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ALKYLLITHIUM ANIONIC POLYMERIZATION INITIATORS IN HYDROCARBON SOLVENTS

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The very large effect of solvents in the reactions of organometallic compounds when changing from non-polar to polar solvents is generally recognized. But the marked difference in behaviour of alkyllithiums, at least in their reactions with olefins, when the reaction medium is changed from saturated hydrocarbons to the more polarizable aromatic solvents is generally overlooked.

In hydrocarbon solvents generally, the alkyllithiums are associated, sixfold for ethyl and n-butyllithium[1], and fourfold for tert-butyllithium[2]. In aromatic solvents the kinetics of the addition of these alkyllithiums to olefins are consistent with a simple equilibrium dissociation to a small amount of a monomeric form which then adds in a simple bimolecular reaction to the olefin. This scheme is valid for the addition of n-butyllithium to styrene[3] and to diphenylethylene where the order is $\frac{1}{6}$ [4], and the addition of tert-butyllithium to diphenylethylene[5] where the order found was $\frac{1}{4}$.

$$[\mathrm{RLi}]_n \rightleftarrows n\,\mathrm{RLi}$$

$$\mathrm{RLi} + \mathrm{C_6H_5CH{=}CH_2} \rightarrow \mathrm{C_6H_5\overset{-}{C}HCH_2R\cdot Li^+}$$

In the saturated solvent cyclohexane, this scheme breaks down, and completely different behaviour is found. In the addition of n-butyllithium to styrene, isoprene and butadiene[6,7] it was found that initially there is a period of increasing rate, and that if an order is found for the period of maximum rate it is between $\frac{1}{2}$ and 1. The rate is also considerably slower than in benzene. No detailed mechanism has been proposed for this complex behaviour.

The validity of the scheme proposed for the aromatic solvents has recently been challenged[8], but no differentiation was made between the two types of behaviour in the two different types of solvent. The criticism was based largely on behaviour found in aliphatic solvents although the distinction between the two solvent types had already been drawn.

To extend the basis of data on which the solvent effect may be judged, the reaction of the secondary alkyllithium sec-butyllithium, has been studied in both benzene and in cyclohexane solution with two monomers, styrene and isoprene, and compared with the association number. The rate of reaction of this isomer has been found to be far greater than that of the normal isomer[9] and should show if the behaviour difference is general.

EXPERIMENTAL

The sec-butyllithium was obtained as a 12% solution from Foote Mineral Co. Before use it was freed from solvent by pumping, and given a short path distillation at 75° onto a cold finger. The Foote technical data bulletin suggests the thermal decomposition would be less than 1% in the time taken to distill a small quantity. That used for kinetic measurements was then diluted into fragile bulbs with the appropriate solvent, in an all glass apparatus by methods described before.

The solvent and monomer purification were as previously described[3,6,7].

The measurement of the rate of formation of the polymer anion from the butyllithium and the monomer was done spectrophotometrically in all glass vessels, prewashed with butyllithium solution, as before. The reactions in cyclohexane were at 40°, in benzene at 30°. All rates are given in units of moles, litres and seconds.

The degree of association of the sec-butyllithium was found by measuring its apparent molecular weight by freezing point depression in both benzene and cyclohexane. The cells in which the freezing points were measured were all glass, test-tube shaped and contained a deep well for a thermistor probe, and a magnetic stirrer bar. They were all sealed onto a larger apparatus onto which were joined via breakseals, vessels containing the solvent and sec-butyllithium. The apparatus was washed under vacuum conditions with a solution of butyllithium, then the solvent distilled around many times and drained to a side vessel. The side vessel was frozen and removed. The solvent was allowed into the apparatus and one of the freezing point cells sealed off with the solvent. The breakseal to the butyllithium was then broken, and the solution manipulated in such a way as to fill the remaining cells with solutions of different concentrations, and then sealed off. The sec-butyllithium was at all times kept chilled. The freezing point depressions were measured with a thermistor probe coupled with an Aminco–Bowman bridge, calibrated with triphenylmethane solutions.

