produced in the CD_4–H_2 experiments is less than a third of the decrease in CD^+.)

The rate constants for reaction of CH_3^+, CH_2^+, and CH^+ with D_2 are about one-fourth of the rate constants for the reaction of these ions with CH_4.[4] If the rate constants are proportional to $(\alpha/\mu)^{1/2}$, the polarizability of the molecule divided by the reduced mass of the complex,[11] then the rate constant for the reaction of CH_2^+ with H_2 would be equal to the rate constant for CH_2^+ with CH_4. (The differences in reduced mass balance the differences in polarizability.) The observed ratio of rate constants is very different from this calculated value and is actually about the same as the ratio of the polarizabilities of H_2 and CH_4.

Pratt and Wolfgang[2a] in their paper suggest exchange between CH_5^+ and T_2 to give CH_4T^+ followed by proton exchange with CH_4 to give the neutral CH_3T. According to our data this exchange reaction of CH_5^+ with D_2 does not occur or if it does occur its rate constant must be less than 10^{-12} cc./molecule-sec. Similarly, direct reaction between CH_4^+ and D_2 to give CH_4D^+ was observed to have a very small cross section, similar to the direct atom-exchange reaction. Some CH_4T^+ could presumably be formed by the reaction of T_3^+ with CH_4 which we observed between D_3^+ and H_3^+ and CH_4, but we found that very rapid exchange occurs in CH_3^+ and its product $C_2H_5^+$ as did Wexler[2b] (Wexler did not observe the disappearance of CH_3^+ and formation of CH_2D^+ from the reaction of CH_3^+ with D_2 as we report; he merely observed the presence of the substituted ethyl ions.) It seems reasonable to us that the exchange should proceed through the methyl and ethyl ions and their neutralization products.

Acknowledgments.—We are indebted to Mr. W. C. Gieger for performing these experiments with his accustomed skill.

(11) H. Eyring, J. O. Hirschfelder, and H. S. Taylor, *J. Chem. Phys.*, **4**, 479 (1936).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, VANDERBILT UNIVERSITY, NASHVILLE, TENN.]

The Monte Carlo Integration of Rate Equations[1]

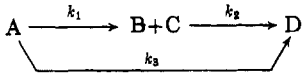
BY L. J. SCHAAD

RECEIVED JULY 11, 1963

The difficult problem of analytic integration of rate equations can be circumvented by constructing a digital computer model of the reacting system. Concentration–time curves, accurate to 1 or 2%, are obtained directly from the model for all components of the system.

Introduction

One often accepts or rejects a proposed reaction mechanism by comparing experimental concentration–time data with those predicted by that proposed mechanism. It is easy enough to write down differential equations governing the model mechanism, but unfortunately their integration to give the desired concentration–time curves is usually difficult. In even the relatively simple case



(1)

Pearson, King, and Langer[2] have shown that integration of the rate equations

$$\begin{aligned} d[A]/dt &= -k_1[A] - k_3[A] \\ d[B]/dt &= d[C]/dt = k_1[A] - k_2[B][C] \\ d[D]/dt &= k_3[A] + k_2[B][C] \end{aligned} \qquad (2)$$

gives

$$[B] = [A]_0 \frac{k_1}{k_1 + k_3} (\tau/K)^{1/2} \frac{iJ_1(2i\sqrt{\tau K}) - \beta H_1^1(2i\sqrt{\tau K})}{J_0(2i\sqrt{\tau K}) + i\beta H_0^1(2i\sqrt{\tau K})} \qquad (3)$$

where

$$\tau = e^{-(k_1+k_2)t},\ K = k_1k_2[A]_0/(k_1 + k_3)^2,$$
$$\beta = iJ_1(2i\sqrt{K})/H_1^1(2i\sqrt{K})$$

and J's and H's are Bessel functions. For mechanisms even slightly more complex, integration in closed analytical form is impossible.

A method is therefore presented here which avoids this integration. A digital computer is used to set up a statistical (*i.e.*, Monte Carlo[3]) model of the reacting system from which concentration–time curves are obtained directly. This is described first in general to show the scope of the method and then in detail for mechanism 1.

