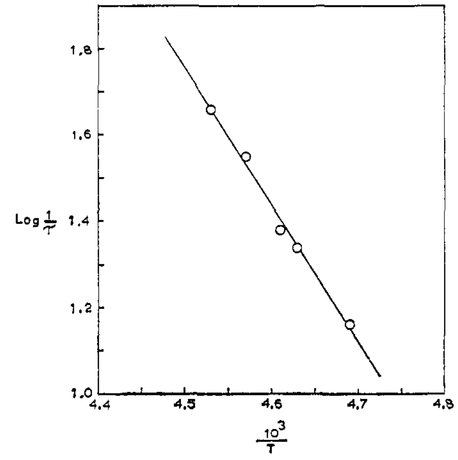


Figure 9. $1/\tau$ *vs.* $1/T$ from ^{1}H spectra in $Mg(CH_3)_2$–$Li_2Mg(CH_3)_4$ system, Li/Mg = 0.915. The concentrations in solution are $(CH_3)_2Mg$ = 0.21 *M* and $Li_2Mg(CH_3)_4$ = 0.18 *M*.

A similar approach leads to the following for ^{1}H exchange, assuming that a methyl group is exchanged each time a lithium is.

$$1/\tau_T = \frac{k_1}{2} \qquad 1/\tau_C = \frac{2k_1}{5}\frac{(T)}{(C)} \tag{8}$$

$$1/\tau_H = \frac{k_1}{2}\left(\frac{4}{5}\frac{(T)}{(C)} + 1\right) \tag{9}$$

The complexity of the spectra, resulting from the presence of two complexes, precludes really satisfactory testing of the mechanism. There are, however, a few pertinent observations. The ratio $(1/\tau_{Li})/(1/\tau_H)$ for a particular solution is given by $[4(T)/3(C) + 1]/[4(T)/5(C) + 1]$. In the sample Li/Zn = 5.6 employed in obtaining the data of Figure 8, (T)/(C) = 1.7, corresponding to a ratio of 1.4. In the graphs of $1/\tau$ *vs.* $1/T$ in Figure 8, the line for methyl-exchange data should then run about 0.15 log unit lower than the line for the ^{7}Li data. The observed value is approximately 0.3, which is reasonable agreement when experimental error is considered.

Equations 6 and 7 also yield a relationship between $1/\tau_T$ and $1/\tau_{Li}$ in the ^{7}Li spectra.

$$(1/\tau_{Li})/(1/\tau_T) = 4(T)/3(C) + 1$$

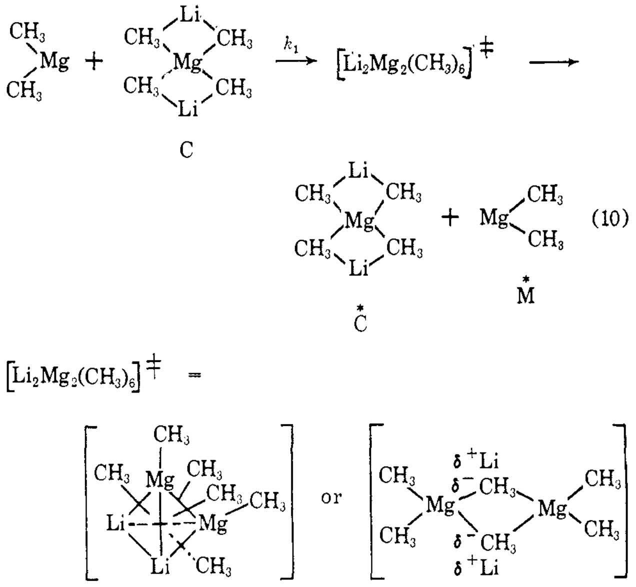
For (T)/(C) = 1.7, the ratio is thus 3.2. The difference in log τ values should then be about 0.51. The observed value is about 0.68 (Figure 8), in quite satisfactory agreement.

The $LiCH_3$–$Zn(CH_3)_2$ system is thus akin to the LiR–$LiM(CH_3)_4$ system, in that ^{7}Li exchange is determined by dissociation of alkyllithium tetramers. It is clear, however, that ^{7}Li exchange is slower than in the group III systems, indicating that the condition $k_{-1} \ll k_2'(C)$ is not strictly met. The group II systems differ dramatically from the group III systems, however, in exhibiting comparably rapid methyl group exchange. There is probably an intermediate formed between dimer and 3:1 complex which requires the transfer of a methyllithium molecule. More detailed kinetic studies, including evaluation of concentration dependences, are needed, however, to further our understanding of these exchanges.

The most important observation about the $LiCH_3$–$Mg(CH_3)_2$ system is that both lithium and methyl group exchanges are slower than their counterparts in the zinc system. This is particularly noteworthy in light of the observation discussed above, that the zinc complexes seem to be more stable (Table I). It further points up the probability that exchange between methyllithium and the complexes does not occur *via* dissociation of the complexes.

