pendent work being carried out in his laboratories, and for stimulating discussions regarding our own studies also. Helpful discussions were also provided by Professors G. S. Hammond and J. D. Roberts, and we are pleased to acknowledge financial support from the Petroleum Research Fund of the American Chemical Society (Grant No. 1053-G1), the Arthur A. Noyes Fund, and a Du Pont Young Faculty Grant.

The Ethylenation of Secondary and Tertiary Alkyllithiums. II. Its Kinetics and the Nature of the Active Species

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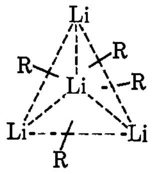
Abstract: The degree of etheration by dimethyl ether at its boiling point (−24.8°) has been measured for *n*-heptane solutions of isopropyl-, *sec*-butyl-, and *n*-butyllithium over a range of ether partial pressures. The primary alkyllithium is appreciably more strongly etherated than the secondary ones. *n*-Butyllithium approaches a limit of four ether molecules coordinated with a tetrameric organolithium aggregate. The ethylenation of isopropyl-, *sec*-butyl-, and *t*-butyllithium at −24.8° is of the first order with respect to organolithium tetramer and of the first order with respect to ethylene. With diethyl ether in 5.7- to 113-fold excess over [RLi] in *n*-pentane, the ethylenation of isopropyl- and *sec*-butyllithium is of second order in ether. With the less hindered ether, tetrahydrofuran, the rate of ethylenation of *t*-butyllithium at −40.8° in *n*-pentane passes through a maximum and later becomes inversely proportional to [THF]. Triethylamine and N-methylpyrrolidine produce a first-order catalysis of ethylenation, over a concentration range similar to that in which diethyl ether behaves in a second-order manner. 1,4-Dimethoxybutane is a strong first-order catalyst at low concentrations, but was not examined at high [ether]/[RLi] ratios. The activation parameters of the ethylenations observed lie in the range $\Delta H^{\ddagger} = 9.0$–$11.5$ kcal/mole and $\Delta S^{\ddagger} = -41.5$ to -25.4 eu/mole. The implications of these facts for diethyl ether catalysis are discussed in terms of a transition state (Chart I) containing one molecule of ethylene, four units of RLi, and $(2 + n)$ molecules of ether, where $n = 0$ or 1 and represents the prevalent degree of etheration over the range of conditions examined. The model predicts reaction orders which may vary with the case and the conditions. If RLi-initiated polymerization of styrene is a carbanion reaction, ethylenation is probably not one.

Alkyllithiums have long been known to exist as aggregates in hydrocarbon solvents by cryoscopic and ebullioscopic measurements.[1–4] The average molecular weight changes little or not at all with dilution. Ethyllithium has been shown to be in the form of tetrameric and hexameric aggregates in the vapor phase by mass spectroscopy.[5,6] Methyl- and ethyllithium have been shown to be tetrameric aggregates in the crystalline solid phase by X-ray crystallography.[7,8] Most recently methyl- and ethyllithium have been shown to be tetrameric in ethyl ether by ^{7}Li nmr;[9] the ^{7}Li–^{13}C coupling patterns[10] in methyllithium are in best agreement with the local-environment tetrahedral model[9] **1**.

Formula **1** shows four lithium atoms held together by electron-deficient bonding and occupying the corners of a tetrahedron. The alkyl groups are not at the corners, but on the faces, of the tetrahedron, so that each alkyl group has three lithium atoms for nearest neighbors and each lithium atom has three nearest neighbor alkyl groups. The organolithium tetramer has 16 bonding lithium orbitals and only four electron pairs. The exchange of lithium atoms in the tetrahedral aggregate is rapid compared to the transitions involved in nmr absorption at room temperature but is slower than these at −60°.[10]



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These considerations are fundamental to any kinetic study of alkyllithium reactions. Whatever equilibrium exists between organolithium aggregates of different sizes and the organolithium monomer, any reaction of an alkyllithium will be channeled through that species for which the most favorable mechanism exists. If that species is the same as the predominant one under the reaction conditions, whatever that species may be, the reaction will appear to be of the first order with respect to alkyllithium. A reaction channeled through a higher aggregate than the prevailing one will

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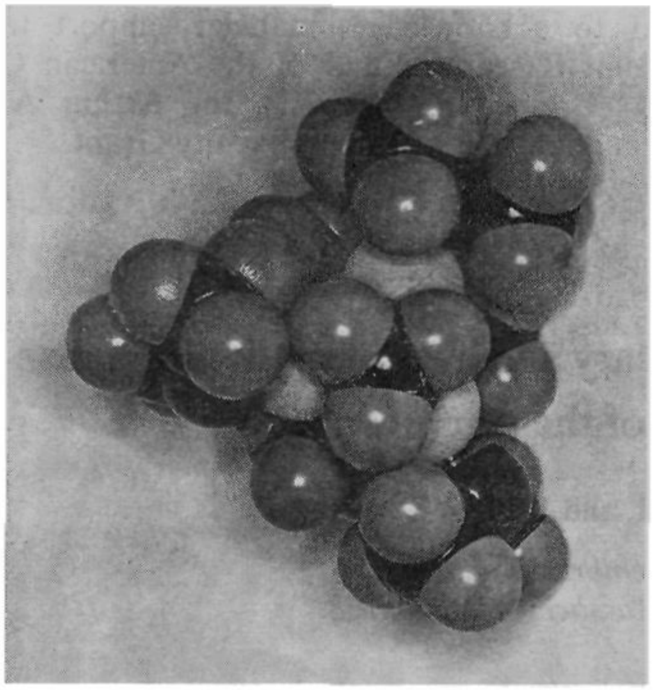

Figure 1. Model of methyllithium tetramer, complexed with four molecules of dimethyl ether. The methyl groups are shown bonded on the faces of the Li_4 tetrahedron, as in formula **1**.[9] The ethers are assigned bonding sites at the lithium atoms. The entire structure is still electron deficient, and the etheration does not destroy the four-center bonds.

appear to be of higher order with respect to RLi and a reaction channeled through a lower aggregate will appear to be of lower order. A striking example of the latter case is the initiation of the polymerization of styrene by *n*-butyllithium in benzene.[11-13] The dependence of the rate upon the sixth root of *n*-butyllithium concentration is taken to mean that the initiation reaction is an attack on styrene by *n*-butyllithium *monomer*, present in exceedingly low concentration in equilibrium with predominant hexamer in benzene solution. Similar fractional reaction orders have been observed for the reaction of ethyllithium and *t*-butyllithium with 1,1-diphenylethylene.[14] Thus rate studies can reveal, in principle, the size of the molecular aggregate which is involved in a particular reaction, when the rate studies are taken in conjunction with a knowledge of the prevailing state of aggregation in solution.

Reactions of organolithium reagents are also strongly dependent on catalysis by basic ligands.[15] In styrene polymerization, small amounts of ethers accelerate the *initiation* so greatly that it ceases to be rate determining. The rate of the *propagation* reaction depends upon the ratio of concentrations of ether and alkyllithium, but in a different manner from the initiation reaction.[16] Catalytic effects of tetrahydrofuran following no regular kinetic order were observed in the addition of *n*-butyllithium to 1,1-diphenylethylene.[17] Despite the formal similarity of this reaction to the initiation of styrene polymerization, it was impossible to establish a definite order of the reaction with respect to butyllithium. Indeed at a fixed THF concentration the dependence of rate on [RLi] at low concentrations became negative.

