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Zero-Order Conversion Kinetics of Dilithium Adduct of Diphenyl Acetylene: Enhanced Stationary State Approximation

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Experiments by Maerker et al.[1] in 1998 showed that the conversion of the dilithium adduct of diphenyl acetylene, (*Z*)-2, to its trans derivative (*E*)-5 occurred at a rate that was independent of time, leading them to propose a model for this reaction. We present a detailed numerical example to illustrate that this model predicts a reaction that proceeds nearly linearly with time almost from the start to the end of the conversion. We then introduce an enhanced stationary state approximation (ESSA), with a network representation, to get accurate analytical solutions for the time-dependent reagent concentrations predicted by this model, along with estimates of the accuracy of the solutions. Unlike the usual stationary state approximation (SSA), this ESSA allows for analytical solution during the initial transient induction period as well as the main phase of the reaction. Examinations of the network and of the analytical solutions provide an explanation for the mechanism by which this model maintains nearly zero-order kinetics throughout the reaction. This mechanism is more general than the particular reagents described here; it requires only the reaction scheme which satisfies certain inequalities. The analytical solutions show also that the conversion rate is determined mainly by the total concentration of monolithiated compounds present (a total which remains constant throughout the reactions), and the rate constant for cis-to-trans conversion of these monolithiated compounds.

1. Introduction

Note: General conventions, specific notation, and abbreviations used in this paper are listed in Appendix A. Conversion of the cis dilithium adduct of diphenyl acetylene (*Z*)-2 into its trans derivative (*E*)-2 (also referred to as the 253−278 conversion) was studied experimentally by Maerker et al.[1] They found that the conversion proceeded linearly with time, indicating a somewhat surprising zero-order chemical kinetics. They suggested a reaction model, and used a stationary state approximation (SSA) to estimate the reaction rate in terms of the parameters of the model. However, their approximations were somewhat oversimplified, leading to some inconsistent and incomplete results. The aims of the present study were to better explain the mechanism by which the model reaction maintains zero-order kinetics throughout the conversion and to find accurate analytical solutions to the model.

We used the Maerker[1]−Kemmer[2] reaction model, but used a new *enhanced* version (enhanced stationary state approximation, ESSA) of the usual SSA to eliminate inconsistencies of the SSA and to obtain accurate analytical results for the time dependence of all reagent concentrations throughout the full conversion. The ESSA also provides self-estimates of its own accuracy. As a further check, we did numerical integrations of the differential equations for representative values of the model parameters. One such integration is provided as a detailed example to illustrate the remarkable accuracy of the analytical approximation. Although the numerical solutions are more accurate, the analytical solutions have very important advantages: they show directly the effects of varying parameters without requiring repeated numerical integrations, and they show which results are applicable more generally, even when parameters are changed. A network representation and the analytical results provide insight into the mechanism by which this model succeeds so well to maintain nearly zero-order kinetics throughout the reaction. We show that the rate of (*Z*)-2 to (*E*)-5 conversion is determined essentially by the total initial concentration of both stilbenes [cis stilbene, (*Z*)-3, plus trans stilbene, (*E*)-3] multiplied by the rate constant for the cis-to-trans conversion of stilbene. We show also that the zero-order nature of the reaction (called reaction scheme I) is not limited to a particular choice of reagents but depends only on certain inequalities being satisfied.

2. Reactions

Conversion of the cis dilithium adduct of diphenyl acetylene [tolane, (*Z*)-2], (herein denoted z_1 for simplicity) into its trans derivative (*E*)-5 (herein denoted z_4) was reported in a recent note by Maerker et al.[1] The reaction was performed in diethyl ether solution at ambient temperature. Experimentally, the reaction kinetics was found to be zero-order in the concentration

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of z_1. The formation rate of z_4 appeared to be constant, despite the decreasing concentration of z_1 (see Figure 2 of Maerker).[1]

The isosbestic points in the optical absorption spectra (see Figure 1 of Maerker)[1] showed that there were only the two major species present. However, it was further deduced that two intermediates both present in minute concentration (trans stilbene (*E*)-3 and cis stilbene (*Z*)-3, the monolithium adducts of tolane, herein denoted z_2 and z_3 respectively), did participate in the reaction; their concentrations being sufficiently small to not affect the optical absorption spectra. Detailed study of the reaction led them[1,2] to the following mechanism for the overall process (shown below with our new notation as reaction scheme I). They assumed a simple bimolecular reaction for Ia and monomolecular kinetics for Ib.

$$z_1 + z_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} z_3 + z_4 \quad (k_1 >>> k_{-1}) \tag{Ia}$$

followed by the rapid conversion of z3 back to z2

$$z_3 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} z_2 \quad (k_2 \gg k_{-2}) \tag{Ib}$$

The rapidity of the conversion of z_3 back to z_2 suggested that $k_2 \gg k_{-2}$. (Note: by "rapid conversion" in this scheme, we mean that the monomolecular reaction $z_3 \rightarrow z_2$ is a rapid one. The actual concentration of z_3 remains nearly constant because of an equally rapid generation of z_3 from z_1 and z_2 in Ia)

The overall reaction is determined by the following four differential equations.

$$\mathrm{d}z_1/\mathrm{d}t = -(k_1 z_1 z_2 - k_{-1} z_3 z_4) = -j_{14} \tag{1}$$

$$\mathrm{d}z_2/\mathrm{d}t = -(k_1 z_1 z_2 - k_{-1} z_3 z_4) - (k_{-2} z_2 - k_2 z_3) = -j_{14} - j_{23} \tag{2}$$

$$\mathrm{d}z_3/\mathrm{d}t = (k_1 z_1 z_2 - k_{-1} z_3 z_4) + (k_{-2} z_2 - k_2 z_3) = j_{14} + j_{23} \tag{3}$$

$$\mathrm{d}z_4/\mathrm{d}t = (k_1 z_1 z_2 - k_{-1} z_3 z_4) = j_{14} \tag{4}$$

In these equations, j_{23} and j_{14}, which appear as important elements in our network representation of section 5, are also introduced here to simplify notation in the differential equations.

The reverse reactions, governed by the small rate constants $k_{-1} \ll k_1$ and $k_{-2} \ll k_2$, were thought to be negligible during the main phase of the process (they were not included in Maerker's reaction scheme shown on p 2138 of ref 1), making the reaction nearly irreversible, so

$$k_{-1} z_3 z_4 \ll k_1 z_1 z_2 \tag{5a}$$

$$k_{-2} z_2 \ll k_2 z_3 \tag{5b}$$

3. Traditional Stationary State Approximation

Many textbooks[4] discussing chemical kinetics teach that a functional expression helpful in deriving rate laws of some complex reactions can be obtained from the so-called stationary state approximation or steady state approximation (SSA). SSA is usually used when the concentration of some intermediate species x is always small, so that its time derivative can be neglected relative to the time derivatives of concentration of the main species y. In other words, if $[x] \ll [y]$, it often turns out that also $|\mathrm{d}[x]/\mathrm{d}t| \ll |\mathrm{d}[y]/\mathrm{d}t|$, at least for some large fraction of the reaction time.

