Digital Computer Program for Calculating Selectivities of Hydrogenation Catalysts

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Abstract

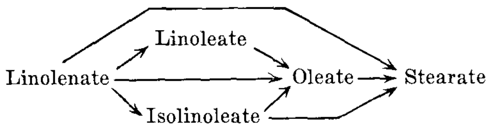
Linolenate and linoleate selectivities of hydrogenation catalysts are determined by a digital computer program which solves the kinetic equations of consecutive first-order reactions. The described program is applicable to any initial oil or degree of hydrogenation.

Introduction

In the literature on hydrogenation of fats, catalyst selectivity has been evaluated by a variety of approaches. Graphical methods for determining catalyst selectivities were exploited by Moore et al. (11) using triangular coordinates. Later Bailey (4) and Boelhouwer et al. (5) qualitatively compared selectivity by plotting against iodine values. In 1965, Albright (1) published computer-generated curves for given oils from which linoleate selectivity can be estimated. Generally, the limitations of these graphical procedures are that linolenate selectivity is not determined, that only oils for which curves have been calculated can be evaluated and that variations in initial compositions of oils are not taken into account.

Bailey (3) was perhaps the first to give a rigorous mathematical treatment of catalyst selectivity, basing his analysis on the kinetics of first-order consecutive and concurrent reactions. By laborious and repeated hand calculations, he arrived at approximate values for rate constants and provided dual mathematical evidence for the existence of an oleate shunt. This laborious process of arithmetic calculation and matching of kinetic data was later applied by Scholfield et al. (13). While their use of radioactively labeled intermediates improved experimental design and confidence in resultant conclusions, it also multiplied the calculations required.

With the advent and widespread availability of analog and digital computers to research workers, methods of evaluating proposed models for reaction schemes and of more accurately determining linolenate and linoleate selectivities became feasible. Examples of the application of analog computer simulation of experimental data are reported by Butterfield et al. (6), Albright and Wisniak (2) and Mounts and Dutton (12). The last-named workers invoked the following model to simulate their experimental results in microvapor-phase hydrogenation.



Besides the need for this comprehensive type of reaction analysis, there is also a continuing demand for a simplified method of calculation to survey and evaluate catalyst selectivity based on initial composition and one set of experimental data points. However, to obtain a solution with only one set of experimental data for a given hydrogenation necessarily limits the scheme to that of the simple consecutive reactions

$$\text{Triene} \xrightarrow{k_1} \text{Diene} \xrightarrow{k_2} \text{Monoene} \xrightarrow{k_3} \text{Saturates}$$

since any more complex scheme would have an infinite number of solutions.

The consecutive reaction scheme was used by Dutton (7) to calculate linolenate selectivity. He added 0.5 mole equivalent of hydrogen to a 50:50 mixture of methyl linolenate and methyl linoleate and then determined the amount of linolenate left which is related to linolenate selectivity. Although this procedure has been used routinely for catalyst surveys (8,9), it does not determine linoleate selectivity, a synthetic mixture must be used for the starting material, and a specific amount of hydrogen has to be added. Circumventing these difficulties is the method of Riesz and Weber (10). Their method permits the calculation of both selectivities and is not limited to any specific initial oil. However, it provides only a good approximation of selectivities.

A more precise determination of catalyst selectivities can be made by the use of an analog computer. Such an analog program, similar to that described by Butterfield et al. (6), has been used in this Laboratory. This program is applicable to any oil with its specific analysis and does not require a specific degree of hydrogenation.

Now a digital computer program can be described which is also in routine but wider use in this Laboratory and combines all the advantages of the analog computer method with those inherent to digital computer systems, such as the elimination of human judgment. A listing of the program in Fortran IV written for an IBM 1130 computer system can be obtained from the authors.

