

NEGATIVE REACTION RATES OF THE POLYMERIZATION OF ISOPRENE INITIATED WITH ALKYL LITHIUM

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The polymerization kinetics of isoprene in benzene initiated with ethyl, n-butyl, and n-hexyllithium was investigated, using gas chromatography as the analytical method. In the range of high concentration of the initiator, negative formal reaction orders of polymerization with respect to the initial concentration of monomer and initiator were found. Such anomaly was proved to be due to the initiation step of the reaction; orders were zero at a constant initiator concentration/solvent concentration ratio. If the ratio increases, the signs of the reaction orders assume negative values.

The formal reaction orders of the polymerization of isoprene with organolithium compounds in nonpolar media are known to be strongly dependent on the concentration range of the reaction components. Data of various authors greatly differ in this respect¹⁻³. For the polymerization of isoprene with ethyllithium in toluene, Spirin⁴ found a linear dependence of the reaction rate on the initial concentration of ethyllithium up to concentrations of c. $5 \cdot 10^{-3}$ mol/l; with further increase of the concentration of the initiator the polymerization rate remained unchanged up to $1.5 \cdot 10^{-2}$ mol/l, after which there was a considerable drop in the reaction rate. Sinn⁵ also found a negative reaction order with respect to the concentration of the initiator. At a concentration of butyllithium between $6.5 \cdot 10^{-3}$ and $13 \cdot 10^{-3}$ mol/l the rate of the polymerization of isoprene without solvent attained maximum, while at higher initiator concentrations it was decreasing steeply. However, in the majority of the other papers there is no mention of the occurrence of negative reaction rates; only a decrease in the polymerization rate to zero rate with respect to the initial concentration of the initiator was generally observed. This decrease in the reaction orders was satisfactorily explained by Brown⁶, who suggested a mechanism of the initiation with alkyl lithium, in the first step of which he considers the formation of a π -complex of the diene with an alkyl lithium associate (tetramer or hexamer). Unfortunately, the occurrence of negative polymerization orders cannot be explained in terms of Brown's theory. Papers^{4,5} do not allow to decide if the anomaly is due to the propagation or to the initiation reaction, or to the effect of the so-called cross-association of living polyisopropenyllithium with alkyl lithium⁷.

It has been an aim of this work to determine which reaction step of the polymerization of isoprene initiated with alkyl lithium is responsible for the occurrence of the negative reaction rate, and to attempt a qualitative interpretation of the phenomenon. In order to obtain plausible results in the analytical determination of the reaction components we used the gas chromatographic method, which provides

absolute values independent of the different association equilibria of the system under study.

EXPERIMENTAL

Chemicals

Isoprene was purified by distillation with sodium metal, rectified over calcium hydride in argon and stored over calcium hydride in a protective argon atmosphere at low temperature. Benzene, pentane and cyclohexane were shaken with concentrated sulphuric acid, washed with water and a solution of potassium hydroxide; on drying with calcium hydride they were distilled over a Na/K alloy over which they were also stored. Ethyllithium was prepared by reacting 15 g of lithium suspension in 0.6 l of dry benzene at room temperature in argon with 60 ml of ethyl bromide with intensive stirring for seven hours. *n*-Butyllithium was prepared in a similar way, by reacting 100 ml of *n*-butyl chloride with 20 g of a lithium suspension in 0.5 l benzene; the concentration of the product was 1.8 mol/l. More concentrated solutions of butyllithium were prepared by evaporating one part of the solvent *in vacuo*. *n*-Hexyllithium was prepared by reacting 10 g of lithium suspension with 60 ml of *n*-hexyl chloride in 0.4 l of dry benzene; the concentration of the product was 1.05 mol/l.

Polymerization

The reaction was carried out with intensive stirring under argon in a thermostated apparatus dried by washing with the initiator and provided with a capillary for taking samples. The volume of the reaction mixture was 50 ml. The samples (c. 0.3 ml) were immediately shaken with 0.05 ml of water and the content of unreacted components was immediately determined by gas chromatography.

Gas Chromatography

Column 2.5 m, 20% silicone elastomer SE 30 on Chromosorb N—AW, catharometer as detector. Isoprene and *n*-butane were analyzed at the column temperature 80°C and the evaporator temperature 200°C and at the pressure of the carrier gas (hydrogen) 0.05 MPa. The samples were injected with syringes produced by Hamilton Co., 1, 5 and 10 μ l in volume. Internal standards added to the reaction mixture were c. 10% of the monomer (pentane or cyclohexane); the chromatograms were evaluated with respect to the peak heights by using calibration mixtures of the compounds being determined with an internal standard having a known ratio of components. We checked up if the internal standard used did not affect the reaction rate.

