Absorption spectra of some of the processed oils indicated that high shear was more effective than ordinary mixing in removing from an oil the gossypol-like and carotenoid color bodies.

Acknowledgment

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The Kinetics of the Hydrogenation of Pure Fatty Esters. I. Mono-Olefinic Systems: Methyl Oleate

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A RECENT PAPER by Swicklik *et al.* (11) has presented, along with their own interesting contribution, a survey of the literature concerning the kinetics of fatty oil hydrogenation. The considerable confusion which existed in this field of research prior to 1941 was complicated, as they pointed out, by unsatisfactory data. As evidenced by the more recent publications on the subject, this state of affairs is being corrected gradually by studying the hydrogenation of simple, pure unsaturated compounds, carried out under well-controlled conditions, thus allowing the basic features of the problem to emerge. A further step would be to make use of the fact that the reactions involved are taking place on the surface of a catalyst and, as such, are governed by the laws of adsorption. These should be involved in any attempt at setting up rate equations.

The present series describes work accomplished with simple alkyl esters under conditions designed to suppress complicating side reactions and to permit accurate measurement of the rate of hydrogen absorption. Absorption rate data obtained in this way reflect the simple kinetics involved in the reaction.

The present article discusses data obtained on hydrogenating methyl oleate. Their implications are basic in interpreting the more complicated systems described in the following articles of this series.

Experimental

REAGENTS

Methyl oleate was obtained from olive oil through methanolysis, fractional molecular distillation of the crude esters, several fractional crystallizations from acetone, and a final fractional distillation, using the Podbielniak semi-automatic microanalyzer. The product showed the following analysis:

hydrogen value, 0.680 (13); required, 0.680.
refractive index at 20°C., 1.4515; reported, 1.4515 (7).

Spectrophotometric analyses (before and after alkali-isomerization) detected no conjugated or polyunsaturated impurities.

Stored under nitrogen in sealed ampoules kept in the refrigerator, the ester was transferred to hypodermic syringes for weighing according to a technique already described (14).

Ethyl alcohol was obtained by refluxing under nitrogen 95% fermentation alcohol over caustic soda for several hours and fractionally distilling the product under nitrogen. The water content was 5%; transmittance against distilled water was 60% at 220 mμ.

Dibutyl-ether was obtained by careful fractional distillation over sodium of Eastman Kodak (white label) product. Found: B.P. 142.5°C. under 760 mm.; reported, 142.4°C. (12).

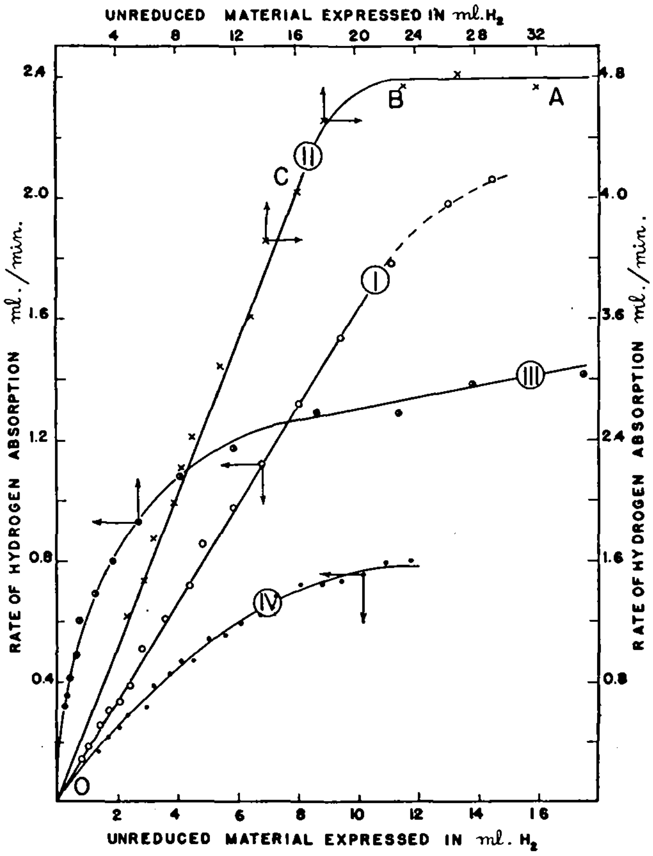

FIG. 1. Hydrogenation Rate Curves.