Description of Computer Program

To determine linolenate and linoleate selectivities, the computer must determine A, B and C from the following equations:

$$\mathrm{Ll} = \mathrm{Ll}_o e^{-A} \qquad [1]$$

$$\mathrm{L} = \mathrm{Ll}_o \frac{A}{B-A} (e^{-A}-e^{-B}) + \mathrm{L}_o e^{-B} \qquad [2]$$

$$\mathrm{Ol} = \mathrm{Ll}_o \frac{A}{B-A} \frac{B}{C-A} (e^{-A}-e^{-C}) - \mathrm{Ll}_o \frac{A}{B-A} \frac{B}{C-B} (e^{-B}-e^{-C}) + \mathrm{L}_o \frac{B}{C-B} (e^{-B}-e^{-C}) + \mathrm{Ol}_o e^{-C} \qquad [3]$$

where Ll, L and Ol are the mole fractions of linolenate, linoleate and oleate in the hydrogenated sample and where Ll_o, L_o and Ol_o are the mole fractions of linolenate, linoleate and oleate in the initial oil. These three equations are equivalent to those published by Albright (1) if simple substitutions are made: $A = k_1t$; $B = k_2t$; $C = k_3t$ where k_1, k_2 and k_3 are rate constants and t is time.

Equation 1 is solved for A directly, but equations 2 and 3 have no formal solution for B and C, respectively. Thus, the computer approximates these values by initializing B as a fraction of A, calculating an L

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SAMPLE 8100-56-7A                TRIENE          DIENE       MONOENE     SATURATES
INITIAL OIL                       0.0800          0.5480      0.2200      0.1520
HYDROGENATED OIL                  0.0470          0.5570      0.2440      0.1520
LINOLENATE SELECTIVITY            0.1227E 02a
LINOLEATE SELECTIVITY CAN NOT BE DETERMINED FROM THE DATA
SAMPLE 8100-56-7B                TRIENE          DIENE       MONOENE     SATURATES
INITIAL OIL                       0.0800          0.5480      0.2200      0.1520
HYDROGENATED OIL                  0.0140          0.5260      0.3060      0.1540
LINOLENATE SELECTIVITY            0.1081E 02
LINOLEATE SELECTIVITY             0.2125E 02
SAMPLE 8100-56-7C                TRIENE          DIENE       MONOENE     SATURATES
INITIAL OIL                       0.0800          0.5480      0.2200      0.1520
HYDROGENATED OIL                  0.0000          0.5025      0.3457      0.1517
LINOLENATE SELECTIVITY CAN NOT BE DETERMINED FROM THE DATA
LINOLEATE SELECTIVITY CAN NOT BE DETERMINED FROM THE DATA
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[a] Read as 0.1227×10^2 or 12.27

FIG. 1. Typical computer output of a selectivity calculation.

value, comparing it to the experimental L value and then incrementing B so as to converge on the correct value. The converging process is stopped when B is determined within 0.1%. If experimental accuracy warrants, a more precise determination of B can be made. C is then determined by the same converging process. Linolenate and linoleate selectivities are the ratios A/B and B/C, respectively, which are printed out by the computer.

The program proceeds by entering the molar composition of the initial oil and the hydrogenated oil into the computer. Data are normalized so that material balance is exactly one, and all components are as mole fractions. To prevent the possibility of division by zero, data are then checked to see whether either or neither of the selectivities can be calculated. Linolenate selectivity cannot be calculated if linolenate is not present in the initial oil; linoleate selectivity cannot be calculated if there has been no increase in saturates; neither can be calculated if linoleate is present in the initial oil but not in the hydrogenated oil. The calculation of one or both selectivities, if permitted, proceeds in less than 10 sec on our IBM 1130 computer system. Print out consists of sample identification, the normalized mole fractions of the initial oil and of the hydrogenated oil and the two selectivities, or a statement that either or both could not be calculated. A typical print-out is shown in Fig. 1.

Within the limitation of a consecutive order reaction, the computer program rapidly determines, if data permit, the linolenate and linoleate selectivities of any initial oil composition. The accuracy of the determination is 0.1%, which generally is better than the experimental data warrant.

Discussion

It becomes increasingly apparent that the behavior of the catalyst is best described in terms of the rate constants for the reactions it promotes. Whereas the magnitude of the absolute reaction rates allows the speed with which the reaction will be completed to be predicted, the ratios of reaction rates concurrently determine characteristics of the product. For example, it is the relative rate by which linoleate is reduced to monoene compared to the rate with which monoene is reduced to saturate is one of several factors which determine whether the final product is liquid or solid, *trans* content being another factor. The more widespread use of specific reaction rates and calculation of reaction rate ratios for the characterization of catalysts should be facilitated by the digital computer program described.

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[Received May 29, 1967]