RESULTS AND DISCUSSION

The reaction of ethyllithium with isoprene was carried out in benzene solution at a relatively high content of alkylolithium. The initial monomer concentration varied from 0.04 to 0.1 mol/l, the initial initiator concentration, $[I]_0$, lay within 0.05–0.2 mol/l. The conversion curves of the monomer at 280–310 K were found to characterize only the initiation step of the reaction, while the propagation was

strongly suppressed. The only reaction product detected up to more than 50% of the conversion of monomer was the monoadduct C_7H_{14} . No negative reaction orders were found in this concentration range; the initial reaction rate, v_0 , determined by extrapolation of the instantaneous rate to zero conversion is linearly dependent on the initial monomer concentration, $[M]_0$ and the reaction order with respect to the initial initiator concentration is approximately $1/2$ (Fig. 1). The energy of activation, 13.8 kcal/mol, and the frequency factor, $2 \cdot 10^8 \text{ l}^{0.5} \text{ mol}^{-0.5} \text{ min}^{-1}$ ($3.3 \cdot 10^6 \cdot \text{l}^{0.5} \text{ mol}^{-0.5} \text{ s}^{-1}$) indicate the exacting entropy demands of the transition state of the reaction (Fig. 2). Further increase in the initial isoprene concentration did not lead to any deviation from the dependence given in Fig. 1. Higher initiator concentrations were difficult to obtain for experimental reasons; this is why *n*-butyllithium was used for initiation in further measurements, while following at the same time the conversion of both the monomer and the initiator (through hydrocarbon arising by the hydrolysis of the latter). Because of the weaker initiation power of butyllithium the propagation reaction is much more operative here (Fig. 3). Table I, which summarizes the resulting initial polymerization rates, gives at low concentrations of the initial compounds the relationship

$$v_0 = k[M]_0 [I]_0,$$

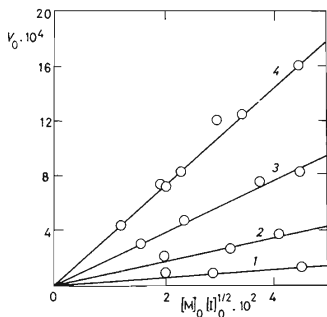


FIG. 1

Relationship between the Initial Rate, v_0 ($\text{mol l}^{-1} \text{ min}^{-1}$) and the Initial Monomer $[M]_0$ and Initiator $[I]_0$ Concentrations (in mol/l) in the Reaction of Ethyllithium with Isoprene in Benzene

Temperatures, K: 1 280, 2 290, 3 300, 4 310.

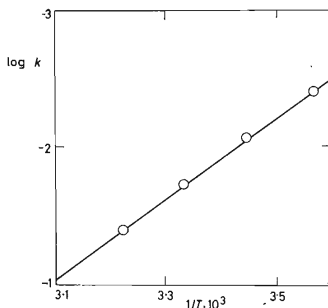


FIG. 2

Dependence of the Rate Constant (k in $\text{l}^{0.5} \text{ mol}^{-0.5} \text{ min}^{-1}$) on Absolute Temperature in the Reaction of Ethyllithium with Isoprene in Benzene

i.e. the reaction rates with respect to the initial concentrations of the substrate (monomer) and initiator are equal to unity. At the highest monomer concentration (Table I) there was a steep decrease in the reaction rate. With the further increase in the monomer concentration the conversion curves ($[M]$ vs time) became sigmoidal, and the decrease in the polymerization rate was more distinct.

The reaction kinetics at a high monomer concentration (8 mol/l) was studied. A solution of butyllithium from which the solvent had been partly evaporated had to be used for the highest initiator concentrations. The maximal polymerization rate, v_m , was calculated from the slope of the linear part of the sigmoidal curve of the monomer conversion. At low concentrations of butyllithium the formal reaction order with respect to the initiator concentration is $1/5$; at highest concentrations of butyllithium the reaction rate is inversely proportional to that of the initiator (Fig. 4).

In an attempt to demonstrate that the anomalies mentioned above are not characteristic of *n*-butyllithium only, and also for an easier analysis of hydrocarbons, *n*-hexyllithium was used in the initiation in further tests. It was found that besides a decrease in the polymerization rate, a strong decrease in the rate of initiation determined from the conversion curves of the initiator also became operative at high concentrations. At the beginning the initiation rates are unity with respect to the initial monomer concentration and $1/2$ with respect to the initial initiator concentra-

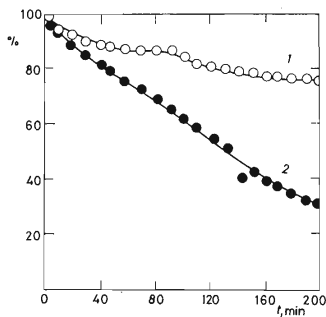


FIG. 3

Conversion Curve of *n*-Butyllithium 1 and Isoprene 2 in the Reaction in Benzene (300 K; initial concentration of the active components 0.3 mol/l)

