## Conclusion

Butyllithium in THF consists of a tetramer in equilibrium with a dimer; the proportion of dimer increases as the temperature is lowered. No evidence could be obtained for the presence of monomeric butyllithium in THF. Traces of alcohol or oxygen in the solvent lead to mixed alkyllithium–lithium alkoxide complexes with up to three alkoxide ligands. The dimer and the mixed complexes appear to have increased polarization of the carbon–lithium bond, relative to the tetramer, and may possess different reactivity. The testing of this latter expectation by use of our RINMR system is described in the following paper.

# A Rapid-Injection NMR Study of the Reactivity of Butyllithium Aggregates in Tetrahydrofuran[1]

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**Abstract:** The influence of aggregation on the reactivity of butyllithium toward benzaldehyde and cyclopentadiene in THF was studied at –85 °C by the RINMR method. It was found that the dimer is more reactive than the tetramer toward each of the substrates; in the case of benzaldehyde the difference in rate is tenfold. When the aldehyde is injected into a stoichiometric excess of butyllithium dimer, the reaction is complete in 50 ms. In mixed butyllithium–lithium butoxide aggregates, the reactivity of the butyllithium increases with the number of alkoxy ligands. The aggregate $Bu_2Li_4(OBu)_2$ is of comparable reactivity to the dimer. When butyllithium adds to benzaldehyde, the product lithium 1-phenylpentanolate is formed in a nonequilibrated highly reactive state. It can compete with tetrameric butyllithium for benzaldehyde to reversibly form a hemiacetal salt. One can follow by RINMR the conversion of this reactive alcoholate into free alcoholate and then the complexation of this alcoholate onto the outside of the dimeric and tetrameric butyllithium aggregates. The rates of conversion of hexameric butyllithium into tetramer and dimer and of tetramer into dimer can be directly measured.

In the preceding paper[4] we have established that butyllithium exists in THF as a tetramer in equilibrium with a dimer and that the presence of lithium butoxide, due to oxygen contamination, leads to successive replacement of alkyl groups in the tetrameric structure by alkoxide ligands. It is obviously very desirable to determine the relative reactivity of these species, as the effects of concentration, temperature, and impurities on the reactions of organolithium compounds is of great synthetic importance.

Until now the high reactivity of butyllithium in THF, and toward THF, has limited the number of kinetic investigations on this system. Waack has established that the kinetic order with respect to butyllithium is 0.4 in its reaction with diphenylethylene[5] and is 0.25 in the reaction with triphenylmethane.[6] These partial orders and those for a variety of other organometallic reactions in various solvents[7] have been interpreted in terms of an initial rapid dissociation of aggregated butyllithium into monomer, which is considered to be the predominantly reactive species.[8] Such an interpretation has been supported by the observed change in reaction order in butyllithium, from approximately 0.33 to 1 in its reaction with the solvent THF, as the concentration is lowered

from 100 to 1.5 mM.[9] We have, however, shown that *no* direct evidence for monomeric butyllithium in THF could be found at concentrations down to 100 μM and that at 25 °C the tetramer will be 50% dissociated into *dimer* at a total butyllithium concentration of 8.6 mM.[4]

Having at our disposal the rapid injection NMR (RINMR) technique[10,11] which allows us to follow several concurrent reactions that are complete in 1s at temperatures down to –90 °C, we chose to examine the reactions of butyllithium with cyclopentadiene (deprotonation) and with benzaldehyde (addition) with the goal of answering the following questions: (a) are the reactions too rapid to be followed, (b) do dimeric butyllithium and mixed butyllithium–lithium alkoxide complexes react more rapidly than the tetramer, (c) can the tetramer react, and (d) are the products incorporated into the aggregates?

## Experimental Section

**Instrumentation.** NMR spectra were run on a Bruker WH-360 spectrometer. Chemical shifts ($\delta$) were measured relative to the residual $\alpha$-methylene protons in the THF solvent and are reported relative to Me$_4$Si. The rapid injection insert has been described.[11] The shortest acquistion time (AQT) used was 36 ms (corresponding to a sweep width of 14 000 Hz on 1 K data points, with digital resolution of 28 Hz). For most injections an AQT of 72 ms (SW = 14 000, SI = 2 K) was used. A delay of 30 ms was systematically imposed before the first acquistion, and normally a 30° pulse was used. Quantitative estimation of peak areas was carried out by weighing the cutouts. In some cases when differing butyllithium peaks were compared among themselves, a minor

(1) Presented in part at the Autumn Meeting of the Swiss Chemical Society, Bern, October 14, 1983.
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(4) McGarrity, J. F.; Ogle, C. A. *J. Am. Chem. Soc.*, preceding paper in this issue.
(5) Waack, R.; Doran, M. A. *J. Am. Chem. Soc.* **1969**, *91*, 2456–2461.
(6) West, P.; Waack, R.; Purmont, J. I. *J. Am. Chem. Soc.* **1970**, *92*, 840–845.
(7) Schlosser, M. "Struktur and Reaktivität Polarer Organometalle"; Springer-Verlag: Berlin 1973; p 131 (this work has not been translated).
(8) See: Wakefield, B. J. "The Chemistry of Organolithium Compounds"; Pergamon Press: New York, 1974; p 14.

