THE EFFECT OF ELECTRONDONORS
ON THE POLYMERIZATION KINETICS OF ISOPRENE

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The effect of small additions of 1-octene, butyl ethyl ether and triethyl amine on the polymerization kinetics of isoprene (2-methyl-1,3-butadiene) in benzene initiated by butyllithium was investigated by employing the GLC analysis. The addition of 1-octane was reflected only in a shorter induction period of the reaction; the effect on the propagation rate was insignificant. With the increasing amount of butyl ethyl ether, the polymerization rate increases linearly, while the reaction order with respect to the concentration of triethylamine is variable and increases from 0·33 to 0·66 with the increasing concentration of the initiator. For a constant concentration of triethyl amine, the reaction order with respect to the initial concentration of the initiator was found to vary considerably, reaching even negative values. A reaction scheme was suggested, taking into account the competition between two different solvates of alkyllithium.
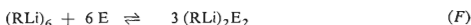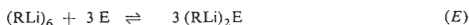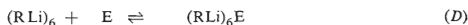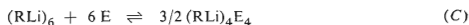
A strong effect of the addition of the Lewis acids on the rate of the anionic polymerization of dienes is sometimes explained by a decrease in the degree of association of alkyllithium. Cheema, Gibson, Settle and Eastham[1,2] believe that complexes of alkyllithium with compounds containing one atom-electrondonor (E), such as triethyl amine, diethyl ether, tetrahydrofuran, have the composition 2 : 1 even at a large excess of these compounds; such a composition corresponds to the dimer of an organic metal solvated with one molecule of amine or ether. The solvation process may be represented[3] by the equilibrium

$$(RLi)_n + \tfrac{1}{2}n\,E \;\rightleftharpoons\; \tfrac{1}{2}n\,(RLi)_2\,E. \tag{A}$$
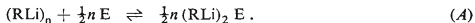
In some cases, information on the composition of complexes of organolithium compounds with electrondonors may be obtained indirectly from the kinetics of the reaction of alkyllithium. On the curve representing the dependence of the reaction rate on the molar ratio (r) of ether to alkyllithium, a discontinuity was found[4,5] at $r = 0.5$, which suggests complex formation between two molecules of alkyllithium and one molecule of diethyl ether or tetrahydrofuran. Also, IR and NMR spectra[3,6,7] indicate a strong reduction of the degree of association of alkyllithium due to electrondonors. By employing the cryoscopic method, Brown[8] determined the mechanism of decomposition of the hexameric associate of ethyllithium into tetrameric and dimeric associates after the addition of trimethyl amine to a benzene solution of ethyllithium. This author suggested that in the range of low concentrations of the electrondonor (E) the associate, though solved, did not undergo decomposition:

$$(RLi)_6 + 2\,E \;\rightleftharpoons\; (RLi)_6E_2. \tag{B}$$
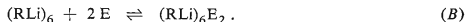
With an excess of the base, it dissociates to a solvated dimeric associate. Using NMR spectra and the dependence of the dielectric constant[2] on the content of the Lewis base in solution[1,3], changes were examined in the composition of a number of alkyllithium compound in mixtures of ether and hexane. The curves representing the dependences always exhibited a discontinuity on reaching the molar ratio of the base to alkyllithium equal to 1 : 2. Further additions of the base did not show any influence on the composition of the complex. The authors' statements concerning the dimeric structure of butyllithium and isobutyllithium in ether cannot be regarded as unambiguous however, because their results suggest only the existence of the molar ratio relating the individual components of the complex. More reliable data on the degree of association of organolithium compounds in ether solutions were obtained by West and Waack[9]; some of their conclusions are at variance with the data published earlier[3,5,8]. They found that the degree of association of methyllithium in tetrahydrofuran was four, that of phenyllithium was two, while benzyllithium remained nonassociated under such conditions. In a more recent paper, Lewis and Brown[10] consider that in solvation equilibria of alkyllithium compounds with tetrahydrofuran, diethyl ether, quinuclidine *etc.*, also solvates of the type

$$(RLi)_6 + 6E \rightleftharpoons 3/2 (RLi)_4E_4 \qquad (C)$$

$$(RLi)_6 + E \rightleftharpoons (RLi)_6E \qquad (D)$$

$$(RLi)_6 + 3E \rightleftharpoons 3 (RLi)_2E \qquad (E)$$

$$(RLi)_6 + 6E \rightleftharpoons 3 (RLi)_2E_2 \qquad (F)$$

may be formed, and discuss the probability of such formation.

