• TECHNICAL

Cis-Trans Isomerization of Oleic Acid by Nitrous Acid[1]

CARTER LITCHFIELD, R. D. HARLOW, A. F. ISBELL[2] and RAYMOND REISER,
Department of Biochemistry & Nutrition, Texas Agricultural Experiment Station, College Station, Texas

Abstract

Oleic acid was *cis-trans* isomerized by HNO_2 generated *in situ* by reacting $NaNO_2$ with a mineral acid. The influence on the reaction of time, temp, agitation, solvent, amt of catalyst and type of mineral acid was investigated. Optimum reaction conditions were defined for achieving equilibrium isomerization in 30 min with minimum by-product formation. After isomerization, nitrogenous by-products were efficiently removed using silicic acid. The active species causing *cis-trans* isomerization was tentatively identified as free radical nitrogen dioxide.

Introduction

Since 1819 when Poutet (1) first reported the solidification of olive oil by "oxides of nitrogen," there has been considerable interest in the various reagents which will *cis-trans* isomerize unsaturated fatty acids. A large number of such catalysts have been reported: "oxides of nitrogen" (2–5), selenium (6–8), tellurium (8), sulfur dioxide (9), various phosphorus compounds (10), catalytic hydrogenation (11–14), mercaptans (15), silicates (16,17), iodine (18,19), UV light (20), and electron radiation (21). Selenium and "oxides of nitrogen" have been the most widely used of these catalysts.

Considerable interest has been shown in the possible commercial applications of *cis-trans* isomerization to natural fats and fatty acids. *Trans* fatty acids have a higher melting point than the corresponding *cis* acids; hence *cis-trans* isomerization can be used to harden fats with no loss of unsaturation. Peanut oil or olive oil can be converted to satisfactory semisolid margarine oils by such a process (22). *Trans* fatty acids are more resistant to oxidation than the corresponding *cis* acids (23,24). Soaps made from *trans* acids also have superior wetting and detergency properties (25,26).

The oxides of nitrogen used to catalyze *cis-trans* isomerization have been produced in a number of ways. Poutet (1) *cis-trans* isomerized olive oil using the reaction of mercury with nitric acid. Griffiths and Hilditch (2) verified Poutet's results and showed that the reaction of copper with HNO_3, As_2O_3 with HNO_3, or $NaNO_2$ with H_2SO_4 had a similar isomerizing action on oleic acid. Cook and Light (27) recommended heating ammonium nitrate or nitric acid with starch, a sulfite, a bisulfite, or a nitrate. By far the most popular method for generating the oxides of nitrogen has been the reaction of $NaNO_2$ with HNO_3. These latter conditions produce nitrous acid *in situ* (28), and the HNO_2 then breaks down into the oxides of nitrogen which probably produce the *cis-trans* isomerization.

A difference of opinion exists on the identity of the active catalytic species in the oxides of nitrogen. Eipper (29) claimed that N_2O, NO, N_2O_3 and NO_2 were all effective. Cook and Light (27) reported that N_2O, NO and NO_2 were the active species. On the other hand, Kahn (30) found that NO_2 would *cis-trans* isomerize oleic acid but NO and N_2O would not.

Many workers (2,5,31,32) report the production of undesirable nitrogenous by-products during the *cis-trans* isomerization of unsaturated fatty acids by oxides of nitrogen. Little attention has been paid, however, to the analysis and removal of these by-products. Recently, while preparing 9-*trans*,12-*trans* octadecadienoic acid by HNO_2 isomerization of linoleic acid (32), we found that the nitrogenous by-products could be quickly and easily removed on a column of silicic acid. Subsequent experiments showed that the same purification method could also remove most of the nitrogenous by-products from HNO_2 isomerized oleic acid.

