

Geometrical Isomerization of Fatty Acids with Sulfur as a Catalyst

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The kinetics of the geometrical isomerization of oleic and palmitoleic acids, both contained in U.S.P. oleic acid, were studied. Sulfur powder was used as a catalyst. The methyl esters of fatty acids were analyzed by GLC with 15% OV-275 columns. The sulfur-catalyzed isomerization at 180 and 225 °C proceeds via two consecutive mechanisms. The position of equilibrium is reached by the second mechanism. For this, at any particular initial concentration of sulfur, the pseudo-first-order rate dependence on substrate for a reversible reaction holds. The full rate has been shown to be proportional to the initial sulfur concentration taken to the 1.2 power. The rate constants at both temperatures and the activation energies were calculated.

Introduction

Conversion of lower melting *cis* forms to higher melting *trans* forms has been a goal in edible as well as industrial products (cosmetics, transparent soaps, etc.). Much research has been done to find a convenient method for geometrical isomerization of unsaturated fatty acids. *Cis* isomers are converted to *trans* isomers by many catalysts, but publications are usually about the determination of the equilibrium position.

When an industrial catalyst is necessary, not only the price but also the rate of reaction and the formation of byproducts (polymers, positional isomers, etc.) must be taken into account. Thus, it is important to determine not only the yield but also the kinetics.

Information about sulfur as a catalyst for the geometrical isomerization of fatty acids is scarce (Johnson and Pryde, 1979; Sonntag, 1979; Sastry et al., 1970). Reactions with sulfur compounds are better known. Another type of catalyst is the thiyl radical (RS^{\bullet}) produced from mercaptans or sulfides (Johnson and Pryde, 1979) or *p*-toluenesulfinic acid (Snyder and Scholfield, 1982). Sulfur powder was also used as a catalyst in other reactions that are combined with geometrical isomerization. Balakrishna et al. (1971) used sulfur in Diels-Alder reactions with safflower oil fatty acids. Totani et al. (1978) carried out the cyclization of tung oil with sulfur as a catalyst.

None of the above-mentioned papers studies the kinetics of the reactions. It is also not common to study the geometrical isomerization of monounsaturated fatty acids that are different from oleic acid (Grompone and Moyna, 1986) and that are usually found in fats and oils.

In the present paper, the kinetics of the geometrical isomerization of oleic and palmitoleic acids (contained in U.S.P. oleic acid) with sulfur as a catalyst is studied.

Theory

If the mechanism of the reaction of geometrical isomerization corresponds to a reversible reaction with first-order kinetics for the monounsaturated fatty acids and with n th-order kinetics for the catalyst, at constant temperature, the integrated rate law is

$$\ln \frac{C_{c,0} - C_{c,e}}{C_c - C_{c,e}} = (k_1 + k_2) C_s^n t \quad (1)$$

The values of such concentrations are

$$C_c = \frac{10dP_c}{M_c} \quad (2)$$

$$C_s = \frac{10dP_s}{M_s} \quad (3)$$

By using percentages, the rate equation becomes

$$\ln \frac{P_{c,0} - P_{c,e}}{P_c - P_{c,e}} = (k_1 + k_2) \left(\frac{10d}{M_s} \right)^n P_s^n t \quad (4)$$

When there is more than one monounsaturated fatty acid, the percentages of its *cis* and *trans* configurations can be taken in relation to 100 g of itself (and not to 100 g of sample).

$$P_c + P_t = A < 100 \quad (5)$$

$$P_c' = \frac{100P_c}{A} \quad (6)$$

$$\ln \frac{P_{c,0}' - P_{c,e}'}{P_c' - P_{c,e}'} = (k_1 + k_2) \left(\frac{10d}{M_s} \right)^n P_s^n t \quad (7)$$

$$\ln (P_c' - P_{c,e}') =$$

$$-(k_1 + k_2) \left(\frac{10d}{M_s} \right)^n P_s^n t + \ln (P_{c,0}' - P_{c,e}') \quad (8)$$

When $\ln (P_c' - P_{c,e}')$ is plotted against time, a straight line is secured. The slope, p , of this line is

$$p = -(k_1 + k_2) \left(\frac{10d}{M_s} \right)^n P_s^n \quad (9)$$

$$\log |p| = \log (k_1 + k_2) \left(\frac{10d}{M_s} \right)^n + n \log P_s \quad (10)$$

The slope of the plot of $\log |p|$ versus $\log P_s$ gives the n th order with respect to the catalyst. With such a value, eq 9 allows us to determine the sum, $k_1 + k_2$, at different temperatures.