A quantitative description of the solvation effect is so far lacking, and obtaining experimental data which would be reproducible, at least in part, is a difficult task. Since data reported on the polymerization kinetics of isoprene,* especially in the range of low concentrations of bases, are very scarce, we re-investigated this range. The paper is a continuation of the preceding paper[11].

EXPERIMENTAL

Chemicals

Isoprene was purified by distillation with sodium metal and distillation with calcium hydride in argon and stored over calcium hydride in a protective argon atmosphere at low temperature. Benzene and pentane (GLC internal standard) were shaken with conc. sulphuric acid, washed with water and a solution of potassium hydroxide; after drying with calcium hydride, they were distilled with a Na/K alloy, over which they were also kept. 1-Octane, tetrahydrofuran, butyl ethyl ether and triethyl amine were dried with sodium metal and purified by distillation with calcium hydride, over which they were stored in a protective argon atmosphere. Butyllithium was prepared by reacting 80 g of butyl chloride and 20 g of lithium suspension in 0·4 l of dry

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* Instead of 2-methyl-2,3-butadiene, "isoprene" is used as a name usual in technological applications.

benzene at room temperature in an argon atmosphere with virgorous stirring for several hours[11]; the concentration of the product varied about 1·8 mol/l.

Polymerization

The reaction was carried out in a special reactor, 100 ml total volume, with a lower ground glass joint providing direct connection with an automatic sampling system for the GLC analysis. The sampling system made possible an immediate transfer of the sample into the evaporator of a gas chromatograph without polymerization occurring in the process. The reactor was thermostated to 300 K, and its contents were vigorously stirred. The volume of the reacting mixture was 24·0 ml, the samples were about 15 microlitres in volume. Argon served as the protective atmosphere. The components were dosed into the reactor in the following order: benzene, initiator, electrondonor, monomer.

Gas Chromatography

The gas chromatograph was of our own construction, specially adapted for sampling. The column was 2·5 m 20% Carbowax 20M on Chromosorb N-AW, with a catharometer manufactured by Giede, GDR, as the detector. Pentane (10 vol.% to the reaction mixture) was used as the internal standard. The column temperature was 80°C, the pressure of the carrier gas (hydrogen) was 0·1 MPA. The chromatograms were evaluated according to the peak heights using a calibration plot. The recorder was a Perkin–Elmer, type 56 device.

RESULTS AND DISCUSSION

The reactions were carried out in benzene solution at 300 K. The first electrondonor (E) was tetrahydrofuran; the results obtained resembled those with butyl ethyl ether, but the reproducibility was very poor. The rate varied at the same concentrations of the initial compounds by ±25%, depending on the time for which the mixture of tetrahydrofuran and butyllithium was left to stand before the addition of the monomer (minutes by the order of magnitude). Tetrahydrofuran reacts with alkyllithium only slowly, but at concentrations comparable with the initial concentrations of the initiator $[I]_0$ its effect may be quite considerable. This explanation is corroborated by the fact that at higher THF concentrations the reproducibility increased. 1-Octene does not affect the overall reaction rate to any essential degree (within the limits of experimental error, some ±2%), but strongly affects the so-called induction period. For the initial concentrations of butyllithium and isoprene 0·5 mol/l the induction period became shorter after the addition of small quantities of 1-octene (2 and 4% related to the reaction mixture), while with higher quantities added (8% and more) it disappeared completely. The rate of the propagation reaction remains unchanged if the addition of 1-octene does not raise the concentration of the product from the initiation reaction, the conversion of which is only several per cent; it merely accelerates the reaction and possibly also restricts the slowing-down effect of the "cross" association, so that identical kinetic curves are mutually shifted in time only.

