NOTATION

C_1, C_2, C_3, = constants defined in the text
D = diameter, cm.
g = gravitational constant
m = mass, g.
Q = flow rate, cc./sec.
R = radius, cm.
t = time, sec.
U = velocity, cm./sec.
V = volume, cc.

Greek Letters

β = term in Equation (10) as defined in Equation (13)
Ψ = Harkins' correction factor
ρ = density, g./cc.
σ = interfacial tension, dynes/cm.

Subscripts

D = drop
j = jet
N = nozzle
t = terminal, applying to the drop after detachment
1 = first phase of drop formation
2 = second phase of drop formation

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Computerized Catalytic Kinetics: A Useful Extension of the Method of Wei and Prater

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An extension of the method of Wei and Prater has been devised for determining the relative rate constants for an isothermal, first-order, reversible, three-component system, namely, the catalyzed isothermal isomerization of *n*-butenes. The new method reduces the required work to one experiment.

Wei and Prater (*1*) developed an interesting and elegant method for evaluating the kinetic parameters of monomolecular or pseudomonomolecular, first-order multicomponent systems. Its application, however, has usually required as much experimental work as the classical approach, where the relative rate constants are derived from the initial product ratios. Because of this, and because the mathematics appear forbidding, the method has not been widely used by catalytic chemists, even for those systems where its utility has already been demonstrated, for example, the isomerization of the *n*-butenes. The real value of this work, then, has been that it has clarified the limitations of kinetic studies and has defined exactly what can and cannot be derived therefrom.

The purpose of the present paper is to present a simple extension of this treatment which leads to a great reduction in the amount of experimental work needed to define the system completely. This was done without excessive complication of the computation involved. The new approach was applied to the isomerization of *n*-butenes (a coupled, first-order, ternary system) over a carefully purified Na-Y-zeolite. It is convenient therefore to limit the following discussion to this system.

Faith and Vermeulen (*2*) also developed a method to calculate the absolute rate constants of a three-component system based on the Wei and Prater analysis. This method used only a few points of a single-reaction path and involved a graphic matching of experimental points to a master plot which had been previously constructed. In order to improve its accuracy, it would be necessary to apply curve fitting techniques to the graphic step, to increase the number of experimental points, and, perhaps, to apply an iterative method to the results obtained from the master plots. Although a computer could obviously be adopted for this purpose, a more direct method was derived.

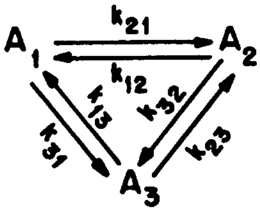
THEORY

Wei and Prater (*1*) have shown that given a first-order real system (where $A_1 \equiv$ 1-butene, $A_2 \equiv$ cis-2-butene, and $A_3 \equiv$ trans-2-butene), it is possible to find a mathematically equivalent system of hypothetical species B_i of the type

B_0 does not react ($\lambda_0 = 0$)

$$B_1 \xrightarrow{\lambda_1} 0$$

$$B_2 \xrightarrow{\lambda_2} 0$$



This mathematical transformation uncouples the variables and thus eliminates the principal feature of the A_i system which makes it difficult to evaluate the rate constants k_{ij}. The time evolution of the A_i system in matrix notation is

$$d\vec{\alpha}/dt = K\vec{\alpha} \tag{1}$$

Similarly, the time evolution of the B_i system is represented by:

$$d\vec{\beta}/dt = \Lambda\vec{\beta} \tag{2}$$

where Λ is a diagonal matrix with elements 0, λ_1, λ_2 and $\vec{\beta}$ is the composition vector in the B_i system.

Wei and Prater (*1*) have shown that

$$\vec{\alpha} = X\vec{\beta} \quad \text{and} \quad \vec{\beta} = X^{-1}\vec{\alpha} \tag{3}$$

where $XX^{-1} = I$ and $X = (\vec{x}_0, \vec{x}_1, \vec{x}_2)$; $\vec{x}_0, \vec{x}_1, \vec{x}_2$ are the three unit characteristic vectors. When only relative rate constants are required, it is sufficient to determine the ratio λ_1/λ_2. For this purpose they (*1*) derived

$$\log b_1/b_1^0 = (\lambda_1/\lambda_2) \log b_2/b_2^0 \tag{4}$$

where b_1 and b_2 are the concentrations of the hypothetical species B_1 and B_2, and b_1^0 and b_2^0 the initial values of these variables. Therefore the ratio λ_1/λ_2 can be obtained from the *best fit* of the concentration data in the B_i system.

