Hydrogenation Research

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(Robert R. Allen, former AOCS president and winner of the 1983 Bailey Award, was the recipient of the 1986 Supelco AOCS Research Award presented in May at the 1986 AOCS annual meeting in Honolulu, Hawaii. Allen received the award for his pioneering work in hydrogenation and for other research. The following is the address given by Allen after receiving the award.)

During the 33 years I have spent in industrial fats and oils research and development I have been fortunate to have both R&D managers who let me stay in the laboratory and do my own research, and capable assistants who worked with me in the laboratory. Of course, much of my work could never have been done without them, so this award is theirs, too. My laboratory assistant in Taiwan, Dorothy Chu, wrote me, "You are my boss, so it is my honor, too." This is not just my award; you are also honoring those who worked with me during the past.

One of the most interesting problems in the fats and oils field is the hydrogenation of vegetable oils to produce the semi-solid fats that constitute a great part of our products. Discovered by Normann in 1901, the process has been developed so that today millions of pound of oils are hydrogenated every day, and they do not know, or need to know, what actually is happening in the reactors. But human curiosity being as it is, a chemist, observing a reaction that is not understood, will try to find out what is happening.

My own work in hydrogenation started in 1953 at Armour & Co., Central Research. An article in the *Journal of the American Oil Chemists' Society*, written by Boelhouwer (1), reported large amounts of unsaturated isomeric monoenes were formed by hydrogenation. However, migration of the double bond toward the carboxyl was restricted, and the bonds migrated away from the normal 9 position toward the methyl end of the fatty acid. This work interested me because I could not understand why a carboxyl group 9 carbons away should affect the double bond. So Art Kiess and I started work on this. Since this was before gas liquid chromatography, we used liquid-liquid chromatography to separate the dibasic acids that resulted from oxidation of the double bond (2). The length of the dibasic acid gave the position of the double bond. Also, we used ozone to oxidize the double bonds while Boelhouwer had used permanganate. Figure 1 shows a typical separation of the dibasic acids. The preparation of the column and elution of the dibasic acids took from two to three hours, and the titration of each of some 50 fractions took at least another hour. We could do only two analyses per day. Art Kiess did most of the titrations, and I am sure his patience was sorely tried when faced with hundreds of them. But he did them and we found, when pure oleic was hydrogenated, some bonds were saturated and others were geometrically isomerized to give *trans*, but others were positionally isomerized, and the bonds moved equally in both directions from the 9 position (Fig. 2). We found permanganate oxidations degraded the dibasic acids so

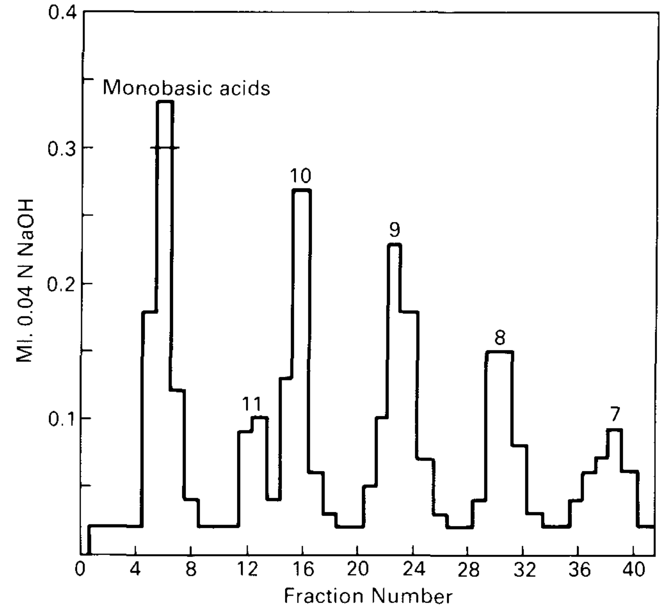

FIG. 1. Separation of dibasic acids by partition chromatography. Numbers indicate chain length of the acid.