These and other observations show that one must consider a wide range of possibilities for the active participant in any organolithium reaction, and that the establishment of the reaction order with respect to each participant is by no means trivial.

Results and Discussion

The Extent of Etheration of the Alkyllithiums. Complexing of alkyllithiums with triethylamine has been studied previously by freezing-point depression[18] and the formation of complexes between *n*-butyllithium and ethyl ether has been studied by nmr, vapor pressure lowering, and dielectric constant measurements.[19] Such studies have led to the important conclusion that the predominant *n*-butyllithium etherate contains RLi and ether units in the ratio of 2:1 and that therefore etheration does not break up the electron-deficient organolithium aggregate. The same conclusion follows from the tetrameric character of alkyllithiums in ether solvents.[9] Although Eastham and coworkers have considered the unit $[(RLi)_2 \cdot \text{ether}]$ to be the fundamental building block of the etherated organolithium species, the actual molecular weight measurements have never indicated such small aggregates to be prevalent in any solution of a saturated organolithium compound.[20]

The organolithium tetramer of structure **1** would still have eight fewer bonding electrons than orbitals after coordination with four ether molecules, and therefore could continue to be held together by electron-deficient bonding. Figure 1 shows a model of structure **1** ($R = CH_3$) further coordinated at the lithium atoms with four molecules of dimethyl ether.

Since we were mainly concerned here with secondary and tertiary alkyllithiums, it was desirable to find a method of directly measuring the extent of etheration, applicable to low temperatures where ether was not destroyed. This was accomplished by adding increments of gaseous dimethyl ether to *n*-heptane solutions of the alkyllithiums at −25°, the apparatus being thermostated by a jacket of refluxing dimethyl ether. Plots of vapor pressure against equivalents of ether added all showed initial lags in the development of vapor pressure, followed by a rising line approaching the slope of the regular Henry's law plot for pure heptane, but displaced from it by the amount of ether bound to the organolithium aggregate. Figures 2, 3, and 4 show the curves for dimethyl ether with 1.115 *N* isopropyl-, 1.85 *N sec*-butyl, and 1.69 *N n*-butyllithium, respectively. The degree of etheration of the alkyllithium can be read from these graphs as the horizontal distance from the points back to the dashed line. In all three cases the first molecule added per $(RLi)_4$ aggregate is tightly bound at these concentrations. When four dimethyl ether molecules have entered the solution per tetrameric aggregate, the numbers of ether molecules bound are about 2.2 for isopropyl-, 2.5 for *sec*-butyl-, and 3.6 for *n*-butyllithium. The slightly greater etheration of the *sec*-butyl than of the isopropyl compound reflects the greater concentration of the former solution, and not a difference in electrophilic character of the two reagents.

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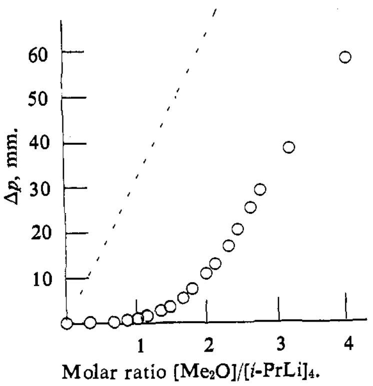

Figure 2. Extent of complexing of dimethyl ether with 1.115 *N* isopropyllithium at −24.8° in *n*-heptane. Dashed line, dimethyl ether in pure *n*-heptane, no RLi present.

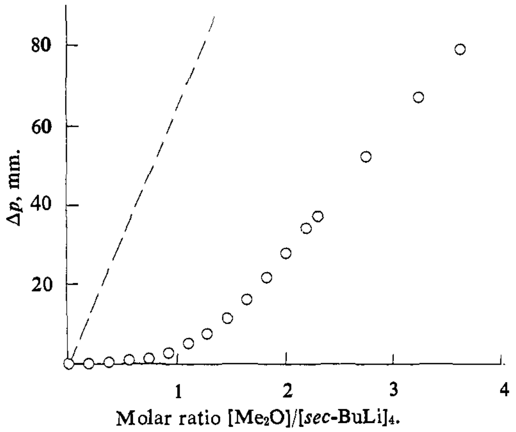

Figure 3. Extent of complexing of dimethyl ether with 1.85 *N sec*-butyllithium at −24.8° in *n*-heptane. Dashed line, dimethyl ether in pure *n*-heptane, no RLi present.

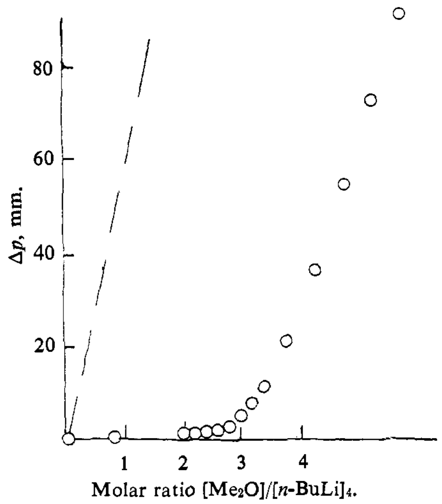

Figure 4. Extent of complexing of dimethyl ether with 1.69 *N* *n*-butyllithium at −24.8° in *n*-heptane. Dashed line, dimethyl ether in pure *n*-heptane, no RLi present.

Reproducibility of Rates—A Transition Metal Effect. When we first began to measure the rates of ethylenation of secondary and tertiary alkyllithiums, although first-order rate behavior was observed, the values of the rate constants themselves were subject to unexplained variations over about a 20-fold range. This was eventually traced to the use of a nichrome wire stirrer in preparing the lithium sand from which the alkyllithium was made. As soon as this stirrer was replaced by a Teflon stirrer for the preparation of the lithium, the subsequent ethylenations became reproducible and the rates dropped to a small fraction of what they had been. This identification of the responsible factor was confirmed by returning to the nichrome stirrer after a long series of reproducible runs; the fast and unreliable rates were again encountered.

Attempts were made to influence the rate of ethylenation by introducing transition metal compounds after the preparation of the alkyllithium from Teflon-stirred lithium sand. These attempts were uniformly unsuccessful. In experiments with *t*-butyllithium and 4.8 *M* ether at −40.8°, addition of nichrome, nickel oxide, ferric, cobaltous, cupric, titanium, and dicyclopentadienyltitanium chlorides, manganese dioxide, and chromic bromide all gave rates of ethylenation within an extreme variation of twofold. It seems likely that when some nichrome component is actually present in the lithium (the stirrer was pitted after use) the formation of *t*-butyllithium is attended by the formation of a transition metal–organic compound which affects the rate of ethylenation. In view of the ease with which exchange takes place in the electron-deficient organometallic aggregates, it is an intriguing possibility that some of the lithium tetrahedra under these conditions may have a transition metal substituted for one of the lithiums. This could be a way of stabilizing an otherwise very unstable alkyl–transition metal compound capable of superposing some Ziegler polymerization upon the ethylenation of the alkyllithiums.

Kinetic Procedure. Ethers, amines, and transition metals are not the only foreign materials that may affect the rate of ethylenation. To avoid lithium alkoxides, which readily become built into the alkyllithium aggregates,[9] all our alkyllithiums to be used for rate measurements were prepared in pentane solution in a drybox, sealed in bottles under argon before removal, and then introduced by syringe into the reaction vessel. For use in converting measurements of the volume and pressure of ethylene into concentrations in solution, the solubility of ethylene was determined in pentane–ether and pentane–THF mixtures over the entire range of composition. The apparatus used for these measurements, for the determinations of the extent of etheration, and for the rates of ethylene uptake by the solutions containing alkyllithium and ether, is described in the Experimental Section. Each kinetic run was started by mixing a solution of alkyllithium in pentane with a solution of the ether in pentane, each solution having been separately saturated with ethylene at the temperature of the reaction. Thus the appreciable heat of solution of ethylene was dissipated before the reaction began. In the absence of ether the solubility of ethylene in the alkyllithium solutions was the same as in pure pentane. Tables I and II record the solubilities in the solvent mixtures.

