pomace as a protein source indicated that the material was not of high biological value. Microbiological analysis of the total seed protein for the principal amino acids showed that the protein contained relatively large amounts of glutamic acid and was seriously deficient in tryptophan. The methionine content was also inadequate and the lysine was marginal.

Acknowledgments

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Some Additional Notes on the Kinetics and Theory of Fatty Oil Hydrogenation*

A. E. BAILEY, Votator Division, The Girdler Corporation, Louisville, Ky.

SOME time ago Bailey and Fisher (2) examined a series of hydrogenated linseed, soybean, and cottonseed oils, and from the composition of samples taken at different iodine values were able, by methods of approximation, to calculate roughly the reaction rates of the different unsaturated fatty acids in the oils, under conditions leading to "selective" and to "non-selective" hydrogenation. Somewhat surprisingly, it appeared that the reactivity of the different acids was by no means determined by the total degree of unsaturation but depended in any case upon the position as well as the number of double bonds. Furthermore by operating under conditions conducive to increased "selectivity" it was not possible materially to increase the differences in reactivities amongst all the unsaturated acids but merely between two groups of acids, comprising linolenic and linoleic on one hand, and isolinoleic (9:10, 15:16 octadecadienoic) and oleic on the other. Although the saturation of linoleic or isolinoleic acid proceeded in a step-wise manner, *e.g.*, linoleic → oleic → stearic, it was noted that, of the linolenic acid reacting, a portion apparently was hydrogenated directly to oleic acid without intermediate desorption of linoleic (or isolinoleic) acid from the catalyst. However no attempt was made to evaluate this effect quantitatively.

Later it was pointed out by Hilditch (4, 5) that these results indicated a fundamental difference in the properties and reactivities of unsaturated aliphatic compounds containing isolated double bonds and those with double bonds separated by a single CH_2 group and that the behavior of the different fatty acids upon hydrogenation was closely paralleled by their behavior upon reaction with atmospheric oxygen.

In view of the considerable theoretical and practical interest attached to the hydrogenation reaction it was considered worthwhile to go back to the original data of Bailey and Fisher and attempt a more careful analysis of the reaction kinetics through a somewhat different mathematical approach. The present communication will set forth the results of this analysis and will also discuss the theory of hydrogenation and catalyst action in view of the present as well as previous data.

Equations for the Reactions

The different reactions which occur simultaneously and consecutively in the hydrogenation of an oil containing linolenic, linoleic, isolinoleic, and oleic acids are shown diagrammatically in Figure 1.

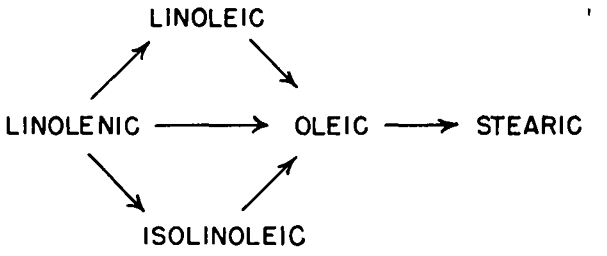

FIG. 1. Schematic representation of reactions occurring in the hydrogenation of a fatty oil containing oleic, linoleic, and linolenic acids.

In setting up expressions relating the composition of the oil to the reaction rates of the different fatty acids it is assumed here, as assumed previously by Bailey and Fisher, that, of an increment of hydrogen taken up by the oil in an infinitesimal period, the fraction going to each acid is proportional to the concentration of the acid times a figure determined by the reactivity of the acid. It is to be noted that this is not quite equivalent to assuming that the reaction rate at any instant is equal to the concentration times

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a velocity constant, which is the criterion for a first order reaction. The difference is that in the former case a proportion results that does not necessarily involve consideration of absolute reaction rates.

