the main source of a pressure shift at constant temperature between these two processes for the same fall-off parameter n lies in mechanism A in the modification of the collision constant by the factor $(2k_2/k_3 + 1)$. It should be remembered that the summations in equations 1 and 2 are over different energy regions and the factor cited is not given by the ratio of observed rate constants.

The Kinetic Isotope Effect.—An average ratio of observed rate constants of 1.22 was found for structural isomerization of light and deuterated cyclopropane at 718°K., which gives a value of $k_H/k_D = 2.18$ after correction for the hydrogen in propylene-d_2.[21] This is a reasonable order of magnitude. Over the range of pressures studied, comparison of the fall-off for light and heavy cyclopropane reveals no change in the ratio (Fig. 2). This indicates that for this range of pressure and the comparatively small region of fall-off covered the value of k_H/k_D underwent no change outside of experimental error. However, accurate determination of the isotopic rate ratio should be based on an internal comparison method; our data do not provide a proper basis for further discussion, except the remark that they do not support the results of a previous isotope rate study.[21a] The isotope effect would not be expected to disappear entirely at the low pressure limit.

Average Rate Constant.—The high pressure average rate constant of the reacting molecule, for geometric isomerization, may be represented in the manner of Johnston and White[19] as

$$<k_E>^T_\infty = k_d M(k_{g\infty}/k_g - 1)$$

The value of this quantity obtained from the data of Fig. 1 is 2.27×10^7 sec.$^{-1}$. This magnitude is adequately encompassed by a modified expression of the form

$$k_{\bar{E}} = A \left\{ \frac{\bar{E} - E_0 + E'_z}{\bar{E} + E_z} \right\}^{s-1}$$

used earlier by us elsewhere,[18] where $s = 20$–21, and the other quantities have their usual significance. A value of $s \simeq 20$ is much greater than the value obtained from the classical expression for $k_{\bar{E}}$ and contrasts also with the value of $s = 11$ obtained for fit of the fall-off with the classical Kassel expression; the value of s needed to fit experimental data on a quantum model is considerably larger than that obtained from a classical calculation; a detailed quantum calculation of the fall-off behavior by Marcus[22] indicates that a value of $s = 21$ gives a fit of the data for structural isomerization.

The Value of n.—From this study of cyclopropane and cyclopropane-d_2, the value of n determined from the fall-off of k_p by an application of the classical Slater theory is 13–14; this is the same as the value found previously for light cyclopropane.[5] In Slater's theory, $n = 14$ is the highest value which n can assume for light cyclopropane, which has seven doubly degenerate vibrational modes. For the cyclopropane-d_2 molecule, for which only twofold symmetry operations are possible, there are no degenerate vibrations, and according to the theory this should result in an increase in the value of n toward 20 or 21. This is not found here to be the case. This invariance of n in cyclopropane-d_2, as found from the fall-off, or non-equilibrium behavior, of the system, may be the most unequivocal test to date of the postulates of the theory.

---

[21] (a) R. E. Weston, *J. Chem. Phys.*, **23**, 988 (1955); **26**, 975 (1957); (b) J. Bigeleisen and M. Wolfsberg, *Adv. Chem. Phys.*, 1, 15 (1958).

[22] R. A. Marcus, private communication. We thank Prof. Marcus for permission to quote these unpublished results.

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, UNION CARBIDE CHEMICALS COMPANY, SOUTH CHARLESTON, WEST VIRGINIA]

Polymerization of Styrene by *n*-Butyllithium. II. Effect of Lewis Acids and Bases[1]

BY F. J. WELCH

RECEIVED APRIL 25, 1960

The rate of polymerization of styrene initiated by *n*-butyllithium is greatly accelerated by small quantities of Lewis bases, such as ethers or amines, and retarded by Lewis acids, such as zinc or aluminum alkyls. From the dependence of rate on acid and base concentration information was obtained concerning the nature of the interaction of these additives with lithium alkyls. Evidence is presented which confirms that acids form complexes of the type RLi·A with lithium alkyls, whereas bases form complexes of the type RLi·2B. Equilibrium constants for complex formation have been calculated from the rate data. The strength of the complexes with bases decreases in the order tetrahydrofuran > 2,5-dimethyltetrahydrofuran > ethyl ether, triethylamine. With acids the order is triisobutylaluminum > di-*n*-butylzinc. Ethyl sulfide, tri-*n*-butylphosphine, di-*n*-butylmercury and alkyl halides do not form strong complexes with lithium alkyls in benzene solution.

