• TECHNICAL

Isotopic Effects During Catalytic Hydrogenation[1]

E. D. BITNER, E. SELKE, W. K. ROHWEDDER, and H. J. DUTTON,
Northern Regional Research Laboratory,[2] Peoria, Illinois

Abstract

No isotopic discrimination is observed during catalytic reduction of methyl oleate with hydrogen-tritium gas mixtures. One explanation may be that at atmospheric pressure and 40C the isotopic effect on solubility is small and the concentration of the dissolved hydrogen isotopes is rate limiting. Tritium in methyl 9-octadecenoate-9,10-T is not released during saturation of the double bond but appears in the gaseous phase upon completion of hydrogenation, as indicated by an ion chamber. No isotopic discrimination is observed in the reduction of methyl oleate with mixtures of hydrogen, deuterium, and tritium; however, a mass spectrometer indicates an increase in the hydrogen-deuterium ratio during hydrogenation. Under the conditions described, tritium and deuterium may be used to study the mechanism of hydrogenation without significant isotopic effects.

Introduction

The validity of tracer experiments, particularly for the isotopes of hydrogen, depends on a knowledge of the magnitude of the isotopic discrimination. This isotopic effect on rate constants for hydrogen over tritium has been calculated to be a factor of 60 and, for hydrogen over deuterium, 18. Accordingly, the magnitude of an isotope effect involving tritium or deuterium may be large (1).

This paper presents the measurement of the isotopic discrimination of tritium and deuterium during catalytic hydrogenation of methyl oleate with a) a mixture of hydrogen and tritium, and b) a mixture of hydrogen, deuterium, and tritium. The catalytic hydrogenation of a tritium-labeled compound, methyl 9-octadecenoate-9,10-T, and the description of various specialized equipment and methods of analyses are included.

Experimental

An automatic manometric apparatus was used to perform all hydrogenations. As shown in Figure 1, a servomechanism held the pressure constant within the system by employing a sensor and compensating syringe. A transducer enabled the position of the syringe, or the amount of hydrogen uptake during the reaction, to be recorded by one pen of a dual-pen strip chart potentiometer. The reaction vessel consisted of a 25-ml flask with a slightly rounded bottom, a ground-glass joint, and two side arms; one was fitted with a serum cap to inject or remove methyl ester samples, the other completed the closed circuit loop of the gas system. A magnetic stirrer and thermostated oil bath completed the reactor. The gas was circulated through the ion chamber-syringe reservoir and over the reaction surface by a magetically operated pump. A precision leak valve (Granville Phillips Company) was inserted into the system allowing approximately 0.01 ml per min to flow to the mass spectrometer in order to monitor the gaseous phase for hydrogen and deuterium during a reaction. The level of radioactivity within the system was monitored by a flow-through ion chamber and its associated electrometer and recorded on the second pen of the dual-pen recorder.

One of the important features of the design of this system is its small "dead" volume. Since small changes in concentration of tritium needed to be detected during hydrogenations to measure small isotopic effects, the diluting volume of tubing, pump, and ion-chamber was minimized. The volume of the entire closed-loop system is 100 ml, and the gas uptake is usually 25–50 ml. Thus, the observed concentration change will be a fourth to a half of the maximum effect and can be appropriately corrected.

The procedure for an experiment consisted of weighing the catalyst into the reaction flask, evacuating the system 3 times with hydrogen flushing between evacuations, filling with the mixture of hydrogen isotopes, allowing 15–20 min for the electronic equipment to stabilize, then injecting the methyl oleate, and finally starting the stirrer. The introduction of tritium into the system was accomplished before the final hydrogen filling by allowing successive 0.1 ml aliquots (at 1.0-mm pressure) to expand into the evacuated manometer from a tritium dispenser until the desired level of radioactivity was reached.

