Conversion of Conjugated *cis-trans* Octadecadienoates to the *trans-trans* Isomers[1, 2, 3]

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ADDUCTS of the Diels-Alder type form readily when dienophiles react with conjugated *trans-trans* unsaturation, but the reaction is slow and incomplete with *cis-trans* conjugation (4). Conjugated dienes can be prepared in high yields by isomerization of linoleic acid or of oils rich in linoleic acid, with concentrated alkali, but this process yields a mixture of conjugated *cis-trans* 9,11- and 10,12-octadecadienoic acids with little or no *trans-trans* isomers (5).

The conversion of *cis* double bonds to the *trans* configuration (elaidinization) has been accomplished with a number of catalysts. However all catalysts are not equally efficient, and the ease with which elaidinization takes place, with any particular catalyst, depends on the type of unsaturation. Sulfur and iodine are relatively ineffective for changing isolated *cis* double bonds to the *trans* form, but traces of these materials rapidly produce isomerization of conjugated unsaturated systems. The conversion of *trans-trans-cis* α-eleostearic acid to the all-*trans* β isomer takes place easily at room temperature, in the presence of sulfur, and contact with sulfur-containing rubber tubing or stoppers must be avoided during preparation of α-eleostearic acid from tung oil.

Iodine has been used frequently for the preparation of conjugated *trans-trans* octadecadienoates, and Tolberg and Wheeler (6) have studied the spectral changes taking place during the reaction. They have found that an equilibrium was obtained when approximately 68% of the conjugated diene was in the *trans-trans* form. However the conditions that affect the rate and extent of the reaction have not been reported, and this investigation was undertaken to provide this information.

Experimental Procedures

Materials Used. Concentrates of *cis-trans* octadecadienoic acids were prepared by urea fractionation of the fatty acids of safflower seed oil, followed by isomerization with alkali (1). For most experiments the methyl esters obtained by esterifying the acids with methanol in the presence of sulfuric acid were used. In a few instances the acids themselves or the sodium soaps were used as starting materials.

Analytical reagent carbon disulfide was used, without further purification, as a solvent for the reaction, and for spectroscopic measurements in the infrared region. Methanol and Skellysolve C were distilled before use.

Conversion of Conjugated cis-trans Octadecadienoate to the trans-trans Isomer. When possible, the reaction and measurements were performed in the same solvent without isolation of the product. However in several instances it was necessary to isolate the reaction product before the extent of conversion could be measured. In these cases the *cis-trans* and *trans-trans* contents were measured on weighed amounts of the recovered fat dissolved in carbon disulfide.

a) *Direct Measurement of Isomerization in the Reaction Mixture.* An amount of conjugated *cis-trans* octadecadienoate sufficient to give a 5% solution was weighed into a volumetric flask and dissolved in a solution of iodine in Skellysolve C or carbon disulfide. At suitable intervals aliquots of the solution were used directly in the spectrophotometer for the determination of the *cis-trans* and *trans-trans* contents. Pure solvent was used in the reference cell.

b) *Measurement of Isomerization on Recovered Fat.* The reaction mixture was prepared as above, except that the fat concentration was usually higher. At intervals an aliquot of the mixture, equivalent to about 1 g. of fat, was transferred to a separatory funnel containing 10 ml. of 0.5 N sodium thiosulfate. The mixture was shaken to destroy the excess iodine, and the fat was extracted with 10 to 15 ml. of Skellysolve F. The solvent layer was washed several times with water and dried over anhydrous sodium sulfate; finally the solvent was removed under vacuum. In some cases the iodine color returned in the sample after initial treatment with sodium thiosulfate, and it was necessary to shake the sample with the sodium thiosulfate solution several times to remove the iodine completely. This technique gave more erratic results than direct measurement in the reaction mixture, probably because of losses and further changes which may take place during the additional steps necessary to destroy the iodine, extract the fat from the mixture, and prepare the methyl esters before the measurements are made.

Spectrophotometric Measurements. The conjugated *cis-trans* and *trans-trans* contents of the samples were determined by an infrared spectrophotometric method (1), using a Perkin-Elmer Model 21 double-beam instrument with sodium chloride prism and 0.1-mm. sodium chloride cells. The measurements were made between 10 and 11 μ, using the two absorption bands at 10.16 and 10.55 μ characteristic of pure conjugated *cis-trans* material and the single peak at 10.11 μ of the conjugated *trans-trans* compounds. In most cases the analyses were made with carbon disulfide solutions, and pure carbon disulfide was used in the reference cell. The total lack of absorption of iodine between 10 and 11 μ made it unnecessary to compensate for the iodine present in the samples when the isomerization mixtures were analyzed directly.

One series of measurements was performed with Skellysolve C solutions, and during these experiments it was noticed that the absorptivities of the pure *cis-trans* and *trans-trans* octadecadienoates were lower by factors of 0.845 and 0.836 than the values obtained for these compounds in carbon disulfide solutions. The

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[1] A report of work done partly under contract with the U. S. Department of Agriculture and authorized by the Research and Marketing Act. The contract was supervised by the Northern Utilization Research and Development Division of the Agricultural Research Service, Peoria, Ill. This research was supported also by the Hormel Foundation.