RESULTS

Both monomers behaved similarly with sec-butyllithium in each solvent, but the behaviour in the two solvents was different in much the same way that the behaviour of n-butyllithium was different. With both monomers the rate of formation of the polymer anion was at its maximum at the beginning of the reaction in benzene solution, and fell as the reagents became exhausted. In cyclohexane solution, however, both monomers gave sigmoidal curves of formation of polymer anions, the initial rate being very slow and increasing to a maximum, to decline again as the reagents were consumed. The period of maximum rate began after about a quarter of the reaction was completed. These two types of reaction curve are shown in Fig. 1.

The order of the reaction with respect to the initial butyllithium is close to $\frac{1}{4}$ with both monomers in benzene solution, as is shown in Fig. 2. In cyclohexane solution, however, the corresponding order for the period of maximum rate is 0.75 for isoprene, and 1.4 for styrene (Fig. 3). Moreover, the rates are hundreds of times slower in cyclohexane than in benzene at the same temperature, at 10^{-3} M butyllithium. In cyclohexane solution with isoprene the very initial rate appears to have an order even closer to first in butyllithium.

The results of the association studies are in Table 1 and show a degree of

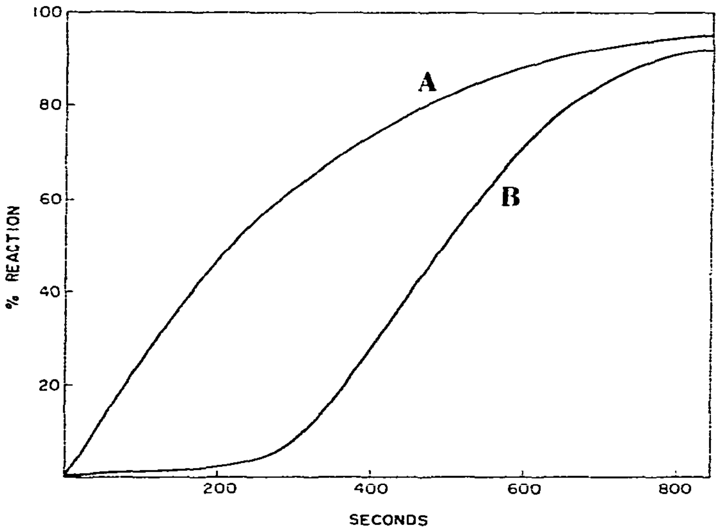

Fig. 1. Typical curves for the appearance of the UV absorption of polystyryllithium. A. Reaction of 1.09×10^{-3} *M* sec-butyllithium with 5.33×10^{-4} *M* styrene in benzene solution at 30°. *B*. Reaction of 1.34×10^{-3} *M* sec-butyllithium with 8.67×10^{-2} *M* styrene in cyclohexane solution at 40°.

association for sec-butyllithium of 4, within the experimental error. This compares with the sixfold association of ethyl- and n-butyllithium, and the fourfold association of tert-butyllithium.

In cyclohexane solution it was found that the sec-butyllithium had a very low light absorption below 300 mμ which increased monotonically to 220 mμ, the end of the scan. In benzene solution this absorption was many times greater in the region of 290 mμ (ε_{290} 352), where the absorption of benzene is still low, and appeared to be

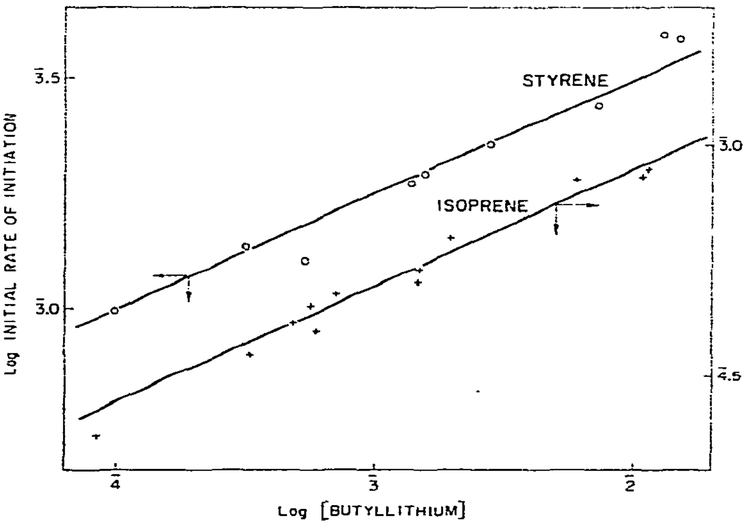

Fig. 2. Dependence of initial rate of reaction of styrene and isoprene with sec-butyllithium in benzene solution at 30°.