For example, consider the initiation of radical polymerizations involving an initiator (In), a monomer (M), a small concentration of radical (R), and a polymer (P). The process can be described by reaction scheme II.

$$\mathrm{In} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\mathrm{R} \qquad \mathrm{R} + \mathrm{M} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{P} \tag{II}$$

It follows that $\mathrm{dR}/\mathrm{d}t = 2k_1\ \mathrm{In} - k_{-1}\ \mathrm{R}^2 - k_2\ \mathrm{R\ M} + k_{-2}\ \mathrm{P}$.

In the SSA, after some initial induction period, $\mathrm{dR}/\mathrm{d}t \approx 0$. If, in addition, $k_{-2}\ \mathrm{P} \ll k_2\ \mathrm{RM}$, then

$$0 \approx k_{-1}\mathrm{R}^2 + k_2\mathrm{RM} - 2k_1\mathrm{In} \tag{6}$$

This is a quadratic equation that determines R from In, M, and the rate constants k_1, k_{-1}, k_2.

4. Problems of the SSA Applied to Reaction Scheme I

The SSA does not apply so obviously for more complicated cases, such as reaction scheme I. Maerker[1] neglected the small reverse reactions $k_{-1}z_3z_4$ and $k_{-2}z_2$, and made the plausible assumption that the concentration of z_2 is stationary, leading them to the relations

$$0 = \mathrm{d}z_2/\mathrm{d}t = k_2 z_3 - k_1 z_1 z_2 \tag{7}$$

$$z_2 = k_2 z_3 / k_1 z_1 \tag{8}$$

so that the conversion rate

$$\mathrm{d}z_4/\mathrm{d}t = k_1 z_1 z_2 \tag{9}$$

was claimed to be, from eq 8,

$$\mathrm{d}z_4/\mathrm{d}t = k_2 z_3 \tag{10}$$

formally independent of z_1.

Reviewing the situation shows that this formal independence was not sufficient to prove real independence, since the dependence of z_3 on z_1 was not known. In order for the reaction kinetics to be zero order, eq 9 required the dominant term $k_1z_1z_2$ to be nearly constant, implying that the concentration z_2 increases in inverse proportion to z_1, as z_1 is depleted. This requirement seems to conflict with the SSA assumption of eq 7, that $\mathrm{d}z_2/\mathrm{d}t = 0$. Furthermore, the SSA does not treat the initial transient induction period.

In section 7, we develop an extended SSA (ESSA) to remove these problems. We will find that neither eq 5a nor eq 8 nor eq 9 is accurate. However, the errors fortuitously seem to cancel out so that eq 10 is actually quite accurate during most of the conversion, even though 5a, 8, and 9 are inaccurate.

5. Network Representation

More insight into the general problem can be obtained by representing the system of equations as a network. Figure 1 shows an electrical network representation.

Fixed capacitors labeled C_i, $i = 1, 2, 3, 4$, represent the chemicals. All capacitors have the same value. Without loss of generality, for the sake of convenience of the discussion, we choose all C_i to be one Farad. Then, because $Q = CV$, their charges Q_i (in Coulombs) are equal numerically to their voltages V_i (in volts). Charges Q_i (or V_i) and currents I_i represent the concentrations and their time derivatives, respectively. Voltage controlled current sources (VCCS), labeled j_{14} and j_{23}, represent the driving terms in the differential equations. The network gives an easy visual realization of the relations among the currents, and the fact that there are only two independent current sources.

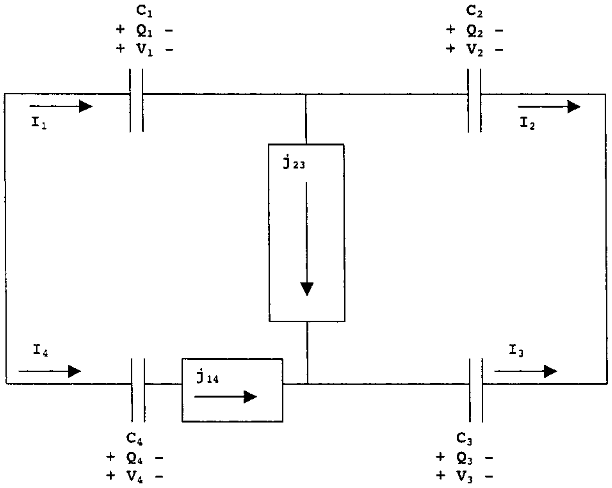

Figure 1. Electrical network analogue of reaction scheme I. For $i = 1, 2, 3, 4$, capacitors $C_i = 1$ Farad, charges Q_i represent the concentrations z_i, voltages $V_i = Q_i/C_i$ also represent z_i, currents $I_i = dQ_i/dt$ represent dz_i/dt, voltage controlled current sources (VCCS): $j_{14} = k_1Q_1Q_2 - k_{-1}Q_3Q_4$ represents $j_{14} = k_1z_1z_2 - k_{-1}z_3z_4$; $j_{23} = k_{-2}Q_2 - k_2Q_3$ represents $j_{23} = k_{-2}z_2 - k_2z_3$.

One sees also quite easily the effects of the ESSA; it allows us to temporarily disconnect some branches, which have nearly zero current. In section 7, it will be seen that the middle branch (with VCCS j_{23}) can be removed for the initial transient phase of the reaction ($t < t_1$ in section 7), whereas the right-hand branch (with C_2 and C_3) can be removed during the main phase of the reaction ($t_1 < t < t_2$ in section 7). It also makes clear that combinations j_{23} and j_{14} of time derivatives in the kinetic equations (currents in the network) are important variables, leading us to the insight for the approximations needed to develop the solutions.

6. Numerical Computer Solutions

Methods. It is helpful to study results of a numerical integration of the differential equations for a particular example. This was done using a Turbo-Pascal program based on Bulirsch[5] and repeated using PSpice and the network of Figure 1 to confirm the results.

Example. The model parameters and computed results for a typical numerical example are presented in Table 1, and shown graphically in Figure 2.

The initial concentrations of z_2 ($Z_{20} = 2$) and of z_3 ($Z_{30} = 0.2$) are chosen in the ratio $Z_{20}/Z_{30} = k_2/k_{-2} = 10$, which represents an experimental situation for which z_2 and z_3 are in equilibrium with each other before being added to z_1. The final concentration is thus in the same ratio, making z_2 and z_3 act essentially as catalysts, in the sense that neither one is permanently used up in the reaction.

The initial concentration z_1 is $Z_{10} = 100$ (for approximately 100% of this major ingredient), and z_4 is $Z_{40} = 0.001$ representing a trace amount that might be present in real experiments.

A striking and significant result is the dramatic decrease of z_2 in the initial stage of the process. In the time needed to convert about 2% of z_1 to z_4, the concentration z_2 is reduced more than 100-fold from 2.0 to 0.012, while z_3 increases accordingly more than 10-fold from 0.2 to 2.188. The greatly enhanced concentration z_3, formed during the initial transient, is now a source for continuous production of extra z_2 needed to maintain the production of z_4 during the main reaction phase.

