ADDITION OF ORGANOLITHIUM REAGENTS TO 1,1-DIPHENYLETHYLENE IN DIETHYL ETHER, KINETICS AND STRUCTURE REACTIVITY BEHAVIORS

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(Received January 12th, 1971)

SUMMARY

Kinetic studies of the addition of benzyllithium, allyllithium, phenyllithium, methyllithium and n-butyllithium to 1,1-diphenylethylene in diethyl ether solution show the reactions are first order in DPE and variable order in organolithium reagent. A consequence of the differences in effective reaction orders is that the relative reactivity of these reagents is concentration dependent. Vinyllithium does not give the normal 1/1 adduct with DPE in Et_2O. In the concentration range investigated, *i.e.* between 10^{-3} and 1 M organolithium, methyllithium is the least reactive and n-butyllithium is the most reactive, by a factor of $\sim 1/4000$. The effective organolithium reaction orders and relative reactivity order in Et_2O are similar to those reported in tetrahydrofuran. The rate increase between Et_2O and THF reaction media is smallest for phenyllithium (*i.e.*, 90) and largest for benzyllithium, (*i.e.*, 1700).

A consequence of the dipolar nature of organolithium reagents is that their properties and behaviors depend markedly on the solvent media. The influence of solvation is exemplified by NMR[1] and electronic spectral studies[2]. Sensitivity of an organolithium reagent to its environment is expected to vary with reagent structure. Kinetic studies are reported here for six organolithium reagents in diethyl ether. The findings are compared to those reported in tetrahydrofuran (THF)[3]. Although differences in reaction rate are substantial, kinetic behaviors are similar between the two solvents.

The reaction examined is addition of the organolithium reagent to 1,1-diphenylethylene (DPE) to form a substituted (diphenylmethyl)lithium. Only monoadduct forms under the present reaction conditions. This reaction was used by Ziegler and co-workers[4] in benzene solution and by Evans and co-workers who have reported detailed kinetic studies for addition of alkyllithiums to DPE in benzene[5]. The reagents examined here are methyllithium, n-butyllithium, phenyllithium, vinyllithium, allyllithium, and benzyllithium.

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Kinetic evaluation in ether has the advantage that the organolithium species that reacted too fast in THF for accurate kinetics[3], *i.e.*, n-butyllithium, are in a measurable rate range for detailed study. A complicating feature is that the reaction of species of lower reactivity, *i.e.*, phenyllithium and methyllithium, exhibit induction periods. Induction periods introduced by a solvent change have been reported[6,7].

A surprising finding is that vinyllithium does not form a normal mono-DPE adduct in diethyl ether. Vinyllithium adduct formation is normal in THF[8]. There are other examples of a solvent change altering the product course of organolithium reactions[9,10].

The reactivity behaviors resulting from a change in solvent can arise from differences in the nature of the organolithium species in solution, *i.e.*, the aggregate nature and equilibrium position, and the solvent dependence of the energetics of the transition state complex. These factors will be discussed.

The effects of solvents on the rates and kinetics of the propagation reaction of organolithium initiated olefin addition polymerization is reported for several systems. Earlier studies showed the accelerating effects of polar solvents on the propagation reaction of styrene polymerization, but showed the kinetics to be little changed[11,12]. The significance of the structure of the organolithium species to its dependence on solvent for its reactivity is illustrated by the report that the addition of THF to the n-butyllithium initiated polymerization of styrene, in benzene, has a pronounced effect on the initiation rate[13]. Strikingly different behaviors are reported for poly-styryllithium in dioxane and THF[14,15]. The effect of dielectric constant on the prop-agation rate of polystyryllithium polymerization is reported for benzene/THF mixture[16]. The addition of THF is shown not to have as significant an effect on the propagation rate of polyisoprenyllithium in cyclohexane[17]. Kinetic studies of the propagation rates of polybutadienyllithium and polyisoprenyllithium in hexane and THF show that the reactivity of these structures are not as sensitive to solvent chan-ges[18] as is polystyryllithium. As well as changing the reaction rates, the polymer microstructure of n-butyllithium initiated polymerization of dienes is sensitive to the solvent media[19,20]. The nature of the solvent also alters copolymerization parameters in organolithium polymerizations[21]. The acceleration of organolithium reactions, other than polymerization, resulting from low concentrations of ether or amines is also great[22,23].