Finally, it was shown (*1*)

$$K = X\Lambda X^{-1} \tag{5}$$

and this relationship also holds for the relative rate constant matrices:

$$K^* = X\Lambda_r X^{-1} \tag{6}$$

where K^* is the relative rate constant matrix which can be normalized by making one of the $k_{ij} = 1$ (in our case $K^* = k_{21} K_r$).

The method of Wei and Prater required the following experiments: (1) the determination of one highly curved reaction path, for example, that for reactant pure cis-2-butene; (2) performing several additional experiments (usually three to five) to locate by successive approximations the initial composition of the straight line reaction path. Therefore, a way was sought to calculate all of the kinetic parameters from the results of a single experiment.

The degree of fit of the experimental points to the straight line given by Equation (4) depends on two factors: the intrinsic experimental error in the determination of the points of a highly curved path, and the error in establishing the initial composition of the linear path. Provided that the experimental points are sufficiently accurate, the fitting of the equation will be very sensitive to small changes in the second variable.[†] This suggested the possibility of choosing as the initial composition of the linear reaction path that value which provides the best fit of the data in the B_i system. In developing a statistical method to apply this criterion, it must be borne in mind that both b_1 and b_2 are subject to comparable errors, since both are derived from the concentration measurements. Equation (4) can be written $\ell_1 Y + \ell_2 Z = 0$. The measured variables will be z_i and y_i, which are related to the true values, Y_i and Z_i by $z_i = Z_i + \nu_i$ and $y_i = Y_i + \mu_i$. By assuming that the expectations of the errors, $E\mu_i = E\nu_i = 0$, that the errors μ_i and ν_i are uncorrelated with each other, that the successive observations are uncorrelated, and that var μ_i = var ν_i, Madansky (*3*) derived an unbiased estimator of the slope $(-\ell_1/\ell_2)$. The last assumption is the most critical in our case, but it would appear to be the best approach since both variables are of the same kind and are derived from measurements made with the same instrument. This estimator will be derived here by an alternative method which adapts itself for computational purposes. It was assumed, for this problem, that the sum of the squares of the *perpendicular* distances to the best fitting line is a minimum, that is

$$\Sigma(\ell_1 y_i + \ell_2 z_i)^2 = \min \tag{7}$$

Differentiating Equation (7) with respect to ℓ_1 and ℓ_2 and setting them equal to zero, lead in matrix notation to

$$\begin{bmatrix} \Sigma y_i^2 & \Sigma y_i z_i \\ \Sigma y_i z_i & \Sigma z_i^2 \end{bmatrix} \begin{bmatrix} \ell_1 \\ \ell_2 \end{bmatrix} = 0 \quad \text{or} \quad S\ell = 0 \tag{8}$$

For simplification, let $\Sigma y_i^2 = p$, $\Sigma z_i^2 = q$, and $\Sigma y_i z_i = r$. If δ represents the eigenvalues of the system, then $|S - \delta I| = 0$. Solving the determinant

$$\begin{vmatrix} p - \delta & r \\ r & q - \delta \end{vmatrix} = 0 \tag{8a}$$

one finds that

$$\delta = \frac{p + q \pm \sqrt{(p - q)^2 + 4r^2}}{2} \tag{9}$$

The roots δ_1 and δ_2 are both positive, but of course the smallest, δ_2, is chosen. It can be easily demonstrated, using simple matrix algebra, that

$$\delta_2 = \Sigma(\ell_1 y_i + \ell_2 z_i)^2 = \min \tag{10}$$

The proof is as follows:

$$\Sigma(\ell_1 y_i + \ell_2 z_i)^2 = \Sigma(\ell_1^2 y_i^2 + \ell_2^2 z_i^2 + 2\ell_1 \ell_2 y_i z_i) = \ell' S \ell \tag{11}$$

where $\ell' = (\ell_1 \ell_2)$. Multiplying $S\ell = \delta_2 \ell$ by ℓ' yields $\ell' S \ell = \delta_2 \ell' \ell$. Therefore $\ell' S \ell = \delta_2$; Q.E.D.