Introduction

In the presence of small quantities of lithium alkyls styrene polymerizes by a mechanism involving the successive additions of lithium alkyl to the double-bond of the monomer forming a new lithium alkyl.[2] For *n*-butyllithium concentrations <0.020 *M* polymerization in hydrocarbon solvents obeys the simple rate law

$$\frac{-d(M)}{dt} = k\,(RLi)\,(M)$$

However, the addition of small quantities of ethers, particularly tetrahydrofuran, or tertiary amines causes a large increase in the rate of polymerization.[2,3] Lewis bases of this type also have a marked effect on the stereospecificity[4-6] and rate[6] of diene

---

[1] Presented in part at the 135th Meeting of the American Chemical Society, Boston, April, 1959

[2] F. J. Welch, THIS JOURNAL, **81**, 1345 (1959).

[3] K. F. O'Driscoll and A. V. Tobolsky, *J. Polymer Sci.*, **35**, 259 (1959).

[4] H. Morita and A. V. Tobolsky, THIS JOURNAL, **79**, 5853 (1957); A. V. Tobolsky and C. E. Rogers, *J. Polymer Sci.*, **40**, 73 (1959).

polymerizations catalyzed by lithium alkyls. Apparently, these substances increase the rate of addition of the lithium alkyl to the double-bond by interacting with the lithium alkyl in such a manner that its polarity is increased. Therefore, the rate of polymerization is a sensitive measure of the interaction of the lithium–carbon bond in the growing species with its environment.

The dependence of the rate of polymerization on the concentration of a number of compounds which interact with lithium alkyls has been studied in benzene solution by a convenient dilatometric procedure.

Experimental

Materials.—Commercial styrene was distilled at 20 mm. pressure from Linde 5-A Molecular Sieve shortly before use. Tetrahydrofuran (E. I. DuPont) was refluxed over sodium hydroxide pellets and distilled from lithium aluminum hydride through a fifteen-plate column. Commercial triethylamine and *n*-butyl chloride were distilled through a fifteen-plate column. *n*-Butyllithium was prepared from *n*-butyl chloride and lithium sand in benzene or hexane solution.[2] Di-*n*-butylzinc was prepared according to the method of Noller.[7] Di-*n*-butylmercury[8] and tri-*n*-butylphosphine were prepared from the Grignard reagent and the corresponding metal chloride. 2,5-Dimethyltetrahydrofuran was prepared from 1,5-hexadiene and aqueous sulfuric acid by the procedure of Cortese,[9] b.p. 93–95°, $n^{30}\text{D} = 1.4025$. Reagent grade benzene, ethyl sulfide (Eastman White Label), ethyl ether (Mallinckrodt anhydrous reagent grade) and triisobutylaluminum were used as received.

Apparatus.—The dilatometer had a bulb of about 130-ml. volume and a stem of 10 mm. tubing. It was connected near the top through stopcocks to a solvent reservoir and to a vacuum line. An opening at the top sealed with a rubber serum bottle cap permitted the injection of reagents with a syringe. A magnetic bar was used to stir the contents of the dilatometer.

Procedure.—Solvent, monomer and all reagents except the metal alkyls were stored over calcium hydride under a nitrogen atmosphere to insure dryness. The dilatometer was dried by heating under reduced pressure. After breaking the vacuum with high purity nitrogen, benzene was added from the reservoir by nitrogen pressure. Styrene and complexing agents were added by syringe, and the solution was brought to constant temperature in a water-bath. *n*-Butyllithium solution was added by syringe, and the solution was mixed rapidly by magnetic stirring. Polymerization was followed to essentially complete conversion. The rate of propagation was determined from the limiting slope of the rate curves.[2]

Temperature of the bath was maintained at 30.0 ± 0.05°. When polymerization was complete, the polystyrene formed was recovered by precipitation with methanol, and its intrinsic viscosity in benzene solution determined at 30°. *n*-Butyllithium concentrations in the range 0.002–0.012 *M* and styrene concentrations in the range of 0.32 to 0.65 *M* were used in the various experiments. In all experiments the mixtures were homogeneous throughout the polymerizations except for the experiments using high concentrations of lithium butoxide.

Results

Effect of Lewis Bases.—The dependence of the rate of polymerization of styrene on tetrahydrofuran (THF) concentration is illustrated in Fig. 1. For THF concentrations less than about 0.004 *M* the rate increases nearly linearly with THF concentration, but for THF concentrations above about 0.005 *M* the rate is relatively insensitive to variations in the ether concentration. These quantities of THF are not enough to affect the dielectric constant of the medium significantly. The break in the curve occurring near a (THF)/(BuLi) ratio of two is indicative of the formation of a strong complex of the type RLi·2THF. This complex is a more active catalyst for the polymerization of styrene than the free lithium alkyl.