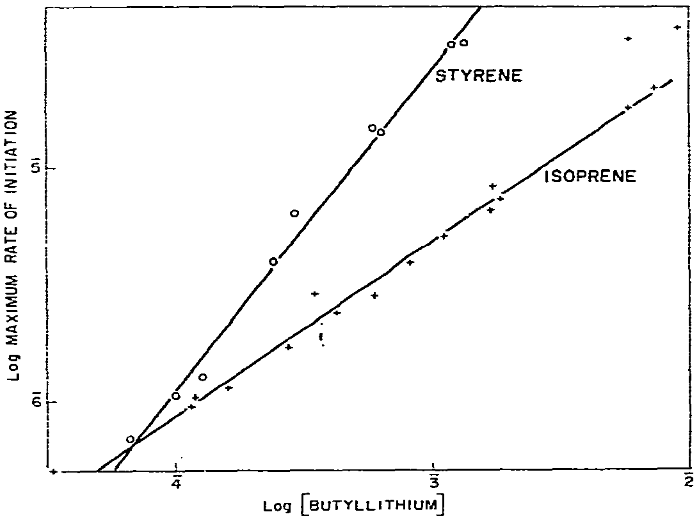

Fig. 3. Dependence of maximum rate of reaction of styrene and isoprene with sec-butyllithium in cyclohexane solution at 40°.

still increasing at lower wavelengths. There must be some interaction between benzene and the butyllithium to cause this absorption.

DISCUSSION

The literature contains a number of examples of a fractional order with butyllithium in aromatic solvents, similar to the above results. Evans *et al.* have studied the reaction of ethyl-, n-butyl- and tert-butyllithium with diphenylethylene and with fluorene[4,5,10,11] and found low order in all cases, despite the fact that one is an addition reaction, and the other a substitution reaction. The order in n-butyllithium was $\frac{1}{6}$ in both cases, and $\frac{1}{4}$ order with tert-butyllithium, both in agreement with their measured degrees of association, but the orders for ethyllithium were rather lower than expected. The initiation reaction of styrene with n-butyllithium has been shown to have a low order in toluene, and $\frac{1}{6}$ in benzene. Burnett has reacted n-butyllithium with many substituted styrenes and found orders between $\frac{1}{4}$ and $\frac{1}{6}$ under rather open conditions[12]. One reaction in which a first order dependence of ethyllithium was found is the reaction with benzyl chloride in benzene[13].

TABLE 1

DEGREE OF ASSOCIATION OF sec-BUTYLLITHIUM

Solvent	*[sec-Butyllithium] Formal (M)*	*n*	*Solvent*	*[sec-Butyllithium] Formal (M)*	*n*
Benzene	0.172	4.13	Cyclohexane	0.107	4.07
	0.286	4.08		0.289	4.30
	0.491	4.10		0.345	3.99
	0.502	4.20		0.363	4.09
				0.399	4.23

With the exception of the last, which differs in being a reaction with a polar substrate, all these reactions in aromatic solvents have been explained in terms of a small amount of a reactive monomeric alkyllithium in equilibrium with the unreactive associated form. The frequent coincidence of the fractional order with the degree of association lends considerable support to this scheme, although direct evidence is difficult to obtain as the dissociations are too small to measure. Support is also gained from the behaviour of the propagation reactions of the polymerization of styrene, isoprene and butadiene, where the propagating species is a resonance stabilized anion–Li^+ ion pair which forms aggregates. The order of reaction is again in accord with the found association numbers even though some are in aliphatic solvents.