The advantage of dealing only in relative rather than absolute reaction rates is that it eliminates the necessity of dealing with absolute reaction times and permits one to proceed with the analysis of reaction kinetics purely in terms of the composition of the oil. For this analysis the conventional equations for first order reactions are valid, regardless of whether each reaction proceeds in true first order fashion, or progressively slows or quickens with change in the effective hydrogen or catalyst concentration in the system. They become invalid only if the different reactions do not maintain their relative rates.

The equations for consecutive irreversible first order reactions were published by Rakowski (6). The proper modifications of these for the hydrogenation of a fatty oil will be given here in detail, since they are not obvious from the original publication.

Let,

a = % linolenic acid in original oil
F_b = fraction of *a* going to linoleic acid
F_c = fraction of *a* going to isolinoleic acid
F_d = fraction of *a* going to oleic acid

b = % linoleic acid in original oil
c = % isolinoleic acid in original oil
d = % oleic acid in original oil

At end of time, *t*, let,

A_t = %linolenic acid in oil
B_t = % linoleic acid in oil
C_t = %isolinoleic acid in oil
D_t = % oleic acid in oil
E_t = % saturated acids in oil

Let,

k_a = relative reaction rate of linolenic acid
k_b = relative reaction rate of linoleic acid
k_c = relative reaction rate of isolinoleic acid
k_d = relative reaction rate of oleic acid

Then,

$$A_t = ae^{-k_a t}$$

$$B_t = be^{-k_b t} + aF_b\left(\frac{k_a}{k_b - k_a}\right)\left(e^{-k_a t} - e^{-k_b t}\right)$$

$$C_t = ce^{-k_c t} + aF_c\left(\frac{k_a}{k_c - k_a}\right)\left(e^{-k_a t} - e^{-k_c t}\right)$$

$$D_t = de^{-k_d t} + aF_d\left(\frac{k_a}{k_d - k_a}\right)\left(e^{-k_a t} - e^{-k_d t}\right)$$

$$+ aF_b k_a k_b \left[\frac{e^{-k_a t}}{(k_b - k_a)(k_d - k_a)} - \frac{e^{-k_b t}}{(k_b - k_a)(k_d - k_b)} + \frac{e^{-k_d t}}{(k_d - k_b)(k_d - k_a)}\right]$$

$$+ aF_c k_a k_c \left[\frac{e^{-k_a t}}{(k_c - k_a)(k_d - k_a)} - \frac{e^{-k_c t}}{(k_c - k_a)(k_d - k_c)} + \frac{e^{-k_d t}}{(k_d - k_c)(k_d - k_a)}\right]$$

$$+ b\left(\frac{k_b}{k_d - k_b}\right)\left(e^{-k_b t} - e^{-k_d t}\right)$$

$$+ c\left(\frac{k_c}{k_d - k_c}\right)\left(e^{-k_c t} - e^{-k_d t}\right)$$

$$E_t = 100 - (A_t + B_t + C_t + D_t)$$

Calculations and Results

Samples of oil upon which the original investigation was based included two series of linseed oils, one of which was hydrogenated under relatively "selective" and the other under relatively "non-selective" conditions; and one series of cottonseed and one series of soybean oils, each of which was hydrogenated "selectively." Analytical data on these were published not only by Bailey and Fisher (2), but also by Fisher, O'Connor, and Dollear (3). For the original soybean oil the composition given by the latter authors represents a correction of the analysis reported earlier and is the one used in the present calculations. All of the other analytical data are identical in the two papers.

The procedure followed in outlining theoretical iodine value-composition curves was to first assume values for F_b, F_c, and F_d, and for k_a, k_b, k_c, and k_d, and then, from these and the experimentally determined values of *a*, *b*, *c*, and *d*, to calculate the composition in terms of A_t, B_t, C_t, D_t, and E_t, and from the composition the iodine value at successive arbitrarily chosen values of *t*. As explained previously, such curves are determined by the relative values of k_a, k_b, k_c, and k_d, and are not influenced by the absolute values of these terms or the absolute values taken for *t*, each of which are to be chosen merely for convenience.

