Micro Vapor-Phase Hydrogenation Monitored With Tanden Chromatography-Radioactivity: III. Isomeric Monoenes[1]

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Abstract

Micro vapor-phase hydrogenation and radiotracer techniques have been utilized to investigate the effect of geometric configuration and double bond position on the rate of hydrogenation of octadecenoates. These techniques provide for simultaneously monitoring the time course of vapor-phase hydrogenation both for an essentially pure monoene isomer by thermal conductivity and for methyl oleate by radioactivity. The two hydrogenations proceed independently but have identical parameters of temperature, flow rate and catalyst activity. The experimental data are plotted, relative reaction rates are calculated and theoretical curves are drawn by a digital computer system with plotter accessory. Experiments with nickel catalysts indicate that rates of reduction are affected by both the position and configuration of the double bond. *cis*-15-Octadecenoate is reduced 1.4 times faster than its *cis*-9 isomer. Both *cis*-9- and -12-octadecenoate are reduced at approximately equal rates. *cis*-9-Octadecenoate was reduced 1.4 times as fast as the *cis*-6 isomer. Oleate was reduced 1.27 times as fast as elaidate.

Introduction

Hydrogenation rates for various geometric and positional isomers of oleic acid have not been the subject of a comprehensive investigation. Allen and Kiess (1) studying the isomerization occurring during hydrogenation of oleic acid concluded that their data supported the view of Feuge et al. (7) that all geometric and positional isomers react with equal ease. Dunworth and Nord (4), using paladium and rhodium catalysts, compared the hydrogenation rates of four hexenoic acids. They observed that the rate increases with increasing distance of the double bond from the carboxyl group. Pigulevskii and Artamonov (11) comparatively hydrogenated the 2-, 3-, 6- and 9-octadecenoic acids with platinum. They found that rate of hydrogenation increased with the 6- and 9-isomers. Several other papers have reported the comparative hydrogenations of *cis-trans* isomers of particular double bond positions. For example, petroselinic acid hydrogenated more rapidly than petroselaidic acid (12,13), and oleic acid compared to elaidic acid had a ratio of 1.15:1 (14). It has also been stated that the rate constant of oxidation increases as the double bond moves away from the carboxyl group (12). Scholfield et al. (15) observed that in the monoene produced from a nickel-catalyzed linolenate, there are less 12 monoenes than 9 or 15. While this observation may indicate that the 12 double bond hydrogenates most easily, the difference in monoene composition was thought to be caused by differences in the relative rates of hydrogenation of the dienes. In the same paper they said that platinum-catalyzed reduction of linolenate produced monoenes, the composition of which indicated that the double bonds farthest from the carboxyl group are reduced more rapidly. This concept had also been postulated by Inoue and Suzuki (9). In work on the hydrogenation of methyl linoleate and methyl oleate, Cousins et al. (3) and Feuge and Cousins (6) have supported the thesis that the most distant double bond is hydrogenated most rapidly.

In the third paper of this series the vapor-phase hydrogenation rates of isomeric monoenes have been determined relative to that of the *cis*-9 monoene. Both *cis* and *trans* octadecenoates having double bonds in positions 6 through 12 and 15 have been hydrogenated in the presence of trace amounts of 1-^{14}C-methyl oleate using the micro vapor-phase hydrogenator (MVPH) with a tandem gas liquid chromatography radioactivity system (GLCR) (10).

Experimental Procedures

Each isomeric monoene (>80% purity) has hydrogenated in a mixture with high specific activity 1-^{14}C-methyl oleate. Sufficient 1-^{14}C-methyl oleate 9.2 mc/mM, was added to make the specific activity of the resulting mixture about 1 μc/mg. The catalyst tube was packed with a 0.81% nickel catalyst as used previously (10). Ten separate injections into the MVPH at varying depths provided data for subsequent simulation and determination of relative reaction rates. The series of injections was performed in duplicate for each monoene.

Figure 1 presents a block diagram of the GLCR and data acquisition system. Specific instruments and equipment used are named on the diagram as a part of exact experimental conditions. The partially hydrogenated sample elutes from the MVPH accessory directly into the chromatographic column. Separated constituents are detected by thermal conductivity and, subsequently, by an ion chamber. The electronic signal from each of these detectors is simultaneously displayed on a dual-pen strip chart recorder and stored on a two-channel magnetic tape recorder.

