1. 1% TIRE SULFUR (BY WT. OF SULFUR-ASPHALT BLEND)
2. ASPHALT TEMPERATURE = 300°F (149°C)

Figure 20. Effect of some additives on H_2S emission—delayed addition.

cated: (1) the addition of sulfur to asphalt at working temperature of 300°F (149°C) resulted in an increase in asphaltene content, percent bonded sulfur, and evolution of hydrogen sulfide; however, more than 75% of added sulfur remained unreacted in colloidal suspension; (2) for a particular asphalt and a particular set of mixing temperatures, there is an "optimum" sulfur content; (3) the addition of a small amount of sulfur to asphalt (5–20% by weight of asphalt) at 300°F (149°C) resulted in an increase in penetration and reduction in viscosity and ductility; (4) addition of sulfur to asphalt–concentration mixtures significantly increased the stability, resistance to water action, and tensile strength of the compacted mixtures. For practical considerations, the post-mix procedure with sulfur added at the end of normal mixing cycle is recommended; (5) there are definite improvements in certain sulfur-treated aggregates in reducing asphalt and water absorption and in increasing

mechanical stability of the mixes: (6) natural weathering of sulfur–asphalt concrete up to 30 months increased the mechanical stability of the mixes with little change in flow value; and (7) hydrogen sulfide emission during sulfur–asphalt mixing increased with sulfur concentration and mixing temperature; cupric oxide, calcium carbonate, activated carbon, lime, zinc oxide, sodium carbonate, aluminum oxide, and calcium chloride were found effective in controlling H_2S emission.

Literature Cited

Abraham, H., "Asphalts and Allied Substances", 6th ed, pp 168–169; 178–179, D. Van Nostrand, New York, N.Y., 1961.
Asphalt Institute, "Mix Design Methods For Asphalt Concrete", MS-2 (1969).
Bocca, P. L., Petrossi, U., Pinoni, V. Chim. Ind. (Paris), 55, 427 (1973).
Burgess, R. A., Deme, I., paper presented at the 167th National Meeting of the American Chemical Society, Sulfur Use Symposium, Los Angeles, Calif., Apr 1974.
Crow, L. J., Bates, R. C. U. S. Bur. Mines, Rept. Invest., 7349 (1970).
Csanyi, L. H., Fung, H. P. Proc. Assoc. Asphalt Paving Tech., 23, 64 (1954).
Dale, J. M., Ludwig, A. C. Civil Eng., 37, 66 (1967).
Davis, J. C., Chem. Eng., 79, 30 (1972).
Deme, I. Proc. Assoc. Asphalt Paving Tech., 43 (1974).
Fike, H. L. Adv. Chem. Ser., No. 110 (1972).
Gallaway, B. M., Saylak, D., paper presented at the 167th National Meeting of the American Chemical Society, Sulfur Use Symposium, Los Angeles, Calif., 1974.
Hammond, R., Deme, I. Proc. Can. Tech. Asphalt Assoc., (1971).
Heithau, J. J., Johnson, R. W. Proc. Assoc. Asphalt Paving Tech., 27, 17 (1958).
Horio, R. J. Petroleum Inst. (Japan), 15, 997 (1972).
Lee, D. Y., Highw. Res. Rec., 468, 43 (1973).
Lee, D. Y., "Modification of Asphalt and Asphalt Paving Mixtures by Sulfur Additives", Iowa State University, Ames, Iowa, 1971.
Petrossi, U., Bocca, P. L., Pacor, P. Ind. Eng. Chem., Prod. Res. Dev., 11, 214 (1972).
Tucker, J. R., Schweyer, H. E. Ind. Eng. Chem., Prod. Res. Dev., 4, 51 (1965).

Geometrical Isomerization of Jojoba Oil

Jaime Wisniak* and Pnina Alfandary

Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel

Jojoba oil has been isomerized with selenium and NO_2 catalysts under a wide range of conditions. The reaction with selenium is first order in the isomer and $\frac{1}{3}$ order in the catalyst, with an activation energy of 35 kcal/mol, yields up to 56% trans isomer, and melting points 36 to 40°C. The reaction with NO_2 is faster, proceeds under milder conditions with a yield of 75% trans isomer, and raises the melting point to 42°C.