Typical examples of the three types of catalytic hydrogenations are tabulated in Table I with accompanying reaction conditions. They consisted of methyl oleate with a mixture of hydrogen and tritium gas (Experiment 1), methyl oleate with a mixture of hydrogen, deuterium, and tritium gas (Experiment 2), and a mixture of methyl oleate and methyl 9-octadecenoate-9,10-T with hydrogen gas (Experiment 3).

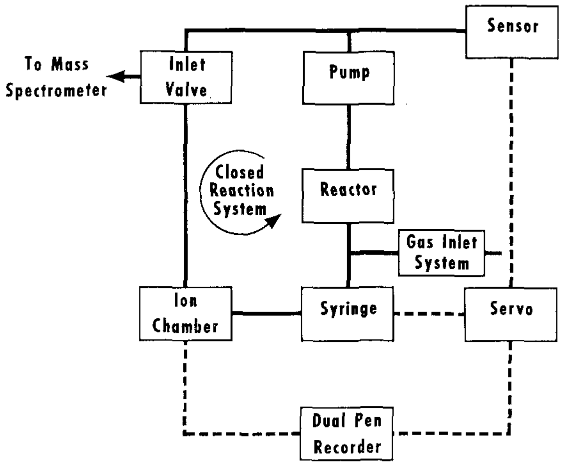

FIG. 1. Block diagram showing manometric system used for hydrogenation experiments.

---

[1] Presented at the AOCS meeting, Toronto, October, 1962.
[2] No. Utiliz. Res. & Dev. Div., ARS, U.S.D.A.

TABLE I

Reaction Conditions of Typical Hydrogenation Experiments (Atmospheric Pressure)

Exp. no.	Starting compound	Gas used	Temp C	Rate of reaction	Radioactivity, μc	
				cc/min	Initial condition	In product
1	Methyl oleate	H,T	Rm.	0.625	163.2	80.4
2	Methyl oleate	H,D,T	40	0.611	21.8	5.9
3	Methyl oleate[a]	H	40	0.542	315.5	251.3

[a] Methyl oleate + methyl 9-octadecenoate-9,10-T.

All experiments were run at atmospheric pressure and either 40C or room temp. The 40C was finally chosen as the desired operating temp to insure a liquid ester phase at complete saturation since methyl stearate, the product, has a mp of ca. 38.5C (6).

The reactions were carried out on a scale of 0.35–0.45 g of ester with a catalyst-ester ratio of ca. 1:4 (wt–wt). A commercial catalyst, 5% palladium-on-carbon powder (5) which has high reactivity at moderate temp and pressure, was used for all runs. Reaction rates as shown in Table I were fairly uniform, and induction periods were observed to vary from 0 to ca. 5 min.

Methyl oleate was obtained by low-temp crystallization, and its purity was determined by gas liquid chromatography (GLC) to be 99.8% with an impurity of 0.2% methyl palmitate.

Methyl 9-octadecenoate-9,10-T was prepared by exposing methyl stearolate to tritium (3).

The thermal conductivity curve of Figure 2 indicates the purity of the parent methyl stearolate and its retention time for comparison with the ion-chamber electrometer trace of the tritiated product. As shown by the electrometer trace, several volatile radiochemical decomposition products precede the elution of methyl 9-octadecenoate-9,10-T. The major and most volatile material is believed to be dissolved tritium gas (7). The radiochemical products consisted of tritiated octadecenoate (88.6% for B in Fig. 2), tritiated stearate (8.7% for A in Fig. 2), and tritiated stearolate (2.7% for C in Fig. 2).