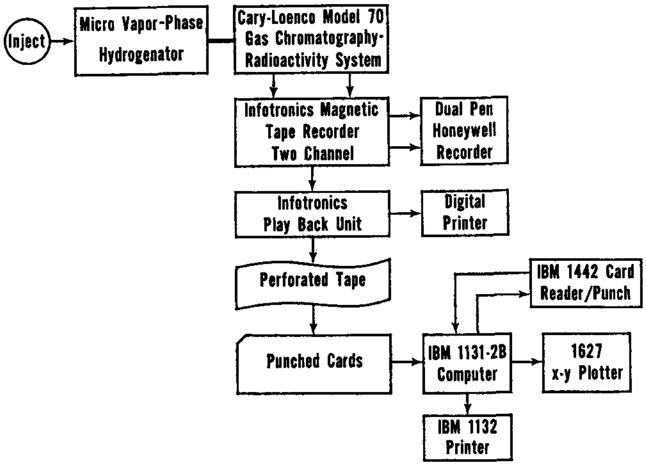

FIG. 1. Block diagram—MVPH, GLCR, data acquisition and data processing.

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[1] Presented at AOCS Meeting, Chicago, October 1967.

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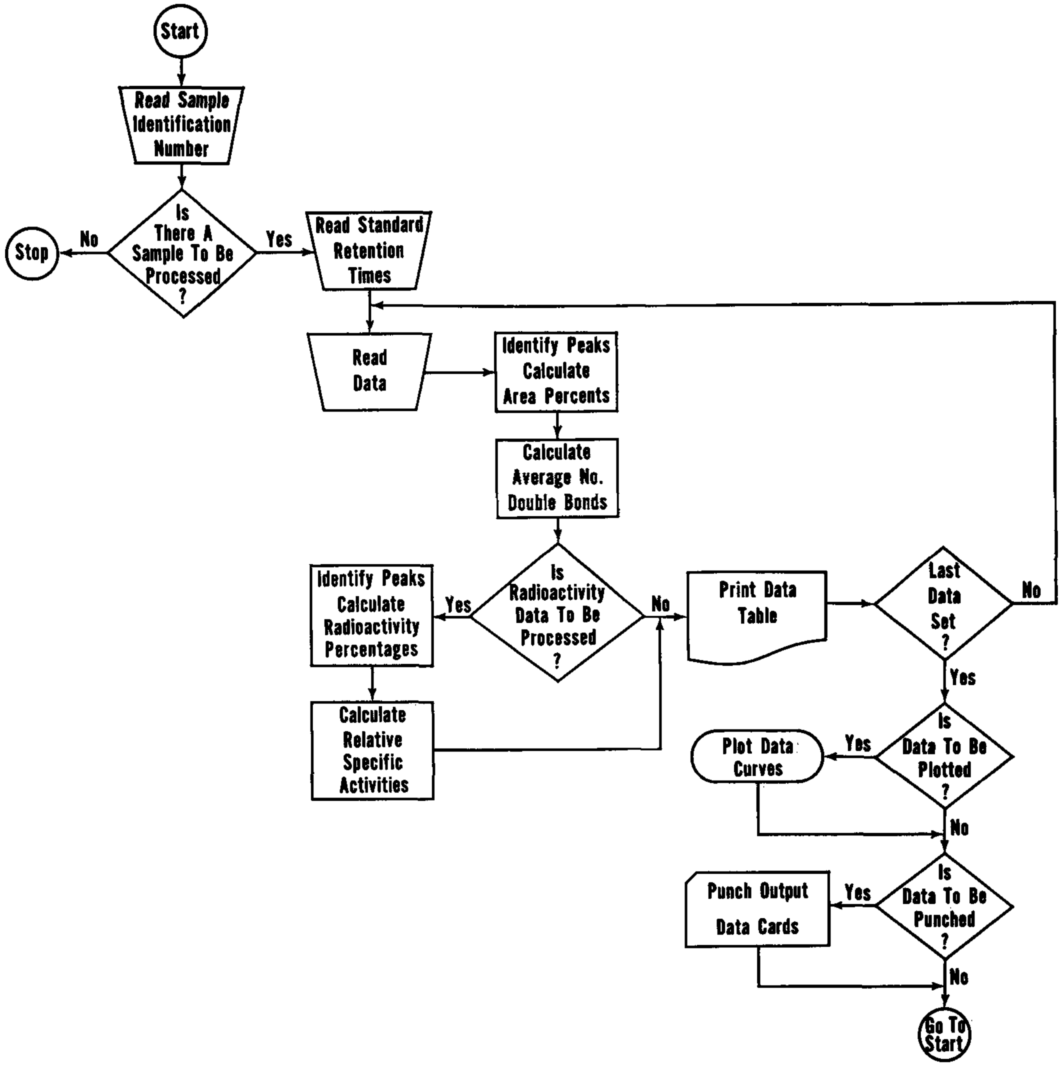

FIG. 2. Flow diagram of digital computer program.