The mechanism described for exchange in the zinc system is applicable to the magnesium system. It seems probable that the same general pathway is involved, but that k_2' is relatively slower than in the zinc system.[15]

We now consider the exchange systems arising when Li/Mg(Zn) < 2. In the magnesium system a resonance representing excess dimethylmagnesium can be observed below −50°. This is a more straightforward system than those treated earlier, since exchange occurs between only two species, dimethylmagnesium and $Li_2Mg(CH_3)_4$. Analysis of the temperature dependence of the spectrum by use of the computer program yields an activation energy of 15 ± 3 kcal/mole (Figure 9). A mechanism for the exchange process is offered in eq 10. The transition state may be thought of as the transient existence of a 1:1 complex. The structure of the transition state is not clear, but it could involve the formation of a tetramer like the 3:1 complex. A dissociative mechanism is considered unlikely. Rate expressions applicable to this case are as follows



(10)

$$\frac{d(M^*)}{dt} = \frac{d(C^*)}{dt} = k_1(C)(M)$$

$$\frac{1}{\tau_M} = \frac{1}{2}\frac{1}{(M)}\frac{d(M^*)}{dt} = \frac{k_1}{2}(C)$$

and

$$\frac{1}{\tau_C} = \frac{1}{4}\frac{1}{(C)}\frac{d(C^*)}{dt} = \frac{k_1}{4}(M)$$

$$\frac{1}{\tau} = \frac{1}{\tau_M} + \frac{1}{\tau_C} = \frac{k_1}{2}\left((C) + \frac{1}{2}(M)\right) \tag{11}$$

Table II. Summary of Kinetic Data Obtained for $LiCH_3$–$Mg(CH_3)_2$ and $LiCH_3$–$Zn(CH_3)_2$ Systems in Ether

System	Nucleus exchanging	Arrhenius activation energy	Temp dependence of log k_1[a]
$LiCH_3$–$Li_2Zn(CH_3)_4$	^7Li	10.9	$-2380\,(1/T) + 11.6$
$LiCH_3$–$Li_2Zn(CH_3)_4$[b]	^7Li	12.0	$-2630\,(1/T) + 12.7$
$LiCH_3$–$Li_2Zn(CH_3)_4$	^1H	8.5	$-1860\,(1/T) + 9.33$
$LiCH_3$–$Li_2Mg(CH_3)_4$	^7Li	10.3	$-2260\,(1/T) + 10.6$
$LiCH_3$–$Li_2Mg(CH_3)_4$	^1H	≈ 10	
$Mg(CH_3)_2$–$Li_2Mg(CH_3)_4$	^1H	15.0	$-3180\,(1/T) + 16.9$

[a] k_1 is derived from $1/\tau$ in each case by use of eq 6–9 as appropriate for $Li/Mg(Zn) > 2$, and eq 11 for $Li/Mg < 2$. [b] From observation of $1/\tau_T$ alone; see text.

where eq 11 gives the relationship between $1/\tau$ obtained from the computer program and the rate constant, k_1.

In the zinc system, a separate resonance representing dimethylzinc was not observed, even at −107°. Methyl-group exchange is clearly more rapid than in the magnesium system. The mechanism of exchange is probably the same. The difference in rate may be associated with the fact that solvent is coordinated more strongly to dimethylmagnesium than dimethylzinc, as evidenced by dipole moment measurements.[16]

Finally, it has been noted that methyl group exchange between dimethylmagnesium and dimethylzinc in ether is rapid even at −103°. Table II provides a summary of all the quantitative results obtained.

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Kinetics of Electrochemical Oxidative Coupling of Decahydroclovodecaborate(2−) in Acetonitrile[1]

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Abstract: A variety of electrochemical techniques have been used to establish that the oxidation of $B_{10}H_{10}^{2-}$ at a platinum electrode in acetonitrile proceeds by an initial one-electron transfer to form a free radical which undergoes a second-order chemical reaction to form $B_{20}H_{19}^{3-}$, which is oxidized to $B_{20}H_{18}^{2-}$ at a slightly greater potential than $B_{10}H_{10}^{2-}$. The second-order rate constant for the chemical coupling reaction has been determined by chronopotentiometry with current reversal. Twenty determinations gave an average value of $k = 2.8 \times 10^3$ l. mole^{-1} sec^{-1}, with a standard deviation of 0.2×10^3 l. mole^{-1} sec^{-1}.

The aqueous chemical oxidation of $B_{10}H_{10}^{2-}$ produces $B_{20}H_{18}^{2-}$, the result of a two-electron oxidation per B_{10} unit.[2–6] Under milder conditions, it is also possible to isolate good yields of $B_{20}H_{19}^{3-}$, the result of a one-electron oxidation of $B_{10}H_{10}^{2-}$.[4–6] Under appropriate conditions, $B_{20}H_{19}^{3-}$ can be converted to $B_{20}H_{18}^{2-}$ and *vice versa*, but neither has been reduced back to $B_{10}H_{10}^{2-}$.[4–6] It is logical to suggest, on the basis of this chemical evidence, that $B_{10}H_{10}^{2-}$ undergoes an initial oxidation followed by an irreversible coupling reaction to form $B_{20}H_{19}^{3-}$, which is subsequently oxidized to $B_{20}H_{18}^{2-}$. If the electrochemical oxidation of $B_{10}H_{10}^{2-}$ were to follow a similar scheme, some of the more rapid electrochemical techniques should be applicable to the study of the coupling reaction itself.

Results

Voltammetry. At a rotating platinum electrode, a split anodic wave is observed for solutions of $B_{10}H_{10}^{2-}$ in acetonitrile containing 1.0, 0.63, or 0.10 M $(C_2H_5)_4NClO_4$ as supporting electrolyte. The apparent heights of the two parts of the wave are unequal, the less anodic predominating. As the concentration of $B_{10}H_{10}^{2-}$ is decreased, holding the concentration of supporting electrolyte constant, two changes are observed. The first wave (less anodic portion of the split wave) seems to increase at the expense of the second, and the second part now occurs at a less anodic potential. The first

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