TABLE 1: Concentrations of All Reagents vs Time for a Numerical Example of Reaction Scheme I[a]

k_1	k_{-1}	k_2	k_{-2}
20.000	0.200	10.000	1.000

Z_{10}	Z_{20}	Z_{30}	Z_{40}
100.000	2.000	0.200	0.001

t	z_1	z_2	z_3	z_4	dz_4/dt	$k_1z_1z_2$
0.0000	100.000	2.000	0.200	0.001	4000.00	4000.00
0.0001	99.638	1.638	0.562	0.363	3264.10	3264.14
0.0002	99.342	1.343	0.857	0.659	2668.21	2668.33
0.0005	98.740	0.744	1.456	1.261	1468.88	1469.25
0.0010	98.271	0.284	1.916	1.730	557.52	558.18
0.0020	98.016	0.049	2.151	1.985	95.20	96.06
0.0025	97.982	0.026	2.174	2.019	50.07	50.95
0.0026	97.977	0.023	2.177	2.024	44.19	45.07
0.0027	97.973	0.021	2.179	2.028	40.26	41.15
0.0030	97.962	0.017	2.183	2.039	32.42	33.31
0.0035	97.948	0.014	2.186	2.053	26.53	27.43
0.0040	97.936	0.012	2.188	2.065	22.60	23.50
0.0050	97.913	0.012	2.188	2.088	22.59	23.50
0.0100	97.804	0.012	2.188	2.197	22.51	23.47
0.0200	97.585	0.012	2.188	2.416	22.36	23.42
0.0500	96.929	0.012	2.188	3.072	21.92	23.26
0.1000	95.837	0.012	2.188	4.164	21.18	23.00
0.2000	93.651	0.013	2.187	6.350	21.57	24.35
0.5000	87.102	0.016	2.184	12.899	22.24	27.87
1.0000	76.208	0.021	2.179	23.793	21.64	32.01
2.0000	54.538	0.038	2.162	45.463	21.79	41.45
3.0000	33.162	0.075	2.125	66.839	21.34	49.74
3.5000	22.716	0.116	2.084	77.285	20.49	52.70
3.9000	14.628	0.185	2.015	85.373	19.72	54.12
4.0000	12.675	0.213	1.987	87.326	19.29	54.00
4.2000	8.911	0.297	1.903	91.090	18.26	52.93
4.4800	4.261	0.552	1.648	95.740	15.49	47.04
4.6000	2.651	0.752	1.448	97.350	11.68	39.87
4.8000	0.949	1.262	0.938	99.052	5.37	23.95
5.0000	0.325	1.717	0.483	99.676	1.53	11.16

[a] Results were found by computer numerical integration and shown here and also graphically in Figure 3. The corresponding conversion rate dz_4/dt is compared with the reaction rate $k_1z_1z_2$. Also shown are the parameters of this numerical example.

Note that the reaction is remarkably very close to zero-order; the reaction rate remains 21 ± 10% as the conversion of z_1 to z_4 proceeds from 2% to 90%. This is despite the fact that the product z_1z_2 actually increases more than 2-fold from a minimum of 1.1 to a maximum of 2.7 during this same time interval, further contradicting the SSA result of eq 9. Beyond 90% conversion, the reaction slows down markedly as all of the reagents approach their equilibrium concentrations.

We notice also that contrary to eq 5a, $(k_{-1}z_3z_4)/(k_1z_1z_2)$ is not negligible, being more than 50% for the second half of the conversion. Thus, neither SSA eq 5a nor eq 8 nor eq 9 is accurate. However, these errors (somewhat fortuitously) seem to cancel, so that the final SSA result of eq 10 is quite accurate, even though eqs 5a, 8, and 9, on which it was based, are not.

The Need for Analytical Solution. The numerical results apply only to the particular numerical example. However, variation of the parameters indicated that many features of the results are rather general.

Analytic solutions are needed to provide additional understanding, and allow easier generalization and/or optimization than does a numerical solution that has to be recomputed for each new set of rate constants and initial conditions.

7. Analytical Extended Stationary State Approximation (ESSA)

In Appendix B, we present detailed analytical solutions and justification for the approximations used. In this section we briefly summarize our methods and results from Appendix B.

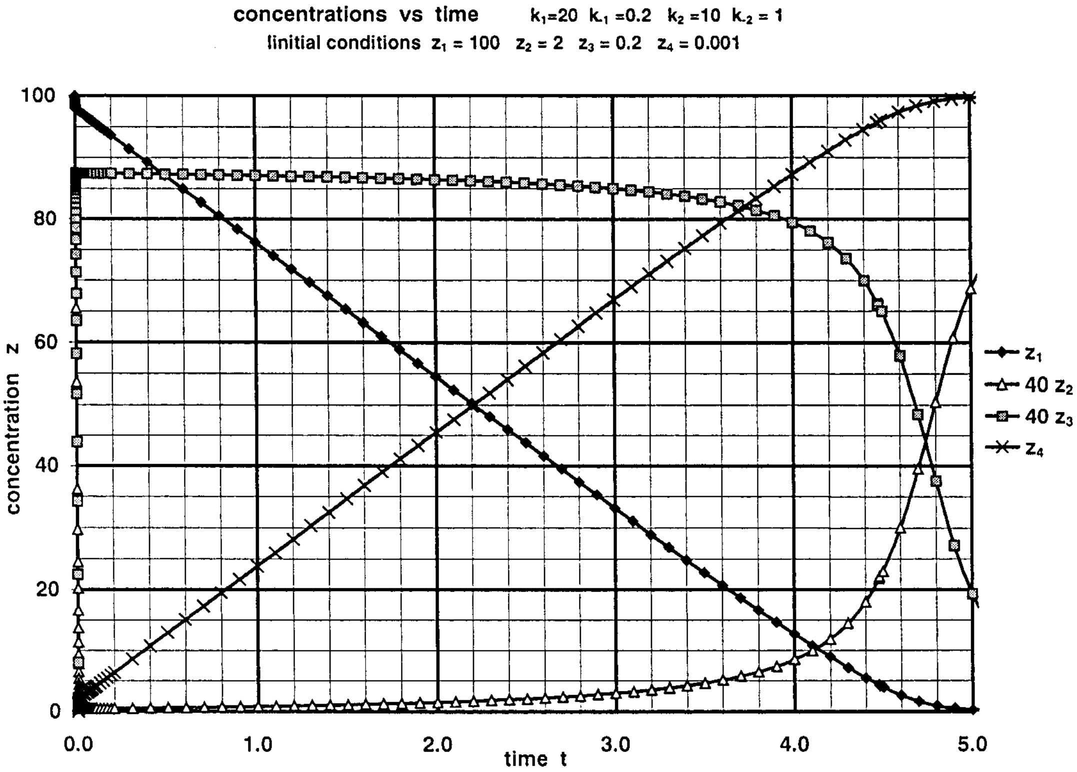

Figure 2. Concentrations of all reagents vs time for reaction scheme I and parameters of the numerical example. Results were found by computer numerical integration and listed in Table 1.

Equations 11−14 in this section correspond to equations B4.1, B4.2, B5.3, and B13.2, respectively, in Appendix B.

To understand the situation better, we analyze the problem analytically, albeit approximately, using an extension of the SSA that is more elaborate than the simple application of the SSA used by Maerker.[1] We find that extensions of the usual SSA can be used to solve the differential equations analytically, with remarkably high accuracy and very little effort. The analytical solutions can also explain the reasons that eqs 5a, 8, and 9 are not accurate, but still eq 10 is very accurate.

