Reaction Mechanics of Sodium Methoxide Treatment of Lard[1]

THEODORE J. WEISS, GLEN A. JACOBSON,[2] and LARS H. WIEDERMANN,[3] Research Laboratories, Swift and Company, Chicago, Illinois

Lard was treated at several temperatures with sodium methoxide catalyst. Samples were taken frequently during the course of the reaction and were subjected to measurements of glyceride distribution, especially the trisaturated triglyceride fraction, in terms of melting point, cooling curve, aniline point, and x-ray diffraction pattern. The over-all reaction could be broken down into several phases.

I. Catalyst Formation. The sodium methoxide reacts with a fat to form an active catalyst. Infrared spectra show the formation of *beta*-keto esters during the reaction, probably intermediates in the ester-ester interchange.

II. Crystal Modification. This phase is characterized by a complete and permanent change in crystal structure with a simultaneous loss of GS_2U peak in the cooling curve. The GS_3 content is only slightly increased from the original lard at this point.

III, IV, etc. Interesterification. During these phases the fatty acids of the triglycerides approach random distribution. Intra-esterification occurs simultaneously but at a different rate. These phases are distinguishable from each other by their apparent GS_3 contents, which increase beyond that of phase II.

Although much work has been done on the treatment of lard with interesterification catalysts (1), little has been reported on the mechanics of the reactions involved. Difficulties have been encountered in differentiating between lard and treated lard because of the fact that standard analytical methods such as melting point, iodine value, etc., did not show measurable differences between these products (2).

Development of the differential cooling-curve technique (3) offers a more sensitive tool for the measurement of certain characteristics of glyceride composition than had been previously available. Preliminary results showed that lard could be distinguished from crystal-modified lard and that further treatment with interesterification catalysts brought about further changes. Therefore a systematic study of the reactions occurring during the treatment of lard with sodium methoxide was undertaken.

Experimental

Preparation of Sample. Filtered, dried, low free-fatty-acid lard was treated with 0.5% sodium methoxide (commercial) at several temperatures. Samples were withdrawn at frequent intervals in order to be able to follow all of the changes which might occur during the treatment, which ends in a fully-randomized product.

Analytical Methods. The sample obtained were subjected to analyses by a differential cooling curve (3), which indicated both point of crystal modification and apparent GS_3 content, also aniline point (4).

Results and Discussion

The discovery that a characteristic peak of the differential cooling curve is indicative of the apparent GS_3 content of treated lard facilitated the following of the course of the over-all reaction. Plots of GS_3 peak height *versus* time for lard treated at various temperatures indicate the presence of several phases which occur during the reaction (Figure 1). The cooling curve of lard does not show a distinct GS_3 peak. The GS_3 peak develops as the reaction progresses towards crystal-modified lard. The peak heights of partially-modified lard however could not be correlated with those of crystal-modified lard. These two products are in reality quite dissimilar. For this reason the GS_3 peak plots omit treated lards prior to complete crystal modification. By this time the typical GS_2U peak of lard has disappeared. Point CM on the curve refers to the point of complete modification, as determined by cooling curve and confirmed by x-ray diffraction analysis (1).

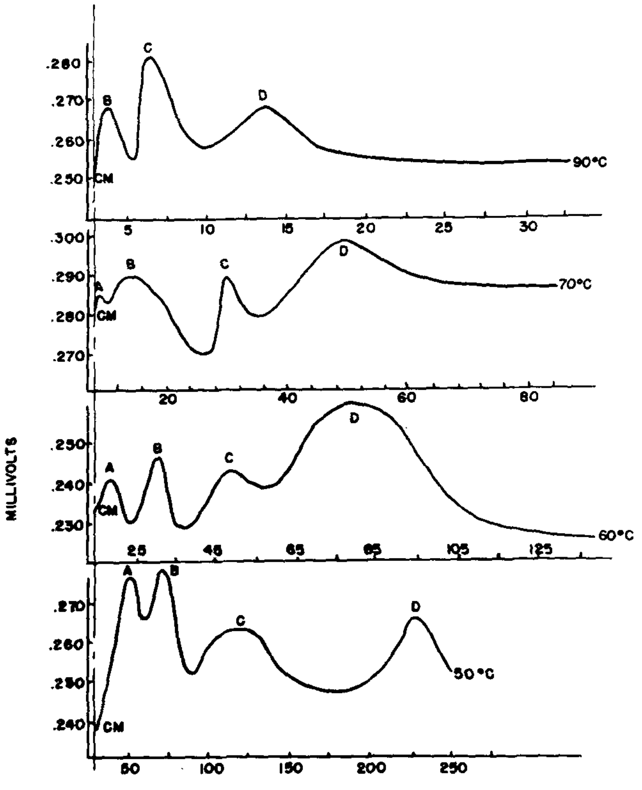

FIG. 1. Differential cooling-curve peak heights for treated lards plotted against time of reaction at various temperatures.

