ACKNOWLEDGMENT

A.B.B.H Hussin acknowledges the receipt of a scholarship from the Malaysian Government.

We would like to thank our colleagues in the Procter Department for valuable discussions, and particularly, Dr. J. E. McKay, for his encouragement. We also acknowledge the contribution of Dr. J. Lydon of the Biophysics Department, Leeds University, in supervising the microscopy and X-ray structure work.

REFERENCES

1. Povey, M.J.W., JAOCS 6163 xxx-xxx (1984).
2. Hussin, A.B.B.H., An Investigation into the Use of Ultrasonics to Monitor Phase Changes and Dilatations in Fats and Oils. Ph.D. Thesis, University of Leeds, U.K. (1982).
3. A.O.C.S. Official Method Cd 10.57.
4. Povey, M.J.W., and J.M. Wilkinson, British Poultry Science, 21:489 (1980).
5. Pellam, J.R., and J.K. Galt, Chemistry and Physics, 14:608 (1946).
6. Greenspan, M. and C.E. Tschiegg, J. Res. National Bureau of Stds 59:249 (1957).
7. Greenspan, M. and C.E. Tschiegg, J. Acoust. Soc. Am. 31:75 (1959).
8. Zacharias, E.M. and R.A. Parnell, Fd. Techn. 26(4):160 (1972).
9. Hannewijk, J., A.J Haighton, and P.W. Hendriske, in Analysis and Characterization of Oils, Fats and Fat Products Vol. 1., ed. Boekenoogen, H.A., Interscience Publishers, Longon, 1964, pp. 119-182.

Thermal Isomerization of Jojoba Wax

ARJEH B. GALUN and **ELEONORA SHAUBI**, The Institutes for Applied Research, Ben-Gurion University of the Negev, Beer-Sheva, Israel

ABSTRACT

Jojoba wax was thermally isomerized over a range of temperatures. The equilibrium constant and the rates of *cis-trans* and *trans-cis* conversions were measured. Activation energy ($\sim$ 24 kcal/m) and enthalpy were calculated.

INTRODUCTION

The chemical homogeneity (1,2) and unique physical properties (3) of jojoba wax and its *trans* isomer, mentioned in some earlier works (4,5), motivated us to investigate the kinetics of its geometrical isomerization. The *cis* isomer has a higher heat of combustion, indicating lower thermal stability, and can be transformed into the *trans* form by heating to temperatures that supply enough energy to cause rotation about the double bond (6).

A large number of thermal isomerizations of simple olefins in the gas phase (7-12) and in the liquid phase (13-15) have been reported. The data from the early work can be divided into two classes: those with low frequency factors (A) and activation energies (E_a), and those with high (normal) frequency factors and activation energies. Surface effects and side reactions involving decomposition lead to apparent decreases in both A and E_a.

PROCEDURES

Materials

The crude jojoba wax used in this work was obtained in 1978 from the natural population of an Apache reservation in the U.S.A.

Gas chromatographic analyses, infrared spectra and NMR were performed. The material had an iodine value, refractive index, melting point, freezing point, ester number, acid number and saponification number identical to those given in reference 5. The crude jojoba wax (11) was mixed with 10 g of bleaching earth at 80 C for 15 min, and filtered.

Method

Gas chromatography. The gas chromatographic analyses were performed according to the method suggested by Miwa (1).

Infrared spectroscopy. IR analyses to determine the amount of isolated *trans* bonds were performed on a Perkin-Elmer model 357 spectrophotometer with a 0.2 mm KBr cell, according to AOCS method Cd-14-61 (1962) with brassidyl brassidate and erucyl erucate standards for calibration.

Heating. A micro carius furnace was used for thermal isomerizations.

Thin layer chromatography (TLC). Silica-gel coated glass plates were impregnated with a solution of 20% silver nitrate. The plates were dried in an oven for 3 hr at 110 C. The acids were converted to methyl esters by diazomethane and dropped on plates.

