Kinetic Rate Constants Determined by a Digital Computer

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Abstract

The difficulty of determining rate constants for complex reactions has been overcome with the development of a general digital computer program that can determine up to 10 rate constants in any reaction scheme which can contain as many as 10 components. A given reaction to which the experimental data are to be fit is described to the computer in a short one-step integration subprogram, which solves the differential equations representing the scheme. Only this subprogram needs to be rewritten to change the reaction scheme. Special features of the program and length of calculations are discussed. A copper-chromite hydrogenation of a mixture of linolenate and conjugated linoleate demonstrates what the program does and what is a typical output.

Introduction

Rate constants of simple one-step reactions can be easily determined graphically. When more than one reaction is involved, the determination of all rate constants becomes difficult. The more complex the reaction scheme, the more difficult the determination of each constant.

Complex schemes can be simulated by either analog or digital computers (1,2). Analog computers are easily programmed and are quite useful in determining rate constants when reaction schemes are being developed and different programs are being tried. A disadvantage of the analog is that an operator is required to visually fit the data by a trial and error procedure. The time involved makes this a laborious task when quantities of data are to be analyzed. A digital computer does not require an operator during the fitting process, and a least squares fit replaces a visual fit. Generally, a new and complete digital fitting program has been required for every new reaction scheme. This task involves much time and expense. These problems have been overcome by the development of a general digital fitting program, DRATE, which needs only a minimal reprogramming for differing reaction schemes. The operation, its limitations and special features are discussed here.

Experimental Procedures

The program, DRATE, has been written in Fortran IV for an IBM 1130 computer system with 8 K core, card reader, disk, printer and plotter. The complexity of the program required that it be split into several linked programs and subroutines (subprograms). Further program information will be furnished upon request.

It is necessary to write a one-step integration subroutine, named SKEME, for the differential equations which describe the particular reaction. This subroutine is usually short and can use any integration technique including those supplied by the computer vendor. Thus, to change the reaction scheme only a new integration subroutine needs to be written.

The writing of such a subroutine can be illustrated by using the simple consecutive reaction scheme which follows:

$$A \xrightarrow{\ k_A\ } B \xrightarrow{\ k_B\ } C$$
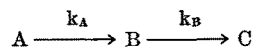
The differential equations describing the concentrations of A and B at time t are given in equations 1 and 2.

$$d[A] = -k_A[A]dt \tag{1}$$
$$d[B] = k_A[A]dt - k_B[B]dt \tag{2}$$

These equations can be formally integrated; however, the integration can be done by the computer. The digital integration method of choice for most kinetic equations is the trapezoidal approximation. In this method the actual difference between the initial values (A_0 and B_0) at time t and the values (A_1 and B_1) at time t + Δt is used to approximate the differential resulting in Equations 3 and 4. Average values of A and B (Equations 5 and 6)

$$d[A] = A_1 - A_0 \tag{3}$$
$$d[B] = B_1 - B_0 \tag{4}$$
$$[A] = (A_1 + A_0)/2 \tag{5}$$
$$[B] = (B_1 + B_0)/2 \tag{6}$$

are used to represent the instantaneous concentrations. Substituting Equations 3 through 6 into Equations 1 and 2 and solving for A_1 and B_1 yields Equations 7 and 8. These equations are then used in the one

$$A_1 = A_0(2 - k_A \cdot dt)/(2 + k_A \cdot dt) \tag{7}$$
$$B_1 = (k_A(A_1 + A_0) + B_0(2 - k_B \cdot dt))/(2 + k_B \cdot dt) \tag{8}$$

step integration subroutine listed below.