(9) Holm, T. *Acta Chem. Scand., Ser. B* **1978**, *B32*, 162–166.
(10) McGarrity, J. F.; Prodolliet, J.; Smyth, T. *Org. Magn. Reson.* **1981**, *17*, 59–65.
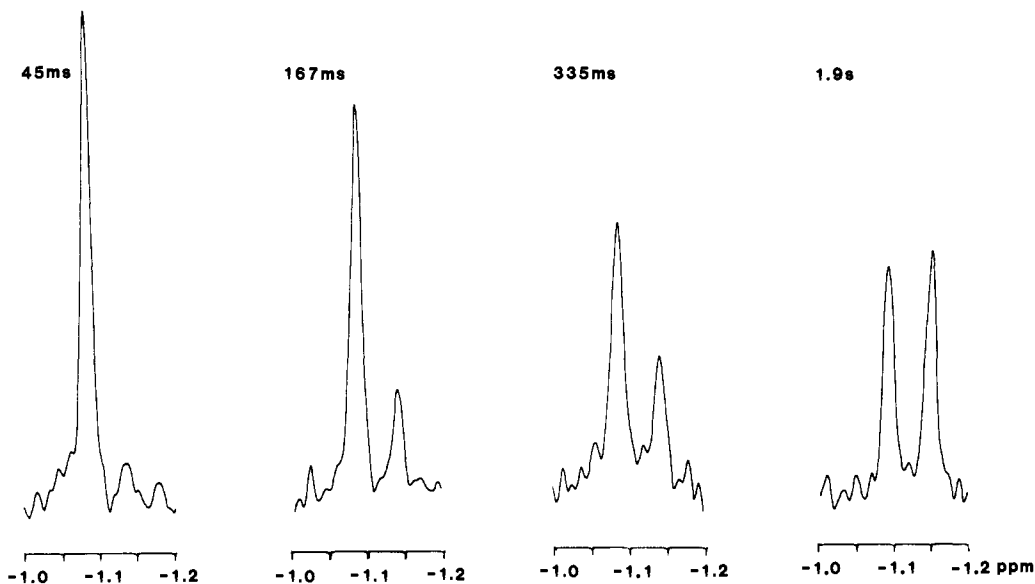(11) McGarrity, J. F.; Prodolliet, J. *J. Org. Chem.* **1984**, *49*, 4465.

**Figure 1.** Evolution of the $\alpha$-CH$_2$ resonance of butyllithium-$\beta,\beta$-$d_2$ after injection as a toluene-$d_8$ solution into THF-$d_8$ at $-84$ °C, [BuLi] = 60 mM.

Lorentzian to Gaussian line shape modification (LB = $-5$, GB = 0.5) was applied.

**Sample Preparation.** Benzaldehyde was freshly distilled; dicyclopentadiene was distilled and cracked immediately before use. Solvents were dried and butyllithium solutions were prepared as described previously.[4] The NMR tubes, truncated to a length of 11.0 cm and containing a weighed amount of pentamethylbenzene reference, were evacuated, filled with argon on a Schlenk line, and fitted with rubber septums, and then 330 $\mu$L dry THF-$d_8$ was added with a gas-tight syringe. For reactions in which the substrate was to be injected, the butyllithium was added by syringe to the cooled ($-78$ °C) THF solution in the NMR tube. The tube was transferred at $-78$ °C and wiped off before introduction in the spectrometer. The purity and concentration of the samples were checked, and modified if necessary, before removal of the rubber septum.

For experiments in which butyllithium was to be injected, the rapid injection syringe was filled so that the reagent solution (in toluene-$d_8$) did not quite reach the capillary tip. A fine lithium oxide crust invariably formed on the outside of the capillary tip after filling or after injections. This crust did not noticably affect the injections and probably helped to protect the solution from too much air contact. The solution in the capillary tip was purged several times by a series of 5-$\mu$L injections into a paper tissue in a well-ventilated hood (as the fine suspension of Li$_2$O formed is irritating), and then the volume to be injected was selected and the insert was introduced into the spectrometer. Solutions of up to 6 M butyllithium in toluene could be handled without problem (such as local conflagration of the tissue used to wipe off the capillary tip). However, solutions above 3 M in alkane solvents were much less convenient to manipulate.

## Results and Discussion

**Relaxation-Induced Errors in Kinetic Experiments.** For very rapid reactions where minimum acquisition times and delays are essential, systematic errors in the peak areas of different resonances will arise as a result of unequal longitudinal relaxation times. The solution to this problem that we previously employed, of adding a paramagnetic relaxation agent, is of course inapplicable to organolithium reactions. However, whereas the relaxation error cannot be avoided, it can be estimated. Whenever a kinetic experiment has been run with a rapid repetition of pulses, the reagents and/or products are subjected to exactly the same sequence of pulses without any injection. This relaxation experiment is run normally five times and each series of (e.g., 32) FIDs is superimposed on the previous ones to give an averaged series. The relative variations in the different species' peak areas from this series can be used to correct those in the kinetic run. We found that this procedure was necessary whenever the time interval between 30° pulses was less that 150 ms.