The curves all have similar maxima, which occur at regular intervals and are a function of reaction temperature. The variation in the exact shapes of the

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[2] Present address: Campbell Soup Company, Camden, N. J.

[3] Present address: National Dairy Products Corporation, Glenview, Ill.

curves at the different reaction temperatures as well as the erratic relationships between the peak heights cannot be explained at this time. The presence of the peaks and their positions on the time scale however can be explained. At 90°C. the reaction phase, represented by peak A, does not appear as it does at the other temperatures where the reaction is sufficiently slow.

The Arrhenius plot, reciprocal of temperature *vs.* log of reciprocal time, for the modification point gives a straight line, CM (Figure 2).

This plot is based on the equation:

$$2.303 \log\left(\frac{k}{t}\right) = \frac{-E}{RT} + \text{constant}$$

where k = a constant
t = time
E = activation energy
R = the gas constant
T = temperature

The equation is in the form of a straight line, the slope of which is a function of the activation energy of the reaction plotted. The activation energy of the crystal-modification reaction was calculated from the slope of this line and was found to be 13,600 calories per mole per degree Kelvin. This value is approximately that expected for ester-ester interchange reactions.

The fact that the peaks A, B, C, D also plot as straight lines, but with a different slope from the modification curve, show that these result from a different reaction than that causing crystal modification. This second reaction has an activation energy of 17,200 calories per mole per degree Kelvin and would therefore be expected to be slower than the crystal-modification reaction.

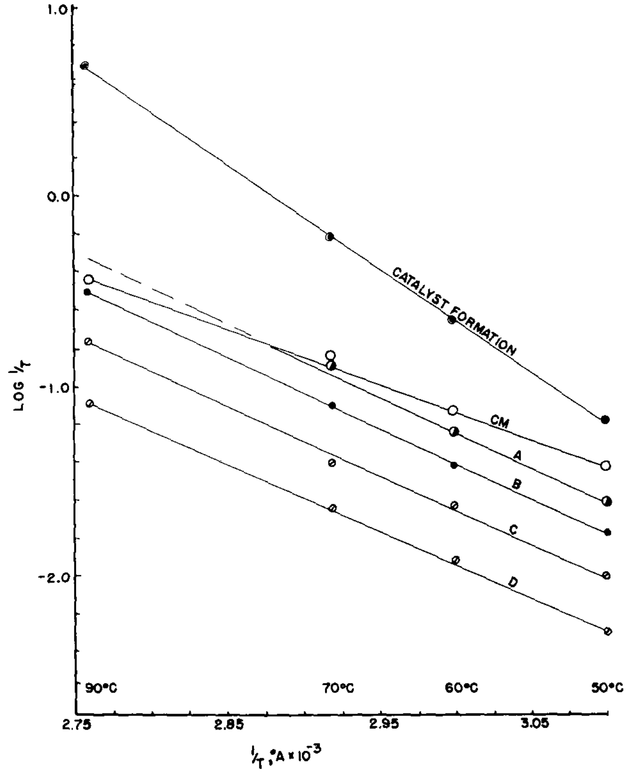

Fig. 2. Plot of reaction rate *versus* reciprocal time for different reaction phases that take place when lard is treated at various temperatures.

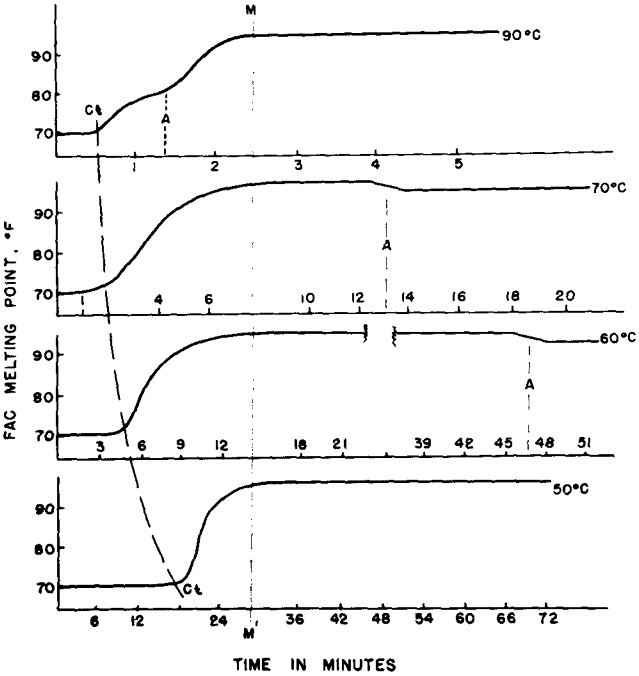

Fig. 3. Destearinated lard melting-points plotted against time of reaction with sodium methoxide at various temperatures.