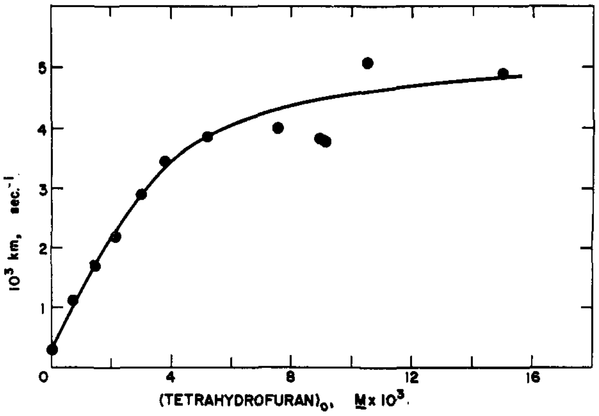

Fig. 1.—Dependence of the rate of polymerization on the concentration of tetrahydrofuran: 0.0020 ± 0.0003 *M* *n*-butyllithium.

The observed rate of polymerization can be considered to be composed of the rates for the two reactions[10]

$$\text{RLi} + \text{M} \xrightarrow{k_1} \text{R(M)Li}$$

$$\text{RLi}\cdot 2\text{THF} + \text{M} \xrightarrow{k_2} \text{R(M)Li}\cdot 2\text{THF}$$

Then k_m, the experimentally measured pseudo first order rate constant for the disappearance of styrene, is given by

$$k_m = k_1(\text{RLi}) + k_2(\text{RLi}\cdot 2\text{THF}) \qquad (1)$$

In the absence of THF the second term drops out and $k_m = k_1$ (RLi). For THF concentrations which are sufficiently high that essentially all of the alkyllithium is present as the complex the first term becomes zero and $k_m = k_2$ (RLi·2THF). Therefore, a plot of k_m against $(\text{THF})_0$ at constant $(\text{RLi})_0$ (where the subscripts refer to concentrations added initially) gives k_1(RLi) as the intercept and k_2(RLi·2THF) as the limiting value of k_m (Fig. 1). If the ratio $k_m/(\text{RLi})_0$ instead of k_m is plotted against $(\text{THF})_0$, the limiting value of the rate at high $(\text{THF})_0$ is the specific rate constant k_2 (Fig. 2). The value of k_2 obtained in this manner is independent of $(\text{RLi})_0$ provided that the tetrahydrofuran concentration is sufficiently high that the concentration of uncomplexed alkyllithium is essentially zero.

The amount of lithium alkyl added initially, $(\text{RLi})_0$, is equal to the amount present as the complex, (RLi·2THF), plus the amount remaining uncomplexed, (RLi). Making the appropriate substitutions in equation 1

$$k_m = k_1\,(\text{RLi})_0 + (k_2 - k_1)(\text{RLi}\cdot 2\text{THF}) \qquad (2)$$

Therefore, the concentration of (RLi·2THF) may

---

(5) R. S. Stearns and L. E. Forman, *J. Polymer Sci.*, **41**, 381 (1959).

(6) A. A. Korotkov, *Angew. Chem.*, **70**, 85 (1958).

(7) C. R. Noller, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 184.

(8) H. Gilman and R. E. Brown, THIS JOURNAL, **52**, 3314 (1930).

(9) F. Cortese, *Ber.*, **62**, 504 (1929).

(10) Presumably a 1:1 complex of the type RLi·THF is also present in low concentration in equilibrium with RLi·2THF and the free ether and alkyllithium. It would also add to styrene and contribute to the observed rate. However, these experiments do not furnish information concerning this species.

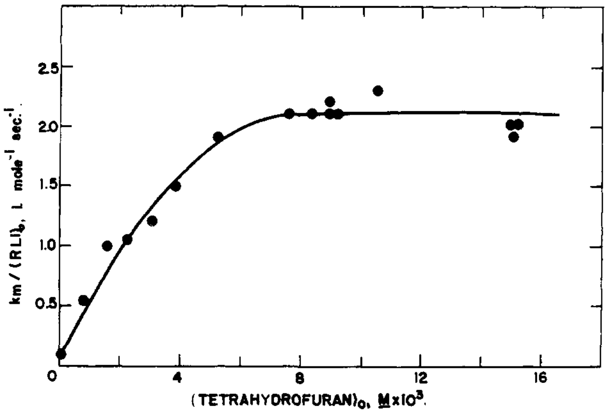

Fig. 2.—Dependence of the specific polymerization rate on the concentration of tetrahydrofuran: 0.0010–0.0025 *M* *n*-butyllithium.

be calculated from the various rate constants and the initial catalyst concentration. Once the concentration of the complex is known, the equilibrium concentrations of (RLi) and (THF) and the equilibrium constant *K* can be calculated for the reaction

$$\text{RLi} + \text{THF} \underset{}{\overset{K}{\rightleftarrows}} \text{RLi}\cdot 2\text{THF}$$

The specific rate constant k_1 has a value of 0.12 l. mole^{-1} sec.$^{-1}$ at 30° in benzene,[2] and from Fig. 2 the value of k_2 is 2.1 l. mole^{-1} sec.$^{-1}$. In Table I values for *K* are calculated from the data presented in Fig. 2. Only the data in the intermediate portion of the curve can be used for these calculations because the concentration of (THF) is essentially zero at low $(\text{THF})_0$ and that of (RLi) is nearly zero at high $(\text{THF})_0$.