At equilibrium, we obtain

$$K = \frac{P_{t,e}'}{P_{c,e}'} = \frac{k_1}{k_2} \quad (11)$$

With such values, k_1 and k_2 at each temperature can be calculated. From the Arrhenius equation, the activation energies for the reverse and direct reactions can be determined.

Experimental Procedures

A distilled U.S.P. oleic acid (from Emery) was used, whose composition was 2.5% myristic acid, 2.0% *cis*-myristoleic acid, 5.3% palmitic acid, 11.0% *cis*-palmitoleic acid, 2.8% stearic acid, 69.5% *cis*-oleic acid, 4.8% *trans*-oleic acid, and 2.1% *cis,cis*-linoleic acid.

Black selenium GPR (BDH Laboratory Reagents) and purified sulfur powder (Merck) were used as catalysts. Both reagents were previously scattered in lampblack to 1/10th of their weight in order to prevent their agglomeration when in contact with hot oil.

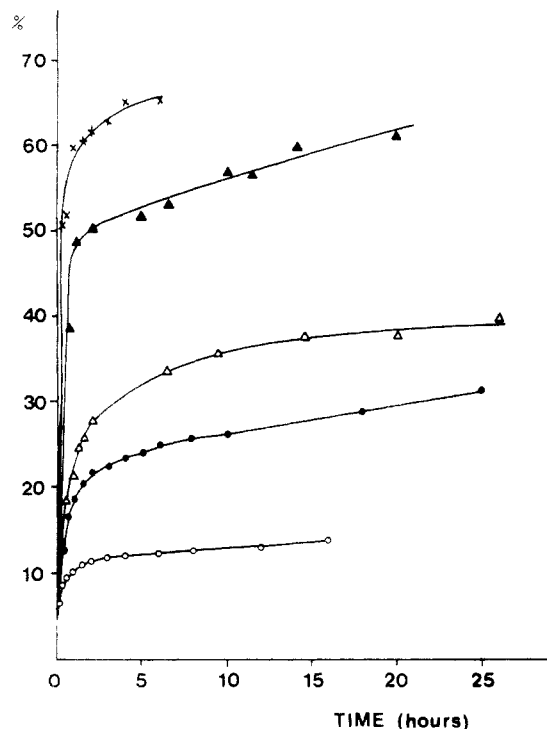


Figure 1. Rate curves for *trans*-oleic acid obtained at various temperatures and various initial sulfur concentrations. (x) 225 °C, 1.0% S; (Δ) 225 °C, 0.5% S; (▲) 180 °C, 0.5% S; (●) 225 °C, 0.1% S; (○) 180 °C, 0.1% S.

The method employed for the isomerization reactions was similar to that provided by the literature (Fitzpatrick and Orchin, 1957; Litchfield et al., 1963; Subrahmanyam and Quackenbush, 1964). The fatty material was heated in a three-neck flask, the temperature of which was maintained within ± 1 °C. A stream of CO₂ was allowed to flow through the flask to agitate and prevent diffusion of air into the system. When the desired temperature was reached, the catalyst was added (time zero). The reaction was performed in a fume hood to avoid harmful effects from the sulfur vapors carried out by the CO₂.

Samples were taken at definite intervals, cooled, and filtered before preparing the methyl esters of fatty acids (AOAC, 1980). A Shimadzu Model GC-6 AMPrF gas chromatograph equipped with a 15% OV-275 on 100/120 Chromosorb P AW-DMCS, 20-ft \times 1/8-in., stainless steel column from Supelco Inc. was used for gas chromatographic analysis of the methyl esters of the fatty acids. This column has been developed specifically to separate *cis*-*trans* isomers.

Results

(1) Chemical Equilibrium. Since the compositions at equilibrium do not depend upon the catalyst used, a run with U.S.P. oleic acid with 1% selenium at 190 °C was carried out. The latter was used since it is the most efficient catalyst according to the bibliography (Fitzpatrick and Orchin, 1957; Litchfield et al., 1963; Subrahmanyam and Quackenbush, 1964). The values obtained are shown in Table I. According to eq 11, the equilibrium constant has the value of 2.82 for oleic acid and 2.62 for palmitoleic acid.