We use reaction scheme I, with differential eqs 1−4. We also use rate constants and initial conditions that satisfy the following general inequalities:

$$k_1 \gg k_{-1} \qquad (11) = (\text{B4.1})$$

$$k_2 \gg k_{-2} \qquad (12) = (\text{B4.2})$$

$$Z_{10} \gg Z_{20} \gg Z_{30} \gg Z_{40}; \quad C_{14} \gg C_{23} \qquad (13) = (\text{B5.3})$$

Other than the requirement of having to satisfy these inequalities, the rate constants and initial conditions may be chosen freely. Thus, the results of using the ESSA will apply more generally than for just these particular reagents or for the numerical example chosen.

The reaction time is divided into three intervals, with a different analysis for each. Detailed analytical ESSA solutions for all concentrations are in Table 2 (part A), with numerical example results in Table 2 (part B). Figure 3 shows a graphic representation of z_4 to compare with numerical computer integrations. Note that changes in the conditions above might require that changes in the details of some approximations be made in the ESSA.

ESSA Compared With the Usual SSA. The usual SSA focuses on the smallest reagent concentrations and assumes that because they remain small, their time derivatives can be approximated as zero. The extended ESSA focuses on larger concentrations that happen to have sufficiently small time derivatives to be considered “stationary”. These larger nearly stationary concentrations are treated as constants when computing the other concentrations. The predicted values of those other concentrations are then used to recompute the changes in the nearly stationary concentration and thus to find the time at which this stage of approximation fails to be self-consistent, and at which a new approximation is needed. Thus, as in our example, the ESSA can deal with the initial induction period during which the large concentration of the source reagent is nearly stationary, as well as the main phase of the reaction during which only the larger concentration intermediate (z_3) of the two intermediates (z_2, z_3) is stationary.

ESSA Interval 1 ($0 \leq t \leq t_1$). This interval is characterized by a nearly stationary z_1.

For t near zero, $|dz_2/dt| = |dz_3/dt| \approx |dz_4/dt| = |dz_1/dt| = j_{14} \approx k_1 z_1 z_2$. This condition differs from the usual SSA condition, because here the rate of change of the small quantities is approximately equal to the rate of change of the large quantities. We note, however, that because z_1 is the largest concentration, the percentage changes in z_1 are smallest. Thus, the largest concentration, z_1, may be considered to be nearly constant ($z_1 \approx Z_{10}$) on the right-hand side of eqs 1−4 when computing the time derivatives.

In the network of Figure 1, we can neglect j_{23}, and thus can disconnect the central branch, leaving a much simpler network to be analyzed.

Initially, the large concentration of the starting source material z_1 is far from equilibrium with the final product z_4. The major term in the rate equations is $k_1 z_1 z_2$. It causes major (percentage) changes in the small concentrations of the intermediates z_2 and z_3, driving them far from equilibrium, with only minor (percentage) changes in the large concentration z_1. Thus, during this

TABLE 2: Analytical Results from the Extended Stationary State Approximation (ESSA)[a]

(A) General Case

time (t or $T = t - t_1$)	z_1	z_2	z_3	z_4	eq #
0	Z_{10}	Z_{20}	Z_{30}	Z_{40}	
$0 < t < t_1$	$Z_{10} + z_2 - Z_{20}$	$Z_{20}\exp(-R_{10}t)$	$Z_{30} - z_2 + Z_{20}$	$Z_{40} - z_2 + Z_{20}$	B11.1a−11.4a
$t_1 = (1/R_{10})\mathrm{Ln}(R_{10}/k_2)$	$Z_{11} = Z_{10} + Z_{21} - Z_{20}$	$Z_{21} = k_2C_{23}/R_{10}$	$Z_{31} = C_{23} - Z_{21}$ $\approx C_{23}$	$Z_{41} = Z_{40} + Z_{20} - Z_{21}$	B10.3; B11.1b−11.4b
$T = t - t_1 > 0$	$C_{14} - z_4$	$[C_{23}k_2(1 + k_{-1}Z_{31}T)]/$ $k_1(Z_{11} - k_2Z_{31}T)$	$C_{23} - z_2$	$Z_{41} + k_2Z_{31}T$ $\approx Z_{41} + k_2C_{23}T$	B14.1−14.4
$T_{2\_inf} \approx C_{14}/(k_2C_{23})$					B15.2
$T_{3\_p} \approx 1 + (k_{-1}C_{14}/k_2)/nk_1C_{23}$					B15.3
$T_{2\_p} = T_{2\_inf} - T_{3\_p}$		$Z_{21} + nZ_{31}$	$Z_{31}(1 - n)$		
equilibrium	$(k_{-1}k_{-2}C_{14})/k_1k_2 + k_{-1}k_{-2}$ $\approx (k_{-1}k_{-2}C_{14})/k_1k_2$	$k_2C_{23}/k_2 + k_{-2}$	$k_{-2}C_{23}/k_2 + k_{-2}$	$k_1k_2C_{14}/k_1k_2 + k_{-1}k_{-2}$ $\approx C_{14}$	B17.1−17.4

(B) Numerical Example

k_1	k_{-1}	k_2	k_{-2}
20.000	0.200	10.000	1.000

time (t or $T = t - t_1$)	z_1	z_2	z_3	z_4	eq #
0	100.000	2.000	0.200	0.001	
$0 < t < t_1$	$98.0 + 2\exp(-2000t)$	$2\exp(-2000t)$	$0.20 - 2\exp(-2000t)$	$2.001 - 2\exp(-2000t)$	B11.1a−11.4a
$t_1 \approx 0.00260$	98.011	0.011	2.189	1.990	B10.3; B11.1b −11.4b
$T = t - t_1 > 0$	$98.011 - 21.89T$	$0.011\{1 + 0.421T\}/$ $1 - 0.2233T$	$C_{23} - z_2$	$1.990 + 21.89T$	B14.1−14.4
$T_{2\_inf} \approx 4.55$					B15.2
$T_{3\_p} \approx 0.0682/n$					B15.3
$T_{2\_p} = 4.55 - 0.0682/n$		0.230	1.970		
equilibrium	$= 0.0999011$ ≈ 0.1	2.00	0.20	99.9010989 ≈ 99.9	B17.1−17.4

[a] $T_{2\_p} = T_{2\_inf} - T_{3\_p}$; $C_{14} = Z_{10} + Z_{40}$; $C_{23} = Z_{20} + Z_{30}$; $R_{10} = k_1 Z_{10}$; p = % error; $n = p/100$.

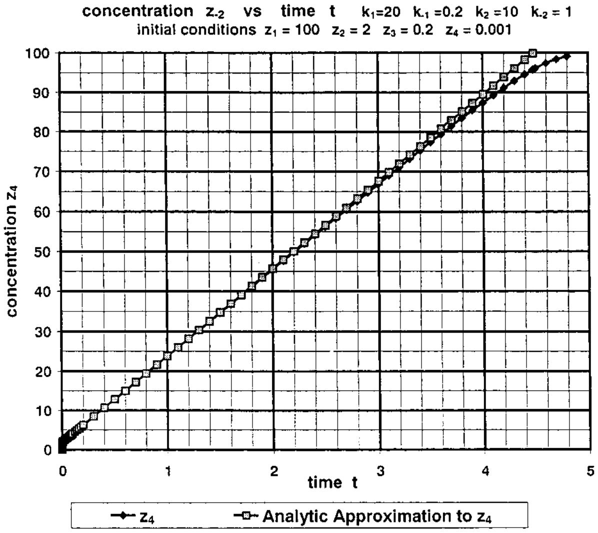

Figure 3. Concentration of final product z_4 vs time t for reaction scheme I and parameters of numerical example. Lower curve is computer numerical integration. Upper curve is analytical approximation using ESSA.

phase, we make use of the fact that the large concentration z_1 is nearly stationary and that $z_4/z_1 \ll 1$.