TABLE I

EQUILIBRIUM CONSTANT FOR ASSOCIATION OF RLi WITH TETRAHYDROFURAN

$(\text{RLi})_0$, *M*	$(\text{THF})_0$, *M*	$10^3 k_m$, sec.$^{-1}$	(RLi·2THF), *M*	$\frac{(\text{RLi}\cdot 2\text{THF})}{(\text{RLi})(\text{THF})^2}$, l.^{2} mole^{-2} × 10^6
0.00090	0.0022	1.51	0.00067	3.6
.0019	.0023	2.18	.00093	4.6
.0025	.0030	2.91	.0012	2.6
.0023	.0038	3.44	.0015	2.9
.0021	.0052	3.87	.0017	1.3
			Average	3.0 × 10^6

In Figs. 3 to 5 the dependence of rate on the concentrations of 2,5-dimethyltetrahydrofuran (DMTHF), ethyl ether and triethylamine are illustrated. These compounds also effect a marked increase in the rate of polymerization, but the complexes formed with the lithium alkyl are much weaker than that formed by tetrahydrofuran. Although the stoichiometry of the complexes is not apparent from these data, it was assumed to be the same as that established for tetrahydrofuran. In the experiments with DMTHF and ethyl ether data were not obtained at sufficiently high concentrations of base to clearly define the limiting value of the rate of polymerization. However, in both cases k_2 must be at least 2.1 l. mole^{-1} sec.$^{-1}$, the value obtained using THF, and there is no reason to suspect that it should be higher than this. The limiting rate in the presence of triethylamine is considerably less than that observed in the presence of ethers. From Fig. 5 the value of k_2 is 0.70 l. mole^{-1} sec.$^{-1}$ In Tables II to IV values of the equilibrium constants for association of DMTHF, ethyl ether and triethylamine with alkyllithium are calculated.

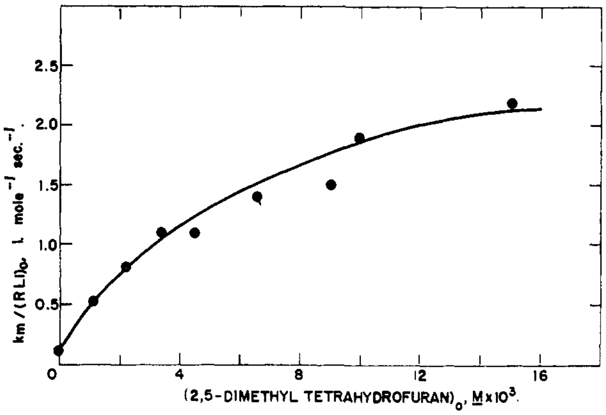

Fig. 3.—Dependence of the specific polymerization rate on the concentration of 2,5-dimethyl-tetrahydrofuran: 0.001–0.003 *M* *n*-butyllithium.

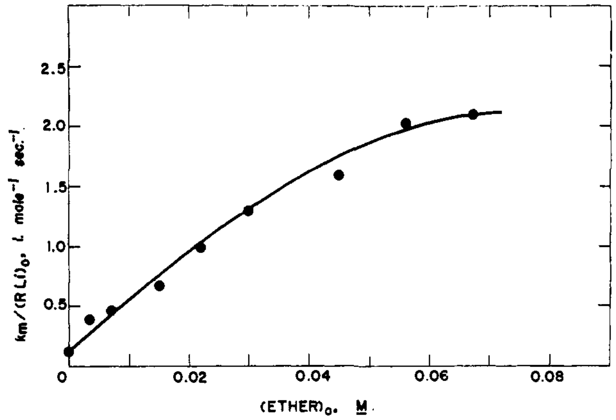

Fig. 4.—Dependence of the specific polymerization rate on the concentration of ethyl ether: 0.002–0.004 *M* *n*-butyllithium.

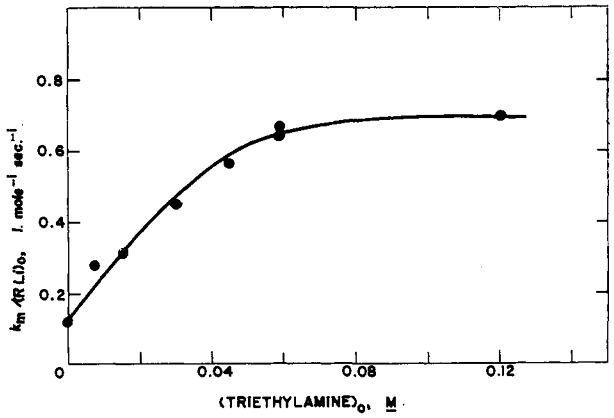

Fig. 5. Dependence of the specific polymerization rate on the concentration of triethylamine: 0.002–0.004 *M* *n*-butyllithium.