Since it was difficult to interpret the premodification phase of the reaction, destearinated lard was treated with sodium methoxide in the same manner as was the lard. Destearinated lard is similar to lard and, in addition, exhibits a melting-point rise of about 25°F. on randomization. The results obtained are shown in Figure 3. These curves show an induction period, which is interpreted as the time required for catalyst formation. The end of this period is marked Ct. on the plot.

The Arrhenius plot of the time-temperature relationship of catalyst formation (Figure 2) gives a straight line curve which is not parallel to the other curves, indicating that the catalyst development phase does not involve ester-ester interchange. The activation energy was calculated to be 25,800 calories per mole per degree Kelvin. This amount of energy is considerably more than is required for ester-ester interchange, and could be sufficient for the formation of the enolate ion (Figure 4).

From this it would seem that the sodium methoxide is, as suggested by Eckey (5), only a catalyst activator, while the true catalyst is a compound resulting from the action of the activator on the triglyceride molecule. Figure 4 shows a proposed catalyst formation reaction. This is a typical reaction in which the enolate ion is formed by the action of a base on an ester. The proposed mechanisms for the ester-ester interchange by intra-esterification (Figure 5) and interesterification (Figure 6) follow logically the formation of the enolate ion. These reactions are characteristic of normal ester condensations.

The postulated formation of the *beta*-keto ester as an intermediate is supported by the presence of the *beta*-keto ester maximum absorption peak in infra-red

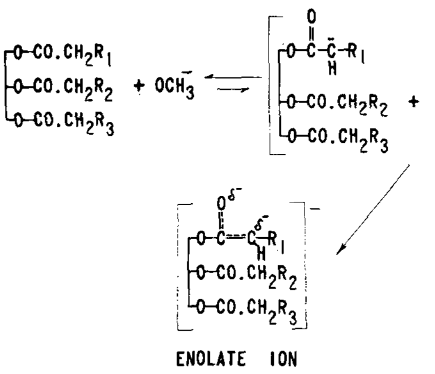

FIG. 4. Enolate ion formation.

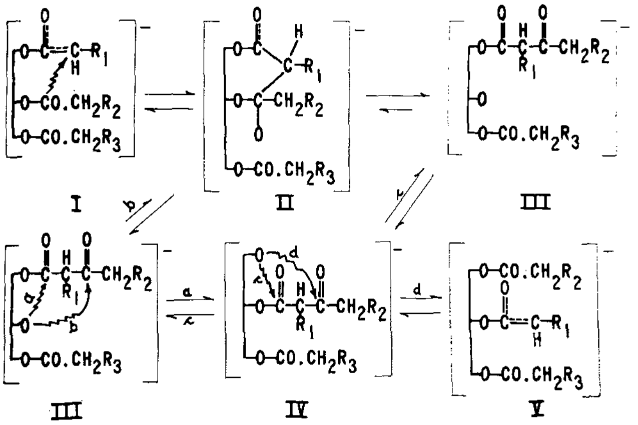

FIG. 5. Mechanism for intramolecular ester-ester interchange. The enolate ion (I) reacts with another ester group in the triglyceride molecule to produce a *beta*-keto ester (III), which because of its reduced acidity will not react further with another ethoxide ion but will undergo further reaction by either paths a or b; the former gives another *beta*-keto ester intermediate (IV), which yields an intramolecularly esterified product (V).

