Kinetic Studies on Hydrogenation of Fat. An Effect of Poison Formed in Catalysis on the Rate of Hydrogenation[*]

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Despite the considerable experimental studies conducted during these fifty years, there is still much remaining to be cleared up as to the facts regarding the hydrogenation rate, and no satisfactory method has been obtained so far of analyzing the reaction rate mathematically, since hydrogenation has several peculiarities which render mathematical analysis of it difficult. For instance, even the reaction order[1] of an unsaturated molecule, a fundamental problem in kinetics has not yet been clarified. The present discussion is based upon the results of experiments using copper catalysts and whale oil. The conclusions obtained in this study are applicable not only to a specific catalyst and oil, but also to the common reaction of hydrogenation of fat. Further reports confirming these points in greater detail will be issued in the near future. Throughout this experiment, the pressure of hydrogen is kept constant, so the kinetic behavior of the hydrogen molecule is left out of consideration.

Experimental and Results

The hydrogenation of finback whale oil was carried out throughout this series of experiments under atmospheric pressure of hydrogen and at 180°C by using somewhat modified H. Adkin's[2] Cu-Cr-O catalysts.

The experimental technique is outlined here which is practically identical with those employed previously[3]. A static method was employed. The whole glass apparatus was used, which consists of a reaction bulb (a 25 mm. height and a 45 mm. in diameter) connected through a flexible spiral glass tube to a gas burett. The reaction bulb was immersed in an oil bath and was given a horizontal rotation of R. P. M. 200 by a piston of 3 cm. in diameter. The reaction periods from start to end of the motion were recorded.

Two types of slightly modified H. Adkin's Cu-Cr-O catalyst[4] were used.

Type (a): Without barium chromate. Copper content amounting to 43% as a metal on an average.

Type (b): With barium chromate. The amount of barium chromate was adjusted so as to contain 10% of metallic copper in the catalyst.

The activity of those catalysts is satisfactorily uniform when the decomposition temperature of copper ammonium chromate is strictly controlled at about 350°C. Their characteristic features will be briefly described.

The Cu-Cr-O catalyst readily reduced accompanying initial induction period to an active metallic copper and to chromium oxide (Cr_2O_3) at above 120°C consuming about 18 cc. (N. T. P.) of hydrogen per 0.1 g. of type (a) catalyst about 8 cc. per 0.1 g. of the type (b) catalyst in hydrogen atmosphere, and somewhat less volume of hydrogen is consumed in the wet reducing process at the same temperature in each case. In hydrogenation of whale oil with this catalyst under low pressure of hydrogen, highly unsaturated acids are partly saturated while those of oleic acid series are not hydrogenated. The selection is perfect[3,5]. The catalyst is usually added to oil after it is reduced, but sometimes it may be used without reduction. In the latter case reduction of the catalyst takes place within thirty minutes at 180°C accompanying simultaneous hydrogenation of oil.

The results[6] of the analysis using finback whale oil indicate that when selective hydrogenation goes on completely, unsaturated acids ($|\overline{\overline{_{3\sim}}}$-acids) higher than acids of linoleic acid series ($|\overline{\overline{_{2}}}$-acid) are converted to those of linoleic acid series ($|\overline{\overline{_{2}}}$-acid) at iodine value (I. V. in short) 90, and that acids of linoleic acid series which are unsaturated

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[*] A principal part of the present work was presented at the Monthly Meeting of the Pharmaceutical Society of Japan held on March 17th, 1951 in Tokyo Univ.

[1] F. L. Morritz, E. Lieber and R. B. Bernstein, *J. Am. Chem. Soc.*, **75**, 3116 (1953).

[2] H. Adkins, R. Connor and K. Folkers, *J. Am. Chem. Soc.*, **54**, 1138 (1932).

[3] R. Miyake, *J. Pharm. Soc. Japan*, **68**, 9 (1948).

[4] ibid., 68, 18-31 (1948).