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SUBROUTINE SKEME (CONC,RATE,DT,XAXIS,
   IDNO)
DIMENSION CONC(10),RATE(12)
IDNO=3
A=CONC(1)
CONC(1)=A*(2.-RATE(1)*DT)/
   (2.+RATE(1)*DT)
A=A+CONC(1)
B=CONC(2)
CONC(2)=(A*RATE(1)*DT+B*(2.-RATE(2)
   *DT))/(2.+RATE(2)*DT)
CONC(3)=1.-CONC(1)-CONC(2)
XAXIS=XAXIS+DT
RETURN
END
```

Component C [CONC(3)] is determined by material balance and the position on the x axis (XAXIS) is calculated by summing the delta time (DT) units for each integration step taken. The variable IDNO is used to identify the subroutine. The total integration is accomplished by the main line program repeatedly calling this subroutine until the last set of experimental data is reached.

Input data to the mainline program consist of (a) an identification card, which provides up to 80 characters of any type of information; (b) a control card for instructing the computer how to handle the data and what units are being used; (c) a rate constant card, which contains an initial guess as to the values of the rate constants and a time increment for the integration; (d) data cards, which are the experimental data points that are to be fit; and (e) a data

termination card, which indicates that all data has been entered.

The program requires, for plotting purposes, that compositional data have a magnitude of 1 or less. This limitation means that mole fraction, weight fraction or some similar unit needs to be used for the input data. An option is provided to normalize the input data if needed or desired, thus, eliminating any manual calculation. The data are then arranged into a proper time sequence if they were not originally in the correct order. The minimization process then begins. The program follows the minimization technique of Rosenbrock and Story (4) to minimize the summed squared error between the calculated and the experimental data. Once it is determined that all rate constants vary less than 1% between axis rotations in the minimization program, the final printout occurs. The operator has an option to terminate the minimization before this criterion is met and still obtain the final printout. The program can be restarted from the point of operator intervention if desired, and the minimization will continue until the 1% criterion is met. The printout consists of the identification information, the experimental data, the determined rate constants and all possible ratios of them, a sensitivities table which indicates to what precision the rate constants were determined, and finally, a plotted graph of the experimental data and the best fit theoretical curve.

Results and Discussion

The program, DRATE, can be used to determine as many as 10 rate constants from a reaction scheme that may have from 1 to 10 measured components. Two additional rate constants can be entered if they are known and are to be held constant during the fitting process. The limitations of 10 components and 12 rate constants can easily be removed by minor programming changes if the available computer has sufficient storage (core) for the increased number of variables. Actually, to determine as many as 10 rate constants in a complex scheme takes a large amount of computer time and might make such an operation too costly to be worthwhile.

Solution times vary in accordance with the complexity of the integration routine. Since many trials are made to determine the best fit rate constants, the longer the integration, the longer the solution. The more rate constants to be determined, the more trials needed, and the longer the solution. Determining three rate constants in a three-component scheme takes about 15 min on our 1130 computer. Of this 15 min, minimization takes about 5 min and input-output the rest. In a more complex problem where six rate constants were determined from a five-component reaction scheme, the computing time was 5½ hr. Floating point (decimal number) arithmetic
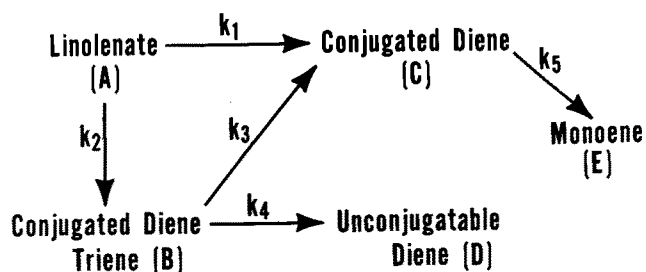
on a 1130 computer is quite slow and the times would be much shorter, possibly by a factor of 10, on computers that have floating point hardware. Thus, the complexity of the reaction scheme and the number of rate constants to be determined are limited only by the speed and size of the computer available. The precision and amount of input data also limit what scheme can be used, but this is not a computer limitation.