Combination of Equations (8), (8*a*), and (10) yields the estimator of the slope

$$-\ell_1/\ell_2 = (q - \delta_2)/r \tag{12}$$

which is identical with Madansky's result (*3*).

In brief, the fitting technique consists of assuming various values of the initial composition of the linear path of reaction until the one is found which gives minimum value of δ. Note that once a value for the initial composition of the linear reaction path is assumed, this, together with the equilibrium composition, is sufficient to determine the matrix X. Data can then be transformed to the B_i system, fit to the straight line [Equation (4)] and δ determined. A Control Data 1604A computer was programmed to search for the minimum value of δ and to print the results corresponding to this choice. The output includes the computation of K_r and the calculation of six theoretical reaction paths starting from different points on the reaction simplex. The calculated theoretical paths were recorded on magnetic

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[†] The composition vector $\vec{\beta}$ is related to $\vec{\alpha}$ through Equation (3). If $\vec{\alpha}$ is accurately known, $\vec{\beta}$ will reflect small variation in X and it is the latter which depends upon the initial composition of the linear path.

tape which then was fed into a 30-in. digital X-Y CALCOMP plotter. In this way the theoretical paths were plotted directly on the triangular diagram. The computer program will be furnished on request.

EXPERIMENTAL

Reactor

A static reactor similar to that used earlier (4) was employed in the present work. It was a 300-cc. spherical Pyrex bulb with a 20 mm. O.D. thimble which extended 11 cm. below the bulb. This thimble contained a glass thermocouple well which permitted the measurement of the reaction temperature in the center of the catalyst bed. The temperature was continuously recorded and controlled to within ±0.5°C. of a given temperature by a Thyratron controller. The gas was stirred by convection, which proved to be satisfactory. The reactor was connected through a standard taper joint to a BET-type gas handling system.

Catalyst and Pretreatment

The catalyst was Linde Na-Y zeolite (lot No. 1280-133). After repeated exchange with NaAc, the CaO analysis dropped to 0.028% and the degree of cation deficiency was greatly reduced.

Before each experiment the catalyst was evacuated and pretreated with oxygen at 1 atm. pressure at 500°C. twice for half an hour each time, and finally was evacuated at the same temperature until a flat vacuum in a McLeod gauge was obtained. The catalyst was white and remained so after the reaction.

Reactants

The 1-butene and cis- and trans-2-butene (Phillips Research Grade) were at least 99.8% pure. Where traces of moisture were a factor, the gas was vacuum transferred from −78° to −195°C.

Procedure

In all these experiments 76 mg. dry weight of catalyst were used. After pretreatment, an amount of water equivalent to 2.0 molecules/cage was admitted into the reactor at room temperature. The reactor thimble was surrounded by the furnace before the reactant was admitted. In each run 55 cc. (NTP) of reactant were used and 1.5-cc. samples were withdrawn periodically during the reaction and analyzed by GLC.

The reaction was clean for all practical purposes, but some secondary products did develop after long reaction time, when the *n*-butene mixture was close to equilibrium. These products were isobutene, *n*-butene, iso-butane, and butadiene, but they never totaled more than 0.5%.

RESULTS

A series of experiments was carried out at 260° starting at six different points in the reaction simplex. The results are shown as the points in Figure 1. Note that three duplicate experiments (I, II, and IV) were made to define the highly curved path obtained when starting with pure cis-2-butene. The six relative rate constants were calculated by the method outlined above from the results of each of these experiments. The results are listed in Table 1, where also are given (column 3) the calculated values of the initial composition of the straight line reaction path. A mixture of about this composition was made and the straight line was verified experimentally (experiment III of Figure 1). This initial composition, together with the results of experiment I, were used to calculate the relative rate constants by the method of Wei and Prater (*1*), and these are listed for experiment III in Table 1.