The rate dependence on both the ethyl ether and triethylamine concentrations was studied at several

TABLE II

EQUILIBRIUM CONSTANT FOR ASSOCIATION OF RLi WITH 2,5-DIMETHYLTETRAHYDROFURAN

$(\mathrm{RLi})_0$ M	$(\mathrm{DMTHF})_0$ M	$10^3 k_m$, sec.$^{-1}$	$(\mathrm{RLi\cdot 2\text{-}DMTHF})$ M	$\frac{(\mathrm{RLi\cdot 2DMTHF})}{(\mathrm{RLi})(\mathrm{DMTHF})^2}$, $1.^2$ mole^{-2} $\times 10^5$
0.0022	0.0022	1.80	0.00073	0.8
.0019	.0033	2.00	.00084	2.9
.0024	.0045	2.55	.0011	1.6
.0026	.0066	3.62	.0016	1.5
.0021	.010	4.03	.0018	1.5
.0029	.0090	4.42	.0019	0.7
			Average	1.5×10^5

TABLE III

EQUILIBRIUM CONSTANT FOR ASSOCIATION OF RLi WITH ETHYL ETHER

$(\mathrm{RLi})_0$ M	$(\mathrm{Et_2O})_0$ M	$10^3 k_m$, sec.$^{-1}$	$(\mathrm{RLi\cdot 2Et_2O})$ M	$\frac{(\mathrm{RLi\cdot Et_2O})}{(\mathrm{RLi})(\mathrm{Et_2O})^2}$, $1.^2$ mole^{-2} $\times 10^3$
0.011	0.0092	3.65	0.0011	2.2
.010	.0135	4.84	.0017	2.1
.0038	.015	2.60	.0010	2.1
.0032	.022	3.33	.0014	2.2
.0035	.030	4.40	.0019	1.7
.0035	.045	5.48	.0024	1.4
			Average	2.0×10^3

TABLE IV

EQUILIBRIUM CONSTANT FOR ASSOCIATION OF RLi WITH TRIETHYLAMINE

$(\mathrm{RLi})_0$ M	$(\mathrm{Et_3N})_0$ M	$10^3 k_m$, sec.$^{-1}$	$(\mathrm{RLi\cdot 2Et_3N})$ M	$\frac{(\mathrm{RLi\cdot 2Et_3N})}{(\mathrm{RLi})(\mathrm{Et_3N})^2}$, $1.^2$ mole^{-2} $\times 10^3$
0.0092	0.0135	2.21	0.0016	2.1
.0096	.019	2.67	.0021	1.6
.0096	.029	2.95	.0026	0.6
.0092	.048	5.00	.0070	2.7
.0038	.015	1.19	.0010	2.1
.0030	.030	1.36	.0014	1.2
.0026	.059	1.67	.0019	0.8
.0031	.045	1.78	.0020	1.1
.0030	.059	2.00	.0023	1.0
			Average	1.4×10^3

catalyst concentrations. Similar values for the equilibrium constant result from data obtained at the various catalyst concentrations in accord with the equilibrium requirements.

The molecular weight of the polymers formed as indicated by the intrinsic viscosity was independent of the concentration of the ethers or amine. For the data shown in Fig. 1 the intrinsic viscosities of the polymers were 0.25 to 0.31, corresponding to molecular weights of 21,000 to 28,000 based on the viscosity molecular weight relation of Szwarc, *et al.*[11] The molecular weight calculated from the ratio of monomer to catalyst assuming absence of termination was 21,000. Although the presence of small quantities of ethers or amines does not affect the molecular weights of the polymers, it may affect the molecular weight distribution. No information is available concerning this point.

Some of the catalyst added is inevitably destroyed by trace impurities in the system. Since one mole of polystyrene is produced per mole of catalyst irrespective of the concentrations of Lewis base, the effective catalyst concentration can be calculated readily from the molecular weight of polystyrene obtained. The catalyst concentrations used in the calculations in this section were obtained in this manner.

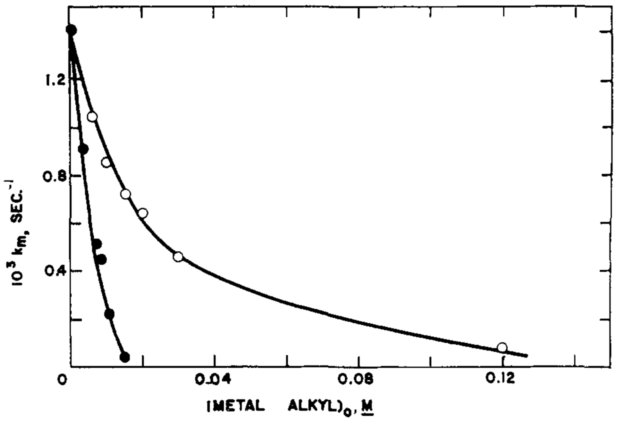

Fig. 6.—Dependence of the rate of polymerization on the concentration of triisobutylaluminum (black circles) and di-*n*-butylzinc (open circles): 0.012 *M* *n*-butyllithium.

