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KINETICS OF ADDITION OF BUTYLLITHIUM ONTO DIISOPROPENYLBENZENE

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Abstract—The kinetics of the addition reaction between butyllithium and diisopropenylbenzene (DIB) were investigated in non-polar solvents. It has been established that the two double bonds of *meta*-DIB are almost isoreactive, as expected; for the *para*-isomer however the first addition is faster than the second. The overall rate of reaction is also greater for *para*-DIB. This kinetic study is of great use, since the diadduct behaves as an efficient bifunctional anionic initiator which can be used in non-polar solvents.

INTRODUCTION

Upon search for an efficient difunctional anionic initiator soluble in non-polar solvents, it was found [1, 2] that butyllithium adds to *meta*-diisopropenylbenzene. The red adduct solution can be used to initiate polymerizations in the absence of polar additives; it was shown that the polymers formed are bifunctional, well defined and of low polydispersity [1]. However the reaction between butyllithium and *m*-DIB is slow in non-polar solvents, and precipitation usually occurs when the reaction approaches quantitative (i.e. when the diadduct is formed).

It was of interest to investigate the kinetics of this reaction as such, to establish whether the reactivities of the two double bonds with respect to butyllithium are the same or not, and whether the scheme of consecutive reactions is applicable. It has to be remembered that, like α-methylstyrene, *m*- and *p*-diisopropenylbenzenes polymerize reversibly. Thus, by choosing properly the temperature and the initial monomer concentration, polymer formation can be prevented.

EXPERIMENTAL PART

Solvents

Benzene and cyclohexane were purified by repeated distillation in the presence of a small amount of butyllithium.

Monomers

α-Methylstyrene was distilled twice over sodium wire and collected under vacuum.

The two diisopropenylbenzene isomers were synthesized according to the following procedures.

meta-*Diisopropenylbenzene*

The reaction of dimethylisophthalate with methylmagnesium iodide in ether solution gives after hydrolysis 1.3 di(1'-hydroxy-1' methylethyl) benzene, which is recrystallized from benzene. Yield: 77%. The NMR spectrum exhibits peaks at 7.45 and 7.10 ppm (Ar protons), 4.60 ppm (OH), 1.45 ppm (CH_3). The dicarbinol is then vacuum distilled into a column filled with Al_2O_3 heated to 250°, where dehydration occurs. The obtained crude product is dried and then distilled under vacuum b.p. 107°/16 mm Hg. Yield: 87%. NMR data: peaks at 7.20 and 7.00 ppm (Ar protons), 5.10 and 4.80 ppm ($=CH_2$), 2.00 ppm (CH_3 protons).

para-*Diisopropenylbenzene*

The procedure used to synthesize the *para*-isomer of DIB is similar to that for the *meta*-isomer. The starting materials is dimethylterephthalate. The dicarbinol exhibits NMR peaks at 6.90 ppm (Ar protons), 4.30 ppm (OH), 1.10 ppm (CH_3 protons). The *para*-DIB boils at 106°/16 mm Hg and its NMR spectrum shows peaks at 7.10 ppm (Ar protons), 5.15 ppm and 4.85 ppm ($=CH_2$) and 2 ppm (CH_3). The yields are slightly lower than those for the *meta*-isomer. The two DIB isomers have been carefully purified before use, by distillation over Na wire.

The kinetic experiments were carried out in cyclohexane solution, using a 10-fold excess of butyllithium, at 25° over a period of 24–48 hr. The reaction was followed spectrophotometrically using a Beckman Acta CV recording spectrophotometer. Low concentrations of DIB were chosen in the order of 10^{-3} mol/l to ensure the validity of Beer's law; the optical path in the cell was 0.2 cm. The absorption maxima were located at 315 nm for α-methylstyrene, at 318 nm for *meta*-diisopropenylbenzene and at 418 nm for the *para*-isomer. Figure 1 gives examples of absorption curves registered at various times.