EXPERIMENTAL

The rate measurements, preparation of organolithium reagents and other general experimental procedures are identical to those reported previously[3]. Diethyl ether was distilled from lithium dispersion under argon. Reaction rates were followed at $22 \pm 1°$ spectroscopically using a Cary-14 recording spectrophotometer. The absorption maxima of the respective adducts are substantially different from those reported in THF in accord with the solvent dependence reported for 1,1-diphenyl-n-hexyllithium[2]. All the adducts have symmetrical absorption envelopes like that described for the n-butyllithium adduct[2]. The absorption maxima and molar ab-sorptivities of each adduct are listed in Table 1.

Organolithium concentrations were determined by titration of total alkalinity[3]. Only freshly prepared reagents were used. In some of the benzyllithium experiments

TABLE 1

ABSORPTION MAXIMA AND MOLAR ABSORPTIVITIES OF RLi–DPE ADDUCTS IN DIETHYL ETHER SOLUTION

R	λ_{max} (nm)	$\varepsilon(\times 10^{-4})^a$
Phenyl	430	2.5
Methyl	438	2.0
n-Butyl	438	2.5
Allyl	428	2.6
Benzyl	438	2.5

^{a} Width of absorption band at half-height typically $\sim 3900\ cm^{-1}$.

TABLE 2

GLC MOLAR CORRECTION FACTORS FOR ORGANOLITHIUM–DPE ADDUCTS AND RELATED COMPOUNDS

No.	Compound	Formula	Molar correction factor ^{a}
1	$C_6H_5-C_6H_5$	$C_{12}H_{10}$	1.07
2	$(C_6H_5)_2CH_2$	$C_{13}H_{12}$	1.01
3	$(C_6H_5)_2C=CH_2$	$C_{14}H_{12}$	1.00
4	DPE adduct of CH_3Li	$C_{15}H_{16}^b$	0.97
5	DPE adduct of $CH_2=CHLi$	$C_{16}H_{16}^b$	
6	DPE adduct of C_2H_5Li	$C_{16}H_{18}^b$	1.00
7	DPE adduct of $CH_2=CH-CH_2Li$	$C_{17}H_{18}^b$	1.02
8	DPE adduct of n-C_4H_9Li	$C_{18}H_{22}^b$	0.90
9	$(C_6H_5)_2C=CHC_6H_5$	$C_{20}H_{16}$	0.70
10	DPE adduct of C_6H_5Li	$C_{20}H_{18}^b$	0.82
11	DPE adduct of $C_6H_5CH_2Li$	$C_{21}H_{20}^b$	0.82
12	$(C_6H_5)_2C=C(C_6H_5)_2$	$C_{26}H_{20}$	0.66

^{a} Relative to DPE, *i.e.* area $Ph_2CHCH_2R \times$ molar correction factor = DPE equivalent. GLC F&M 609, flame ionization detector, Infotronics integrator; QF-1 column $4' \times 0.25''$, or $2' \times 0.25''$. Att. 2×100, μl 0.2 ± 0.1 M solution; DET = IP = 300°; 1–4 140° isothermal, 7–11 200–225° isothermal. ^{b} Isolated reaction product identified by ^1H NMR.

(*i.e.*, those points in Fig. 1 designated by a line), benzyllithium concentration was measured spectroscopically at $\lambda_{max} = 330$ nm. $\varepsilon = 1.3 \times 10^4$.

Analysis of the reaction products, by GLC, established that, with the exception of vinyllithium, the addition of each of these reagents to DPE gives exclusively the mono-adduct[3]. Data pertaining to the quantitative GLC detection of these adducts are listed in Table 2.

Vinyllithium was prepared in hexane from tetravinyltin and one equivalent of n-butyllithium to insure that no residual butyllithium precipitates with the vinyl-lithium. Vinyllithium was also prepared in diethyl ether by adding 3.3 equivalents of methyllithium to tetravinyltin. The methylvinyltin compounds were removed by evaporation to dryness in high vacuum. In THF solution these vinyllithiums gave the same reaction rates as reported previously[8]. Vinyllithium was also prepared by reaction of lithium with divinylmercury in ether. The reaction went in good con-version, as measured by titration of soluble alkalinity, but the very strong odor of trace residual divinylmercury forced abandonment of the use of this reagent.

Allyllithium was prepared from phenyllithium and tetraallyltin in diethyl

ether. This route avoids the co-precipitation of n-butyllithium allyllithium which occurs when allyllithium is prepared in hexane from n-butyllithium and tetraallyltin. Tetraphenyltin precipitates and after cooling in ice and centrifuging the clear supernate allyllithium ether solution was withdrawn; final molarity 0.3.