By a procedure of successive approximations and trial and error the theoretical curve best fitting the experimental data was plotted for each series of hydrogenated oils. The results are shown graphically in Figures 2, 3, 4, and 5. In Table I are listed the values of *a*, *b*, *c*, and *d*, of F_b, F_c, and F_d, and of k_a, k_b, k_c, and k_d from which the theoretical curves were obtained. In the case of the cottonseed and soybean oils the values of *a*, *b*, *c*, and *d* are those of the unhardened oil. For the linseed oil however the starting oil was taken in each case as the first hydrogenated sample, rather than the unhardened oil, as this gave a much more satisfactory correspondence between subsequent observed and calculated compositions. It seems probable that the analysis of the raw oil is erroneously low with respect to the content of lino-

TABLE I

Relative Reaction Rates of Different Unsaturated Fatty Acids in the Hydrogenation of Cottonseed, Linseed, and Soybean Oils, and Fractions of Linolenic Acid Going to Linoleic, Isolinoleic, and Oleic Acids

	Linseed (Non-selective)	Linseed (Selective)	Soybean (Selective)	Cottonseed (Selective)
	Relative Reaction Rates			
Oleic	1	1	1	1
Isolinoleic	2.5	3.85	5	....
Linoleic	7.5	31	50	38
Linolenic	12.5	77	100	....
	Fraction of Linolenic to Acid Indicated			
Linoleic	0.24	0	0	....
Isolinoleic	0.65	0.54	0.53	....
Oleic	0.11	0.46	0.47	....

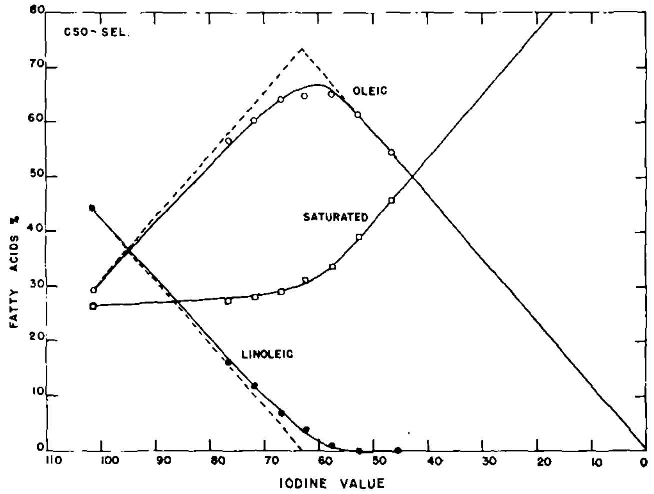

Fig. 2. Selective hydrogenation of cottonseed oil. Calculated composition is represented by solid lines, experimentally determined composition by plotted points.

lenic and possibly also linoleic acid, and that the initial content of isolinoleic acid (5.0%) is fictitious.

Although a number of methods may be followed in fitting together the calculated and observed composition curves, it will be found convenient in practice to begin by tabulating values for A_t for a succession of assumed values of t, with k_a taken as unity (or better, as 100 or 1,000), and thereafter to develop suitable values for the other variables in the order: F_b and k_b, F_c and k_c, and F_d and k_d. There is no explicit solution of the set of equations given above, and in general there appears to be no alternative to a somewhat tedious cut-and-try process.

Discussion of Results

In all cases the experimentally determined compositions of the oil samples agreed quite closely with calculated compositions, over the entire iodine value-composition diagram; this appears to confirm in general the validity of the assumptions and the methods involved in the calculations. As will be explained later, there are theoretical reasons for expecting some deviation to occur, or more specifically, for expecting the selectivity of the reaction to decrease as hydrogenation progresses. There is, in fact, some slight evidence of such an effect, *e.g.*, in Figure 2 it will be seen that the first values for linoleic acid content tend to fall a little below the theoretical curve and the last values a little above. However, the influence of this effect is not large and is obviously very much less than the influence of changes in selectivity brought about by varying the temperature, pressure, or catalyst concentration.