Order with Respect to Alkyllithium. The greatest number of runs were made by measuring the absorption of ethylene from a gas buret at 1 atm pressure over a vigorously stirred solution of isopropyl-, *sec*-butyl-, or *t*-butyllithium in pentane containing an ether. Under these conditions in all experiments $\log(V - V_\infty)$

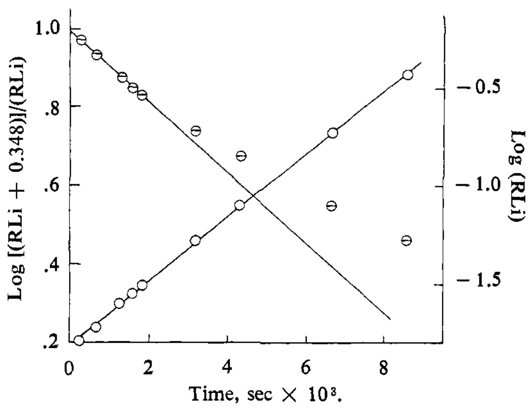

Figure 5. Order of the ethylenation reaction with respect to ethylene: $[Et_2O] = 5.74$ *M* in 250 ml of ether–pentane; [*sec*-BuLi] = 0.620 *N*; total moles of ethylene initially, 0.2417. Ethylene pressure declined during run from 785 to 332 mm, [RLi] from 0.620 to 0.0529 *N*: open circles (left-hand ordinate scale), plotted as a second-order reaction between RLi and ethylene; barred circles (right-hand ordinate scale); plotted as a first-order reaction in RLi. The points plotted are randomly selected from 100 experimental readings showing no appreciable scatter.

was a linear function of time until *V*, the remaining volume of ethylene, became too close to V_∞, the final ethylene volume, for accurate determination of the difference. Experimentally this shows that the maintenance of saturation of the solution with ethylene is rapid and never rate determining. It also establishes a highly significant fact about the mechanism: *the ethylenation rate is controlled by something that happens to the (RLi) aggregate prevalent in the solution, and not to monomeric RLi nor any other aggregate in equilibrium with it.* The reaction is therefore of first order with respect to $(RLi)_4$.

Table I. Solubility of Ethylene at 1 Atm Pressure in Ether–Pentane Mixtures

	Ethylene solubility, *M*			
Et_2O, *M*	−11.7°	−24.8°	−40.8°	−47.7°
0		0.359		
0.955		0.363		
1.91		0.389		
2.39		0.396		
2.86		0.400		
3.34		0.404		
3.82		0.416		
4.76		0.418		
5.13	0.286	0.428	0.704	0.880
5.78		0.432		
6.82		0.432		
7.64		0.439		

Table II. Solubility of Ethylene at 1 Atm Pressure in *n*-Pentane–Tetrahydrofuran Mixtures

	Ethylene solubility, *M*		
THF, *M*	−11.7	−24.8	−40.8
0			0.572
0.328	0.240	0.365	0.583
0.379			0.590
0.949			0.605
1.90			0.639
3.79			0.658
6.64			0.653
10.43			0.615

Order with Respect to Ethylene. In view of the fractional order of the initiation of styrene polymerization by alkyllithiums[11–13,21] we thought it possible that our monomeric alkyllithiums might be so much more reactive than the tetramers toward ethylene that the rate of ethylenation would be determined by the rate of deaggregation of $(RLi)_4$. If such were the case it would mean that the ethylene was a highly efficient scavenger for RLi monomer, and the rate would be independent of ethylene concentration. The way to test this is to follow the rate of the reaction, not by the decline in ethylene volume at constant pressure, but by the decline in ethylene pressure at constant volume. Under the latter set of conditions the ethylene concentration in the solution is not constant during a run, and the participation of this reactant in the rate-determining step can be tested.

In an apparatus combining the pressure-measuring feature used in the etheration measurements with the double preequilibration used in the previous rate measurements, 16 ethylenations were followed by the change in ethylene pressure in *n*-pentane solutions containing different concentrations of added diethyl ether at −24.8°. Six of the runs were with isopropyllithium, eight with *sec*-butyllithium, and two with *t*-butyllithium. The drop in ethylene pressure during the measurement was usually about 50%, but sometimes as high as 70%, while the alkyllithium became completely consumed. Up to 90% disappearance of the alkyllithium, good adherence was observed to the requirement of a second-order reaction that the logarithm of y/x, the ratio of reactant concentrations, be a linear function of time (see Appendix for the treatment of a second-order reaction in which one reactant is distributed between liquid and vapor phases).

Figure 5 shows a rate measurement of this kind in a solvent of 100 ml of pentane and 150 ml of ether at −24.8°, in which the *sec*-butyllithium concentration was followed from 0.620 down to 0.053 *M*, and the ethylene pressure over the solution fell from 785 to 292 mm. The second-order plot is linear throughout its course. For comparison a plot is shown of log [RLi] *vs. t*, which should have been linear if ethylene were not involved in the rate-determining step. This plot is far from straight.

It follows from these rate measurements that the ethylenation of isopropyl-, sec-butyl-, and t-butyllithium is a direct reaction between ethylene and an etherated alkyllithium tetramer, and that dissociation of the molecular aggregate is not the rate-determining step.

Order with Respect to Ether. The measurement of ethylenation rate was somewhat more conveniently carried out at constant pressure, by measuring the change in ethylene volume, than by the method just described. Therefore, having established that the reaction is of first order in ethylene, we carried out the later runs at constant ethylene pressure, determined the pseudo-first-order rate constant with respect to alkyllithium, and converted it to a second-order rate constant by dividing by the measured ethylene solubility under the conditions of the reaction. In this way a number of ethylenation rates were measured for isopropyl- and *sec*-butyllithium in the presence of different

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(21) For a critical discussion of the kinetics of these reactions see ref 4a, especially pp 487–489.

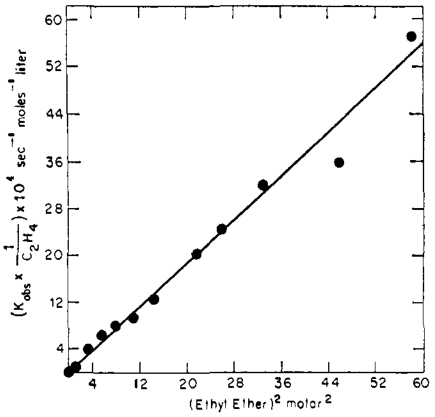

Figure 6. The dependence of the rate of addition of isopropyllithium to ethylene on ethyl ether concentration at −24.8°.

concentrations of diethyl ether and for *t*-butyllithium with tetrahydrofuran. The measured rate constants with diethyl ether are shown in Table III and their dependence on ether contrations is shown in Figures 6 and 7. The ethylenation of isopropyl- and *sec*-butyllithium in the presence of diethyl ether proceeds at a rate much more nearly proportional to the square than to any other power of the ether concentration. In the experiments on which this conclusion is based the ether was always present in excess over the organolithium reagent, the ratio (Ether/RLi) being from 5.7 to 113.