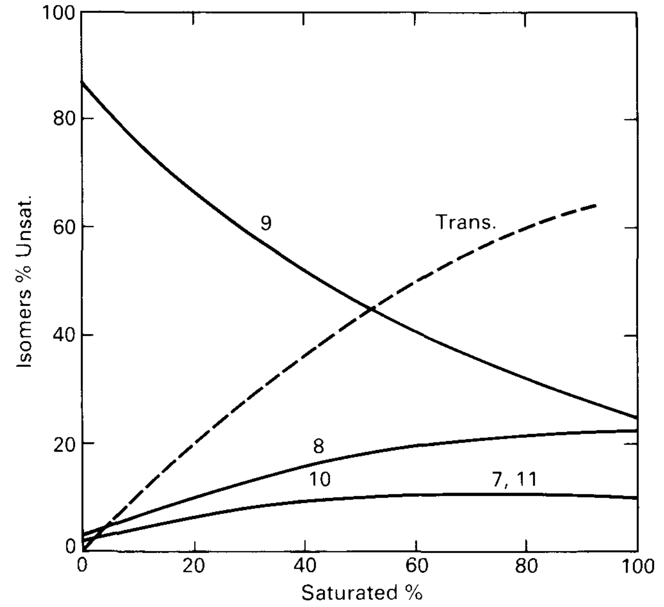

FIG. 2. Positional and geometric isomers formed during hydrogenation of methyl oleate.

the analyses were not accurate. The only mechanism we could devise was the "half hydrogenation" theory shown in Figure 3.

We found this mechanism was accepted, and we moved on to the two-double-bond fatty acid, linoleic (5). We found the reaction sequence was confined to the 5 carbon, penta diene system, and that 9,10,11,12 monoenes were produced. Art and I devised a mechanism that involved a conjugation of the two double bonds before hydrogenation. But before we published this we decided to test the hydrogenation of a conjugated diene system (3). Because a pure *cis,cis* conjugated diene had not been reported in the literature, we had to synthesize some (4) and a few grams were hydrogenated. We found the expected three monoenes but were surprised that the *trans* monoene was pure 11 isomer. We built a scale model (Fig. 4) of the *cis,cis* conjugated and found the hydrogens on the 11,12 carbons had to be *trans*. So, when the diene was hydrogenated 1,4 the resulting double bond at the 11 position had to be *trans*.

From this study of conjugated diene, we believed that about half of the penta diene system of linoleic was conjugated before hydrogenation so that both the conjugated and non-conjugated dienes produced the isomeric monoenes by hydrogenation (Fig. 5). You can imagine the hundreds of separations and titrations Art Kiess did.

Several years later, after moving to Anderson Clayton Foods in the warm South, I was working with a new laboratory assistant, Jesse Covey. At this time there was some controversy in the literature about the rate of hydrogenation of the different positional isomers. We prepared some pure *cis* 6, *cis* 9 and *cis* 12 octadecenoates. The *cis* 6 was prepared from parsley seed oil. The purchasing agent thought we were going into parsley culture when I ordered 10 lbs of parsley seed.

We had gas chromatography by now. Russell Walker and I had built two that worked, but finally several were on the market that could obtain the high temperatures necessary for fatty acid analysis. What a pleasure—no more titrations, just inject a sample and get a recording of the peaks.

We found by hydrogenation of the mix that 6,9,12 isomers hydrogenated at the same rate (Fig. 6).

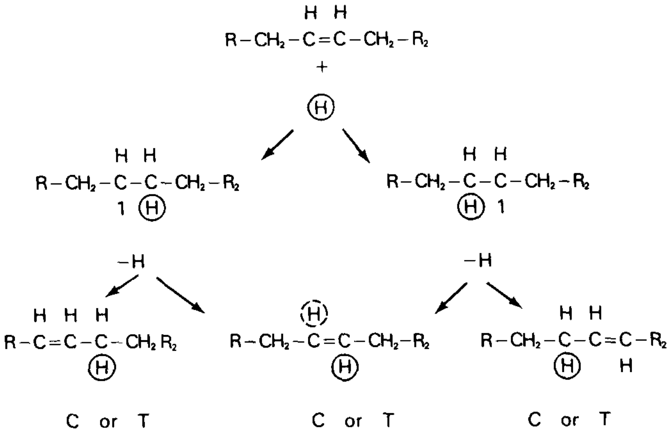

FIG. 3. Theory of half hydrogenation of oleate.

