hydrolyzed with an ice-H_2O slurry (500 ml). The hydrolysate was stirred for 30 min and was then neutralized with sodium acetate (296 g), whereupon the product precipitated as a yellow solid. The crude product was isolated, washed with H_2O, and dried. The yield was 52.5 g (66.3%) of a light yellow powder, mp 114–118°. Recrystallization (2-propanol-*p*-dioxane) gave a product with mp 123.5–127°. The nmr spectrum (CH_3NO_2) was consistent with the structure of 1,3-bis(1-chloropropen-3-al)benzene (**8**): δ 6.7 (d, 2 H, -CH=, J = 6.5 Hz), 7.8 (m, 4 H, H_{arom}), 10.1 ppm (d, 2 H, -CHO, J = 6.5 Hz). The ir spectrum contained a strong band at 1660 cm^{-1} (C=O).

1,3-Bis(1-chloropropen-3-al)benzene using $COCl_2$. Dimethylformamide (100 ml) was added to a 250-ml flask fitted with a gas dispersion tube and a dewar condenser, and $COCl_2$ (17.3 g, 0.17 mol) was dispersed thereinto over a 4-hr period. The resulting complex was treated with *m*-diacetylbenzene (13.8 g, 0.085 mol) with cooling to maintain the reaction temperature at 60° and was then stirred overnight at ambient temperature. Addition of H_2O (750 ml) caused the precipitation of crude product which was isolated and washed with additional H_2O. The yield was 17.0 g (78.5%) of a light yellow powder, mp 92–103°.

1,4-Bis(1-chloropropen-3-al)benzene using $POCl_3$. The 1,4 isomer was prepared in a manner identical with that employed tor the 1,3 isomer (described above). The yield was 81% of a yellow powder, mp 145–155°.

1,4-Bis(1-chloropropen-3-al)benzene using $COCl_2$. The 1,4 isomer was prepared in a manner identical to that employed tor the 1,3-isomer (described above). The yield was 74.2% of a light yellow powder, mp 150–158°.

***m*-Diethynylbenzene.** Crude 1,3-bis(1-chloropropen-3-al)benzene (mp 114–118°, 30 g, 0.11 mol) was added to a solution of NaOH (20.0 g, 0.5 mol) in H_2O (250 ml) and *p*-dioxane (400 ml) at 75°. The resulting mixture was stirred at 75° for 45 min, cooled to room temperature, neutralized with 10% aqueous HCl (125 ml), and saturated with NaCl. Extraction with ether gave an organic solution which upon distillation gave a product, bp 46–48° (1.0 mm), which was shown to be *m*-diethynylbenzene by comparison with authentic material (prepared by the method of Hay, Scheme I). The yield was 9.7 g (69.5%).

***p*-Diethynylbenzene.** *p*-Diethynylbenzene was prepared in a manner analogous to that described above for *m*-diethynylbenzene with the exception that the product was isolated by sublimation. Owing to extensive polymerization during the isolation process, yields were limited to 20%. Analysis was by comparison with authentic *p*-diethynylbenzene (prepared by the method of Hay, Scheme I).

Communications to the Editor

On the Kinetics of Cooperative Processes. Closure Approximations

In recent years we have formulated in analytical hierarchic form the master equation for the kinetics of cooperative processes for a two-state model with nearest-neighbor interactions on a linear lattice.[1,2] In the equilibrium limit of the theory, well-known results previously derived from a partition function are obtained for infinite as well as finite chains by means of the principle of detailed balancing.[2,3]

A basic difficulty, already encountered by Glauber,[4] whose starting point is a master equation for the state probability of the whole system, arises in the nonequilibrium case. The variables in our theory are the time-dependent probabilities $n(X_j)$ for a specific sequence of states X_j with length $j > 1$. Under reversible conditions and in contrast to the irreversible case, no rate equations for sequences of arbitrary length can be formulated by inspection. A general procedure for obtaining the successive rate equations for the $n(X_j)$'s was developed[1] and applied to sequences up to length six,[2] but it becomes rapidly impracticable to carry out such a program as j increases, since the rate equations do not "close." That is, they are of the type

$$\mathrm{d}n(X_j)/\mathrm{d}t = \sum_{i=1}^{j+1} A_i n(Y_i) \qquad \text{not all } A_{j+1} = 0 \qquad (1)$$

where the A_i's are linear combinations of the rate constants. Thus, when $j = 6$, the limit to which the equations for the infinite chain have been formulated explicitly,[2] runs of length seven must be introduced, and so forth. In finite chains of sufficiently short length, this presents no difficulties, and the appropriate equations have been developed[5] for chains of up to length seven.