Curve I: Methyl oleate in 95% ethyl alcohol with Raney nickel showing first order relationship.

Curve II: Same system as for Curve I but with larger amounts of both methyl oleate and Raney nickel resulting in zero order kinetics (AB) during the early stages.

Curve III: Methyl oleate in 95% ethyl alcohol with a platinum catalyst.

Curve IV: Methyl oleate in dibutyl ether with a platinum catalyst.

Related coordinates for the various curves are indicated by the arrows.

CATALYSTS

The *Raney nickel* catalysts were different preparations of the W-5 type (5) obtained and kept as suspensions in ethyl alcohol. All were stored in the refrigerator between uses, some under hydrogen, others without this extra precaution. Pipetting from these well-stirred suspensions provided approximate amounts of catalyst. An accurate determination of the nickel involved in each experiment was made after it was completed.

The *platinum catalyst, PS 14,* was described in a previous paper (15).

APPARATUS AND TECHNIQUE

The hydrogenations were conducted at 25.0°C., under 760 mm. Hg., in ethyl alcohol or dibutyl ether, using an apparatus and a technique already described (14). Readings of the buret were taken every minute, and the rate of absorption at minute *i* was taken as half the volume change observed between minute $i-1$ and $i+1$. Hydrogen absorption rates were then plotted against the volume of hydrogen still to be absorbed. Obviously this volume is proportional to the concentration of double bonds present in the medium.

Results

When methyl oleate was hydrogenated in the presence of Raney nickel W-5, the absorption curves closely approximated a straight line as shown by curve I, Figure 1; deviations were small (Table I) except for the initial points which showed the effect of a lag resulting from delayed solution of the sample when dropped into the alcohol-catalyst suspension. A linear relationship was found regardless of wide variations in the age, effectiveness, and method of storage of the catalyst as well as in the catalyst-methyl oleate ratio. The only limitation was imposed by the necessity of working at absorption rates no greater than 4.5 ml. of hydrogen per minute; somewhat beyond this limit distortion of the rate curves would occur (Figure 1, curve II). Assuming an initial horizontal course AB (constant rate), they would curve down gradually until, when the 4.5 ml. per minute limit was attained, a straight line OC was formed. If all other conditions are equal, the length of the initial plateau would be greater at lower agitation rates; however once the straight, oblique branch had been reached, increasing the agitation could not induce a change of course. This showed conclusively that saturation of the medium with hydrogen had occurred. Consequently data typified by curve I, Figure 1, are comparable in having been obtained under conditions identical with respect to the hydrogen supply. This effect of agitation has also been reported elsewhere (9).

TABLE I

Hydrogenation Rate of Methyl Oleate with Raney Nickel
(Me oleate W5 – 1. Run 9–266. $H_o = 16.80$)

T Time	H, Concn.	1n H_o/H	k = 1/T 1n H_o/H
4	10.66	0.455	0.1137
5	9.49	0.571	0.1142
6	8.45	0.687	0.1145
7	7.49	0.808	0.1154
8	6.65	0.926	0.1158
9	5.93	1.041	0.1157
10	5.25	1.163	0.1163
11	4.66	1.282	0.1166
12	4.15	1.398	0.1165
13	3.71	1.510	0.1162
14	3.34	1.610	0.1150
18	2.15	2.056	0.1142
22	1.34	2.528	0.1148
24	1.04	2.782	0.1159

Curve III, Figure 1, shows the completely different type of curve obtained when, if all other conditions are equal, platinum catalyst PS 14 was substituted for Raney nickel W-5.