INTERPRETATION OF THE KINETIC DATA

The two steps of adduct formation between butyllithium and diisopropenylbenzene can be treated as consecutive reactions [3]:

$$A + L \rightarrow B \quad k_1$$

$$B + L \rightarrow C \quad k_2$$

Here A is the DIB, B the monoadduct, C the diadduct, L the BuLi; the concentration of BuLi can be considered as constant. k_1 and k_2 are the rate constants characterizing the two steps. The differential equations characterizing this system can be written as:

$$-\frac{d[A]}{dt} = k_1[L][A]$$

$$-\frac{d[B]}{dt} = k_2[L][B] - k_1[L][A]$$

$$\frac{d[C]}{dt} = k_2[L][B].$$

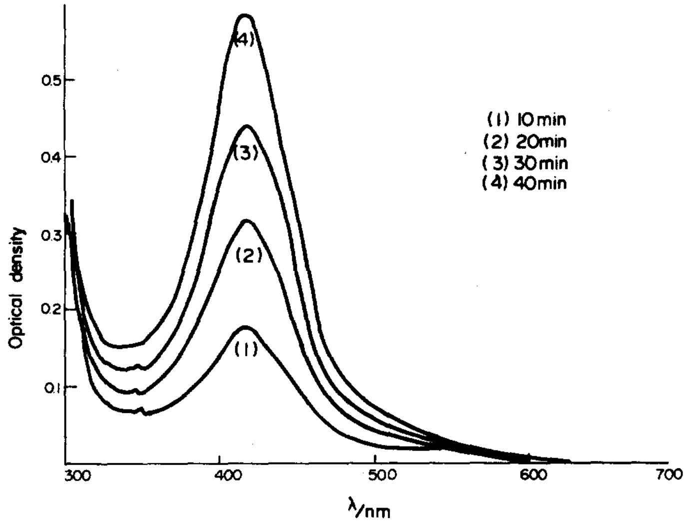

Fig. 1. Example of absorption curves registered at various times for the addition product of a 10 excess of sec. butyllithium onto *p*-diisopropenylbenzene in cyclohexane ($T = 25°$).

1. Consider first the simple case in which

$$k_1 = k_2 = k$$

In that case the concentrations of species A, B and C, at time t can be expressed as:

$$[A] = [A_0]\,e^{-k[L]t}$$

$$[B] = [A_0]k[L]t\,e^{-k[L]t}$$

$$[C] = [A_0][1 - (k[L]t + 1)e^{-k[L]t}]$$

Here $[A_0]$ is the initial DIB concentration.

2. If the two steps of the adduct formation are governed by different rate constants ($k_1 \neq k_2$), integration of the above differential equations leads to

$$[A] = [A_0]e^{-k_1[L]t}$$

$$[B] = [A_0]\frac{k_1}{k_1 - k_2}(e^{-k_2[L]t} - e^{-k_1[L]t})$$

$$[C] = [A_0]\left[1 - \frac{k_1}{k_1 - k_2}e^{-k_2[L]t} + \frac{k_2}{k_1 - k_2}e^{-k_1[L]t}\right]$$

3. Both the monoadduct and the diadduct contribute to the optical density measured at time t, OD_t. If the extinction coefficient of the diadduct is twice that of the monoadduct, then OD_t is proportional to $[B] + 2[C]$; at infinite time, if conversion is quantitative and if no precipitation occurs, OD_{max} should be proportional to $2[C]_\infty = 2[A_0]$.

However it is not established that the extinction coefficient per double bond is the same for both types of adducts. If ϵ_B and ϵ_C are the true extinction coefficients, per double bond reacted, of species B and C, and r the ratio of the two ($r = \epsilon_B/\epsilon_C$), we can express OD_t/OD_{max} as:

$$\frac{OD_t}{OD_{max}} = \frac{r[B] + 2[C]}{2[A_0]}.$$

This expression can be written as:

(a) in the case in which one rate constant governs both steps of the reaction:

$$\frac{OD_t}{OD_{max}} = 1 - \left[k[L]t\left(1 - \frac{r}{2}\right) + 1\right]e^{-k[L]t}. \quad (1)$$

(b) in the case of two rate constants being used:

$$\frac{OD_t}{OD_{max}} = 1 + \frac{k_2 - \frac{r}{2}k_1}{k_1 - k_2}e^{-k_1[L]t} - \frac{\left(1 - \frac{r}{2}\right)k_1}{k_1 - k_2}e^{-k_2[L]t}.$$