[5] Mr. T. Namba kindly informed us about the result of his observation several years ago, that in the hydrogenation of soybean oil by a hydrogen bubbling method some acids in oleic acid series are saturated in the presence of Cu-Cr-O catalyst under the same conditions as in this experiment.

[6] R. Miyake, *J. Pharm. Soc. Japan*, **68**, 2 (1948).

in middle grade are reduced to those of oleic acids series at I. V. 70.

Experiment No. 1.—*A case in which velocity of hydrogenation apparently obeys unimolecular law.*

In the run V. 317 a sintered catalyst reduced at rather high temperature was used. 0.1252 g. of catalyst (a) was completely reduced in the reaction bulb in hydrogen at 270°C for twenty minutes absorbing 14.9 cc. of hydrogen (N. T. P.); then the reduced catalyst was covered by 0.9572 g. of whale oil (I. V. 98.6) to avoid exposure to the air before it was used for hydrogenation. The I. V. of hydrogenated oil was 74.4. The hydrogen adsorption rate is shown in Fig. 1 and the experimental formula obtained by the method of least square from the data of Fig. 2 is as follows:

$$2.303 \log (23.07 - x) = -0.008475t + 3.914.$$

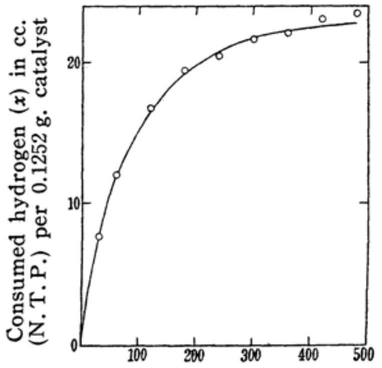

Fig. 1. Run V 317. 0.1252 g. of catalyst was used after reduction at 270°C. The curve is the calculated one from the formula V 317.3 and V 317.4.

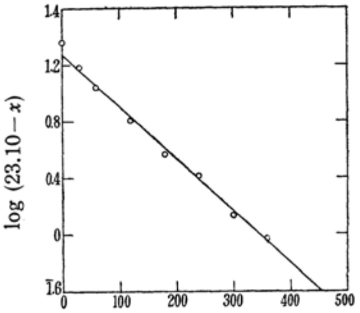

Fig. 2. Run V 317. The logarithum of concentration of highly unsaturated compounds in cc. is plotted against time. The reaction is seemingly of the first order.

Experiment No. 2.—This experiment was carried out to show that the velocity of hydrogenation was independent of the concentrations of highly unsaturated acids in oil. The unreduced catalyst (a) was used. Within the range of the experiment the velocity may be regarded as equal regardless of the change of the concentration. Results are summarized in Table I and in Fig. 3.

TABLE I

Run no.	Catalyst	Whale oil	Refined hydrogenated whale oil	Highly unsaturated compounds
	(g.)	(g.)	(g.)	(%)
V 321	0.1023	0.8894	1.9570	4.5
V 322	0.1200	1.0759	3.006	3.8
V 323	0.1040	0.8970	—	14.3

Whale oil: I. V. 110, n_{d}^{40} 1.4655; content of highly unsaturated compounds, weight % 14.3. Refined hydrogenated whale oil: I. V. 70.6, n_{d}^{40} 1.4603.

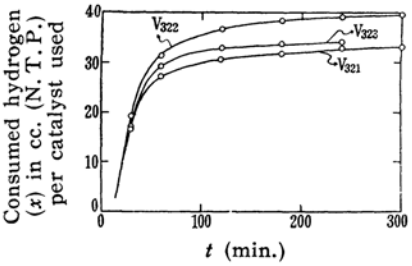

Fig. 3. The independence of the rate upon the concentration of acceptor. In run V 323 whale oil and in run V 321 and V 322 mixtures if whale oil and refined hydrogenated whale oil are hydrogenated with unreduced catalysts listed in Table I.