Introduction

It is a well known fact of the chemistry of unsaturated fatty material that they can be converted into solid materials by geometrical isomerization of the double bonds. The trans isomer is thermodynamically more stable than the cis form and has a much higher melting point. The reaction has never had any commercial significance probably because the same results can be achieved by partial hydrogenation with the additional advantage of higher oxidation stability.

The unusual properties of jojoba oil suggest that this phenomenon can be used to enhance the uses of this material, and thus it seems appropriate to investigate its behavior under isomerizing conditions. Simmondsia californica, or jojoba, is an evergreen shrub of the Buxaceae family that grows in semi-desertic areas and yields a nut that contains about 50% of an oil composed of the C_{20} and C_{22} alcohols and acids, with one double bond each. This oil is tasteless, colorless, and odorless and is not digestible by humans because it is not hydrolyzed by the enzyme lipase. Jojoba oil

has a high thermal stability and seems to have remarkable medicinal properties, is one of the best stabilizers for penicillin, and exhibits an intense inhibition action on tubercle bacilli (Knoepfer and Vix, 1958). No doubt these pharmaceutical characteristics could be advantageously used if the wax had a natural creamy structure.

A large number of catalysts have been proposed and tested for the isomerization of fatty materials. Among them, mention can be made of the oxides of nitrogen, selenium, sulfur dioxide, and catalytic hydrogenation (Litchfield et al., 1965). Sulfur dioxide isomerization is effected at 110 to 115°C with dry liquid catalyst and increases the melting point of peanut oil to 27.9°C, of soybean oil to 18.9°C, and of whale oil to 33.8°C (Waterman et al., 1948). The reaction is thought to proceed through the addition of SO_2 to one of the double bonds, its subsequent split and restoral of the double bond with both possible geometrical configurations (Waterman et al., 1949). Fitzpatrick and Orchin (1957) have shown that the selenium catalyzed elaidinization of oleic acid proceeds via a π-complex formation between oleic and selenium, resulting in the solution of the selenium. At 200°C there is the possibility of conversion of the π complex into a σ complex where the selenium attaches itself to a particular carbon atom, in the form of a hydroperselenide. The reaction is pseudo first order in the acid and $\frac{1}{3}$ order in selenium, with an activation energy of 30 kcal/mol. At 210°C and selenium concentrations of 0.2% or higher, the maximum of 67% trans isomer content was obtained after 45 min, corroborating the findings of Skellon and Spence (1953).

The maximum content trans isomer and the conditions of isomerization with NO_2 have been thoroughly investigated by Litchfield (1963, 1965). According to their work, the equilibrium mixture of cis–trans isomers contains 75–80% elaidic acid instead of the generally accepted 66% value. The fatty acid (oleic, linoleic, linolenic) was isomerized with in situ generation of HNO_2 produced by reaction of $NaNO_2$ with a suitable acid. Conditions of reaction were 30, 65, and 90°C with amounts of HNO_2 varying between 0.80 and 2.74 g of HNO_2/100 g of acid, and equilibrium was usually achieved after 60 min. A reaction mechanism was proposed in which the active catalytic species was the free radical nitrogen oxide. Infrared and GLC analyses indicated that for linoleic and linolenic acid the equilibrium trans content was 80%.

The elaidinization of erucic acid, one of the major components of crambe oil, has been investigated by Chang and Miwa (1972) by heating it at 70°C for 30 min with 4 mol % nitrous acid. A 70% yield to trans isomer was obtained with no migration of the double bond. Their results indicated that the isomerization is induced initially by the nitrogen dioxide anion and followed immediately by complex formation between the excited triplet anion and the olefin. Crystallization of the final product yielded a solid that contained 96–97% of the trans form (brassidic acid) melting at 58–59°C.