To make something useful of this work, we started looking at catalysts. Producers of commercial hydrogenated fat and oil usually buy their catalysts from manufacturers specializing in various types of catalyst. The most desired catalyst for oil hydrogenation is one that is very active and selective, i.e., one that will

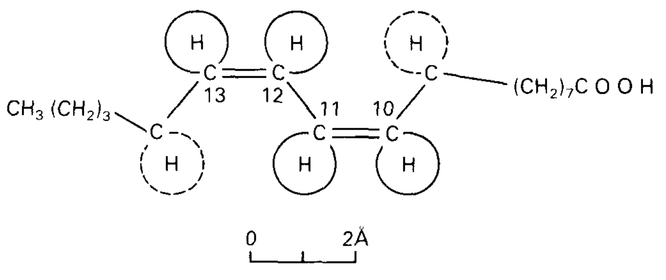

FIG. 4. Model of 10,12 *cis,cis* octadecadienoic acid.

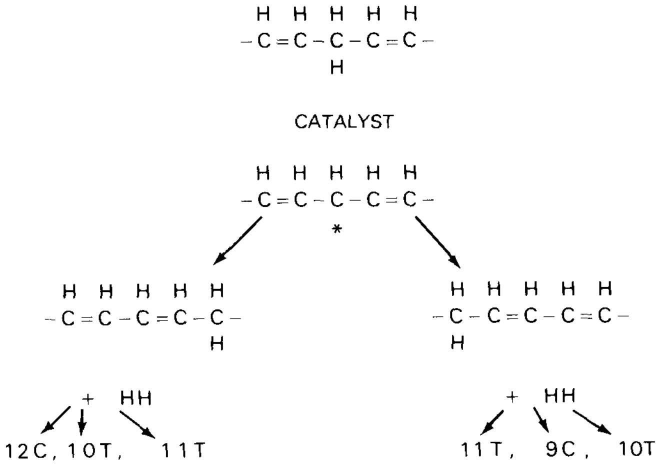

FIG. 5. Theory of hydrogenation of linoleic.

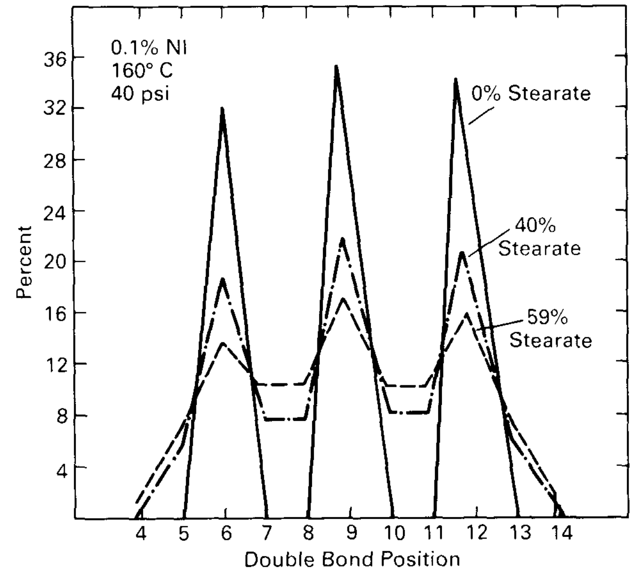

FIG. 6. Hydrogenation of mix of 6 *cis*, 9 *cis*, 12 *cis* octadecenoates.

hydrogenate rapidly and will reduce linoleic to oleic without hydrogenating much of the oleic to saturation. By use of a very selective catalyst, high oxidative stable oils are produced without becoming too hard. The selectivity of a catalyst was a somewhat general term that could not be measured. Thus, what was needed was a method to measure the reaction rates of each of the series of reactions. L.F. Albright of Purdue University published the integrated rate equations (Fig. 7) and graphs to determine the selectivity ratios of a catalyst (7). We began using these graphs to measure the selectivity of the catalysts we were buying for plant use. We found some variation in the catalysts of different manufacturers.