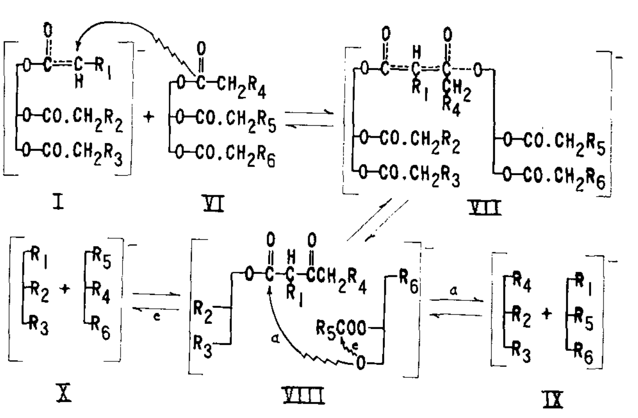

FIG. 6. Mechanism for intermolecular ester-ester interchange. The enolate ion (I) can react with another triglyceride molecule (VI) to produce a *beta*-keto ester between two glyceride molecules (VII). This intermediate can undergo stepwise reaction, through the intermediate VIII, to form an intermolecularly-esterified product (IX). The paths followed are similar to those of a and d for products III and V in Figure 5. An intramolecularly esterified product (X) can also be formed from the intermediate (VIII) through the path of b (III) after undergoing a shift in electrons *via* path e (VIII). This results in an equilibrium similar to that described by path c between III and IV in Figure 5.

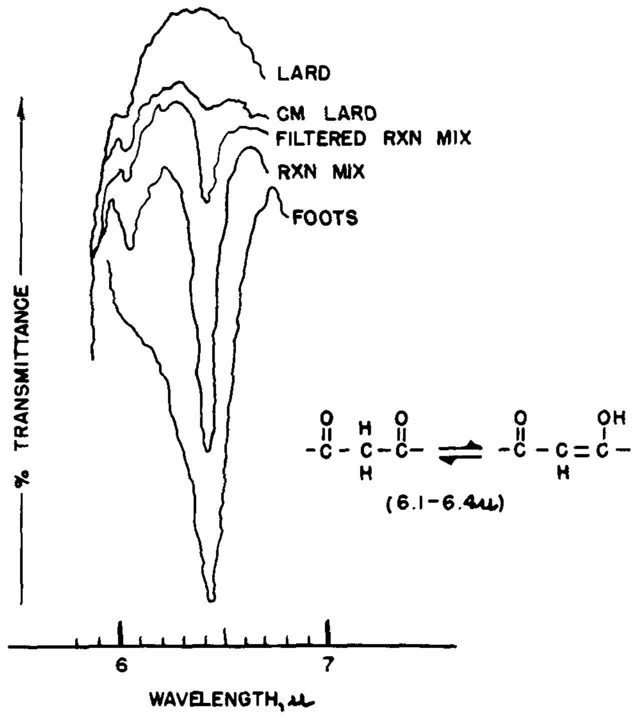

FIG. 7. Infrared patterns of various samples from the treatment of lard with sodium methoxide.

spectra (Figure 7). This peak was found in the reaction mixture and in the foots removed from this mixture after terminating the reaction by addition of water. The original lard did not show this peak. Crystal modified lard had only traces of this compound.

The proposed mechanisms imply that the *intra* ester-ester interchange would predominate in the initial stages of the reaction and would be the principal reaction involved in the formation of crystal-modified lard. This is in agreement with the closing statement by Bailey (2) that the crystal habits of the glycerides are caused by the position of oleic acid in the triglyceride molecule. No appreciable change in the GS_3 content at the point of crystal modification would be expected since intra-esterification would merely involve a change in symmetry of the individual triglyceride molecule.

The subsequent phases, marked by GS_3 peaks A, B, C, and D (Figure 1) are probably due to a constantly-shifting balance of glyceride species resulting from *inter* and *intra* esterification that takes place simultaneously but at different rates until a point approaching complete randomization is reached.

Destearinated lard usually exhibits a melting-point drop (Figure 3) after the maximum melting-point has been reached. However at 90° an apparent change (point A) takes place before the maximum melting-point is reached. It is interesting to note that peak A in lard (Figure 1) would have appeared before crystal modification at 90° and is also indicated by the broken part of the peak A line of Figure 2.

Because of the softness of the destearinated lard products, cooling curves do not give sufficiently definite peaks for accurate measurement. Aniline points (Figure 8) however confirmed the fact that some change was taking place after reaching the maximum melting-point. The vertical lines A, M, and M-prime in Figure 8 indicate the times at which changes in slope occur. These changes correspond to the melting-point changes shown in Figure 3.

