The Metalation of Triphenylmethane by Organolithium Compounds in Tetrahydrofuran

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Abstract: Reaction rate studies of the metalation of triphenylmethane by six organolithium reagents show that kinetic behaviors and relative reactivities vary substantially with reagent structure and reagent concentration. The latter dependence is due to changes in the effective reaction order in organolithium with reagent structure. Kinetic orders in RLi are ~1 for benzyllithium and allyllithium, ~0.25 for *n*-butyllithium, methyllithium, and vinyllithium, and 0.64 for phenyllithium. The effective reactivity order at 0.1 *F* RLi is benzyllithium > allyllithium > *n*-butyllithium > phenyllithium > vinyllithium > methyllithium; at 0.01 *F* RLi the reactivity sequence is benzyllithium > *n*-butyllithium > allyllithium > vinyllithium > phenyllithium > methyllithium. Fractional reaction orders are in accord with aggregation state of the respective RLi reagent in tetrahydrofuran. Colligative measurements are reported for vinyllithium and allylithium. The kinetic examination covers a concentration of ~0.005 to ~1 *F* in RLi. Experiments in which RLi is in excess over triphenylmethane show effective first-order dependence on triphenylmethane and complete conversion of it to triphenylmethyllithium. When triphenylmethane is in excess over RLi only a fraction of RLi is effective in initially producing triphenylmethyllithium; this is attributed to multimetalation.

The kinetic behavior and relative reactivities of six organolithium (RLi) reagents as metalatin greagents toward triphenylmethane in tetrahydrofuran (THF) solution are reported here. This report illustrates the dependence of metalation rate on the structure of organolithium metalating reagents, whereas the majority of previous metalation studies pertained to reaction rate dependence on substrate structure (*i.e.*, hydrocarbon acidities).[1]

An earlier communication[2] disclosed the relative reactivity sequence of these reagents at a formal concentration of $\{\text{RLi}\} \simeq 7.0 \times 10^{-2}$ *F*. Evaluation over a range of concentrations shows this reactivity sequence is concentration dependent, a consequence of the reaction order in organolithium reagent varying with reagent structure.[3-6] Organolithium reaction orders vary from ~1.0 to ~0.25. This behavior is attributed to the propensity of certain organolithium compounds to aggregate in THF. Colligative property measurements[7] are in accord with degrees of aggregation inferred from reaction orders.

Reaction orders in organolithium reagents reported here for metalation of triphenylmethane are analogous to those recorded for addition to 1,1-diphenylethylene.[5,8,9] Relative reactivities of the organolithium reagents in the metalation and olefin addition reactions are not the same.[8,9]

Experimental Section

Reagents. Tetrahydrofuran was preliminarily dried over calcium hydride and, just prior to use, distilled under argon from lithium benzophenone ketyl. Diethyl ether and hexane were distilled from lithium metal dispersion. Triphenylmethane (Eastman Organic Chemicals) was recrystallized from ethanol. Zone-refined triphenylmethane was used as received from James Hinton, Valparaiso, Fla. Dibenzylmercury (Metallomer Laboratories) was recrystallized from a methylene chloride–ethanol mixture. Commercially available materials used without further purification were dimethylmercury and diphenylmercury (Eastman Organic Chemicals), diallylmercury (Orgmet, Inc.), tetrallyltin and tetravinyltin (M and T Chemicals, Inc.), ethyllithium in benzene (Alfa Inorganics, Inc.), and *n*-butyllithium in hexane (Foote Mineral Co.).

Preparation of Organolithium Compounds. Throughout all preparations and handling of organolithium reagents high vacuum techniques and argon "blankets" were used.[8] Preparative methods for the organolithium reagents were chosen to be lithium halide free, since such salts effect reactivity.[10] The total alkalinity, measured by titration with 0.10 *M* HCl using phenolphthalein as indicator, was shown by electronic spectra, gasometric analysis, or glpc analysis of the vapors over the organolithium solution before and after quenching, as described earlier,[9] to be equivalent to the formal organolithium concentration $\{\text{RLi}\}$.

Methyllithium, phenyllithium, benzyllithium, and allyllithium were prepared in diethyl ether at ~0.6 *F* concentration from the corresponding bismercury compound and excess lithium metal.[11,12] Allyllithium and vinyllithium were prepared from the appropriate tetraorganotin compound (R_4Sn) *via* reaction in hexane solution with *n*-butyllithium.[13] The RLi precipitate was washed with hexane, pumped dry on a high-vacuum line, and dissolved in THF.[8]

