—10°. This NMR behavior can be understood by the assumption of the following valence tautomerism (Fig. 1) occurring rapidly even at —10° in the solution. This rapid tautomerism averages out all the protons and the NMR spectrum will have a single peak. The τ-value observed can be approximately calculated as follows on the assumption of the tautomerism. The calculation involves averaging out all the τ-values of the terminal protons of butadiene(tricarbonyl)iron[4] and the hypothetical τ-values for π-allyl(tricarbonyl)iron* and results in a value of 8.35 τ.

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1 A. NAKAMURA, P.-J. KIM AND N. HAGIHARA, *J. Organometal. Chem.*, 3 (1965) 7.
2 A. C. COPE AND F. KAGAN, *J. Am. Chem. Soc.*, 80 (1958) 5499.
3 G. F. EMERSON, J. E. MAHLER, R. PETTIT AND R. COLLINS, *J. Am. Chem. Soc.*, 86 (1964) 3590.
4 M. L. H. GREEN, L. PRATT AND G. WILKINSON, *J. Chem. Soc.*, (1959) 3753.
5 H. D. MURDOCH AND E. A. C. LUCKEN, *Helv. Chim. Acta*, 47 (1964) 1517.
6 W. R. MCCLELLAN, H. H. HOEHN, H. N. CRIPPS, E. L. MUETTERTIES AND B. W. HOWK, *J. Am. Chem. Soc.*, 83 (1961) 1601.

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* π-Allyltricarbonyliron is paramagnetic in solution[5]. The hypothetical τ-value was calculated by averaging the known τ-values of the terminal protons in π-allyltetracarbonylmanganese and in π-allyltricarbonylcobalt (*cf.* ref. 6).

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Solvent and concentration effects on the rate of addition of *n*-butyllithium to 1,1-diphenylethylene

Enhancement of rates of organolithium reactions by ether solvents has been recognized for many years, but quantitative knowledge is wanting. We report here measurements of the rate of reaction (1) in hydrocarbon solutions containing small amounts of tetrahydrofuran (THF)*. The rate increases a factor of 400–700 with a 160-fold change in THF level at each of seven *n*-butyllithium concentrations. On the other hand, with increasing amounts of *n*-butyllithium at constant THF concentrations, the rate of reaction (1) is found to decrease. Since *n*-butyllithium is one of the formal reactants, this decrease in rate is unusual. The only previously reported kinetic

$$n\text{-}C_4H_9Li + CH_2{=}C(C_6H_5)_2 \longrightarrow n\text{-}C_5H_{11}C(C_6H_5)_2Li \tag{1}$$

studies of organolithium olefin addition reactions which relate to solvent effects are the propagation reaction of *n*-butyllithium-initiated polymerization of styrene in benzene solution containing small amounts of THF[2–4] and the propagation reaction of *n*-butyllithium-initiated polymerization of dienes in hexane or THF[5] or $(C_2H_5)_2O$[6]. Initiation of these polymerizations was reported to be too fast to measure. A kinetic

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* See ref. 1 for a kinetic study of reaction (1) in benzene.

study of the effect of ethers on a different type of organolithium reaction demonstrates the accelerating effect of diethyl ether on the coupling reaction between *n*-butyllithium and 1-bromooctane in predominantly hexane solution[7].

n-Butyllithium adds to 1,1-diphenylethylene (DPE) to form 1,1-diphenyl-*n*-hexyllithium[8]. Addition of a second DPE molecule does not occur except when DPE is present in large excess[9]. In the experiments reported here the amount of DPE (0.045 mmoles) and the total volume (5.0 ml) are constant. Concentrations of THF and *n*-butyllithium are varied. Rates were measured spectroscopically by monitoring the absorbance of the adduct 1,1-diphenyl-*n*-hexyllithium on a Cary recording spectrophotometer using an absorption cell described previously[10]. Initial rates of reaction (1), determined from the initial slopes of the absorbance *vs.* time curves, are given in Table 1. The molar ratio THF/n-C_4H_9Li ranges from 0.008 to 25.

Rates of reaction (1) appear to be primarily determined by the *n*-butyllithium concentration and the ratio THF/*n*-butyllithium, as shown by a plot of rate$_i$/$[n\text{-}C_4H_9Li]_i$ versus THF/$[n\text{-}C_4H_9Li]_i$, in which all the data of Table 1 fall on the same semi-parabolic curve.