When the same platinum catalyst was used and alcohol was replaced by dibutyl ether, curves exemplified by curve IV, Figure 1, were obtained. Under the same conditions the family of curves shown in Figure 2 was obtained when methyl stearate was added to the medium. A progressive decrease in hydrogenation rate was observed when the amount of methyl stearate was increased.

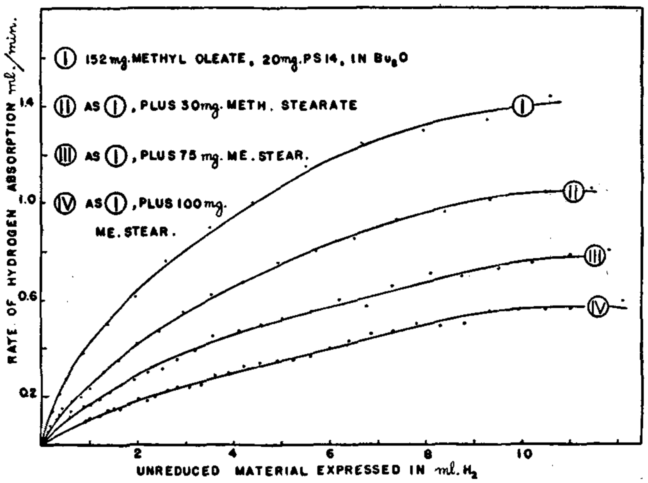

FIG. 2. Family of hydrogenation rate curves obtained with methyl oleate, a platinum catalyst, in dibutyl ether with increasing amounts of methyl stearate.

No significant decrease could be detected when methyl stearate was added to methyl oleate-alcohol-Raney nickel W-5 systems.

Discussion

The results show that the kinetics of the oleate-alcohol-Raney nickel system are adequately described by

$$\text{methyl oleate} \xrightarrow{k_O} \text{methyl stearate}$$

$$\text{Hydrogen absorption rate} = dH/dt = -k_OH \quad (1)$$

where k_O is a constant equal to the slope of the absorption rate line, and H the volume of hydrogen still to be absorbed to complete the reaction. In this reaction the hydrogen absorbed corresponds mole for mole to the ester hydrogenated; thus:

$$dA/dt = -k_OA \quad (2)$$

where A is the concentration of methyl oleate.

In writing expression 2, it is assumed that no *trans* or *iso* oleate is formed during the reaction. This is reasonable in view of the results of Feuge *et al.* (4) and of those of Swicklik *et al.,* showing a considerable decrease in isomerization as the temperature decreases.

Bailey (1) has made, concerning the rate of hydrogenation of double bonds, an assumption leading to an apparently similar expression. However he made it quite clear that only relative rates were considered while expression 2 involves the absolute rate. A first order relationship between the rate and the concentration of the reactant is remarkable, although not unique, for heterogeneous reactions involving adsorption. The rate is dependent on catalyst densities of coverage, and these are usually complex functions of reactant concentrations. As shown by curve III, Figure 1, a more complex relationship is found when a platinum catalyst is used. Expression 2, which appears to be the rule with nickel catalysts, is highly suggestive of a mechanism similar to that proposed by Rideal (8) and applied by Rideal and Eley (3) to the interpretation of para-ortho hydrogenation conversion. This mechanism differs from the classical Langmuir-Hinshelwood concept of heterogeneous catalytic reactions in that it necessitates the adsorption of one of the reactants only. The impact of molecules of the other reactant with activated molecules of the adsorbed reactant would bring about the reaction. If methyl oleate reacted as a result of impacts against activated hydrogen molecules or atoms covering the catalyst, the over-all rate of reaction would indeed be proportional to the concentration of methyl oleate in the medium since the number of impacts would be proportional to this concentration.

However Laidler (6) considers the classical mechanism as the more frequent and also the more probable since it would involve lower energies of activation; the reactants both are adsorbed. Furthermore he concludes that one characteristic of the Rideal type of mechanism would be a strong adsorption of the product of reaction. Our results have shown that this is definitely not the case since addition of methyl stearate does not alter the rate of reaction. It is the case with a platinum catalyst however (Figure 2).