This paper presents a study of the *cis-trans* isomerization of technical oleic acid by HNO_2 generated *in situ* by reacting $NaNO_2$ with a mineral acid. The influence on the reaction of time, temp, agitation, solvent, amt of $NaNO_2$ and type of mineral acid were investigated; and optimum reaction conditions were defined. The removal of nitrogenous by-products by silicic acid was evaluated, and the active species catalyzing *cis-trans* isomerization was tentatively identified.

Procedures

Materials

Technical grade oleic acid (Eastman Organic Chemicals, Rochester, N.Y.) was used for all *cis-trans* isomerization reactions except where otherwise noted. This material had an iodine value (I.V.) of 87.5 and contained 382 ppm elemental nitrogen. The fatty acid composition of the oleic acid was determined by gas-liquid chromatography (GLC), and the results are shown in Table 1. IR spectroscopy indicated that the fatty acid already contained 7.9% isolated *trans* bonds, probably due to its origin or method of manufacture.

Refined edible grade cottonseed oil (Procter & Gamble, Cincinnati, Ohio) was used as received. 98 + % N_2O, NO, NO_2 and N_2O_3 gases were purchased commercially (Matheson Co., East Rutherford, N.J.) and used without further purification.

Methods

Gas Chromatography. Samples of oleic acid were converted to their corresponding methyl esters using the BF_3/methanol esterification procedures of Metcalfe

TABLE I

Fatty Acid Composition of Technical Oleic Acid (wt %)

Fatty acid	Before isomerization	After isomerization[a]
12:0	trace	trace
14:0	3.6	3.7
14:1 (?)	2.6	2.9
Unknown	0.2	0.2
16:0	4.2	3.9
16:1	12.7	11.7
Unknown	1.7	1.8
18:0	0.6	0.6
18:1	71.5	73.0
18:2	3.0	2.3

[a] Optimum *cis-trans* isomerization reaction conditions described in Figure 5.

---

[1] Presented at the AOCS Meeting in New Orleans, 1964.

[2] Department of Chemistry, Texas A&M University, College Station, Texas.

and Schmitz (33). Total fatty acid compositions were determined by GLC analysis of the methyl esters on a 6 ft x 1/8 in. diethyleneglycol succinate polyester column as previously described (42).

The *trans* content of isomerized oleic acid was determined by separating the *cis* and *trans* isomers of 16 and 18 carbon monoenes using a 100 ft x 0.010 in. ID capillary column coated with Apeizon L at 200C as described before (34). The sum of the 16 and 18 carbon *trans* monoenes was then reported as the "per cent *trans* monoene" in the mixture. Although the technical oleic acid contained a peak corresponding to the elution time of 14:1, capillary GLC did not show any separation of *cis* and *trans* 14:1 isomers after isomerization with HNO_2. The identity of this supposed 14:1 component was therefore open to question, and it was not used in calculating per cent *trans* monoene values. Some 18:1 positional isomers present in the technical oleic acid were eluted at the same time as methyl elaidate on the capillary GLC column. For this reason, the per cent *trans* monoene content of the unisomerized oleic acid was 14.6% determined by capillary GLC and 7.9% determined by IR spectroscopy. After substantial *cis-trans* isomerization, most of these positional isomers eluted after methyl elaidate, and GLC results were more accurate. Error from this source was estimated to be less than 2% (absolute) on samples containing over 50% *trans* monoene, thus making capillary GLC results quite satisfactory for the present study.