[2] Hormel Institute Publication No. 180.

[3] Presented at the 32nd Fall Meeting, American Oil Chemists' Society, October 1958, Chicago, Ill.

results obtained with Skellysolve C were corrected to compensate for these differences in absorptivity.

Reaction in Darkness. To estimate the extent of the reaction in absence of light, samples of fats dissolved in carbon disulfide solutions of iodine were prepared and stored in total darkness. At intervals aliquots of the solutions were transferred, in the dark, to the spectrophotometer cell, and the cell was brought to the infrared laboratory in a dark box. The instrument was adjusted in the usual manner and set at 10.10 μ. The room lights were turned off, both light beams were closed, and the other lights of the instrument were covered to keep the room as dark as possible. Then, as rapidly as possible, the cell was put into place, the light beams were opened, and the instrument was started. In this manner the *trans-trans* peak was recorded within five seconds after exposure of the sample to the light beam of the instrument, and the amount of conversion occurring after the sample had been placed in the light beam was negligible. Although no quantitative measurements could be made, the absorbance of the peak in the 10.15 μ region indicates the change which occurred during storage in the dark.

Results

Reaction in Skellysolve C. Figure 1 shows the effect of iodine concentration on the formation of *trans-trans* isomers in Skellysolve C under a light intensity of approximately 30 foot-candles. The excellent reproducibility of the reaction is indicated by the curve for 0.03 N iodine, where the points shown were obtained from two experiments performed three weeks apart.

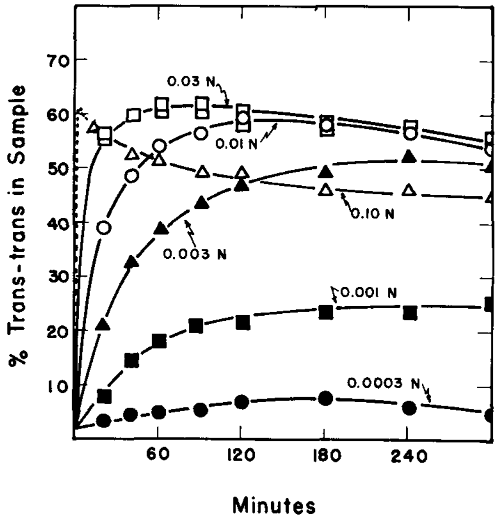

Fig. 1. Isomerization of *cis-trans* octadecadienoate with iodine in Skellysolve C, 5% fat solution.

Very little isomerization took place in the presence of 0.0003 N iodine, but the rate of formation of *trans-trans* compounds increased rapidly with iodine concentration. At higher iodine levels a second reaction, involving destruction of conjugation, became evident. This already is noticeable in the curve for 0.01 N iodine, and the disappearance of conjugation is much more rapid at higher iodine concentrations. An insoluble, dark, viscous material also formed in the solutions containing high concentrations of iodine.

With high levels of iodine it was not possible to make quantitative determinations during the initial stages of the reaction. The reaction rates were so great that the composition of the mixtures changed appreciably during the time required to obtain the infrared spectra of the samples. The time necessary to attain the maximum *trans-trans* content was estimated by placing the samples in the spectrophotometer immediately after mixing and recording the intensity of the *trans-trans* peak as a function of time by operating the instrument at a constant wavelength of 10.11 μ.

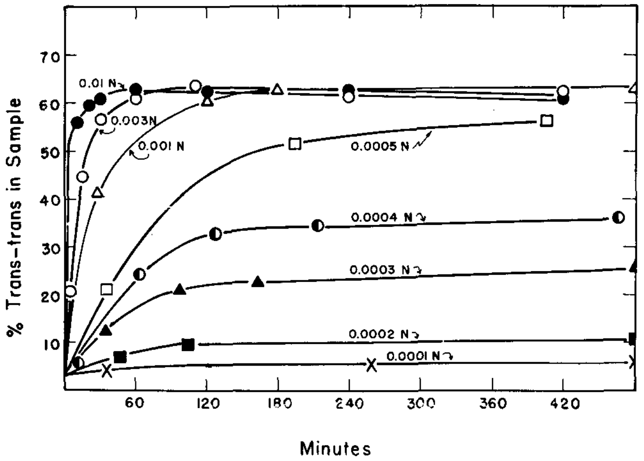

Fig. 2. Isomerization of *cis-trans* octadecadienoate with iodine in carbon disulfide, 5% fat solution.

The *trans-trans* peak of the sample containing 0.1 N iodine reached a maximum value 1.2 min. after mixing, and the decrease during the next 10 min. amounted to 16% of the maximum value.

The light intensity of the spectrophotometer beam was about 30 foot-candles, and since this was approximately the same as the light intensity received by the samples represented in Figure 1, the curves for 0.1 N iodine has been extrapolated to give the highest *trans-trans* content approximately 1 min. after mixing. Samples containing 0.07 and 0.05 N I_2 gave curves intermediate between the 0.1 and 0.03 N I_2 concentrations. These have been omitted from the figure for clarity. The 0.07 N sample reached a maximum *trans-trans* content 3 min. after mixing, and the loss in absorbance was only 4% of the maximum value after 10 more minutes.

