Addition of Organolithium Reagents to 1,1-Diphenylethylene in Tetrahydrofuran. Kinetics and Structure-Reactivity Relationship[1a]

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Abstract: Kinetic studies of the addition of six organolithium reagents to 1,1-diphenylethylene in tetrahydrofuran solution show the reaction to be first order in DPE but of variable order in organolithium reagent. Benzyllithium and allyllithium follow approximate first-order dependence, methyllithium and vinyllithium show approximate 0.25-order dependence, and phenyllithium shows 0.66-order dependence. Reaction rates of these species were obtained by monitoring the increase in the visible spectrum of the respective adduct. A competitive technique was required to evaluate the rate of adduct formation with *n*-butyllithium. These latter data are not extensive, but a fractional reaction order, *i.e.*, ~0.25, is indicated. The result of the differences in effective reaction order is that the relative reactivity of these species is strongly concentration dependent. Comparative reactivities in this series differ by approximately four powers of ten. The reactivity order of these organolithium species is seen to depend on factors other than the foreseeable basicities, *e.g.*, differences in aggregation behaviors and ion-pair interactions.

Toward the goal of elucidating the structure–reactivity relationship and of providing information relating to reaction mechanism, the kinetics of reaction of six organolithium reagents with 1,1-diphenylethylene (DPE) were examined. These kinetic experiments establish the effective reactivity behavior for three structural classes of organolithium reagents. Tetrahydrofuran (THF), the solvent in these studies, is advantageous in that all the organolithium reagents are soluble over a large concentration range. It is disadvantageous in that some of the reaction rates are extremely fast.[2]

These studies provide insight to the mechanism of organolithium–olefin addition reactions in donor solvents. As contrasted with hydrocarbon solvents, ether solvents interact strongly with the incipient lithium cation. Thus, mechanistic differences could be anticipated between such reaction media. A most significant finding of these experiments is that some of the organolithium reagents have fractional reaction orders and some behave in a first-order manner. An important consequence of the differing reaction orders is that the relative reactivities of these organolithium reagents are concentration dependent.

A study of the structure dependence of the relative reactivities of a series of organolithium reagents toward addition to styrene was recently reported.[3] Previous general organolithium reactivity literature is reviewed there. Of note is that the majority of published studies of organolithium reactions with olefins in ether solutions pertain to the *propagation* reaction in vinyl polymerizations. Addition of organolithium reagents to DPE is comparable to the *initiation* step in the anionic polymerization of vinyl monomers.

The reaction examined is eq 1, where in these studies

$$\mathrm{RLi} + \mathrm{CH_2{=}C(C_6H_5)_2} \rightarrow \mathrm{RCH_2C(C_6H_5)_2Li} \qquad (1)$$

RLi is benzyllithium, allyllithium, phenyllithium, vinyllithium, *n*-butyllithium, and methyllithium. The addition to DPE gives exclusively the monoadduct. Kinetic results are identical when organolithium reagent or DPE is in excess.

Early use of this reaction was made by Ziegler and coworkers[4] to evaluate relative reactivities of three alkyllithium reagents in benzene solution. Detailed kinetic studies in benzene solution were reported by Evans and coworkers[5] for addition of *n*-butyllithium, ethyllithium, and *t*-butyllithium to DPE.

In a kinetic study in THF solution[6] the comparatively moderate rate of adduct formation between DPE and vinyllithium was contrasted with the comparatively instantaneous formation of the *n*-butyllithium–DPE adduct in this solvent. The fractional reaction order found for vinyllithium was interpreted as evidence for its being aggregated in THF solution. Measurements of the rate of addition of *n*-butyllithium to DPE in benzene with added aliquots of THF illustrate the accelerating effect of this solvent on this reaction rate.[7] A study of the kinetics of addition of the three methylphenylsilyllithium reagents to DPE reported[8] these reagents behave in a first-order manner in THF.

Experimental Section

Organolithium reagents are notable for their high reactivity toward oxygen or proton-active substances such as water. Consequently studies of these reagents must be done with extreme care.