Table III. Rate of Reaction of Ethylene with Alkyllithiums in *n*-Pentane Containing Diethyl Ether, at −24.8°

[RLi], *N*	[Et$_2$O], *M*	[C$_2$H$_4$], *M* solubility	$k_1 \times 10^4$, sec^{-1}	$k_2 \times 10^4$, M^{-1} sec^{-1} av	% of total reaction followed
		Isopropyllithium			
0.169	0	0.359	0	0	
0.169	0.955	0.363	0.458	1.22	84
			0.433		86
0.169	1.91	0.389	1.59	4.01	94
			1.53		94
0.169	2.39	0.396	2.44	6.22	95
			2.49		95
0.169	2.86	0.400	3.07	7.93	95
			3.27		93
0.169	3.34	0.404	3.78	9.20	95
			3.65		94
0.169	3.82	0.416	5.43	12.5	93
			4.98		94
0.169	4.76	0.418	8.30	20.4	88
			8.73		94
0.135	5.13	0.433	10.5	24.5	92
			10.7		92
0.135	5.78	0.432	14.2	32.4	95
			13.8		95
0.966	6.82	0.432	14.7	35.6	84
			16.1		94
0.0676	7.64	0.439	26.0	56.5	94
			23.6		96
		sec-Butyllithium			
0.153	1.28	0.380	1.12	3.03	94
			1.19		96
0.153	2.57	0.398	3.40	8.82	83
			3.62		90
0.153	3.86	0.413	7.46	18.0	96
			7.42		94
0.153	5.13	0.425	11.3	27.0	95
			11.7		94
0.153	6.42	0.429	16.8	39.5	96
			17.1		94

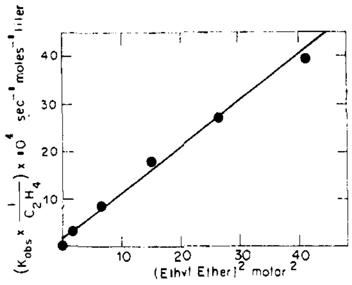

Figure 7. The dependence of the rate of reaction of *sec*-butyl lithium with ethylene on ethyl ether concentration at −24.8°.

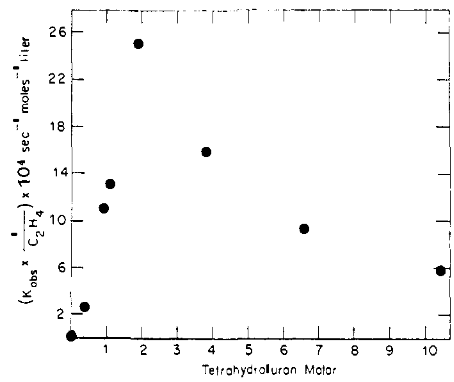

Figure 8. Rate of reaction of *t*-butyllithium with ethylene catalyzed by tetrahydrofuran at −40.8°.

Rate Maximum with Tetrahydrofuran. A series of rate measurements carried out with *t*-butyllithium in pentane at −40.8° in the presence of different concentrations of tetrahydrofuran proved especially informative. As shown in Table IV and Figure 8, the rate of ethylenation at first increased rapidly with THF concentration, but passed through a maximum at about 2 *M* THF, declining steadily as the concentration of tetrahydrofuran was further increased. Examination of the curve of Figure 8 in sections reveals that the lower end of the declining portion of the curve corresponds to rate con-

Table IV. Rate of Reaction of Ethylene with 0.242 *N* *t*-Butyllithium in *n*-Pentane Containing Tetrahydrofuran at −40.8°

THF, *M*	[C$_2$H$_4$], *M* solubility	$k_1 \times 10^4$, sec^{-1}	$k_2 \times 10^4$, M^{-1}sec^{-1}av	% of total reaction followed
0	0.572	0	0	
0.38	0.590	1.51	2.64	96
		1.61		95
0.95	0.605	6.80	10.9	95
		6.43		96
1.12	0.615	7.97	13.0	91
1.90	0.639	15.8		96
		15.9	24.8	95
3.79	0.658	10.4		96
		10.7	16.0	97
6.64	0.653	6.05	9.37	95
		6.19		96
10.4	0.615	3.54		96
		3.45	5.68	96

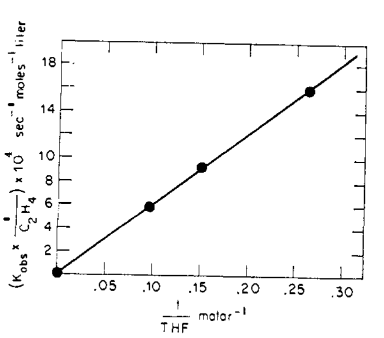

Figure 9. The rate of reaction of *t*-butyllithium with ethylene at −40.8° *vs.* 1/[THF] (at high concentration of tetrahydrofuran).

stants which are inversely proportional to the concentration of tetrahydrofuran (Figure 9). This is what would be expected if the ethylene reacts *at the last vacant coordination site of the etherated tetramer*, this site being blocked off when the activating ligand is itself a strongly basic and unhindered molecule. This result is consistent with a mechanism involving coordination of the reacting ethylene at one of the lithium atoms of the aggregate, followed by its insertion into the C–Li bond which has been activated by the double coordination of ether on the aggregate. A similar effect of THF has been observed in the propagation rate of styrene polymerization.[15,22]

t-Butyllithium was considered a convenient organolithium compound for this type of study because it is less reactive toward ethylene than isopropyllithium and the entire range of tetrahydrofuran concentrations could be studied without encountering inconveniently rapid reactions at −40.8°. Work is now in progress to extend such measurements to secondary organolithiums at still lower temperatures. Presumably the reason for the absence of self-inhibition by diethyl ether is a combination of its lesser basicity and greater bulkiness compared with THF, resulting in low values of the successive etheration equilibrium constants, with the result that a maximum relative concentration of the triply etherated tetramer is never attained with available concentrations of diethyl ether.

Other Catalyzing Ligands. A preliminary experiment with 1,2-dimethoxyethane (glyme) in place of ether failed to show the expected catalysis of ethylenation. However, a *first-order* catalytic effect was shown by 1,4-dimethoxybutane on the ethylenation of isopropyllithium, indicated in Table V and Figure 10. By comparison with the other catalytic ethers this first-order activation appears to be due to the functioning of 1,4-dimethoxybutane as a bifunctional ligand which occupies two sites on an organolithium tetramer. Possibly glyme is effectively bidentate only when the two coordination sites are on the same atom, which is not true of $(RLi)_4$. This series was not carried to high concentrations of ether, and it is not known whether a saturation effect like that with THF would be observed at higher concentration, or not.

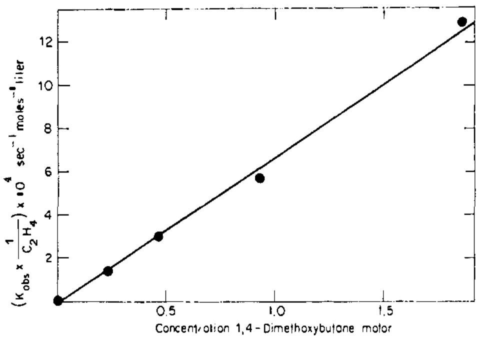

Figure 10. The dependence of the rate of reaction of isopropyllithium with ethylene on the concentration of 1,4-dimethoxybutane at −24.8°.