Reaction in Carbon Disulfide. Iodine concentrations greater than 0.01 N were not used in this series of experiments in order to avoid the formation of insoluble materials similar to those obtained with Skellysolve C. Figure 2 shows the formation of *trans-trans* compounds with various concentrations of iodine in carbon disulfide solutions.

The rate of reaction is more rapid in carbon disulfide than in Skellysolve C, and with 0.01 N iodine maximum *trans-trans* formation was attained in 60 min. (150 min. in Skellysolve C). This more rapid rate of reaction also makes it possible to obtain maximum *trans-trans* formation with iodine concentrations as low as 0.001 N whereas not more than 25% of *trans-trans* material was formed with the same iodine concentration in Skellysolve C.

Reaction in Methanol. When methanol was used as the reaction solvent, the conversion of *cis-trans* to *trans-trans* compounds was much lower than in the other two solvents studied, and low *trans-trans* contents were attained even with high iodine concentrations. The results obtained with methanol have been summarized in Table I. The highest *trans-trans* content was obtained 20 min. after the fat had been mixed with a 0.10 N iodine solution. However in this sample more than 26% of the total conjugation originally present in the fat had been destroyed, and aliquots analyzed at later times indicated further destruction. Lowest destruction of conjugation occurred with 0.01 N and 0.03 N iodine solutions, but the amounts of *trans-trans* material formed were considerably lower than those obtained with carbon disulfide or Skellysolve C.

TABLE I

Isomerization of Conjugated *cis-trans* Octadecadienoate with Iodine in Methanol

Iodine concentrations	Time to reach max. *trans-trans*	Total conjugation [a]	Maximum *trans-trans* content	
			of total sample	of conj. material
N	*min.*	%	%	%
0 [b]	0	93.6	2.3	2.5
0.0001	240	74.3	5.6	7.6
0.001	180	74.7	15.9	21.3
0.003	300 [c]	73.1	23.7	32.4
0.01	300 [c]	81.3	37.6	46.2
0.03	300 [c]	78.4	38.4	49.0
0.05	300 [c]	69.8	22.4	32.0
0.07	240	67.6	24.2	35.0
0.1	20	68.9	48.5	70.4

[a] *Cis-trans* and *trans-trans* only, as measured by the infrared method.
[b] Original conjugated *cis-trans* concentrate used as substrate.
[c] End of experiment.

Effect of Temperature. Figure 3 shows that when samples containing 5% conjugated *cis-trans* concentrate in 0.03 N iodine in CS_2 were stored at room temperature (23°C.), 0°C., and −20°C., the reaction rate, the extent of conversion, and the loss of conjugation all increased with temperature.

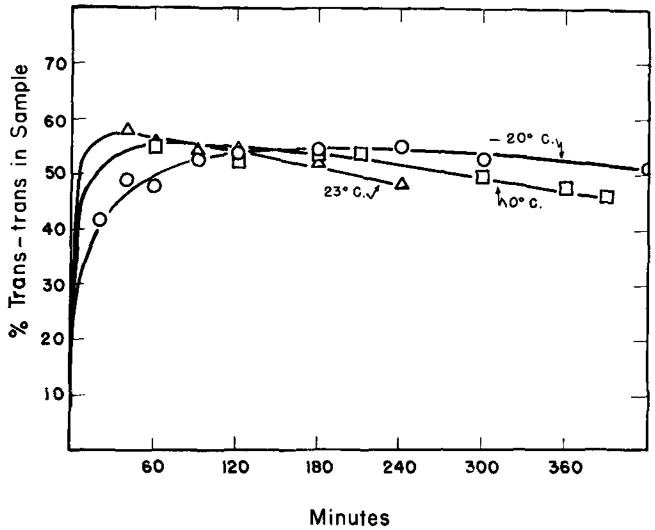

FIG. 3. Effect of temperature on isomerization of *cis-trans* octadecadienoate, 5% fat in 0.03 N iodine in CS_2.

Effect of Light Intensity. The effect of light intensity on the formation of *trans-trans* isomers is shown in Figure 4. Identical samples in 10-ml. volumetric flasks were placed at various distances from two day-light fluorescent lamps, and the amount of light falling on the flasks was measured with a photoelectric light meter. The rate and extent of conversion were approximately the same in the two samples receiving 50 and 100 foot-candles of light, indicating that, under the conditions used, a light intensity of approximately 50 foot-candles is sufficient to give maximum isomerization. With an exposure of 20 foot-candles the reaction rate was slower, and the extent of conversion reached a plateau near 45% *trans-trans* compounds in the sample. At 2 foot-candles the reaction was very slow, and the maximum conversion attained was only 20% *trans-trans* compounds. These results indicate that the conversion of *cis-trans* to the *trans-trans* isomer is catalyzed by light.