The data in Table 1 shows that at a constant *n*-butyllithium concentration the increase produced by THF in the rate of (1) is small at low THF concentrations, and it increases at higher THF concentrations. Plots of rate *vs.* [THF] show two approximately linear sections. The slopes of the first sections at low THF concentration increase with decreasing *n*-butyllithium concentration; the slopes at higher THF levels are similar for all the *n*-butyllithium concentrations. Presumably at even lower *n*-butyllithium concentrations the rate increase would appear to be proportional to the amount of THF as is found for the dependence of the rate of addition of styrene to polystyryllithium on THF[2]. However, the small effect of small amounts of THF is in contrast to the finding that virtually all of the acceleration of the rate of *n*-butyllithium–1-bromooctane coupling reaction by diethyl ether occurs when Et_2O/n-$C_4H_9Li < 0.5$ (ref. 7).

At a given ratio of THF to *n*-butyllithium, the rate of (1) is faster the higher the n-C_4H_9Li concentration, but at a given THF level the rate is faster the lower the n-C_4H_9Li concentration. The propagation rate of styrene polymerization did not show this inverse rate dependence with increasing polystyryllithium concentration[2]. An indication of a further possible fundamental difference between the effect of THF on *n*-butyllithium and polystyryllithium[2] or polyisoprenyllithium[5,6] is that initiation of polymerization of styrene or isoprene by n-C_4H_9Li is enormously accelerated by THF whereas propagation is only a few-fold faster than in hydrocarbon solution[2,5,6]. In fact, even at the lowest THF concentration initiation was too fast to measure[2].

Apparent orders of reaction (1) in n-C_4H_9Li as indicated by plots of log rate *vs.* log [*n*-BuLi], vary from a fractional negative value at low THF levels to approximate zero order at high THF levels. Non-linear plots are obtained at intermediate THF concentrations. Similar treatment to obtain the apparent reaction order in THF (at constant n-C_4H_9Li) also result in non-linear plots except at low THF levels.

The increase in rate caused by the addition of THF could be a result of a greater number of reactive species of approximately the same reactivity as those in the absence of THF* or of an increase in the reactivity of the species already present. Although

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* In hydrocarbon solution, *n*-butyllithium exists predominantly as hexamers[11], which are in equilibrium with reactive monomeric *n*-butyllithium[2].

activation energies for addition of organolithium compounds to olefins are less in ether solutions[2,5,6] than in hydrocarbon solutions[12], the principal factor causing increased rates in the presence of THF is probably the formation of a greater number of reactive species.

n-Butyllithium in hydrocarbon solutions in the presence of small amounts of THF might be considered to be participating in several equilibria consisting of relatively unreactive, unsolvated *n*-butyllithium hexamers and equilibrium concentrations of reactive, unsolvated monomeric *n*-butyllithium and etherates of monomeric *n*-butyllithium*. The existence of a solvated but unreactive *n*-butyllithium aggregate (which may or may not be a hexamer) may also be required to explain the data of Table 1, as described below. Evidence that *n*-butyllithium and ethyllithium exist as solvated dimers in hydrocarbon solutions containing excess diethyl ether[13] or triethylamine[14] has led to the conclusion that the reactive species in such solutions is the solvated dimer. Kinetic evidence for the extent of aggregation of *n*-butyllithium in 100% THF is not, however, consistent with the predominant species being a dimer, but indicates at least trimers[15].

TABLE 1

INITIAL RATES[a] OF REACTION (I) IN BENZENE CONTAINING SMALL AMOUNTS OF TETRAHYDROFURAN

Mmoles n-C_4H_9Li[b]	*Mmoles THF*								$[n$-$C_4H_9Li]/[DPE]$ (*molar*)
	0.0123	0.037	0.123	0.247	0.37	0.618	1.23	1.84	
0.075	0.29	0.93	5.0	8.0	24.8	36.	85.	124	1.7
0.105	0.26	1.0	4.8	10.4	18.2	36.	84.	120.	2.4
0.30	0.32	0.71	3.9	6.0	11.2	34.	99.	140.	6.7
0.75	0.16	0.45	1.34	2.9	9.5	21.	86.	108.	16.6
1.5	0.16	0.42	0.98	2.0	3.0	6.2	41.	66.	33.
3.0			0.34		2.5				67.
7.5			0.18		0.58				166.
[THF]/[DPE] (molar)	0.27	0.82	2.7	5.5	8.2	13.7	27.	41.	