Kinetic Measurements. The closed reactor–spectroscopic cell used in these studies was described earlier.[12] Cells with path lengths between 4.6×10^{-3} and 2.0 cm were used, the appropriate path length being determined by the reaction rate and reagent concentrations. In all runs the cell was first oven-dried at 150° and then subjected to three cycles of high-vacuum pumping and filling with argon. Desired quantities of RLi solution in THF or in diethyl ether were added to the cell using Hamilton gas-tight syringes, initially dried in a vacuum oven and stored under nitrogen. If the organolithium solution was in diethyl ether, the latter was pumped away and replaced by THF. A measured quantity of triphenylmethane stock solution in THF was added. The rea-

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[1] (a) A. I. Shatenstein, *Advan. Phys. Org. Chem.*, **1**, 155 (1963); (b) H. F. Ebel and G. Ritterbusch. *Ann.*, **704**, 15 (1967); (c) A. Streitwieser, Jr., E. Ciuffarin, and J. H. Hammons, *J. Am. Chem. Soc.*, **89**, 63 (1967), and references therein.

[2] R. Waack and P. West, *ibid.*, **86**, 4494 (1964).

[3] R. Waack and P. West, *J. Organometal. Chem.*, **5**, 188 (1966).

[4] R. Waack, P. West, and M. A. Doran, *Chem. Ind.* (London), 1035 (1966).

[5] R. Waack, P. West, and M. A. Doran, Symposium on Hydrocarbon Ions, Abstracts, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, U41.

[6] R. Waack, M. A. Doran, E. B. Baker, and P. West, Abstracts, Third International Conference on Organometallic Chemistry, Munich, Germany, 1967.

[7] P. West and R. Waack, *J. Am. Chem. Soc.*, **89**, 4395 (1967).

[8] R. Waack and P. E. Stevenson, *ibid.*, **87**, 1183 (1965).

[9] R. Waack and M. A. Doran, *ibid.*, **91**, 2456 (1969).

[10] (a) D. Y. Curtin and E. W. Flynn, *ibid.*, **81**, 4714 (1959); (b) R. Huisgen and W. Mack, *Chem. Ber.*, **93**, 332 (1960); (c) R. Waack and M. A. Doran, *Chem. Ind.* (London), 496 (1964).

[11] G. Wittig, F. J. Meyer, and G. Lange, *Ann.*, **571**, 167 (1951).

[12] R. Waack and M. A. Doran, *J. Am. Chem. Soc.*, **85**, 1651 (1963).

[13] D. Seyferth and M. A. Weiner, *ibid.*, **83**, 3583 (1961).

gents were mixed by vigorous magnetic stirring. Within 45 sec of mixing, the cell was placed in a Cary Model 14 recording spectrophotometer and the optical density at 500 mμ monitored as a function of time. Absorption at this wavelength is due to product, triphenylmethyllithium. The spectrum of triphenylmethyllithium is not changed by the presence of excess metalating organolithium reagent. Reversal in the order of addition of RLi and substrate solutions to the cell gave similar results. Exceptions to the above procedure were the studies involving *n*-butyllithium and ethyllithium. The short lifetime of *n*-butyllithium and ethyllithium in THF prohibited use of stock solutions in this solvent. Hydrocarbon solutions of these organolithiums were used. The hydrocarbon solvent was pumped off and a THF solution of triphenylmethane added directly to the liquid *n*-butyllithium. The same kinetic results were obtained when a small amount of THF was initially added to the *n*-butyllithium, quickly followed by the addition of triphenylmethane in THF. The concentration of a triphenylmethane stock solution in THF was determined spectrophotometrically at 262 mμ ($\epsilon = 1.0 \times 10^3\ M^{-1}\ \mathrm{cm}^{-1}$). Kinetics were conducted at 22 ± 1°, except during variable-temperature studies. At the end of each kinetic run the total alkalinity was measured by titration with 0.10 *M* HCl to a phenophthalein end point, to substantiate the initial formal organolithium concentration $\{\mathrm{RLi}\}_i$ calculated from the amount of stock RLi solution used.

Kinetic runs were also conducted at temperatures between −40 and 22° using a variable-temperature unit,[14] cooled by a flow of thermally regulated nitrogen gas controlled by a thermistor positioned next to the cell and above the light path. Reaction temperatures were measured with a thermocouple sealed into a stainless steel needle and positioned in the solution. The presence of the thermocouple did not change the optical density reading. The reaction cell used was similar to that described earlier[12] but permitted reagents to be added directly into the spectroscopic cell. Approximately 4.0 ml of substrate solution was placed in the reaction cell and allowed to come to the desired temperature. Less than 0.5 ml of RLi stock solution was introduced *via* syringe, and, to promote adequate mixing, the majority of the side-arm contents were without delay drawn into the syringe and promptly flushed back into the cell. The latter procedure was repeated using 4.0 ml of RLi solution and less than 0.5 ml of triphenylmethane solution with equivalent results. The effective extinction coefficient as measured at the 500 mμ absorption maximum of triphenylmethyllithium increases with decrease in temperature between −40 and 22°, because of narrowing of the absorption envelope. This was taken into account when comparing reaction rates at different temperatures.

