Geometric Isomerization of Fatty Acids with Nickel Catalyst[1]

Maria A. Grompone[a] and **Patrick Moyna**[b]
[a]Compañia BAO S.A., Laureles 573, Montevideo, Uruguay, and [b]Facultad de Quimica, Avda, Gral. Flores 2124, Montevideo, Uruguay

Cis-trans **isomerization studies were performed on commercial oleic acid and refined sunflower oil. Reactions were carried out at constant temperature, under inert atmosphere (without hydrogen), using an industrial nickel-containing hydrogenation catalyst.**

With sunflower oil, hydrogen transfer and polymerization were concurrent with the formation of *trans* isomers.

Many papers about the *cis-trans* isomerization reactions of unsaturated fatty acids and related compounds (ethyl or methyl esters) have been published. Catalysts such as sulphur, iodine, selenium and its derivatives (oxide, sulfide, hydride), telurium, nitrogen derivatives, mercaptans, etc., have been used (1-6). The literature does not provide precise information about geometric isomerization using nickel as the catalyst.

This report describes the geometric isomerization of commercial oleic acid and refined sunflower oil. An industrial nickel-containing hydrogenation catalyst (Resan 22, Harshaw Chemical Company) was used. All reactions were carried out at constant temperature in a carbon dioxide atmosphere.

EXPERIMENTAL PROCEDURES

The fatty material was heated and agitated by bubbling CO_2 through it. When the desired temperature was reached, the catalyst (Resan 22 with a metallic nickel content of 20.5%) was added (time zero) at 10% of the oil weight. Samples were taken then and at definite intervals, and saponification and iodine numbers (7,8) were determined. Fatty acid methyl esters were prepared (8) and analyzed. A Shimadzu Model GC-6 AMPrF gas chromatograph equipped with 15% OV-275 columns on 100/120 Chromosorb P AW-DMCS, 20′ × 1/8″ stainless steel, from Supelco Inc., Bellefonte, Pennsylvania, was used for all gas chromatographic analyses. This column has been developed specifically to separate *cis-trans* isomers of fatty acid methyl esters (9).

RESULTS AND DISCUSSION

The effectiveness of the catalyst used for *cis-trans* isomerization of a monounsaturated fatty acid under CO_2 is demonstrated in Table 1. Working at a lower temperature, much lower catalyst concentration and shorter reaction time, Feuge et al. (10) did not obtain those products.

TABLE 1

Isomerization of U.S.P. Oleic Acid with 10% Resan 22, at 210 C

Time (hr)	Myristic (%)	*trans* myristoleic (%)	*cis* myristoleic (%)	Total myristoleic (%)	Palmitic (%)	*trans* palmitoleic (%)	*cis* palmitoleic (%)	Total palmitoleic (%)	Stearic (%)	*trans* oleic (%)	*cis* oleic (%)	Total oleic (%)	*cis-cis* linoleic (%)
0	2.3	—	2.1	2.1	5.1	—	11.7	11.7	1.5	7.0	68.3	75.3	2.0
4	2.0	0.8	0.6	1.4	5.3	4.6	5.9	10.5	8.7	28.8	43.4	72.2	—
7	2.0	1.1	0.7	1.8	5.8	5.5	5.2	10.7	9.4	30.9	39.4	70.3	—
12	2.0	1.1	0.4	1.5	5.9	6.0	4.7	10.7	9.4	39.2	31.2	70.4	—
19	1.8	0.8	0.3	1.1	5.0	5.9	4.7	10.6	10.0	45.6	25.9	71.5	—

TABLE 2

Isomerization of Sunflower Oil with 10% Resan 22

Temperature (°C)	Time (hr)	Palmitic (%)	Stearic (%)	*trans* oleic (%)	*cis* oleic (%)	Total oleic (%)	*trans-trans* linoleic (%)	*trans-cis* linoleic (%)	*cis-cis* linoleic (%)	Total linoleic (%)	Iodine number	Saponification number
210	0	9.8	12.5	+	28.6	28.6	—	—	49.1	49.1	121.2	190.5
210	6	10.2	12.2	5.9	27.6	33.5	0.9	1.9	41.3	44.1	115.6	190.5
210	14	10.8	14.9	12.3	30.8	43.1	2.7	4.5	24.0	31.2	114.0	188.6
210	22	11.6	19.0	24.2	28.3	52.5	3.3	3.5	10.0	16.8	107.4	179.5
210	30	12.3	22.3	31.9	21.7	53.6	4.5	4.3	3.1	11.9	103.0	159.6
230	0	9.1	5.9	+	32.6	32.6	—	—	52.3	52.3	—	—
230	4	9.7	8.6	5.8	30.2	36.0	1.7	3.0	41.0	45.7	—	—
230	7	10.0	11.7	8.6	30.3	38.9	2.8	4.2	32.5	39.5	—	—
230	14	11.5	17.1	18.7	26.9	45.6	5.2	5.6	15.1	25.9	—	—
230	21	13.3	18.8	30.7	26.8	57.5	6.5	4.0	—	10.5	—	—

---

[1] Based on work done in partial fulfillment of requirements for completion of the doctoral dissertation of Maria A. Grompone.