The developing solvent was petroleum ether (40-60 C) containing 5% ether. Spots were made visible by spraying an aqueous solution of 7.5% cuprous acetate and 0.5% potassium permanganate or by spraying with 50% sulphuric acid and heating to 250 C to char organic components. The latter procedure is not very effective with silver nitrate-impregnated plates, presumably because the nitric acid liberated causes overoxidation to carbon dioxide, leading to the loss of the charred spots. Silver(I) ions complex the *cis* double bond, thus the *cis* compound has a lower R_f value than the *trans* isomer, enabling differentiation between *cis* and *trans* forms (16).

Experimental

Thermal isomerization. Samples of bleached jojoba wax were isomerized in vacuum-sealed ampoules at temperatures between 250 C and 400 C (Table I). Heating for 192 hr at 300 C isomerized 53.3% *trans* jojoba wax to 37.6% with partial decomposition. Heating for 216 hr at 300 C in vacuum-sealed ampoules isomerized 65% brassidyl brassidate (containing 35% erucyl erucate) to 38%.

SYNTHESIS OF MODEL COMPOUNDS FOR THE DETERMINATION OF THE AMOUNT OF trans BONDS

Jojoba wax is a mixture of esters of varying compositions, and therefore its properties, such as melting range and molecular weight, are not constant, making analytical and spectroscopic calculations difficult.

Since C_{22} mono-13-unsaturated acids and alcohols are components (5) of this wax, we found it necessary to synthesize the pure *cis* and pure *trans* isomers of these esters as model compounds. The pure *cis* isomer is erucyl

TABLE I

Thermal Isomerization of Bleached Jojoba Wax

250 C		300 C		350 C		400 C	
Trans %	Time (h)	Trans %	Time (h)	Trans %	Time (h)	Trans %	Time (h)
0	0	0	0	0	0	0	0
4.6	120	0.8	1	1.3	1	14.5	1
4.9	166	1.6	2	3.2	2	17.6	3
7.9	286	3.2	4	3.6	4	17.1	5
7.7	504	19.1	24				
		20.9	48				
		19.3	72				

erucate, and the pure *trans* isomer is brassidyl brassidate. Mixtures of these pure isomers were taken as standards for spectroscopic analyses and calibration curves were based on them.

The synthetic pathway of brassidyl brassidate (pure *trans* compound), brassidyl erucate *(trans-cis)*, erucyl brassidate *(cis-trans)* and erucyl erucate (pure *cis* compound) is outlined below.

Erucic Acid

A solution of 206 g of erucamide and 60 g of sodium hydroxide in 500 mL of H_2O and 150 mL of ethanol was refluxed for 180 hr and acidified with concentrated hydrochloric acid to pH 1. Sodium chloride was filtered off, and the ethanol was evaporated. Petroleum ether (60-80 C) was added to the oily phase, which was washed with water, aqueous sodium bicarbonate, and again with water until neutral, and the solvent was evaporated. The erucic acid was recrystallized from 95% ethanol at 10 C and dried in vacuo for 24 hr. The hydrolysis of erucamide was followed by IR spectroscopy. The end of the reaction was observed when the absorption bands at 3,200 cm^{-1} and 3,400 cm^{-1} ($-NH_2$ stretching) disappeared, and a broad absorption band appeared at 3,400-2,500 cm^{-1} (O—H stretch of the erucic acid).

The NMR spectrum shows 2 absorption peaks (2:2) at 5.3 and 2.2 ppm caused by the hydrogen atoms at the double bond and the carboxyl group, respectively. Since the model compounds are new, their properties are summarized in Table II.

Brassidic Acid

This compound was prepared according to Miwa (17). The 970 cm^{-1} IR absorption peak is caused by the out-of-plane C—H bending of the *trans* isomer. The NMR peak at 5.2 ppm lost its symmetry from the *trans* configuration of the double bond.

The separation of brassidic acid from erucic acid was achieved by TLC. Additional characteristics are listed in Table II.

Methyl Erucate and Methyl Brassidate

Erucic and brassidic acids were esterified by adding diazomethane drop by drop to ether solutions of the corresponding acids and evaporating the solvent.

The infrared absorption at 2,500-3,500 cm^{-1} and the carboxylic C=O stretch at 1,690 cm^{-1} disappeared because of the carboxylic hydroxyl group. The ester carbonyl absorbed at 1,740 cm^{-1}.