The behaviour in cyclohexane of alkyllithiums is markedly different. The rate curves are sigmoidal and even the maximum rate is factors of two powers of ten slower than those in benzene, the real initial rates are even slower. Moreover, in all cases, the kinetic orders for the rate maximum are nearer to first order, varying from 0.57 found by Burnett[12] for the reactions of n-butyllithium with substituted styrenes, to 0.67, 1 and 1.4 for the reaction of various butyllithiums with styrene, butadiene and isoprene found by Hsieh and by Worsfold *et al.*[6,7,9]. It is evident that the reaction scheme that was adequate in aromatic solvents, fails in aliphatic solvents. The most likely reason for its failure is perhaps a much smaller dissociation to give the monomeric alkyllithium. Alternatively in this non-polarizable solvent there may well be a reluctance on the part of a perhaps moderately co-valent monomeric alkyllithium to give the more polar resonance stabilized polymer anion–Li^+ ion pair. In both cases the reaction with the comparatively unreactive aggregate, or a partial dissociation fragment of it, could then be the preferred path. The simultaneous incorporation of the ion pair in the aggregate would aid in stabilizing it. The increase in rate during the course of the reaction is perhaps due to a greater reactivity of aggregates already containing some of the polar polymer anions. This mechanism would be masked in aromatic solvents by the more rapid alternate process.

That there is more interaction of sec-butyllithium with benzene than with cyclohexane is shown by the presence of absorption in the region of 290 mμ. This interaction could well promote the dissociation over that found in cyclohexane. Also Brown[14] has found that the exchange reaction of tert-butyllithium (I) with (lithiomethyl)trimethylsilane (II) is of the order of 10^3 to 10^4 times faster in toluene than in cyclopentane. This he attributed to a faster rate of dissociation of the tetramers into dimeric forms through which he thought the exchange proceeded. The rate of dissociation of the tert-butyllithium he showed to be rate determining. It is significant, however, that he reports that the first mixed species formed in cyclopentane was that rich in (II), presumably $(II)_3(I)$. If the exchange went through the dimers the first product formed would be $(II)_2(I)_2$. If the exchange of this latter mixed species with $(II)_4$ was very rapid the first observed species would of course be $(II)_3(I)$. But unless this exchange is very fast the initial production of $(II)_3(I)$ could be interpreted in favour of exchange via monomeric species.

Brown[8] has criticized generally the mechanism whereby the initiation of polymerization is thought to go via an equilibrium concentration of the monomeric alkyllithium, on the grounds that the rate of dissociation to a monomeric form would be too slow to account for the rates. In doing so he used data derived from a reaction in an aliphatic solvent, although there was already data that this initiation mechanism did not apply in aliphatic solvents. The data he used was that of Morton[15] on the heat and entropy of dissociation of a suggested dimeric polyisoprenyllithium into a monomeric form in hexane solution. The validity of even this data is questioned as the degree of association of polyisoprenyllithium is held to be greater than twofold by several authors. Moreover the high dissociation energy is quite inconsistent with the mechanism proposed by Morton for the polymerization, from kinetic data obtained under the same conditions, which depends on a rapid equilibration between monomeric and associated species to give monodisperse polymer. There seems little reason yet to discard the first proposed mechanism in aromatic solvents, although it can by no means be considered conclusively proved. The mechanism in aliphatic solvents is still quite obscure, though obviously different. More and different data is needed before much progress can be made.

The large increase in rate between the hexameric n-butyllithium and the tetrameric sec-butyllithium and tert-butyllithium, may well be a consequence of a more extensive dissociation accompanying the smaller degree of association. The reactivity of an unassociated normal isomer also might be expected to be less than that of a secondary or a tertiary isomer, except for steric factors.

SUMMARY

The degree of association of sec-butyllithium has been shown to be fourfold in both benzene and cyclohexane solution. In benzene solution the order of reaction in butyllithium when sec-butyllithium reacts with either styrene or isoprene has been shown to be $\frac{1}{4}$. In cyclohexane, however, the reaction curves with both monomers are sigmoidal, and the maximum rate shows a dependence on butyllithium nearer first. This behaviour difference is compared with the behaviour of other lithium alkyls in their reactions in aromatic and aliphatic solvents. It is suggested that two different mechanisms apply in aromatic and in aliphatic solvents because of the large difference in the rates of dissociation of the aggregates in the two types of solvent.

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