As in other many-body problems, a closure of the hierarchy of equations is one way out to be explored. That is, we *assume*[1,2]

$$n(Y_i; Z_j; U) = n(Y_i; Z_j)n(Z_j; U)/n(Z_j) \qquad i = 0, 1, \ldots \qquad (2)$$

Here Y_i and Z_j represent specified sequences of the two states of lengths i and j, respectively, and U is a singlet. Physically, this implies the hope that with increasing length, the behavior of short sequences should become increasingly less dependent on that of long runs.

We have tested numerical solutions of the now nonlinear differential equations by varying the magnitudes of the rate parameters over a wide range and assuming closure at levels j = 3 and 4, respectively.[2] Singlet, doublet, and triplet probabilities as well as number- and weight-average sequence lengths are examined as the system passes from one toward a second equilibrium state. No significant differences between the two sets of approximations are observed. This, of course, may be indicative of a good approximation or of results which vary but slowly with the level at which closure is imposed. This question remains to be investigated.

Recently, in dealing with the same subject, and based on the identical model, certain results have been put forward.[6] These involve some misconceptions about the nature of our solution and a rederivation of several of our relationships. Most basically, however, this paper includes the hypothesis that the closure approximation, eq 2, is rigorous at the triplet (j = 2) level. This assertion, apparently, is deduced from the fact that interactions between adjacent sites only are assumed in the elementary reaction processes. At equilibrium, of course, exact closure obtains already at the doublet (j = 1)

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(1) A. Silberberg and R. Simha, *Biopolymers*, **6**, 479 (1968).

(2) P. Rabinowitz, A. Silberberg, R. Simha, and E. Loftus in "Stochastic Processes in Chemical Physics," K. E. Shuler, Ed., Wiley, New York, N. Y., 1969, p 231.

(3) R. Simha and R. H. Lacombe, *J. Chem. Phys.*, **55**, 2936 (1971).

(4) R. J. Glauber, *J. Math. Phys.*, **4**, 294 (1963).

(5) R. Simha and E. Loftus, unpublished work.

(6) For example, G. Schwarz, *Ber. Bunsenges. Phys. Chem.*, **75**, 40 (1971).

level. To say the least, it is intuitively doubtful that the system should be able to pass from one to a second equilibrium, *i.e.*, doublet closure state, *via* a series of immutable triplet closure states.

However, since the ultimate proof is, of course, provided by the rate equations, one may examine to what extent eq 2 is consistent with these. We shall deal here only with infinite chains, since it is only with respect to these that the assertion is claimed to hold. Here the location of a particular lattice site need not be specified.[3] Our rate equations have already been extended to a sufficiently high level so that quadruplets and quintuplets (and higher tuplets) can be considered.

Development. The basic procedure then is to select a particular species X_j, $j = 4$, in eq 1 and to express by means of eq 2 all quadruplets and quintuplets in terms of shorter sequences. We shall derive explicitly the results for the particular case of the sequence 0001 and then cite the final results for the other two "canonical" quadruplets 0011 and 0111. Here 0 and 1 indicate, as in previous work, the two alternative states a given lattice site can assume.