Experiment No. 3.—An experiment was undertaken to discover the cause of the fall of catalyst activity. With 0.1 g. of unreduced catalyst 1 g. of whale oil was hydrogenated (V 283 (1)). Then 1 g. of whale oil was added and hydrogenated (V 283 (2)), and once again 1 g. of whale oil was added and hydrogenated (V 283 (3)). The catalyst thus deactivated was thoroughly washed with ether in Soxhlet apparatus and then used again as a catalyst of hydrogenation of fresh whale oil (V 285). In experiments V 283 (2) and (3), catalyst was evidently in reduced state. In V 285 catalyst was slightly oxidized due to exposure to the air during washing by either. The data are shown in Table II and in Fig. 4. In Fig. 5 to show more clearly the reactivation of catalyst, the net amount of hydrogen absorbed per one g. of whale oil, i. e. a corrected value obtained by substrating from the total absorbed hydrogen the volume of hydrogen consumed for the reduction of catalyst which are calculated from the drop of iodine value, are plotted against the reaction time.

TABLE II

Run no.	Catalyst (g.)	Whale oil (g.)	Iodine value of hydrogenated oil
283 (1)	0.1192	1.0265	69.2 (calculated)
283 (2)	0.1192	0.1192	
283 (3)	0.1192	0.9826	
285	0.0508	0.5099	70.2 (experimental)

Iodine value of whale oil: 107

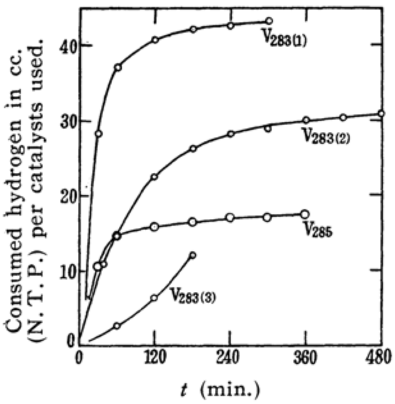

Fig. 4. The deactivation feature of catalyst in hydrogenation with succesive addition of 1 g. oil and reactivation of waste catalyst by washing with ether.

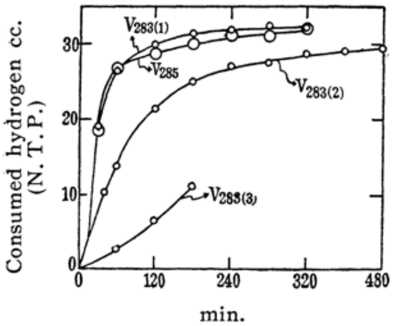

Fig. 5. The net amount of hydrogen absorbed per one g. of oil, calculated from Fig. 4 and Table II.

Experiment No. 4.—The fact that the reaction rate was increased when the amount of catalyst increased in a certain range is illustrated here using the unreduced catalyst type (a). The hydrogenation conditions were similar to those of the foregoing experiments. 1–2 g. of whale oil was used. The results are summarized in Fig. 6., in which the maximum rate (cc./min.) of hydrogenation of the higher unsaturated acids ($|_{\overline{\overline{3}}}$-acid) are plotted against the amounts of catalyst used. The rate is proportional to the amounts of catalysts used, when too much catalyst is not applied. If sufficient catalyst is used, the rate of reaction becomes nearly constant, being independent of the amount of catalyst. This fact might induce an opinion that the diffusion rate of hydrogen into an oil phase may be the limiting factor[7] in this case. Discussion on this follows. The diffusion theory, however, is not tenable in this case, because faster consumption of hydrogen can be observed in the same apparatus by using a more effective catalyst such as nickel. A study on this phenomenon is now being undertaken by Yajima. It will suffice here to state that oil is saturated with hydrogen under the conditions of this experiment.