The rate of buildup of adduct at 22 ± 1° was followed spectroscopically using a Cary Model 14 recording spectrophotometer. The closed-reactor spectroscopic cell used in these studies has been described.[9] In use, the cell was evacuated to high vacuum and then put under a positive argon pressure. Reactants were introduced with Hamilton gas-tight syringes. Cells of various path lengths were used which, depending upon the rate of reaction, provided a time–absorbance trace suitable for accurate evaluation.

The absorption maxima of the respective adducts are listed in Table I. The variation in $\lambda_{\max}$ for the phenyl and vinyl adducts is

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[1] This paper was reported in part at the Symposium on Hydrocarbon Ions, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, Abstract U-41; (b) Polaroid Corporation, Cambridge, Mass. 02139.

[2] In this respect diethyl ether is favorable and kinetic studies in this solvent will be reported in a subsequent paper.

[3] R. Waack and M. A. Doran, *J. Org. Chem.*, **32**, 3395 (1967).

[4] K. Ziegler, F. Crossman, H. Kleiner, and O. Schäffer, *Ann.*, **473**, 1 (1929); see pp 14–17.

[5] R. A. H. Casling, A. G. Evans, and N. H. Rees, *J. Chem. Soc.*, 519 (1966).

[6] R. Waack and P. E. Stevenson, *J. Am. Chem. Soc.*, **87**, 1183 (1965).

[7] R. Waack and M. A. Doran, *J. Organometal. Chem.*, **3**, 481 (1965).

[8] A. G. Evans, M. Ll. Jones, and N. H. Rees, *J. Chem. Soc., B*, 961 (1967).

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

Table I. Absorption Maxima of RLi–DPE Adducts in THF Solution

RLi	λ_{max}, mμ	Log ε
Phenyl	482	4.48
Vinyl	486	4.48
Methyl	497	4.49
n-Butyl	495	4.45
Allyl	495	4.48
Benzyl	492	4.48

larger than might be expected to be caused by a substituent situated one saturated carbon removed from the chromophoric center. All adducts have symmetrical absorption envelopes like that pictured for the *n*-butyl adduct[10] in THF. Molar absorptivities are all consistent.

It is established that excess organolithium, *e.g.*, *n*-butyllithium,[10] does not influence the spectrum of the adduct in THF solution. The organolithium reagents were prepared by well-proven standard procedures.[3,9,11] Benzyllithium, methyllithium, and phenyllithium are prepared from the appropriate bismercury compound and lithium at ~0.6 *M* in diethyl ether solution.[12] After stirring from 2 to 4 hr. a clear solution was obtained by centrifuging. Conversion of starting mercury compound determined by total alkalinity and recovery of metallic mercury was ≥90%. Vinyllithium and allyllithium were prepared from the respective tetrasubstituted tin compounds *via* transmetalation[13] with *n*-butyllithium in hexane or phenyllithium in diethyl ether. The former reaction was carried out on a sintered-glass filter plate. The insoluble organolithium reagents were washed three times with dry *n*-hexane before dissolving in THF. In the latter preparation the clear supernatant solution was separated from precipitated tetraphenyltin after cooling. Evaporation to dryness was followed by dissolving in THF.

The Hamilton syringes used to transfer reagents were stored in a nitrogen atmosphere after a drying period in a vacuum oven. The spectroscopic cell was oven dried at 150° and alternately evacuated and argon filled. THF was distilled under argon from a lithium dispersion–benzophenone complex. DPE was vacuum distilled from calcium hydride and stored under argon. Samples of DPE purified by preparative glpc gave identical results.

Rate measurements were carried out as follows. An aliquot of organolithium was transferred to the cell. The solvent, if diethyl ether, was pumped off and THF added. The desired amount of DPE was added, undiluted or as a stock solution. Mixing was done by magnetic stirring and tipping the solution back and forth in the cell several times. The absorbance at the absorption maximum of the adduct being formed was monitored continuously *vs.* time in the Cary Model 14 spectrophotometer. Mixing and positioning of the cell in the spectrophotometer required 30 to 40 sec. Reactions were also carried out in the reverse manner, *i.e.*, the organolithium reagents in THF being added to a solution of DPE, with equivalent results. Titration of each experiment for total alkalinity (with 0.1 *N* HCl to phenolphthalein end point) corroborated the accuracy of addition of the aliquot of the organolithium reactant.