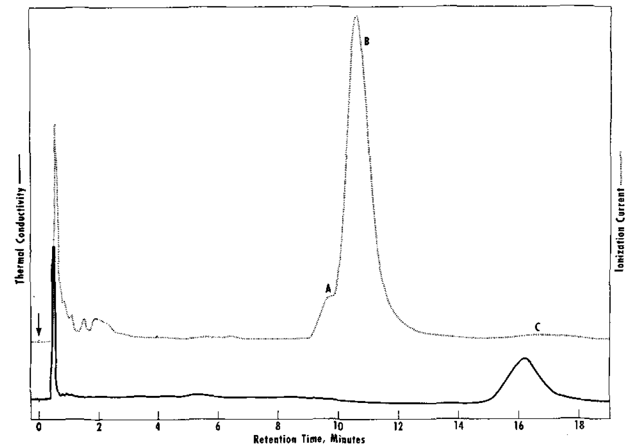

FIG. 2. Thermal conductivity and ion-current records from chromatogram for tritiated methyl stearolate.

Radioactivity was increased in some runs to study the effect of higher tritium concentration. Radiochemical analysis of initial and final products was performed by dissolving the sample in toluene in a 25-ml flask. An aliquot, normally 10 μl, was then placed into vials of scintillation solvent and the radioactivity determined by a liquid scintillation spectrometer.

Results

Typical results of the class of experiments (1 in Table I) involving hydrogen, tritium, and methyl oleate are shown in Figure 3, which is a photograph of a recording. In this figure and successive ones, arrows mark the points of interest on the gas-uptake curve. Point a indicates the place of the injection of