The results from experiments I, II, and IV are plotted in another way in Figure 2. The ratio k_{12}/k_{32} was taken from the zero conversion intercept. Using this ratio and the experimental ratio k_{21}/k_{31}, obtained in the same way from experiments V and VI, together with the three equilibrium constants from Golden, Egger, and Benson (5), another set of relative rate constants was calculated. The initial 1-butene/cis-2-butene ratio was also determined experimentally $k_{13}/k_{23} = 2.3$, starting with pure trans-2-butene (experiment VII), and it was found to be in good agreement with the results shown in the last column of Table 1.

Despite the fact that the computer determines and prints only the minimum value of δ, it was considered worthwhile for better visualization to plot the results for several choices of the initial composition of the linear reaction path. The example given in Figure 3 shows the variation of δ with the change in choice of initial composition (for experiment II). Figure 4 shows how the plot of log b_1/b_1^0 versus log b_2/b_2^0 changed from a straight line to a curve when the initial composition was varied toward either side of the best value.

All of the lines drawn through the points in Figure 1 are theoretical paths calculated by the computer using only the data from experiment I. The agreement with experiment demonstrated that the system was first order on a conversion basis and also verified the ability of the method to predict new theoretical paths. It was shown that the reaction was also first order on a time basis. Following the criterion of Hightower and Hall (5) the data were plotted in

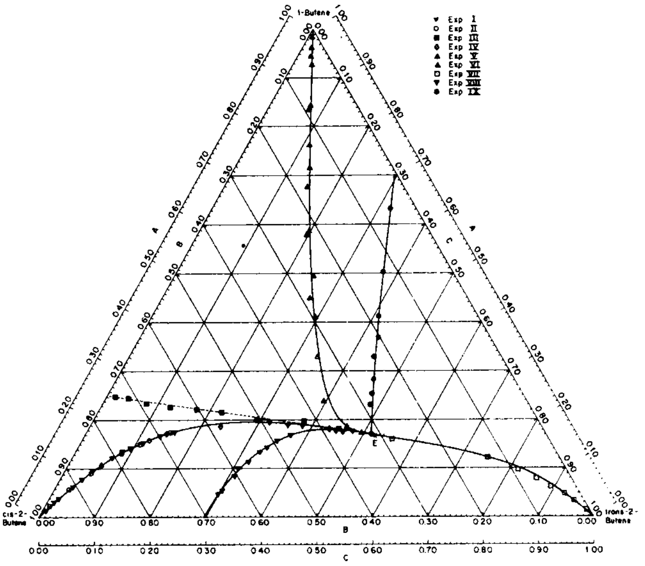

Fig. 1. Composition plot for *n*-butene isomerization over Na-Y-zeolite.

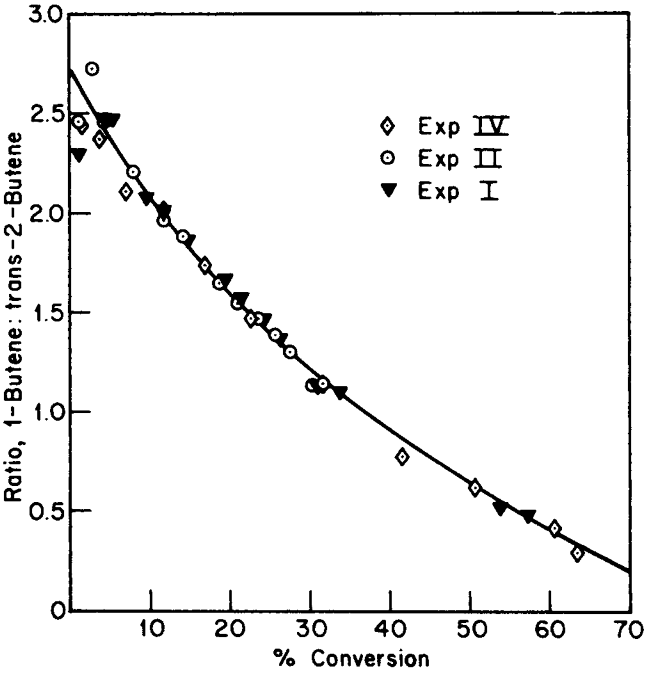

Fig. 2. Product ratio for isomerization of *cis*-2-butene.

