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Micro Vapor-Phase Hydrogenation Monitored with Tandem Chromatography-Radioactivity

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Reaction kinetics and selectivity of hydrogenation catalysis have been studied by the microreactor chromatography–radioactivity technique as described.

Vapor-phase reactors monitored by gas chromatography (*1*) have been reported for catalytic oxidation (*2*), polymerization, and cracking (*3*), but so far catalytic vapor-phase hydrogenation studies have been limited to unsaturated hydrocarbons (*4–6*). Beroza (*7*) found that fission takes place with esters and other hetero compounds under conditions which are mandatory for vapor-phase hydrogenation; he exploited this observation, identifying hydrocarbon fragments to determine molecular structures.

In preliminary phases of our work, conditions were discovered which permitted hydrogenation of fatty acid methyl esters. By varying the depth of injection, and thus the effective length of the reactor column, a differential type of kinetic data was obtained. Kinetic patterns for radioinactive compounds and those obtained concurrently for radioactively labeled compounds have been simulated and the ratios of specific reaction rate constants calculated by an analog computer.

Equipment

The micro vapor-phase hydrogenator (Fig. 1) is so designed that it forms an accessory to a gas chromatograph and substitutes for the injection nut and septum. The hydrogen stream normally entering the injection port is diverted to the head of the micro-hydrogenator, and after passing by the silicone diaphragm and through a wool plug, it enters a 43 × 6.3-mm column of packed hydrogenation catalyst. By means of a heating coil and a thermocouple mounted on the exterior of the reactor, its temperature is controlled independently of the column temperature. Effective column lengths up to 43 mm are obtained by injecting a sample into the column with a Hamilton† microsyringe at predetermined distances. Injection at the specified depths is achieved by slipping calibrated sleeves over the syringe needle just before puncture of the septum. Sleeve lengths were calculated from first order kinetics to give equal increments of reaction.

The partially hydrogenated esters pass directly from the microreactor to the head of the gas chromatographic column, move through the column, and finally elute through a thermal-conductivity detector. Radioactivity of the effluent gas is monitored by a continuous flow ion chamber modified for high temperatures (*8*). To facilitate calculation, thermal-conductivity voltages are fed into a Ridgefield electronic integrator, which reads out the value of the integral by means of a bar graph and the

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† The mention of firm names or trade products does not imply that they are endorsed or recommended by the Department of Agriculture over other firms or similar products not mentioned.

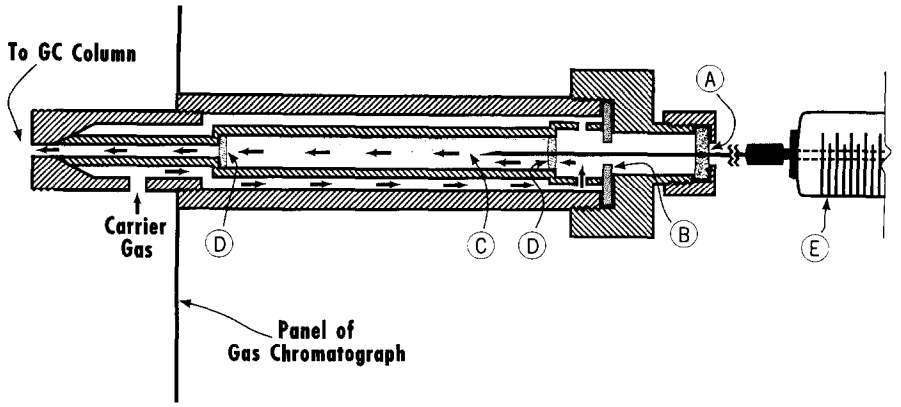

FIG. 1. Diagram of micro vapor-phase hydrogenator: A, silicone rubber septum; B, Teflon gasket; C, catalyst; D, glass wool; E, microsyringe with 4-inch needle.

pip of an operational pen on the recorder chart. Radioactivity data (ion currents) are displayed by a second pen of a two-pen recorder. The integral of this curve, provided by a Pye electronic integrator, is displayed on a second recorder in the familiar stair-step pattern.

PROCEDURE

Preliminary attempts at vapor-phase hydrogenation of fatty esters invariably resulted in fission of the ester molecule. While unsaturated hydrocarbons were successfully reduced, even the lowest chain esters broke up into hydrocarbon fragments when the temperature of the hydrogenator was raised to a degree sufficient to move them through the column. This phenomenon, described by Beroza (7) during the course of our work, seemed to preclude the possibility of achieving a successful reduction of esters in vapor phase; however, by dilution of a catalyst (nickel on Kieselguhr) 100-fold with Chromosorb P (60/80 mesh), complete hydrogenation was achieved in a 43-mm column with no detectable fission. Because hydrogenation is faster than fission, the complete hydrogenation would have occurred on the undiluted catalyst in the first 0.5 mm of column length, leaving the remaining 42.5 mm for rupturing the molecules.