In this latter case, it appears that the expression

$$\left(1 - \frac{OD_t}{OD_{max}}\right)$$

is the sum of two exponentials:

$$\left(1 - \frac{OD_t}{OD_{max}}\right) = C_1\exp(-k_1[L]t) + C_2\exp(-k_2[L]t)$$

with

$$C_1 = \frac{\frac{r}{2}k_1 - k_2}{k_1 - k_2} \qquad C_2 = \frac{\left(1 - \frac{r}{2}\right)k_1}{k_1 - k_2}.$$

The interesting feature is that, even though the value of r is not experimentally accessible, the decomposition of the kinetic curve

$$\left(1 - \frac{OD_t}{OD_{max}}\right)$$

vs time into its constituent exponentials should yield the true rate constants k_1 and k_2 of the two steps of the addition reaction.

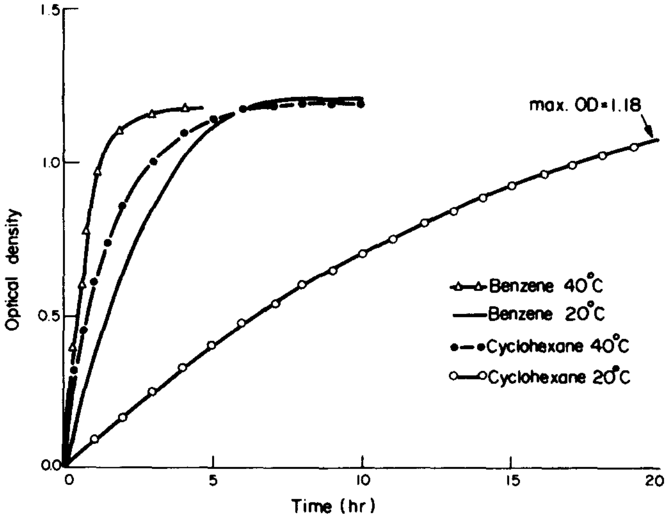

Fig. 2. Plot of OD vs time for the reaction of a stoichiometric amount of sec. butyllithium onto *m*-diisopropenylbenzene in cyclohexane at 20°, 40°; in benzene at 20°, 40°.

DISCUSSION OF THE EXPERIMENTAL RESULTS

1. *Preliminary experiments*

A few experiments were carried out under the conditions used to prepare the bifunctional initiator solutions, i.e. by mixing *m*-DIB and sec·butyllithium in a 1:2 stoichiometric ratio, in benzene or in cyclohexane, the concentrations being of the order of 10^{-2} M and the temperatures ranging from 20° to 40°. The optical absorption at 315 nm (in benzene) or 310 nm (in cyclohexane) is recorded, and Fig. 2 shows the plots of the optical density OD_t vs time.

The reaction is much faster in benzene than in cyclohexane. The rate of addition also increases with temperature.

From the concentration used and the optical density measured, the values of ϵ (per double bond reacted) are found to be close to 8000. However the experimental accuracy on the value of ϵ is questionable because these experiments were run at relatively high concentrations (10^{-2} M), and also because precipitation of the diadduct occurs slowly for conversions above 90%. All further experiments were carried out at high dilution (to ensure the validity of Beer's law) and using a large excess of BuLi, the concentration of which can thus be considered constant. No precipitation occurs under those conditions.

2. *Kinetics of reaction of butyllithium with α-methylstyrene*

In this simple case, which was studied under the same conditions, ($[\alpha MS] = 10^{-3}$ M, $[BuLi] = 10^{-2}$ M), for comparison, the reaction can be expected to be first order with respect to α-methylstyrene. Thus a plot of log $(1 - OD_t/OD_{max})$ vs time should be linear. Figure 3 show the experimental results plotted for the reaction of α-methylstyrene with sec·butyllithium in cyclohexane at 20°. A satisfactory straight line is observed, the slope yielding the rate constant k

$$k = 5.7\ l\cdot mol^{-1}hr^{-1} = 1.6\cdot 10^{-3}\ l\,mol^{-1}sec^{-1}$$

The slight curvature observed in the plot of Fig. 3 for the first hours of the reaction is not easy to explain. It may be related to propagation-depropagation equilibria since, according to Leonard [4], the "ceiling" conditions are not the same for low oligomers as for "living" high molecular weight polymers. Evidence in favour of this interpretation is the fact that the λ_{max} of absorption of the living sites shifts from an initial value of 335 nm (characteristic of "living" poly-α-methylstyrene) to 315 nm which is reached when the plot becomes linear.