Colligative Property Measurements. The technique used to investigate the colligative properties of allyllithium and vinyllithium solutions in THF has been reported,[7] as have the colligative properties of the other reagents.[7]

Results

The absorption spectrum of triphenylmethyllithium in THF at 22° has a peak at 500 mμ ($\epsilon = 3.5 \times 10^4\ M^{-1}\ \mathrm{cm}^{-1}$) with a broad shoulder on the short wavelength side. At lower temperatures, the absorption envelope sharpens and the maximum moves to longer wavelength (see Table I). Values of $(\mathrm{d}\{(C_6H_5)_3CLi\}/\mathrm{d}t)_i$ were computed from changes in optical density at 500 mμ recorded as a function of time, after correction for base-line absorption.

Table I

	$(C_6H_5)_3CLi$–THF		
T, °C	$\lambda_{\max}$, mμ	$\epsilon\ (\lambda_{\max})$, $M^{-1}\ \mathrm{cm}^{-1} \times 10^{-4}$	$^1/_2\Delta w_{1/2}$, Å[a]
22	500	3.5	51
0	505	3.6	50
−20	510	3.8	48
−40	510	4.2	45

[a] Half the width of the absorption envelope measured from the long-wavelength side to the peak center.

For a particular initial formal organolithium concentration $\{\mathrm{RLi}\}_i$, the quantity

$$\left(\frac{\mathrm{d}\{(C_6H_5)_3CLi\}/\mathrm{d}t}{[(C_6H_5)_3CH]}\right)_i = \left(\frac{\mathrm{rate}}{S}\right)_i$$

is a first-order function of substrate concentration, *S*, when $[(C_6H_5)_3CH]_i < \{\mathrm{RLi}\}_i$. Non-first-order behavior in triphenylmethane is observed when $[(C_6H_5)_3CH]_i \gg \{\mathrm{RLi}\}_i$. A decrease in $(\mathrm{rate}/S)_i$ is recorded with increase in initial ratio of substrate to metalating reagent beyond the value of unity. This is illustrated by data taken using $\{C_6H_5Li\}_i = 10^{-2}\ F$, summarized in Table II.

Addition of an aliquot of organolithium reagent to an appreciable excess of triphenylmethane in THF produces an initial major increase in optical density at 500 mμ corresponding to a quantity of triphenylmethyllithium equivalent to only a fraction of the amount of reactant RLi used. This is followed by a very much slower increase in 500 mμ absorption with time. Addition of another aliquot of RLi produces more triphenylmethyllithium but again in fractional amount compared to the RLi added, and the corresponding $(\mathrm{rate}/S)_i$ value is lower than that associated with the first aliquot added. The overall yield of triphenylmethyllithium increases toward the 100% conversion of metalating RLi over a long period of time. The use of either repeatedly recrystallized reagent grade triphenylmethane or zone-refined material results in no change in this behavior.

The majority of metalation experiments was conducted using a substantial excess of reactant RLi. No change was observed in the electronic spectrum of triphenylmethyllithium with time in the presence of excess RLi. Initial (rate/S) quantities were evaluated where only a small fraction of RLi was consumed. Because of the predominance of reagent RLi, such rate values are not complicated by triphenylmethyllithium–RLi interactions. Initial rate measurements invariably agreed with those calculated from pseudo-first-order plots, showing product–reactant interactions do not influence these metalation rates. Metalation rates for each organolithium were generally determined with $\{\mathrm{RLi}\}_i$ in the range 5×10^{-3} to 1.0 *F*, and first-order behavior in substrate was assured by keeping $[(C_6H_5)_3CH]_i < 2.0 \times 10^{-3}\ M$. Variations in $\log(\mathrm{rate}/S)_i$ as a function of $\log\{\mathrm{RLi}\}_i$ are shown in Figure 1. Effective reaction orders in $\{\mathrm{RLi}\}_i$ are obtained from linear regression analyses of the data. These values, together with their 95% confidence limits, are listed in Table III.

The output of the differential vapor pressure evaluation of the colligative properties of allyllithium and vinyllithium solutions in THF is given as normalized $\Delta R(\Omega)$ readings as a function of $\{\mathrm{RLi}\}$.[7] The apparent degrees of organolithium association (n_{app}) for allyllithium–THF and vinyllithium–THF system are given in Table IV. The reaction orders in $\{\mathrm{RLi}\}_i$ determined for metalation of triphenylmethane at −40° are 0.25 ± 0.04 for *n*-butyllithium and 0.68 ± 0.04 for phenyllithium (Figure 2). Since these least-square values differ somewhat from the corresponding reaction orders at 22°, the ratio of measured effective reactivities at 22 and −40° for each particular RLi is dependent on $\{\mathrm{RLi}\}_i$ (Figure 2 and Table V). Reaction rates using *n*-butyllithium, phenyllithium, and methyllithium at

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(14) R. Waack, M. A. Doran, and P. E. Stevenson, *J. Am. Chem. Soc.*, 88, 2109 (1966).