The more probable mechanism is thus the classical one which assumes that the reaction takes place between adsorption complexes of the reactant.

In establishing rate equations for heterogeneous catalytic reactions, the concept of "reactant coverage" is used instead of the "reactant concentration" concept applied in homogeneous systems. The same reaction rate expressions can be used, providing such substitution be made. In the case at hand the reaction would be considered "bimolecular," *i.e.*, the rate is proportional to the mole fraction ϕ of methyl oleate and the mole fraction ψ of hydrogen adsorbed per unit area. Let D be the total area and F a "velocity constant," then

$$da/dt = -FD\phi\psi \qquad (3)$$

would express the over-all rate of reaction. Terms ϕ and ψ are complex functions of the variables, *i.e.*, the concentrations of all solutes engaged in adsorptive competition. The results have shown that methyl stearate, one of the solutes, is not involved.

Before attempting to formulate ϕ and ψ, the adsorption model for both hydrogen and oleate has to be defined. For the strongly chemisorbed hydrogen there is little doubt that the adsorption is of the monolayer type. A multilayer model for methyl oleate is excluded since the observed linear relationship between rate and concentration is incompatible with the existence of a gradient in energy of activation. This would be manifest at some point of the concentration range if multilayer coverage were replaced by a monolayer one. The type of curve obtained with a platinum catalyst, on the other hand (Figure 1, curve III), is reminiscent of the B. E. T. isotherms and strongly suggestive of a multilayer model.

There is thus every suggestion that the simple Langmuir theory of adsorption applies in the case of a nickel catalyst. Hence one can write the classical expressions of catalyst density of coverage, assuming ϕ and ψ to be proportional to these densities; G and J are the appropriate proportionality constants:

$$\phi = GMA/(1 + MA + RH) \qquad (4)$$
$$\psi = JRH/(1 + MA + RH)$$

In the above expressions M and A are, respectively, the adsorption constant and the concentration of methyl oleate in the medium; R and H represent the corresponding quantities for hydrogen. Substituting these values for ϕ and ψ in expression 3:

$$dA/dt = -GJFDMARH/(1 + MA + RH)^2 \qquad (5)$$

H is a constant corresponding to the saturation concentration of hydrogen. The expression will describe the experimental results when term MA in the denominator is negligible since it then can be written in the following form, identical to expression 2:

$$dA/dt = -k_0A$$

with

$$k_0 = GJFDMRH/(1 + RH)^2 \qquad (6)$$

all terms in expression 6 being constants.

Since term MA is negligible when M is very small, one must conclude that methyl oleate is very weakly adsorbed.

ZERO ORDER KINETICS

Zero order kinetics, such as indicated by branch AB, curve II in Figure 1, occur when the rate of hydrogen diffusion is constant and lower than the rate of the reaction with a hydrogen-saturated medium. Conditions for the establishment of this type of kinetics can be found by assuming any change in the factors in equation 5 which will tend to increase the rate of reaction. Zero order kinetics are thus likely to occur:

a) when F is large, *i.e.*, when the catalyst is very effective or when the temperature is high;

b) when D is large, *i.e.*, when the amount of catalyst or its effective area for unit weight is large; and

c) when A is large, *i.e.*, when the concentration of unsaturated compound is high.

The same result would be obtained by decreasing the rate of diffusion by one of the following means: reducing the gas-liquid interface; lowering the pressure; increasing the temperature to reduce hydrogen solubility; reducing the rate of admission.

It is evident from c) that a change from zero order to a higher order of kinetics must occur in the course of any batch hydrogenation experiment whenever zero order conditions existed at the start (Figure 1, curve II).

The above rules apply to hydrogenations carried out under industrial conditions. In the recent article by Swicklik *et al.* (11) their Figure 3 shows the rate of tristearate formation at 175°C., under 1 atmosphere, to be a linear function of time. At the same temperature, but under 65 lb. of pressure (Figure 4), this rate is proportional to time only until about 50% stearate has formed; from then on, the plot indicates kinetics of a higher order. Under 1 atmosphere but at a lower temperature (125°C., Figure 2), the rate of hydrogenation is of a higher order throughout. See also the data of Feuge *et al.* (4) containing many examples of over-all zero order kinetics.