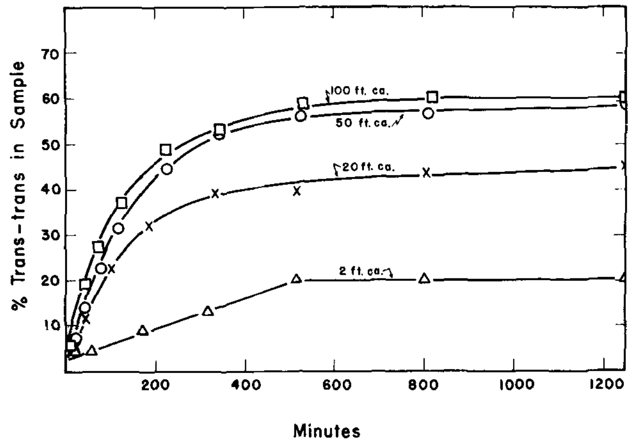

FIG. 4. Effect of light intensity on isomerization of *cis-trans* octadecadienoate, 5% fat in 0.0005 N iodine in CS_2.

Effect of Fat Concentration. Three samples, containing approximately 5%, 1%, and 0.5% fat dissolved in a 0.0005 N iodine solution in carbon disulfide, were exposed to equal light intensity, and the *cis-trans* and *trans-trans* contents of the samples were measured from time to time. The measurements were made directly on the solutions by using cells with thicknesses of 0.1, 0.5, and 1.0 mm., respectively, so that the total amount of sample in the light beam was approximately constant and equivalent to a 5% solution in a 0.1-mm. cell. The results given in Figure 5 show that the rate of conversion is greater at lower fat concentrations. The effect of decreasing fat concentration, while iodine concentration remains constant, is similar to that obtained by increasing iodine concentration while the fat content remains the same, as shown in Figure 2.

Reaction in Darkness in the Presence of Iodine. The extent of conversion taking place in the absence of

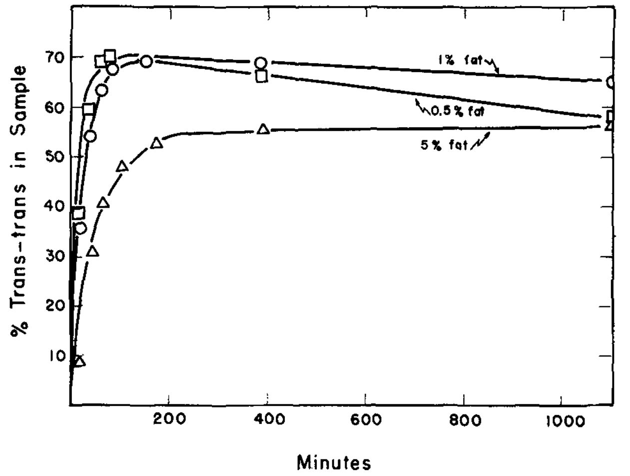

FIG. 5. Effect of fat concentration on isomerization of *cis-trans* octadecadienoate, 5% fat in 0.0005 N iodine in CS_2.

TABLE II

Isomerization of Conjugated *cis-trans* Octadecadienoate in the Dark with Iodine

Days in darkness	Absorbance of *trans-trans* peak				
	0.005 N I_2	0.001 N I_2	0.0005 N I_2	0.0001 N I_2	No I_2
0	0.270	0.280	0.280	0.280	0.280
2	......	0.321	0.365	0.280	0.279
4	......	0.357	0.362	0.272	......
6	......	0.397	0.390	0.275	0.273
11	0.570	......	......	......	......
12	......	0.450	0.421	0.277	......
35	0.550	......	......	......	......
47	......	0.468	0.520	0.279	0.289
76	......	......	0.490	0.270	0.282

light is shown in Table II, where the absorbance of the *trans-trans* peak, obtained within 5 sec. after the samples were exposed to the light of the spectrophotometer, has been recorded for samples stored for up to 76 days in total darkness. The results indicate that the reaction takes place slowly in the dark and that the rate of conversion increases with increasing iodine concentration. No reaction took place in the absence of iodine or when the iodine solution was 0.0001 N.

Isomerization of trans-trans Compounds and Composition of the Equilibrium Mixture. Figure 6 shows the changes in composition with time when the methyl esters of either conjugated *cis-trans* or conjugated *trans-trans* octadecadienoic acids were treated with 0.003 N iodine in carbon disulfide. The *cis-trans* concentrate originally used contained 91.2% *cis-trans* and 3.9% *trans-trans* dienes while the *trans-trans* material contained 4.0% *cis-trans* and 94.8% *trans-trans* compounds.

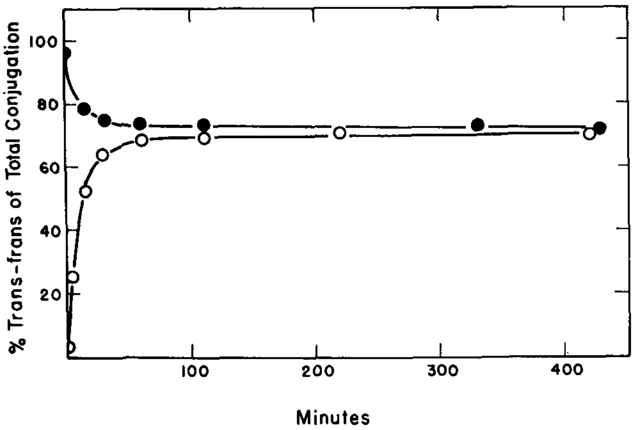

FIG. 6. Isomerization of conjugated *cis-trans* and *trans-trans* octadecadienoates, 5% fat in 0.003 N iodine in CS_2.