Experimental Materials and Procedures

The jojoba seeds used in this work were obtained from shrubs grown at the Negev Institute for Arid Zone Research, now a part of the Ben-Gurion University of the Negev. Cold-pressing produced a medium color oil that had the following characteristics: refractive index (20°C), 1.4652; iodine value (Wijs), 83.2; melting point, 13.0°C; acid number, 6.7; saponification number, 107. The gas chromatographic analysis was performed according to the method suggested by Miwa (1971), namely, 3% OV-1 on Gas Chrom Q, 100–120 mesh, stainless steel column 100 cm
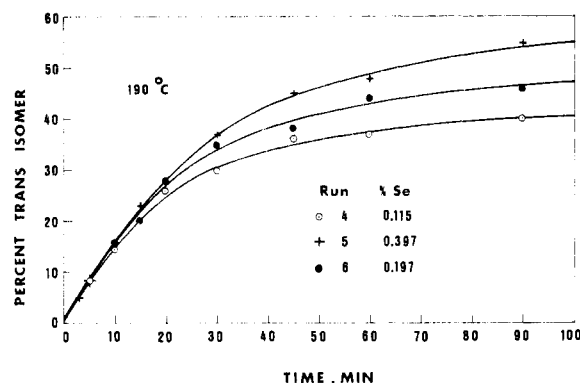
Figure 1. Isomerization with selenium. Effect of catalyst concentration.

long and 0.2 cm i.d., temperature programming of 3°C/min between 275 and 300°C, injection port 350°, flame ionization oven 380°C, Packard-Becker Model 417 chromatograph. The following results were obtained: C_{34}, 0.1%; C_{36}, 1.6%; C_{38}, 7%; C_{40}, 32%; C_{42}, 49%; C_{44}, 9%; C_{46}, 0.9%; C_{48}, 0.1%. The oil was used as such without further purification. Selenium powder black was purchased from E. Merck, Darmstadt (Cat. No. 7714). All other reagents used were analytical grade.

Isomerization runs with selenium were conducted as follows. A given amount of oil was introduced in a resin flask provided with an electric heating mantle and agitation. At the proper temperature level the adequate quantity of catalyst was added signaling the start of the run. Except at 180°C the time of dissolution of selenium was short and did not affect the measurements. Samples were taken at agreed time intervals, rapidly filtered, and analyzed for trans content. Overall time of reaction varied between 45 and 150 min.

Isomerization with NO_2 was conducted on a double-wall resin flask connected to a constant-temperature bath and provided with mechanical agitation, thermometer, reflux condenser, and dropping funnel. The jojoba oil was heated to the specified temperature and volumes of HNO_3 and $NaNO_2$ of the required strength were added under vigorous agitation. Samples were taken at given time intervals, diluted in ethyl ether, and washed with water. They were then dried by passing through a column containing anhydrous Na_2SO_4. Removal of organic nitrogenous by-products was done by passing the product through a column of activated silicic acid (Litchfield et al., 1965).

The infrared absorption of the samples was measured by the AOCS method Cd-14-61 (1962) on a Perkin-Elmer Model 457 spectrophotometer with a 1-mm sodium chloride cell, elaidic and brassidic methyl esters standards (Applied Science Laboratories), using the correction suggested by Schofield et al. (1966).

Results

Selenium isomerization was conducted in the following range of variables: percentage of selenium, 0.094 to 0.400; temperature, 180–210°C. Typical curves appear in Figure 1 for 190°C and different catalyst concentrations. The rate of reaction increases with higher selenium concentration and the concentration of trans isomer tends to an equilibrium value. The isomerization of the double bond is a reversible reaction of order one

$$C \underset{k_T}{\overset{k_C}{\rightleftharpoons}} T \tag{1}$$

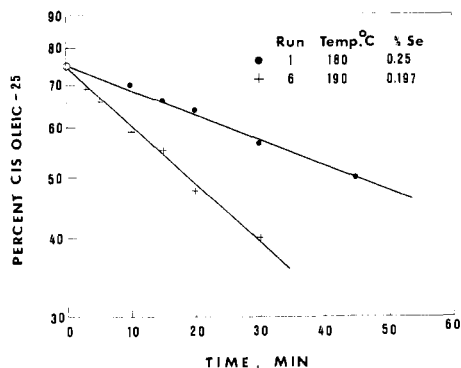that can be described analytically as

Figure 2. Change in cis content during isomerization with selenium catalyst.