Experimental scatter becomes substantial at concentrations below 5×10^{-3} *M* in organolithium reagents. This is presumably a consequence of a low level of impurities remaining on the walls of the reaction cell. *n*-Butyllithium is quite reactive to THF at room temperature. The reaction with DPE is so much faster that this is not a problem in these studies.

For the organolithium having appropriate absorption features, *i.e.*, benzyllithium, log ε_{330} 4.14, and allyllithium, log ε_{315} 3.7, the initial concentration values were determined from absorption measurements. This was especially useful with these reagents because their rapid reaction rates made it advantageous to work at low organolithium concentrations.

Two procedures for evaluating a differential rate expression were used. (1) In the case of a reasonably linear time–absorbance curve, the curve was extrapolated to zero time for an initial rate value at initial reactant concentration. (2) Where there was pronounced curvature in the initial portion of the time–absorbance curve, rates were measured by drawing tangents to the curve at various times, corresponding to a number of values of reactant concentrations.

The rate of addition of *n*-butyllithium to DPE in THF is extremely rapid. Rate measurements by the usual technique were, thus, not possible. Rate measurements at low temperatures using a thermostated cell[10] in the spectrophotometer were attempted. Although rate values were obtained in the temperature range −60 to −30°, the rate was still extremely rapid, making reliability of the measurements owing to incomplete mixing or temperature equilibration questionable. Reliability of the *n*-butyllithium concentrations as a result of handling at these low temperatures was also uncertain.

To obtain rate data for *n*-butyllithium, a competitive technique was devised. Equimolar mixtures of benzyllithium and *n*-butyllithium at various concentrations of total lithium were allowed to compete for a limited amount of DPE. The reactions were quenched with methanol after a few seconds. Analysis by glpc gave the ratios of hydrolysis products. This permits calculation of the ratio of rate of adduct formation with *n*-butyllithium relative to that for benzyllithium. Separate experiments in diethyl ether showed that the *relative rates* of the two reagents are not affected by the presence of the other species. A report of these rate studies of mixed organolithiums is being prepared.

Analysis of the reaction products, by glpc, established that reaction 1 goes essentially to completion with the formation of a single adduct. This is true whether DPE or the organolithium is the limiting reagent. Each of the adducts was isolated from separate preparative experiments and its structure confirmed by proton nmr and other physical constants when available. Only with vinyllithium was there evidence for a second product in the preparative-scale experiment.

Results

First-order behavior in olefin for reactions with organolithium reagents is typical.[5,7] This is also true for each of the organolithium reagents investigated here. An example is illustrated in Figure 1 in which phenyllithium was in 40-fold excess over DPE.

The experimental data are treated directly by the differential rate method.[14] Plotting the logarithm of the differential rate expression against the logarithm of the formal organolithium concentration is expected to give a straight line, the slope of which is the reaction order with respect to organolithium species. Two differential procedures were employed. In one of them, initial rates are measured at various initial concentrations of organolithium reagent. Use of initial rates avoids possible complications due to interaction of products with reactant. The second procedure involves measuring slopes at various times in a single experiment corresponding to various values of the reactant concentration. By this procedure, in an experiment in which DPE is in excess over organolithium reagent, an effective reaction order with respect to the organolithium reagent can be derived from a single experiment.[15] This method was used with some of the organolithium reagents reported here and found to give reaction orders in agreement with those obtained when the organolithium reagent is in large excess.

Data for phenyllithium are given as typical. Table II illustrates the constancy of the obtained reaction rate as measured from initial reaction rate, from rates at various reaction times, and from a first-order plot for the same reaction illustrated in Figure 1. Table III shows that the

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

(11) R. Waack and M. A. Doran, *J. Phys. Chem.*, **67**, 148 (1963).

(12) G. Wittig, F. J. Meyer, and G. Lange, *Ann.*, **517**, 167 (1951).

(13) D. Seyferth and M. A. Weiner, *J. Am. Chem. Soc.*, **83**, 3583 (1961).

(14) K. J. Laidler, "Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1965, pp 15–17.

(15) K. F. O'Driscoll, E. N. Ricchezza, and J. G. Clark, *J. Polym. Sci., Part A*, **3**, 3241 (1965).