The NMR spectrum shows absorptions at 3.6 and 5.3 ppm at a ratio of 3:2, caused by the oxygen-bound methyl and the double-bond hydrogen atoms, respectively.

Brassidol and Erucol

Erucol was prepared by two methods: reduction of methyl erucate with lithium aluminum hydride; and reduction of erucic acid with lithium aluminum hydride.

Lithium aluminum hydride, 0.5 g in 200 mL of absolute either, was gently refluxed, and a solution of 0.2 g of methyl erucate in 100 mL of absolute ether was slowly added. The residual lithium aluminum hydride was destroyed by the slow addition of water. After separation of the phases, the ether solution was dried over $MgSO_4$ and filtered, the ether was evaporated, and the product was crystallized from ether. The yield and properties are presented in Table II.

Brassidol was prepared in a similar way. The IR spectrum showed an absorption peak at 3,330 cm^{-1}, which was assigned to the hydroxyl group. The peak at 1740 cm^{-1} of the ester carbonyl disappeared. In the NMR spectrum a triplet appeared at 3.5 ppm due to the hydrogen atoms of the methylenic group near oxygen atom. The ratio of the peaks at 5.2 ppm and 3.5 ppm was 2:2.

The second reduction proved to be more difficult than the reduction of the ester; it is slower and gives a lower yield (10%). It was, therefore, not used for routine syntheses.

Brassidyl Brassidate, Erucyl Erucate, Brassidyl Erucate and Erucyl Brassidate

Erucyl erucate was synthesized by two methods: transesterification of erucol and methyl erucate with p-toluene sulphonic acid as catalyst; and esterification of erucol and erucic acid using phosphoric acid as catalyst (8).

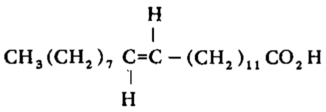
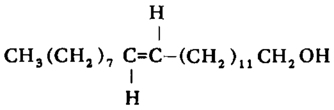
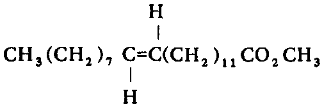
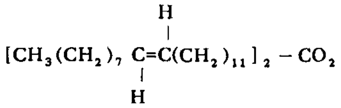
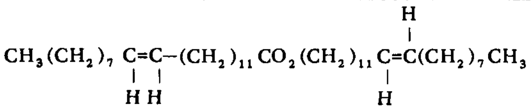
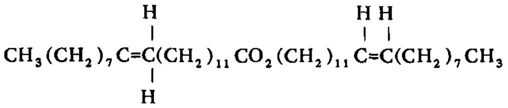
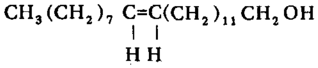
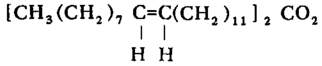
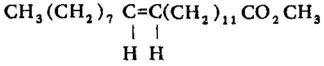
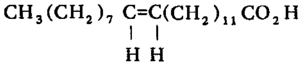
In the first method, 1 m erucol, 1 m methyl erucate, and 1% catalyst were heated to 140 C for 3 hr, and the product was distilled in vacuo. It contained some *trans* isomer.

Differentiation between the starting material and the desired product by infrared absorption is difficult owing to the similarity of their spectra. Their R_f values are also very close, rendering TLC separation impractical.

In the second method, the four model esters were synthesized by esterification of the corresponding acids and alcohols. One m carboxylic acid, 1 m alcohol and 1.5% (of the total weight) of phosphoric acid were heated in vacuo to 220 C for 1.5 hr. This method was found to be effective for wax synthesis, without *cis-trans* isomerization (18). The mixture was dissolved in ether, and the solution was washed successively with water, aqueous sodium bicarbonate, and water and then dried. After the solvent was removed, the product was recrystallized from a mixture of ether-petroleum ether (except erucyl erucate, which is a liquid). The *trans* derivatives were further purified by passing through a silica column containing 10% silver nitrate, which retains the *cis* configurations. Other deriva-