Table I. Kinetic Data for Selenium Isomerization

Temp, °C	Run	% Se	$k' = k_C' + k_T'$, min⁻¹
180	1	0.250	0.00880
	2	0.397	0.0108
	3	0.098	0.00722
190	4	0.115	0.0202
	5	0.397	0.0252
	6	0.197	0.0225
200	7	0.094	0.0405
	8	0.400	0.0590
	9	0.190	0.0498
210	10	0.198	0.103
	11	0.300	0.116
	12	0.400	0.125

$$-\frac{dC}{d\theta} = k_C'C - k_T'T \qquad (2)$$

which on integration gives

$$\ln\frac{C_0 - C_e}{C - C_e} = (k_C' + k_T')\theta \qquad (3)$$

where C_0 is the initial concentration of cis isomer and C_e its equilibrium value at infinite time. In the particular case under consideration all the fresh double bonds are in the cis configuration ($C_0 = 100$) and the equilibrium concentration $C_e = 25$ based on the data obtained in this work with NO_2 and the data of Lichtfield et al. (1963, 1965).

Equation 3 indicates that a straight line is obtained when plotting log ($C - C_e$) against reaction time, at least for the largest part of the time interval. Figure 2 gives some typical results for two temperature and selenium levels. Table I reports all the major data obtained in this work.

The dependence of the rate on the selenium catalyst can be obtained following the reasoning developed by Fitzpatrick and Orchin (1957). The true kinetic equation is

$$-\frac{dC}{d\theta} = k_C \cdot CS\, e^{1/n} - k_T \cdot T \cdot Se^{1/n} \qquad (4)$$

where Se is the catalyst concentration and n is some integer. From eq 3 and 4 we obtain

$$k_C' + k_T' = (k_C + k_T)Se^{1/n}; k' = kSe^{1/n} \qquad (5)$$

where $k_C' + k_T' = k'$ and $k_C + k_T = k$. The values of n can be obtained by plotting in a log–log graph the results for k' and Se that appear in Table I. This is shown in Figure 3 for the four temperature levels tested. It is seen that the exper-
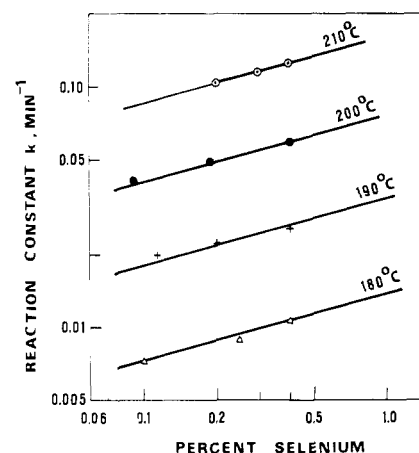

Figure 3. Isomerization with selenium. Order of the reaction with the catalyst.
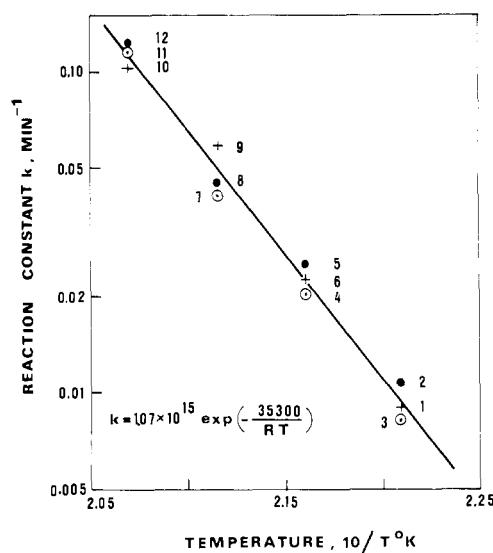

Figure 4. Arrhenius plot for isomerization with selenium.

imental data fall on reasonable parallel lines that have a slope of 0.275, so that $n = 3.64$. In other words, it can be assumed that every mole of jojoba oil is associated with 3 atoms of selenium. The average distance between the two double bonds present in each molecule of jojoba oil is about 24 carbon atoms so that there are no steric hindrances for simultaneous complexing and isomerization of both bonds. This is in accord with the results of Fitzpatrick and Orchin for the isomerization of oleic acid (1957). According to their data the initial reaction of selenium with oleic or elaidic acid appear to be due to the formation of some type of reversible complex which involves bonding between the double bond of the substrate and selenium (π complex). The complexing selenium is a diatomic species that originates by decomposition of powdered six atomic selenium at temperatures of around 200°C. In this way the rate of isomerization of pure oleic acid is shown to vary with the ⅓ power of the catalyst concentration.