After completion of the series of hydrogenations, data from each were stored individually on the magnetic tape; the digital presentation of the curves was provided by a playback unit which integrates the curves at accelerated speeds. The data were obtained on a digital printer and as a paper tape punched in an appropriate mode compatible with an IBM 1130 computer. Either this tape may be read directly into the computer or punched cards can be produced for manual editing of the data.

The principal steps of the program (Fortran IV, for an IBM 1130) are outlined below and summarized in the flow diagram (Fig. 2). Thermal conductivity peaks were identified by comparison of the peak relative retention time to a series of standard relative retention times. Weight percentages of the individual components are calculated as follows:

$$(m_i/W) = \frac{A_i \quad \sqrt{M_i}}{\sum\limits_i A_i \sqrt{M_i}} \times 100$$

where (m_i/W) is the weight percentage of the ith component; A_i, the integrated area under the chromatographic peak corresponding to the ith component and M_i, the molecular weight of the ith component. The square root of the molecular weight serves as a factor to correct the response of the thermal conductivity detector (5). Average number of double bonds is calculated by multiplying the weight percentage times the number of double bonds in that constituent and summing. Peaks of the radioactivity curve are also identified by comparison of peak relative retention times with standard relative retention times. Radioactivity percentages are calculated, as is the weight percentage; however, the square root function $(\sqrt{M_i})$ is not applied. Relative specific activity data are determined for constituents which have both thermal conductivity and radioactivity peaks and calculated on the basis of the percentage composition as follows: radioactivity per cent/weight per cent. The results are presented as follows: (a) tabular form, (b) as a plot of composition vs. average double bonds and (c) punch cards. Relative reaction rates are determined according to the computer program described by Butterfield (2).

Results and Discussion

Inherent in the design of this isotopic experiment is the concept of two separate compounds being hydrogenated simultaneously but independently. Ther-

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SAMPLE NO.        79.200    CIS 12 / CIS 9 PT
                  CATALYST  DOUBLE  RETENTION WEIGHT     RADIOACTIVITY  RELATIVE
                   BED      BONDS     TIME    PERCENT       PERCENT      SPECIFIC
                   DEPTH                                                 ACTIVITY

                     1       0.84
 CONSTITUENT
18-STEARATE                          7.11    15.6466       12.7704         0.816
18-MONOENE                           8.92    84.3533       87.2295         1.034
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FIG. 3. Computer print-out of calculated data.

TABLE I

Relative Hydrogenation Rates (k isomer/k oleate)[a]

Double bond position	Geometric isomers							
	cis				*trans*			
	Run 1	Error × 10^{-2}	Run 2	Error × 10^{-2}	Run 1	Error × 10^{-2}	Run 2	Error × 10^{-2}
6	0.693	2.0	0.690	0.35	0.734	0.69	0.744	0.25
7	0.783	0.66	0.773	2.3	0.842	0.37	0.815	0.14
8	0.868	0.46	0.851	0.18	0.813	0.60	0.810	0.40
9	0.981	0.97	0.981	0.11	0.793	0.60	0.795	0.96
10	0.868	0.54	0.820	0.54	0.788	0.24	0.781	0.15
11	0.896	0.52	0.860	0.22	0.901	0.08	0.903	0.27
12	0.962	0.59	0.921	0.47	0.928	0.18	0.948	0.89
15	1.422	0.51	1.400	0.39	1.391	0.10	1.350	0.13

[a] All values in table are determined relative to 1-^{14}C-methyl oleate.

mal conductivity presents the analysis for the unlabeled component which, within the limits of detection, is free of methyl oleate. Since the only radioactive component in the sample is 1-^{14}C-methyl oleate, the radioactivity analysis measures the hydrogenation of methyl oleate only. Because of the large amount of catalyst surface compared to the amount of sample injected, competitive interference could not be expected to be a factor in micro vapor-phase hydrogenation (8).