(2) Reactions with Sulfur as a Catalyst. Runs with 0.1%, 0.5%, and 1.0% sulfur at 180 and 225 °C were carried out. In each one, the percentages of *cis*- and *trans*-oleic acids and *cis*- and *trans*-palmitoleic acids versus time were determined. The results of these rate studies are shown in Figures 1 and 2.

Table I. Equilibrium Composition for the Isomerization of Oleic and Palmitoleic Acids

fatty acid	P'_c	P'_t
palmitoleic acid	27.6	72.4
oleic acid	26.2	73.8

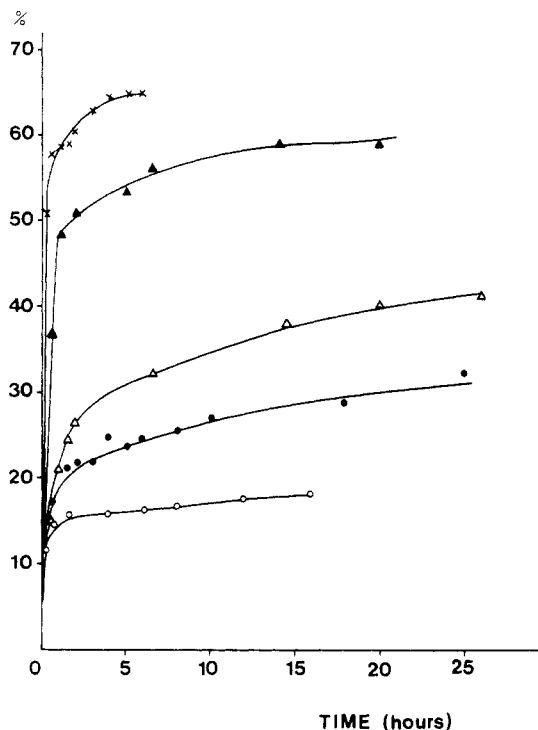


Figure 2. Rate curves for *trans*-palmitoleic acid obtained at various temperatures and various initial sulfur concentrations. (x) 225 °C, 1.0% S; (Δ) 225 °C, 0.5% S; (▲) 180 °C, 0.5% S; (●) 225 °C, 0.1% S; (○) 180 °C, 0.1% S.

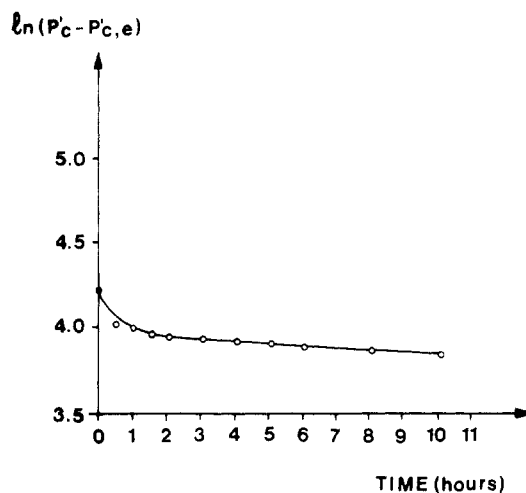


Figure 3. Integrated rate law for geometrical isomerization of *cis*-oleic acid. Temperature 225 °C. Catalyst: 0.1% sulfur.

In order to verify the integrated rate law (eq 8), $\ln(P'_c - P_{c,e})$ versus time was plotted. As a typical example, the data for the experiment at 225 °C with 0.1% sulfur is shown in Figure 3.

Conclusions

From Table I, it appears that the percent of *trans* isomers at equilibrium was about the same for both fatty acids tested. Geometrical isomerization is known to be accompanied with polymerization and hydrogen-transfer reactions. The GLC analysis shows that no such byproducts were observed.