The data of Table I can be further used to calculate the energy of activation of the reaction. As shown in Figure 4, the data for all catalyst concentrations yield a good fit of the Arrhenius equation with an activation energy of 35 kcal/mol, a value that agrees very well with the figure of 30 kcal/mol reported by Fitzpatrick and Orchin (1937). Under similar conditions the overall pseudo-first-order constant
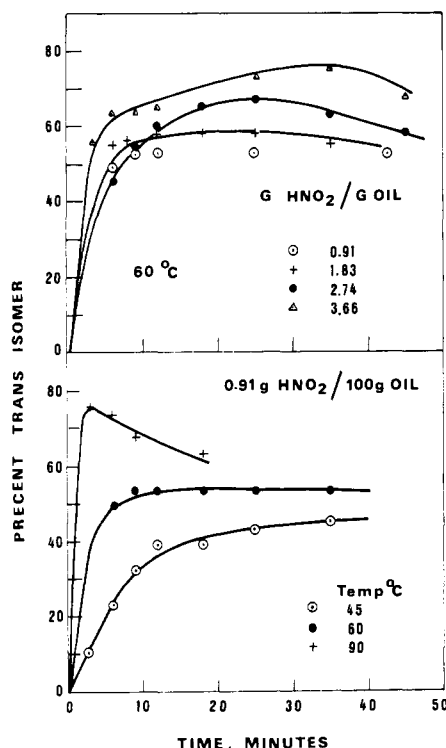
Figure 5. Isomerization with HNO₂. Influence of temperature and catalyst concentration.

for oleic acid isomerization is about double that for jojoba oil so that the frequency factor in the Arrhenius equation for oleic acid is twice that for jojoba oil.

The NO₂-catalyzed runs were made in the following range of variables: temperature, 45–90°C; wt of HNO₂/100 g of jojoba oil, 0.91–3.66 g.

Typical curves appear in Figure 5 for several catalyst and temperature levels. It is seen that the reaction is very fast and that the rate increases with an increase in temperature and catalyst concentration. In every case it was found that

under the more drastic conditions the maximum amount of isomer is achieved very rapidly and then begins to decrease. This behavior was also found by Litchfield (1965) when working with soybean oil and explained by the formation of stable NO₂ complexes with the double bonds. This explanation seems plausible if one considers the fact that the reaction product has a yellow color that is darker under more drastic conditions and that it is not removed by successive treatments with silicic acid. The maximum of trans isomer achieved was about 75%, particularly at the higher levels of temperature and catalyst.

In general, it can be said that the isomerization process with HNO₂ is simpler than that with selenium, proceeds faster and at lower temperatures, and yields a higher percentage of trans isomers.

Nomenclature

C = concentration of cis isomer
T = concentration of trans isomer; temperature °K
R = gas constant, cal/mol °K
Se = selenium concentration
n = integer
k_C, k_C' = velocity constant for the cis isomer, min⁻¹
k_T, k_T' = velocity constant for the trans isomer, min⁻¹

Literature Cited

Chang, S-P, Miwa, T. K., *J. Am. Oil Chem. Soc.*, **49**, 422 (1972).
Fitzpatrick, J. D. Orchin, M., *J. Am. Chem. Soc.*, **79**, 4765 (1957).
Knoepfer, N. B., Vix, H. L. E., *J. Agr. Food Chem.*, **6**, 118 (1958).
Litchfield, C., Lord, J. E., Isbell, A. F., Deisen, R., *J. Am. Oil Chem. Soc.*, **40**, 553 (1963).
Litchfield, C., Harlow, R. D., Isbell, A. F., Reiser, R., *J. Am. Oil Chem. Soc.*, **42**, 73 (1965).
Miwa, T. W., *J. Am. Oil Chem. Soc.*, **48**, 259 (1971).
Official and Tentative Methods of the American Oil Chemists' Society, Chicago, Ill., 1962.
Schofield, C. R., Butterfield, R. O., Dutton, H. J., *Anal. Chem.*, **38**, 1694 (1966).
Waterman, H. I., van Vlodrop, C., Gannewyk, J., *Research*, **1**, 183 (1948).
Waterman, H. I., van Steenis, J., de Boer, J. H., *Research*, **2**, 583 (1949).