Effect of Lewis Acids.—Alkyl derivatives of metals such as aluminum and zinc retard polymerizations catalyzed by lithium alkyls. Figure 6 shows the effect of di-*n*-butylzinc and triisobutylaluminum on the rate of polymerization. Although little more than an equimolar amount of trialkaluminum completely prevents polymerization, greater than a ten-fold excess of dibutylzinc is necessary for inhibition.

Metal alkyls which are acidic with respect to lithium alkyls, such as trialkylaluminums, form 1:1 complexes of the type $\mathrm{Li^+[AlR_4]^-}$ with lithium alkyls.[12,13] The data in Fig. 6 confirm the formation of a strong complex of this stoichiometry with the aluminum alkyl. It is assumed that di-*n*-butylzinc also forms an equimolar complex although the stoichiometry cannot be deduced from the data in Fig. 6. Since the rate of polymerization approaches zero as the concentration of metal alkyl increases, the complexes must not be catalysts for the polymerization of styrene. These metal alkyls reduce the rate of polymerization by reducing the effective concentration of lithium alkyl through complex formation. An equilibrium of the type illustrated here for dibutylzinc is presumably involved.

$$\mathrm{RLi} + \mathrm{Bu_2Zn} \overset{K}{\rightleftarrows} (\mathrm{RLi\cdot Bu_2Zn})$$

Since the rate of polymerization is proportional to the concentration of unassociated alkyllithium,[2] the rate can be used to determine the concentration of uncomplexed alkyllithium. At 30° in benzene solution the lithium alkyl concentration is given by the expression $k_m = 0.12\ (\mathrm{RLi})$. The equilibrium concentrations of the complex and dibutylzinc can be calculated from the expressions

$$(\mathrm{RLi})_0 = (\mathrm{RLi}) + (\mathrm{RLi\cdot Bu_2Zn})$$
$$(\mathrm{Bu_2Zn})_0 = (\mathrm{Bu_2Zn}) + (\mathrm{RLi\cdot Bu_2Zn})$$

---

(11) R. Waack, A. Rembaum, J. D. Coombes and M. Szwarc, THIS JOURNAL, **79**, 2026 (1957).

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

(13) G. Wittig, *Angew. Chem.*, **70**, 65 (1958).

Knowledge of these values permits calculation of the equilibrium constant for association K. In Table V values for K are calculated for the experimental points illustrated in Fig. 6.

TABLE V

EQUILIBRIUM CONSTANT FOR ASSOCIATION OF RLi WITH DI-*n*-BUTYLZINC

$(Bu_2Zn)_0$ M	$(BuLi)_0 = 0.012$ M $(RLi)^a$ M	$\frac{(RLi \cdot Bu_2Zn)}{(RLi)(Bu_2Zn)}$, l. mole^{-1}
0.0060	0.0087	130
.010	.0070	140
.015	.0060	110
.020	.0053	97
.030	.0038	98
.12	.0007	140
	Average	120

[a] Calculated from the rate of polymerization; (RLi) = $k_m/0.12$.

Values for the equilibrium constant for association with triisobutylaluminum calculated in the same manner are listed to Table VI.

TABLE VI

EQUILIBRIUM CONSTANT FOR ASSOCIATION OF RLi WITH TRIISOBUTYLALUMINUM

$(\text{iso-}Bu_3Al)_0$ M	$(BuLi)_0 = 0.012$ M $(RLi)^a$ M	$\frac{(RLi \cdot \text{iso-}Bu_3Al)}{(RLi)(\text{iso-}Bu_3Al)}$, l. mole^{-1} × 10^3
0.0089	0.0037	3.7
.011	.0018	7.1
.015	.0004	8.5
	Average	6.5 × 10^3

[a] Calculated from the rate of polymerization; (RLi) = $k_m/0.12$.

The molecular weight of polystyrene produced increased with increasing concentrations of zinc alkyl (Table VII) supporting the conclusion that the zinc alkyl retards the rate of polymerization by inactivating catalyst. However, the observed molecular weights at high $(Bu_2Zn)_0$ were lower than those calculated from the ratio of monomer to the effective alkylithium concentration derived from the rate.