**Equilibration of Butyllithium Aggregates in THF.** Figure 1 portrays the evolution of the $\alpha$-CH$_2$ resonance of butyllithium-$\beta,\beta$-$d_2$ when its solution in toluene-$d_8$ is injected into THF at $-84$ °C. Initially there is only one resonance visible (at $-1.07$ ppm);

**Table I.** Equilibration of Butyllithium Aggregates after Injection of a Toluene-$d_8$ Solution into THF-$d_8$ at $-85$ °C

| time, s | % peak A[a] | % peak B[b] | concn of dimer,[c] mM |
|---------|-------------|-------------|------------------------|
| 0 | 100 | | 0 |
| 0.13 | 86 | 14 | 1.1 |
| 0.32 | 75 | 25 | 1.9 |
| 0.51 | 61 | 39 | 2.9 |
| 0.70 | 59 | 41 | 3.1 |
| 0.90 | 59 | 41 | 3.1 |
| 1.19 | 55 | 45 | 3.4 |
| 1.77 | 48 | 52 | 3.9 |
| 2.36 | 42 | 58 | 4.3 |
| 2.96 | 40 | 60 | 4.5 |
| 3.04 | 37 | 63 | 4.7 |
| 6.14 | 29 | 71 | 5.3 |
| 11.23 | 29 | 71 | 5.3 |
| 21.32 | 24 | 76 | 5.7 |
| end | 24 | 76 | 5.7 |

$^a\delta = -1.07$.  $^b\delta = -1.19$.  $^c$Total [BuLi] = 15 mM.
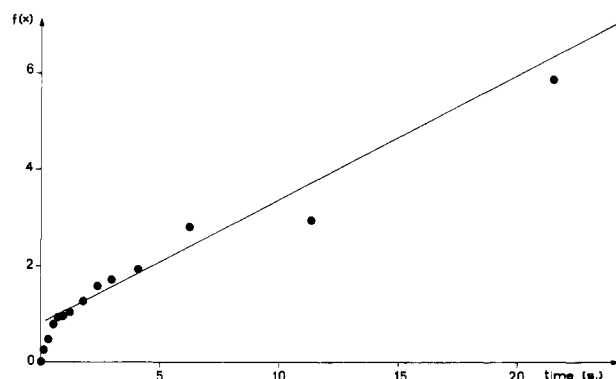


**Figure 2.** Variation of $f(x)$, defined by eq 1 in the text, with time; [x$_e$] = 5.7 mM, 2$a$ = 7.5 mM.

it decreases as that at $\delta$ $-1.19$ emerges and develops. After 2 s no further evolution in the signals was evident, and their areas corresponded to the equilibrium proportions of tetrameric butyllithium-$\beta,\beta$-$d_2$ (at $\delta$ $-1.07$) and dimeric butyllithium-$\beta,\beta$-$d_2$ (at $\delta$ $-1.19$).

The data for a more extensive equilibration where the final ratio of dimer to tetramer was 6:1 are reported in Table I. It is possible to calculate the rate of conversion of tetramer into dimer by applying eq 1 for the attainment of an equilibrium starting from one component and in which the reverse reaction is bimolecular,[12]

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$$f(x) = \ln \frac{2ax_e + x(2a - x_e)}{2a(x_e - x)} = k\frac{4a - x_e}{2x_e} \qquad (1)$$

where $a$ is the initial concentration of tetramer, and $x$ and $x_e$ are the concentrations of dimer at time $t$ and after equilibration. Figure 2 displays a plot of the data in Table I fitted to eq 1, with the assumption that all the butyllithium is initially aggregated as the tetramer ($\delta$ −1.07). It is evident that all the data points are not correlated by eq 1. Clearly there is a discontinuity in the relation: this occurs at a point which corresponds to a 35% conversion in the starting material. Such a discontinuity was observed in all the experiments carried out, independent of the final dimer–tetramer ratio. However, if one evaluates a rate constant for the conversion of tetramer to dimer from the data points that do fit eq 1, the value obtained of $k = (0.28 \pm 0.03$ s$^{-1}$)[13] agrees well with that measured by normal $^7$Li NMR exchange experiments on the equilibrated mixtures ($k = 0.25 \pm 0.05$ s$^{-1}$ at −85 °C).[4] Hence we conclude that the initial, rapid phase of the reaction is due to the irreversible conversion of hexameric butyllithium (the normal aggregation state in toluene) into tetramer and dimer, which further equilibrate at a rate consistent with eq 1.
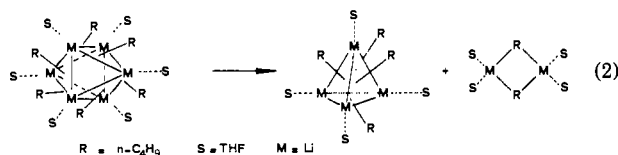


The discontinuity in the kinetic profile at 35% conversion then corresponds to complete scission of hexamer into tetramer and dimer, and consequently the hexamer and tetramer have indistinguishable $^1$H chemical shifts. This is a very reasonable thesis, as the higher aggregates have the same lithium–carbon bond type (4 center, 2 electron) and, as presumably solvation of the hexamer is instantaneous, the same number of solvent ligands per lithium atom.