TABLE II

Characteristics of the Synthesized Compounds

Compound	Empirical formula	Structural formula	m.p. (C)	n_D^{60}	Yield %	State at 23 C	Mol. wt.	Analyses C % Calculated	C % Measured	H % Calculated	H % Measured
Brassidic acid	$C_{22}H_{42}O_2$	 $CH_3(CH_2)_7\,\underset{H}{C}=\overset{H}{C}-(CH_2)_{11}CO_2H$	60		84.0	solid	338.53	78.04	–	12.50	–
Brassidol	$C_{22}H_{44}O$	 $CH_3(CH_2)_7\,\underset{H}{C}=\overset{H}{C}-(CH_2)_{11}CH_2OH$	48	1.4560	77.7	solid	324.94	81.41	81.17	13.66	13.66
Methyl brassidate	$C_{23}H_{44}O_2$	 $CH_3(CH_2)_7\,\underset{H}{C}=\overset{H}{C}(CH_2)_{11}CO_2CH_3$	28	1.4423	95.0	solid	352.61	78.35	78.68	12.58	12.84
Brassidyl brassidate	$C_{44}H_{84}O_2$	 $[CH_3(CH_2)_7\,\underset{H}{C}=\overset{H}{C}(CH_2)_{11}]_2-CO_2$	53	1.4503	60.0	solid	645.16	81.92	81.49	13.12	13.00
Brassidyl erucate	$C_{44}H_{84}O_2$	 $CH_3(CH_2)_7\,\underset{H}{C}=\underset{H}{C}-(CH_2)_{11}CO_2(CH_2)_{11}\underset{H}{C}=\overset{H}{C}(CH_2)_7CH_3$	29-30	1.4572	57.0	solid	645.16	81.92	81.70	13.12	13.00
Erucyl brassidate	$C_{44}H_{84}O_2$	 $CH_3(CH_2)_7C=\overset{H}{\underset{H}{C}}(CH_2)_{11}CO_2(CH_2)_{11}\overset{H}{C}=\overset{H}{C}(CH_2)_7CH_3$	34-35	1.4597	59.0	solid	645.16	81.12	81.65	13.12	13.10
Erucol	$C_{22}H_{44}O$	 $CH_3(CH_2)_7\,\underset{H}{C}=\underset{H}{C}(CH_2)_{11}CH_2OH$	30	1.4425	76.5	solid	324.94	81.41	–	13.66	–
Erucyl erucate	$C_{44}H_{84}O_2$	 $[CH_3(CH_2)_7\,\underset{H}{C}=\underset{H}{C}(CH_2)_{11}]_2\,CO_2$	–	1.4700	50.0	liquid	645.16	81.92	81.87	13.12	13.21
Methyl erucate	$C_{23}H_{44}O_2$	 $CH_3(CH_2)_7\,\underset{H}{C}=\underset{H}{C}(CH_2)_{11}CO_2CH_3$	–	–	95.0	liquid	352.61	78.36	–	12.88	–
Erucic acid	$C_{22}H_{42}O_2$	 $CH_3(CH_2)_7\,\underset{H}{C}=\underset{H}{C}(CH_2)_{11}CO_2H$	33	1.4514	80.0	solid	338.58	78.04	–	12.50	–

tives were passed through a regular silica column.

The infrared spectra were as expected: the hydroxyl stretch at 3,500 cm^{-1} and the carboxylic carbonyl stretch at 1,690 cm^{-1} were absent, and the ester carbonyl stretch at 1,720 cm^{-1} was prominent.

The NMR spectrum showed two absorptions at 5.3 and 3.7 ppm in the ratio of 4:2. The large difference between the R_f values of the alcohols, acids and esters makes it easy to follow the reaction by TLC. Data on these esters are given in Table II.

DISCUSSION

The pictorial presentation of the electronic states of ethylene, as developed by Mulliken and Roothaan (19), is suitable for discussing the mechanism of the isomerization of olefin chains, where the variation in potential energy caused by the rotation of one CH group relative to the other through a 180° angle involves transitions from the ground singlet to an excited singlet. Somewhere in between, a transition to a low-lying triplet state may lead to isomerization by falling back into the singlet ground state of the transformation. Mulliken and Roothaan maintain that hyperconjugation leads to enhanced stability in the perpendicular configuration.