Adsorption of the fatty ester on this catalyst, as well as on the Chromosorb P used to dilute the catalyst, imposes a low temperature limit; 170°C is the minimum temperature usable for eluting the C_{18} fatty acid methyl esters, as judged by the nearly ideal shape of eluted peaks when temperatures above this were tried. Normally, temperature of the chromatographic column is held at 200° for optimal separations.

RESULTS AND DISCUSSION

One application of the instrument, and of the procedures described, is shown in

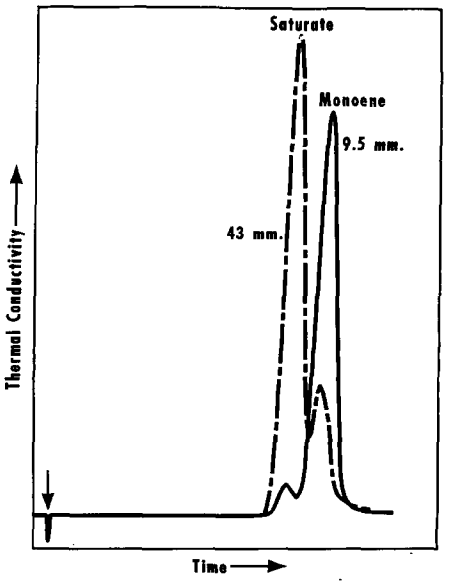

FIG. 2. Chromatogram for methyl oleate hydrogenated in two-column lengths.

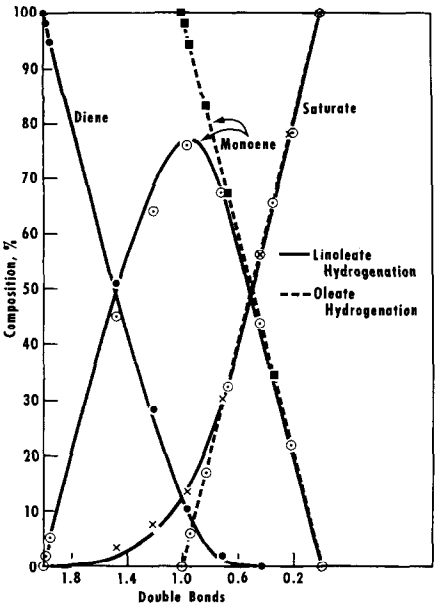

FIG. 3. Percentage composition as a function of double bonds per mole remaining for methyl linoleate and methyl oleate.

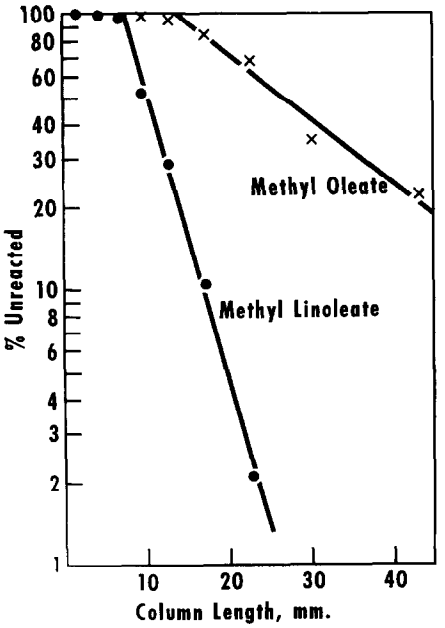

FIG. 4. Log per cent of methyl oleate and methyl linoleate remaining as function of column length.

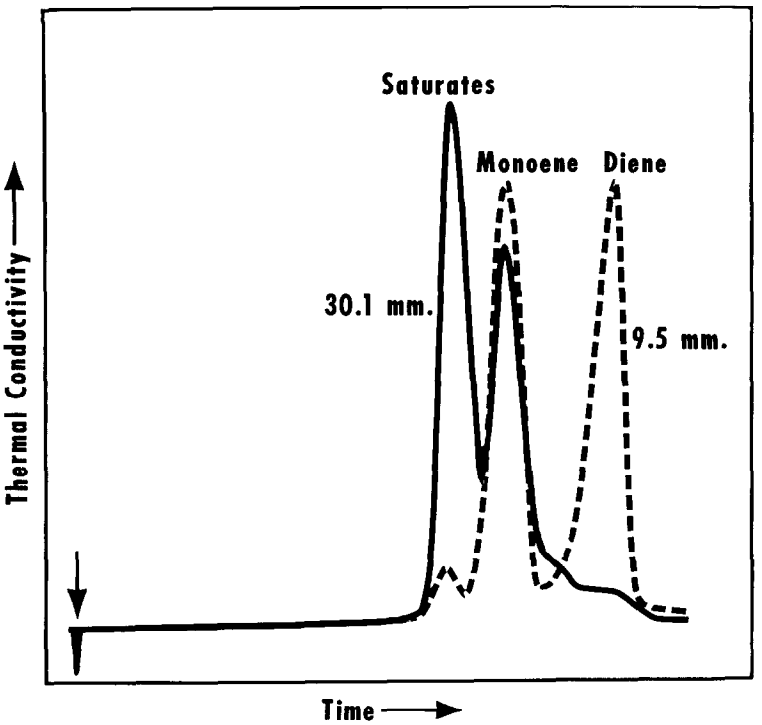

FIG. 5. Chromatograms for methyl linoleate hydrogenated in two-column lengths.