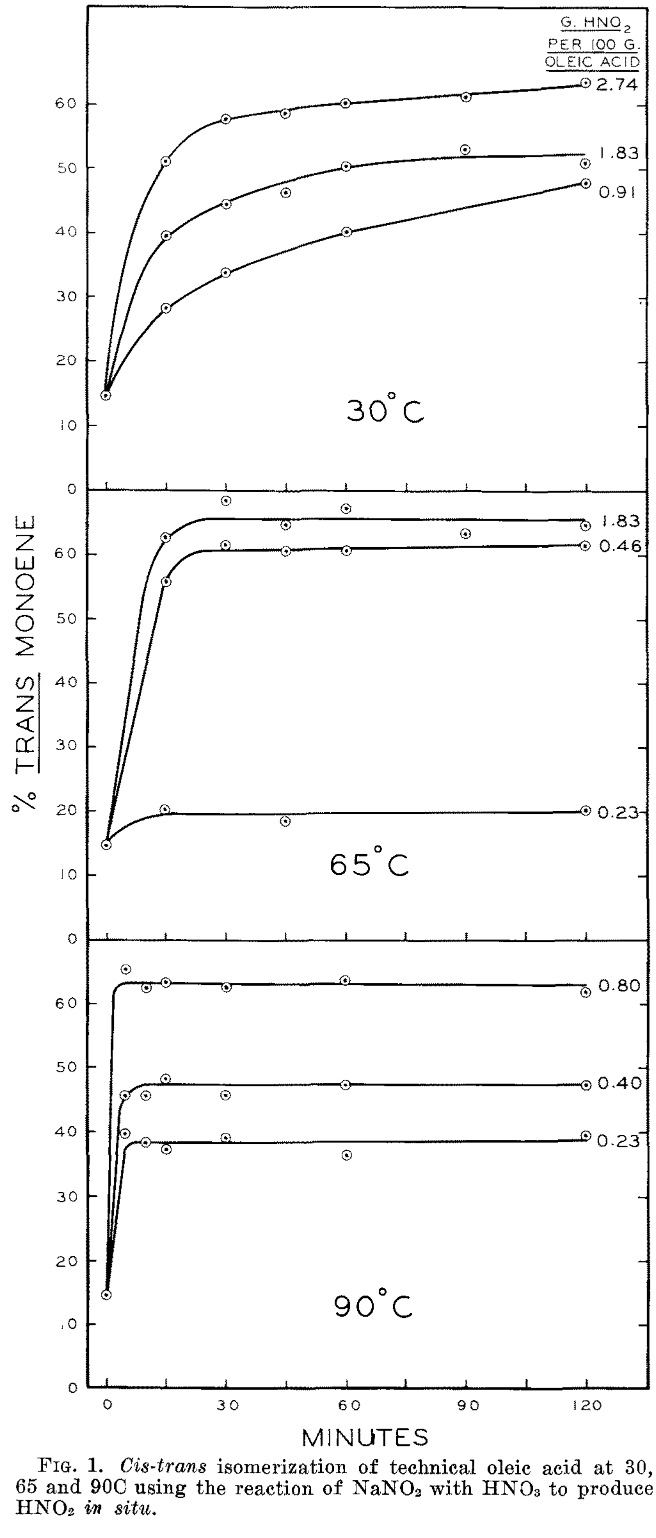


FIG. 1. *Cis-trans* isomerization of technical oleic acid at 30, 65 and 90C using the reaction of $NaNO_2$ with HNO_3 to produce HNO_2 *in situ.*

Iodine Values. I.V. were determined using AOCS method Cd-1-25 (35).

Nitrogen Content. Analyses of the ppm elemental nitrogen content of fatty acids were run by Galbraith Laboratories, Inc., Knoxville, Tenn., using a standard micro-Dumas procedure.

Infrared Spectroscopy. IR analyses to determine the amt of isolated *trans* bonds were run on Beckman IR-4 or IR-8 IR spectrophotometers. AOCS method Cd-14-61 (35) was used with pure methyl elaidate or an AOCS secondary triglyceride standard for calibration.