During this period Anderson-Clayton started a management sciences group and hired a mathematician-statistician-computer expert, Dan Stone. He asked me how he could help in my work, so I showed him Albright's equations and told him I needed to calculate the actual values of K1, K2 and K3. The next day he came back with a computer program to calculate the values from FAC data. This was exactly what we needed, so we started an intensive catalyst evaluation program to make sure our plants were using the most selective, active and consistent catalyst. We used a computer to calculate the rate values and the selectivity ratio from experimental hydrogenations. This way we kept our catalyst suppliers honest.

We were now buying some very selective catalysts but we wanted to know how the conditions of hydrogenation affected selectivity. There are four reaction parameters: temperature, pressure, catalyst concentration and rate of agitation. I consulted the laboratory statistician, Mike Moore, and he introduced me to Response Surface Analysis (Fig. 8). Since I am a strong proponent of the axiom, "Nothing is too much trouble as long as someone else does it," the Response Surface was ideal.

To examine the relationships of four experimental parameters at five different levels, at least 31 experiments must be done. The experimental plans are published, so, to measure the hydrogenation parameters' effect on selectivity, rate of reaction, or *trans*, I assigned the actual experimental values to the plan; Jesse Covey did the 31 hydrogenations and analyzed over 100 samples. The results were submitted to Mike Moore, who came back with a pile of computer printouts and then showed me what they meant. An equation was found by the computer that related the reaction conditions to a response, i.e., selectivity. By using this equation we could do experimental hydrogenations under any set of conditions by a computer, with no lab work. For example, the effect of pressure and temperature on selectivity are shown in Figure 9. This shows, at constant temperature, increasing pressure decreases selectivity and increasing temperature increases selectivity.

I retired from Anderson Clayton in 1983, and in 1984 I had the opportunity to live in Taiwan and do research at the Food Industry Research and Development Institute (FIRDI) and teach at the National Taiwan University Graduate Institute of Food Science and Technology.

$$\text{Linolenic} \xrightarrow{K_1} \text{Linoleic} \xrightarrow{K_2} \text{Oleic} \xrightarrow{K_3} \text{Stearic}$$

$$SR = \frac{K_2}{K_3} \qquad LN\ SR = \frac{K_1}{K_2}$$

FIG. 7. Calculation of composition from rate constants of hydrogenation.

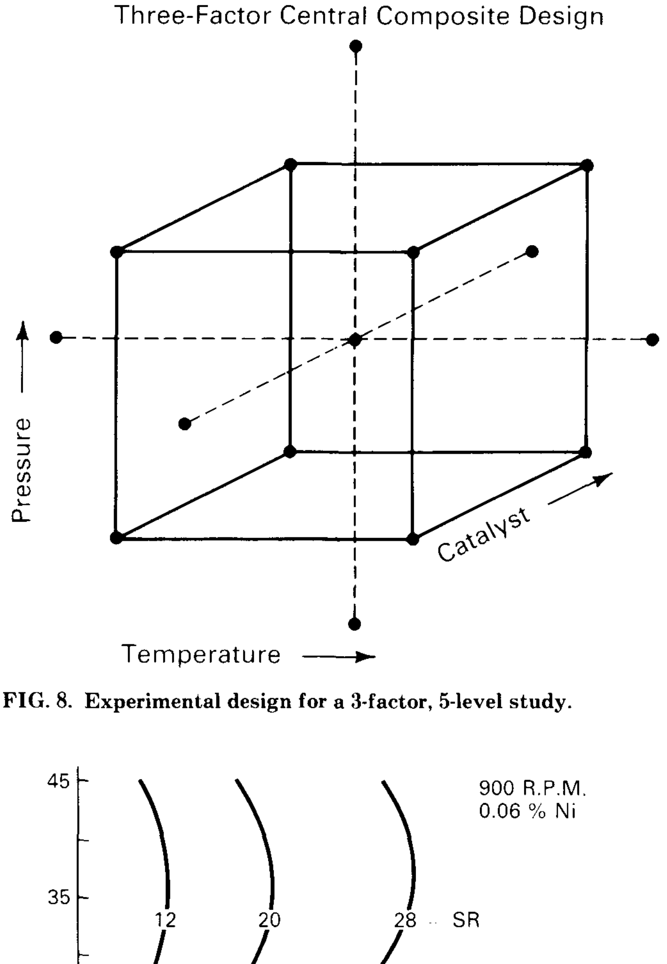

FIG. 8. Experimental design for a 3-factor, 5-level study.

