The Kinetics of the Hydrogenation of Pure Fatty Esters. III. Poly-Olefinic Systems: Selectivity of Raney Nickel

FRANZ A. VANDENHEUVEL, Fisheries Research Board of Canada, Technological Station,
Halifax, Nova Scotia, Canada

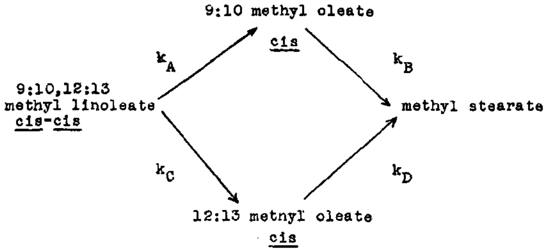
THE PRESENT WORK was undertaken to determine the selectivity displayed by Raney nickel catalysts in the hydrogenation of polyunsaturated fatty esters.

Preliminary work of a semi-quantitative nature had indicated a definite influence of the preparative technique on this property. This was evident from estimations of the relative reactivity of the double bonds of methyl linoleate toward hydrogen in the presence of several Raney nickel preparations. Such determinations can be made by computing the data obtained from the complete analysis of samples from the hydrogenation reaction mixture at timed intervals, a method first used by Bailey (2) with vegetable oils and commercial-type nickel catalysts. This procedure involves a considerable amount of analytical work however, even when the starting material is a simple glyceride or monoester.

A very satisfactory method was found when it was observed that the absorption rate data obtained on hydrogenating methyl linoleate under certain conditions were directly interpretable. This was not surprising since these conditions, *i.e.*, hydrogenation at room temperature in a medium kept saturated with hydrogen, had proved in our work on methyl oleate (7) to be conducive to very simple kinetics; no complicating effect could be detected from *cis-trans* isomerization or double bond shifts, and first order kinetics were obtained throughout. In the case of polyunsaturated esters one could expect under the same conditions the saturation of each particular double bond to proceed at a rate defined by

$$R_U = k_U U \qquad \text{I}$$

where U is the concentration in the medium of the molecular species bearing that particular double bond and k_U a specific constant. A general mechanism for the hydrogenation of *cis-cis* methyl linoleate would then be described by the following system involving two simultaneous routes, each including two consecutive reactions of the first order:



II

Equations giving for any given time the hydrogen H to be absorbed for complete saturation, and R, the hydrogen absorption rate, can be derived from the above mechanism. In these equations, specific constants k_A, k_B, k_C, and k_D are unknown parameters. Since H and R can be obtained by direct measurement (8), values for the constants should be directly computable from absorption data. Such data were obtained from more than 200 hydrogenation experiments, in which the ratio of ester to catalyst and the catalyst itself were the only variables.[1]

Experimental

Materials and Methods. The preparation and properties of *methyl oleate* and 95% *ethyl alcohol* have been described in Part I of this series (7). *Methyl linoleate* was derived from highly purified tetrabromostearic acid (mp. 115°) by debromination followed by esterification and molecular distillation. This ester did not contain any conjugated material detectable by alkali-isomerization techniques (3).

The small amount of *trans* isomer that linoleate obtained by debromination is known to contain did not appear to interfere in the present work. Storage and handling procedures were the same as for methyl oleate. I. V.: 172.5, theoretical: 172.3; hydrogenation value (8): 1.370, theoretical: 1.370; n_D^{20}: 1.4613, reported: 1.4611 (5), 1.4616 (4), 1.4613 (6).

Catalysts. These were prepared through various modifications of the procedure described by Adkins and Billica (1) for the preparation of W 5. They were stored under 95% alcohol in the refrigerator between uses. Some were kept under a blanket of hydrogen, some under nitrogen; for others no protecting blanket was used. Samples were pipetted from thoroughly mechanically-stirred suspensions while bubbling with either nitrogen or hydrogen when these gases were used for blanketing. The exact amount of catalyst used was determined by nickel estimation in the recovered catalyst.