Table II. Slope of the Integrated Rate Law for the Isomerization of Oleic and Palmitoleic Acids

P_s	temp, °C	$\ln (P_{c,0}' - P_{c,e}')$	p, h^{-1}	corr coeff
Oleic Acid				
0.1	225	3.955	-0.0084	-0.991
0.5	225	3.236	-0.0376	-0.980
1.0	225	2.820	-0.1630	-0.960
0.1	180	4.145	-0.0035	-0.942
0.5	180	3.830	-0.0133	-0.930
Palmitoleic Acid				
0.1	225	3.9336	-0.0093	-0.978
0.5	225	3.1259	-0.0391	-0.958
1.0	225	2.8592	-0.1837	-0.996
0.1	180	4.0501	-0.0036	-0.985
0.5	180	3.8329	-0.0172	-0.930

Table III. Values of the Sum of the Rate Constants ($k_1 + k_2$)

P_s	oleic acid		palmitoleic acid	
	at 180 °C	at 225 °C	at 180 °C	at 225 °C
0.1	4.1	9.8	4.2	10.9
0.5	2.2	6.1	2.8	6.4
1.0		11.4		12.8
mean	3.1	9.1	3.5	10.0

At least three important facts are immediately apparent from the curves of Figures 1 and 2: (1) the rate of isomerization increases with increasing initial sulfur concentration at constant temperature; (2) with 1.0% sulfur or less, it is not possible to reach the equilibrium concentration in a reasonable time; (3) the shapes of the curves for oleic and palmitoleic acids identical.

From the shapes of the curves in Figures 1-3, we can conclude that the reaction takes place by two consecutive mechanisms, similar to what was found when using selenium as a catalyst (Fitzpatrick and Orchin, 1957). Over long periods (from 2 h after the beginning of the reaction), a satisfactory straight line is obtained when $\ln (P_c' - P_{c,e}')$ versus time was plotted. This verifies the existence of that second mechanism of reversible pseudo-first-order reactions by which the position of equilibrium is reached (This was verified in every run that was carried out.) This is the step that determines the rate of reaction, and it is very important to the production of trans fatty acids. For such a mechanism, slopes of the straight lines were calculated by means of the least-squares approximation (Table II).

The pseudo-first-order rate dependence on the substrate means that the catalyst remains essentially constant at any particular initial concentration of sulfur.

CO₂ was bubbled to avoid sedimentation of the catalyst. Owing to the long duration of runs, they were interrupted each 8 h, but when they were started again, a strict control of agitation was not done. The linearity of the points for the same run indicates that the variations in the agitation produced during it do not modify the reaction rate.

The complete rate equation (eq 10) shows the catalyst dependence. The order of the reaction with respect to the catalyst at 225 °C (exponential value for the sulfur concentration in rate equation (4)) was determined. The same value of 1.2 for oleic and palmitoleic acids was obtained.

From eq 9, the sum $k_1 + k_2$ (using $d = 0.8 \text{ g mL}^{-1}$ and $M_s = 256$) was determined (Table III). From that sum and the equilibrium constant, K , the values of k_1 and k_2 were calculated at each temperature (Table IV). K was assumed to be independent of temperature between 180 and 225 °C, which is correct only if the activation energies of the direct and reverse reactions were the same. These energies were calculated from the Arrhenius equation and are summarized in Table IV. From this table it is apparent that the activation energies of the reverse and direct re-

Table IV. Rate Constants and Activation Energies for the Isomerization of Oleic and Palmitoleic Acids

	at 180 °C	at 225 °C	act. energy
Oleic Acid			
k_1	2.3	6.8	11
k_2	0.8	2.4	11
Palmitoleic Acid			
k_1	2.5	7.2	10.5
k_2	1.0	2.8	10.5

actions for both oleic acid and palmitoleic acid are identical and it confirms the assumption made before about the equilibrium constant.

The values from Table IV correspond to the second mechanism. The kinetic study of such a mechanism is important since the position of final equilibrium depends upon it. They cannot be compared to the published data for selenium as a catalyst (Fitzpatrick and Orchin, 1957) since these refer to the first mechanism only.