Further experiments were carried out with butyl ethyl ether as the donor. The slope of the kinetic curve (Fig. 1, 2) is identical with the reduced rate $(v_r$ in mol l^{-1} . . h$^{-1})$,

$$v_r = -\frac{d[M]}{[M]\,dt} = -\frac{d \ln [M]}{dt} = k_i[A]^p + k_p[RM_nLi]^q , \qquad (1)$$

where $[M]$ is the concentration of the monomer, $[A]$ is the concentration of the solvated active sites in the initiation reaction, $([A] \equiv [E_n(BuLi)_m])$, $[RM_nLi]$ is the concentration of the "living" polymer, k_i is the initiation constant and k_p is the propagation constant. In a polar solution the exponents p, q are close to unity; as $[RMLi] = m([A]_0 - [A])$, at the beginning of the reaction, where n is small, it holds that

$$v_r = (k_i - mk_p)[A] + mk_p[A]_0 . \qquad (2)$$

The conversion curves are convex or concave according to the sign of the right-hand side of Eq, (2). It follows from Fig. 1, 2 that this term is positive and very small, and that consequently the effect of the initiation reaction predominates. Hence, in the first approximation v_r is proportional to the concentration of the associate active sites in the initiation reaction and may be employed as the association criterion. For the overall effect of ether in the concentration range $0-0.5$ mol/l it was found that

$$v_r = 0.8 + 6.4[E]_0 \qquad (3)$$

for $[M]_0 = [I]_0 = 0.5$ mol/l. The concentration of the active associate sites increases with the concentration of ether linearly; consequently, the equilibrium constant of association is low, because otherwise the effect of the loss of the free hexameric associate of alkyllithium would come into play. The effect of ether concentration on the initiation reaction is documented in Fig. 4 (curve 1), in which the dependence of the monomer conversion has been plotted for such a short time where the propagation reaction does not yet become operative to any essential extent. This dependence is linear too. Curve 3 in Fig. 2 shows the dependence of the reduced rate on the concentration of the equimolar mixture of butyllithium and butyl ethyl ether. Both dependences indicate the role played by the solvation equilibrium, E.

The effect of triethyl amine as electrondonor on the polymerization is much stronger than that of the chosen ether (Fig 3). The reaction order with respect to the initial concentration of butyllithium as the initiator is 2/3 at the beginning and then drops to zero with increasing $[I]_0$, or even becomes negative (Fig. 5). The reaction order with respect to the amine concentration at a given $[I]_0$ is a complicated function of $[I]_0$ (Fig. 6); within the concentration range $[I]_0$ under the investigation, varies from 1/3 to 2/3. With the increasing amine-to-initiator molar ratio, the reaction order increases from 2/3 to unity (Fig. 7). The reaction orders thus determined are summarized
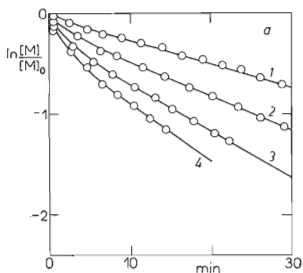
FIG. 1

Conversion Curves of the Polymerization of Isoprene ($[M]_0 = 0.5$ mol/l) with Butyllithium in a Mixture with Butyl Ethyl Ether in the Molar Ratio 1 : 1

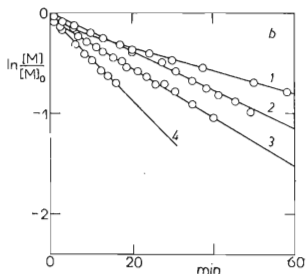Concentration of butyllithium (mol/l): *1* 0.125, *2* 0.250, *3* 0.375, *4* 0.500.

FIG. 2

Conversion Curves of the Polymerization of Isoprene ($[M]_0 = 0.5$ mol/l) with Butyllithium ($[I]_0 = 0.5$ mol/l) and with Butyl Ethyl Ether Added, mol/l:
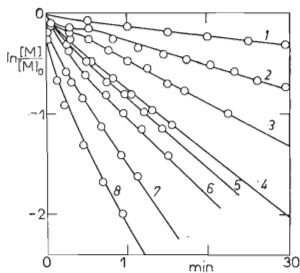*1* 0.0, *2* 0.05, *3* 0.125, *4* 0.25.