Table II. Consistency of Reaction Rates from Different Data Treatments

Time, min	% reaction	ΔD, min^{-1}	[DPE], *M*	R_t/[DPE]$_t$, hr^{-1}
Initial	Initial	0.087	0.0037	2.64
6	27	0.064	0.0027	2.60
15	50	0.044	0.0018	2.68
30	75	0.022	0.0009	2.66
Slope of first-order plot	0 → 84	(Figure 1)		2.76

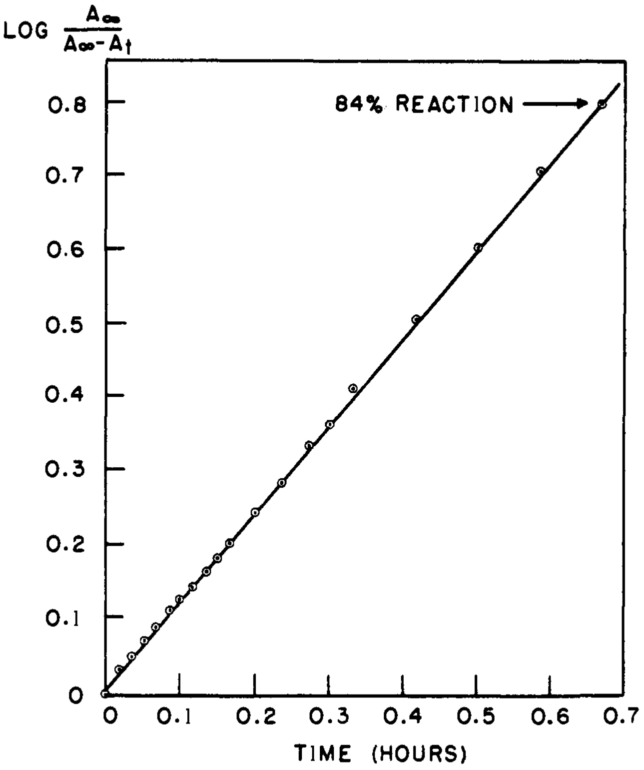

Figure 1. First-order behavior for addition of phenyllithium (0.15 *F*) to 1,1-diphenylethylene (0.0037 *M*) in tetrahydrofuran solution at 22°.

Table III. Independence of Rate and Reaction Ratios

[PhLi]$_i$, *M*	[DPE]$_i$, *M*	R_i/[DPE]$_i$, hr^{-1}
0.08	0.012	1.69
0.08	0.010	1.74
0.08	0.010	1.69
0.08	0.008	1.74
0.08	0.006	1.75
0.08	0.002	1.70
		Av 1.72
		Std dev 0.028

first-order behavior in DPE holds for various ratios of phenyllithium to DPE.

The majority of the rate experiments were done with organolithium reagent in large excess, and initial rates are used. Experimental data for each of the organolithium reagents are listed in Tables IV through VIII. Rates of

Table IV. Initial Rates for Addition of Methyllithium to DPE in THF

[DPE]$_i$ × 10^3, *M*	[MeLi], *M*	R_i/[DPE]$_i$, hr^{-1}
6.54	0.950	4.26^a
15.9	0.550	3.97^a
7.62	0.258	3.16^a
10.3	0.22	3.12
3.4	0.16	2.50
13.6	0.14	3.01^a
2.4	0.136	2.41
3.08	0.103	2.30^a
2.4	0.076	2.02
10.3	0.062	2.19
1.5	0.061	1.79^a
21.6	0.016	1.63
50.4	0.0094	1.23
Data for series × - ×, Method 2^b		
50	0.0092	1.24
49	0.0080	1.22
48	0.0070	1.14
47	0.0060	1.08
46	0.0052	0.98
45	0.0043	0.93

[a] Experiments done in cooperation with Dr. P. West. [b] Least-squares slope 0.269 ± 0.026, 95% confidence limits; does not include series × - × experiments.

Table V. Initial Rates for Addition of Benzyllithium to DPE in THF

[DPE]$_i$ × 10^3, *M*	[PhCH$_2$Li] × 10^3, *M*	R_i/[DPE]$_i$, hr^{-1}
0.12	1.16	68
0.12	0.88	54
0.12	0.59	34
0.08	0.54^a	33
0.12	0.44	21
0.08	0.40^a	21
0.12	0.31	14
0.09	0.28^a	16

[a] Rates from tangent at *t*, method 2.