Table II. The Dependence of $(\text{rate}/S)_i$ on Substrate Concentration, S, $\{C_6H_5Li\}_i \simeq 10^{-2}$ F throughout Experiments A–E

Data set	$\{C_6H_5Li\}_i$, F ($\times 10^2$)	$[(C_6H_5)_3CH]_i$, M ($\times 10^3$)	$([(C_6H_5)_3CH]/\{C_6H_5Li\})_i$	$\left(\frac{d\{(C_6H_5)_3CLi\}/dt}{[(C_6H_5)_3CH]}\right)_i = \left(\frac{\text{rate}}{S}\right)_i$, hr^{-1}
A	1.03	0.90	0.088	1.05
B	1.11	1.60	0.144	1.13[a]
C	1.13	1.65	0.146	0.92
D	1.04	1.59	0.153	1.10
C	1.00	1.68	0.168	0.67
B	1.06	3.16	0.298	0.97[a]
B	1.16	7.16	0.617	1.17[a]
B	1.16	9.31	0.803	0.88[a]
A	1.03	12.1	1.17	0.61
E	1.10	97.7	8.88	0.36
E	1.08	1.18	10.9	0.33
E	1.12	153	13.7	0.31[a]
E	1.17	180	15.4	0.19
E	1.12	280	25.0	0.15[a]

[a] Used zone refined $(C_6H_5)_3CH$.

$\{RLi\}_i = 0.21 \pm 0.01$ F were measured at temperatures ranging from 22 to −40° (Figure 3).

Discussion

The majority of metalation experiments was conducted using excess reactant RLi. Under these conditions the reactions are first order in substrate triphenylmethane. Initial (rate/S) quantities were evaluated as a function of $\{RLi\}_i$ (Figure 1). A significant feature of these results is that by virtue of nonunity reaction orders in some $\{RLi\}_i$ (Table III), the effective reactivities of these organolithiums are a function of formal organolithium concentration (Table VI).[5] At $\{RLi\}_i = 0.01$ F the reactivity sequence is benzyllithium > n-butyllithium > allyllithium > vinyllithium > phenyllithium > methyllithium, whereas at $\{RLi\}_i = 0.10$ F the reactivities decrease in the order benzyllithium > allyllithium > n-butyllithium > phenyllithium > vinyllithium > methyllithium. A similar situation has been observed with the addition of the same organolithiums to 1,1-diphenylethylene in THF,[9] except that a different order of reactivities at any particular $\{RLi\}_i$ applies.[5] These results are compared in Table VII. At $\{RLi\}_i = 0.01$ F there is a 40-fold greater spread in RLi relative reactivities with the olefin addition reaction than in the metalation reaction. The substantially greater effective reactivity of both alkyllithiums, methyllithium,

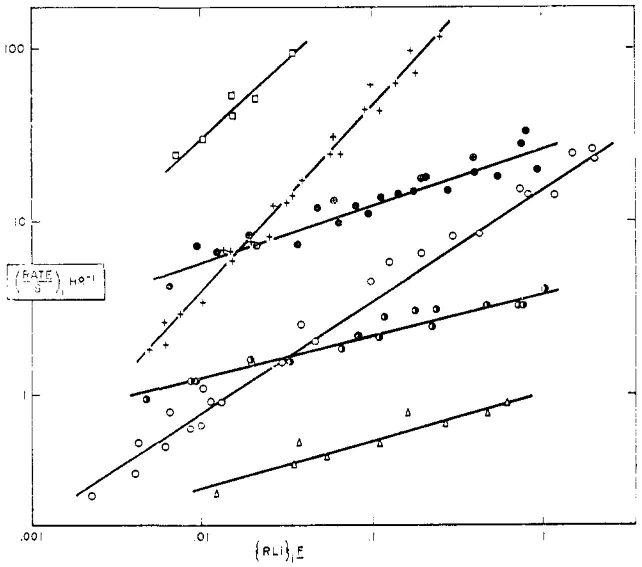

Figure 1. Relative rates of metalation of triphenylmethane in THF at 22° by different organolithiums as a function of {RLi}, F. Least-squares lines are drawn through each set of data points. The apparent orders in {RLi} are given in Table III: □, benzyllithium; +, allyllithium; ⊕, ethyllithium; ●, n-butyllithium; ○, phenyllithium; ◑, vinyllithium; and △, methyllithium.