[a] Moles liters^{-1} min.$^{-1}$ × 10^4. To convert these initial rates into rate constants requires a knowledge of the nature of n-C_4H_9Li in these solutions. If n-C_4H_9Li is monomeric, the rate will be $k_2[n\text{-}C_4H_9Li][DPE]$, but if the n-C_4H_9Li is aggregated, the rate expression is $k_1[(n\text{-}C_4H_9Li)_i]^{1/n}[DPE]$ where $k_1 = k_2K(1/n)^{1/n}$, where K is the aggregate monomer equilibrium constant.
[b] n-C_4H_9Li obtained from Foote Mineral Co., 1.5 molar in hexane. At the highest n-C_4H_9Li levels hexane is the predominant solvent. Rates are slightly slower in hexane than benzene. Experiments in hexane–THF show the same trends as above.

The rate of reaction of polystyryllithium with styrene goes through a maximum (at a THF/n-C_4H_9Li ratio ~ 10) with increasing amounts of THF, leading to the conclusion that the monoetherates of polystyryllithium are more reactive than the dietherates[2]. A maximum rate with added THF is also found for the addition of isoprene to polyisoprenyllithium, but at the much higher THF/RLi ratio of 500:1 (ref. 5). Nevertheless, no indication of a maximum rate is found for reaction (I) up to the

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[*] Evidence suggests the existence of specific etherates which, following the conclusions of Bywater and Worsfold[2] for polystyryllithium, can be thought of as mono- and dietherates. The nature of the reactive *n*-butyllithium species in THF solution are as yet uncertain.

highest experimentally accessible THF/n-C_4H_9Li ratio of 25. In 100% THF the rate is essentially instantaneous. Assuming that reaction (1) does not have a rate maximum at a higher THF/n-C_4H_9Li ratio, the decrease in rate with added n-butyllithium can be interpreted as indicating the existence of a least two etherates of n-butyllithium, and that the higher etherate is more reactive than the lower etherate. If such is the case, the relative reactivities required of the respective etherates are opposite to those invoked to explain a rate maximum. If reaction (1) does have a rate maximum at THF/n-$C_4H_9Li > 25$, the decrease in rate on adding n-butyllithium at constant THF level can only be explained by the existence of a relatively unreactive solvated n-C_4H_9Li cluster[14].

It is apparent from the trends reported here and the behavior of other organolithium systems that the findings for one reaction or a specific organolithium compound should not be extrapolated to other systems. Presumably with the availability of more data, generalities will be forthcoming. This work is continuing and will be reported in detail soon.

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1 A. G. Evans and D. B. George, *J. Chem. Soc.*, (1961) 4653.
2 S. Bywater and D. J. Worsfold, *Can. J. Chem.*, 40 (1962) 1564.
3 F. J. Welch, *J. Am. Chem. Soc.*, 82 (1960) 600.
4 K. F. O'Driscoll and A. V. Tobolsky, *J. Polymer Sci.*, 35 (1959) 259.
5 M. Morton, E. E. Bostick, R. A. Livigni and L. J. Fetters, *J. Polymer Sci.*, A1 (1963) 1735; M. Morton and L. J. Fetters, *J. Polymer Sci.*, A2 (1964) 3311.
6 H. Sinn and F. Bandermann, *Makromol. Chem.*, 62 (1963) 134; H. Sinn and F. Patat, *Angew. Chem.*, 3 (1964) 2.
7 J. F. Eastham and G. W. Gibson, *J. Am. Chem. Soc.*, 85 (1963) 2171.
8 R. Waack and M. A. Doran, *J. Phys. Chem.*, 67 (1963) 148.
9 A. G. Evans and D. B. George, *J. Chem. Soc.*, (1962) 141.
10 R. Waack and M. A. Doran, *J. Am. Chem. Soc.*, 85 (1963) 1651.
11 D. Margerison and J. P. Newport, *Trans. Faraday Soc.*, 59 (1963) 2058.
12 D. J. Worsfold and S. Bywater, *Can. J. Chem.*, 38 (1960) 1891.
13 Z. K. Cheema, G. W. Gibson and J. F. Eastham, *J. Am. Chem. Soc.*, 85 (1963) 2517.
14 T. L. Brown, R. L. Gerteis, D. A. Bafus and J. A. Ladd, *J. Am. Chem. Soc.*, 86 (1964) 2135.
15 R. Waack and P. West, in preparation.

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The preparation of trialkyltin hydrides by thermal decomposition of formates

Organotin hydrides usually are prepared by the reduction of organotin halides or oxides. We now wish to report that tri-n-propyltin or tri-n-butyltin hydride can be prepared by thermal decomposition of the corresponding formate under vacuum:

$$R_3SnOOCH \xrightarrow{\Delta} R_3SnH + CO_2$$

Tri-n-propyltin formate[1] (27.7 g, b.p. 101–104°/3 mm Hg, n_D^{20} 1.5038) was heated at 160–170° under reduced pressure (10–12 mm Hg), using a distillating column