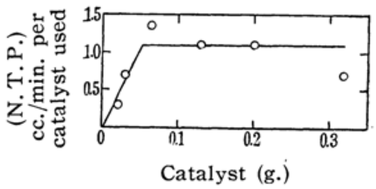

Fig. 6. The dependance of rate upon the amount of catalyst. Differing from the circumstance employing the dry-reduced catalyst, the wet-reduced catalyst becomes partially inactivated by the irreversible poisonous substances, presumably formed from the fat by the accompanying oxidizing action of the oxide catalyst in the reduction period. The injurious effect, however, do not become pronounced until not too much unreduced catalyst (about 0.2 g. in this case) is used.

Kinetic Consideration

The consideration are principally inferred from the behavior of unsaturated oil molecules in the reaction system, quite apart from the behaviour of hydrogen molecule, since the hydrogen pressure was maintained constant throughout this series of experiments, and further, as mentioned in Experiment No. 4, the oil was evidently saturated with hydrogen. The fact that hydrogenation rate is independent of the concentration of the highly unsaturated molecules indicates the rate determining step is the hydrogenation process on the surface of catalyst, that the diffusion of oil molecules to the catalyst surface is fast enough to establish the adsorption equilibrium of oil molecules between the catalyst and the liquid phase, and that the highly unsaturated molecules are strongly adsorbed, although the reaction is sometimes apparently first-order kinetics as shown in Experiment 1.

The decrease in rate of reaction with time is necessarily ascribed to successive deactivation of catalyst, by possible two principal factors, poisoning and sintering. The results of Experiment No. 3 indicate that the effect of the latter can be ignored.

In conclusion, as the equilibrium in the reaction system is established, the rate of hydrogenation is directly proportional to the amount of catalyst, i. e., the decrease in the rate is directly corresponding to the decrease in the number of active centers caused by a catalytic poison in a first approximation.

In order to interpret the change in rate in view of this conclusion, an assumption is made induced from the suggestive results obtained in Experiment No. 1 that the num-

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7) V. I. Gol'danski and S. Yu. Elovich, *C. A.*, **41**, 2973 (1948).

ber of active centers is reduced by the quantity of poison formed in the process of catalysis in proportion to the amount of hydrogenated molecules. Thus, if x cc. of hydrogen reacts at time t min. the rate is assumed

$$dx/dt=K_1(N_o-K_2x),$$

where

K_1 = the hydrogenation rate constant (cc./min.) per unit active center,

N_o = the original number of active centers, which is supposed here to be capable of combining an unsaturated compound and hydrogen together,

K_2 = this term consists principally of the proportional constant of catalytic poison formation reaction, absorption coefficient of poison and proportionality constant so as to make K_2x correspond to the number of active centers deactivated.

This equation, however, has a linear expression with respect to x similar to the first order formula; it involves two reaction rate constants, K_1 and K_2. Although N_o/K_2 corresponds to the initial concentration of reactant in the first order kinetics, it can be determined only from experimental data.

The analysis of Run No. V 317 with the applification of this equation is shown in Fig. 7, wherein an abrupt change in rate at point (b). Hence it is expressed by the following two equations.

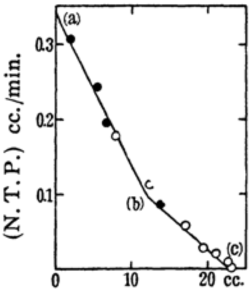

Fig. 7. $dx/dt-x$ relation from V 317.
○ experimental
● interpolated

$$dx/dt=0.3430-0.02021x \quad (\text{V 317.1})$$

$$dx/dt=0.2047-0.00889x \quad (\text{V 317.2})$$

These equations are dissolved and calculated integral constants by adopting suitable experimental points on Fig. 7. The result is