In the figure the percentage of the conjugated material which is in the *trans-trans* form has been plotted against time. It is obvious that the same equilibrium mixture is obtained in both cases and that, at equilibrium, the *trans-trans* material constitutes approximately 71% of the conjugated fraction.

Isomerization in the Absence of Catalyst. Catalysts are unable to initiate reactions but serve merely to accelerate the rate at which the reactions take place. It was of interest to see therefore if the isomerization took place at a measurable rate in the absence of iodine. Five per cent carbon disulfide solutions of conjugated *cis-trans* or *trans-trans* concentrates were exposed to the light of 100 foot-candle intensity and analyzed directly in the spectrophotometer. The curves in Figure 7 show that the conversion of one isomer to the other takes place in the absence of iodine but that the reaction is very slow.

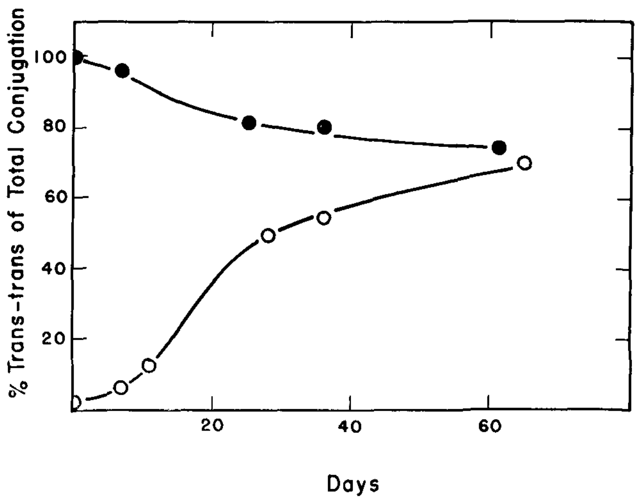

FIG. 7. Isomerization of conjugated *cis-trans* and *trans-trans* octadecadienoates without catalyst, 5% fat in CS_2.

Isomerization of Acids and Soaps. Several experiments were performed to explore the ease with which acids or soaps could be isomerized with iodine.

The acids were readily isomerized with iodine in Skellysolve C in diffuse daylight or in direct sunlight. A mercury vapor "sterilamp" was rather ineffective in catalyzing isomerization and no *trans-trans* isomers were formed when iodine was dissolved directly in *cis-trans* acids without solvent.

The sodium soaps of conjugated *cis-trans* acids dissolved in an aqueous-alcoholic solution (25% ethanol) were isomerized easily in the presence of 0.1 N iodine and 7.5% KI. The *trans-trans* content obtained was approximately the same as during isomerization of esters in Skellysolve C, but the rate of conversion was lower.

Discussion

Composition of Equilibrium Mixtures. Figure 6 shows that in the equilibrium mixture resulting from isomerization of conjugated *cis-trans* or *trans-trans* diene, with 0.003 N iodine in carbon disulfide, 71% of the conjugation is in the *trans-trans* form. Similar values between 70.4 and 72.3% *trans-trans* have been obtained with 0.01 N and 0.001 N iodine in CS_2, with 0.1 N iodine in methanol, and by isomerizing soaps in aqueous-alcoholic solutions with iodine. However direct measurements on equilibrium mixtures obtained in Skellysolve C indicated a *trans-trans* content of 75.2% (74.3 to 76.3) when iodine concentrations of 0.01, 0.03, 0.05, 0.07, and 0.10 N were used. The solvent should have no effect on the composition of the equilibrium mixture, and it is very likely that the values obtained with Skellysolve C solutions are in error, particularly since the absorptivities of the *cis-trans* and *trans-trans* compounds in this solvent are different from those in carbon disulfide, and the results in Skellysolve C were obtained by applying a correction to the measurements. This is supported by a *trans-trans* content of 71.4% for an equilibrium mixture obtained by isomerizing a *cis-trans* sample in Skellysolve C and analyzing the equilibrium mixture in carbon disulfide after isolation from the isomerization solvent.

Tolberg and Wheeler (6) have indicated that little, if any, *cis-cis* material is present in the equilibrium mixture. A comparison of the observed absorbances, at 231 mμ, of several equilibrium mixtures, with the values calculated from the *cis-trans* and *trans-trans* contents determined by the infrared method, and the absorptivities of the pure compounds (1) agrees fully with these observations (Table III).