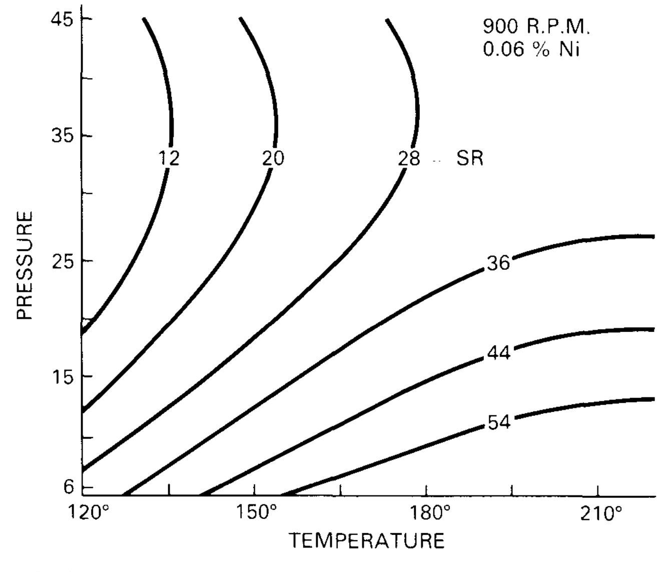

FIG. 9. Effect of hydrogenation temperature and pressure on selectivity.

At FIRDI, my lab assistant was Dorothy Yan Wah Chu. She had attended Ohio State University, so her English is excellent; my Chinese was non-existent. We did several projects including the hydrogenation of pure methyl linoleate. The science of gas chromatography and the instrumentation and separation power available now is almost unbelievable. Fortunately, the flavor lab at FIRDI had the latest instrument to use capillary columns. We obtained the 100-meter (this is over a city block long) capillary that was designed for separating geometric and positional isomers of unsaturated fats. With this column, the isomers produced during the hydrogenation of linoleic were separated (Fig. 10). Since helium is very expensive in Taiwan, we used hydrogen as a carrier gas. Probably because of the lower viscosity of hydrogen compared to helium, we obtained excellent separations of all the isomers in about 35 minutes, quite a contrast to the method we used in the 1950s.

While Dorothy was doing the laboratory work, I was comparing the rates of disappearance of linoleic vs. the rate of formation of *trans* unsaturation, using data from our Response Surface work (Fig. 11). I found that when one mole of linoleic was hydrogenated, about 2/3 mole of *trans* unsaturation was formed during the early part of the reaction. This happened under the wide range of conditions used in the study. So, if only a part of the linoleic is conjugated, the reaction conditions should affect the amount of conjugation and thus the amount of *trans* of the linoleic hydrogenated to monoene. This apparently does not happen. Therefore, a different mechanism must be operating; as shown in Figure 12, if the linoleic is not conjugated but both double bonds are complexed with the catalyst. Then hydrogen can add 1,2 to form a 9 *cis* monoene, 4,5 to form a 12 *cis* monoene, or 1,5. If 1,5, the hydrogen at the 3 position will go either way to form either a *trans* 10 or *trans* 11. If the hydrogen goes 1,2; 4,5; or 1,5 equally, then for every three moles