Two amines, triethylamine and N-methylpyrrolidine, also proved capable of catalyzing the addition of ethylene to *sec*-butyllithium, as shown in Table VI and Figures 11 and 12. These studies showed no indication of double ligancy being required, and no sign of self-inhibition. Again the difference between these amines and the ethers may reside in quantitative differences in their complexation equilibria with the alkyllithium aggregates. In these cases we do not have constant-volume runs showing the order with respect to ethylene, and hence no actual proof that the amine solvation is

Table V. Rate of Reaction of Ethylene with Isopropyllithium at −24.8° in the Presence of 1,4-Dimethoxybutane[a]

[*i*-PrLi], N	[DMB], M	$k_1 \times 10^4$, sec^{-1}	$k_2 \times 10^4$, M^{-1}sec^{-1}av	% of total reaction followed
0.126	0.0238	0.53	1.43	94
		0.50		91
0.126	0.0475	1.07	2.88	86
		1.01		92
0.125	0.0943	1.97	5.57	90
		2.06		90
0.123	0.1861	4.57	12.4	88
		4.40		88

[a] Ethylene solubility, −0.361 ± 0.002 M.

Table VI. Rate of Reaction of Ethylene with *sec*-Butyllithium at −24.8° in the Presence of Tertiary Amines

		$k_1 \times 10^4$, sec^{-1}		
[RLi], N	[Amine], M	Triethylamine	N-Methylpyrrolidine,	% of total reaction followed
0.127	0.587		1.30	96
			1.39	93
0.120	0.953	1.62		88
		1.74		89
0.127	1.17		2.81	97
			2.89	97
0.120	1.90	2.65		95
		2.51		94
0.127	2.35		4.91	93
			4.81	90
0.120	3.81	5.28		93
		5.34		91
0.127	4.70		9.06	92
			9.36	94
0.120	4.76	6.58		78
		6.43		93
0.102	6.46		12.7	95
			11.5	94

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(22) F. A. Settle, M. Haggerty, and J. F. Eastham [*J. Amer. Chem. Soc.*, **86**, 2077 (1964)] have observed that an insoluble complex can be precipitated by the addition of THF to *t*-butyllithium. Precipitation of the organolithium from our solutions containing the higher concentrations of THF would also be a possible reason for the rate depression. However, regular inspections of the reacting solutions never revealed any precipitate; evidently at the concentrations of our experiments the limit of solubility had not been reached.

Table VII. Effect of Temperature on Ethylenation Rates

[RLi], N	Ligand (M)	$k_4 \times 10^4$ [a]			
		−47.7°	−40.8°	−24.8°	−11.7°
i-PrLi, 0.40	Et_2O (5.13)	0.123	0.218	0.929	2.57
sec-BuLi, 0.46	Et_2O (5.13)	0.133	0.270	0.668	0.983
i-PrLi, 0.40	THF (0.328)		92.2	335	885
i-PrLi, 0.38	$CH_3O(CH_2)_4OCH_3$, (0.186)		20.6[b]	66.4[b]	253[b]
sec-BuLi, 0.36	Et_3N (3.81)		0.826[b]	3.95[b]	15.0[b]

[a] k_4 is the fourth-order constant for reaction of one $(RLi)_4$, one ethylene, and two ligand molecules. [b] The k's for DMB and Et_3N catalysis are third-order constants (one $(RLi)_4$, one ethylene, one ligand).

not bringing about a rate-determining cleavage of the alkyllithium tetramer; however, it would be consistent to view the amines as ligands, more bulky than ethers but also more basic, which coordinate with $(RLi)_4$ to an unfavorable equilibrium and in so doing impart greater reactivity than does an ether molecule. In this connection it seems likely that the strong activating effects of tetramethylethylenediamine[23] on organolithium compounds may in fact be by way of conversion of the aggregate to a tightly chelated monomer with strong ionic character.

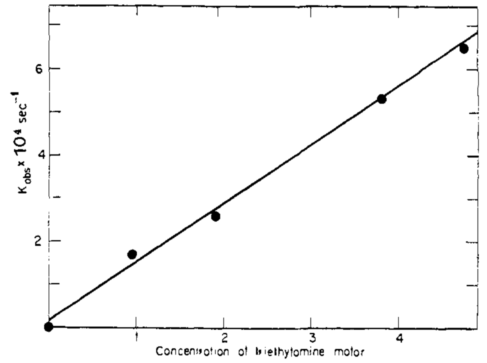


Figure 11. Rate of reaction of *sec*-butyllithium with ethylene *vs.* the concentration of triethylamine at −24.8°.

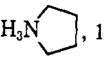
Temperature Coefficients. By jacketing the apparatus with different liquids (Experimental Section) we measured several of the rates over the range of temperature from −11.7 to −40.8 or −47.7°. Table VII lists the results and Table VIII shows the calculated activation parameters. The solubility of ethylene is reduced to less than half by raising the temperature from −40.8 to −11.7°, so that the pseudo-first-order rate constants are less responsive to temperature than the second-order constants.

Table VIII. Activation Parameters for Ethylenation

Alkyllithium	Ligand	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, kcal/(deg mole)
Isopropyl	Et_2O	9.4	−41.5
sec-Butyl	Et_2O	9.3	−39.5
Isopropyl	THF	9.0	−30.6
Isopropyl	DMB	10.0	−27.5
sec-Butyl	Et_3N	11.5	−25.4

Rate Comparisons. Despite the different kinetic orders of catalysis involved, it is of interest to compare the rates of ethylenation attained with different catalysts and different alkyllithiums. Table IX compares the observed rates of ethylenation in the presence of 1 M ligand, regardless of the order of its effect on the rate. The order of reactivity of the alkyllithiums is secondary > tertiary, and the order of effectiveness of catalysts is tetrahydrofuran > 1,4-dimethoxybutane > triethylamine > N-methylpyrrolidine > diethyl ether. However, it appears that, at all concentrations above 4 M, diethyl ether, because it enters the reaction to the second power, is more strongly catalytic than either of the amines. Tetrahydrofuran, though by far the most powerful catalyst, has a ceiling effectiveness at 2 M. 1,4-Dimethoxybutane at 2 M is more effective than diethyl ether at any attainable concentration, despite the lower kinetic order of the catalysis by the former.

Table IX. Relative Rates of Ethylenation at −24.8° of Alkyllithiums with 1 M Ligand

Ligand, kinetic order	Isopropyl	*sec*-Butyl	*t*-Butyl
[Ethyl ether], 2	1	1	[0.3][a]
[THF], 2	355		~46
DMB, 1	71		
Et_3N, 1		4	
, 1	2.5		

[a] Compared at $[Et_2O]$ = 4.78 M.

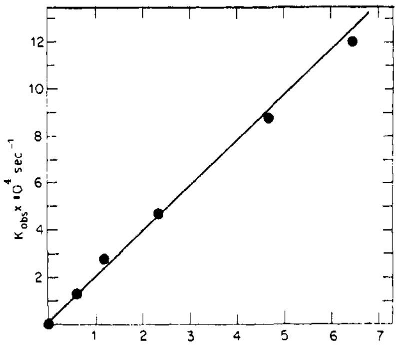


Figure 12. The rate of reaction of *sec*-butyllithium with ethylene *vs.* the concentration of N-methylpyrrolidine at −24.8°.