3. *Kinetics of addition of butyllithium to* p-*diisopropenylbenzene*

The two double bonds of this monomer are conjugated and they are therefore expected to exhibit different reactivities. The results are displayed in Figs 4 and 5. The variation of OD with time (Fig. 4) is monotonous, and the variation of log $(1 - OD_t/OD_{max})$ vs time exhibits curvature; manual attempts to decompose this curve into a sum of two exponentials failed, owing to the rather small difference between the two rate constants k_1 and k_2. Computer calculations (using a Hewlett–Packard HP 30) by successive iteractions yielded the following values for the constants (r being set equal to unity):

$$k_1 = 2.2\cdot 10^{-2}$$

$$k_2 = 1.7\cdot 10^{-2}\ l\cdot mol^{-1}sec^{-1}$$

Figure 6 shows the curve calculated using these two constants together with the experimental points. The agreement can be considered satisfactory. It should be pointed out that the experimental accuracy decreases for high conversion, as it then rests almost exclusively on the determination of OD_{max}; a small error in that value shifts the experimental points noticeably.

It is therefore confirmed that, for *p*-diisopropenylbenzene, the first addition occurs at a rate about 30% higher than the second addition. However this difference is far below what could be expected from a benzene derivative with two conjugated unsaturations. It

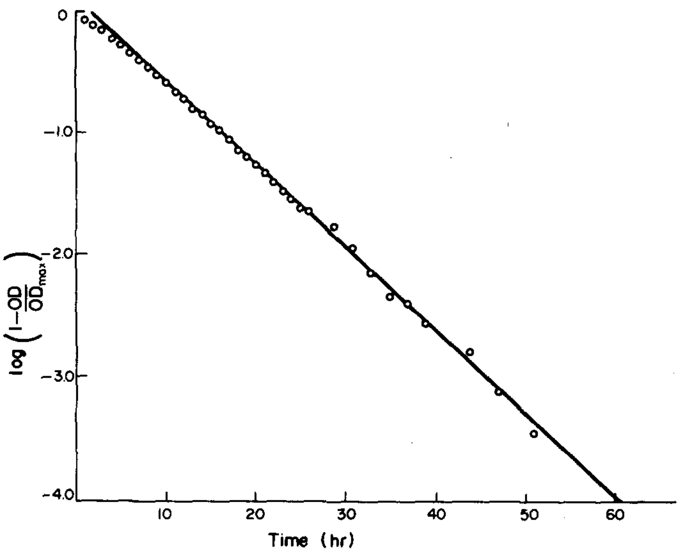

Fig. 3. First order plot log ($1\text{-}OD/OD_{max}$) vs time of the reaction of α-methylstyrene with a 10 excess of butyllithium in cyclohexane ($T = 20°$).

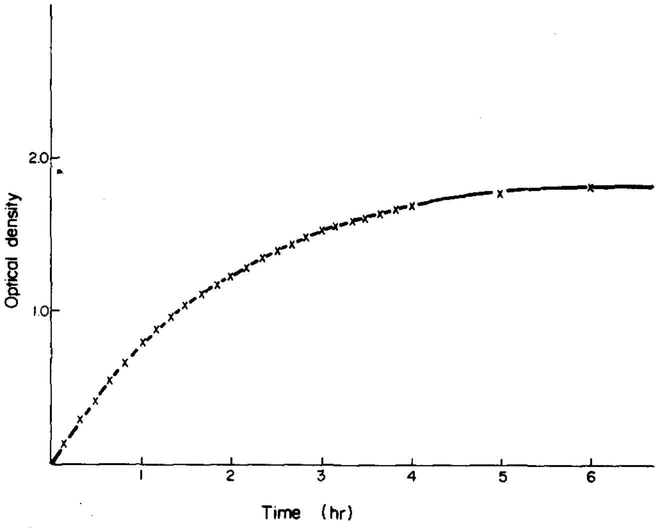

Fig. 4. Kinetics of addition of a 10 excess of butyllithium to *p*-diisopropenylbenzene: plot of OD vs time (solvent: cyclohexane, $T = 25°$).