Fig. 2. The specific example is the hydrogenation of methyl oleate. Progressive disappearance of the peak for methyl oleate and increase in the methyl stearate peak are apparent in each of the curves, corresponding to column lengths of 9.5 and 43 mm. Areas under the peaks of these curves, and also those for curves corresponding to lengths of 12.9, 17.1, 22.5, and 30.1 mm (not shown in Fig. 2), have been calculated and are presented by the broken lines in Fig. 3 drawn against the degree of reaction or specifically, the number of double bonds remaining.

The length along the column, as already suggested, has the elements of a time parameter. Since the percentage of oleate plotted on semilogarithmic paper against the length gives an approximate linear representation (Fig. 4), equations for first order kinetics should approximate the data.

The hydrogenation of methyl linoleate constitutes a series of consecutive reactions of the type:

$$\underset{\text{(Diene)}}{A} \xrightarrow[k_a]{+H_2} \underset{\text{(Monoene)}}{B} \xrightarrow[k_b]{+H_2} \underset{\text{(Saturate)}}{C}$$

corresponding to the reduction of diene to monoene to saturate. Typical chromatographic curves corresponding to the lengths of catalyst columns of 9.5 and 30.1 mm are shown in Fig. 5. When the integrated gas chromatographic data for these and two additional column lengths are plotted against the number of double bonds present, the curves (solid lines) of Fig. 3 are obtained. The change in the logarithm of the methyl linoleate percentage with length (Fig. 4), like that for the methyl oleate, approaches linear characteristics after the initial points, which correspond to short lengths on the hydrogenation column. The curves drawn upon Fig. 3 for linoleate reduction are those provided by an analog computer (*9*) programmed for simple, first-order kinetics of consecutive reactions and for a ratio of k_a/k_b of 9.3. With palladium and platinum catalysts and the same temperature conditions, kinetic patterns were similarly determined, but they differed significantly in form from those shown in Fig. 3. In accordance with the known lower selectivity characteristics of palladium over nickel and of platinum over palladium, the ratio of k_a/k_b for palladium was 2.35 and for platinum, 0.918. Whether this qualitative correlation between performance in gas-phase and practical liquid-phase hydrogenation can be established and whether this vapor-phase hydrogenation procedure can be used for the practical evaluation of catalysts are subjects of current research.

Application of a radioactive monitor to the gas stream coming from the thermal conductivity cell is shown in Fig. 6. In this

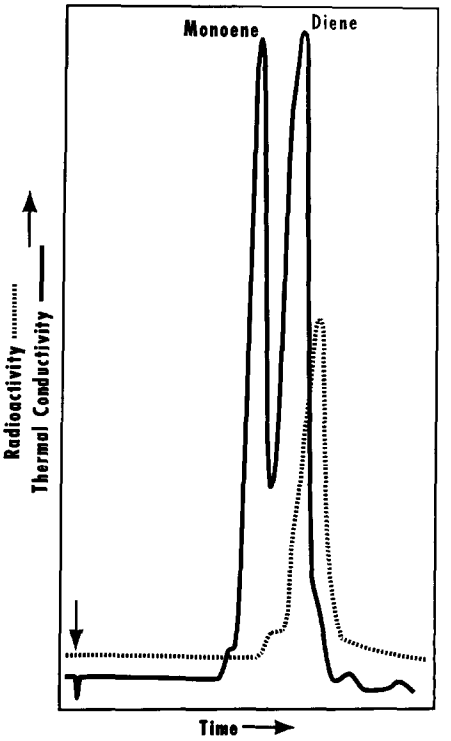

FIG. 6. Thermal conductivity and radioactivity monitoring for vapor-phase hydrogenation of inactive methyl 9,12-octadecadienoate (solid line) and 9,15-octadecadienoate-H^3 (broken line). Column length, 9.5 mm.

experiment 1 μc of 9,15-octadecadienoate labeled with tritium in the 12,13 position (*10*) was injected along with unlabeled 9,12-octadecadienoate (methyl linoleate). The chromatogram for the partially hydrogenated unlabeled 9,12-linoleate is

comparable to that in Fig. 5 (9.5 mm). Obviously, however, with its octadiene structure the labeled 9,15 isomer is quite unreactive compared to the pentadiene structure of methyl linoleate. Because of the isolation of the double bonds in the 9,15 compound, they should, in fact, hydrogenate no more rapidly than does the double bond in methyl oleate.

Other applications and variations of the micro vapor-phase hydrogenation monitored with tandem chromatography–radioactivity immediately suggest themselves. An important analytical application of the microhydrogenation chromatography technique is simplification of the mixture of fatty acids in natural oils by reducing the unsaturated isologs to the corresponding saturated homologs (*11*).

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