$$2.303\log(16.97-x)=-0.0202t+2.826 \quad (\text{V 317.3})$$

$$2.303\log(23.06-x)=-0.00889t+2.935 \quad (\text{V 317.4})$$

From these four equations, the following figures for the point (b) are obtained: 0.0967 cc./min., 12.18 cc. and sixty two minutes respectively for dx/dt, x and t. The iodine value at (b) is estimated as 88. This is in good agreement with the calculated iodine value 90, at which $\overline{|3\sim}$-acids will disappear. Thus, the equation (V 317.3) can be used for the former stage of hydrogenation of $\overline{|3\sim}$-acids before sixty-two minutes and thereafter the equation (V 317.4). Therefore K_1N_o for $\overline{|2}$-acids must be taken 0.0967 cc./min. (at point b). The slopes of the pair of straight lines in Fig. 7 are shown respectively in terms of K_1K_2 for $\overline{|3\sim}$-acids and K_1K_2 for $\overline{|2}$-acids in the equations (V 317.3 and V 317.4) and the ratio of these $K_1(\overline{|3\sim})/K_1(\overline{|2})$ can be calculated from the ratio of the value of these slopes if the value of $K_2(\overline{|3\sim})/K_2(\overline{|2})$ is known. If an assumption is made that $K_2(\overline{|3\sim})/K_2(\overline{|2})$ is unity, then $K_1(\overline{|3\sim})/K_1(\overline{|2})=0.0202/0.00899=2.25$, which is comparably consistent with the value obtained from instances in which $K_2(\overline{|3\sim})$ and $K_2(\overline{|2})$ happen to be negligible compared with the change in K_1 terms as will be reported in the next work. The appearance of the breaking point (b) in Fig. 7 indicates the occurrence of good selectivity which is also consistent with being indifferent to the reaction rate with the concentration of the highly unsaturated molecules.

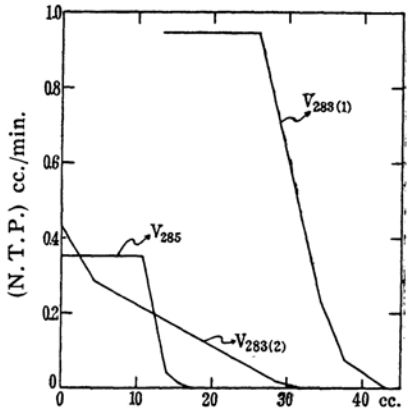

Fig. 8. $dx/dt-x$ relation from Experiment No. 3 (Fig. 4). The graph of V 283 (1) will proceed same in shape from this position to the left through decreasing values of 9.9 cc. to x, provided correction is made on it by substracting the required hydrogen for the reduction of catalyst in Fig. 4.

Reviewing Fig. 8, it deserves special notice here for the arising of different types of active center in the hydrogenation range of $\overline{|2}$-acids, their slopes being respectively 0.0861 and 0.0476. An assumption being made of the equality of both K_2 again here concerning both types of active center, the ratio of slope is nearly 2** which corresponds to the ratio of K_1 term in two types of active center, catalyzing the same substance in this case.

The reaction rate after passing over the point of about I. V. 75 changes to the very slow one in this catalyst indicating the possibility of the appearanse of some special constitution of fatty molecule ($\overline{\overline{|2}}'$) (Table III).

TABLE III

THE STRAIGHT LINES IN FIG. 8 ARE EXPRESSED BY TWO TYPES OF FORMULAS EITHER $dx/dt = a$ OR $2.303 \log(b-x) = -ct+d$. THE ESTIMATED VALUE OF THESE TERMS ARE TABULATED. $(dx/dt)_i$, $(x)_i$ AND $(I.V.)_i$ ARE THE RESPECTIVELY THE CALCULATED VALUES AT THE POINT OF INTERSECTION OF CROSSING TWO LINES