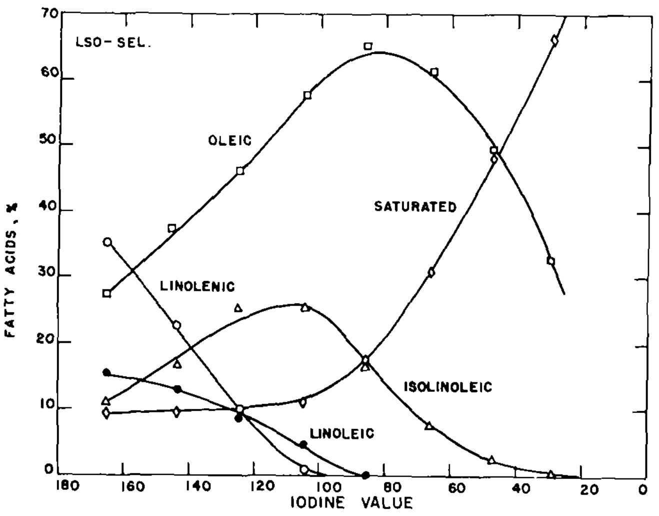

Fig. 3. Selective hydrogenation of linseed oil. Calculated composition is represented by solid lines, experimentally determined compositions by plotted points.

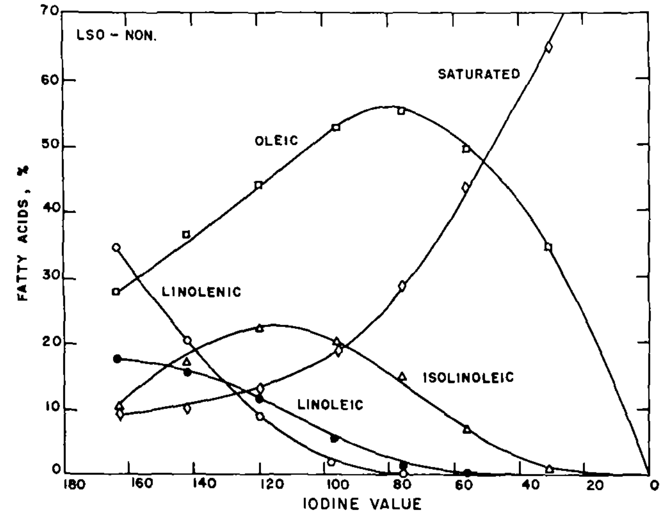

Fig. 4. Non-selective hydrogenation of linseed oil. Calculated composition is represented by solid lines, experimentally determined composition by plotted points.

There are minor differences in the relative reaction rates of the different fatty acids as determined by the present method, and as reported earlier (2) from less accurate calculations. In the case of the cottonseed oil hydrogenated selectively, the revised ratio of reactivities, linoleic acid to oleic acid, is 38 to 1, rather than 19 to 1. The difference here lies in the difficulty of placing the oleic acid maximum accurately by inspection alone and the failure to realize before that the maximum does not lie at or near the critical iodine value corresponding to maximum possible oleic acid formation but at a substantially lower iodine value. The examination of records in the author's possession of numerous other laboratory runs, made in a similar apparatus at pressures in the range of 0-150 p.s.i.g., at temperatures of 225-375°F., and with catalyst concentrations of 0.01-0.30% nickel, reveals ratios varying from about 4 to 1 to 50 to 1.