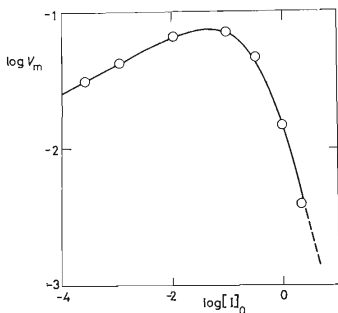


FIG. 4

Reaction of Isoprene ($[M]_0 = 8.0$ mol/l) with *n*-butyllithium at 290 K in Benzene

v_m is the maximum polymerization rate ($\text{mol l}^{-1} \text{min}^{-1}$), $[I]_0$ is the initial initiator concentration (mol/l).

tion. At certain selected initial concentrations of the reaction components ($[M]_0$, $[I]_0$) and of the solvent ($[S]$) in the given system it holds that the reaction orders are zero; under these critical conditions the ratio $[S]/[I]_0$ is constant (Table II). As soon as the ratio drops below c. 33, which may be due both to an increase in the initiator concentration and to an increase in the monomer concentration (the concentration of the solvent is lowered), the reaction orders change their sign (Fig. 5a,b). It is unequi-

TABLE I

Initial Polymerization Rate, v_0 , of Isoprene Initiated with n-Butyllithium (benzene, 300 K)
 $[M]_0$ Initial monomer concentration, $[I]_0$ initial initiator concentration.

$[M]_0$ mol/l	$[I]_0$ mol/l	v_0 mol/l min	$v_0/[M]_0 [I]_0$ l/mol min
0.20	0.20	0.0013	0.032
0.24	0.15	0.0010	0.028
0.17	1.00	0.0050	0.030
0.30	0.30	0.0018	0.020
0.50	0.50	0.0083	0.033
0.50	1.00	0.0170	0.034
1.00	1.00	0.0070	0.007

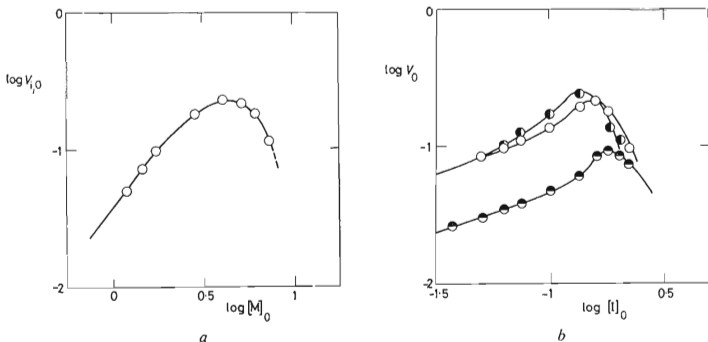


FIG. 5

Reaction of Isoprene (M) with n-Hexyllithium in Benzene at 300 K

Dependence of the initial initiation rate ($v_{i,0} = (d[I] dt)_{t=0}$ mol l⁻¹ h⁻¹) on (a) $[M]_0$ (mol/l) at $[I]_0$ 0.2 mol/l; (b) $[I]_0$ (mol/l) at $[M]_0$ 1.0 ●, 2.0 ○ and 4.0 ◐ mol/l.

TABLE II

Initial Initiator $[I]_0$, Monomer $[M]_0$ and Benzene $[S]$ Concentrations under Critical Conditions of the Reaction of Isoprene with *n*-Hexyllithium at 300 K

$[I]_0$ mol/l	$[M]_0$ mol/l	$[S]$ mol/l	$\frac{[S]}{[I]_0}$	Figure
0.19	4.0	6.47	34.00	5b
0.26	2.0	8.60	33.07	5b
0.29	1.0	9.68	33.37	5b
0.20	3.7	6.80	34.00	5a
0.06 ^a	8.0	2.20	37.00	4

^a Initiation with *n*-butyllithium.

vocally clear that the negative reaction polymerization orders are due to an anomalous course of the initiation reaction and that below the critical concentration of the initial compounds the course of the reaction is normal and in accordance with numerous literature data.

The negative polymerization orders cannot be explained by means of simple association equilibria; the dependence has a character similar to the finding described by Waack⁸, concerning the addition of *n*-butyllithium to 1,1-diphenylethylene with small amounts of tetrahydrofuran added. At a constant THF/butyllithium ratio the reaction rate increases with increasing amount of alkyllithium. If, on the other hand, the concentration of alkyllithium was increased at a constant THF content, the reaction was slowed down.

Since the molecule of the initiator cannot fix tens of molecules of benzene (one molecule of alkyllithium hexamer would have to bind hundreds of molecules of benzene) for the loss of the free solvent due to complexation to become operative, the above dependence cannot be explained by the classical solvation equilibrium. Apparently, here we have a competition between two different solvates of the initiator in the transitional state of the reaction, the lower solvate being the less reactive.

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