In Appendix B, we obtain quite accurate results for this rapid initial transient, as summarized in Table 2. This interval ends when $dz_3/dt = -dz_2/dt$ decreases to zero, at a time we call t_1. At that time, z_3 and z_2 are then (momentarily) exactly stationary. We estimate, quite accurately, the concentrations Z_{21} and Z_{31} (the values of z_2 and z_3 at time $t = t_1$) and use those to determine Z_{11} and Z_{41} (the values of z_1 and z_4 at time t_1). Even more important, we determine the production rate (dz_4/dt) at t_1 when we have an exact stationary state.

With somewhat less accuracy, we determine the value of the time t_1. The ESSA found $t_1 \approx 0.0026$, whereas the computer integrations found $t_1 \approx 0.0067$. Although this is a very large % error, the actual time difference 0.0041 is extremely small compared with the overall time span of the reaction ($t \approx 5$). Because this does not affect any of the other estimates, we did not find it necessary to improve the approximation to find t_1 more accurately analytically in the ESSA.

ESSA Interval 2 ($t_1 < t < t_{2\_p}$). This interval is characterized by nearly stationary $z_3 = Z_{31} \approx C_{23}$ and $|dz_2/dt| = |dz_3/dt| \ll |dz_4/dt| = |dz_1/dt|$, so $j_{23} \approx -j_{14}$. Thus, we can effectively remove the right-hand branch in the network of Figure 1, again leading to a much simpler network to be analyzed.

The changes in z_2 and z_3 are slow. However, z_2 starts out very small at t_1, so the percentage changes in z_2 are fairly large. On the other hand, z_3 starts out much larger at t_1, so the percentage changes in z_3 are indeed small. Thus, it is z_3, not z_2, that is nearly stationary in this time interval.

After t_1, the concentration ratio $z_2/z_3 \ll 1$ is very far from its equilibrium value $z_2/z_3 \gg 1$, and in effect drives the reaction rate as z_2/z_3 tries to return to equilibrium. The term $k_1z_1z_2$ is no longer the only important term in the rate equations. Instead of concentrating on $z_2' = z_3' = 0$ as in the usual SSA, we concentrate on the fact that $j_{14} \approx -j_{23} \approx k_2Z_{31} \approx k_2C_{23}$, a constant. Thus, from the analysis shown in Appendix B, we find

$$z_4' = dz_4/dt \approx k_2Z_{31} \approx k_2C_{23} \qquad (14) = (B13.2)$$

so z_4 increases linearly with time. However, as time progresses, z_3 decreases slowly from Z_{31}. We define t_{2-p} as the time at which z_3 has changed by p% from Z_{31} . From then on, eq 14 is no longer accurate to p%. In our numerical example, for $p = 10$% this is $t_{2\_10} \approx 3.9$, for which the ESSA predicts 87% of z_1 has been converted to z_4 (Table 1 shows 85%).

Although the production rate z'_4 decreases significantly from then on, the integrated effect on z_4 is much smaller, so that in our example, analytical eq B14.1 predicts $z_4 \approx 100$% at $t = 4.8$, whereas the more accurate numerical integration (Table 1) finds $z_4 \approx 96$% at that time; an error of only 4%. Comparison of the analytical ESSA and the computer solutions for z_4 is shown graphically in Figure 3; the fit is remarkably good. Detailed results for all concentrations are shown in Table 2.

ESSA Interval 3 ($t > t_2$). In this interval, all reagents approach equilibrium. There are no very simple approximations based on one stationary reagent or one dominant process. The approach to equilibrium is more difficult to compute accurately analytically. However, the final equilibrium solutions are found easily and are shown in Table 2.

We found above that deviations of eq B14.1 from the numerical integrations are sufficiently small to be within the accuracy of the experiments,[1] and thus are not worth much effort to find more accurate analytical solutions. Thus, we extend the use of eqs B14 into this time interval but cut off at $z_i = Z_{i(\mathrm{equil})}$.

8. Comparison of Theory with Experiment

We have not specified the scales (units) used for the time t or rate constants k. In principle, these could be determined by fitting to experiments.

The report of Maerker et al.[1] of their experiment explicitly shows a linear conversion rate graphically (their Figure 1) for only 250 min, while reporting in the text that the "conversion is completed within 24 hours". The growth of z_4 in our model remains approximately linear ($z_4 \approx Z_{41} + k_2C_{23}T \approx 1.990 + 21.89T$) until $T \approx t \approx 4$. This would mean that our time $t = 4$ corresponds to the experimental 24 h, indicating that our unit of time would be about 6 h.

On the other hand, Maerker et al.[1] did not report any actual concentrations, thus we cannot determine scales for our concentrations and rate constants.

As suggested by an anonymous reviewer, "Experiments with added known concentrations of these monolithium compounds should be very interesting". They could be used to check the theoretical prediction that the conversion rate is proportional to the total concentration of these two (cis + trans) monolithium compounds, and almost independent of their initial relative concentrations. Maerker et al.[1] did one such experiment which showed that a large initial concentration of (E)-3, i.e., $Z_{20} = \approx 0.83\ Z_{10}$, increased the reaction rate. There were, however, insufficient data for a quantitative comparison with the predictions of the model. Also, the large initial concentration of Z_{20} violates the inequalities required for the approximations in our analytical treatment.

9. Conclusions

The enhanced stationary state approximation (ESSA) and the network representation provide analytical solutions for the time-dependent concentrations of each of the reagents as well as the reaction rates in the conversion of the dilithium adduct of diphenyl acetylene to its trans derivative (E)-5. The ESSA also provides self-estimates on the limits of its own accuracy for predicting conversion rates.

It is seen from the analytical ESSA solutions that the initial trace concentration z_3 [(Z)-3] increases rapidly during the first phase of the reaction, as z_2 is almost completely depleted, driven by the large deviation from equilibrium of the diphenyl acetylene concentration z_4. The absolute value of changes to all four reagent concentrations are nearly equal; however, the percentage change in the z_1 concentration is very small, whereas the percentage changes in the other three reagent concentrations are all large. It is this contrast that makes the ESSA so accurate in this time interval. During the main phase of the reaction, the increased z_3 acts as a nearly constant reservoir to produce extra z_2 [(E)-3]] at a nearly constant rate. This extra z_2 then rapidly reacts with the cis diphenyl acetylene (source z_1) to form the trans derivative product, $z_4 = (E)$-5 at the same nearly constant rate. Thus, the combination of a reservoir z_3 as a steady source for extra z_2, and the rapid reaction of z_1 with this extra z_2, is very effective in maintaining the nearly zero-order reaction over the wide range of source concentrations. We found a very rapid initial transient reaction, during which the amount of cis diphenyl acetylene (source z_1) converted to its trans derivative (product z_4) is equal to approximately Z_{20} (the initial trace concentration of monolithiated stilbene).