Experimental

Cis-Trans Isomerization Reaction. Oleic acid was *cis-trans* isomerized with *in situ* generation of HNO_2 produced by reacting $NaNO_2$ with a suitable acid. In a typical isomerization reaction, 350 g of technical oleic acid was placed in a closed, 2-liter, heated resin reactor fitted with a dropping funnel, a stirring shaft equipped with a Teflon paddle, a thermometer, an outlet to a bubble trap, and a sampling tube extending into the fatty acid. The reactor was purged with nitrogen, and the fatty acid was heated to the required temp. The desired 6 *M* acid (HNO_3 unless otherwise specified) was added, and the system was again flushed with nitrogen. 2 *M* $NaNO_2$ solution was then added through the dropping funnel with vigorous stirring, and the reaction was continued for two hr. A 2:1 molar ratio of acid to $NaNO_2$ was always used. 10 g samples were withdrawn at the desired sampling times by applying suction to the sampling tube without stopping the stirring. To assure that a representative sample was obtained, the sampling tube was thoroughly flushed with reaction mixture immediately prior to taking a sample. Each sample was diluted in three times its volume of diethyl ether, and the catalyst was quickly removed by washing several times with distilled water. The wash waters were combined and extracted three times with ether to remove any remaining fatty material. All the ether solutions were combined and dried by passing through a column containing 40 g of anhydrous powdered Na_2SO_4. The column was flushed with 50 ml of dry ether, and the solvent was removed from the total eluate under reduced pressure. Each sample was then analyzed for percentage of *trans* monoene, I.V. and ppm nitrogen as required.

Evaluation of Reaction Variables. The influence of various reaction conditions was studied to try to achieve equilibrium *cis-trans* isomerization within 60 min with minimum loss due to by-product formation. Equilibrium *cis-trans* isomerization of pure oleic acid converts 75–80% of the *cis* double bonds into *trans* double bonds (31). Since the total 16:1 plus 18:1 content of the technical oleic acid was only 84.2%, this meant that a maximum of ca. 62% *trans* monoene could be produced by HNO_2 isomerization.

Reactions were carried out at 30,65 and 90C using varying amt of HNO_2. The *trans* monoene content of the oleic acid was determined by GLC at intervals as the reaction progressed (Fig. 1). The minimum amt of catalyst necessary to achieve equilibrium isomerization within one hr was determined for each temp. At 30, 65 and 90C, these minimum catalyst levels were, respectively, 2.74, 0.46 and 0.80 g HNO_2/100 g oleic acid.

The effect of using various acids for reaction with $NaNO_2$ to generate HNO_2 was also investigated. HNO_3, H_2SO_4, HCl, H_3PO_4, and CH_3COOH were compared at 30C using sufficient $NaNO_2$ and 6 *M* acid to produce 1.83 g of HNO_2/100 g of oleic acid. (With polyprotic acids, only one proton was calculated as participating in HNO_2 generation). The *trans* monoene content of oleic acid was determined by GLC at intervals as the reaction progressed (Fig. 2). HNO_3 produced the greatest amount of *cis-trans* isomerization, HCl and H_2SO_4 produced a moderate amt, and H_3PO_4 and CH_3COOH produced very little isomerization.

The use of H_2SO_4 and HNO_3 to produce higher levels of HNO_2 was also compared at 30C (Figs. 1 and 2). Results indicated that 2–3 times as much H_2SO_4 is needed to produce the same amt of *cis-trans* isomerization as HNO_3.

To check the influence of agitation on HNO_2 catalyzed *cis-trans* isomerization, a reaction was run at 30C with 2.74 g HNO_2/100 g oleic acid and using only enough magnetic stirring to give a slight vortex in the fatty acid. The *trans* monoene content of the oleic acid was followed by GLC as before. Results showed that this milder agitation gave the same rate of isomerization as obtained with the much higher rpm Teflon paddle used before under equivalent reaction conditions (shown in Fig. 1).

Previous HNO_2 catalyzed isomerizations all involved two liquid phases (water and fatty acid) in the reaction system. To determine if a single liquid phase would speed up the reaction, a common solvent for all the reactants was sought. Three such solvents were found: bis[2-(2-methoxyethoxy)ethyl]ether (commonly called tetraglyme), methanol, and N,N-dimethylformamide. Subsequent evaluation showed that methanol and N,N-dimethylformamide were unsatisfactory since they reacted with HNO_2. A single phase reaction was run in tetraglyme at 30C using 1.83 g HNO_2/100 g of oleic acid. Samples were withdrawn at the desired sampling times and diluted in three times their volume of petroleum ether (30–60C bp). Water washing removed the tetraglyme, and the petroleum ether solution was dried over Na_2SO_4 and evaporated to recover the fatty acid. The *trans* monoene content was determined by GLC as before. Results (Fig. 3) showed that HNO_2 catalyzed isomerization was not as rapid in the single phase reaction as in the equivalent two-phase system.