Formulating our reaction as

$$A \underset{k_b}{\overset{k_a}{\rightleftharpoons}} B \qquad [1]$$

and assuming these thermal isomerizations to be first order opposing unimolecular reactions (Fig. 1,2), we have (20):

$$k_a + k_b = (2.303/t) \log (([B_o]-[\bar{B}])/([B]-[\bar{B}])) \qquad [2]$$

where k_a and k_b are the rate constants of the forward and reverse reactions respectively, t is the time since inception, $[B_o]$ is the initial concentration of B and $[\bar{B}]$ is the concentration of B at equilibrium.

Starting from pure A, $[B_o]$ equals zero, so that equation 2 reduces to:

$$k_a + k_b = (2.303/t) \log ([\bar{B}]/([\bar{B}] - [B])). \qquad [3]$$

By these kinetics, the time dependence of $\log ([\bar{B}]/([\bar{B}]-[B]))$ must be linear, and the sum of the rate constants of the forward and reverse reactions can easily be determined from the slope of this line. This is shown in Figures 1 and 2.

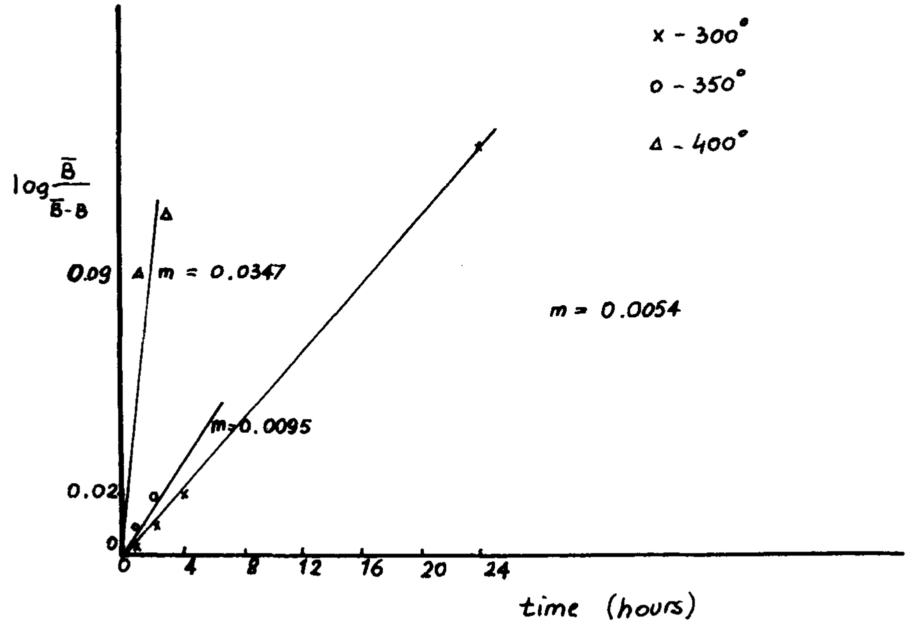


FIG. 1. Relation between $\log ([\bar{B}]/([\bar{B}]-[B]))$ and reaction time at various temperatures.

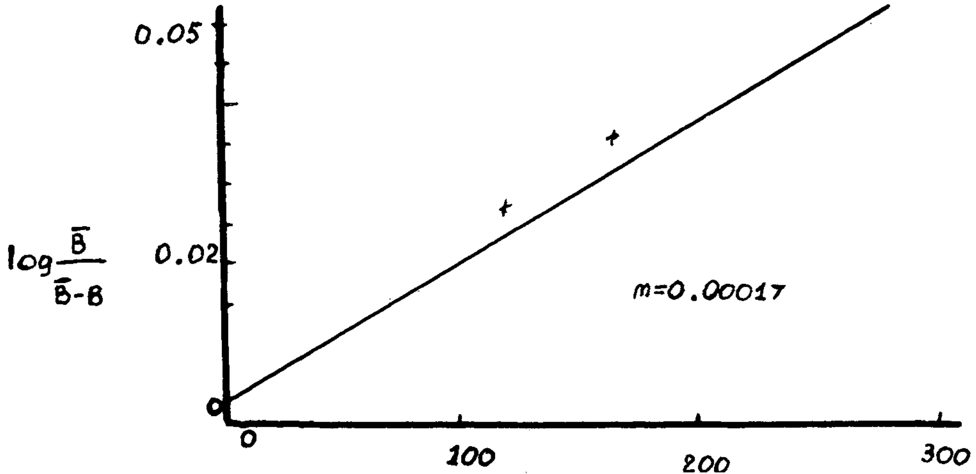


FIG. 2. Relation between $\log ([\bar{B}]/([\bar{B}]-[B]))$ and reaction time at 250 C.