A very important point must be made in relation to all these cases. Because of the slow, constant rate of diffusion of the hydrogen, the hydrogen coverage of the catalyst is very small and constant. But the Langmuir equilibrium is maintained in the case of the unsaturated compounds. In the case of methyl oleate equation 4 assumes, under zero order conditions, the simple form:

$$\phi = \mathrm{GMA} \qquad (7)$$

since H has now become very small and term RH is negligible. Variation of A in the course of the reaction does not influence the rate simply because ϕ is so much larger than the constant hydrogen coverage. The case is analogous to that of a bimolecular homogeneous reaction where concentration of one reactant is much higher than the concentration of the other one and when, by some device, the latter is kept constant.

If several unsaturated species are present in the system, a relation such as 7 would apply to their respective coverages, and the small, constant hydrogen coverage available would be competitively shared by all adsorbed reactants proportionally to both their respective coverages and reactivities. This principle was postulated in a somewhat different form by Bailey and Fisher (2). Its successful application in interpreting the kinetics of the more complex systems constitutes the subject of the next article of the present series.

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Reaction of Methyl Alpha-Eleostearate with Mercuric Acetate

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THE ADDITION of mercuric salts at the ethylenic bonds of olefins has been investigated extensively (3), but little has been published on the reaction of these salts with long-chain unsaturated fatty acids and their esters. Early work by Leys (6) showed that mercuric acetate in acetic acid solution adds to oleic acid producing a mercurated compound reported to contain acetoxymercuri- (CH_3CO_2Hg-) groups. In the preparation of pure oleic acid Bertram (2) made a mercurated oleic acid which he separated from the unreacted saturated acids before regenerating the oleic acid by heating the mercurated product with hydrochloric acid. Ralston *et al.* (10) reacted mercuric acetate with ethyl oleate in boiling methanol and obtained a stable compound, readily soluble in kerosene, to which he attributed the structure, ethyl 9-acetoxymercuri-, 10-methoxy stearate. Patents (11) were obtained on the use of this and similar oxymercurated fatty materials for use as weed killers. Connor and Wright (4) found that methoxymercuration could be used as an analytical method for determining *cis-trans* ratios in certain fatty materials because oleic esters (*cis* form) reacted appreciably faster than elaidic esters (*trans* form).

A number of references to the use of mercury compounds to accelerate iodine value determinations were cited by Benham and Klee (1), who used mercuric acetate as a "catalyst" to cause complete saturation of conjugated double bond systems such as those in dehydrated castor oil and tung oil. Later it was observed in this laboratory that the order of adding mercuric acetate and halogenating solution affects the results of iodine value determinations on tung oils (9). More recently Inouye *et al.* (5) listed the R_F value of the addition compound obtained by reacting methyl beta-eleostearate with mercuric acetate in methanol but noted that the mercury content was "considerably lower than theoretical." This result is in accord with our results obtained on mercuration of methyl alpha-eleostearate and focuses attention on the fact that the reaction of mercuric acetate with fatty acids containing conjugated unsaturation has not previously been reported.

Preliminary experiments indicated that mercuric acetate adds readily at room temperature to tung oil or to purified methyl alpha-eleostearate in either methanol or acetic acid solution. The refluxing of a solution of mercuric acetate and methyl alpha-eleostearate in acetic acid gave a product with unexpectedly low mercury content (13%) and a copious precipitate of metallic mercury. This, together with the high acetoxyl content (25%), indicated that extensive addition followed by decomposition had occurred. Although reaction occurred readily at room temperature, giving products of increased mercury content, reaction at still lower temperatures (0 to 20°C.) afforded products of the highest mercury content, up to 27%. It was noted that the presence of inert solvents such as petroleum ether or ethyl ether retarded addition while exposure to light accelerated it.

On the basis of these preliminary observations methyl alpha-eleostearate was reacted with mercuric

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