TABLE VII

DEPENDENCE OF THE MOLECULAR WEIGHT OF POLYSTYRENE ON THE DI-*n*-BUTYLZINC CONCENTRATION

$(Bu_2Zn)_0$ M	(RLi) M	$\overline{DP}^a$	$\frac{(\text{Stryene})}{(RLi)}$
....	0.012	54	54
0.0060	.0087	77	75
.015	.0060	90	110
.030	.0038	120	170
.12	.0007	300	900

[a] Degree of polymerization calculated from [η] of polystyrene produced.[11]

These results indicate that the equilibrium between complexed and uncomplexed lithium alkyl is established slowly with respect to polymerization but that some exchange of lithium alkyl between complex and solution does occur. Data from the triisobutylaluminum experiments lead to similar conclusions.

It follows from these results that the compounds $LiAlR_4$ and $LiZnR_3$ are also catalysts for the polymerization of styrene but only to the extent that they dissociate in solution to give LiR, the actual initiator.

Effect of Some Other Additives.—The effect of a number of other compounds on the rate of polymerization at 30° was examined. Chlorobenzene had no appreciable effect on either the rate or the molecular weight. In fact it probably could be used as a solvent in the polymerizations. On the other hand *n*-butyl chloride seemed to react slowly with the growing polymer chains, leading to a decrease in rate with increasing conversion and to polymers of higher intrinsic viscosities than expected from the initial catalyst concentrations. However, the propagation rates during the early part of the polymerizations were largely unaffected by the concentration of *n*-butyl chloride. Apparently alkyl and aryl chlorides do not complex appreciably with lithium alkyls.

Ethyl sulfide and di-*n*-butylmercury had no significant effect on either the rate or the viscosity of the polymer formed. They do not seem to complex appreciably with lithium alkyls in benzene solution. However, alkyl sulfides do affect the stereospecificity of the polymerization of butadiene in petroleum ether.[14] Tri-*n*-butylphosphine had no effect on the polymer viscosity, but it had a slight accelerating effect on the rate. However, these experiments were less precise than desired, and the effect may result from experimental error. In any case the complex formed is weak at best.

The effect of lithium *n*-butoxide on the polymerization is of particular significance since it is a contaminant of *n*-butyllithium solutions which have been exposed to air. It has been reported that lithium alkoxides affect the per cent. of 1,2-linkages in polybutadiene produced using *n*-butyllithium catalyst in petroleum ether.[14] Alkoxide was prepared *in situ* by reaction of anhydrous 1-butanol with excess *n*-butyllithium. Reaction was assumed to be quantitative. Solutions were homogeneous for lithium butoxide concentrations less than 0.030 M but were heterogeneous at higher concentrations.

As illustrated in Table VIII the rate of polymerization is reduced by the presence of lithium alkoxide, although the intrinsic viscosity of polystyrene produced remained essentially unchanged.

TABLE VIII

EFFECT OF LITHIUM BUTOXIDE ON THE RATE OF POLYMERIZATION AND THE INTRINSIC VISCOSITY OF POLYSTYRENE

$(BuLi)_0 = 0.010$ M

(LiOBu) M	$10^3 k_m$, sec.$^{-1}$	[η]
...	1.22	0.095
0.024	0.87	.103
0.048	0.65	.106

Lithium alkyls associate appreciably in hydrocarbon solution only at concentrations greater than about 0.020 M.[2] Only the unassociated lithium alkyl adds to styrene at appreciable rates. However, the molecular weight of polystyrene formed is unaffected by the association.[2] From this study it appears that lithium alkoxides also associate with

---

[14] V. A. Kropacheff, B. A. Dolgoplosk and I. N. Nikolayeff, *Doklady Akad. Nauk S.S.S.R.*, **115**, 516 (1957).

lithium alkyls, thereby effectively reducing the concentration of free lithium alkyl. Because of the rapid attainment of equilibrium between the associated and unassociated lithium alkyl, molecular weight is not affected.

The concentrations of lithium alkoxide considered here would correspond to 25 to 80% oxidation of lithium alkyl. This is above the range of oxidation to be expected on chance exposure of the catalyst to air. However, these experiments do emphasize the need for careful preparation and handling of lithium alkyls to prevent exposure to air if meaningful quantitative polymerization data are to be obtained.

Discussion

Compounds which are basic compared to the lithium alkyl increase the polarity of the lithium–carbon bond by coördination with the lithium atom in the sense that a greater negative charge is placed on carbon.[13]

$$\mathrm{R{-}Li} + 2\mathrm{B} \longrightarrow \mathrm{R}^{-}\ {}^{+}[\mathrm{Li{\cdot}2B}]$$

Therefore, in the presence of such basic compounds the reactivity of lithium alkyls is enhanced. The magnitude of rate of polymerization in the presence of excess base where all of the lithium alkyl is present as the complex is a measure of the degree of polarization of the lithium–carbon bone. This study indicates that all of the ethers examined induce the same degree of polarization in the lithium alkyl and ethers induce a greater degree of polarization than does triethylamine.