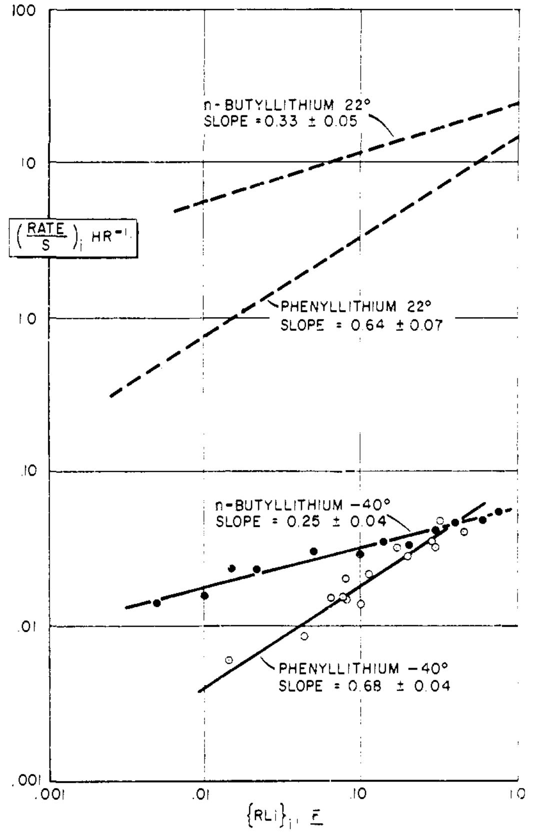

Figure 2. The effect of a change in temperature from 22° (Figure 1) to −40° on the relative rates of metalation of triphenylmethane in THF by n-butyllithium (●) and phenyllithium (○).

Table III. Effective Reaction Orders in Formal Organolithium Concentration $\{\mathrm{RLi}\}_i$ Deduced by Least-Squares Analyses

RLi	Effective reaction order in $\{\mathrm{RLi}\}^a$
Benzyllithium	0.90 ± 0.27
Allyllithium	1.07 ± 0.05
Phenyllithium	0.64 ± 0.07[b]
Vinyllithium	0.24 ± 0.04
n-Butyllithium	0.33 ± 0.05
Methyllithium	0.28 ± 0.08

[a] The 95% confidence limits are also given. [b] More experimental points covering a wider concentration range are given here than in the data reported earlier.[4]

Table IV. Colligative Property Measurements on Allyllithium and Vinyllithium in THF at 25.0 ± 0.2°

RLi	$\{\mathrm{RLi}\}$, *F*	Normalized $\Delta R(\Omega)$ *vs.* THF[a]	n_{app} (apparent degree of RLi aggregation)[a,b]
Allyllithium	0.107	28.7	1.28
	0.160	39.9	1.39
	0.214	58.2	1.25
	0.288	83.7	1.17
	0.414	108.6	1.31
	0.427	119.7	1.23
	0.535	144.0	1.28
	0.700	179.5	1.34
Vinyllithium	0.110	10.0	4.10
	0.222	20.9	3.88
	0.314	31.2	3.64
	0.414	41.7	3.48
	0.544	54.5	3.45
	0.672	70.5	3.25
	0.772	79.5	3.36
	0.886	90.9	3.40

[a] See ref 7 for full explanation of these terms. [b] Computed assuming RLi does not form an etherate. If THF were considered as bound in etherates (see discussion in ref 7), then n_{app} would be larger, particularly at high [RLi] concentrations.

Table V. The Effect of Formal Organolithium Concentration $\{\mathrm{RLi}\}$ on the Ratio of RLi Reactivities at 22 and −40°

RLi	$\{\mathrm{RLi}\}_i$, *F*	$(\mathrm{rate}/S)_i$, hr^{-1} 22°	−40°	Ratio of RLi reactivities at 22 and −40°
n-Butyllithium	0.01	5.8	0.019	305
	0.50	21	0.049	430
Phenyllithium	0.01	0.80	0.0039	205
	0.50	9.8	0.056	175

Table VI. Variation in Relative Reactivities of Organolithiums toward Triphenylmethane as a Function of $\{\mathrm{RLi}\}_i$ in THF at 22°

RLi	Relative reactivities[a] $\{\mathrm{RLi}\}$ = 0.01 *F*	$\{\mathrm{RLi}\}$ = 0.10 *F*
Methyllithium	1.0	1.0[b]
Phenyllithium	2.8	6.3
Vinyllithium	4.3	4.2
Allyllithium	14	90
n-Butyllithium	20	23
Benzyllithium	150	450[c]

[a] $(\mathrm{Rate}/S)_i$ values compared to $(\mathrm{rate}/S)_i$ for methyllithium. [b] Ratio of $(\mathrm{rate}/S)_i$ values for methyllithium at 0.10 and 0.01 *F* = 1.9. [c] Obtained by extrapolation.