Table VI. Rate of Addition of Allyllithium to DPE in THF

[DPE] × 10^3, *M*	[AllylLi],^{a} *M*	R^b/[DPE], hr^{-1}
5	0.014	45
1.1	0.005	25
3.4	0.0009	3.5

[a] [Allyllithium] from ε_{308} 5 × 10^3. [b] Rates at given time, method 2.

Table VII. Initial Rates for Addition of Vinyllithium to DPE in THF^a

[DPE]$_i$ × 10^3, *M*	[ViLi], *M*	R_i/[DPE]$_i$, hr^{-1}
22.8	0.49	3.3
11.4	0.48	2.8
34.0	0.45	2.3
3.8	0.074	1.9
4.0	0.068	1.8
4.8	0.028	0.95

[a] Data in addition to that reported in ref 6.

Table VIII. Initial Rates for Addition of Phenyllithium to DPE in THF

$[DPE]_i \times 10^3$, M	$[PhLi]_i$, M	$R_i/[DPE]_i$, hr^{-1}
10.3	0.288	4.16
10.3	0.288	3.80
10.3	0.286	4.22
10.3	0.192	2.60
9.1	0.178	2.64
10.0	0.083	1.69
10.0	0.082	1.74
10.3	0.080	1.69
6.8	0.058	1.46
10.0	0.043	1.21
6.8	0.041	1.11
8.0	0.031	0.79
11.4	0.026	0.82
228.0	0.021	0.63
17.1	0.017	0.57
10.0	0.015	0.60
9.1	0.0084	0.30
8.35	0.47	5.8

Table IX. Competitive Rates of Adduct Formation for *n*-Butyllithium and Benzyllithium with 1,1-Diphenylethylene

$[DPE]_i \times 10^3$, M	[*n*-BuLi], M	A/B^a	R^c/DPE, hr^{-1}
11.4	0.096	0.64	6100
1.65	0.0145	2.6	2800
0.46	0.006	4.4	1840
0.28	0.005	4.6	1600

[a] $A = [(C_6H_5)_2CHCH_2C_4H_9]$ and $B = [(C_6H_5)_2CHCH_2CH_2C_6H_5]$. Molar correction factors, relative to DPE, are 0.90 for *A* and 0.82 for *B*. [c] Calculated rate of addition of *n*-butyllithium to DPE based on extrapolated rate for benzyllithium addition.

adduct formation with *n*-butyllithium determined relative to that for benzyllithium are shown in Table IX. Concentration units are moles per liter.

Figure 2 is a double-logarithmic plot of reaction rates *vs.* formal reagent concentration for each of the organolithium species. The slope of each line defines the effective reaction order in organolithium reagent. Figure 2 illustrates the effective relative reactivities of these organolithium reagents. Of particular significance in Figure 2 is its illustration that effective reaction order in organolithium reagent changes with structure of the organolithium reagent. *A most important consequence of this behavior is that the effective relative reactivity of these reagents is concentration dependent.*

At the low concentration end of the methyllithium line in Figure 2 are data (×-×) derived from an experiment in which the concentration of DPE was 0.050 *M* and that of initial methyllithium 0.0094 *M*. Rate values *vs.* methyllithium concentration are derived by the previously described method 2 of measuring slopes of the rate *vs.* time curve. These rate values fit the line described by the initial rate values up to 50% consumption of the methyllithium. Below this concentration of methyllithium the points deviate somewhat. The experiment demonstrates that interference by product on the measured reaction rate is not significant.