TABLE III

Absorbance of Equilibrium Mixtures at 231 mμ

Sample	*cis-trans*	*trans-trans*	Total	A_{231}	
				Calculated[a]	Measured
	%	%	%		
A	22.1	55.0	77.1	82.0	81.4
B	22.0	60.3	82.4	87.5	87.4
C	28.1	58.7	86.8	91.4	87.4

[a] Assuming the absorptivities at 231 mμ to be 89.7 for pure *cis-trans* and 112.7 for pure *trans-trans*.

Thus it seems well established that the isomerization mixture contains approximately 71% *trans-trans* and 29% *cis-trans* isomers. These values are in reasonable agreement with those of Tolberg and Wheeler (6).

Kinetics of the Reaction. The isomerization of *cis-trans* octadecadienoate to the *trans-trans* isomer may be represented by the following reversible equilibrium reaction:

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$$

where k_1 and k_2 are the rate constants for the forward and reverse reactions, respectively.

The over-all rate at which the forward reaction approaches equilibrium is given by the equation

$$-dA/dt = k_1 [A] - k_2 [B] \qquad (I)$$

which on integration gives

$$k_1 + k_2 = \frac{1}{t} \ln [B_e]/([B_e] - [B]) \qquad (II)$$

where $[B_e]$ is the concentration of B at equilibrium and [B] the concentration of B at time t.

In this case [B] is the concentration of *trans-trans* isomer (%TT) and $[B_e] = 71$. Equation II becomes

$$\log (71 - \%TT) = \frac{-k't}{2.303} + \log 71 \qquad (III)$$

where $k' = k_1 + k_2$. A plot of log (71−%TT) against t should give a straight line with a slope from which k′, the over-all rate constant can be calculated. Figure 8 shows such a plot for isomerization with 0.003 N iodine in CS_2. The over-all rate constant k′ calculated from the slope of the line is 0.082 $min.^{-1}$

It should be possible to obtain rate constants in a similar manner for experiments performed under different conditions. However the curves in Figures 1 and 2 indicate that the rate of isomerization depends on catalyst concentration, also that the catalyst is destroyed or inactivated. The straight line relationship shown in Figure 8 therefore should exist only during the early stages of the reaction, while using relatively large amounts of catalyst, when the catalyst concentration remains reasonably constant. Under these conditions isomerization is so rapid that accurate measurements at the beginning of the reaction are not possible.

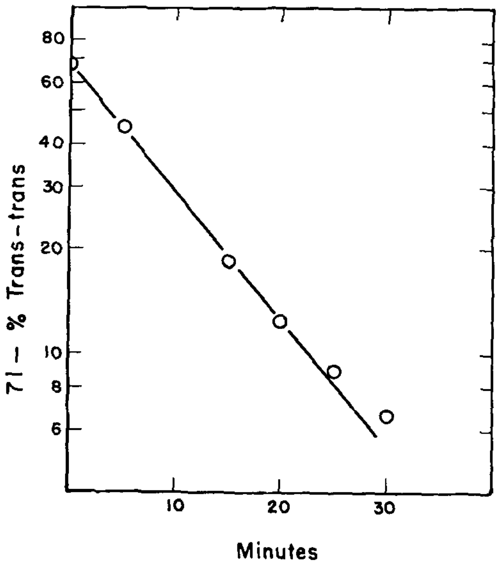

FIG. 8. Evaluation of isomerization rate constant for *cis-trans* octadecadienoate, 5% fat solution in 0.003 N iodine in CS_2.

The isomerization therefore appears to be pseudo-first order with respect to the substrate, but the exact relationship of catalyst concentration and temperature to reaction rate has not been established.

Catalyst Inactivation. Figures 1 and 2 show that with iodine concentration less than 0.01 N in Skellysolve C or 0.001 N in CS_2 the equilibrium mixture is not attained, presumably because the catalyst is used up in other ways. Visual observations also indicate the disappearance of iodine, and Figure 9 shows that isomerization can be made to proceed in stages by the repeated addition of small amounts of catalyst to the reaction mixture. This indicates clearly that the failure to reach equilibrium with low iodine concentration results from the disappearance or inactivation of the catalyst. At the same time, with high iodine concentrations, conjugation disappears, and a dark, viscous, insoluble material forms. It is very possible that the disappearance of conjugation and of iodine are caused by reactions probably involving direct addition of iodine to the conjugated double bond system to form a stable covalent compound. The dark, insoluble material formed at high iodine concentrations probably results from some sort of polymerization and may account also for part of the loss of conjugation and iodine.