Characteristics of the Mechanism. Over-all, the ethylenation is a fourth-order reaction, first order in alkyllithium tetramer, second order in ether, and first order in ethylene. Chart I indicates some of the pre-equilibria and possible rate-determining steps. The simplified over-all dissociation equilibrium (a) is important only as a path for exchanges in the tetramer. Its rate constants are at least of the order of 10 sec^{-1},

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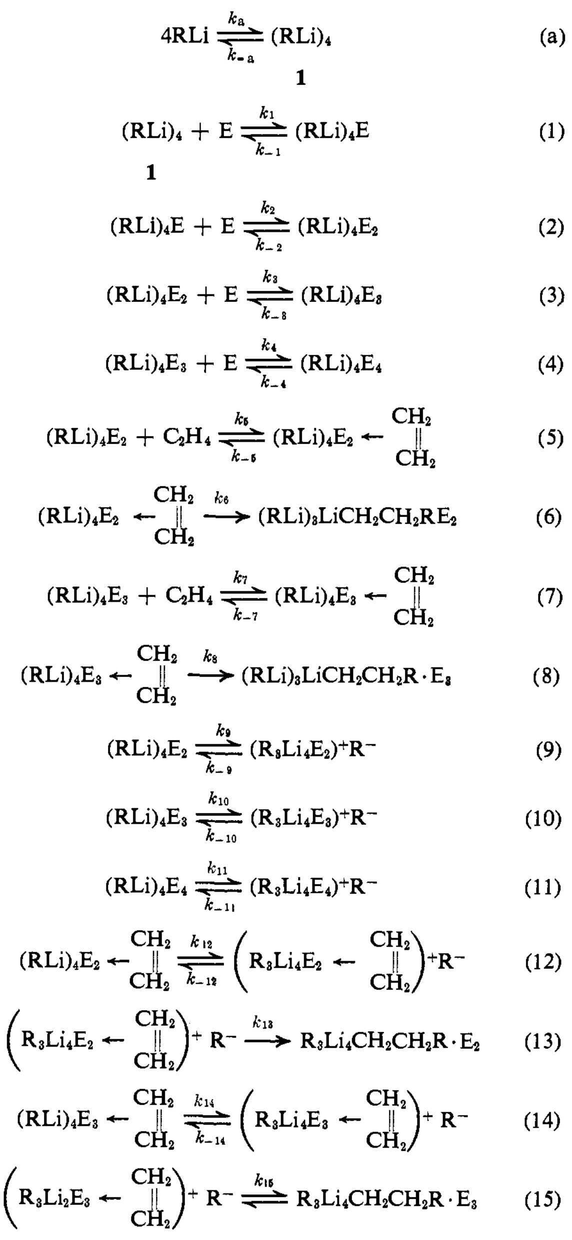
(23) Reference 15, footnotes 5 and 6.

Chart I



$$4\mathrm{RLi} \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} \underset{\mathbf{1}}{(\mathrm{RLi})_4} \qquad \text{(a)}$$

$$\underset{\mathbf{1}}{(\mathrm{RLi})_4} + \mathrm{E} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (\mathrm{RLi})_4\mathrm{E} \qquad (1)$$

$$(\mathrm{RLi})_4\mathrm{E} + \mathrm{E} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} (\mathrm{RLi})_4\mathrm{E}_2 \qquad (2)$$

$$(\mathrm{RLi})_4\mathrm{E}_2 + \mathrm{E} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} (\mathrm{RLi})_4\mathrm{E}_3 \qquad (3)$$

$$(\mathrm{RLi})_4\mathrm{E}_3 + \mathrm{E} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} (\mathrm{RLi})_4\mathrm{E}_4 \qquad (4)$$

$$(\mathrm{RLi})_4\mathrm{E}_2 + \mathrm{C_2H_4} \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} (\mathrm{RLi})_4\mathrm{E}_2 \leftarrow \begin{matrix}\mathrm{CH_2}\\ \|\\ \mathrm{CH_2}\end{matrix} \qquad (5)$$

$$(\mathrm{RLi})_4\mathrm{E}_2 \leftarrow \begin{matrix}\mathrm{CH_2}\\ \|\\ \mathrm{CH_2}\end{matrix} \xrightarrow{k_6} (\mathrm{RLi})_3\mathrm{LiCH_2CH_2RE_2} \qquad (6)$$

$$(\mathrm{RLi})_4\mathrm{E}_3 + \mathrm{C_2H_4} \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} (\mathrm{RLi})_4\mathrm{E}_3 \leftarrow \begin{matrix}\mathrm{CH_2}\\ \|\\ \mathrm{CH_2}\end{matrix} \qquad (7)$$

$$(\mathrm{RLi})_4\mathrm{E}_3 \leftarrow \begin{matrix}\mathrm{CH_2}\\ \|\\ \mathrm{CH_2}\end{matrix} \xrightarrow{k_8} (\mathrm{RLi})_3\mathrm{LiCH_2CH_2R\cdot E_3} \qquad (8)$$

$$(\mathrm{RLi})_4\mathrm{E}_2 \underset{k_{-9}}{\overset{k_9}{\rightleftharpoons}} (\mathrm{R_3Li_4E_2})^+\mathrm{R}^- \qquad (9)$$

$$(\mathrm{RLi})_4\mathrm{E}_3 \underset{k_{-10}}{\overset{k_{10}}{\rightleftharpoons}} (\mathrm{R_3Li_4E_3})^+\mathrm{R}^- \qquad (10)$$

$$(\mathrm{RLi})_4\mathrm{E}_4 \underset{k_{-11}}{\overset{k_{11}}{\rightleftharpoons}} (\mathrm{R_3Li_4E_4})^+\mathrm{R}^- \qquad (11)$$

$$(\mathrm{RLi})_4\mathrm{E}_2 \leftarrow \begin{matrix}\mathrm{CH_2}\\ \|\\ \mathrm{CH_2}\end{matrix} \underset{k_{-12}}{\overset{k_{12}}{\rightleftharpoons}} \left(\mathrm{R_3Li_4E_2} \leftarrow \begin{matrix}\mathrm{CH_2}\\ \|\\ \mathrm{CH_2}\end{matrix}\right)^+\mathrm{R}^- \qquad (12)$$

$$\left(\mathrm{R_3Li_4E_2} \leftarrow \begin{matrix}\mathrm{CH_2}\\ \|\\ \mathrm{CH_2}\end{matrix}\right)^+ \mathrm{R}^- \xrightarrow{k_{13}} \mathrm{R_3Li_4CH_2CH_2R\cdot E_2} \qquad (13)$$

$$(\mathrm{RLi})_4\mathrm{E}_3 \leftarrow \begin{matrix}\mathrm{CH_2}\\ \|\\ \mathrm{CH_2}\end{matrix} \underset{k_{-14}}{\overset{k_{14}}{\rightleftharpoons}} \left(\mathrm{R_3Li_4E_3} \leftarrow \begin{matrix}\mathrm{CH_2}\\ \|\\ \mathrm{CH_2}\end{matrix}\right)^+ \mathrm{R}^- \qquad (14)$$

$$\left(\mathrm{R_3Li_2E_3} \leftarrow \begin{matrix}\mathrm{CH_2}\\ \|\\ \mathrm{CH_2}\end{matrix}\right)^+ \mathrm{R}^- \overset{k_{15}}{\rightleftharpoons} \mathrm{R_3Li_4CH_2CH_2R\cdot E_3} \qquad (15)$$

since the ^{7}Li nmr spectrum corresponds to rapid exchange of R groups in the aggregates.[9]

It would be difficult to account for the regular dependences of rate on ether concentration unless all the equilibria of eq 1–4 were rapidly established relative to the rate-determining step. Since we know that ethylene is in the rate-determining step, this step might be defined by k_5, k_6, k_7, k_8, k_{12}, k_{13}, k_{14}, or k_{15}. The last four are considered because the importance of ionic dissociation in so many organolithium reactions[4a] requires the examination of its possible involvement here.