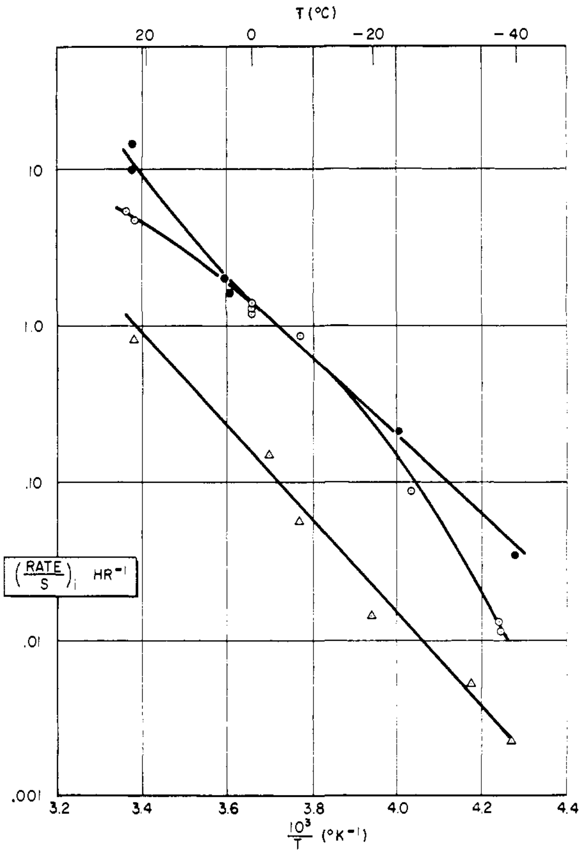

Figure 3. The temperature dependence of organolithium reactivities toward triphenylmethane in THF at $\{\mathrm{RLi}\}_i$ = 0.21 ± 0.01 *F*: ●, *n*-butyllithium; ○, phenyllithium; and △, methyllithium.

and especially *n*-butyllithium, toward 1,1-diphenylethylene compared to triphenylmethane is notable. The relative reactivities of organolithiums are thus dependent on the nature of the reaction (*e.g.*, metalations *vs.* olefin additions) and formal RLi concentration. Relative reactivity orders for each type of reaction are presumably substrate independent,[9] although absolute rate comparisons would not be so.

Table VII. Relative Reactivities of Organolithiums at $\{\mathrm{RLi}\}_i$ = 0.01 *F* toward Triphenylmethane and 1,1-Diphenylethylene in THF at 22°

RLi	Relative reactivities[a] Triphenylmethane	1,1-Diphenylethylene
Methyllithium	1.0	1.0[b]
Phenyllithium	2.8	0.34
Vinyllithium	4.3	0.72
Allyllithium	14	33
n-Butyllithium	20	1900
Benzyllithium	150	650[c]

[a] $(\mathrm{Rate}/S)_i$ values compared to $(\mathrm{rate}/S)_i$ for methyllithium. [b] $(\mathrm{Rate}/S)_i$ for 0.01 *F* methyllithium reacting with 1,1-diphenylethylene = 4.3 $(\mathrm{rate}/S)_i$ corresponding to reaction with triphenylmethane. [c] Obtained by extrapolation.

The observed nonunity orders in $\{\mathrm{RLi}\}$ (Table III) are a result of aggregation of the organolithiums in THF.[3,4] In THF at 25° the colligative properties of benzyllithium,[7] allyllithium (Table IV), and phenyllithium[7] can be explained in terms of a solvated dimer–solvated monomer equilibrium, whereas the colligative

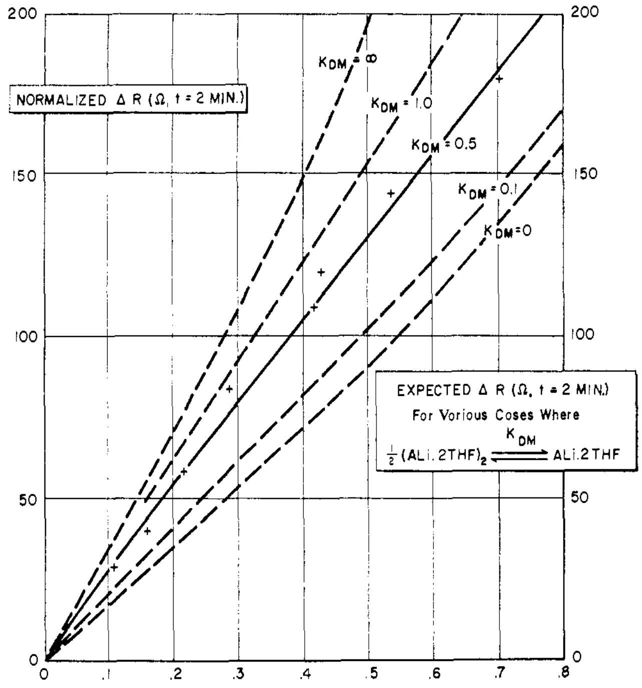

Figure 4. A comparison between colligative property measurements (+) made on allyllithium in THF at 25° and the expected behavior of the model system described at the right-hand ordinate axis and in the text.