TABLE 1. RELATIVE RATE CONSTANTS FOR *n*-BUTENE ISOMERIZATION CALCULATED BY DIFFERENT METHODS*

Exp. No.	$\delta \times 10^5$	Initial Composition** (% 1-butene)	k_{21}	k_{31}	k_{12}	k_{32}	k_{13}	k_{23}	$\frac{k_{21}}{k_{31}}$	$\frac{k_{12}}{k_{32}}$	$\frac{k_{13}}{k_{23}}$
I	0.75	25.1	1.0	0.860	0.547	0.199	0.279	0.118	1.16	2.75	2.36
II	1.43	25.3	1.0	0.847	0.547	0.202	0.274	0.120	1.18	2.71	2.28
III†	0.75	25.1	1.0	0.860	0.547	0.199	0.279	0.118	1.16	2.75	2.36
IV	0.27	25.1	1.0	0.865	0.547	0.207	0.280	0.123	1.16	2.64	2.28
(I, II, IV, V, VI)‡	—	—	1.0	0.860	0.547	0.203	0.280	0.120	1.16	2.70	2.33

*Experiments were made in a static reactor at 260°; catalyst was 76 mg. Na-Y zeolite (dry basis); two molecules/cage of

**Composition of 1-butene, *cis*-2-butene mixture required for straight line reaction path.

water were added as cocatalyst; total gas was 55 cc. (NTP) at 150 torr.

†The rate constants were calculated using the data of experiment I, together with experimentally determined initial composition corresponding to linear reaction path.

‡The rate constants were calculated from the initial product ratios and equilibrium constants.

Figure 5 according to $-\log (N_e - N) = kt - \log N_e$, where N and N_e correspond to conversion at time t and at equilibrium, respectively. Although based on an incorrect model, this kind of plot is valid up to 65% conversion when 1-butene is isomerized under the conditions used. Starting with cis-2-butene, however, this model only holds up to about 15% conversion.

To ascertain the effect of varying temperature during a run, two experiments were performed. In the first, the temperature drifted downward from 325° to 315°C. during the run, while in the second the temperature was held constant at 320° ±0.5°C. The ratio $\log (b_1/b_1^0)/\log (b_2/b_2^0)$, although not needed for actual computation, is a very useful check to determine whether a straight line is really being fitted or if there is a curvature in the plot. When the temperature drifted downward, it was clear that the variation of temperature produced a definite curvature, while at constant temperature the data were randomly distributed on both sides of the best fitting straight line. With the first situation, the results were meaningless. In cases of this kind the computer may not be able to find a minimum value of δ.

Wei and Prater (*1*) suggested a value of $\sigma = 0.5\%$ for careful work with clean systems. This is consistent with our data. When *random* errors of 1% were introduced into a set of theoretical (error-free) data, the computer output showed a comparable increase in the random variation of the $(\log b_1/b_1^0)/(\log b_2/b_2^0)$ ratio. However, no curvature appeared in the log-log plot of these variables. As random errors increase, less accurate values of the relative rate constants are obtained, independent of the method employed in their evaluation. Points close to equilibrium are very sensitive to small errors, because of the increased sensitivity of the $\log b_i/b_i^0$ ratio, and should be avoided.

Obviously if the reaction path turns out to be linear, the method cannot be applied. However, a second isomer can be tested. If its reaction path is also linear, this is the