FIG. 3

Conversion Curves of the Polymerization of Isoprene ($[M]_0 = 1.0$ mol/l) with Butyllithium ($[I]_0 = 0.5$ mol/l) with Triethylamine Added. mol/l:
1 0.0, *2* 0.05, *3* 0.10, *4* 0.20, *5* 0.25, *6* 0.30, *7* 0.50, *8* 1.00.
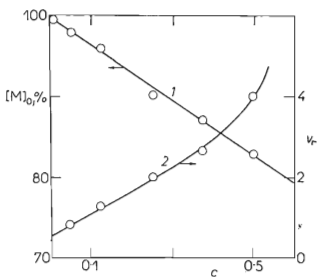

FIG. 4

Polymerization of Isoprene (0.5 mol/l) with Butyllithium and with Butyl Ethyl Ether Added

1 Conversion of monomer at constant time $t = 0.7$ min as a function of concentration (c) of the equimolar mixture BuLi + + Et_3N in mol/l. Point nearest to the beginning of coordinates holds for pure butyllithium (0.5 mol/l). *2* Dependence of reduced rate v_r (mol l^{-1} h^{-1}) of linear parts of conversion curves in Fig. 1.

in Table I. The only possible explanation of the decrease in the concentration of the solvated active sites in the initiation reaction with the increasing concentration of alkyllithium (Fig. 5) is that two different solvates A_1, A_2 arising in the equilibria (D), (E) and compete in the solvation equilibria. A_1 does not participate in the initiation
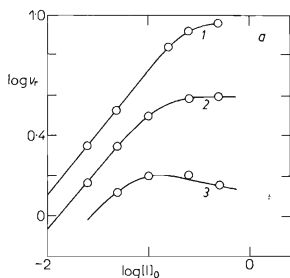

Fig. 5

Polymerization of Isoprene ($[M]_0 = 1.0$ mol/l) with Butyllithium, Dependence of Reduced Rate v_r on the Initial Concentration of Butyllithium ($[I]_0$) in mol/l, with Triethylamine Added, mol/l:
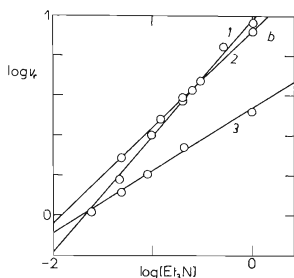
1 1·0, 2 0·2, 3 0·05.

Fig. 6

Dependence of Reduced Rate v_r (mol/l h) of the Polymerization of Isoprene ($[M]_0 = 1.0$ mol/l) on the Concentration of Et_3N (mol/l) for the Initial Concentration of Butyllithium, mol/l:

1 0·50, 2 0·25, 3 0·05.

Fig. 7

Dependence of Reduced Rate v_r (mol/l h) of the Polymerization of Isoprene ($[M_0] = 1.0$ mol/l) on Concentration of the Mixture BuLi : Et_3N in Ratios

1 1 : 4, 2 1 : 2, 3 1 : 1, 4 2 : 1. c is analytical concentration of butyllithium.
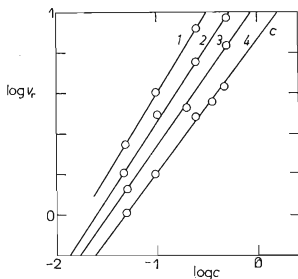
reaction (or only little) and A_2 is considerably active in the same reaction; the respective equilibrium constants are given by

$$K_1 = [A_1]/[H][E] \quad K_2 = [A_2]^3/[H][E]^3 , \qquad (4a,b)$$

where H is the concentration of alkyllithium hexamer. It holds, further, that

$$[H]_0 = [H] + [A_1] + \tfrac{1}{3}[A_2] , \qquad (5)$$

$$[E]_0 = [E] + [A]_1 + [A_2] . \qquad (6)$$

By substituting (5, 6) (5) and (6) into (4a) and after rearrangement, we obtain

$$[A_1] = \tfrac{1}{2}([H]_0 + [E]_0 + 1/K_1 - \tfrac{4}{3}[A_2]) (1 - \sqrt{(1 - a)}) , \qquad (7)$$

where

$$a = \frac{4([H]_0 - \tfrac{1}{3}[A_2]) ([E]_0 - [A_2])}{([H]_0 + [E] + 1/K_1 - \tfrac{4}{3}[A_2])^2} . \qquad (8)$$

If $a \ll 1$, the expression for $[A]$ may be considerably simplified. By subsequent substitution into an expression which is obtained by dividing (4a) and (4b),

$$[A_2]^3 = \frac{K_2}{K_1} [E]^2 [A_1] , \qquad (9)$$

TABLE I
Reaction Order in the Polymerization of Isoprene Initiated with Butyllithium with the Addition of Triethyl Amine (benzene $[M]_0 = 1 \cdot 0$ mol/l, 300 K)

c Concentration of the mixture BuLi and Et_3N with respect to the analytical concentration of lithium.