Contrary to the impression gained previously (2), it appears definite that an increase in the selectivity of the reaction slightly increases the spread in reactivity between linoleic and linolenic acids and also between oleic and isolinoleic acids, as well as greatly increasing the spread between the two groups of acids. The data derived from the two linseed oil runs may be summarized as follows:

	Non-selective	Selective
$k_{linolenic}/k_{linoleic}$	1.7	2.5
$k_{isolinoleic}/k_{oleic}$	2.5	3.8
$k_{linoleic}/k_{oleic}$	7.5	31

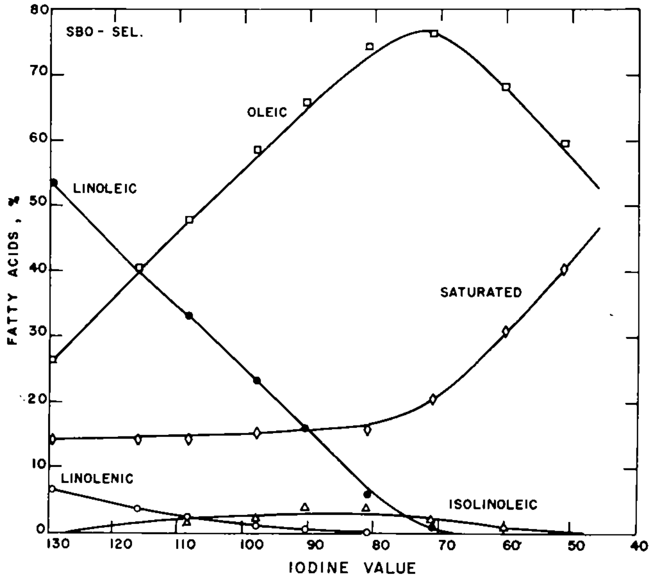

FIG. 5. Selective hydrogenation of soybean oil. Calculated composition is represented by solid lines, experimentally determined composition by plotted points.

Theoretical Discussion

Current theories of liquid-phase hydrogenation and catalyst action envision the following sequence of operations:

1. Transfer of hydrogen from the gas to the liquid phase by solution in the oil.
2. Adsorption from the liquid of hydrogen upon an active spot on the nickel catalyst surface.
3. Prior, simultaneous, or later adsorption of an unsaturated fatty acid radical, in near proximity to the hydrogen.
4. Reaction of hydrogen, nickel, and unsaturated radical, to form an unstable hydrogen-nickel-oil complex.
5. Breakdown of the complex to yield nickel and a hydrogenated radical adsorbed thereon.
6. Desorption of the radical to leave the nickel free to participate in a new cycle.

The first order character of the reaction, as well as certain other phenomena, appear to be best explained by assuming that Steps 1 and 3 are controlling with respect to the reaction rate. According to this view, the concentration of hydrogen in different parts of the system will be as shown diagrammatically in Figure 6. There will be a near approach to equilibrium between hydrogen in the liquid phase and on the catalyst surface (the actual reaction zone), but a large departure from equilibrium between the liquid and gas phases, and a consequent steep concentration gradient in the gas-liquid interface. Under such conditions the concentration of hydrogen in the reaction zone may be considered fixed by the concentration in the gas phase and the aforementioned interface gradient. With the concentration of hydrogen fixed, the reaction rate of any specific fatty acid will of course be proportional to its concentration in the oil.

"Selective" hydrogenation, *i.e.*, preferential saturation of the fatty acids according to their degree of unsaturation, is favored by a low concentration of hydrogen in the sphere of reaction or, under the conditions outlined, a low concentration of hydrogen dissolved in the oil. The reason for this effect is not altogether clear even though a superficial view would be that a limited supply of hydrogen should logically go to the more reactive compounds. It may be that a low concentration of hydrogen on the catalyst leads to a relatively long period for the adsorption and desorption of unsaturated molecules before they react, with the consequence that there is increased opportunity for the more reactive fatty acid radicals to crowd out those which are less reactive and less strongly adsorbed.

The effect of variations in the hydrogen pressure and the dispersion of hydrogen in the oil are evident from Figure 6. A high pressure, as represented at G_1, will lead to a high level of dissolved hydrogen, O_1, and a high adsorbed hydrogen concentration, C_1. With other conditions constant, lowering the pressure or gas phase concentration, for example, to G_2, will lower the dissolved and adsorbed hydrogen concentrations to O_2 and C_2, respectively, and make the reaction more selective. Increasing the dispersion of hydrogen through more violent agitation or increased hydrogen circulation will increase the magnitude of the gas-liquid interface. This in turn, will reduce the gradient in the interface, raise the dissolved and adsorbed hydrogen concentrations, as for example, from O_2 and C_2 to O_2' and C_2', and make the reaction less selective.