Reaction Mechanism. It has been observed that when an iodine solution is added to conjugated *cis-trans* or *trans-trans* octadecadienoate, a visible decrease in the intensity of the iodine color occurs immediately, perhaps indicating the formation of a colorless iodine-fat complex. This change does not seem to take place stoichiometrically as, even at low iodine concentration, the color does not disappear completely. Furthermore the change is partly reversible. Shaking of the iodine-fat solution with sodium thiosulfate completely removes the free iodine remaining in the the mixture, but, on standing for several minutes in light, the color of iodine returns in the organic phase and this color can be removed again with thiosulfate. With iodine concentrations of 0.05 N or above, this process can be repeated several times, but the intensity of the returning iodine color is decreased each time. When identical experiments were

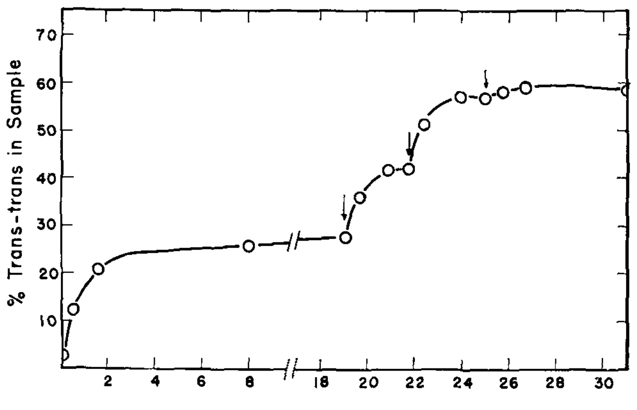

FIG. 9. Effect of stepwise addition of small increments of iodine on isomerization of *cis-trans* octadecadienoate, 5% fat solution, original iodine solution 0.0003 N in CS_2.

performed with natural *cis*-9, *cis*-12-linoleate, a slight change in the color of the solution occurred, probably because of a small degree of solvation of the iodine induced by the oxygen of the ester group, but no iodine color returned in the fat-organic solvent layer after treatment with thiosulfate. Although no quantitative measurements have been made, these observations indicate the existence of an equilibrium between the free components of the mixture and a fat-iodine coordination complex.

In addition, when a sample of conjugated *cis-trans* octadecadienoate was mixed with 0.01 N iodine in Skellysolve C in the dark, decolorized with thiosulfate in the dark 15 min. later, and then left standing in darkness for an additional 65 min., no iodine color returned to the fat solution. However, when the sample later was exposed to light, the color of iodine returned within 10 min.

Evidently the conjugated fat-iodine complex forms readily in the dark, but the reverse reaction, whereby the complex is dissociated and free iodine again liberated, is catalyzed by light.

It is probable that the conversion of *cis-trans* octadecadienoate to the *trans-trans* isomer is associated with the formation of this reversible iodine complex and that light catalyzes the conversion because of its effect on the decomposition of the complex.

The mechanism of the reaction therefore is probably:

$$\begin{tikzcd}
\mathrm{CT}\cdot\mathrm{I}_2 & \mathrm{CT}+\mathrm{I}_2 \arrow[l] \arrow[r, shift left, "\text{fast}"] & {[\mathrm{CT}\cdot\mathrm{I}_2]} \arrow[l, shift left, "\text{light}"] \arrow[d, shift left, "\text{slow}"] \\
\mathrm{TT}\cdot\mathrm{I}_2 & \mathrm{TT}+\mathrm{I}_2 \arrow[l] \arrow[r, shift left, "\text{fast}"] & {[\mathrm{TT}\cdot\mathrm{I}_2]} \arrow[l, shift left, "\text{light}"] \arrow[u, shift left] \\
\text{stable covalent compounds} & & \text{unstable coordination complexes}
\end{tikzcd}$$

Conditions Influencing the Reaction. Catalyst concentration, temperature, light intensity, fat concentration, and type of solvent which influence the rate of isomerization also affect the extent of isomerization by changing the relative rates of the two reactions competing for the iodine catalyst.

At low iodine concentrations or at high fat levels when the ratio of catalyst to substrate is low, isomerization proceeds slowly, and the formation of the stable covalent compounds effectively removes the catalyst from the mixture before isomerization has progressed to the equilibrium point. This seems to occur when iodine concentrations are 0.003 N or less in Skellysolve C and 0.0005 N or less in carbon disulfide. Visual observations indicate that the rates of disappearance of iodine in the presence of conjugated material in these two solvents are approximately equal. Consequently, the greater efficiency of the catalyst in CS_2 must be caused by a higher rate of isomerization resulting in the formation of more *trans-trans* material before the iodine is inactivated by forming the stable compound.

In carbon disulfide and Skellysolve C, iodine gives violet solutions and is presumably present in the diatomic (I_2) state. In methanol however a brown solution is obtained, and it has been postulated that this results from solvation between iodine and the oxygen of methanol (2). It has been shown also that "brown" iodine in polar solvents is more reactive than "violet" iodine in nonpolar solvents (3). The low efficiency of iodine, as an isomerization catalyst, in methanol and the high loss of conjugated diene may be caused by the increased formation of the stable covalent compound in this solvent.

The effect of light intensity on the rate of conversion may result from the catalytic action of light on the decomposition of the fat-iodine complex. However the low maximum *trans-trans* content of the samples under poor illumination, even after prolonged exposure (Figure 4), cannot be explained in the same manner. The gradual disappearance of iodine color from the samples under different illumination appeared to be independent of light intensity, and all samples were nearly colorless after 800 min., and only slightly yellow, with no trace of pink iodine color after 1,300 minutes when the experiment was stopped. Consequently, under poor illumination, the iodine present in the sample reacts with the substrate to form the stable compound before complete conversion to the equilibrium mixture can occur. When the samples exposed at 2 or 20 foot-candles for 1,300 min. were exposed further to a light intensity of 100 foot-candles, the *trans-trans* content increased only very slightly, at a rate corresponding approximately to that observed in the absence of catalyst.