Consequently we can treat the first five points in Table I according to a first-order kinetic expression and derive a value of the rate constant for conversion of hexamer into tetramer and dimer. The value obtained of $k = (0.65 \pm 0.07$ s$^{-1}$) ($r = 0.987$) is approximately twice that for the conversion of tetramer into dimer.

**Relative Reactivity of Dimeric and Tetrameric Butyllithium.** Figure 3A displays spectra obtained when cyclopentadiene is injected into a solution of butyllithium containing equal concentrations of tetramer and dimer in THF. Under these conditions all of the cyclopentadiene is metalated in less than 1 s. It is apparent that the dimer peak diminishes in intensity more rapidly than does the tetramer peak. On completion of the reaction, a new equilibrium between the two oligomers is established, corresponding to a lower overall concentration of butyllithium. The same phenomenon is noticeable in the spectra of Figure 3B, illustrating the reaction of benzaldehyde with an identical solution of butyllithium. The reaction is much more rapid than the cyclopentadiene metalation, as all the benzaldehyde is consumed in 100 ms. The initial decrease in the dimer peak relative to that of the tetramer is even more apparent than in the previous example. Close examination of the spectra also reveals a greater complexity in the reaction, to be discussed in the next section.

We conclude that in both these reactions the dimer reacts more rapidly than the tetramer and that in the initial stages the reaction of the dimer is faster than its generation from tetramer. One can roughly quantify the difference in reactivity between the butyllithium oligomers toward benzaldehyde. The variation in concentration of each species with time will be a complex function, as their relative concentrations, and hence rates of reaction, vary
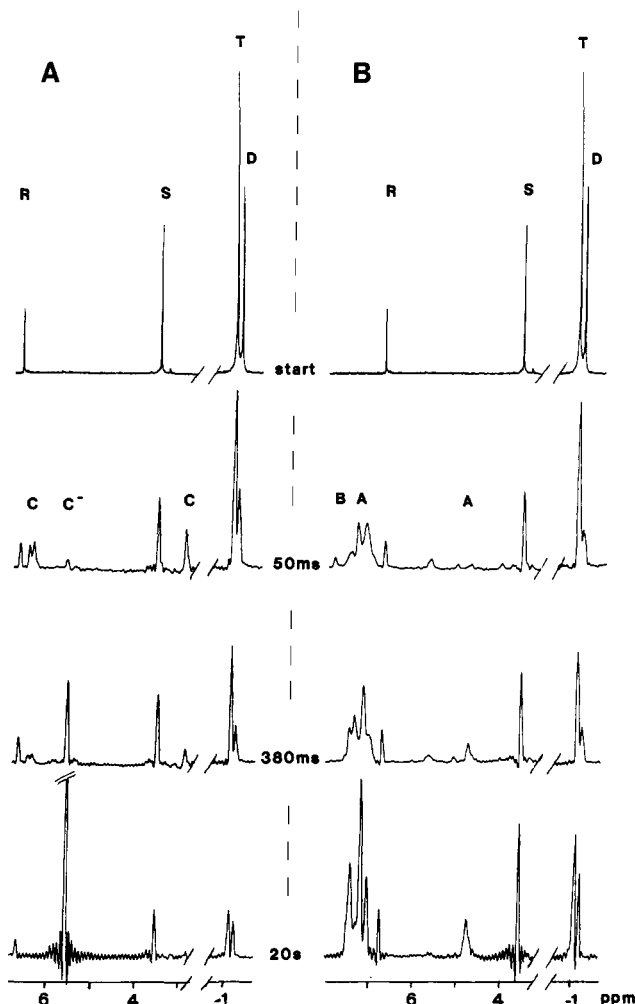
(12) Moore, J. W.; Pearson, R. G. "Kinetics and Mechanism"; John Wiley & Sons: New York, 1981; p 305. The expression is modified to account for the equilibrium A ⇌ 2B rather than A ⇌ B + C.

(13) The errors quoted in this paper are in each case one standard deviation.



**Figure 3.** RINMR spectra following the injection of cyclopentadiene (86 mM) (final concentration) (A) and benzaldehyde (97 mM) (final concentration) (B) into butyllithium-$\beta$-$d_2$ (120 mM) in THF-$d_8$ at −86 °C: R = reference, S = solvent, T = tetramer, D = dimer, C = cyclopentadiene, C$^-$ = cyclopentadienyllithium, B = benzaldehyde, A = alcoholate.