Monte Carlo Integration of a First-Order Rate Equation.—Consider, to take an example, the uncatalyzed thermal decomposition of H_2O_2. Here the first-order rate equation

$$d[H_2O_2]/dt = k[H_2O_2]$$

can easily be integrated to give

$$\log [H_2O_2] = (\text{a constant}) - kt$$

To construct a Monte Carlo model of this reaction, a portion of computer storage is set aside to represent the reaction flask, and an H_2O_2 molecule is represented in the computer by the digit 1. Decomposition is indicated by replacing these 1's by 0's. To start the reaction, the flask is filled with H_2O_2 by loading 1's into the computer storage. Suppose there are 1000 1's in storage at the start of the reaction. Each is in a particular location and hence each can be distinguished as the 0th, 1st, . . . 999th molecule. The remaining part of storage is used to generate a random number between 0 and 999. If the number 215 (say) is generated, the 215th H_2O_2 molecule is reacted by replacing the 1 representing it by a 0. Another random number is generated and the reaction continued. If 215 is generated again, a 0 will be replaced by another 0 giving in effect no reaction. This is repeated some specified number of times; then H_2O_2 is "titrated" by counting the number of 1's remaining

(1) Presented in part at the Southeastern Regional Meeting of the American Chemical Society, Gatlinburg, Tenn., November, 1962.

(2) R. G. Pearson, L. C. King, and S. H. Langer, *J. Am. Chem. Soc.*, **73**, 4149 (1951).

(3) A. S. Householder, G. E. Forsythe, and H. H. Germond, "Monte Carlo Method," National Bureau of Standards, Applied Mathematics Series 12 (1951).

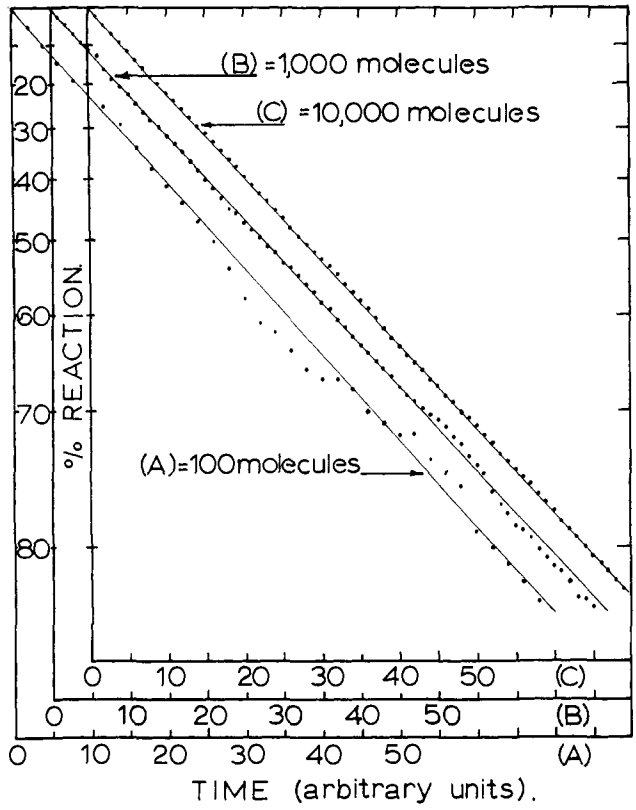


Fig. 1.—Three Monte Carlo models of a first-order reaction showing the effect of model size on accuracy.

in storage. The entire process is repeated until the reaction is as complete as required.

To see that this computer model does correspond to a first-order reaction, compare the rate of decomposition of H_2O_2 with the rate of disappearance of 1's. In a first-order reaction each molecule has a constant probability P of decomposing in unit time. The number of H_2O_2 molecules decomposing in time Δt is therefore $nP\Delta t$, where n is the number of molecules present. In the computer model each location containing a 1 or a 0 has a constant probability P' of being selected in unit time. The number of 1's replaced by 0's in Δt is therefore $n'P'\Delta t$, where n' is the number of 1's present. The two systems are therefore analogous, and a plot of the logarithm of number of 1's *vs.* time does give the expected straight line (Fig. 1).

Notice that the computer model does not require information about the structure of the reacting molecules nor about the nature of the transition state.

The more 1's used to represent the reacting system, the more accurate are the results, but the greater are the computing time and storage needed. Figure 1 shows the accuracy obtained using 100, 1000, and 10,000 1's. To compare the three, the time unit varies and represents, respectively, the time required to generate 2.5, 25, and 250 random numbers. The accuracy with 10,000 1's seems sufficient for most experimental rate data, and the 45 min. of computing time required on an IBM 650 is reasonable.