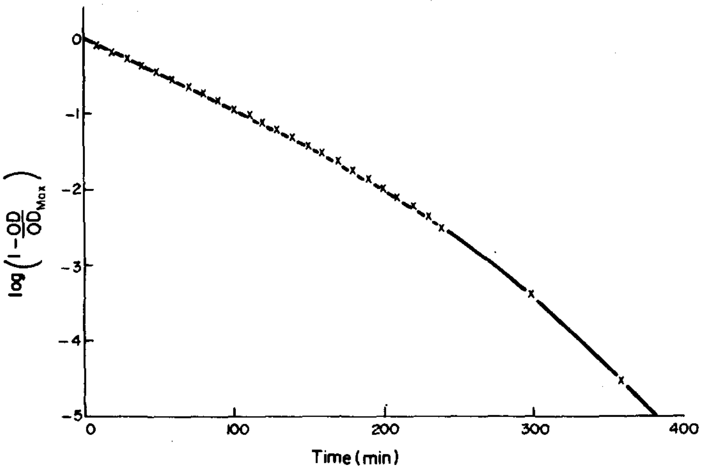

Fig. 5. Kinetics of addition of butyllithium to *p*-diisopropenylbenzene: plot of log ($1\text{-}OD/OD_{max}$) vs time (solvent: cyclohexane, $T = 25°$).

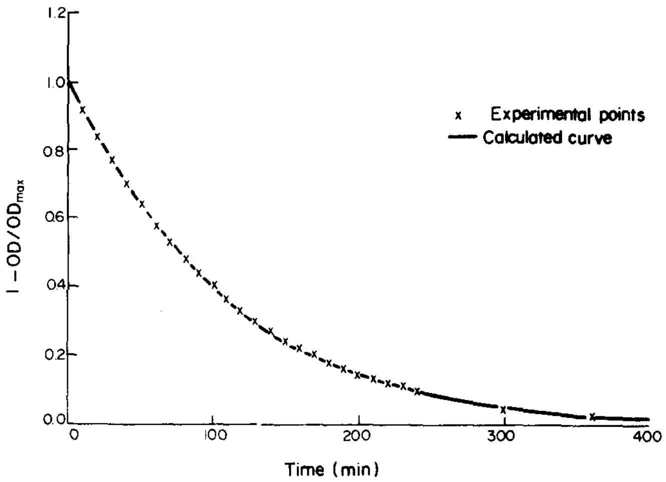

Fig. 6. Comparison between experimental points and curve calculated using the values of the kinetic constant according to Eqn (1), $k_1 = 2.2 \cdot 10^{-2}$, $k_2 = 1.7 \cdot 10^{-2}\,\mathrm{l \cdot mol^{-1} sec^{-1}}$.

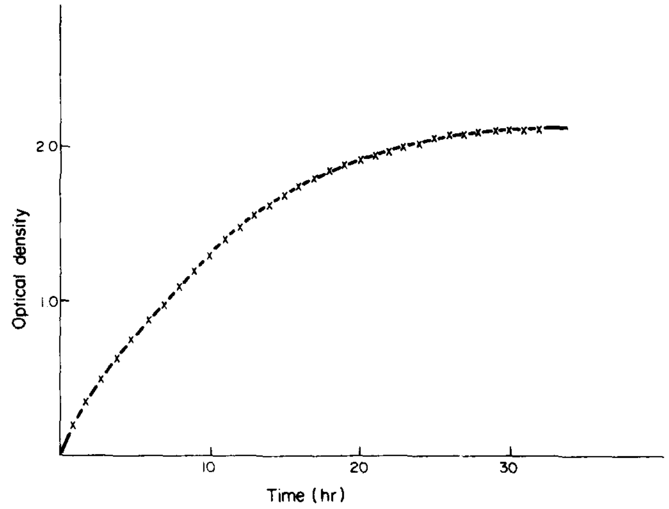

Fig. 7. Kinetics of addition of a 10 excess of butyllithium to *m*-diisopropenylbenzene: plot of OD vs time (solvent: cyclohexane, $T = 20°$).