properties of methyllithium[7] and vinyllithium (Table IV) indicate that solvated tetramer species dominate in THF at 25°. The rapid reaction of *n*-butyllithium with THF at 25° precludes colligative property measurements in this solvent, but measurements in diethyl ether indicate that *n*-butyllithium is largely tetrameric in that solvent.[7] Since methyllithium is dominantly tetrameric in both these solvents at 25°,[7] it is concluded that in all likelihood *n*-butyllithium exists predominantly as solvated tetramers in THF at 25°. It is not possible to evaluate the extent to which other solvated RLi species, such as dimers and monomers, exist in equilibrium with the tetrameric aggregates; the concentrations of these are presumably small.

Recent reports describe studies of the metalation of triphenylmethane by *n*-butyllithium at $\{\text{RLi}\}_i \sim 0.10$ *F* in a series of different electron-donor solvents,[15] and by lithium N-methylanilide in N-methylaniline as solvent over a range of RLi concentrations.[1b] These reactions are reported to be first order in substrate. The order derived with respect to formal organolithium concentration {RLi} was 0.316 for lithium N-methylanilide in N-methylaniline.[1b]

In hydrocarbon solution the analogous fractional reaction orders demonstrated for *n*-butyllithium[16] and *t*-butyllithium[17] in the metalation of fluorene in benzene are consistent with the colligative properties of these species in benzene. Concentration-dependent reaction orders in lithium cyclohexylamide observed for metalation in cyclohexylamine[18] were, likewise, correlated with organolithium aggregation. A rationale in accord with these fractional reaction orders is that the organolithiums are predominantly aggregated, but that product formation occurs largely *via* reaction of a less aggregated species, presumably monomer.

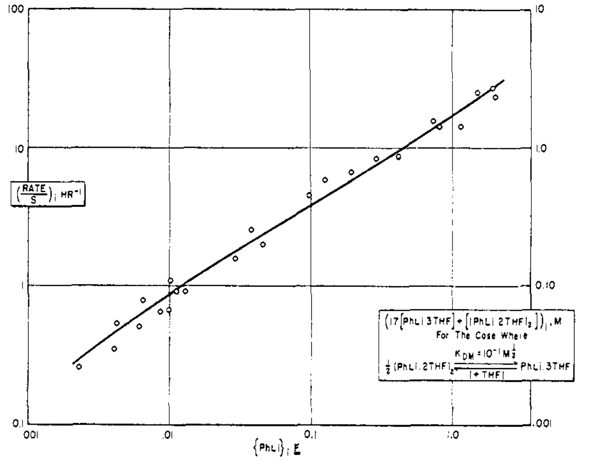

Figure 5. Kinetic data (O) derived from the metalation of triphenylmethane by phenyllithium in THF at 22°, compared with the behavior of the model system described both at the right-hand ordinate axis and in the text.

The colligative property and kinetic study findings on benzyllithium, phenyllithium, and allyllithium in THF at 22–25° can be rationalized in terms of the equilibrium

$$^1/_2(\text{solvated dimer}) \underset{}{\overset{K_{\text{DM}}}{\rightleftharpoons}} \text{solvated monomer}$$

between solvated dimeric and monomeric RLi species, both of which show reactivity[4] toward the substrate triphenylmethane. Equilibrium constants deduced by curve fitting, as illustrated in Figure 4, are K_{DM}(benzyl Li) $\gtrsim 1.0\ M^{1/2}$, K_{DM}(allyl Li) $\simeq 0.5\ M^{1/2}$ (Figure 4), and K_{DM}(phenyl Li) $\simeq 10^{-1}\ M^{1/2}$.[7] A relationship that applies to these systems is

$$\log\left(\frac{\text{rate}}{S}\right)_i = \log\,(k[\text{RLi}] + [(\text{RLi})_2])_i + \text{constant}$$

where *k* is equal to the ratio of monomer and dimer metalation velocity constants. Analysis of the kinetic data suggests that the dimeric species is more reactive than the monomeric form in the case of phenyllithium, *k*(phenyllithium) ≃ 17 (Figure 5), whereas the opposite is true for allyllithium, *k*(allyllithium) = 0.4 (Figure 6).