RESULTS

   Addition of these organolithium reagents to DPE, is first order in the latter, a behavior which has been demonstrated many times for organolithium olefin addition reactions[3,4,6,8,13,18]. The reaction order in organolithium, however, varies with reagent structure, as found in THF solution[3]. Fig. 1 is a log-log plot of the differential rate expression, i.e., rate/DPE $= k(RLi)^{1/n}$. The slope of each reaction rate–organolithium concentration dependence line is the reaction order in organolithium reagent. The intercept gives the rate constant, which in the case of fractional reaction orders is a composite, $k = k' \cdot K \cdot (1/n)^{1/n}$, where K is the equilibrium constant for aggregate dissociation, n is the average effective aggregate size, and k' is the true rate constant.
   The practical significance of the different effective reaction orders is that the relative reactivity of these organolithium reagents is concentration dependent.
   Absolute reaction rates are listed in Table 3 for two concentrations of organolithium reactant. Rates relative to that of methyllithium at each concentration are given in parentheses. The effect of varying reaction orders is apparent in the relative rates at the two concentrations. The relative rates of those species which have
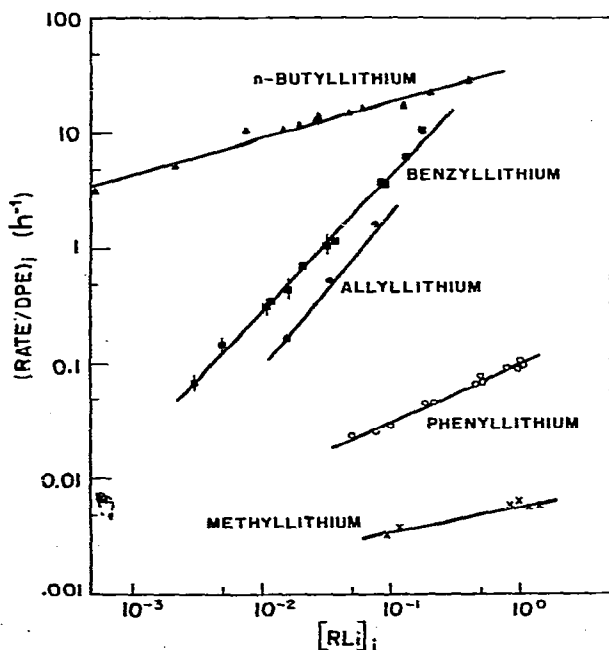

Fig. 1. Log–log differential rate plot for addition of the indicated organolithium reagent to DPE in diethyl ether at $22 \pm 1°$.

TABLE 3

ABSOLUTE REACTION RATES FOR ADDITION OF RLi TO $CH_2=CPh_2$ IN Et_2O AT 22°

RLi	RLi concentration			
	0.01 M		0.1 M	
Methyllithium	0.07^a	$(1)^b$	0.12	(1)
Phenyllithium	0.33	(4.7)	1.1	(9.2)
Allyllithium	2.8	(40)	53	(440)
n-Butyllithium	280	(4000)	580	(4800)
Benzyllithium	8.3	(120)	120	(1000)

^{a} Expressed as $(Rate/DPE)_i sec^{-1} (\times 10^5) = k(RLi)_i^{1/n}$. ^{b} Reaction rates relative to MeLi at indicated concentration given in parentheses.

TABLE 4

COMPARISON OF KINETIC BEHAVIOR IN THF AND Et_2O FOR ADDITION OF ORGANOLITHIUM REAGENTS TO 1,1-DIPHENYLETHYLENE

Organolithium	Effective reaction order		Rate constant $(k)^a$		k(THF)
	Et_2O	THF	Et_2O	THF	$k(Et_2O)$
Methyllithium	0.21 ± 0.09	0.27 ± 0.05	0.00017	0.12	700
Phenyllithium	0.51 ± 0.03	0.66 ± 0.04	0.0028	0.25	90
Vinyllithium		0.34 ± 0.1		0.11	
Allyllithium	~ 1.3	~ 1	1.1	110	100
n-Butyllithium	0.30 ± 0.05	$\sim 0.4^b$	1.0	$\sim 500^b$	500
Benzyllithium	1.2 ± 0.06	1.1 ± 0.2	1.8	3000	1700

^{a} $l^{1/n} \cdot mole^{-1/n} \cdot sec^{-1} (\times 10^2)$, $k = k_2 \cdot K \cdot (1/n)^{1/n}$. ^{b} Evaluated relative to benzyllithium; only four data points.

approximately the same effective reaction order are similar at the two concentrations.

The effective reactivities of these reagents are more widely separated than in THF[3]. Within the investigated concentration range n-butyllithium and benzyllithium undergo a change in relative reactivity with concentration; at ~ 0.5 formal their reactivities are similar. Extrapolation to lower concentrations shows that at $\sim 10^{-4}$ formal concentration phenyllithium will be about as reactive as benzyllithium, providing the kinetic patterns hold.