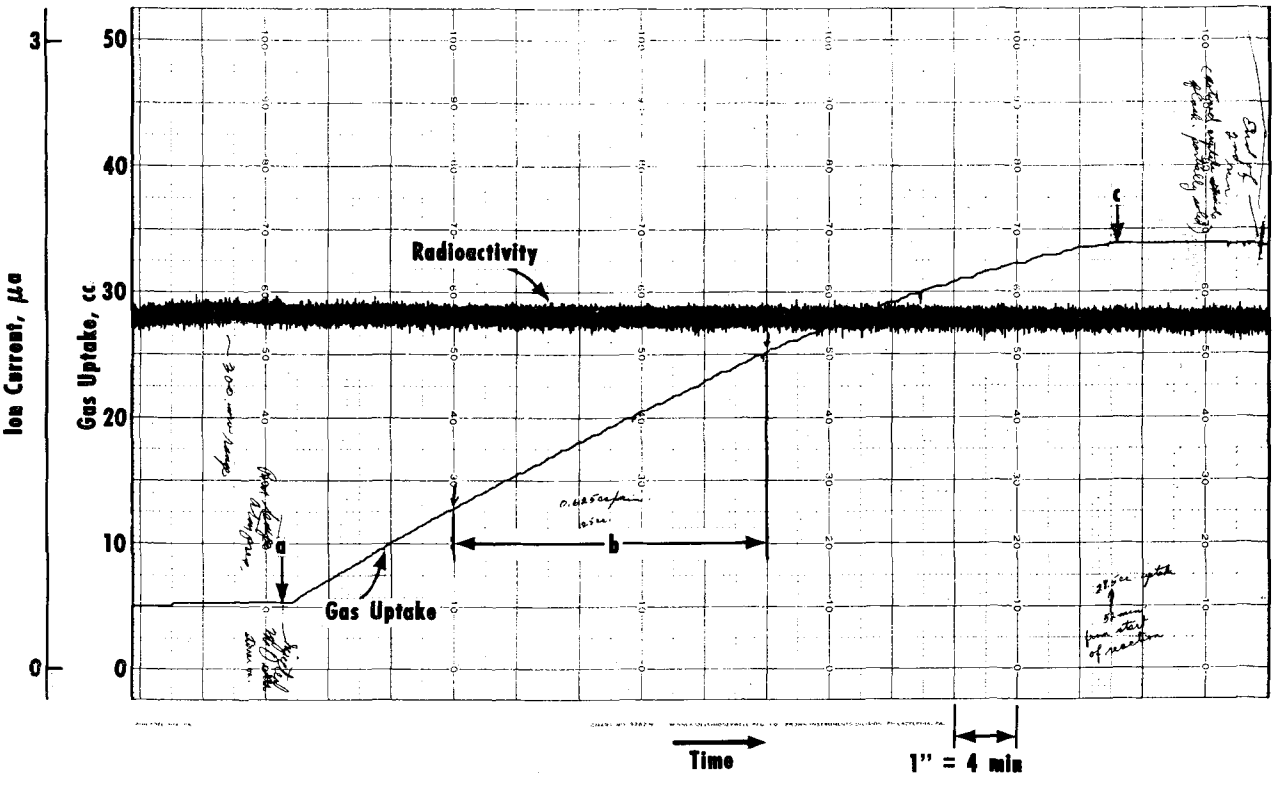

FIG. 3. Hydrogenation of methyl oleate with a hydrogen-tritium gas mixture.

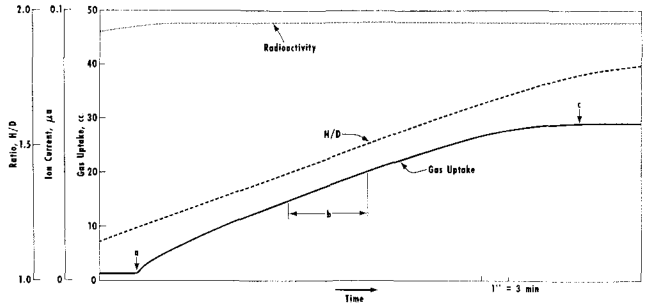

FIG. 4. Hydrogenation of methyl oleate with a mixture of H,D, and T gases.

methyl ester; b the portion of the curve used for calculating rate of reaction; and c the saturation point of the reaction. No isotopic effect is observed since the radioactivity level varies but little during the reaction. The slight change in the ion current of approximately 1% could have been caused by noise, vibrations, drift, or other external factors. This observation means that tritium and hydrogen were absorbed proportionally and without discrimination, leaving their ratio in the gaseous phase unchanged. The conclusion was confirmed upon repeating the experiment five times and increasing the radioactivity concentration fivefold.

The type of experiment employing the 3 isotopes of hydrogen simultaneously in the gaseous phase is exemplified by the results in Figure 4 (2 in Table I). Again, no isotopic effect involving tritium is observed since the radioactivity level does not change during the reaction. However, the monitoring mass spectrometer indicated an increase in the hydrogen-deuterium (H/D) ratio. This phenomenon is in the opposite direction of the anticipated isotopic effect and is discussed in a concurrent paper on deuterium-hydrogen exchange (8).

The results of the third class of experiments, which employed the tritiated ester and hydrogen gas, are shown in Figure 5 (3 in Table I). The gas-uptake curve was typical of previous hydrogenations, but radioactivity varied unexpectedly. An immediate release of radioactive material occurred upon injection of the sample. This initial burst corresponds to the activity produced by the volatile material (largely dissolved tritium gas) in the original compound (Fig. 2). No further release is observed during absorption of hydrogen. At saturation, gradual release of tritium is seen (Fig. 5, d to e). The constant level of radioactivity during the addition reaction indicates that no tritium exchange is taking place and, as in Experiments 1 and 2, that tritium gas is being absorbed at the same rate as hydrogen. The gradual increase in radioactivity in the gaseous phase observed after saturation of the double bonds was evident in seven experiments and has a magnitude of 5–10% of the tritium-labeled octadecenoate injected.

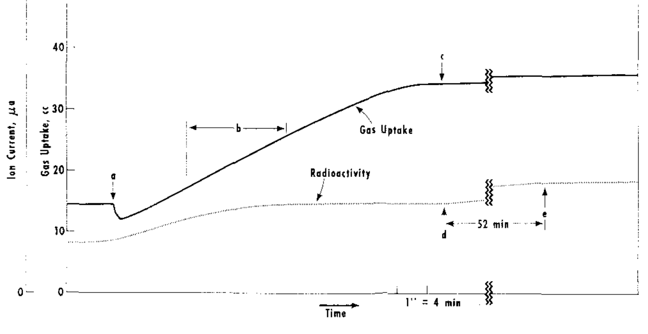

FIG. 5. Catalytic hydrogenation of a mixture of methyl oleate and methyl 9-octadecenoate-9,10-T.