At a given pressure, represented in the figures by G_1, and a given degree of hydrogen dispersion an increase in the catalyst concentration will take the hydrogen out of the oil more rapidly by reaction. This will produce a steeper concentration gradient between the gas and liquid phases, lowering the concentration of dissolved and adsorbed hydrogen, as for example, from O_1 and C_1 to O_1' and C_1', and increasing the selectivity.

High temperatures promote selectivity in hydrogenation. This effect is usually attributed to an increase in temperature having a greater effect upon the reaction rate of linoleic acid, for example, than oleic acid, but without qualification this seems an inadequate explanation. The differences in reaction rates caused by temperature variation are much greater than could be attributed to any reasonable difference in the energies of activation for the two acids, and in any case the activation energy for oleic

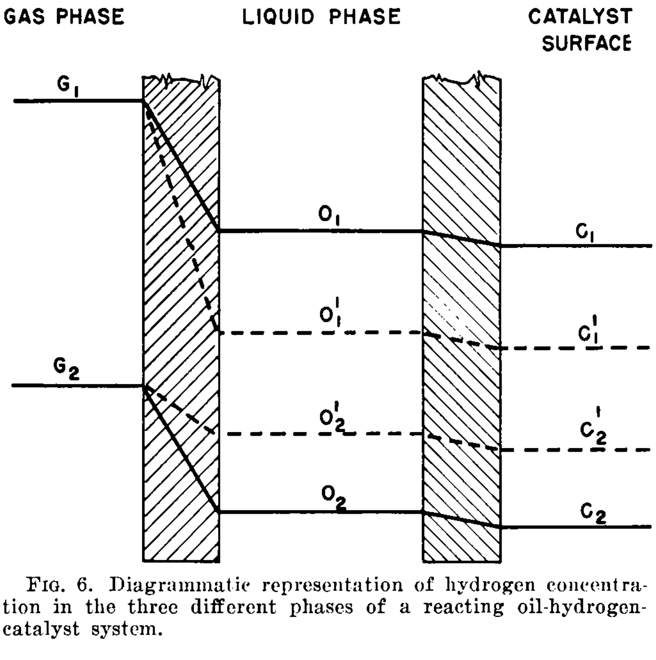

FIG. 6. Diagrammatic representation of hydrogen concentration in the three different phases of a reacting oil-hydrogen-catalyst system.

acid should be the higher, and consequently the reaction rate of this acid should be more influenced by temperature. The reaction is of course much complicated by the presence of the catalyst, but still it is difficult to conceive of any plausible combination of activation energies and heat effects, for either reaction or adsorption, that will lend itself to a satisfactory explanation.

It is one of the chief purposes of the present discussion to point out that the effect of temperature can alternatively be explained on the basis of the hydrogen concentration model set up in Figure 6. Since with hydrogen pressure and hydrogen dispersion constant an increase in temperature increases the reaction rate, it will at the same time lower the concentration of dissolved and of adsorbed hydrogen. In other words, raising the temperature can be expected to have precisely the same effect as increasing the concentration of catalyst.

If both temperature and catalyst concentration influence selectivity through their effect on the reaction rate, it follows that the reaction rate is a measure of their influence. Hence if the pressure and the degree of hydrogen dispersion are held constant, the selectivity should be a function of the reaction rate, increasing as the reaction rate increases from the effect of *either* temperature or catalyst concentration. And with equal reaction rates the selectivity in two different experiments should be the same, regardless of the temperature and amount of catalyst employed in each case.