Extension to Complex Reactions.—Any reaction mechanism, no matter how complex, can add only three kinds of complication to the simple first-order process: (a) higher order, (b) competing reactions, (c) sequential reactions.

Higher Order.—To represent the second-order reaction

$$A + B \longrightarrow \text{products} \qquad (4)$$

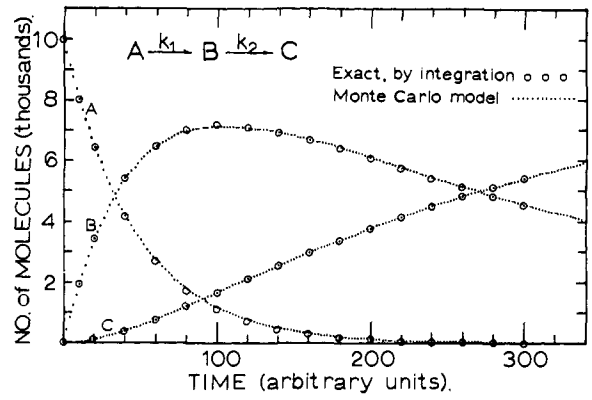


Fig. 2.—Monte Carlo model of two sequential first-order reactions with $k_1/k_2 = 7$.

two portions of storage are set aside. An A molecule is represented by a 1 in the first portion; a B by a 1 in the second. To begin the reaction, the ratio of 1's in part A to 1's in part B is set equal to the ratio of initial concentrations of A and B. Two random numbers are generated, one specifying an A and a B location. If both these locations contain 1's, a reaction is indicated by replacing both by 0's. If one or both already contain 0's, no reaction occurs. After a specified number of random numbers are generated, A and B are titrated by counting the 1's in the two sections of storage.

An alternative, sometimes more convenient, is the use of a single portion of storage in which A is represented by 1 and B by 2.

A reaction, second order in the single component A, can be simulated by randomly picking two A locations instead of one A and one B location. Extension to higher orders is obvious; the number of storage locations that must be chosen randomly each time the reaction is tried equals the order of the reaction. Reaction take place only if all locations chosen contain unreacted molecules.

Competing Reactions.—If one wishes to follow the concentration of all three components in the reaction

$$C \xleftarrow{k_2} A \xrightarrow{k_1} B \qquad (5)$$

three portions of storage are used. The A portion is filled with 1's and the B and C portions with 0's (*i.e.*, if the concentrations of B and C are initially 0). Random numbers are generated to represent the branch A → B. Each time a reaction takes place a 1 is replaced by a 0 in the A section and a 0 by a 1 in the B section. The branch A → C is treated similarly. The ratio of number of random numbers representing A → B to that representing A → C must equal the ratio k_1/k_2.

Again there is the alternative of using one portion of storage and different digits to represent each component and again generalization is obvious.

Sequential Reactions.—Sequential reactions such as

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \qquad (6)$$

are simulated much like competing reactions. Three sections representing A, B, and C are filled with 1's to represent correct initial concentrations, and the reaction is run by generating two sets of random numbers in the ratio k_1/k_2. Figure 2 compares the Monte Carlo model of (6) for $k_1/k_2 = 7$ to the exact result obtained by integrating the rate equations. Two components in equilibrium might be considered a special case of (6). Monte Carlo results for such a system are shown in

Fig. 3. Variations in the curves after about 150 time units give an idea of the errors to be expected from the model.

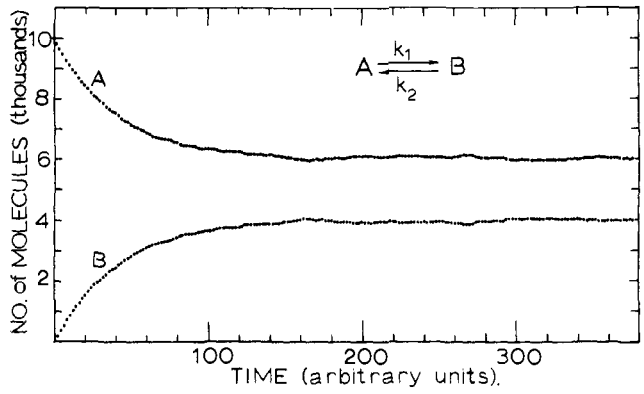


Fig. 3.—Monte Carlo model of two components in equilibrium with $K = k_1/k_2 = 4/6$.