Both *cis* oleic and *cis-cis* linoleic acids from sunflower oil were isomerized at 210 C and 230 C. At 120 C no reaction took place (Table 2).

During reaction at 210 C and 230 C, the amount of linoleic acid was found to decrease. In these conditions, the amounts of stearic and oleic acids changed with time. This means that even with no hydrogen present in the atmosphere over the system, hydrogenation took place. At 210 C a decrease of the iodine number also indicated an increase in saturation.

Some hydrogen-transfer reaction accompanies the *cis-trans* isomerization of polyunsaturated fatty acids with selenium (5,6,11-13). Apparently, similar by-products were formed when Resan 22 was used as a catalyst. No such by-products were observed when oleic acid was isomerized, except during the first four hr. During this interval, the small amount of polyunsaturated acids initially present would allow hydrogen transfer.

Because polymers do not give volatile methyl esters, they are not detected in our chromatographic analysis. There are several publications on indirect determinations of polymers with GLC (14,15). Palmitic acid can be used as a sort of internal standard (stearic acid is not useful because its concentration increases with hydrogen transfer), and the growth of its relative peak area indicates polymer formation. For sunflower oil (Table 2) at 210 C and 230 C there is an increase in palmitic acid, but with oleic acid (Table 1) such an increase is not observed.

Polymerization reactions may also be detected by the decrease in saponification number. At 210 C the saponification number of sunflower oil decreased as the reaction progressed. That is, the combined fatty acids increased their mean molecular weight. A saponification number of 190.5 (initial value) indicates a fatty acid mean molecular weight of 282; a saponification number of 159.6 (final value) indicates a fatty acid mean molecular weight of 338, whose equivalent chain length value is 22. As the carbon chain lengths of sunflower fatty acids range from C_{16} to C_{18}, those results mean that polymerization must have occurred, as it has already been found with selenium (5,6,11-13). Diels-Alder addition has been proposed as a mechanism for chain elongation.

Only polyunsaturated acids can form conjugated dienes that are responsible for hydrogen transfer and polymerization reactions (5,6,11-13). This can explain why those reactions occurred more readily with sunflower oil than commercial oleic acid.

Cis-trans isomerization of polyethenoid acids accompanied by polymerization and hydrogenation transfer (without a hydrogen atmosphere) is of considerable importance in the practice of industrial hydrogenation. Contact between the catalyst and fatty materials may lead to isomerization or polymerization even though there is no hydrogen in the atmosphere. It should be noted that the amount of catalyst used in this work is significantly greater than that usually used.

REFERENCES

1. Kass, J.P., and G.O. Burr, *J. Am. Chem. Soc. 61:*1062 (1939).
2. Kass, J.P., J. Nichols and G.O. Burr, *Ibid. 63:*1060 (1941).
3. Fitzpatrick, J.D., and M. Orchin, *Ibid. 79:*4765 (1957).
4. McCutchon, M.A., R.T. O'Connor, E.F. Du Pre and L.A. Goldblatt, *J. Am. Oil Chem. Soc. 36:*115 (1959).
5. Litchfield, C., J.E. Lord, A.F. Isbell and R. Reiser, *Ibid. 40:*553 (1963).
6. Subrahmanyam, V.V.R., and F.W. Quackenbush, *Ibid. 41:*275 (1964).
7. *Official and Tentative Methods of the American Oil Chemists' Society,* 3rd Edn., revised to 1984, AOCS, Champaign, IL.
8. *Official Methods of Analysis of the Association of Official Analytical Chemists,* 13th Edn., AOAC, Washington, DC, 1980.
9. Ottenstein, D.M., L.A. Witting, P.H. Silvis, D.J. Hometchko and N. Pelick, *J. Am. Oil Chem. Soc. 61:*390 (1984).
10. Feuge, R.O., M.B. Pepper, R.T. O'Connor and E.T. Field, *Ibid. 28:*420 (1951).
11. Kass, J.P., J. Nichols and G.O. Burr, *J. Am. Chem. Soc. 41:*275 (1964).
12. Teeter, H.M., E.W. Bell and M.J. Danzig, *J. Org. Chem. 23:*1156 (1958).
13. Floyd, D.E., R.F. Paschke, D.H. Wheeler and W.S. Baldwin, *J. Am. Oil Chem. Soc. 33:*609 (1956).
14. Prevot, A., *Rev. Fr. Corps Gras 12:*299 (1965).
15. Zielinski, W.L., *J. Am. Oil Chem. Soc. 41:*249 (1964).

[Received August 8, 1985]