Effective reaction orders calculated by regression analysis[24] of the data in Fig. 1 are listed in Table 4. Error limits are the 95% confidence limits of the slopes of the regression lines.

Effective rate constants are also listed in Table 4. Values obtained in THF[3] are listed for comparison.

The data given for methyllithium and phenyllithium is taken after a constant rate of reaction was obtained. Reactions of these reagents with DPE have induction periods in diethyl ether. Substantial experimentation indicates that these induction periods are true characteristics of these reactions, but the experiments are not definitive regarding the mechanistic origin of the induction period. Induction periods are usually

greater for methyllithium than for phenyllithium. Generally, at substantially less than 1% conversion a constant rate is attained which then stays constant up to high conversion, as in the reactions in THF[3]. Times to constant rate ranged from 0 to ~60 min.

DPE, vacuum distilled from calcium hydride, or purified by GLC behaved the same regarding induction periods. To test for impurities as the cause, sufficient methyllithium was mixed with DPE to produce the colored adduct. Reaction of this DPE with additional methyllithium had induction periods.

It is revealing that these induction periods are confined to very low extents of conversion. Possibly, then, induction periods in reactions in other solvents, e.g. THF, in which reaction was not monitored at such very low conversions, may have been overlooked. Examination of a series of reactions in THF with methyllithium, at very low DPE concentrations so that conversion rates are comparable to those with methyllithium in ether after induction did not show induction periods. Examination of the reaction of n-butyllithium with DPE in benzene at low conversions showed no induction period.

Experiments established that possible introduction of alkoxides, i.e., via reaction with oxygen, were not a factor influencing the induction period. In identical experiments with methyllithium partial quenching with ethanol or methanol did not substantially alter the induction periods.

In a series of experiments with phenyllithium the ratio of DPE/phenyllithium was changed over a wide range. The induction period did not show a trend with changes in either reagent independently. Slow rates, whether resulting from low DPE concentration or low phenyllithium concentration, have longer induction periods.

These experiments indicate the induction periods are a characteristic of the methyllithium and phenyllithium reaction in diethyl ether. Because extent of reaction at cessation of induction period is very low, it does not dominate the time conversion findings. It is interesting that the reactions of n-butyllithium plus DPE in benzene containing small amounts of THF do not show an induction period. Similar experiments with phenyllithium have pronounced induction periods. A previous example of the occurrence of the induction periods with a solvent change is the behavior of n-butyllithium in benzene and cyclohexane in olefin addition reactions[25]. In benzene there is no induction period, whereas reactions in cyclohexane have induction periods. In these cases, the presence of alkoxides reduces the induction period [26].

It is surprising that vinyllithium does not react with DPE in the same manner as the other organolithium reagents under these conditions. Vinyllithium does initiate the polymerization of styrene in ether, although at much slower rates than in THF[27]. A mixture of vinyllithium and DPE in diethyl ether will sit for several hours at room temperature without forming color. Addition of sufficient THF produces color showing the vinyllithium is active.

Vinyllithium and DPE in ether apparently react slowly to give a product of higher molecular weight than the normal adduct and not absorbing in the normal adduct range. Quantitative GLC analysis shows that DPE is consumed and that the normal vinyllithium adduct is formed in only a small fraction of the amount of consumed DPE. When THF is present at 2–3 equivalents of the vinyllithium, again some normal adduct is formed, by the bulk of the DPE is otherwise consumed. No other products are evident in the GLC trace at normal analysis (250° after 30 min) tempera-

tures. Possibly adduct decomposition[8] occurs at rates comparable to its formation in diethyl ether. An isolated white solid was not investigated further.