Run no.	a	b	c	d	$(dx/dt)_i$	$(x)_i$	$(I.V.)_i$	Acids range being hydrogenated
V 283 (1)	0.944							$\overline{\overline{|3\sim}}$-acids
					0.944	26.2	89	
		37.1	0.0861	4.76				$\overline{\overline{|2}}$-acids
					0.229	34.5	79	
		39.2	0.0476	3.66				$\overline{\overline{|2}}$-acids
					0.080	37.6	76	
		43.4	0.0138	2.64				$\overline{\overline{|2}}'$-acids
V 283 (2)		13.0	0.0331	2.56				$\overline{\overline{|3\sim}}$-acids
					0.288	4.32	103	
		30.3	0.0111	3.42				$\overline{|3\sim}$, $\overline{\overline{|2}}$-acids
					0.0195	28.6	77	
		31.6	0.00641	2.78				$\overline{\overline{|2}}'$-acids
V 285	0.3505							$\overline{\overline{|3\sim}}$-acids
					0.350	10.6	85	
		14.4	0.0946	4.355				$\overline{\overline{|2}}$-acids
					0.0425	13.9	78	
		16.8	0.0159	1.881				$\overline{\overline{|2}}'$-acids
					0.0162	15.7	74	
		17.5	0.00921	1.653				$\overline{\overline{|2}}'$-acids

The occurrence of linear sector of rate in the early stage is evidently the direct proof of zero order reaction with unsaturated molecules, but it is of interest in view of the point of poison formation. It is suggested that the solubility of poison must be taken into account. In fact, the hydrogenated whale oil contains poisonous substance in it, so hydrogenized oil must be re-refined by alkali and bleaching clay before applying it in Experiment No. 2. Some reactivation of activity accompanied by adding a fresh oil as will be seen in V 283 (2) and (3) might be attributed to, apart from the change in constitution of oil by adding new whale oil, the desorption of poison from catalyst and this concept is introduced into K_2, although it is not expressed in explicit form for the present.

The features under the above consideration, however, are shown in very few instances; they hold true also for many examples we have tested. On the other hand, the occurrence of induction period incidentally which appeared in Experiment No. V 283 (3) in the reduced state catalyst is not so rare but is not reproducible, and of course quite different from that which was experienced with the unreduced catalyst as noticed before.

Some other criteria will be afforded here as regards to the phenomena which are encountered in the hydrogenation of fat aside from the one as discussed above. The inherent impurities present in oil are irreversible poison, leading to permanent inactivation of the catalyst, and bearlittle relation to the change in rate under the condition wherein the absorption equilibrium is established.

The gaseous poisons which happen to occur as impurities in hydrogen may damage a catalyst in the very similar manner proportional to the consumed hydrogen. There is evidence, however, against this in the experiments using the same hydrogen in a gas bubbling hydrogenation method, in which the extent of volume of hydrogen passed had no effect on the activity of catalyst. Another

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** This figure will be shown as a characteristic one of this catalyst in the next report.

effect might be raised from the pyrolysis of oil. It can be left out of consideration in view of kinetics also because time effects were not observed in the above analytical treatments. All these factors can be left out of consideration in the first approximation.

The present criterion appears to be in general accord with the view originally set forth by Armstrong and Hilditch[8], which unfortunately has not been developed to further kinetic treatments. The present authors in writing this report are feeling utmost reverence toward their foresight. In addition it will be pertinent here to recall the Ubbelohde's observations[9], whose data are seemingly all responsible for the present conception, although he did not interpret his results from the viewpoint of catalytic poison.

Summary

Estimation of the volume of hydrogen consumed by a static method with Cu-Cr-O under atmospheric pressure of hydrogen at 180°C by hydrogenation of whale oil was studied kinetically.

It was observed that the reaction is zero order to the concentration of the molecule to be hydrogenized, and, in spite of it, the reaction velocity gradually decreases due to the reversible poisoning of catalyst. An assumption was made that a poisonous substance is formed in the process of catalysis, and that its amount is proportional to the degree of hydrogenation. The following formula is presented.

$$\mathrm{d}x/\mathrm{d}t=K_1(N_0-K_2x)$$

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[8] E.F. Armstrong and T.P. Hilditch, *Proc. Roy. Soc. London*, A **96**, 137 (1919).

[9] L. Ubbelohde and R. Schönfeld, *Z. angew. Chem.*, **44**, 184 (1931).