Apparatus and Hydrogenation Procedure. All experiments were carried out in the precision semimicro hydrogenator described in a previous paper (8), using 95% ethyl alcohol as solvent (17 ml.), at 25.00°C. and under 760.0-mm. Hg pressure. Readings were taken every minute.

Determination of Absorption Rate Curves. The rate R_i at minute i was taken as half the volume change observed between minute $i - 1$ and minute $i + 1$.

Rates were plotted against H_i defined as the volume change from minute i until the system was completely saturated. H_i is an expression of the concentration of unreduced double bonds provided the sample were completely dissolved.

A Mathematical Expression of the Data. All absorption rate curves displayed the characteristics shown by the experimental curve in Figure 1. Branch AB of this curve reflects the marked lag affecting the first experimental points, as in the case of methyl oleate discussed in Part I of this series.

A little more than one minute usually elapsed from the time the sample was dropped into the stirred alcohol-catalyst mixture to the moment when the sample was completely dissolved and the catalyst had reached

---

[1] Most of the experiments were carried out under the author's direct supervision by J. D. Nickerson (Dalhousie University, M.Sc. Thesis, 1950), and A. B. Cann (Acadia University, M.Sc. Thesis, 1951).

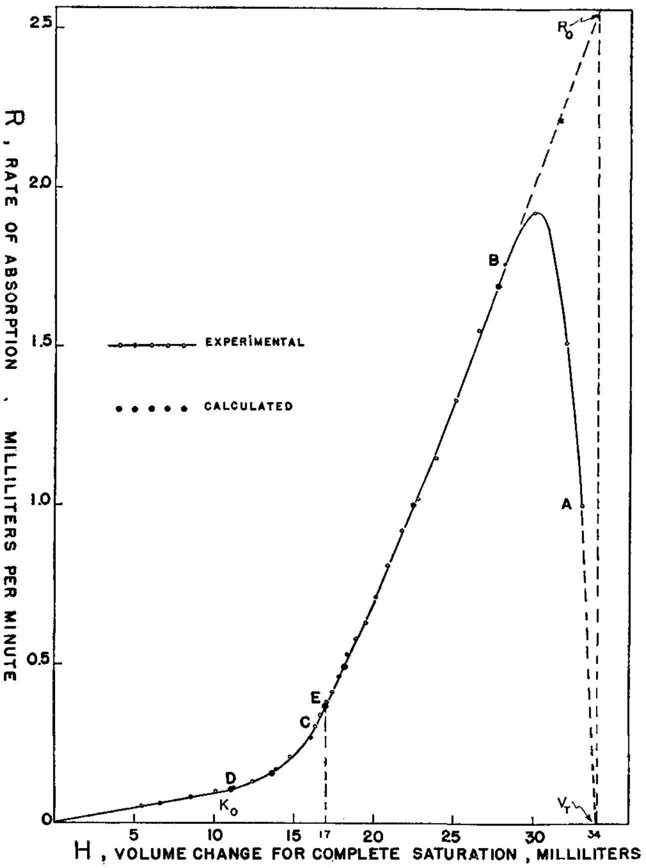


FIG. 1. Typical absorption rate curve obtained with methyl linoleate. Comparison between experimental and calculated values.

full activity. The first two readings corresponded to this non-ideal state of the system. The first two values of H_i and the first three values of R_i calculated from them are in error. From then on (Point B on the curve) the relationship between H_i and R_i was normal.

Branch BC, which is almost a straight line, is joined to DO, a line straight to the origin, by a curved section CD. The latter is located somewhat beyond E, the point corresponding to the absorption of half the theoretical amount of hydrogen. The above features are suggestive of a system of two consecutive reactions of the first order such as described by:

$$\text{Me. linoleate} \xrightarrow{k_L} \text{Me. oleate} \xrightarrow{k_O} \text{Me. stearate} \qquad \text{III}$$

where k_L and k_O are velocity constants with k_L much larger than k_O. This system is a particular case arising from the general system II when only one route is followed by the reaction or, alternatively, when $k_A = k_C$ and $k_B = k_D$ simultaneously.