$[I]_0$ mol/l	Order with respect to $[Et_3N]$	$[I]_0/ [Et_3N]$	Order with respect to c
0·50	0·62	0·25	0·80
0·25	0·47	0·50	0·75
0·10	0·44	1·00	0·71
0·05	0·32	2·00	0·66

we obtain:

$$[A_2]^3 = K_2 \frac{([H]_0 - \tfrac{1}{3}[A_2])([E]_0 - [A_2])^3}{(K_1[H]_0 + K_1[E]_0 + 1 - \tfrac{4}{3}K_1[Q_2])^3}(K_1[E]_0 - K_1[A]_2 + 1)^2 . \quad (10)$$

Solution with the simplification $[E]_0 \gg [H]_0$ yields:

$$[A_2] = \sqrt[3]{[-q + \sqrt{(q^2 + p^3)}]} + \sqrt[3]{[-q - \sqrt{(q^2 + p^3)}]} , \quad (11)$$

where:

$$p = \frac{K_2}{9}\frac{[E]_0^3}{K_1[E]_0 + 1} , \quad q = \frac{-K_2}{2}\frac{[H]_0[E]_0^3}{K_1[E]_0 + 1} . \quad (12a,b)$$

Expression (11) may also be written as

$$[A_2] = \sqrt{p}\{\sqrt[3]{[(x + \sqrt{(1 + x^2)}]} - \sqrt[3]{[-x + \sqrt{(1 + x^2)}]}\} = z\sqrt{p} , \quad (13)$$

where

$$x = -\frac{q}{p\sqrt{p}} = \frac{27}{2}\frac{[H]_0}{[E]_0}\sqrt{\frac{K_1[E]_0 + 1}{K_2[E]_0}} \quad (14)$$

Fig. 8 shows the dependence $z = z(x)$ in the logarithmic coordinates. For a small x we have $z \approx bx$, for a large x we have $z \approx b . \sqrt[3]{x}$ where b is a constant.

The following consequences may be derived from Eqs (13), (14):
a) At a low initial concentration of the initiator, where x is small, the reaction rate is independent of the amine concentration. b) With the increasing concentration
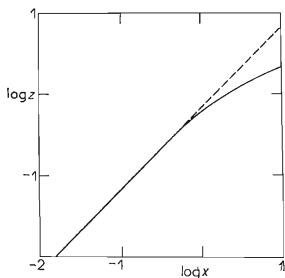

FIG. 8

Function $z = z_{(x)}$ in Eq. (13) Shown in Logarithmic Coordinates

of the initiator, the reaction order with respect to the initial concentration of the electrondonor increases, until at a high x it reaches $2/3$, and is constant, if $K_1[E]_0 \gg 1$. *c*) At a high concentration of the donor and a low concentration of the initiator, the rate of initiation is proportional to the initial concentration of the initiator. *d*) With the increasing concentration of the initiator the reaction order with respect to the concentration of the initiator decreases, according to (*13*), as much as to $1/3$; from here onwards, however, Eq. (*13*) loses its validity owing to the simplification involved in deriving it. At comparable donor and initiator concentrations the term $K_1[H]_0$ becomes operative in the numerator of Eq. (*10*), which further reduced the concentration of the active complex; if this effect predominates, the reaction order passes into the range of negative values. *e*) Numerical treatment of Eq. (*10*) has revealed that in the concentration range of the initial compounds used in the experiments, the reaction order with respect to the initial concentration of the initiator varies from 0.8 for the lowest butyllithium concentrations to $-1/2$ for the lowest concentrations of the donor, that is in an excellent agreement with the results obtained. *f*) For a constant and very low $[H]_0 : [E]_0$, *i.e.* for a small x, Eqs (*12*)−(*14*) give the first order with respect to the concentration of the initiating mixture alkyllithium − donor. If this ratio is large or close to unity, the reaction order decreases according to Eq. (*10*).

All these conclusions agree very well with the measured data. No exact calculation of the constants could be carried out, however, because of difficulties involved in the numerical treatment of Eq. (*10*). A rough estimate using approximate Eqs (*12*)−(*14*) gives

$$K_1 \approx 10^3 \text{ l/mol } (4a), \quad K_2 \equiv 0.5 . 10^2 \text{ l/mol } (4b), \quad k_i = 2 . 10^2 \text{ l/mol}^{-1} \text{ h}^{-1} (1).$$

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