An example of the print-out from the digital computer is seen in Figure 3. The results of each calculation are documented: double bonds remaining, retention time, weight per cent, radioactivity per cent and relative specific activity. Each peak is associated with the appropriate standard and so identified. The data, again prepared by the computer, are plotted in Figure 4. These data are then processed by further computer computations (2) to yield the reaction rates of the isomeric monoene relative to that for methyl oleate (k isomer/k oleate).

The relative reaction rates so determined are presented in Table I.

Rate constants have been fit to the data with the sum squared error as indicated (2). Differences between duplicate runs were less than 2%.

The contention that the rate of hydrogenation in a series of *cis* alkenoic acids increases as the double bond is moved farther from the carboxyl group (3,4,6,9,15) is generally supported by the results presented here. The *cis*-6 monoene hydrogenates at a substantially slower rate than does the *cis*-9 monoene. The double bond in position 15 was highly susceptible to hydrogenation; the rate of hydrogenation of this monoene was 1.41 times as great as that of the *cis*-9 monoene. Some variation from this general trend was noted. First, in that there was little difference between the rates of hydrogenation for the *cis*-12 and *cis*-9 monoenes. Secondly, *cis*-10 and *cis*-11 hydrogenated at rates which were significantly lower than that for *cis*-9.

The *trans*-9 monoene hydrogenates at a much lower rate than does the *cis*-9. This observation confirms that geometric configuration affects the rate of hydrogenation. While the difference in the rates for *cis*- and *trans*-9 is significant, this difference was not reflected in the relative reaction rates of the *cis* and *trans* isomers of monoenes having other double bond positions. Since each reaction rate is determined relative to that of *cis*-9, possibly the double bond position has a greater effect on relative rate of hydrogenation than does geometric configuration.

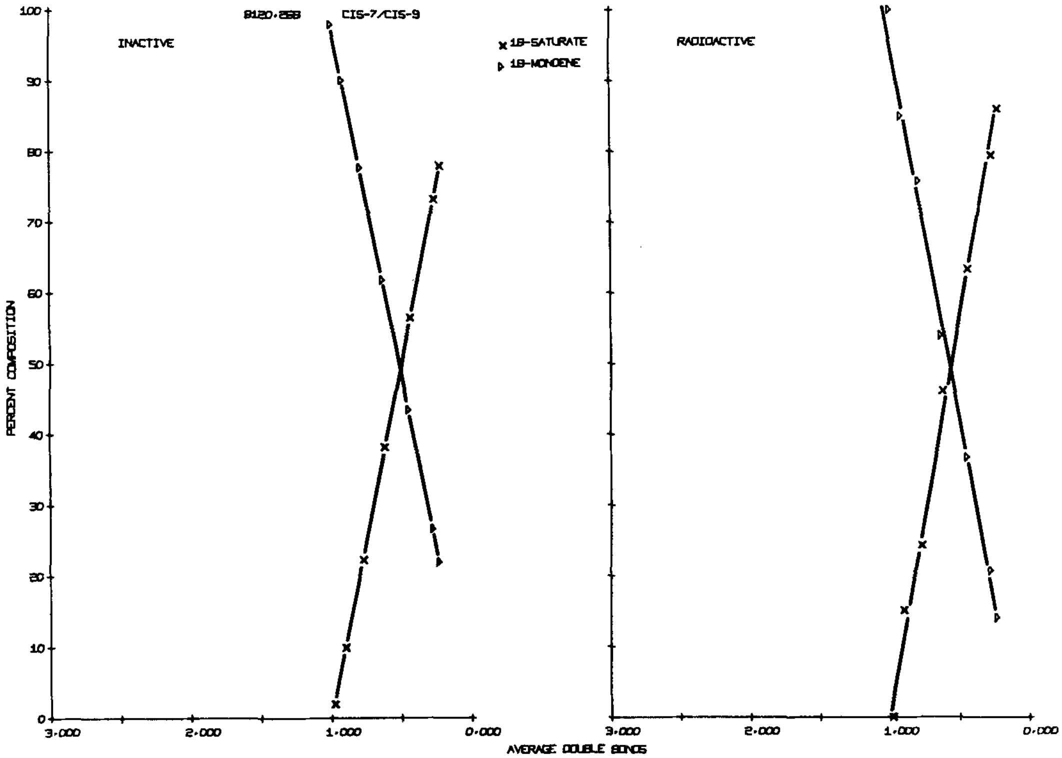

FIG. 4. Computer plot of calculated data.

ACKNOWLEDGMENT

R. J. Meyer (deceased), Morton Chemical Company, prepared the synthetic monoenoic acids.

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[Received June 18, 1969]