Any combination of these three kinds of processes, and hence any chemical reaction, can be represented by a Monte Carlo model either by allowing one storage section for each component or by representing each by a different digit in a single section.

Details

We return now to (1) and consider setting up a Monte Carlo model of Pearson's[2] specific case: $[A]_0 = 4.25 \times 10^{-3}$ M, $[B]_0 = [C]_0 = [D]_0 = 0$, $k_1 = 0.0044$ min.$^{-1}$, $k_2 = 2.96$ (min. mole/l.)$^{-1}$, $k_3 = 0.0021$ min.$^{-1}$.

Initial Concentrations.—Let the first 1000 10-digit words in computer storage represent the reaction flask. Each word could then be used to represent one molecule, but 10 times as many molecules can be put into the same space by using each digit instead. Picking out a molecule then requires two random numbers. A 3-digit random number (000 to 999) picks the word, and a 1-digit random number (0 to 9) specifies the digit within the word.

If A is represented by 1, B by 2, C by 3, and D by 4, the initial concentrations can be simulated by putting 4250 1's anywhere in the first 1000 words of storage. Any number of 1's could be used, but since $[A]_0 = 4.25 \times 10^{-3}$ M, this make it especially easy to convert from number of 1's to molarity. The remaining digits are set equal to 0.

Random Number Generation.—Older methods such as squaring a number and taking the central digits from the product are unreliable. The newer Power Residue Method has been shown to generate long nonrepeating sequences which have so far passed all tests for randomness.[4] Reference 4 gives a number theory justification of the method and also recipes for use without understanding the justification. The 10 low-order digits (*i.e.*, the right-hand half) from the 20-digit product of a 10-digit X by a 10-digit U_0 form the random number U_1. The low-order digits of XU_1 are then U_2; those of XU_2 are U_3 and so on. The starting numbers X = 0000100003 and U_0 = 0123456789 were chosen according to prescription and give a nonrepeating sequence of 5×10^8 10-digit random numbers. None of our Monte Carlo models have yet required more than 8×10^5 of these. Random numbers with fewer digits may be obtained by taking a high-order portion of the 10-digit random number.

(4) Anonymous, Reference Manual on Random Number Generation and Testing, International Business Machines Corporation, 1959.

Rate Constants.—Mechanism 1 contains the three branches A → B + C, B + C → D, and A → D. Denote these as the first, second, and third branches, in that order. Each random number generated is used to try one of the three. Whether or not a particular try leads to reaction depends upon what is in the location specified by the random number. Unlike (5) or (6), all branches are not of the same order, and therefore the number of times each is tried is not simply proportional to its rate constant. Let us determine first the relative number of times each branch should be tried and then how to achieve this with the computer model.

To choose a branch, the computer makes two decisions: first whether to do branch 1 or not; then if not, whether to do branch 3 or branch 2. It is therefore convenient to work with the ratios $R = N_1/(N_2 + N_3)$ and $R' = N_3/N_2$, where N_i is the number of times branch i is tried. If the model is to represent (1) correctly, it must be that

$$\frac{\text{rate of formation of D from A}}{\text{rate of formation of D from B + C}} = \frac{\text{rate of formation of 4's from 1's}}{\text{rate of formation of 4's from 2's and 3's}} \quad (7a)$$

or

$$\frac{k_3[A]}{k_2[B][C]} = \frac{N_3[1]}{N_2[2][3]} = R'\frac{[1]}{[2][3]} \quad (7b)$$

and

$$\frac{\text{rate of formation of B from A}}{\text{total rate of formation of D}} = \frac{\text{rate of formation of 2's from 1's}}{\text{total rate of formation of 4's}} \quad (8a)$$

or

$$\frac{k_1[A]}{k_3[A] + k_2[B][C]} = \frac{N_1[1]}{N_3[1] + N_2[2][3]} = \frac{R(R'+1)[1]}{R'[1] + [2][3]} \quad (8b)$$

where [1] = the ratio of number of 1's representing A to the total number of digits representing the reaction flask; [1] might be thought of as the concentration of 1's in the model; [2] and [3] are defined analogously. Other similar relations could be written down, but these two are sufficient to fix R and R'. It is also necessary that the concentration of a digit be proportional to the concentration of the molecule it represents

$$[1] = \alpha[A] \qquad [3] = \alpha[C]$$
$$[2] = \alpha[B] \qquad [4] = \alpha[D] \quad (9)$$

Since 4250 1's are equivalent to 4.25×10^{-3} M A, [1] = 4250/10,000 and $\alpha = 10^2$ (moles/l.)$^{-1}$. Combining (9) and (7b) gives $R' = \alpha k_3/k_2$. Substitution of R' into (8b) at $t = 0$ gives $R = \alpha k_1/(k_2 + \alpha k_3)$.