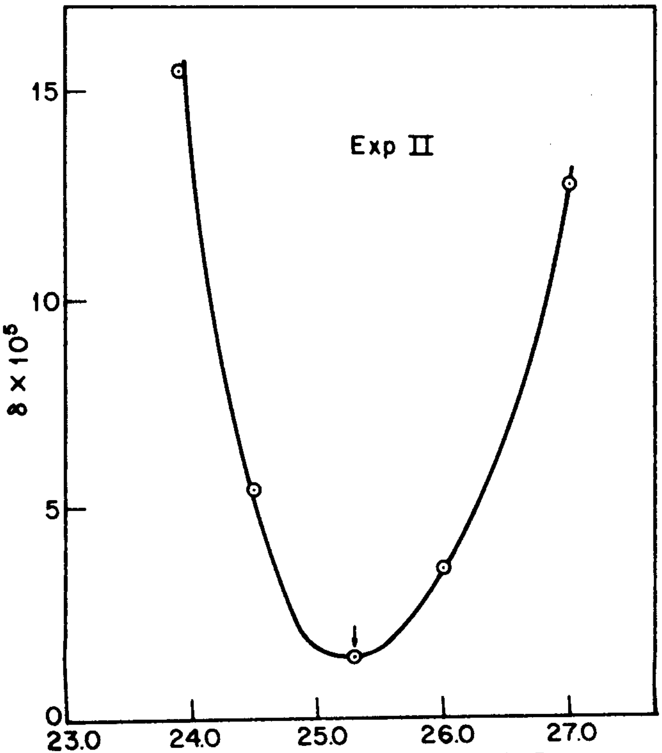

Fig. 3. Choice of initial composition for minimal error.

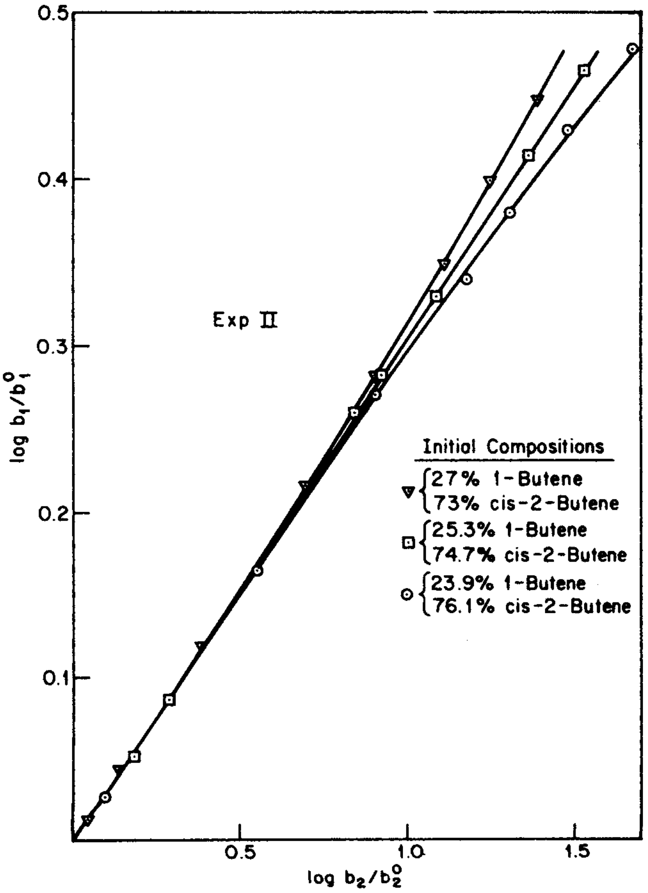

Fig. 4. Effect of choice of initial composition on log-log plot of normalized hypothetical compositions.