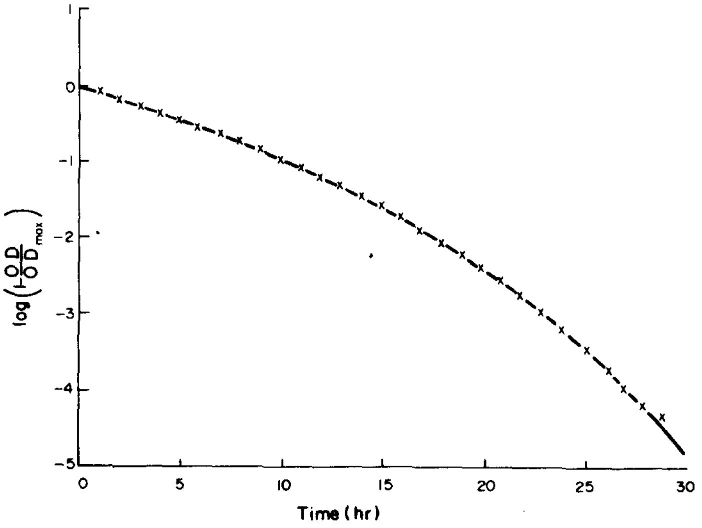

Fig. 8. Kinetics of addition of butyllithium to *m*-diisopropenylbenzene: plot of log (1-OD/OD$_{max}$) vs time (solvent: cyclohexane, $T = 20°$).

is of interest that the reaction is much faster than with α-methylstyrene.

4. *Kinetics of addition of sec·BuLi onto* meta-*diisopropenylbenzene*

In this case no conjugation exists between the two double bonds of the *m*-DIB molecule. One can therefore expect the two double bonds to react independently, and the rate constants to be similar to that characterizing the reaction of α-methylstyrene with BuLi under the same conditions.

The experimental results are displayed in Figs 7 and 8. The plot of log $(1 - OD/OD_{max})$ vs time shows curvature, as in the case of the *para*-isomer. However no curve fit could be achieved by either manual or computer treatment of the data, assuming two different rate constants for the two steps of the reaction.

It was then supposed that the same rate constant governs the two steps and Eqn (1) was used to interpret the experimental data. The best fit was obtained using a rate constant $k = 3.2 \cdot 10^{-3}\,\mathrm{l\,mol^{-1} \cdot sec^{-1}}$, when the value of r is set equal to 0.8. This fit is shown in Fig. 9.

There are a few comments to be made about these results:

1. The reactivity of *m*-DIB with respect to BuLi is about twice that of α-methylstyrene; the reactivity of *p*.-DIB is much higher than that of the *meta*-isomer. This latter enhancement may be due to the effect of conjugation, which is also responsible for the difference of reactivity between the two double bonds of the *para*-isomer.

2. The rate constants obtained from the mathematical treatment of experimental data are not absolute values; they are however comparable. To explain that, consider the case of α-methylstyrene. Here the slope of the straight line characterizes the product: (rate constant) × (concentration of active sites). The latter concentration is assumed to be the amount of BuLi present, which is in fact erroneous. It is well known that BuLi molecules associate in non-polar solvents and that only the "fraction" of "free" BuLi is active. Thus the first differential equation should be written as:

$$-\frac{dA}{dt} = k\,K^{1/n}[L]^{1/n}[A]$$

K being the equilibrium constant for the association of BuLi and n the degree of association. Several authors [5–7] have studied this equilibrium and have established that such reactions are effectively of fractional order with respect to the butyllithium concentration. In the present case, once the adducts are formed they can in turn undergo cross associations with butyllithium. This is probably why no precipitation occurs when excess butyllithium is present. However neither the association constant K nor the degree of association n is accessible for these cross associations, and no account can be taken of this phenomenon.

However, all kinetic experiments were carried out at the same low concentration, and with a 10-fold excess of butyllithium with respect to the antagonist functions. Thus comparisons between the measured rate constants are valid, even though they have no absolute meaning.