If the equilibrium constant, K, is also known, k_a and k_b can be determined separately (Table III).

$$k_a = [K/(1+K)]\ (k_a+k_b) \qquad [4]$$

$$k_b = (k_a+k_b)/(1+K) \qquad [5]$$

TABLE III

Rate Constants of the Thermal Isomerization of Jojoba Wax as a Function of Temperature

Temperature K	k_a+k_b sec^{-1}	k_b sec^{-1}	k_a sec^{-1}
523	$1.08\ 10^{-7}$	$2.70\ 10^{-8}$	$8.10\ 10^{-8}$
573	$3.42\ 10^{-6}$	$8.53\ 10^{-7}$	$2.56\ 10^{-6}$
623	$6.06\ 10^{-6}$	$1.52\ 10^{-6}$	$4.55\ 10^{-6}$
673	$2.22\ 10^{-5}$	$5.53\ 10^{-6}$	$1.66\ 10^{-5}$

TABLE IV

Activation Energy, Frequency Factor and Enthalpy of the Thermal *cis-trans* Isomerization of Jojoba Wax

	Overall reaction	*trans* → *cis*	*cis* → *trans*
E (kcal/mole)	24.9	23.2	21.2
A (sec^{-1})	1.91×10^4		
ΔH_0 250 C (kcal/mole)	24.0	22.3	20.2
ΔH_0 300 C (kcal/mole)	23.8	22.1	20.0
ΔH_0 350 C (kcal/mole)	23.7	22.0	19.9
ΔH_0 400 C (kcal/mole)	23.6	21.9	19.8

The frequency factor (A) is determined from the intercept with the ln k coordinate.

The concentrations of the products were determined from calibration curves of the model compounds. Erucyl erucate *(cis-cis)*, brassidyl brassidate *(trans-trans)*, erucyl brassidate *(cis-trans)*, and brassidyl erucate *(trans-cis)* were synthesized for this purpose.

The activation energy can be determined if the rate constants of the reaction at several temperatures are known. Assuming that the Arrhenius equation ($k = A \exp(E_a/RT)$, where E_a is the activation energy, A the frequency factor, k the rate constant, and T the temperature of the reaction) is applicable to our reaction, ln k must be linearly dependent on T^{-1}, the plot of ln k vs T^{-1} is a straight line and the activation energy is determined from the slope (Fig. 3, Table IV).

The difference per mole between the zero point energies of the initial and final states is the thermal effect of the reactions (Q) at absolute zero. Consequently, the difference Q between the activation energies of the reverse and direct processes is equal to the thermal effect of the reaction, as shown in Figure 4.

We can calculate the free enthalpy, ΔH_0 (Table IV) from equation 8, derived from equations 6 and 7:

$$\Delta G = \Delta H - T\Delta S \qquad [6]$$

$$E = RT^2\ d \ln k/dT \qquad [7]$$

$$\Delta H \cong \Delta E \qquad [8]$$

where ΔS is entropy, ΔH_0 is the free enthalpy, E is activation energy and ΔG is free energy.

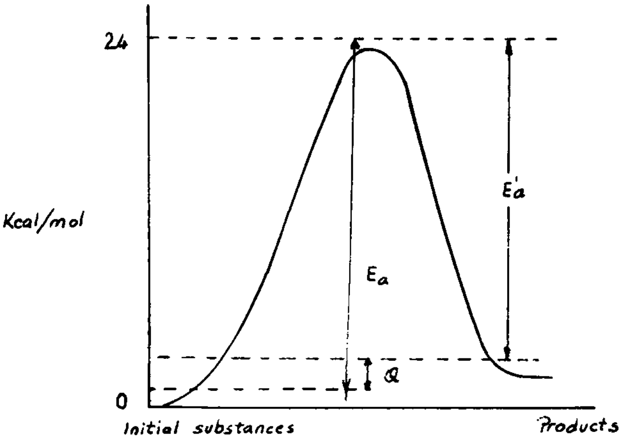


FIG. 4. Relationship between the activation energies of the direct and reverse processes and the thermal effect of the reaction.