during the course of the reaction. A further complication stems from the conversion of tetramer into dimer, as the latter reacts preferentially and as the overall concentration is lowered. However, we can consider two extreme cases. In the first case where the conversion of tetramer to dimer is negligeable during time interval $dt$, we can evaluate the ratio of rate constants, as a function of the change in concentration of each species. As

$$-d[T]/dt = k_T[T][B] \text{ and } -d[D]/dt = k_D[D][B]$$

then

$$d[T]/d[D] = k_T[T]/k_D[D] \qquad (3)$$

and

$$1/k_T \log \{[T_0]/[T_t]\} = (1/k_D) \log \{[D_0]/[D_t]\} \qquad (4)$$

where [T] = concentration of tetramer, [D] = concentration of dimer, [B] = concentration of benzaldehyde, and $k_T$ = rate constant for the reaction of tetramer. From the first two spectra in Figure 3B we evaluate $k_D/k_T$ as 7. Note that a comparison of the spectrum before injection with the first spectrum after injection will be free of any relaxation-induced integration errors. We know the rate of conversion of tetramer into dimer to be 0.25 s$^{-1}$ at −85°,[4] so we can estimate the amount of conversion in 50 ms. In the second extreme case, we assume that this conversion was instantaneous and complete before the reaction with benzaldehyde, then with the starting concentrations of tetramer and dimer modified accordingly, we calculate $k_D/k_T = 11$. Obviously the quality of the data will not support a more refined analysis.
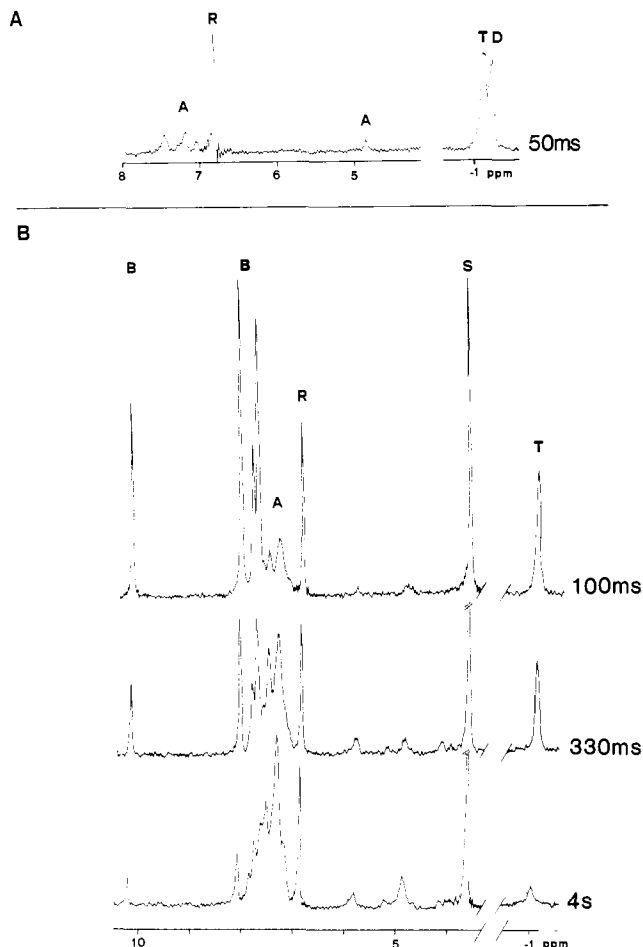
**Figure 4.** RINMR spectra following the injection (A) of benzaldehyde (14 mM) into butyllithium (81 mM) in THF-$d_8$ and (B) of butyllithium in toluene-$d_8$ (48 mM) into benzaldehyde (64 mM) in THF-$d_8$ at -85 °C. Peak attribution as in Figure 3.

We then conclude that dimeric butyllithium is more reactive toward benzaldehyde at -85 °C by factor of 10±3.

**Reaction of Butyllithium with Benzaldehyde.** Figure 4A displays spectra obtained immediately following the injection of benzaldehyde into a large excess of butyllithium pre-equilibrated in THF at -85 °C. It is apparent that the benzaldehyde is no longer present after 50 ms and that the reaction is clean. We found systematically that the reaction was too rapid to be followed even at -95 °C, when the initial concentration of butyllithium dimer was greater than that of benzaldehyde. In contrast, as seen in the spectra of Figure 4B, the reaction can be readily followed when butyllithium in toluene-$d_8$ is injected into benzaldehyde in THF-$d_8$. Furthermore, no butyllithium dimer is visible during the course of the reaction. Obviously under these conditions the dimer is consumed as rapidly as it is formed from higher oligomers. In the spectra in Figures 3B and 4B one can remark that during the reactions not only are the alcoholate aromatic resonances poorly defined but also other aliphatic resonances emerge rapidly at $\delta$ 5.74, 5.13, and 4.09 and then subside to leave the normal alcoholate methine resonance at 4.79. These extra resonances were invariably observed during the reactions whenever benzaldehyde was present in an excess relative to butyllithium dimer. In reactions where butyllithium was in an overall excess, e.g., Figure 3B, these resonances disappeared completely at the end of the reaction.