3. It is of interest to note that the proportions of species A, B and C are not bernouillian (i.e. proportional to the well known factors $(1-p)^2$; $2p(1-p)$; p^2, respectively, p being the degree of conversion). To obey bernouillian statistics, the ratio of the rate constants k_1 and k_2 should be equal to 2. This is illustrated by Fig. 10, in which the amounts of A, B and C are plotted vs "reduced" time $T = k_1[L]t$ for $k_1 = k_2$, also for $k_1 = 2k_2$ and also for $k_1 = 5k_2$. To account for this result is easy: it just means that, in order to obey bernouillian statistics, the probability of reaction for both types of double bonds should be the same: thus the probability for A to react with BuLi should be twice that of B to react, because A bears two double bonds and B one only.

CONCLUSION

The diisopropenylbenzenes react with 2 BuLi molecules to yield diadducts, which can be used as effi-

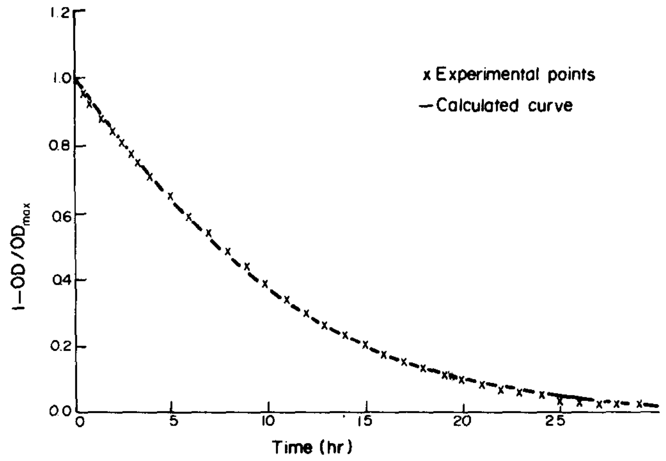

Fig. 9. Comparison between experimental points and curve calculated according to Eqn (1) with $k = 3.2 \cdot 10^{-3}\,\mathrm{l \cdot mol^{-1} \cdot sec^{-1}}$ and $r = 0.8$.

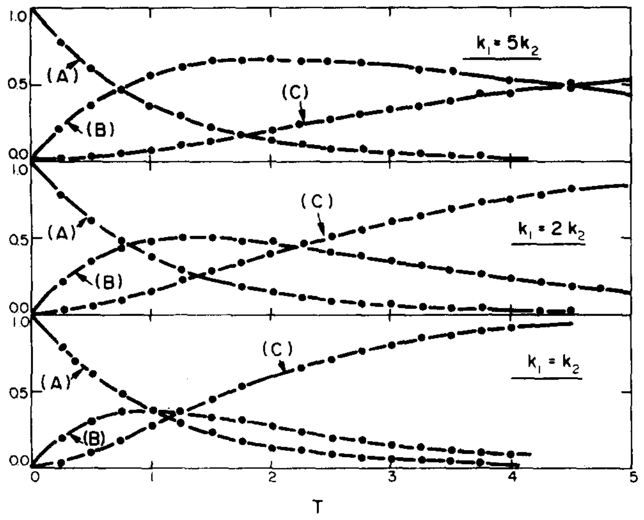

Fig. 10. Relative amounts of A, B and C vs "reduced" time ($T = k_1[L]t$ for a k_1/k_2 ratio of 2, also for a k_1/k_2 ratio of 5 and also for a single rate constant $k = k_1 = k_2$. Only in the former case do bernouillian statistics apply.

cient bifunctional anionic initiators. On the other hand, when polymerized anionically, the two double bonds exhibit quite different reactivites [8, 9]. It was therefore of interest to carry out a detailed kinetic investigation of the adduct formation with butyllithium. It is now established that one single kinetic constant accounts for the two steps of the reaction in the case of *meta*-DIB, and that the constant is close to that observed for α-methylstyrene. The *para*-isomer is far more reactive, and two kinetic constants are necessary to account for the experimental results, because of conjugation effects in that monomer.

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