It is described by the following differential equations:

$$dL/dt = -k_LL$$

and

$$dO/dt = k_LL - k_OO$$

where L and O are, respectively, the amounts of linoleate (moles) and oleate in the reaction mixture.

The solutions to these differential equations are given by:

$$L = L_T\, e^{-k_Lt} \qquad \text{IV}$$

$$O = k_LL_T(k_L - k_O)^{-1}\,(e^{-k_Ot} - e^{-k_Lt}) \qquad \text{V}$$

where L_T is the original amount of linoleate.

Let H_L be the volume change observed in the burette when one double bond is saturated in L moles of linoleate; let H_O be the volume change corresponding to the saturation of O moles of oleate. The change corresponding to the half saturation of L_T moles of linoleate is $V_T/2$, V_T being the volume change observed upon complete saturation of the sample.

Since in each case the hydrogen consumed corresponds mole for mole to the ester involved,

$$H_L/L = H_O/O = V_T/2L_T$$

It follows that L, O, and L_T can be substituted respectively by H_L, H_O, and $V_T/2$ in equations IV and V. Hence,

$$H_L = 2^{-1}\,V_T\,e^{-k_Lt} \qquad \text{VI}$$

$$H_O = 2^{-1}\,k_L\,V_T\,(k_L - k_O)^{-1}\,(e^{-k_Ot} - e^{-k_Lt}) \qquad \text{VII}$$

The sum $2H_L + H_O$ is equal to H; the volume change corresponds to the complete saturation of the system. Thus

$$H = 2^{-1}V_T(k_L - k_O)^{-1}\,[(k_L - 2k_O)e^{-k_Lt} + k_Le^{-k_Ot}] \qquad \text{VIII}$$

The rate at which the hydrogen is consumed, $-dH/dt$, is R, the rate of absorption. Deriving $-H$:

$$R = 2^{-1}k_LV_T(k_L - k_O)^{-1}\,[e^{-k_Lt}(k_L - 2k_O) + k_Oe^{-k_Ot}] \qquad \text{IX}$$

Values for R and H have been determined experimentally for every minute of the reaction. It should be possible therefore to determine k_O and k_L by trial and error, using VIII and IX to compute the data. One complication is that all experimental time values are affected by the same lag error (beyond point B of the curve), which is one more parameter to be determined. To avoid time-consuming computations, the following methods have been used.

Determination of k_O. Since k_L is much larger than k_O, e^{-k_Lt} will much sooner assume insignificant values than e^{-k_Ot} with increasing time values. Making $e^{-k_Lt} = 0$ in VIII and IX, and combining the results, one obtains:

$$R = k_OH \qquad \text{X}$$

indicating that the absorption curve should assume, as it does, the form of a straight line towards the end of the reaction. Moreover X indicates a very simple way of finding k_O as the slope of branch DO.

Determination of k_L. Making $t = 0$ in IX yields an expression of R_O, the initial rate:

$$R_O = k_LV_T/2 \qquad \text{XI}$$

which suggests determining k_L from the value of R_O. Unfortunately R_O cannot be determined with precision because the first experimental points are unreliable.

The following expression was derived from VIII and IX:

$$k_L = [R_1E - R_2]\,(H_1E - H_2)^{-1} \qquad \text{XII}$$

with

$$E = exp. - k_O(t_2 - t_1)$$

It involves k_O, which can be determined from the curve, and two sets of experimental values t_1, R_1, H_1 and t_2, R_2, H_2. When both sets of values are selected from data corresponding to points beyond branch AB of the curve, both t_1 and t_2 are affected by the same lag error; expression XII, which contains their difference, $t_2 - t_1$, is then true regardless of the lag.

With XII any paired combination of the numerous t_i, R_i, H_i sets of values obtained in the course of an experiment can be used.

The validity of equations VIII and IX and therefore of the postulate described by III was established by applying the above methods of analysis to the considerable data which had been obtained.

Application of expression XII to several pairs of experimental H_i, R_i, t_i values corresponding to all sections of the curve, save AB, gave the results shown in Table I.