After an addition most computers are able to test whether or not a carry has occurred from the most significant digit of the sum (*i.e.*, an overflow). This provides a convenient way to send the computer to a given branch the proper number of times. Suppose a random digit is added to the number 3 and the computer is sent to branch 1 if a carry occurs. For random digits 7, 8, and 9 there will be a carry; for 0, 1, . . . 6 there will not. Consequently, $^3/_{10}$ of the time the computer will go to branch 1. In the Monte Carlo model of (1), a random number is added to $R/(R+1)$, and branch 1 is tried if there is a carry. The ratio of number of times a carry occurs to number of times it does not is then $[R/(R+1)]/[1 - R/(R+1)] = R$ as required. If branch 1 is not taken, adding a random number to $R'/(R'+1)$

decides between branches 2 and 3. Figure 4 is an outline of the computer model of (1).

Real *vs.* Computer Time.—After every 250 reaction tries, the computer produces an output card giving the number of each kind of molecule in the reaction flask. Let the time per output card arbitrarily be taken as one unit of computer time. In order that the computer model represent the real system, a plot of number of digits representing a molecule *vs.* computer time must coincide with a plot of concentration of that molecule *vs.* real time. The ordinate scales necessary to achieve this coincidence are known since 4250 digits = 4.25×10^{-3} *M*. The relation between real and model abscissa (*i.e.*, time) scales can be found by considering the relation between real and model rate constants.

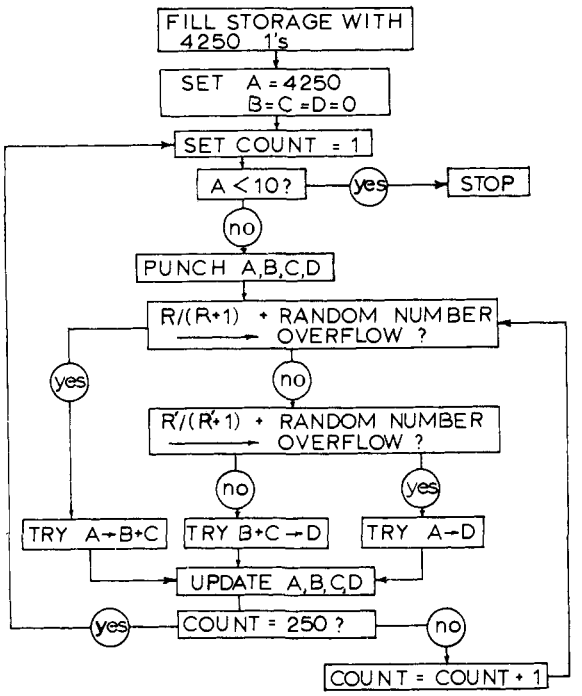


Fig. 4.—Flow chart of the Monte Carlo model of mechanism 1.

Suppose y is a function of the variable x and of the parameters $a_1, a_2, \ldots a_n$; and y' is a function of x' and $a_1', a_2', \ldots a_n'$. Suppose a plot of y *vs.* x coincides with y' *vs.* x' and that abscissa and ordinate scales also coincide for the two cases. If the magnitude and units of the parameter a_1 are

$$a_1 = \kappa\,(x \text{ units})^p\,(y \text{ units})^q \qquad (10)$$

then it must be that

$$a_1' = \kappa\,(x' \text{ units})^p\,(y' \text{ units})^q \qquad (11)$$

since changing from the unprimed to the primed system can be considered simply a renaming of variables. That is, the two parameters have the same magnitude. In general one would not happen to choose units in which scales and curves could both be made to coincide simultaneously. Suppose in this case that when the curves coincide, the scales are such that 1 (x unit) = r (x' units) and 1 (y unit) = s (y' units). One could transform to a case where (10) and (11) hold simply by increasing x' and y' units by factors of r and s.

$$a_1' = \kappa(rx' \text{ units})^p\,(sy' \text{ units})^q = \kappa r^p s^q\,(x' \text{ units})^p\,(y' \text{ units})^q \qquad (12)$$

where $\kappa r^p s^q$ is the magnitude of a_1' in x', y' units and κ is its magnitude in rx', sy' units. But (10) = (11) = (12) giving

$$a_1 \text{ (in } x,y \text{ units)} = a_1' \text{ (in } x',y' \text{ units)} \qquad (13)$$

The same is true for the other parameters.