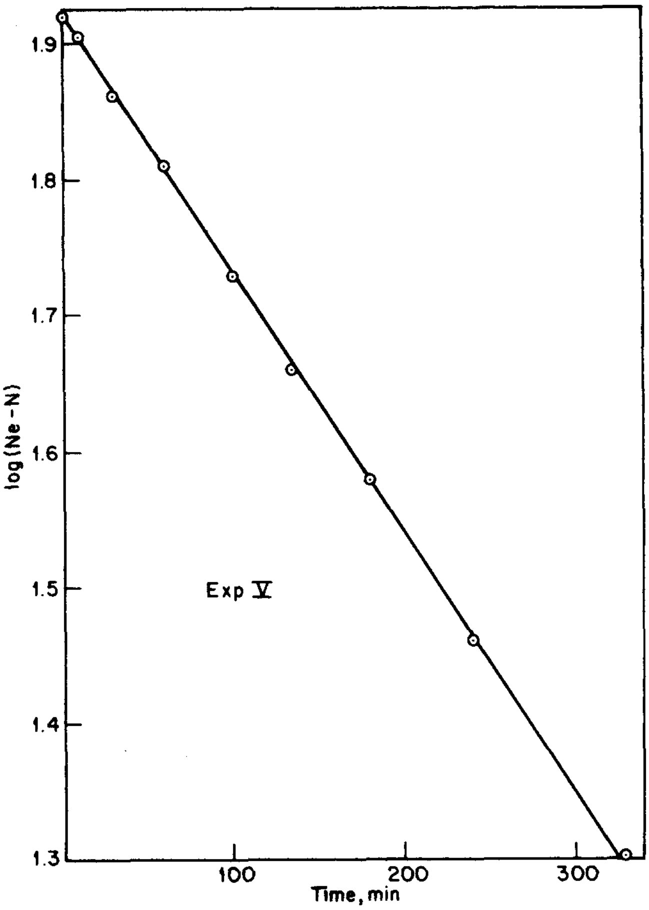

Fig. 5. First order plot for 1-butene isomerization.

trivial case of Wei and Prater (*1*). If the reaction path is curved but very close to a straight line, the rate constants will not be very accurate, but neither will those calculated by any other method.

DISCUSSION

The method of the initial product ratios gave results as reliable as those calculated by the computer method. However, at least two experiments were required and for each of these there was a scattering of the data early in the reaction (Figure 2), which made it difficult to obtain accurate results from a single run. This was not the situation, of course, with the computer method, because the matrix K_r was calculated using the data from many points taken from near 0% conversion to near equilibrium. It follows, then, that the method developed here yields rate constants of comparable accuracy with a minimum of experimental work. There may be some instances, however, where the initial intercept method may provide a more reliable set of relative rate constants than the present method, for example, where serious poisoning occurs during the run. No general statement can be made because the choice will depend on the system, as well as on the object of the experiment.

The computer printout is diagnostic, and this is a useful tool. It distinguishes between random errors and systematic effects by the behavior of the log b_i/b_i^0 ratio printout, which shows either a random scatter or a monotonic change in the variable. In the former case, a straight line will result. In the latter, the extent of curvature will be reflected in the magnitude of the change. Curvature in the log-log plot may be due to systematic errors (for example, drift in temperature), changes in relative rate constants with conversion (poisoning effects), or, perhaps, to such physical phenomena as mass or heat transfer.

Some previously published data (*1*, *4*) for butene isomerization over alumina were processed by the computer method and a definite curvature was found. Although it is impossible to pinpoint the cause in these cases, it can be stated with certainty that it was not from random errors. Additional experiments could now be made, using the diagnostic tool as a guide, to better define the kinetics of this system.

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NOTATION

A_i = three *n*-butenes ($i = 1, 2, 3$)
B_i = three hypothetical species ($i = 0, 1, 2$)
b_i = concentration of B_i
b_i^0 = initial concentration of B_i
K = rate constant matrix
K^* = relative rate constant matrix
K_r = normalized relative rate constant matrix
k_{ij} = first-order rate constants for the reactions relating the product, i, with reactant, j
$k = k_{21} + k_{31}$ = rate constant for the disappearance of 1-butene
ℓ = column matrix with elements ℓ_1 and ℓ_2
ℓ' = row matrix with elements ℓ_1 and ℓ_2
$-\ell_1/\ell_2 = \lambda_1/\lambda_2$ = ratio of the eigenvalues of the system represented by Equation (1)
N = % conversion at time, t
N_e = % conversion at equilibrium
p, q = sum of the squares of y_i and z_i, respectively
r = sum of the products, $y_i z_i$
t = time
X = matrix required for the mathematical transformation from the B_i to the A_i system
$\vec{x}_i$ = unit characteristic vector ($i = 0, 1, 2$)
Y, Z = logarithm of the normalized composition of B_1 and B_2, respectively
Y_i, Z_i = true values of Y and Z
y_i, z_i = measured values of Y and Z

Greek Letters

$\vec{\alpha}$ = composition vector in the A_i system
$\vec{\beta}$ = composition vector in the B_i system
δ_i = eigenvalues of Equation (8) ($i = 1, 2$)
Λ = rate constant matrix in the B_i system
Λ_r = relative rate constant matrix in the B_i system
λ_i = rate constants for the B_i system ($i = 0, 1, 2$)
σ = relative standard deviation
μ_i = absolute error in the measurement of Y_i
ν_i = absolute error in the measurement of Z_i

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