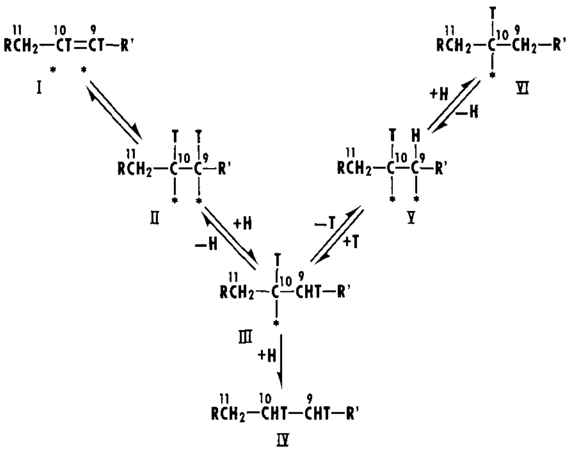

FIG. 6. Horiuti-Polanyi mechanism applied to the catalytic hydrogenation of methyl 9-octadecenoate-9,10-T.

Discussion

The foregoing evidence indicates no discrimination between isotopes when hydrogenating methyl oleate with hydrogen and tritium. With deuterium, an apparent "reverse" isotopic effect is observed. This effect is the subject of a subsequent report (8). While a large isotopic effect may well exist for the step of adsorption on the catalyst, the solubility (2) of the isotopes in ester phase is the rate-limiting step in which the isotopic discrimination is apparently small under the described conditions.

The evolution of tritium during the hydrogenation of methyl 9-octadecenoate-9,10-T may be explained by an extension of the Horiuti-Polanyi (4) mechanism, which is given in part in Figure 6. The initial condition of the compound is depicted at I showing the double bond position with attached tritium. The asterisks represent surface active points on the catalyst. According to this mechanism, tritium perhaps is released by alternation between the mono- (III and VI) and diadsorbed (V) species. During the hydrogenation reaction the tritium released to the catalyst by this alternation is apparently reused (V to III) because the overall direction of the reaction is hydrogen uptake and addition to the double bond. Saturation is achieved by the addition of hydrogen or tritium to either monoadsorbed (III or VI) species and by the subsequent desorption from the catalyst of the saturated ester. Catalyst-adsorbed tritium is then released until equilibrium is attained.

REFERENCES

1. Aronoff, Sam, "Techniques of Radiobiochemistry," Iowa State College Press, Ames, Iowa, 1957, p. 9.
2. Bailey, A. E., "Industrial Oil and Fat Products," 2d ed., Interscience Publishers, Inc., New York, 1951, p. 679–680.
3. Dutton, H. J., E. P. Jones, V. L. Davison, and R. F. Nystrom, J. Org. Chem., *27*, 2648–2649 (1962).
4. Horiuti, J., and M. Polanyi, Trans. Faraday Soc., *30*, 1164–1172 (1934).
5. Johnston, A. E., D. Macmillan, H. J. Dutton, and J. C. Cowan, JAOCS, *39*, 273–276 (1962).
6. Markley, K. S., "Fatty Acids," 2d ed., Part 1, Interscience Publishers, Inc., New York, 1960, p. 590.
7. Nystrom, R. F., L. H. Mason, E. P. Jones, and H. J. Dutton, JAOCS, *36*, 212–214 (1959).
8. Rohwedder, W. K., E. D. Bitner, Helen Ven Horst, and H. J. Dutton, JAOCS, *41*, 33–36 (1964).

[Received April 12, 1963—Accepted July 16, 1963]