During the main phase of the reactions, after the very short initial transient, the conversion rate is predicted quite accurately by the ESSA to be a constant k_2C_{23}, the product of the rate constant k_2 with the total initial concentration of stilbene C_{23} (the total of cis + trans monolithium compounds).

Although the diphenyl acetylene conversion rate slows down in a predictable manner toward the end of the reaction, the integrated concentration of the trans diphenyl acetylene product (z_4) is predicted by the ESSA to increase almost linearly (within the accuracy of the experiments)[1] through the end of the reaction. The analytic ESSA treatment also reproduces the computer computations with accuracy better than the uncertainties in the experiments.[1]

Thus, overall, we see that the reaction scheme I, originally proposed by Kemmer,[2] can indeed explain the nearly linear, apparently zero-order kinetics found experimentally throughout the entire reaction, with conversion rate equal to k_2C_{23}.

Comparison with existing experiments indicates that our model should use a time scale with a unit of time of approximately 6 h. Available experimental results do not give direct information on actual concentrations of the reagents, so we have insufficient information to fix the scales of concentrations and rate constants.

Acknowledgment. Unfortunately, Michael Szwarc passed away shortly after we completed the original manuscript. He was quick to recognize mistakes made in the use of the SSA in his previous work, but firm in his intuitive understanding that the general model of reaction scheme I was correct. We will all miss his insights and probing questions. C.P. thanks the family of Michael Szwarc for their hospitality during the early stages of this work and Prof. Gordon Davies and the Physics Dept at King's College for their hospitality during the final revisions. C.P. thanks in particular also Dr. Joseph Jagur-Grodzinski and Dr. Gideon Levin for their careful reading of the manuscript, for good advice, for the correction of important errors in the nomenclature, and for looking up the CA Registry numbers. We gratefully acknowledge that PSpice was supplied free of charge by Cadence Design Systems (formerly OrCAD/MicroSim).

Appendix A: Notation

General Conventions: For rates and concentrations, variables are indicated by lower case letters r_i, z_i, whereas constants, such as their values at particular times, are indicated by upper case letters R_{ia}, Z_{ia} respectively. The subscript $i = 1, 2, 3, 4$ indicates the particular reagent. The subscript $a = 0, 1, 2\_p, ...$ indicates the time t_a (or T_a) at which this variable is evaluated.

Concentrations C_{14} and C_{23} are upper case because they are constant throughout the reaction.

In the equations, z_i ($i = 1, 2, 3, 4$), In, R, M, & P are used to represent the concentrations of the various reagents. In the text, z_i represents either the names of the four reagents or their respective concentrations, as will be clear from the context. This avoids the need for brackets, e.g. $[z_i]$ etc., to denote concentrations, which would make some of the longer equations rather awkward.

Time derivatives of z_i are indicated by primed variables: z_i' as well as dz_i/dt. Also, j_{14} and j_{23} are used for combinations of time derivatives of concentrations, which appear as voltage controlled current sources in the network representation.

t represents the time from the beginning of the reaction, whereas T represents the time from some intermediate stage of the reaction.

For reaction scheme II, upper case letters are used throughout for variable concentrations; this allows descriptive abbreviations without confusion with similar lower-case letters for reaction scheme I.

Specific Notation: The following notation is used throughout this paper.

Abbreviations:

SSA	stationary state approximation
ESSA	extended stationary state approximation

Rate Constants:

k_i	$i = 1, -1, 2, -2$

Concentrations/Reagents:

In	initiator
M	monomer
P	polymer
R	radical
z_1	(Z)-2 cis dilithium adduct of diphenyl-acetylene, tolane. This has absorption peak at 253 nm [Maerker et al.[1]]
z_2	(E)-3 (trace) trans mono-lithiated adduct of tolane; mono-lithiated trans stilbene [Maerker et al.[1]], CA registry No. 213315-71-0
z_3	(Z)-3 (unstable) cis monolithiated adduct of tolane; cis stilbene [Maerker et al.[1], Levin et al.[3]]
z_4	(E)-5 trans ortho-lithiated. This has absorption peak at 278 nm; [Maerker et al.[1]], CA registry number (RN 213315−73−2) chemical name: (2-2-(Lithiophenyl)-1-phenylvinyl) lithium, or Lithium [.mu.[1,2-phenylene[(1E)-2-phenyl-1,2-etthenediyl]]]di- (9CI)
z_i	$i = 1, 2, 3, 4$ reagent, or its concentration (variable), depending on context
Z_{ia}	$i = 1, 2, 3, 4$; $a = 0, 1, 2\_p$. Value of concentration z_i at time t_a
C_{14}	$= Z_{10} + Z_{40} = z_1 + z_4$
C_{23}	$= Z_{20} + Z_{30} = z_2 + z_3$

Rates:

$r_1 = k_1 z_1$
$r_3 = k_2 z_3$
$R_{10} = k_1 Z_{10}$
$R_{31} = k_2 Z_{31}$

Time Derivatives of Concentrations:

$z_i' = dz_i/dt \qquad i = 1, 2, 3, 4$

$j_{14} = k_1\, z_1\, z_2 - k_{-1}\, z_3\, z_4 = z_4' = -z_1'$ see also Network below

$j_{23} = k_{-2}\, z_2 - k_2\, z_3 = z_1' - z_2' = z_3' = z_4'$ see also Network below

Network:

C_i ($i = 1, 2, 3, 4$ = capacitor corresponding to reagent z_1. (The C_i are all chosen to be 1 Farad).

Q_i ($i = 1, 2, 3, 4$) = charge on C_i, corresponding to concentration of z_i.

$V_i = Q_i/C_i$ = voltage across C_i, corresponding to concentration of z_i.

$I_i = dQ_i/dt$ = current into C_i, corresponding to dz_z/dt.

$j_{14} = k_1 Q_1 Q_2 - k_{-1} Q_3 Q_4$ This is a voltage controlled current source (VCCS). See also Time Derivatives of Concentrations above.

$j_{23} = k_{-2} Q_2 - k_2 Q_3$ This is a volatage controlled source (VCCS). See also Time Derivatives of Concentrations above.