A further curious feature of the reaction emerges when one examines the concentration-time profiles of the reagents. Figure 5 displays such a profile for the experiment from which Figure 4B is derived. It is apparent that the concentration of butyllithium tetramer decreases more rapidly than can be accounted for by its dissociation into dimer. Therefore, the tetramer must also react directly with benzaldehyde. However, the aldehyde apparently
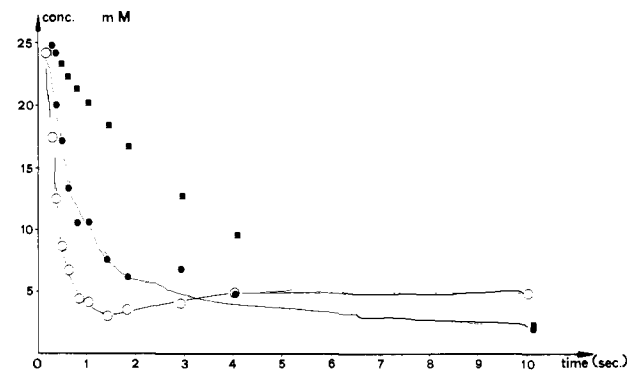


**Figure 5.** Concentration-time profiles for butyllithium (●) injected into an excess of benzaldehyde (O). The calculated curve for a first-order decay of butyllithium with $k = 0.28$ s$^{-1}$ is indicated by (■).
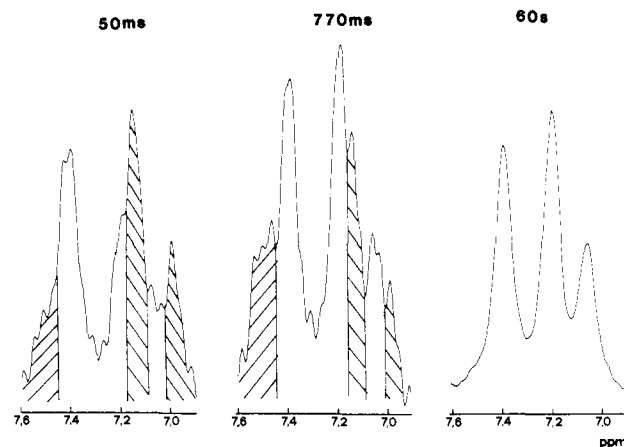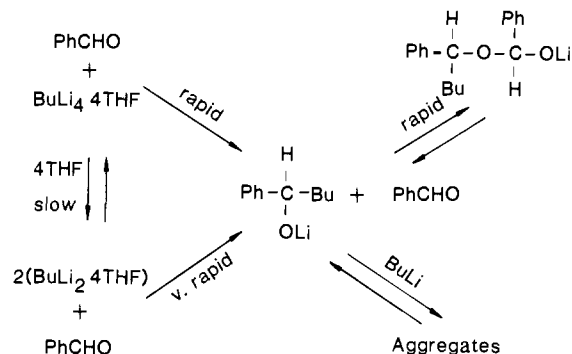


**Figure 6.** Evolution of the aromatic proton resonances of lithium 1-phenylpentanolate in the presence of dimeric butyllithium, immediately after formation.

**Scheme I**



undergoes a further reaction, as its concentration not only decreases more rapidly than that of butyllithium but also goes through a minimum before attaining its final value.

We rationalize both the additional transient peaks and the anomalous variation in benzaldehyde concentration by the reaction sequence outlined in Scheme I. The alcoholate initially formed adds reversibly onto benzaldehyde to give a hemiacetal salt.[14] Nucleophilic addition of the alcoholate can apparently compete only with that of the tetramer, as whenever excess dimer is present no side reaction is evident. As a control experiment lithium 1-phenylpentanolate was added to benzaldehyde. No addition product could be seen when the concentrations that had been used

(14) The resonance at 5.74 ppm, which we attribute to the methine proton on the hemiacetal function, is twice as intense as those at 5.13 and 4.09 ppm. Presumably the first resonance is common to both diastereomers formed (each as a pair of enantiomers), whereas the methine proton on the alcohol-derived carbon experiences very different environments in the two diastereomers.
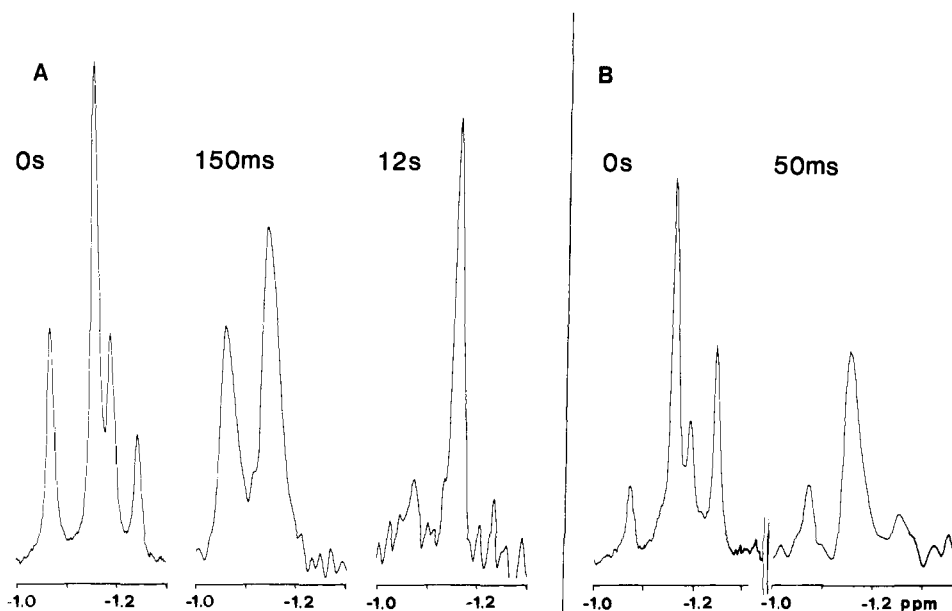
**Figure 7.** RINMR spectra of the injection of benzaldehyde into butyllithium and butyl alcohol in THF-$d_8$ at $-80$ °C: (A) [BuLi] = 149 mM, [BuOH] = 35 mM, [PhCHO] = 106 mM; (B) [BuLi] = 160 mM, [BuOH] = 54 mM, [PhCHO] = 64 mM.