One special feature of the program is that data can be fit to any increasing variate, such as time or the amount of hydrogen used in a hydrogenation. In hydrogenating fats, it is common to fit the compositional data to the average number of double bonds. Even though this average decreases, its negative increases. Since it is desirable to have positive values printed out, the program provides the option of printing the absolute values even though the variate being used in the calculation is negative. Consequently, the data can be fit to almost any variate. If the variate is a function of composition which is normally calculated by hand, for example the average number of double bonds, an option is provided to calculate the abscissa position from the input data. Another feature of DRATE is that the plotted output is self-scaling so that a reasonable size graph is produced for any type of unit used for the abscissa. A third feature is the option of stopping the program in the middle of a calculation with or without printout and being able to restart the program from the point of termination at a later time.

A typical problem would be the determination of rate constants for the hydrogenation of a mixture of linolenate and conjugated linoleate with a copper-chromite catalyst. The proposed scheme for this reaction is shown in Figure 1. Experimental data

FIG. 2. Computer printout of determined rate constants for the copper-chromite reduction of linolenate.

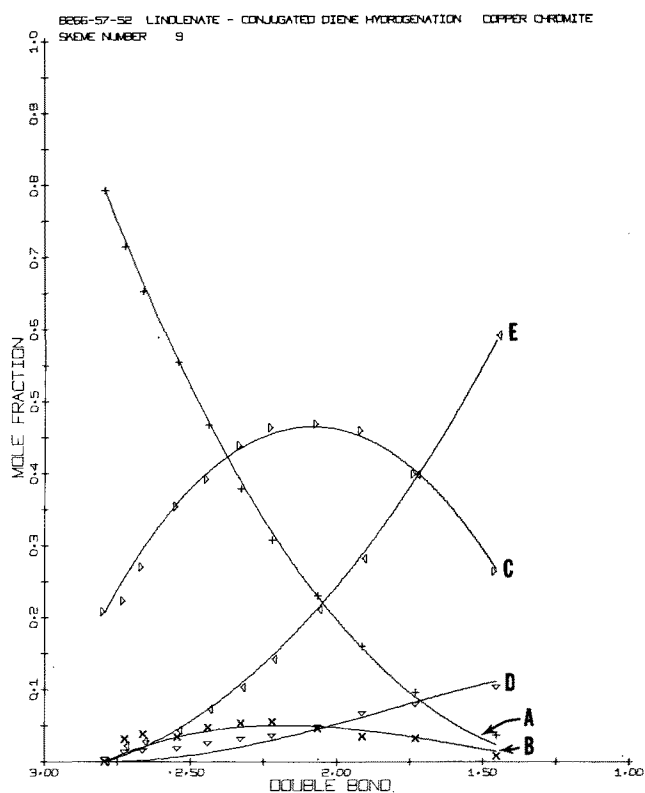FIG. 1. Reaction scheme for copper-chromite reduction of linolenate.

FIG. 3. Computer-drawn graph of experimental data and best fit theoretical curves for linolenate (A), conjugated diene-triene (B), conjugated diene (C), unconjugatable diene (D), and monoene (E).

obtained by Koritala et al. (3) was fit to the scheme by use of DRATE. In this example the data was fit to the average number of double bonds which in effect eliminates time as the independent variable, thus, only ratios of the rate constants determined are of value. To assure that the problem would converge on a set of rate constants, K1 was not permitted to change (a program option allows any specified rate or rates to be held constant) so that the ratios would be established with respect to a rate which was known to have a significant value. The output of DRATE is listed in Figure 2. The first page is printed during the fitting process and shows how the fitting process is proceeding. The number of successful trials (IS), i.e., those reducing the total error; unsuccessful trials (IU); and axis rotations (IC) are printed along with the values of the rate constants used in the last successful trial. When the rate constants are changing less than 1% between axis rotations, the final printout occurs starting on page 2. The data are reproduced in the form used by the computer to check that no errors were made in entering the data. The identification number of the reaction scheme subroutine, SKEME, is printed to assure that the correct one was used along with the total error figure which indicates how good the fit is. The next few lines list the best fit rate constants. Had the data been fit with respect to time, these rates would have been the answer desired, however, in this example only the ratios of these rates are of value. The computer lists all possible ratios permitting easy comparison between runs. Page 3 lists a sensitivity table where each rate is varied, one at a time, by plus and minus 5%. The values in the table represent the ratio of the error for the changed solution to that of the best fit solution. These values demonstrate how much a 5% change in a rate constant will affect the total error and give the operator an idea of how precisely his data have defined the rate constant. The final step of the program is a graph (Fig. 3). This graph is specially useful in indicating poor data points and in giving an impression of how good the fit is, aspects that the total error figure on output page 2 cannot communicate.

Program DRATE should serve anyone who determines rate constants routinely and who has a digital computer available. The program is as general as possible and requires only a minimum of programming for changing reaction schemes.

REFERENCES

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