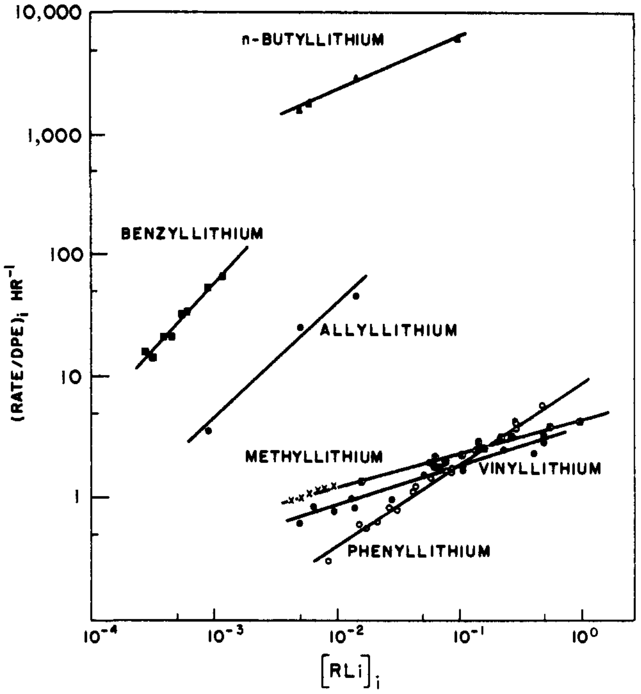

Figure 2. Log-log plot of the differential rate expression for addition of the respective RLi to 1,1-diphenylethylene in tetrahydrofuran solution at 22°.

Discussion

The organolithium reagents examined in this study are representative of three structure groups, *i.e.*, alkyllithiums, *e.g.*, methyllithium and *n*-butyllithium, sp^2 hybridized (in that the lithium is bound to sp^2-hybridized carbon by a σ bond), *e.g.*, phenyllithium and vinyllithium, and resonance-stabilized reagents in which the carbon formally bound to lithium can undergo hybridization change to allow delocalization of the incipient negative charge throughout a π system, *e.g.*, benzyllithium and allyllithium. These three classes of reagents show two distinct kinetic behaviors. Benzyllithium and allyllithium react in an approximate first-order manner. Each of the other species reacts with a fractional kinetic dependence.

The capacity to delocalize, *i.e.*, disperse, negative charge throughout the organic moiety should promote charge separation between incipient anion and cation. This will tend to strengthen interaction between the positively polarized lithium and the solvent. Together these factors favor strong solvation. Hence, interaction with solvent overcomes self-solvation, or aggregation forces and the monomeric species predominates.[16,17]

On the other hand, charge density localized in a σ orbital is favorable to strong cation–anion interaction. The result is that charge separation is minimized and solvation of lithium is weaker than in the above. In these cases energies of solvation by THF appear to be insufficient to overcome forces promoting aggregation. These species are found to be aggregated even in the strong donor solvent THF.[16,17] The aggregates can form specific etherates with THF.[18]

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(16) R. Waack and P. West, *J. Organometal Chem.*, **5**, 188 (1966), and references therein.

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

(18) R. Waack and M. A. Doran, studies to be published.

Table X. Comparative Kinetic Behavior for Addition of Organolithium Reagents to DPE in THF

RLi, *M*	Effective reaction order	Rate constant[a]
Methyl	0.27 ± 0.03	0.12
Phenyl	0.66 ± 0.04	0.25
Vinyl	0.34 ± 0.1	0.11
n-Butyl	~0.4	470 (~240)[b]
Allyl	~1	110
Benzyl	1.1 ± 0.2	3000

[a] $\mathrm{l.}^{1/n}\,\mathrm{mol}^{-1/n}\,\mathrm{sec}^{-1}$ $(\times 10^2)$; $k = k_2K(1/n)^{1/n}$. [b] Taking the mean of four data points and extrapolating the line of slope 0.25 to unit *n*-BuLi concentration.

First-order kinetic behaviors can result from the reagent being monomeric, or predominantly so, in this solution. First-order dependence on organolithium might also result if the aggregated species is the entity responsible for product formation. Colligative measurements show benzyllithium to be monomeric in THF,[17] thus favoring the former interpretation for this reagent.

The interpretation given to these fractional reaction orders is analogous to that proposed to explain fractional reaction orders found for organolithium reagents in hydrocarbon solution.[5,16] The mechanism invokes a preequilibrium of the relatively unreactive aggregated organolithium species and a smaller substantially more reactive entity, presumably the monomer. Providing *K* for the above equilibrium strongly favors the existence of aggregate, the rate of adduct formation is given by $\mathrm{d}A/\mathrm{d}t = kK(1/n)^{1/n}[\mathrm{RLi}]^{1/n}[\mathrm{DPE}]$. Hence rate constants obtained for these species are a composite of a rate constant and an equilibrium constant. Physical measurements capable of evaluating *K* have not been devised, but the kinetic behavior requires it to be very small. In one case, employing curve fitting and a reaction scheme involving monomer, trimer, and hexamer equilibrium, *K*'s of the order 10^{-9} and 10^{-21} were derived for *n*-butyllithium in heptane.[19] Effective reaction orders in organolithium reagent, as determined by least-squares slopes of Figure 2, are listed in Table X.