The minimum amt of HNO_2 necessary to approach equilibrium *cis-trans* isomerization within one hr was now known for four reaction systems: $NaNO_2$ plus HNO_3 at 30, 65 and 90C; and $NaNO_2$ plus H_2SO_4 at 30C. To determine which of these systems gave minimum losses due to nitrogenous by-product formation, the earliest sample containing around 60% *trans* monoene was analyzed for ppm nitrogen and I.V. The increase in nitrogen content and the drop in I.V. caused by isomerization were then computed by comparison with similar analyses on the original oleic acid. These results (Table II) gave an indication of the amt of nitrogenous by-products formed in each reaction. In the $NaNO_2$ plus H_2SO_4 system, a sample containing less than 60% *trans* monoene was analyzed; but since this sample showed a high level of by-product formation, it was evident that the H_2SO_4 system would not give minimum losses. Comparison of the results in Table II indicated that isomerization with $NaNO_2$ plus HNO_3 at 65C for 30 min gave the lowest loss of oleic acid due to by-product formation. These conditions were selected as optimum for maximum *cis-trans* isomerization of technical oleic acid with minimum loss.

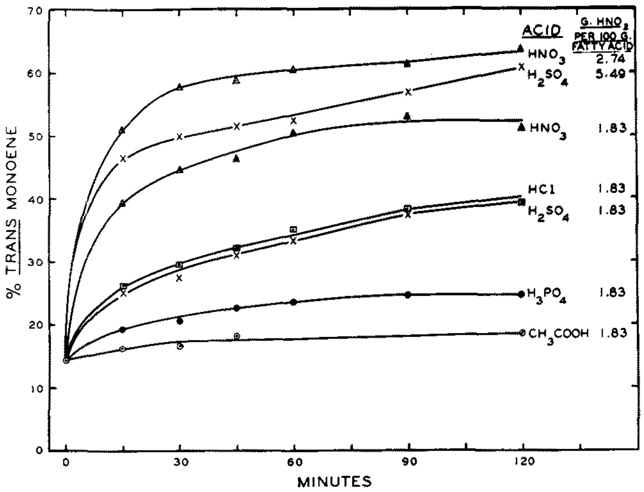


Fig. 2. *Cis-trans* isomerization of technical oleic acid at 30C using various acids to react with $NaNO_2$ to produce HNO_2.

Identification of Active Catalyst Species. Since there have been conflicting reports in the literature as to which "nitrogen oxide" is the active species causing *cis-trans* isomerization, the abilities of N_2O, NO, NO_2 and N_2O_3 to isomerize unsaturated fatty acids were compared. Each gas was bubbled (1–3 bubbles/min) through 820 g of cottonseed oil at 60C with vigorous stirring for 3 hr. Samples were taken at appropriate intervals as the reaction progressed and were analyzed for percentage of isolated *trans* bonds by IR spectroscopy. Results (Fig. 4) indicated that NO_2 was by far the most active catalyst.