In the real system the rate of A → B + C is k_1[A], and in the model let that of 1's → 2's + 3's be $k_1' \times$ (number of 1's). This last rate also equals the number of successful tries of branch 1 per output card. Thus at $t = 0$

$$k_1'(4250) = 250[R/(R+1)](4250/10{,}000) \qquad (14)$$

Application of eq. 13 gives

$$k_1' \text{ (in computer units)} = k_1 \text{ (in real units)} \qquad (15)$$

Then using eq. 14

$$(250/10{,}000)\,R/(R+1)(\text{output cards})^{-1} = 0.0044 \text{ (min.)}^{-1} \qquad (16)$$

1 output card = 0.6925 min.

which is the required relation between real and computer time.

In usual practice one would not be trying to construct a model of a system whose rate constants are known, but rather trying various k's to obtain best fit to observed concentration–time data. Then the steps in these last two sections would be carried out in somewhat inverted order.

Results.—B concentration from the Monte Carlo model of (1) is compared with the integrated result (3) in Fig. 5. Agreement between the two is good. For

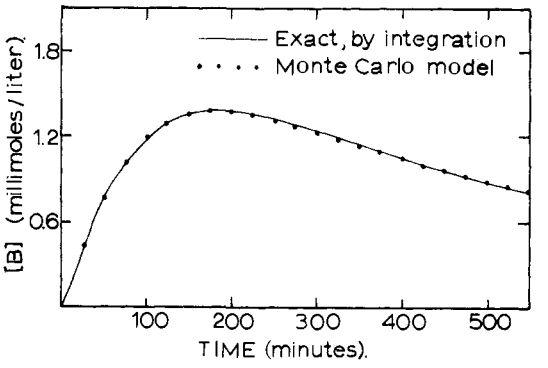


Fig. 5.—B concentration in mechanism 1.

increased accuracy the average of 4 Monte Carlo runs was used. The model would have required 10 hr. computing time on an IBM 650. It was run instead in 45 min. on a IBM 7072 using a 650 simulation program.

Comparison with Other Methods

The difficulty of analytic integration of rate equations increases rapidly with complexity of reaction mechanism and becomes impossible for mechanisms that are not yet very complex. Further, nearly every mechanism that can be integrated must be treated as a separate case, each with its own mathematical techniques. Difficulty of the Monte Carlo method increases more slowly. Just as a complex mechanism consists of individual steps, all of which are essentially similar, so the Monte Carlo model is constructed by combining the essentially similar models of the individual steps. Even for the simple

mechanism 1, and even given the integrated form 3 and tables of Bessel functions, it is easier to get [B] by setting up and running the Monte Carlo model than by evaluating and plotting (3). In usual applications, where to fit the experimental [B] curve (3) would have to be plotted for varying sets of rate constants, the saving would be still greater. The same Monte Carlo program would be used each time, and the rate constants varied by reading in one input card.

On the other hand, it would be difficult to get accuracy greater than 1% with a Monte Carlo model, and greater than 0.1% is probably impossible with present computers. This accuracy is sufficient for most rate studies, but where it is not a Monte Carlo model could give only a first approximation.

Numerical integration of rate equations has been used,[5] but again each mechanism requires a rather different treatment. Accuracy varies from case to case, but would generally exceed that of a Monte Carlo model.

An analog computer method which simulates chemical reaction with models based on electrical circuits has had much application in chemical engineering.[6] The purpose of this method, like that of the Monte Carlo model, is the construction of concentration–time curves without integration of rate equations. Accuracy of the two is about the same. The usual much greater accuracy of digital over analog machine is lost in the Monte Carlo method because of its statistical nature. Choice between the two might often be governed by the type of machine available. One point strongly in favor of the analog method is its speed; only a few seconds of running time are required. On the other hand, a particular reaction either can or cannot be simulated on a given analog computer, but a Monte Carlo model of nearly any reaction can be run on nearly any digital machine by increasing computing time or by decreasing required accuracy.