Changes from Steady State:

$n = [(z_3 - Z_{31})/Z_{31}]$ = relative change of z_3 from Z_{31}
$p = 100n$ = % change of z_3 from Z_{31}

Times t_a, T_a:

$t_0 = 0$ ($a = 0$) is starting time of reactions
t_1 ($a = 1$) is first time at which $dz_2/dt = -dz_3/dt = 0$
t_{2_p} ($a = 2\_p$) is time at which z_3 changes by p% from Z_{31}
$T = t - t_1$ is time interval after t_1
$T_{2\_p} = t_{2\_p} - t_1$ ($a = 2\_p$) is time interval from t_1 to t_{2_p}
T_{2_inf} ($a = 2\_inf$) is the value of T when the denominator of eq A14.3c becomes zero so the fraction becomes "infinite"
T_{3_p} ($a = 3\_p$) $= T_{2\_inf} - T_{2\_p}$

Appendix B

Independent constants:

$$C_{14} = z_1 + z_4 = Z_{10} + Z_{40} = 100.001 \tag{B1.1}$$

$$C_{23} = z_2 + z_3 = Z_{20} + Z_{30} = 2.2 \tag{B1.2}$$

Independent rates:

$$j_{14} = k_1 z_1 z_2 - k_{-1} z_3 z_4 = z_4' = -z_1' \tag{B2.1}$$

$$j_{23} = k_{-2} z_2 - k_2 z_3 = z_1' - z_2' = z_3' - z_4' \tag{B2.2}$$

Rate equations for the reactions.

$$-z_1' = z_4' = j_{14} \tag{B3.1}$$

$$-z_2' = z_3' = j_{14} + j_{23} \tag{B3.2}$$

Choice of rate constants in general:

$$k_1 \gg k_{-1} \tag{B4.1}$$

$$k_2 \gg k_{-2} \tag{B4.2}$$

Note that units of k_1, k_{-1} differ from units of k_2, k_{-2}, so they cannot be directly compared.

Choice of rate constants for numerical example:

$$k_1 = 20; \qquad k_{-2} = 1.0 \tag{B5.1}$$

$$k_{-1} = 0.2; \qquad k_2 = 10.0 \tag{B5.2}$$

Choice of initial concentrations in general:

$$Z_{10} \gg Z_{20} \gg Z_{30} \gg Z_{40} \tag{B5.3}$$

Choice of initial concentrations for numerical example:

$$Z_{10} = 100; \quad Z_{20} = 2.0; \quad Z_{30} = 0.20; \quad Z_{40} = 0.001 \tag{B6.1}$$

so the two independent constants are:

$$C_{14} = z_1 + z_4 = 100.001 \tag{B7.1}$$

$$C_{23} = z_2 + z_3 = 2.2 \tag{B7.2}$$

First Time Interval (0 ≤ t ≤ t_1). At $t = 0$, and for a short time thereafter, the first term of j_{14} dominates the reaction rates. Also, the largest concentration, z_1, changes by only a very small percentage, so this "stationary state" regime can be characterized by nearly stationary z_1 so

$$z_1 \approx Z_{10} \tag{B8.1}$$

$$j_{14} \approx k_1 z_1 z_2 = r_1 z_2 \approx k_1 Z_{10} z_2 = R_{10} z_2 \tag{B8.2}$$

and nearly stationary $(z_1 - z_2)$ so

$$j_{23} \approx 0 \text{ (more precisely } j_{23} \ll j_{14}) \tag{B8.3}$$

Thus, all of the rates of change of concentrations are nearly equal:

$$z_1' = -z_4' \approx z_2' = -z_3' \approx -j_{14} \approx -R_{10} z_2 \tag{B9.1}$$

Note that although the absolute values of all the time derivatives are nearly equal, because Z_{10} is the largest initial concentration, the percentage changes in z_1 are the smallest. Thus, $z_1 \approx Z_{10}$ can remain nearly stationary when there are large percentage changes in some other concentrations.

Of the differential equations B9.1, only the one for z_2' is uncoupled. It is easy to integrate.

$$z_2 = Z_{20} \exp(-R_{10} t) \tag{B9.2}$$

However, z_2 decreases while z_3 and z_4 both increase to the point that $k_1 z_1 z_2$ no longer dominates, and eventually, at $t = t_1$, z_2' decreases to zero. This time, t_1, is the end of the first time interval.

From eq B3.2 we find at that instant t_1

$$j_{14} + j_{23} = 0 \tag{B10.1}$$

Solving for $Z_{21} = z_2(t = t_1)$ and using $Z_{11} \approx Z_{10}$, $k_2 \gg k_{-1} z_4$, and $k_1 z_1 \gg k_2 \gg k_{-2}$, we get in general,

$$Z_{21} \approx k_2 C_{23}/R_{10} \tag{B10.2a}$$

and for our numerical example

$$Z_{21} \approx 0.011 \tag{B10.2b}$$

Comparing with eq B9.2 at $t = t_1$, we can solve for t_1

$$t_1 \approx (1/R_{10})\,\mathrm{Ln}(Z_{20}/Z_{21}) \approx (1/R_{10})\,\mathrm{Ln}([R_{10}Z_{20}]/[k_2 C_{23}]) \approx 0.00260 \tag{B10.3}$$

$$\approx (1/R_{10})\,\mathrm{Ln}(R_{10}/k_2) \quad \text{since } Z_{20} \gg Z_{30}$$

Note that t_1 is very short compared to the overall reaction time and can often be neglected in the main phase of the reaction.

From eq B9.1, we see that the absolute values of all the concentration changes are nearly equal, so we can find all of the concentrations at $t = t_1$.

$$z_1 \approx Z_{10} + z_2 - Z_{20} \approx 98.0 + 2\exp(-2000\, t) \tag{B11.1a}$$

$$z_2 \approx Z_{20} \exp(-R_{10} t) \approx 2\exp(-2000 t) \tag{B11.2a}$$

$$z_3 \approx Z_{30} - z_2 + Z_{20} \approx 0.200 - 2\exp(-2000 t) \tag{B11.3a}$$

$$z_4 \approx Z_{40} - z_2 + Z_{20} \approx 2.001 - 2\exp(-2000 t) \tag{B11.4a}$$

$$Z_{11} \approx Z_{10} + Z_{21} - Z_{20} \approx 98.011 \tag{B11.1b}$$

$$Z_{21} \approx k_2 C_{23}/R_{10} \approx 0.011 \tag{B11.2b}$$

$$Z_{31} \approx C_{23} - Z_{21} \approx 2.189 \approx C_{23} = 2.20 \tag{B11.3b}$$

$$Z_{41} \approx Z_{40} + Z_{20} - Z_{21} \approx 1.990 \tag{B11.4b}$$

In eqs B11, the algebraic terms are more general than the particular numerical values for our particular numerical example. Note that there is only a very short time just before t_1 when the approximation $j_{23} \ll j_{14}$ of eq B8.4 is not valid. Thus we get only very small integrated errors in t_1 and the values of z at $t = t_1$ by using this approximation until $t = t_1$.

Second Time Interval (t_1 ≤ t ≤ t_{2_N}). By our definition of $t = t_1$, (see B10.1), at this time $j_{23} + j_{14} = 0$. For much of the succeeding time, z_3 is nearly stationary, so

$$z_3 \approx Z_{31} \tag{B12.1}$$

$$z_3' = j_{23} + j_{14} \approx 0 \quad \text{(or more precisely } |j_{23} + j_{14}| \ll |j_{23}| \approx |j_{14}|) \tag{B12.2}$$

Note that since $Z_{21} \ll Z_{31}$ and $|z_2'| = |z_3'|$, the percentage changes in z_2 are much larger than the percentage changes in z_3. Thus, z_3 can be nearly stationary, even at times when there are large percentage changes in z_2.