The least-squares slopes of the reaction order plots for methyllithium, vinyllithium, and *n*-butyllithium are interpreted as resulting from tetrameric association of the species in THF. Colligative measurements in THF solution established that methyllithium is tetrameric in THF solution[17] at 22° over the concentrations used in these studies. Although reactivity with solvent precludes such colligative measurements of *n*-butyllithium in THF, identical tetrameric association is found for methyllithium and butyllithium in diethyl ether. Mechanistic pathways other than the one illustrated above may be operative, but it seems clear that the fractional reaction orders arise from the organolithium reagent's being aggregated in solution.[16]

The reaction order of 0.66 found for phenyllithium is not consistent either with a monomeric species or a dimeric species. Such a fractional reaction order can arise from the phenyllithium being dimeric[17] and both the monomer and the dimer reacting to give product.[20] One consideration is that the dimer–monomer equilibrium constant, *K*, is very small. An alternate consideration is that the value of *K*, rather than being very small, is such that the relative concentrations of dimer–monomer change over the concentration of these experiments. A third possibility is that *K* is as in the preceding and that only monomeric reagent is responsible for product formation.[21] Colligative measurements do not permit distinguishing between these situations.

The structure–reactivity order depicted in Figure 2 was not foreseeable from a consideration of the relative basicities predictable for each of the organolithium species from the acidity[22] of the corresponding hydrocarbon. Thus, contrary to the finding that relative rates of proton exchange relate to the thermodynamic stabilities of the respective "carbanions,"[23] the kinetic activity of these organolithium species is dictated by factors other than those influencing relative thermodynamic stabilities. The fact that the reaction orders in organolithium vary from unity to fractional values indicates that factors other than the intrinsic structure of the organic moiety is influencing the rate of reaction of these organolithium species.

The reactive entities in these solutions are probably ion-pair type species. Variations in ion-pair interaction, as well as differences in aggregation behavior, are assuredly influential to the relative kinetic activity of these reagents. Notably these factors would not be present in kinetic acidity evaluations[23] or in thermodynamic evaluations in more ionizing media.

The spread and relative positions of the measured effective reactivities is extremely significant. In the concentration range examined the sp^2 organolithium species are the least reactive. Presuming its kinetic behavior is maintained with increasing concentration, the reactivity of benzyllithium exceeds that of *n*-butyllithium at $>5 \times 10^{-2}\,F$ organolithium. At $5 \times 10^{-2}\,F$ organolithium, the relative magnitudes of reactivities are *n*-butyl (1800), benzyl (330), allyl (21), methyl (1), vinyl (0.7), and phenyl (0.25). At $5 \times 10^{-1}\,F$ organolithium, presuming extrapolation of benzyl and allyl measurements is permissible, the relative magnitude of reactivities is benzyl (17,000), *n*-butyl (3600), allyl (470), phenyl (1.5), methyl (1), and vinyl (0.9).

Reaction rates within each structure group are, with one exception, consistent. The notable discrepancy is the large rate difference between *n*-butyllithium and methyllithium. The former is believed to be representative of alkyllithiums, with the lower reactivity of methyllithium being the exception.[3]

Presuming the kinetic behaviors will hold upon extrapolation to very dilute solution (or that all will show expected transition to first-order behavior at not too greatly different concentrations), the relative reactivity order would be alkyl > sp^2 > resonance stabilized. This is the reaction order sequence that would be anticipated from a Brønsted relationship.[22]

The relative reactivities illustrated in Figure 2 compare reasonably with those reported for reactivity toward addition of styrene at the concentration (0.19 *F*) of organolithium reagent used in the competitive reactivity experi-

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(19) H. Sinn, C. Lundbord, and O. T. Onsager, *Macromol. Chem.*, **70**, 222 (1964).