DISCUSSION

        The kinetic behavior of these organolithium reagents in diethyl ether is like that in THF[3]; reaction rates are substantially slower in ether than in THF. The fractional reaction orders are in accord with reported colligative measurements[28] on the basis of an aggregate–monomer reaction scheme in which product is formed predominantly by a reaction of the monomeric reagent[3]. The change in reaction order for phenyllithium between THF and diethyl ether may infer monomeric reagent is more reactive, relative to dimer, in ether than it is in THF. The 0.5 effective reaction order indicates monomer is essentially responsible for phenyllithium adduct formation in ether, whereas in THF, appreciable reaction via dimer is indicated[29]. The effective reaction order of n-butyllithium is better defined than in the THF experiments and is, within experimental error, in agreement with tetrameric n-butyllithium in diethyl ether[28].
        As well as influencing relative rate constants, i.e., that between monomer vs. dimer[29], the position of the aggregate–monomer equilibrium is no doubt influenced by the solvent. It is reasonable to expect that poorer less basic solvents shift the equilibrium to favor aggregate. The effective reaction order may not be sensitive to a change in the monomer–aggregate equilibrium, but the reduction in reactive monomer may have a substantial influence on the measured effective reactivities in different solvents. For example, colligative measurements of phenyllithium indicate dimer is the dominant species in THF and diethyl ether; such measurements are not sufficiently sensitive to detect an equilibrium shift in a predominately aggregated species.
        Benzyllithium behaves approximately first order in both THF and diethyl ether. A monomer–aggregate equilibrium is not indicated to be involved. The change in the effective rate constant, listed in Table 4, between THF and diethyl ether, should be a result of relative solvent effects on the rate constant. The kinetic activity of this reagent is enhanced substantially by the better coordinating solvent THF. The difference found here is appreciably larger than the ~160 fold rate enhancement in the propagation rate constant of styryllithium in THF compared to that in dioxane[15]. An inference is that the influence of solvent on the kinetic activity of a reagent also depends on the substrate, a reasonable conclusion since the dipolar nature of the transition state should vary for sufficiently different substrates.
        For methyllithium, butyllithium and phenyllithium, the effects of the solvent on reaction rate must be considered in terms of solvent effects on the rate constant and the equilibrium constant for association. Methyllithium and buyllithium are affected similarly by the change from THF to diethyl ether. If the transition state for reaction of these alkyllithiums with DPE is of similar polarity to that with benzyllithium*, the rate change between THF and ether would be larger. The lower value

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* The controlling factor is the difference in solvation between reactant and transition state; the relative energetics of solvation of monomeric butyllithium and benzyllithium are not known, but if the transition state is sufficiently more polar than either reactant the influence of solvation on this state would overwhelm smaller differences in solvation in the reactants. See for example ref. 30.

could indicate the influence of the solvent change on the monomer aggregate equilibrium.

The reactivity of phenyllithium is least influenced by the THF–Et$_2$O solvent change. The change in reaction order for phenyllithium between THF and diethyl ether may indicate K dimer is greater in diethyl ether than in THF. It was pointed out that the conditions of (1) relative monomer/dimer ratio changing appreciably over the concentration range of these kinetic measurements and (2) that only monomer is responsible for adduct formation[3] can account for the 0.6 reaction order in THF, as well as the condition of product formation via dimer mentioned above. If this is the case, the reactivity of phenyllithium in ether might be expected to be reduced more, relative to THF, than it is, since diethyl ether should shift the monomer–aggregate equilibrium toward aggregation. A possible conclusion is that the transition state for addition of phenyllithium to DPE has less charge separation than, for example, that for benzyllithium addition to DPE. Its reaction rate is, thus, less sensitive to solvent.

The fact that polar solvents accelerate the reaction rates of organolithium reagents, in concentration ranges where ion-pairs are presumably the reactive species, infers that the transition states are more polar and more energetically solvated than are the reactants in the respective solvents[30].

The most obvious influence of a polar solvent on a dipolar transition state is its facilitation of the electrical work of charge separation, which is reflected in the activation energy. An effect more difficult to assess is differing degrees of ordering of the solvent in the transition state relative to that in the reactant, which is reflected in the activation entropy. A high degree of ordering in a polar transition state, compared to a reactant having relatively unstructured solvation, would lead to larger negative activation entropy with a more polar solvent; a rate retarding factor. These opposing effects may moderate the overall effect of solvent polarity on the rate constant, in certain cases. This might be a factor in the insensitivity of phenyllithium reactivity to solvent. The effect of the interplay of these factors with solvent change as well as the effect on K is difficult to distinguish.

It is interesting that the relative order of reactivity of these organolithiums is comparable in both THF and Et$_2$O. The reactivity of benzyllithium and n-butyllithium reverse at a similar concentration in both THF and diethyl ether. The largest difference is that, in diethyl ether, phenyllithium is substantially more reactive, relative to methyllithium compared to its relative reactivity in THF. The difference in reactivity between allyllithium and benzyllithium is less in diethyl ether than it is in THF. Comparison with the rate of addition of n-butyllithium to DPE in benzene[31] shows there is an ~250 fold increase in reactivity in diethyl ether.

The difference in experimental effective reaction orders in diethyl ether and THF results in the relative reaction rates in the two solvents being different at different concentrations. This is illustrated by comparison of the ratios of the rate constants in Table 4, which are the effective relative reactivities obtained by extrapolation at unit organolithium concentration, with relative rate values at 0.01 formal organolithium, which are 510, 33, 390, 300, and 2000 for the same reagent order as given in Table 4.

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