With the analog machine, variation of rate constants must be done by trial-and-error manual adjustment of potentiometers.[7] Because of the greater flexibility of the digital machine, it should be possible to construct a Monte Carlo model which would make an automatic least squares fit of the rate constants to give best agreement between model and experiment. We are at present considering this problem.

Acknowledgment.—The author thanks the Vanderbilt University Computing Center and the National Science Foundation (NSF-G1008) for computing time on the IBM 650 and IBM 7072.

(5) K. B. Wiberg and W. H. Richardson, *J. Am. Chem. Soc.*, **84**, 2800 (1962).

(6) T. J. Williams, *Ind. Eng. Chem.*, **50**, 1631 (1958).

(7) A combined digital–analog computer by Minneapolis–Honeywell which might overcome this difficulty was recently reported in *Chem. Eng.*, **70**, 42 (1963).

[CONTRIBUTION NO. 1154 FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY, BLOOMINGTON, IND.]

Studies of Boron–Nitrogen Compounds. VI.[1] Chemical Properties of the Isomers of 1,3,5-Trimethylcycloborazane

BY DONALD F. GAINES AND RILEY SCHAEFFER

RECEIVED JULY 12, 1963

The unsymmetrical isomer II of 1,3,5-trimethylcycloborazane forms a 2-mono and 2,4-dichloro substitution product with hydrogen chloride at −78° and 0°, respectively. The symmetrical isomer I, however, forms a 2,4,6-trichloro substituted product at 0°. The acid-catalyzed methanolysis of II produces a 2-methoxy product at 0°, and rate studies indicate that the reaction is first order in both catalyst and II. The methanolysis of I under the same conditions, however, results in a mixture of mono-, di-, and trimethoxy substitution products. Dehydrohalogenation of the 2,4-dichloro substitution product of II with trimethylamine gives nearly quantitative yields of hydrogen and 1,3,5-trimethylborazine, presumably *via* the unstable analog of cyclohexadiene, $B_3H_4N_3H(CH_3)_3$. Dehydrogenation of I and II with sodium amide in liquid ammonia or trimethylamine yields 1,3,5-trimethylborazine.

Introduction

The addition to borazines of three equivalents of water, alcohols, and hydrogen halides was described some years ago[2] and was thought to result in cyclohexane-type products. However, little evidence was presented to support this assumption. The first example of an adequately characterized cycloborazane was 1,3,5-trimethylcycloborazane (prepared by Bissot and Parry in 1955).[3,4] Subsequently, 1,3,5-hexamethylcycloborazane[5] was prepared and n.m.r. studies[6] indicated that it had a cyclohexane structure. Its chair-shaped conformation was established by single-crystal X-ray studies.[7]

1,3,5-Triethylcycloborazane[8] and the parent cycloborazane[9,10] have since been prepared by several methods, and two isomers of 1,3,5-trimethylcycloborazane[1] have been separated and characterized. Until recently, however, few chemical properties of the cycloborazanes have been reported.

Making use of the two isomers of 1,3,5-trimethylcycloborazane (both isomers probably are in the chair shape; in isomer I all three methyl groups are equatorial, whereas in isomer II two methyl groups are equatorial and the third axial), it has been possible to demonstrate that several of the reactions are definitely related to the structure of the isomers.

Experimental

I. A New Preparation of Cycloborazanes by Reduction of Hydrogen Chloride Adducts of 2,4,6-Trichloroborazines. A. 2,4,6-Trichloroborazine.—In a typical preparation, 2.49 mmoles

(1) For paper V in this series see D. F. Gaines and R. Schaeffer, *J. Am. Chem. Soc.*, **85**, 395 (1963).

(2) E. Wiberg, *Naturwiss.*, **36**, 182, 212 (1948).

(3) T. C. Bissot and R. W. Parry, *J. Am. Chem. Soc.*, **77**, 3481 (1955).

(4) For a description of the nomenclature of the cycloborazanes see ref. 1 and 10.

(5) A. B. Burg, *J. Am. Chem. Soc.*, **79**, 2129 (1957).

(6) G. W. Campbell and L. Johnson, *ibid.*, **81**, 3800 (1959).

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