in the injection experiments were employed. At higher concentrations of benzaldehyde a complex array of peaks, including those attributed to the hemiacetal salt, could be observed.[15] This result and the release of benzaldehyde at the end of the reaction illustrated in Figure 5 suggest that the alcoholate is initially formed in a more reactive, non-equilibrated state which allows it to compete successfully with butyllithium tetramer. Hitherto we refer to this state as "nascent" alcoholate. Finally the addition equilibrium can relax back to aldehyde and equilibrated ("free") alcoholate.

The enhanced reactivity of the nascent alcoholate could in principle be due to complexation with or incorporation into the butyllithium aggregates. A control experiment showed that when butyllithium is added to lithium 1-phenylpentanolate, the methine proton resonance at δ 4.79 and the ortho aromatic resonance at δ 7.48 are shifted. Furthermore, by varying the excess of butyllithium, and consequently the ratio of tetramer to dimer, one can establish to which aggregate the alcoholate is complexed. The shifts of the methine protons are at δ 4.67 and 4.60 for complexation to dimer and tetramer, respectively, and the corresponding shifts of the ortho protons are δ 7.38 and 7.33. We observe no modification in the β-methylene resonances of the tetramer and dimer. Therefore, the alcoholate does not replace an alkyllithium ligand in the aggregates, as do lithium *n*-butoxide and lithium *tert*-butoxide. The complexation observed is probably replacement of a THF solvate ligand on a lithium atom in the aggregate by the alcoholate oxygen.

For the reactions in which there was an initial excess of dimer over benzaldehyde, and which in consequence are effectively instantaneous, one can remark an evolution of the product alkoxide aromatic resonances with time. Such an evolution is portrayed in Figure 6. In the final spectrum after 60 s, the aromatic resonances correspond to the product complexed to the dimer. In the A and B spectra in Figure 6 we recognize the partial development at δ 7.48 of the ortho proton resonance of the "free" product. A different development is noticable in the resonances of the para and meta protons. Whereas in the "free" and dimer-complexed species they have essentially identical shifts at δ 7.04 (7.06) and 7.20 (7.20), the nascent alkoxide in Figure 6A has the corresponding resonances at δ 6.96 and 7.11. These latter peaks diminish rapidly with time. The ortho resonance of the nascent species at δ 7.38 is identical with that of the dimer-com-

plexed species while the methine resonance is similar to that of the "free" product.

Hence in the above experiment we have been able to identify peaks which are characteristic of "nascent" lithium 1-phenyl-pentanolate, and we believe that it is this nascent product which partakes in side reactions in competition with tetrameric butyllithium. We cannot infer the structure of this species from the spectroscopic data. Reasonable alternatives would include a completely unassociated species, implying that the normal state of lithium 1-phenylpentanolate in THF is an aggregate, or a mixed Li$_2$ aggregate in which the alcoholate has displaced an alkyl group from the dimer structure. Recent calculations by Schleyer, Houk, and co-workers indicate that in the gas-phase reaction of dimeric methyllithium with formaldehyde, such a mixed aggregate is the initially formed product.[18] We could not however observe any new peaks in the CH$_2$ butyllithium region during the lifetime of the nascent alcoholate, and so we cannot confirm this prediction. Seebach[14] has recognized the possibility of sequential incorporation of alcoholate product into alkyllithium tetramers, during the reaction of the latter with aldehydes, and has discussed the consequent variation in the reactivity and selectivity of the remaining *alkyl* ligands. Despite the inconsequential nature of the hemiacetal salt formation, we feel that the recognition of nonequilibrated species with enhanced reactivity is a significant outcome of our experiments.

**Reaction of Mixed Alkyllithium–Lithium Alkoxide Aggregates with Benzaldehyde.** We noted in the preceding paper that incorporation of alkoxy groups into aggregates of butyllithium apparently increases the polarization of the carbon–lithium bonds and, probably as a consequence, the nucleophilicity at carbon. This conclusion was tested by injecting benzaldehyde into different mixtures of aggregates. Two examples are given in Figure 7. For (approximate) quantitative estimation of the reactivity of tetramer relative to the other species, comparison was made between the spectrum prior to injection and the first immediately after injection. From the spectra in Figure 7A it is evident that the tetramer is the least reactive of the species present. After 150 ms the only species visible are the tetramer and the monoalkoxy Li$_4$ complex. The ratio of rate constants for reaction of this complex relative

(15) Analogous amide adducts to benzaldehyde have been reported,[16] and an analogous hemithioacetal salt has been proposed as an intermediate in a different synthetic sequence.[17]