TABLE I

Calculation of k_L, Using Equation XII[a]
$k_L = [R_1E - R_2]\,(H_1E - H_2)^{-1}$ with $E = \mathit{exp.} - k_O(t_2 - t_1)$,
$k_O = 0.01$, d = % deviation from average.

t_1	t_2	E	H_1E	R_1E	H_2	R_2	k_L	d
5	15	0.905	23.97	1.405	17.84	0.46	0.154	+2
6	16	0.905	22.70	1.205	17.41	0.41	0.151	0
7	17	0.905	21.55	1.040	17.02	0.38	0.145	−4
8	18	0.905	20.60	0.923	16.66	0.34	0.148	−2
9	19	0.905	19.70	0.832	16.34	0.30	0.158	+4.6
10	20	0.905	18.95	0.733	16.05	0.27	0.159	+5.3
15	25	0.905	16.15	0.416	14.80	0.21	0.152	+0.6
5	25	0.819	21.70	1.270	14.80	0.21	0.153	+1.3
10	30	0.819	17.15	0.663	13.85	0.17	0.149	−1.3
10	50	0.67	14.05	0.542	11.20	0.11	0.152	+0.6
10	100	0.407	8.51	0.329	6.66	0.066	0.142	−6.0
					Average k_L		0.151	

[a] The H_1, R_1, and t_1 data correspond to the experiment described by the curve in Figure 1.

Both numerator and denominator values in XII result from differences which tend to magnify errors several times. The good correlation obtained is thus highly significant; it is also an indication of the precision attainable with the hydrogenator used. Further proof for the system postulated is shown in Figure 1, where calculated values of H and R have been plotted.

As was to be expected, these points fall on the experimental curve while experimental H and R values do not correspond to calculated ones for the same time value. The lag accounting for the discrepancy is easily determined from a plot against time of a few experimental and calculated values of H. In this case the lag was 1.25 min.

The determination of an approximate value for k_L from the extrapolated value of R_O is only feasible when, as in the example given, the number of points on the BC branch is large. When the reaction time is short relatively few points are obtained on BC and branch AB assumes considerable importance. Equation XII is then particularly useful.

It must be pointed out that it is only necessary to reach point D in order to apply the above methods and that the operation need not be pursued as far as shown in the above example. In many experiments point D was reached in 30 min. The total volume change V_T corresponding to complete saturation of the sample is then calculated from the weight of material used. For 100 mg. of methyl linoleate in 95% ethyl alcohol, $V_T = 18.05$ ml. at 25°C., under 760 mm. Hg.

It must be pointed out that H_i, R_i, and V_T represent volumes of hydrogen saturated with alcohol vapor. The partial pressure of ethyl alcohol at 25°C. is 59 mm. Hg, and the actual volumes of hydrogen are found by multiplying H_i, R_i, and V_T by 701/760.

Results and Discussion

In Part I of this series

$$k_O = GJFDMRH\,(1 + RH)^2$$

gave the slope k_O of the straight line obtained for the absorption rate curve with methyl oleate hydrogenated under the conditions used in the present work. In this expression D represents the total area of the catalyst. Slope k_O, also that of OD in the curve obtained for methyl linoleate, should be proportional to the amount of catalyst used when this amount is the only factor made to vary. This is assuming that the area per unit weight of catalyst is uniform throughout the batch and that the activity does not vary on aging. If Ni designates the nickel content of a sample of Raney nickel, successive hydrogenations of the same amount of methyl oleate, or linoleate, should result in a constant k_O/Ni ratio. Furthermore the ratio should be the same for both esters if the postulate described by III is true.

A study of k_O/Ni ratios showed that all the Raney nickel used aged rapidly. This introduced a difficulty in comparing ratios for the two esters. It was surmounted satisfactorily by alternating hydrogenations of each ester as quickly as possible and by averaging the ratios obtained in both series. Table II shows these averages to be indeed approximately equal.