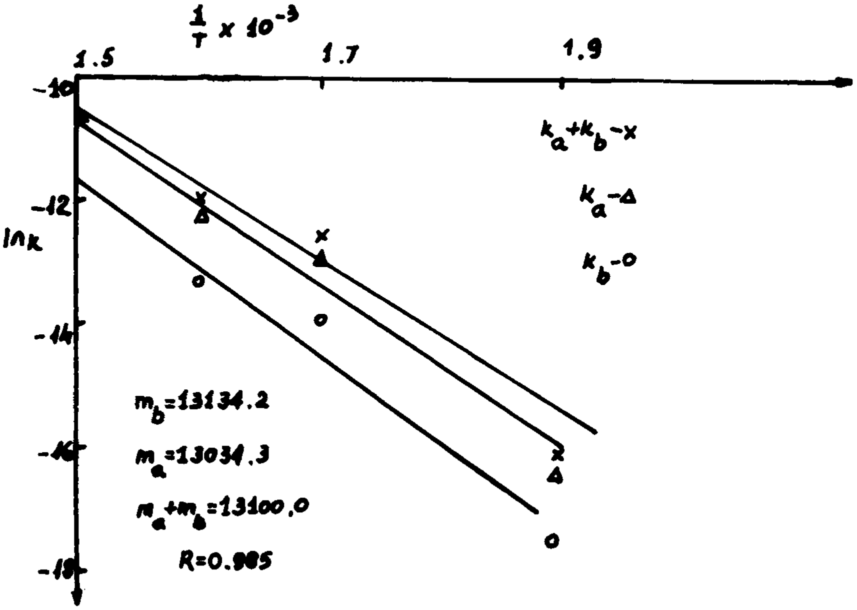


FIG. 3. Arrhenius plot for the thermal isomerization of jojoba wax.

No big difference was found between the Arrhenius parameters of jojoba wax and those of lower esters such as dimethyl maleate (15).

ACKNOWLEDGMENT

This work is part of the Jojoba Project carried out at the Ben-Gurion University for the Negev Jojoba Company, Tel-Aviv.

REFERENCES

1. Miwa, T.K., JAOCS 48:259 (1971).
2. Yermanos, D.M., and C.C. Duncan, JAOCS 53:80 (1976).
3. Products from Jojoba, National Academy of Sciences, Committee of Jojoba Utilization, Washington, DC (1975).
4. Wisniak, J., and P. Alfandary, Ind. Eng. Chem., Prod. Res. Dev., 14(3):177 (1975).
5. Wisniak, J., Prog. Chem. Fats and Other Lipids, 15:167 (1977).
6. Wyman, G.M., Chem. Rev., 55:625 (1955).
7. Douglas, J.E., Rabinovitch, B.S. and F.S. Looney, J. Chem. Phys., 23:315 (1955).
8. Rabinovitch, B.S. and M.J. Hulatt, J. Chem. Phys., 27:592 (1957).
9. Steel, C., J. Phys. Chem., 64:1588 (1960).
10. Anderson, W.F., J.A. Bell, J.M. Diamons and K.R. Wilson, J. Am. Chem. Soc., 80:2384 (1958).
11. Rabinovitch, B.S., and K.N. Michel, J. Am. Chem. Soc., 81:5065 (1959).
12. Cundall, R.B. and T.F. Palmer, Trans. Faraday Soc., 57:1936 (1961).
13. Hojendahl, K., J. Phys. Chem. 28:758 (1924).
14. Tamamushi, B. and H. Akiyama, Bull. Chem. Soc. Japan, 12:382 (1937).
15. Davies, M., and F.P. Evans, Trans. Faraday Soc., 51:1506 (1955).
16. Morris, J.L., Chem. Ind., 1238 (1962).
17. Shu-Pei, Chang, and T.K. Miwa, JAOCS 49:422 (1972).
18. Zajic, J. and M. Buresova, Sbornik Vysoke Skoly Chemicko-Technologicke v. Praze, Oddil Fakulty Potravinarske Technologie 4(2):275 (1960).
19. Mulliken, R.S., and C.C.J. Roothaan, Chem. Rev., 41:219 (1947).
20. Emanuel, N.M., and D.G. Knorre, Chemical Kinetics, John Wiley & Sons, New York, Toronto, 1973, p. 167.