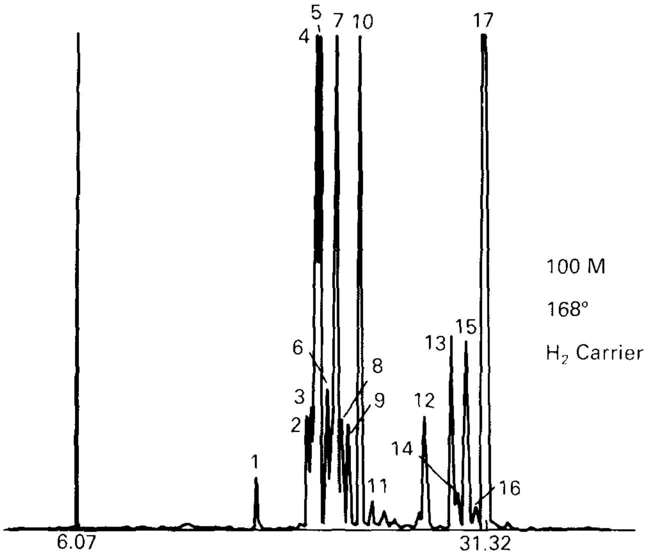

FIG. 10. Separation of geometric and positional isomers formed during hydrogenation of methyl linoleate. 1, methyl stearate; 2, *trans* 8 monoene; 3, *trans* 9; 4, *trans* 10; 5, *trans* 11; 6, *trans* 12; 7, *cis* 9; 8, *cis* 10; 9, *cis* 11; 10, *cis* 12; 11, *cis* 13 monoenes; 12, *trans trans* diene; 13, *cis trans* diene; 14, unknown; 15, *trans cis* diene; 16, unknown; 17, *cis cis* linoleate.

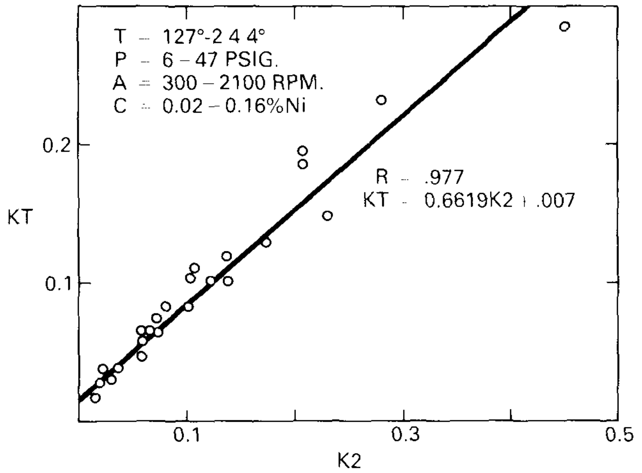

FIG. 11. The rate of formation of *trans* (Kt) vs. rate of hydrogenation of linoleate (K2). t, P, A, C are ranges of experimental parameters.

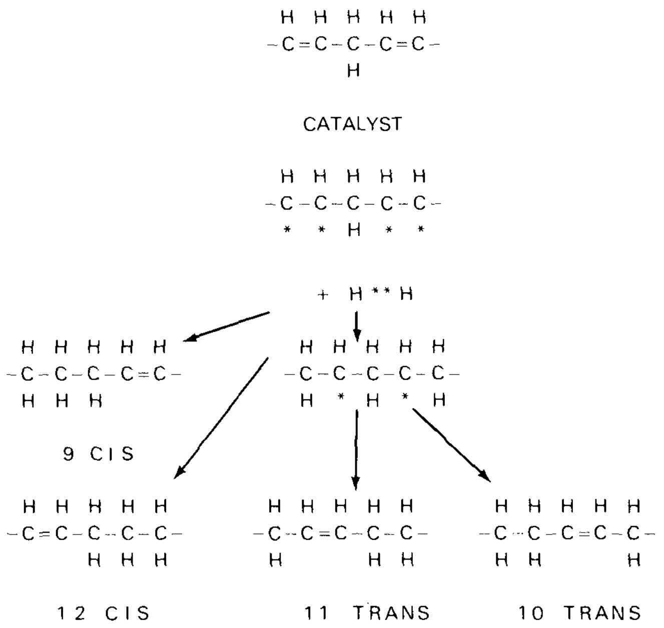

FIG. 12. Theory of hydrogenation of linoleate to a monoene without conjugation.

	Conjugated	Non-conjugated	Found
9	1	2	2
10	2	1	1.15
11	2	1	1
12	1	2	1.62

FIG. 13. Ratio of monoene positional isomers expected from the two theories of hydrogenation of linoleate to oleate.

linoleic hydrogenated—one mole of 9, one mole 12, 1/2 mole 10 and 1/2 mole 11 will be formed. As shown in Figure 13, this agrees fairly well with the ratios found experimentally.

There needs to be much more work on this to show if it is worth considering, but since I do not have a laboratory, someone else must do it. Good luck, whoever you may be, and I hope you enjoy this work as much as I did.

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