From eqs B3.1 and B12.2, we get rate equations

$$z_4' = -z_1' \approx -j_{23} \tag{B13.1}$$

Using conditions B4.2 and B12.1 and the fact that $Z_{31} \gg Z_{21}$, this simplifies to (including numbers for our numerical example)

$$z_4' = -z_1' \approx k_2 Z_{31} = R_{31} \approx 21.89 \approx k_2 C_{23}\,[1 - (k_2/R_{10})] \approx k_2 C_{23} = 22 \tag{B13.2}$$

Looking back at the original reaction scheme, we see that the term $k_2 z_3$ is the rate of conversion of z_3 back to z_2. Thus, it is clear that in this time interval, the major effect is the production of small extra amounts of z_2 at a nearly constant rate from the large "reservoir" of z_3, followed by the quick reaction of the extra z_2 with z_1 to form z_4 at the same nearly constant rate.

Equation B13.2 is easily integrated to solve for z_4 and z_1.

$$z_4 \approx Z_{41} + R_{31}(t - t_1) = Z_{41} + R_{31}T \approx 1.990 + 21.89T$$
$$= (Z_{41} - R_{31}t_1) + R_{31}t \approx 1.933 + 21.89t \qquad \text{(B14.1)}$$

$$z_1 = C_{14} - z_4 \approx 98.011 - 21.89T \approx 98.068 - 21.89t \qquad \text{(B14.2)}$$

Equations B14.1 and B14.2 predict 100% conversion of z_1 to z_4 in time $t = t_1 + [(C_{14} - Z_{41})/R_{31}] \approx 4.480$. The computer solutions show a 96% conversion in that time, so the integrated error of our approximation for z_4 is only 4%.

Now, knowing the time dependence of z_4 and z_1, we find the time dependence of z_2 and z_3 from eqs B12.2, B14.1,2, and B7.2.

$$z_2 \approx [k_{-1}C_{23}z_4 - k_2C_{23}]/[k_1C_{14} + k_2 + k_{-2} - k_1z_4]$$
$$\approx \{C_{23}[(k_2 + k_{-1}Z_{41}) + k_{-1}R_{31}T]\}/\{k_1(Z_{11} - R_{31}T)\}$$
$$\approx \{C_{23}\,[k_2 + k_{-1}R_{31}T\}/\{k_1(Z_{11} - R_{31}T)\}$$
$$\approx 0.011\{1 + 0.421T\}/\{1 - 0.2233T\} \qquad \text{(B14.3a)}$$

$$z_3 = C_{23} - z_2 \qquad \text{(B14.4)}$$

It is clear that eqs B14.1−4 become invalid for large T due to the breakdown in the assumption that $z_3 \approx z_{31}$. Equation B14.3 is valid only as long as the change in z_2 (= negative of change in z_3) is a small percentage of Z_{31}. If, for example, we allow a relative variation of $p\% = p/100 = n$ in Z_{31}, then

$$z_2 = Z_{21} + nZ_{31} = (1 - n)Z_{21} + nC_{23} \approx nC_{23} \qquad \text{(B14.3b)}$$

for $n = p/100 = p\%$ change in z_3.

So, comparing eqs 14.3a and 14.3b, we find at $T = T_{2\_p}$

$$n = k_2[1 + k_{-1}C_{23}T_{2\_p}]/k_1[Z_{11} - k_2C_{23}T_{2\_p}] \qquad \text{(B14.3c)}$$

We define T_{2_inf} as the value of T when the denominator of eq B14.3c goes to zero and $T_{3\_p} = T_{2\_inf} - T_{2\_p}$. We solve B14.3c for both T_{2_inf} and T_{3_p}, for $n \gg k_{-1}/k_1$ (= 0.01 in our example):

$$T_{2\_p} = T_{2\_inf} - T_{3\_p} \qquad \text{(B15.1)}$$

$$T_{2\_inf} = Z_{11}/(k_2C_{23}) = (C_{14} - C_{23})/(k_2C_{23})$$
$$\approx (C_{14})/(k_2C_{23}) \approx 4.55 \qquad \text{(B15.2)}$$

$$T_{3\_p} \approx [k_{-1}/n\,k_1C_{23}]\{(1/k_{-1}) + [(C_{14} - C_{23})/k_2]\}$$
$$\approx [k_{-1}/n\,k_1C_{23}]\{(1/k_{-1}) + (C_{14}/k_2)\} \approx 0.0682/n \qquad \text{(B15.3)}$$

Thus, for 10%, and 20% changes in conversion rate, in our numerical example, we find T and the corresponding values of $z_4 = Z_{42\_p}$ to be $T_{2\_10} \approx 3.9$, $Z_{42\_10} \approx 87$; $T_{2\_20} \approx 4.2$, $Z_{42\_20} \approx 94$. Within 10% (20%) accuracy, the conversion rate of z_1 to z_4 remains 21.9 from 2% through 87% (94%) conversion.

Third Time Interval ($t_{2\_p} < t$). This interval is characterized by a final approach to equilibrium. After t_2, the conversion rate noticeably slows down (nonlinear problem) and becomes more difficult to compute analytically with reasonably accurate approximations. The approximate concentration of z_4, determined by the integration of the approximate conversion rate, differs by much less from the computed solution than does the conversion rate itself, a difference within the experimental accuracy. (See discussion of eqs B14.)

The final equilibrium concentrations are straightforward to compute analytically by setting all of the time derivatives to zero in the rate equations. We find

$$Z_{1(\text{equil})} = [k_{-1}k_{-2}/(k_1k_2 + k_{-1}k_{-2})]C_{14} = 0.0999011 \approx 0.1 \qquad \text{(B17.1)}$$

$$Z_{2(\text{equil})} = [k_2/(k_2 + k_{-2})]C_{23} = 2.00 \qquad \text{(B17.2)}$$

$$Z_{3(\text{equil})} = [k_{-2}/(k_2 + k_{-2})]C_{23} = 0.20 \qquad \text{(B17.3)}$$

$$Z_{4(\text{equil})} = [k_1k_2/(k_1k_2 + k_{-1}k_{-2})]C_{14} = 99.9010989 \approx 99.9 \qquad \text{(B17.4)}$$

Thus, in this time interval, to get concentrations that are accurate within the experimental uncertainty, we simply extend the linear solution of the second time interval beyond t_2, using eqs B14.1−4, but cutting off the values of z_i at $Z_{i(\text{equil})}$ of equations B17.1−4.

References and Notes

(1) Maerker, A.; Kemmer, M.; Wang, H. C.; Dong, H.; Szwarc, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 2136. Note a typographical error in the caption for Figure 1; the symbols for the 2h and 10h seem to be reversed.

(2) Kemmer, M. *Darstellung von vicinalen Dilithioalkenen, Stabilitaten und Folgereactionen*; Shaker, 1997.

(3) Jagur-Grodzinski, J.; Levin, G. private communication providing the CA registry numbers and the various names of these reagents. They also provided a reference to a related study. Levin, G.; Jagur-Grodzinski, J.; Szwarc, M. *J. Org. Chem.* **1969**, *34*, 1702. They pointed out that in this 1969 study, the tentative explanation for the stability of the cis dilithium adduct of diphenyl acetylene was not the right one. It turns out that the bridge structure, and not its dimerization, is responsible for the stability.

(4) See for example, Nichols, John *Chemical Kinetics*; John Wiley: New York, 1976.

(5) Bulirsch, Roland; Stoer, Josef *Numer. Math.* **1966**, *8*, 1.