Isomerization in the Absence of Catalyst. In Figure 7, representing the isomerization of the *cis-trans* and *trans-trans* compounds under the influence of light, but without added catalyst, the first part of both curves has an autocatalytic shape. No effort was made to prevent oxidation of the compounds, and the samples were not kept in an inert atmosphere. It is very likely that some autoxidation occurred during this experiment, and it is possible that peroxides or other oxidation products may have catalyzed the conversion of these compounds into their geometric isomers.

Summary

The conversion of methyl conjugated *cis-trans* octadecadienoate to the *trans-trans* isomer takes place easily in the presence of iodine and light. The reaction is more rapid in carbon disulfide than in Skellysolve C, and it is quite slow and accompanied by loss of conjugation in methanol. The rate of conversion

increases with iodine concentration and light intensity and decreases with increasing fat concentration. It is affected by temperature also, but to a lesser degree. The influence of light may result from its catalytic effect on the decomposition of a reversible fat-iodine complex.

The reaction appears to be pseudo-first order with respect to the substrate but is complicated by side reactions which inactivate the catalyst and destroy conjugation.

The reaction occurs, at a measurable rate, with iodine in the dark, or in light without iodine, but no conversion takes place without iodine in darkness.

The isomerization reaches an equilibrium when approximately 71% of the conjugation present is in the *trans-trans* form. This equilibrium can be attained by starting with either *cis-trans* or *trans-trans* material. Very little, if any, *cis-cis* isomer is present in the equilibrium mixture.

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A Report from the Refining Committee

AT THE FALL MEETING of the Refining Committee of the American Oil Chemists' Society in 1957 questions were raised by one member concerning the refining practice, which has been used by the N.C.P.A. since 1939 (Rule 150), of permitting settlement refining results to be determined on Expeller cottonseed oil by the use of the lye usages and strengths specified for hydraulic oil if the seller so chooses. The rules also include settlement refining conditions for Expeller oil, but as higher amounts of stronger lyes are required, these conditions are seldom chosen by the seller. Some evidence was presented to suggest that while the usage of the refining conditions specified for the settlement refinings on hydraulic oil do result in a fully refined oil with hydraulic oil, the current Expeller oil was significantly under-refined when these same refining conditions were used in the settlement refinings of Expeller oils. It was believed possible that in the continuing efforts to improve Expeller oil yields that the intensity of the seed-conditioning treatment prior to expelling may have been increased, resulting in the presence of materials in crude Expeller oil currently that were either at lower levels or absent under the less severe conditioning-treatment of 20 years ago.

If, in fact, this was the situation, it was pointed out that while a refiner currently would still be able to process hydraulic oil in the plant to a loss equalling the settlement result and obtain thereby an oil of low enough bleach color to be usable in light-color products, with Expeller oil he would find it necessary to refine the oil to a loss substantially greater than the settlement loss to obtain a low enough bleach color on such oil to permit its use in shortenings, for instance, without excessive bleaching costs. In other words, while the inherent minimum bleach color of both hydraulic and Expeller oils had been approached by using the settlement refining conditions for hydraulic oil in 1939, this apparently was no longer the case with Expeller oil as produced currently.

The committee agreed that an investigation of the problem should be made. In 1958 nine laboratories analyzed a sample of Expeller cottonseed oil composited from several score of cars from California and Arizona mills, using stronger lyes than would be required by the hydraulic oil refining conditions to determine if such refinings would reveal evidence of under-refining of the Expeller oil. Mean results (the FFA of the sample was 1.3% so that 12° and 14° Baumé lye would be used for the settlement refining under the rules) are shown in Table I.

TABLE I
% Lye

° Baumé	60%			80%		
	Ref. Loss	Ref. color	Bl. color	Ref. loss	Ref. color	Bl. color
	%	*red*	*red*	%	*red*	*red*
16	6.616	7.394	3.359	7.291	6.466	2.934
20	6.133	6.813	3.025	6.772	5.808	2.446
24	6.752	7.338	3.084	7.400	5.566	2.168

The sharply decreasing bleach color which was found with 80% usage of stronger lyes was accepted as evidence that at least on this sample of Expeller oil the inherent minimum bleach color of such oil could only be obtained by the refiner at the cost of significantly higher refining losses than the settlement loss. Since the hydraulic oil settlement conditions were not run on the oil in question, it was decided to carry out further work. For a measure in terms of bleach color of proper refining of a cottonseed oil, the committee chose the criterion that an oil would be considered fully refined when its bleach color was within 0.2 red of the inherent minimum bleach color of the particular oil.

In the 1959 work nine laboratories each refined four samples of Expeller cottonseed oil representing typical Expeller oils from the Southeast, Valley, Southwest (West Texas), and West Coast areas.

Refinings were made by the hydraulic oil settlement conditions as well as at higher amounts of stronger lyes at each of the oils (including the Expeller oil settlement conditions). Mean results are shown in Table II.