TABLE II

Comparison Between k_O/Ni Ratios for Methyl Oleate and Methyl Linoleate

Age, days	Methyl oleate (200 mg.)				Methyl linoleate (199 mg.)			
	Run No.[a]	Ni (mg.)	$k_O \times 10^3$	$k_O/Ni \times 10^6$	Run No.[a]	Ni (mg.)	$k_O \times 10^3$	$k_O/Ni \times 10^6$
50	1	101.3	61.0	602	2	105.4	65.5	622
50	4	109.7	64.5	588	3	107.6	53.5	576
70	6	110.0	57.5	521	5	115.3	53.5	538
70	7	103.7	56.0	541	8	103.6	50.0	521
81	9	111.2	56.0	504	10	113.7	55.0	484
81	12	111.7	57.0	510	11	115.8	59.0	510
90	14	127.0	62.0	488	13	120.2	56.5	470
90	15	135.3	57.0	421	16	119.4	52.5	440
	$10^6 \times k_O/Ni$, average 521				$10^6 \times k_O/Ni$, average 519			

[a] Runs were carried out in the sequence indicated by run numbers.

Table II also illustrates other difficulties encountered in dealing with Raney nickel suspensions. Although the same pipette was used and the suspension was vigorously stirred in all cases, the amount of catalyst pipetted varied appreciably. Furthermore the variation in activity observed on consecutive runs could not always be accounted for by aging. Both types of variation must result from lack of homogeneity.

In the case just described, catalyst aging had been retarded purposely by storing it under hydrogen. When no protective blanketing was used, the activity, as indicated by k_O/Ni ratios, fell much more rapidly. This is shown by plot I, Figure 2, for 13 successive hydrogenations carried out over a 9-day period, in the course of which the activity declined to about one-third its original value. Rather surprisingly, the k_L/k_O ratio remained remarkably constant as evidenced by plot II, Figure 2, of k_O against k_L values obtained from the corresponding data.

Constancy of the selectivity index defined by k_L/k_O was observed in all cases. It is independent of aging and of lack of homogeneity. A study of the selectivity of Raney nickel catalysts in relation to preparative conditions was thus possible.

It would seem that the present method of investigation is well suited to study such effects. Values of

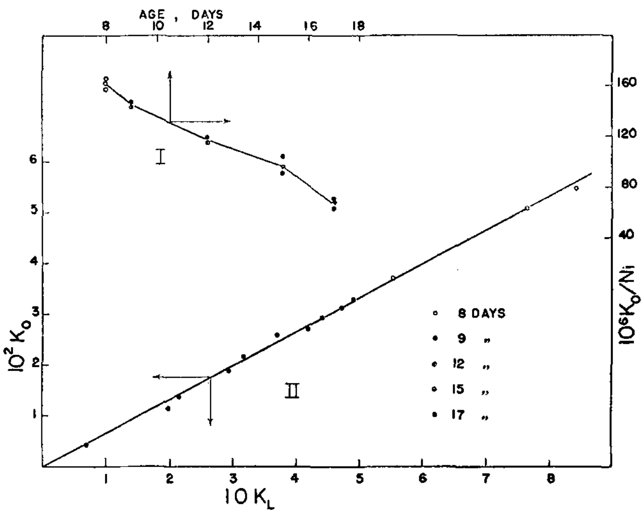


FIG. 2. Plot I. Decline of catalytical activity k_O/Ni on aging. Plot II. Constancy of selectivity index k_L/k_O.

k_L/k_O can be obtained within an hour at little expense of work or material.

The above results do not give any clue as to what alternative route the reaction is taking or whether the two routes are followed simultaneously at an equal rate. A chromatographic study of oxidative material (point D on the absorption curve, Figure 1) gives the answer to this problem. It will be published at a later date.