Methanesulfonic Acid Catalyzed Addition of Aromatic Compounds to Oleic Acid

Y. NAKANO and **T. A. FOGLIA**, Eastern Regional Research Center[1], Philadelphia, Pennsylvania 19118

ABSTRACT

The addition of aromatic compounds to the double bond of oleic acid has been studied using methanesulfonic acid as the acid catalyst. When alkylbenzenes were reacted with oleic acid, the yield of addition product was dependent on the electron density of the benzene ring. For example, a 76% yield of addition product was obtained with toluene, whereas for benzene and monochlorobenzene, the yields of addition products were 60% and 2%. The addition of phenol to oleic acid gave 2 types of addition products, an ether-type (phenylether) product and a ring-substituted product (hydroxyphenylstearic acid). The ratio of the 2 products varied with the reaction temperature and the amount of methanesulfonic acid. The ring-substituted product predominated at a high molar ratio of methanesulfonic acid to oleic acid (6:1) and elevated reaction temperature (50 C). Thiophenol was found to add to oleic acid to form a thioether derivative exclusively.

INTRODUCTION

The addition of aromatic compounds to oleic acid has been studied using various types of Lewis and Bronsted acids as catalysts. Stirton (1) reported the synthesis of arylstearic acid from oleic acid by the Friedel Crafts alkylation reaction. Both sulfuric acid and a strong acid cation exchange resin were used for the addition of phenol to oleic acid by Roe (2). Later, Ault and Eisner reported that methanesulfonic acid was the preferred acid catalyst for the addition of aromatic compounds to unsaturated compounds because this acid gave not only high yields of addition products, but less colored products (3-5).

A structural study of the addition products obtained from the $AlCl_3$ catalyzed reaction of benzene with oleic acid has been made by Smith et al. (6-10). By means of a CrO_3 oxidation procedure, these workers demonstrated that the phenylstearic acid obtained was a mixture of positional isomers with the phenyl substituent located at C_3 to C_{17} of the hydrocarbon chain. Although yields of the addition products have been reported, none of the by-products have been identified, so that overall, the reaction pathway has not been fully studied.

This study was undertaken to elucidate the pathway by which oleic acid reacts with aromatic compounds by identifying all of the reaction products formed when aromatic compounds are reacted with oleic acid in the presence of methanesulfonic acid.

EXPERIMENTAL

Materials

Oleic acid (98%) was obtained from Applied Science Laboratories (State College, PA). Methanesulfonic acid was purchased from Fisher Chemical Company (King of Prussia, PA) and was distilled before it was used. All other reagents were used as received from commercial suppliers. Methyl esters were prepared by the boron trifluoride method (12).

Gas liquid chromatography (GLC) was conducted with a Hewlett Packard Model 7620 chromatograph equipped with dual flame ionization detectors. Separations were obtained on 8-ft × 1/8-in. silanized stainless-steel columns packed with 7.5% EGA + 2% H_3PO_4 on 90/100 mesh Anakron ABS or 3% SP-2100 DOH on 100/120 Supelcoport. Thin layer chromatography (TLC) was performed on Silica gel G plates (250 micron) obtained from Analtech (Newark, DE). Plates were developed with toluene:ether (90:10) and visulalization was accomplished by spraying the plates with 50% H_2SO_4 and charring. A Perkin-Elmer model 720 B infrared spectrophotometer was used for IR analyses. Mass spectra were obtained on a Hewlett Packard Model 5995 GC-MS mass spectrometer. Column chromatography was carried out on Silica gel 60 A (75-150 micron) using hexane: methylene chloride gradients as the eluant. Fractions (100 mL) from the column were monitored by TLC.

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[1] Agricultural Research Service, US Department of Agriculture. Reference to a brand or firm name does not constitute endorsement by the USDA over others of a similar nature that are not mentioned.