Acidic compounds also increase the degree of polarization of lithium alkyls. However, in this case the carbanion is associated with the coördinating acid so that the reactivity of the lithium alkyl is effectively neutralized.[13]

$$\mathrm{R{-}Li} + \mathrm{A} \longrightarrow \mathrm{Li}^{+}\ {}^{-}[\mathrm{AR}]$$

In the discussion of the results the nature of the group R in the lithium alkyl has been ignored. In the case of complexing with Lewis bases, both the complex and the free lithium alkyl add to monomer. Since the rate of propagation was used to indicate the degree of complex formation of the lithium alkyl, the group R must be the species present under these conditions. Therefore, the equilibrium which was studied was that involving the growing polymer chain, $\sim \mathrm{CH_2CH(C_6H_5)Li}$.

This conclusion is probably not true in the case of complexing with the acidic metal alkyls. *n*-Butyllithium probably reacts faster with the metal alkyl than with styrene. Therefore, the complex forms rapidly and only unassociated lithium alkyl is available for addition to monomer. In this case then the equilibrium under consideration is that involving *n*-butyllithium. Since some exchange of lithium alkyl between complex and solution does occur during the polymerization, as evidenced by the data of Table VII, the group $\sim \mathrm{CH_2CH(C_6H_5)Li}$ also must contribute to the equilibrium.

Acknowledgments.—The author wishes to express his appreciation to Dr. R. D. Lundberg and Dr. N. L. Zutty for their advice and helpful discussions.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON, SEATTLE, WASHINGTON]

The Reactions of Trifluoromethyl Hypofluorite with Sulfur Trioxide and Sulfur Dioxide

BY WAYNE P. VAN METER AND GEORGE H. CADY

RECEIVED APRIL 18, 1960

Trifluoromethyl hypofluorite reacts with sulfur trioxide in the temperature range 245 to 260° to form trifluoromethyl peroxyfluorosulfonate, $\mathrm{CF_3OOSO_2F}$, a substance which melts at −117° and boils at 12.9°. Trifluoromethyl hypofluorite reacts with sulfur dioxide in the range 175 to 185° to yield many products, among them being the esters $\mathrm{F_3C{-}O{-}SO_2F}$ (m.p. −121°, b.p. −4.2°), $\mathrm{F_3C{-}O{-}SO_2{-}O{-}CF_3}$ (m.p. −99°, b.p. 31°), $\mathrm{F_3C{-}O{-}SO_2{-}O{-}SO_2F}$ (b.p. 76°) and $\mathrm{F_3C{-}O{-}SO_2{-}O{-}SO_2{-}O{-}CF_3}$ (m.p. −66°, b.p. 98°). The crude mixture of products has been separated into its components by fractional codistillation. Nuclear magnetic resonance, infrared, and mass spectra have been used to establish the structures of the new compounds. Differences in ease of hydrolysis by aqueous sodium hydroxide have been correlated with the proposed structures. Vapor pressure curves and gas and liquid densities have been measured for each of the substances.

Two of the compounds that possess hypofluorite groups have been shown previously to form peroxides upon reaction with compounds having double-bonded oxygen atoms:[1,2]

$$\mathrm{CF_3OF + COF_2 = CF_3OOCF_3}$$

$$\mathrm{FSO_2OF + SO_3 = FSO_2OOSO_2F}$$

The reactions of trifluoromethyl hypofluorite with sulfur trioxide and with sulfur dioxide have been studied in the present research. In the case of sulfur trioxide, an unsymmetrical peroxide, analogous to the products shown above, has been prepared. The reaction with $\mathrm{SO_2}$ has resulted in a series of four new esters which are not peroxides.

Reagents.—Trifluoromethyl hypofluorite was prepared[3] by mixing streams of carbon monoxide and fluorine in a ratio of somewhat more than two volumes of fluorine per volume of carbon monoxide. The gases passed through copper tubing held at about 400° where nearly all of the carbon monoxide was converted to trifluoromethyl hypofluorite. The unused fluorine remained in the stream of gases. Sulfur trioxide ("Sulfan B," General Chemical Division, Allied Chemical and Dye Corp.) and sulfur dioxide (in cylinder, Matheson Company, Inc.) were used as received.

Reaction of $\mathrm{CF_3OF}$ with $\mathrm{SO_3}$.—Mixtures of trifluoromethyl hypofluorite and sulfur trioxide were allowed to react in a nickel vessel of 1.7 liter volume

---

(1) R. S. Porter and G. H. Cady, THIS JOURNAL, **79**, 5628 (1957).

(2) F. B. Dudley and G. H. Cady, *ibid.*, **79**, 513 (1957).

(3) K. B. Kellogg and G. H. Cady, *ibid.*, **70**, 3986 (1948).