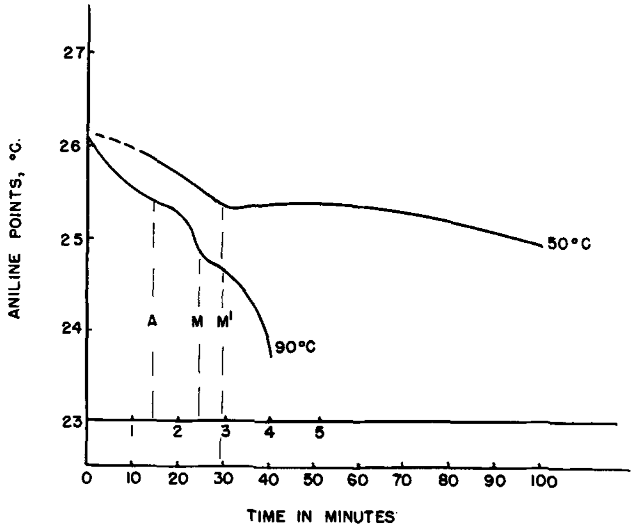

FIG. 8. Plot of aniline points *versus* time for reaction of destearinated lard with sodium methoxide at 90 and 50°C.

It is apparent that the exact times involved to reach specific points in lard treatment are different from the times required to reach equivalent points in the destearinated lard reactions. A change in catalyst activity because of such things as variation in the particle size of the catalyst could easily shift the entire curve on the time scale. In this work all of the lard and the catalyst used for the lard reactions at all temperatures were taken from the same lot. The same is true of the destearinated lard. However a different lot of catalyst was used for each fat, and obviously lard and destearinated lard differ in glyceride composition. Nevertheless similar reaction patterns result from the treatment of each with sodium methoxide.

REFERENCES

1. Weidermann, L. H., Weiss, T. J., Jacobson, G. A., and Mattil, K. F., presented at the 34th Fall Meeting, American Oil Chemists' Society, New York, October 17–19, 1960.

2. Bailey, A. E., Proceedings of the Fifth Research Conference, American Meat Institute, 1953, pp. 11–17.

3. Jacobson, G. A., J. Am. Oil Chemists' Soc., in press.

4. Summerbell, R. K., Franko, B. R., Wiedermann, L. H., and Pollaczek, E., presented at the Minneapolis meeting, American Chemical Society, September, 1955.

5. Eckey, E. W., Ind. Chem., 40, 1183–1190 (1958).

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The Differential Cooling Curve. A Technique for Measuring Certain Fat Characteristics

GLEN A. JACOBSON,[1] P.J. TIEMSTRA,[2] and W.D. POHLE, Research Laboratories, Swift and Company, Chicago, Illinois

The differential cooling-curve technique consists of a measurement of the difference in the cooling rate of a crystallizing and noncrystallizing fat or oil under specific conditions. The temperature differential between the two samples is measured by thermocouples and is plotted as fractions of a millivolt by a recording potentiometer. The significance of the various peaks encountered in the curves is discussed, and a rapid means of determining trisaturated triglyceride content in modified lard and related fats is presented.

The technique is a highly sensitive measurement of the thermal properties of a crystallizing fat, and as such offers an absolute measurement of various degrees of modification of lard. Curves of other fats representing different types of glyceride mixtures are presented.

THE COOLING CURVE has long been recognized as a valuable tool for studying crystallization phenomena of various substances. Among those who have applied this technique to fats were Quimby and coworkers, who noted differences in the cooling curves of tallow, lard, and other triglyceride mixtures (1). More recently Luddy and coworkers used the cooling-curve technique to illustrate changes in cooling characteristics brought about by treatment of lard and tallow by sodium methylate (2). The method described in their paper is based upon the considerable evolution of heat encountered when lard congeals and is of value in the laboratory for determining the end-point of lard crystal modification. Hannewijk, Haighton, and Lavery have demonstrated the usefulness of the differential type of melting and cooling curves in following the melting characteristics and polymorphism of glycerides and glyceride mixtures (3, 4, 5). In this paper are presented some results obtained by using a rapid and sensitive method of measuring the cooling characteristics of fats, the differential cooling curve.

Methods and Apparatus

The differential cooling-curve technique is based upon the difference in cooling rate between a standard oil, which will not crystallize when cooled to 0°C., and an unknown fat, which will crystallize at that temperature. To measure this small difference in temperature, copper constantan thermocouples were employed. The constantan leads of the two thermocouples were connected together (series opposed), and the copper leads were connected to the recording potentiometer. Connected in this manner the thermocouple assembly measures directly the difference in temperature in the two tubes. In actual practice two 15 x 125-mm. tubes are filled to a depth of 6 cm. with the reference and the sample, respectively. The thermocouples are inserted and placed 30 mm. from the bottom and in the center of the tube. The tubes are placed in a

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[1] Present address: Campbell Soup Company, Camden, N.J.
[2] Present address: Swift and Company, Kearny, N.J.