The simple forms of carbanion involvement most frequently considered are ruled out by the combined facts that the prevailing molecular species is $(\mathrm{RLi})_4$ and that the transition state contains this species, two extra ether molecules beyond its prevalent solvation number, and a molecule of ethylene. In some respects the simplest way to involve a carbanion consistent with this requirement would be to postulate that the equilibrium of eq 9, 10, or 11 is rapidly established and that the rate-determining reaction is between the ion pair in one of these equilibria and a molecule of ethylene. This view is undermined by the observed inhibition at high THF concentrations. The more ether there is to solvate the complex cation, the more favorable should be the dissociation to the ion pair in eq 9–11. If the ethylene involved is a free molecule, it is hard to see why the tetraetherate should not react faster than the trietherate. As indicated above, this inhibition becomes intelligible in terms of inclusion of the reacting ethylene at a coordination site from which it may be excluded by full etheration.

Indeed, coordination at a metal atom is one of the few available mechanisms by which ethylene might acquire the out-of-character ability to react with an anion. If this is what is happening, the anion obviously needs to be a powerfully basic anion, and not a mere primary one, to penetrate the electron cloud of the ethylene. Equations 13 and 15 spell out the ethylene insertion as the attack of R^- upon the ethylene part of its associated cation (eq 12 and 14 being regarded as rapid equilibria). Equations 6 and 8 are less literal about resolving the insertion into discrete ionic stages, treating it as a concerted process. The same purpose is served by considering that k_{13} and k_{15} are so large that these reactions would occur immediately on incipient formation of the ion pairs, so that k_{12} or k_{14} would be rate determining.[24]

Special Conditions Required for a Single Kinetic Order. The reaction scheme proposed would not be expected to yield the observed simple dependence of the ethylenation rate upon a single power of the ether or amine concentration except under rather special circumstances. If the transition state includes just two ether molecules, then the condition is that the alkyllithium must remain primarily in the unetherated form over the entire range of ether concentrations employed. On the other hand, if (as seems to be indicated by the *t*-butyllithium results) the transition state contains three ether molecules, then the observed second-order dependence on ether concentration requires that the alkyllithium be predominantly in the monoetherated form over the experimental range of ether concentrations. Defining each equilibrium constant of etheration as $K_n = (\mathrm{LE})_n/[(\mathrm{E})\,(\mathrm{LE}_{n-1})]$ ($\mathrm{L} = (\mathrm{RLi})_4$, E = ether), we can see that the second-order dependence of the ethylenation rate recorded in Table III is possible if K_1 for isopropyl- and *sec*-butyllithium is greater than about 1 while K_2 remains less than about 0.015. If these conditions were not met, the composition of the mixture of etherates would shift in such a way as to produce a more complex dependence of rate upon ether concentration. Some of the runs at the lowest ether concentrations indeed show deviations in the expected direction, and further work is under way to observe and treat the rates outside the simplified conditions described here.

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[24] Actually, it is not necessary to assign any role at all to carbanions in ethylenation. The easy electron conduction within the complexed organolithium aggregate may facilitate a direct migration of the group R from the face of the lithium tetrahedron to the complexed ethylene, the transition state being of no more clearly defined polarity than in a pinacol rearrangement. In such a rearrangement secondary and tertiary alkyl groups commonly show higher migration aptitudes than do primary groups, as in the present case. At one time it was considered important to regard the migrating group in the pinacol rearrangement as moving "with its pair of bonding electrons" [F. C. Whitmore, *J. Amer. Chem. Soc.*, **54**, 3279 (1932)] but the attendant stereochemistry and migration aptitudes are in better accord with a concept of continuous bonding during rearrangement. Three-center, electron-deficient bonding at a transition state is most favorably attained by those same saturated groups which form the most stable cations.

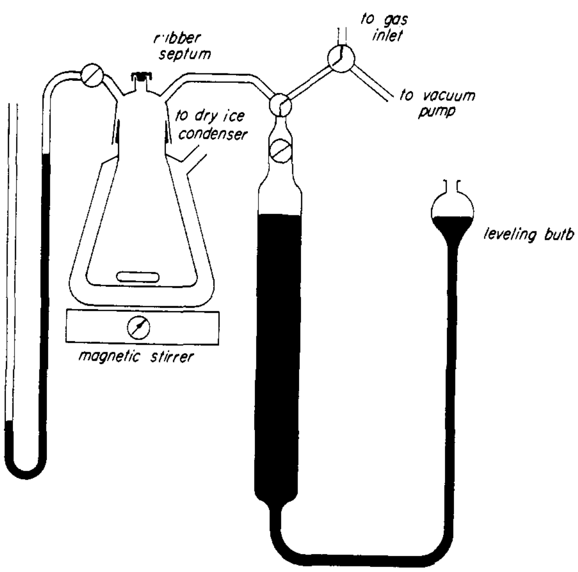

Figure 13. Apparatus used to measure pressure and volume in adding dimethyl ether to alkyllithium solutions.

Also in another respect the simplicity of the experimental results is surprising in the light of the proposed mechanism. Since in our model experiments with dimethyl ether the only primary alkyllithium examined, *n*-butyllithium, was more strongly etherated at equilibrium than either of the secondary alkyllithiums, and since under these conditions a statistical distribution of all RLi's present is rapidly attained in the tetrameric aggregates,[9,10] it would be expected that during ethylenation, as secondary or tertiary alkyllithium is steadily converted into primary alkyllithium at a constant high concentration of ether, the organometallic aggregates would become more tightly etherated with an actual change in the rate constant during the course of a kinetic run. In general there is no indication of any such change, the pseudo-first-order rate plots being linear throughout their course. The degree of conversion to which the runs were followed is indicated in the tables, being usually over 90%. This phenomenon, too, is under further investigation; for the present we can only surmise that the mixing of primary alkyl groups with the secondary in the tetramer brings not only higher etheration but some compensating decrease in inherent reactivity of the secondary groups adjoining them.

In favor of the second-order catalysis being only an approximation based on shifting etherate composition is the fact that several of the ether concentration–rate series are fitted by an equation of the type $k_2 = a[\mathrm{E}] + b[\mathrm{E}]^2$, where the value of a is nowhere near zero. Current work on this topic will be reported later.

Experimental Section

The vapor pressure studies with dimethyl ether, to determine the extent of complexing of the alkyllithiums, were carried out in the apparatus shown in Figure 13. Known volumes of dimethyl ether were measured into the previously evacuated, vapor-jacketed vessel, and after each increment of gas the system was brought to equilibrium with the magnetic stirrer and the pressure measured. The alkyllithium stock solutions were introduced by syringe through the rubber septum shown. Comparison of the measurements with a given alkyllithium and with pure *n*-heptane in the apparatus yielded the data of Figures 2, 3, and 4. A similar apparatus served for the determinations of ethylene solubility in mixtures of *n*-pentane and the ethers or amines.