It is not feasible to analyze unambiguously the THF systems involving methyllithium, ethyllithium, *n*-butyllithium, and vinyllithium in terms of tetramer, dimer, and monomer species, each of which may have the capacity to undergo reaction with triphenylmethane. Tetrameric species $(\text{RLi})_4$ predominate (ref 7 and Table IV) and the observed reaction orders in {RLi} are $\gtrsim 0.25$ (Table III). Reaction orders in $\{\text{RLi}\}_i$ of 0.25 are attributable to either RLi monomer units being the most reactive species present,[3] or to the mechanistic sequence

$$(\text{RLi})_4 + (\text{C}_6\text{H}_5)_3\text{CH} \rightleftharpoons \text{RLi}(\text{C}_6\text{H}_5)_3\text{CH} + (\text{RLi})_3$$

$$\text{RLi}(\text{C}_6\text{H}_5)_3\text{CH} \longrightarrow (\text{C}_6\text{H}_5)_3\text{CLi} + \text{RH}$$

involving reaction between tetrameric RLi species and substrate, $(\text{RLi})_4$ tetramers dominating in solution, fol-

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lowed by rate-controlling decomposition of the RLi·$(C_6H_5)_3CH$ complex yielding triphenylmethyllithium. Organolithium reaction orders in excess of 0.25 obtained using these largely tetrameric reagents indicate that one-step reactions between triphenylmethane and aggregated RLi species, $(RLi)_2$ and/or $(RLi)_4$, are contributing noticeably to the production of triphenylmethyllithium. A measured reaction order in $\{RLi\}_t$ higher than the true value would, however, occur were there significant reaction between RLi and impurities or solvent,[3] a more likely situation at low formal organolithium concentrations.

Optical densities recorded at 500 mμ in metalations where triphenylmethane is in appreciable excess over reactant RLi are lower than is commensurate with 100% conversion of RLi to triphenylmethyllithium. Only a small amount of metalating RLi is accountable as long wavelength absorbing product species. Furthermore, in contrast to the behavior when RLi is in excess, non-first-order character in substrate triphenylmethane is found in the presence of excess triphenylmethane (Table II). On the other hand, for addition of RLi to 1,1-diphenylethylene, first-order behavior in olefin is observed regardless of whether olefin or RLi is in excess.[9] Neither multirecrystallized nor zone-refined triphenylmethane gives different results.

The occurrence of multimetalation[19] is considered to be a likely explanation. Metalation at the α-carbon atom of triphenylmethane produces absorption at 500 mμ. Metalation of the triphenylmethyllithium (or triphenylmethane) on a phenyl ring[20] would consume RLi without producing 500 mμ absorption, and presumably would cause little perturbation of the triphenylmethyllithium chromophore. Consumption of RLi owing to ring metalation is more pronounced in the metalation of $(m\text{-}CF_3C_6H_4)(C_6H_5)_2CH$, $(m\text{-}FC_6H_4)(C_6H_5)_2CH$, and $(m\text{-}CH_3OC_6H_4)(C_6H_5)_2CH$[21] than with $(C_6H_5)_3CH$. The enhancement in acidity of neighboring ring protons by these electronegative substituents is in accord with the proposed ring metalation.[20] The final slow increase observed in 500 mμ absorption is consistent with the idea that ring metalated triphenylmethyl species ultimately α-metalate triphenylmethane present in excess.

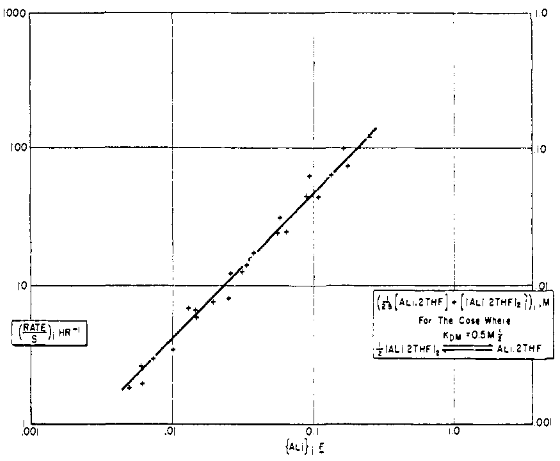

Figure 6. A direct comparison between kinetic data (+) derived from the metalation of triphenylmethane by allyllithium in THF at 22°, and the kinetic results expected for the model system described in the text and at the right-hand ordinate axis.

The effect of variations in temperature on these systems is complex, since equilibria and rate constants are involved, and each will have a temperature dependence. Similar, but not identical, least-square reaction orders in *n*-butyllithium and phenyllithium are obtained at both 22 and −40° (Figure 2), although the difference is perhaps not statistically significant. The measured effective reactivity of each organolithium at 22° compared to −40° is, therefore, a variable function of the formal organolithium concentration {RLi} (Table V). It is observed that at $\{RLi\}_t = 0.21 \pm 0.01$ *F*, the relative reactivities of *n*-butyllithium, phenyllithium, and methyllithium vary with temperature between 22 and −40° (Figure 3).

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