The pertinent rate equations are[1,2]

$$\mathrm{d}n(0)/\mathrm{d}t = k_1[-n(0) + n(01) + n(001)] - 2k_2n(001) + k_3[-n(01) + n(001)] + k_1'[1 - n(0) - n(01) - n(011)] + 2k_2'n(011) + k_3'[n(01) - n(011)] \tag{3a}$$

$$\mathrm{d}n(01)/\mathrm{d}t = k_1[n(0) - n(01) - n(001)] + k_3[-n(01) + n(001)] + k_1'[1 - n(0) - n(01) - n(011)] + k_3'[-n(01) + n(011)] \tag{3b}$$

$$\mathrm{d}n(001)/\mathrm{d}t = k_1[n(0) - n(01) - n(001) - 2n(0_31)] + 2k_2[-n(001) + n(0_31)] + 2k_2'[n(011) - n(0_21_2)] + k_3'[n(01) - 2n(001) - n(011) + 2n(0_21_2)] \tag{3c}$$

$$\mathrm{d}n(0_31)/\mathrm{d}t = k_1[n(0) - n(01) - n(001) - 2n(0_31) - 2n(0_41)] + 2k_2[-n(0_31) + n(0_41)] + 2k_2'[n(0_21_2) - n(0_31_2)] + k_3'[n(01) - n(011) - 2n(0_31) + 2n(0_31_2)] \tag{3d}$$

In these equations

$$n(X_j) = \lim_{N_\mathrm{T}\to\infty} N(X_j)/N_\mathrm{T}$$

where $N(X_j)$ is the number of sequences X_j on a lattice of size N_T. To these *rigorous* equations we add the following expressions, resulting from the assumption of triplet closure

$$n(0_31) = n(000)n(001)/n(00) \tag{4a}$$

$$n(0_21_2) = n(001)n(011)/n(01) \tag{4b}$$

$$n(0_41) = [n(000)/n(00)]^2n(001) \tag{4c}$$

$$n(0_31_2) = n(000)n(001)n(011)/[n(00)n(01)] \tag{4d}$$

Differentiation of eq 4a and elimination of the noncanonical triplet 000 yield

$$\mathrm{d}n(0_31) = [n(001)/n(00)]^2[\mathrm{d}n(0) - \mathrm{d}n(01)] + [1 - 2n(001)/n(00)]\mathrm{d}n(001)$$

By means of eq 3a–3c, 4a, and 4b, the right-hand side is expressed in terms of singlet, doublet, and triplet fractions. An alternative relation for the rate of change of the quadruplet 0_31 results from eq 3d when quadruplets and quintuplets are eliminated by means of eq 4. The two final equations are

$$\mathrm{d}n(0_31)/\mathrm{d}t = k_1n(000)\{1 - 4n(001)/n(00) + 2[n(001)/n(00)]^2\} - 2k_2n(000)[n(001)/n(00)]^2 + 2k_2'n(011)\{[n(000)/n(00)]^2 - [n(001)/n(01)][1 - 2n(001)/n(00)]\} + k_3'n(010)\{2[n(001)/n(00)]^2 + [1 - 2n(001)/n(00)][1 - 2n(001)/n(01)]\} \tag{5a}$$

and

$$\mathrm{d}n(0_31)/\mathrm{d}t = k_1n(000)\{1 - 4n(001)/n(00) + 2[n(001)/n(00)]^2\} - 2k_2n(000)[n(001)/n(00)]^2 + 2k_2'n(011)[n(001)/n(00)][n(001)/n(01)] + k_3'n(010)\{1 - 2[n(000)/n(00)][n(001)/n(01)]\} \tag{5b}$$

A comparison of eq 5a and 5b shows that the coefficients of k_1 and k_2 are indeed identical. In regard to the remaining terms, it will be convenient to introduce the triplet conditional probabilities p_{UVW},[7] defined by the equations

$$p_{UVW} = n(UVW)/n(UV)$$

The k_2' terms then yield the condition

$$p_{000}^2 - p_{100}(1 - 2p_{001}) = p_{001}p_{100}$$

where we have made use of the left–right reading symmetry of a given sequence. The result is either the trivial condition $p_{000} \equiv 0$ or, since $1 - p_{001} = p_{000}$

$$p_{000} = p_{100} \tag{6}$$

This implies a nearest- rather than a second-nearest-neighbor effect in the placement of the terminal 0.