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

(21) We are indebted to Dr. E. C. Steiner for pointing out to us the suitability of this model.

(22) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, pp 19, 20–31, 49–55.

(23) A. I. Shatenshtein, *Advan. Phys. Org. Chem.*, **1**, 187 (1963); A. Streitwieser and D. E. VanSickle, *J. Am. Chem. Soc.*, **84**, 249 (1962).

ments.[3] Of note is that the reactivity order reported here for olefin addition is not the same as the reactivity order found for metalation of triphenylmethane.[24] This will be discussed in forthcoming publication.

In a recent study of rearrangements of certain organolithium species, evidence that the mechanism involves intermediate formation of a molecule of DPE and addition of a new organolithium species was presented.[25] Combining some direct addition studies with those on rearrangement, the authors concluded the reactivity of organolithium compounds toward DPE increases along the series phenyl < *n*-butyl < benzyl. This emphasizes the importance of the dependence of relative reactivity on reagent concentration. The concentrations we estimate for *n*-butyllithium and benzyllithium in the above studies are ~0.14 and 0.09 *F*. Figure 2 shows that this is the critical concentration where the relative reactivities of *n*-butyllithium and benzyllithium change. Considering the effect of concentration, the reactivity order derived from the above study is in accord with that indicated by these kinetic studies.

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Molecular Structure and Photochemical Reactivity. X. Aliphatic Hydroxy Ketones

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Abstract: Irradiation of an α-hydroxy aliphatic ketone, 3-hydroxy-2-butanone (acetoin), at 3130 Å yields acetaldehyde with the same quantum yield, $\Phi = 0.3$, in both gas-phase and liquid solutions. The vapor-phase quantum yield of acetaldehyde is not significantly affected by changes in temperature, but large, temperature-dependent and equal yields of CO and CH_4 were observed along with minor yields of ethanol and biacetyl. A large, solvent-dependent yield of ethanol was noted in the liquid phase. These and other products are found in 3 MeV γ irradiated samples of neat acetoin and acetoin in benzene solution. Results are interpreted on the basis of two primary photochemical reactions: (1) an intramolecular rearrangement of an excited acetoin molecule to form two molecules of acetaldehyde and (2) dissociative processes giving radicals which further react in a sequence of secondary reactions. Irradiation of neat and benzene solutions of a β-hydroxy aliphatic ketone, 1-hydroxy-2-methyl-3-butanone, with $\lambda > 3000$ Å radiation yields acetaldehyde, 2-butanone, *n*-propyl alcohol, allyl alcohol, and biacetyl. The major product of photolysis at 3130 Å and 25° in toluene solution was 2-butanone, $\Phi = 0.05$. With the exception of *n*-propyl alcohol, $\Phi = 0.026$, the quantum yields of the other products were less than 0.01 under these conditions. γ irradiation gives these products plus additional ones. Results of ultraviolet absorption and phosphorescence emission spectroscopy indicate that both hydroxy ketones have n,π^* excited singlet and lowest lying triplet states. In at least one of these, the β-hydroxy compound, the triplet state does not appear to be photochemically important.

The Norrish Type II process, an intramolecular photoelimination of an olefin from aldehydes and ketones, is a mode of decomposition common to carbonyl compounds having hydrogen atoms at the γ position of the alkyl chain.[2,3] The fragmentation occurs in both the liquid and gas phase, is generally not strongly temperature dependent, and involves an internal hydrogen atom abstraction by the carbonyl chromophore *via* a cyclic transition state.[4-7] Both singlet and triplet n,π^* states are important in this process.[8]

A notable exception to this "typical" photochemical behavior was observed in the liquid-phase photolysis of *o*-hydroxybutyrophenone at 3130 Å.[9,10] No Type II cleavage could be observed for this compound in several solvents, whereas the unsubstituted butyrophenone has a quantum yield of 0.42 for this process in both the gas and liquid phase. This quenching effect of the hydroxyl group on the Type II process is ascribed to stabilization by an internal photoenolization analogous to that earlier proposed to explain the stability toward intermolecular photoreduction shown by *o*-hydroxy and *o*-alkyl derivatives of aromatic ketones.[11,12] That such a photo-

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