REFERENCES

1. Adkins, H., and Billica, H. R., J. Am. Chem. Soc., *70*, 695 (1948).
2. Bailey, A. E., J. Am. Oil Chemists' Soc., *26*, 644 (1949).
3. Brice, B. A., and Swain, M. L., J. Opt. Soc. Am., *35*, 532 (1945).
4. Mattil, K. F., and Longenecker, H. E., Oil and Soap, *21*, 16 (1944).
5. Riemenschneider, R. W., Herb, S. F., and Nichols, P. L., J. Am. Oil Chemists' Soc., *26*, 371 (1949).
6. Swift, C. E., Rose, W. G., and Jamieson, G. S., Oil and Soap, *20*, 249 (1943).
7. Vandenheuvel, F. A., J. Am. Oil Chemists' Soc., *33*, 347 (1956).
8. Vandenheuvel, F. A., Anal. Chem., *24*, 847 (1952).

[Received January 18, 1956]

The Migration of Double Bonds During the Isomerization of Methyl Linoleate with Palladium on Carbon Catalyst

K. H. TAKEMURA and L. A. GOLDBLATT, Southern Regional Research Laboratory,[1]
New Orleans, Louisiana

IN CONNECTION with work being carried out in this laboratory on increasing the chemical utility of linoleic acid, a component of cottonseed oil and foots, the catalytic isomerization of the acid to conjugated forms was investigated. Studies on the isomerization of vegetable oils containing linoleic acid have been summarized by Narayan and Kulkarni (8). Radlove *et al.* (10) obtained 30–40% conjugation on treatment of vegetable oils with a nickel-carbon catalyst. Methyl linoleate was reported to give approximately 60% diene conjugation with this catalyst.

In the present work the isomerization of methyl linoleate was studied, using palladium on carbon as catalyst. Moore (7) has studied the formation of "iso-oleic" acids during the hydrogenation of the oleic acid with palladium catalyst. There is mention by Radlove *et al.* (10) of palladium as an isomerization catalyst, and they state "preliminary experiments disclosed that a small amount of conjugation could be achieved by heating either vegetable oils or their methyl esters with platinum, palladium, and nickel catalysts." The Naval Stores industry makes extensive use of palladium-carbon catalysts for the isomerization and disproportionation of rosin (4), but no details concerning the experiments with palladium are given. A survey of the literature yielded no previous report on the use of palladium on carbon as a catalyst for the isomerization of vegetable oils or linoleates. After this work was completed, Floyd, Baldwin, Paschke, and Wheeler reported fairly extensive aromatization and hydrogenation of methyl linoleate by treatment with palladium on carbon catalyst at 275°C. (3a).

In the course of this work it became of interest to determine the location of the double bonds in the isomerized methyl linoleate. The isomerized ester was therefore oxidatively cleaved, and the acids produced were identified by partition chromatography. Studies of this type had been made previously (1, 2) in connection with the migration of double bonds during the partial hydrogenation of esters of oleic elaidic, petroselinic, and linoleic acid.

Experimental

Methyl linoleate was prepared by esterification of linoleic acid obtained from saponification of safflower oil and urea complexing, essentially according to the method of Swern *et al.* (12). Two batches of distilled methyl linoleate were used: one with N_D^{26} 1.4585, iodine-value (Wijs) 163.6 of about 90% purity, and the other distilling at 142 to 146°C. at 0.2 to 0.3 mm., N_D^{27} 1.4590, iodine-value 170.9 of approximately 99% purity.

Isomerization

The ester was heated with stirring under nitrogen at temperatures ranging from 150–250 ± 5°C. in the presence of 2–25% by weight of 10% palladium on carbon (Baker and Company, Newark, N. J., Activity 950, Lot No. 1489).[2] Samples of the reaction mixture were taken at intervals and measured spectrophotometrically for percentage of conjugation.

Hydrogen-iodine values on certain samples were determined by the method described by Pack *et al.* (9).

Oxidation

The distilled, isomerized ester was saponified with dilute (0.25 *N*) alcoholic potassium hydroxide. The acid was then oxidized with ozone by a method similar to that described by R. R. Allen.[3]

---

[1] One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture.

[2] It is not the policy of the Department of Agriculture to recommend commercial firms or their products. The name given above is merely for your information and convenience.

[3] Private communication.