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Nomenclature

C = concentration at a given time, mol L⁻¹

d = specific gravity of the sample, g mL⁻¹

E = activation energy, kcal mol⁻¹

k = rate constant, Lⁿ mol⁻ⁿ h⁻¹

K = equilibrium constant

n = order of the reaction with respect to the catalyst

M = molecular weight

p = slope of $\ln (P_c' - P_{c,e}')$ versus time

P = percentage of a geometrical isomer at a given time with respect to the whole sample

P' = percentage of a geometrical isomer with respect to the fatty acid

t = time, h

Subscripts

c = cis configuration

e = at equilibrium

s = catalyst

t = trans configuration

o = at the initial time

1 = direct reaction

2 = reverse reaction

Registry No. Oleic acid, 112-80-1; palmitoleic acid, 373-49-9; sulfur, 7704-34-9.

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MATERIALS AND INTERFACES

Water Tolerance of Gasoline-Methanol Blends

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A new method based on laser attenuation was devised to accurately measure the phase separation and, in turn, the water tolerance of gasoline-methanol blends with and without cosolvents. Water tolerances were quantified for a variety of blends in model and actual gasolines, as well as in major refinery streams—alkylate, FCC gasoline, and reformate—that make up commercial gasoline pools. Regression analysis of the data shows that the water tolerance behavior of blends with each cosolvent is well-described by a correlation that includes cosolvent concentration, temperature, and base fuel hydrocarbon type.

Introduction

Oxygenate Use in Gasoline Is Growing. Oxygenates are gaining importance as gasoline blending components. They conserve crude oil, supply antiknock quality, and offer potential for pollution reduction. Refiners and marketers have been turning to oxygenates to meet increasing demands for gasoline pool octanes in light of more stringent volatility and fuel composition controls. Several states in the Southwest—Colorado, New Mexico, Arizona, and Nevada—have recently mandated the use of oxygenates in gasoline to reduce CO emissions in urban areas during the winter months. Additional regulatory pressures are likely to increase oxygenate use in gasoline.

Methanol Use in Gasoline Is Limited by Water Tolerance. Oxygenates, which are important as gasoline blending components, include methanol (MeOH), ethanol (EtOH), isopropyl alcohol (IPA), *tert*-butyl alcohol (TBA), and methyl *tert*-butyl ether (MTBE). Because of its low cost and ready availability, MeOH is the most attractive oxygenate from a strictly economic point of view. However, direct use of MeOH as a gasoline blending component in current fuel systems could cause technical problems (Unzelman, 1984). The most serious problem is the separation of blends into hydrocarbon and methanol phases when their water content exceeds a critical level, i.e., water tolerance. This problem is exacerbated at low ambient temperatures.

Cosolvents Can Improve Water Tolerance. Water tolerance is defined as the volume percent of water a blend can retain in solution—"tolerate"—at a given temperature without phase separation. To avoid phase separation, storage tanks and pipe lines must be maintained in essentially dry conditions, a very difficult practical problem. Another approach is addition of cosolvents to increase the water tolerance of the blend. All lower alcohols, up to

hexanol, could be useful as cosolvents; however, TBA has been identified as the most attractive for most commercial gasoline applications. Mixtures of MeOH and TBA have been marketed successfully as an oxygenate blending component for gasoline (American Petroleum Institute, 1988), although such mixtures are currently in very limited use in the U.S.

Current Study Extends Previous Work. Previous studies on the water tolerance of gasoline-MeOH blends have been both qualitative (Rawat et al., 1984; Khinkova et al., 1985) and quantitative (Osten and Sell, 1983; American Petroleum Institute, 1988) in nature. One quantitative study has investigated the water tolerance of gasoline-MeOH blends to compare the relative effectiveness of IPA vs TBA as cosolvents in a regular-grade leaded gasoline (Osten and Sell, 1983). Other quantitative work (American Petroleum Institute, 1988) has examined the relative effectiveness of other alcohols in gasoline, as well as the effect of changing the level of aromatics and cosolvent on phase separation temperatures. One study has reported the findings of the effect of boiling point and hydrocarbon type in gasoline-MeOH mixtures with no cosolvent (Eccleston and Cox, 1977). However, the effect of base gasoline composition over a wide range on the water tolerance of gasoline-MeOH-cosolvent blends has remained largely unexplored. In the current study, the water tolerance behavior of various gasoline-MeOH blends using several cosolvents was investigated to determine and compare the efficacy of the cosolvents and the effect of fuel composition over a wide range. As part of this work, a useful, new technique based on laser attenuation was devised to rapidly and reliably measure phase separations.

Experimental Section

Materials. 1. Base Fuels. Gasolines. Three un-