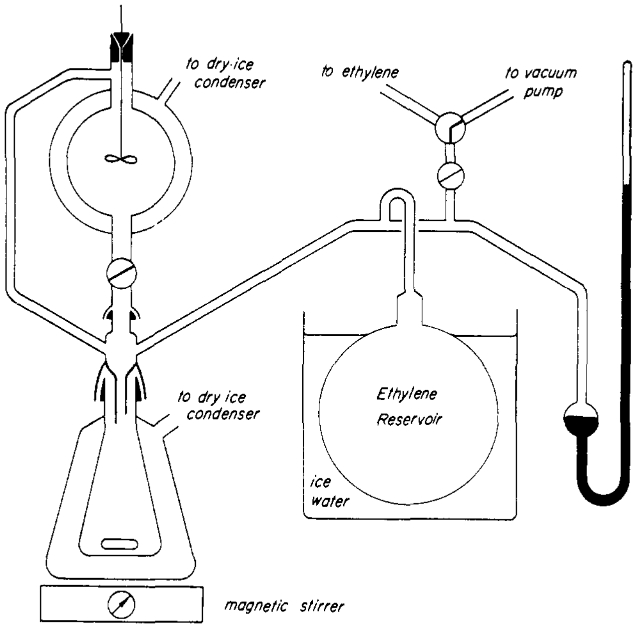

Figure 14. Apparatus for determining order of reaction with respect to ethylene.

In the measurement of rates by following ethylene pressure, in order to ascertain the order of the reaction with respect to ethylene, the apparatus of Figure 14 was employed. As in all the rate runs, the reaction was started by opening the stopcock which allowed mixing of the two preequilibrated solutions in the upper and lower vessels (see Experimental Section of part I).[15] The entire volume of ethylene for the experiment was introduced at the beginning into the reservoir where it was held at 0° and its pressure was read periodically from the manometer. The jacketing of the reaction vessel was efficient enough, and the gas absorption slow enough, so that a constant temperature could be maintained in the reaction vessel as well as in that used for the pressure measurement.

The pseudo-first-order measurements most often used were carried out in the apparatus shown and described in part I of this series.[15] In these runs the ethylene was measured in at constant pressure and its concentration in the saturated reacting solution was constant.

The sources of reagents and solvents, and the technique for preparing and handling the stock solutions of alkyllithiums, have been described in the previous paper.[15]

Tetrahydrofuran. Matheson Coleman and Bell THF was purified according to the method of Fieser.[25] The THF was distilled from lithium aluminum hydride through a 30-cm Vigreux column immediately prior to use. A central fraction bp 64° (uncor) was collected (lit. bp 64–65°).

Dimethyl ether, obtained from the Matheson Co., minimum 99.5% pure (maximum 0.25% water and 0.25% methanol), was purified for use by passing it slowly through two gas drying towers filled with phosphorus pentoxide.

1,4-Dimethoxybutane. Eastman technical butane-1,4-diol was redistilled through a 30-cm vacuum-jacketed Vigreux column. A central fraction, bp 230°, was collected.

Butane-1,4-diol (1 l.) was placed in a 2-l. three-necked flask equipped with a reflux condenser, Tru-bore stirrer, and a nitrogen inlet tube. All operations were carried out under a nitrogen atmosphere. The diol was heated to 70°. Chunks of sodium (46 g) were added with stirring over a period of 4 hr. The nitrogen inlet tube was removed and replaced by a 500-cc pressure-equalizing addition funnel. Eastman White Label methyl iodide (312 g, 2.2 moles) was added dropwise to the reaction over 2 hr with stirring. After cooling the reaction mixture was filtered with suction to remove the sodium iodide. The reaction mixture was then fractionally distilled through a 20-cm vacuum-jacketed Vigreux column. 1-Methoxy-4-butanol, bp 173–175°, was obtained, in 80% yield.

1-Methoxy-4-butanol (156 g, 1.5 moles) was converted to its sodium derivative as above, and 1.6 moles (227 g) of Eastman

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(25) L. F. Fieser, "Experimental Organic Chemistry," 3rd ed, D. C. Heath and Co., Boston, Mass., 1955, p 292.

White Label methyl iodide was added dropwise over 3 hr. The reaction mixture was cooled, filtered, and fractionally distilled through a 20-cm vacuum-jacketed Vigreux column. Crude 1,4-dimethoxybutane, bp 126–136°, was obtained in 80% yield. It was redistilled from lithium aluminum hydride through a 30-cm vacuum-jacketed Vigreux column. A central fraction, bp 132°, was collected.

The infrared spectrum of 1,4-dimethoxybutane is characterized by an intense band at 1120 cm^{-1} due to the ether linkage.

The six hydrogens of the two equivalent methyl groups appear in the nmr as a singlet at 3.24 ppm. The four equivalent methylene hydrogens adjacent to the ether oxygens appear as a complex multiplet centered at 3.30 ppm. The four equivalent methylene hydrogens β to the ether oxygens are coupled to the four equivalent methylene hydrogens α and hence appear as a quintet centered at 1.52 ppm with a coupling constant of about 3 cps. Correct integration of the spectrum was obtained.

N-Methylpyrrolidine, obtained from the Aldrich Chemical Co., was redistilled from lithium aluminum hydride through a 35-cm vacuum jacketed wire spiral packed column. A central fraction, bp 79.5–80.5°, was collected and stored over sodium wire in a ground glass stoppered bottle under argon until use.

Triethylamine. Eastman White Label triethylamine was distilled from lithium aluminum hydride through a 50-cm Vigreux column (wrapped with asbestos tape). A central fraction was collected at a reflux ratio of 6:1, bp 89.5°, and stored over fresh sodium wire under argon in a ground glass bottle until use.

Coolants. Various gases were condensed and were refluxed at their normal boiling points to maintain a fixed temperature for kinetic experiments.[26]

Isobutane, Phillips 99 mole %, bp −11.7°, was used without further purification.

Freon 22 chlorodifluoromethane reagent grade obtained from the Matheson Co., bp −40.8°, was used for temperature control without further purification.

Propylene. CP reagent grade obtained from the Matheson Co., bp −47.7°, was used without further purification.

Freon 12. Dichlorodifluoromethane reagent grade obtained from the Matheson Co., bp −29.8°, was used without further purification.

Acknowledgment. This work was supported by a grant from the National Science Foundation. The junior authors thank the National Science Foundation and the National Institutes of Health for graduate fellowships at different times.

Appendix

Kinetic equations are given for a bimolecular reaction when one reactant, A, is totally dissolved and the second, B, is a gas distributed between solution and vapor phase, where A_T, B_T = total numbers of moles; $[A]_L$, $[B]_L$ = concentrations in solution, moles per liter; V_L, V_G = volumes of liquid and gas phases, liters; h = Henry's law constant = $[B]_L$/(pressure of B) = $[B]_L V_G / B_G RT$ under ideal gas behavior; and f = constant fraction of B which is in the liquid phase = B_L/B_T = $hRTV_L/(V_G + hRTV_L)$.

If one molecule of A reacts with one of B, then $B_T = A_T + a$, where $a = (B_T)_0 - (A_T)_0$ and

$$[B]_L = fB_T/V_L = \frac{f}{V_L}(A_T + a) = \frac{f}{V_L}([A]_L V_L + a) = f\left([A]_L + \frac{a}{V_L}\right)$$

Hence

$$\frac{-d[A]_L}{dt} = k[A]_L[B]_L = kf[A]_L\left([A]_L + \frac{a}{V_L}\right)$$

The integral is

$$\frac{V_L}{a}\ln\frac{[A]_L + \frac{a}{V_L}}{[A]_L} - \ln\frac{([A]_L)_0 + \frac{a}{V_L}}{([A]_L)_0} = kft$$

It follows that a plot of log B_T/A_T *vs.* time will be a straight line whose slope is equal to $akf/2.3V_L$.

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[26] All boiling points and purities of gases reported here are taken from the "Matheson Gas Data Book," 3rd ed, Matheson Co., East Rutherford, N. J., 1961.