Unfortunately the available experimental data are not altogether adequate for evaluating the hydrogen concentration hypothesis on the basis of this criterion. However the limited number of experiments detailed in Table II appear to support it. The data for Runs 1-4 in the table are from Bailey, Feuge, and Smith (1); and for Runs 5-9 are from unpublished work of the author and associates. It will be noted that most of the runs in the table were made with a fairly high concentration of catalyst. Runs with a very small amount of catalyst (*e.g.*, 0.01% nickel), which are not shown in the table, invariably are more selective than is consistent with the hydrogenation rate, as measured by the time required to bring the oil to a definite iodine value. In such cases however it is believed that the running time is not a good indication of the average reaction rate, owing to the considerable degree to which a very small amount of catalyst becomes poisoned by impurities in the oil. Also selectivity may vary from the effect of the poisoning itself.

If the selectivity is related to the reaction rate, it should of course decrease progressively as hydrogenation of the oil proceeds. There is no marked evidence of such decrease in Figures 2 to 5 although it is by no means certain that the effect is large enough or the analytical methods accurate enough for it to be detected in all cases.

It will be noted from Table I that under selective conditions virtually no linolenic acid is hydrogenated to normal linoleic acid and that the proportion of linolenic acid hydrogenating directly to oleic acid is much greater than under non-selective conditions. No explanation of this effect can be offered at present, nor can it be determined from the present data whether it is truly related to the phenomenon of selectivity or simply a result of hydrogenating at different temperatures in the two cases. This point, and also the relation of temperature to selectivity, can only be clarified by experiments in which temperature and the other group of factors governing selectivity are varied consecutively rather than simultaneously.

TABLE II

Relation of Selectivity to Rate of Reaction in the Hydrogenation of Cottonseed Oil to a Specified Iodine Value With Temperature and Catalyst Concentration Varied but Pressure and Agitation Held Constant

Run	Catalyst	Pressure, p.s.i.g.	Temperature °F.	Ni, %	Time, min.	Fatty acids, %	
						Saturated	Linoleic
1	A	27	350	0.05	19	32.5	5.6
2	A	27	300	0.05	31	34.1	7.2
3	A	27	200	0.05	72	39.6	12.6
4	A	27	300	0.10	24	32.8	5.9
5	B	60	375	0.02	41	35.0	9.5
6	B	60	325	0.03	39	35.0	9.5
7	B	60	275	0.06	35	35.0	9.5
8	C	150	275	0.03	14	41.7	12.6
9	C	150	225	0.10	18	42.0	12.9

Summary

1. Equations are given for estimating from the composition of oil samples the relative reaction rates of the different unsaturated fatty acids in an oil subjected to catalytic hydrogenation.

2. Application of the equations to data from the hydrogenation of cottonseed oil reveals that the ratio of reaction rates, linoleic acid to oleic acid, varies from about 4 to 1 in very non-selective to about 50 to 1 in very selective hydrogenation. Re-examination of analytical data on two series of linseed oils hydrogenated selectively and non-selectively showed the following relative reaction rates for oleic, isolinoleic (9:10, 15:16 octadecadienoic), linoleic, and linolenic acids, respectively: non-selective, 1, 2.5, 7.5, 12.5; selective, 1, 3.85, 31, 77. In the non-selective hydrogenation of the oil, 24% of the linolenic acid reacting went to linoleic acid, 65% to isolinoleic acid, and 11% directly to oleic acid. In the selective reaction the corresponding figures were none to linoleic acid, 54% to isolinoleic acid, and 46% to oleic acid. The behavior of soybean oil hydrogenated selectively was quite similar to that of linseed oil.

3. The results are discussed in relation to the theory of catalytic hydrogenation. They indicate that the solution of hydrogen in the oil and the adsorption of unsaturated oil on the catalyst are the two steps which are controlling with respect to the reaction rate. It is suggested that the hydrogen pressure, the degree of hydrogen dispersion through the oil, the catalyst concentration, and the temperature all affect the selectivity of the reaction through their influence on the concentration of hydrogen in the reaction zone, with selectivity being favored by a low concentration.

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