Turning to the k_3' factors, we obtain

$$2p_{001}^2 + (1 - 2p_{001})(1 - 2p_{100}) = 1 - 2p_{000}p_{100}$$

If $p_{001} \neq 0$, and since $1 - p_{100} = p_{101}$, this reduces to

$$p_{001} = p_{101} \tag{6$'$}$$

i.e., the complement of eq 6.

The other two quadruplet equations[1,2] yield the anticipated results. From the sequence 0111 there ensue identities for k_1' and k_2'. Furthermore, we have the following conditions

coefficient of k_2 $p_{111} \equiv 0$ or $p_{111} = p_{011}$

coefficient of k_3 $p_{110} \equiv 0$ or $p_{110} = p_{010}$

From the sequence 0011 one derives identities for k_3 and k_3' and

coefficient of k_1 $p_{000} \equiv 0$ or $p_{101} = p_{001}$

coefficient of k_1' $p_{111} \equiv 0$ or $p_{010} = p_{110}$

coefficient of k_2 $p_{010} \equiv 0$ or $p_{101} = p_{001}$

coefficient of k_2' $p_{101} \equiv 0$ or $p_{010} = p_{110}$

In general, four of the conditional probabilities are independent. Here only two, say, p_{000} and p_{111}, are found to be independent. In other words, if the closure relations 4 are to be consistent with the rate eq 3, a *nearest*-neighbor effect in the formation of sequences must obtain at all times, not just

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(7) For example, R. Simha and J. M. Zimmerman, *J. Theor. Biol.*, 2, 87 (1962).

at equilibrium. The validity of doublet closure may then be examined in the analogous manner as the triplet closure. It suffices to quote the result. Whereas in the latter case it was at least possible to compare appropriate terms with each other, we now observe that *different* rate parameters appear in the two equations to be compared. For example, in considering the triplet 001, we note in eq 3c the appearance of k_1, k_2, k_2', and k_3'. But from eq 3a and 3b and the assumption

$$n(001) = n(00)n(01)/n(0)$$

an equation for $dn(001)/dt$ results, which involves all rates. This inadmissible consequence of doublet closure is not surprising.

In conclusion, we have provided proof that any assertion of *rigorous* closure at the triplet level[6] is erroneous. This, of course, does not necessarily exclude a *numerical* adequacy of the closure approximations used previously by us[2] or others, involving longer sequences. Indeed, results of type (5a–5b) are encouraging in this respect by demonstrating partial identities. Numerical comparisons of the remaining terms in these and analogous equations for longer sequences may prove useful.

At this point one may inquire whether special cases exist other than the trivial one of noncooperativity, where some form of closure of our rate eq 2 for infinite chains is rigorous. For example, consider the special case constructed by Glauber.[4] In our notation, and setting his scale factor a equal to two, it implies

$$k_2 = k_2' = 1; \quad k_1 = k_1' = (1 - \gamma); \quad k_3 = k_3' = (1 + \gamma)$$

and satisfies, of course, the general condition on the rate constants[1,2]

$$(k_2/k_2')^2 = (k_3/k_1')(k_1/k_3')$$

On substituting into the right-hand side of eq 3a, we observe that the coefficients of $n(01)$, $n(011)$, and $n(001)$ all vanish and only the coefficient of $n(0)$ survives, which renders eq 3a immediately integrable. On the other hand, in eq 3b, the analogous substitution does not eliminate the dependence on the triplet sequences. The situation in the further relations of the hierarchy, eq 1, follows the analogous pattern. However, Glauber has shown[4] that in his special case a further closed differential equation for at least pair correlations can be obtained. It should be noted, however, that even the most general mechanism formulated by him represents a special case, namely

$$k_i/k_i' = k_j/k_j' \qquad i, j = 1, 2, 3$$

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CORRECTIONS

"Polymer–Solvent Interactions for Homopolypeptides in Aqueous Solution," by A. J. Hopfinger, Volume 4, Number 6, November–December 1971, page 731.

On page 733, equation 3, the upper limit on the second integral should read $r_j + r_{ij}$. In equation 6, the upper limit on the sum should be n instead of N. The same error occurs in the text two lines above the equation.