(16) Comins, D. L.; Brown, J. D.; Mantlo, N. B. *Tetrahedron Lett.* **1982**, *23*, 3979–3982.
(17) Geiss, K.-H.; Seebach, D.; Seuring, B. *Chem. Ber.* **1977**, *110*, 1833–1851.
(18) Schleyer, P. v. R., personal communication.
(19) D. Seebach, Proceedings of "The Robert A. Welch Foundation Conferences on Chemical Research", Houston, November 1983.

to the tetramer is $k_1/k_T \simeq 3$. This value is a lower limit, as the methylene resonance of the butyllithium remaining at the end of the reaction has a chemical shift identical with that of the monoalkoxy mixed aggregate. In the final state the butyllithium is apparently complexed to the alcoholate product. Although we once again refuse to speculate on the nature of this particular aggregate, we note that we observed it systematically whenever the alcoholate was present in a large excess relative to the butyllithium.

In experiments involving a greater proportion of the dialkoxy mixed aggregate, we find that it has approximately the same reactivity as the dimer relative to the tetramer $k_{DA}/k_T = 7 \pm 4$. The trialkoxy aggregates appeared in other experiments to be even more reactive, but a quantitative estimation proved to be impossible.

We feel that these results may have a direct bearing on the kinetic order of butyllithium in its reactions. Butyllithium which is in a mixed $Li_4$ aggregate with three alkoxide ligands, or in a mixed $Li_2$ aggregate with one alkoxide ligand, will behave *kinetically as a monomer*. Any reaction of butyllithium in THF at room temperature will occur in the presence of enolate ions, formed by the decomposition of the solvent. According to Holm's figures,[9] a solution originally $10^{-2}$ M in butyllithium will form 3 mM acetaldehyde enolate after 30 s at 25 °C. (In our experiments no decomposition was apparent during 1 h at –78 °C.) Adventitious oxygen will give rise to alkoxides. These impurities will lead to partial order kinetics. The significance of this effect will depend of course on the concentration of oxide ligands and

also on the selectivity of the substrate toward different aggregates.

**Conclusions**

By use of the rapid injection NMR technique at temperatures between –80 and –90 °C we have shown the following: (a) The rate of the scission of hexameric butyllithium in THF into tetramer and dimer is twice that of the dissociation of tetramer into dimer. (b) Tetrameric butyllithium can react with benzaldehyde more rapidly than it dissociates into dimer. (c) Dimeric butyllithium is more reactive than the tetramer toward cyclopentadiene and benzaldehyde, and in the latter case the difference is by a factor of 10. (d) Increased substitution of alkyl ligands by alkoxy ligands in mixed $Li_4$ aggregates increases the reactivity of the remaining alkyl groups. (e) In the reaction of butyllithium with benzaldehyde, the product 1-phenylpentanolate is formed in a nonequilibrated, highly reactive state, which allows it to compete with tetrameric butyllithium as a nucleophile. Analogous effects on the reactivity and selectivity of other organometallic reagents are highly probable, and we are confident that the RINMR method will continue to provide insights into this apparently complex, but very important chemistry.

# Kinetics and Mechanism of Self-Protonation Reactions in Organic Electrochemical Processes

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**Abstract:** Anion radicals and dianions produced from the electrochemical reduction of organic molecules are basic species. In the case where the parent compound is a stronger acid than the acids present in the reaction medium, it may react with the basic species resulting from its reduction giving rise to a self-protonation electrochemical process. Determination of the reaction stoichiometry is a necessary first step in the assignment of the reaction mechanism. However, a detailed kinetic analysis is required for identifying the basic species which actually react with the parent molecule, assigning the rate-controlling steps, and determining the pertinent rate constants. This has been carried out on the examples of six molecules bearing acidic hydrogens: phthalimide, 1,3-diphenyl-2-methylindene, 4,5-methylenephenanthrene, and the three nitrophenol isomers, using linear sweep and cyclic voltammetry as well as conventional homogeneous kinetic techniques.

The electrochemical reduction of organic compounds is quite generally associated with the production of basic species in the general sense. Several types of bases and different modes of reactions with the acids present in the reaction medium may occur. A typical example is provided by the reduction of aromatic hydrocarbons or heterocycles leading to the formation of dihydrogenated products.[2]

The use of aprotic solvents such as dimethylformamide (DMF) allows the observation of two different hydrogenation pathways according to the relative strength of the proton donors (DH) present in the medium and of the basic species formed upon successive reduction of the starting molecule, i.e., the anion radical and the dianion.

In carefully dried media[2d] the two latter species are stable in the time scale of low sweep rate cyclic voltammetry, i.e., seconds, giving rise to two reversible waves corresponding to the successive formation of the anion radical and the dianion:

$$AH + e \rightleftarrows AH^{-\cdot}$$

$$AH^{-\cdot} + e \rightleftarrows AH^{2-}$$
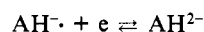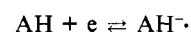
In the presence of small amounts of water, the dianion is protonated whereas the less basic anion radical is not:

$$AH^{2-} + DH \rightarrow AH_2^- + D^-$$
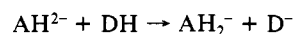
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