Since NO_2 is apparently the active catalyst species in HNO_2 catalyzed *cis-trans* isomerization (see Discussion), a preliminary evaluation was made of pure NO_2 as an isomerization catalyst for oleic acid at 30C. An amt of liquid NO_2 equivalent to 1.83 g of HNO_2/100 g of oleic acid was evaporated into the reactor where extremely vigorous stirring produced intimate gas-liquid mixing. After 5 min, the oleic acid contained 42.2% *trans* monoene and 1995 ppm nitrogen. These results indicated that NO_2 catalysis produces more addition products than the equivalent $NaNO_2$ plus HNO_3 system under similar conditions. Since the use of pure NO_2 offered no apparent advantages

TABLE II

Comparison of Losses During Isomerization

Catalyst		Temp	Reaction time	*Trans* monoene	Nitrogen content	Drop in I.V.
Wt % as HNO_2	Type					
%		C	min	%	ppm	
2.74	$NaNO_2 + HNO_3$	30	60	60.4	4474	7.9
0.46	$NaNO_2 + HNO_3$	65	30	61.3	1221	5.0
0.80	$NaNO_2 + HNO_3$	90	5	65.5	4100	11.0
5.49	$NaNO_2 + H_2SO_4$	30	30	50.0	5830	9.9

TABLE III
Recrystallization of Isomerized Oleic Acid

Sample	Temp	Solvent	Ratio of solvent to fatty acid	Yield	*Trans* monoene in product[a]
	°C			g	%
Original oleic acid before isomerization	....	....	....	100.0	7.9
Isomerized oleic acid eluted from column of silicic acid	....	....	....	93.3	60.5
After first recrystallization	—12	Petroleum ether (30–60C)	5 ml/g	53.6	70.2
After second recrystallization	1	Methanol	7.5 ml/g	28.6	90.8
After third recrystallization	1	Methanol	7.5 ml/g	23.8	97.1

[a] %*trans* monoene in original sample determined by IR spectroscopy. Other values determined by capillary GLC.

over *in situ* HNO_2 generation, no further experiments were run with NO_2.

Removal of Nitrogenous By-Products. The removal of organic nitrogenous by-products by passing the isomerized oleic acid through a column of activated silicic acid was evaluated. A schematic outline of this procedure is shown in Figure 5. 350 g of technical oleic acid was *cis-trans* isomerized for 30 min at 65C by reacting 25 ml of 2 *M* $NaNO_2$ with 17 ml 6 *M* HNO_3 to generate HNO_2 *in situ* (optimum reaction conditions determined above). 1750 ml of petroleum ether (30–60C bp) was then added and the mixture quickly washed four times with distilled water. The solvent layer was dried over anhydrous Na_2SO_4. A chromatographic column was prepared using a slurry of 100 g of silicic acid (Mallinkrodt, 100 mesh, suitable for chromatographic analysis, activated by heating overnight at 110C) in dry petroleum ether. The solvent head was allowed to drop almost to the top of the silicic acid. Then the solution of isomerized fatty acid was added to the column, and the eluate was collected. When the solvent head had once more reached the top of the silicic acid, the column was flushed with 200 ml of petroleum ether. The solvent was then evaporated from the eluate under reduced pressure. 327 g of fatty acid containing 60.5% *trans* monoene and 349 ppm nitrogen was recovered.

The amt of elemental nitrogen added by *cis-trans* isomerization and not removed by the silicic acid was determined by comparing the nitrogen contents of isomerized and unisomerized oleic acids after purification on identical columns of silicic acid. The eluted isomerized fatty acid contained 349 ppm nitrogen, while the eluted unisomerized material contained 187 ppm nitrogen. The difference, 162 ppm nitrogen, represented the net amt of nitrogen added to the acid by the isomerization process.

Solvent recrystallization was used to increase the *trans* monoene content of the product. Best yields of the highest *trans* content material were obtained by three successive overnight crystallizations from petroleum ether, methanol and methanol, respectively (Table III).

Discussion

Nitrous acid is a useful catalyst for the *cis-trans* isomerization of oleic acid. Most nitrogenous by-products can be easily removed by passage through a column of silicic acid. Under optimum reaction and purification conditions, up to 60% *trans* monoene can be introduced into technical grade oleic acid with a 93.3% yield from the starting material. Elemental nitrogen content of the fatty acid increases 162 ppm during processing; this is equivalent to 0.22% 9,10-dinitrostearic acid. Futher purification with silicic acid could probably reduce this nitrogen content even further, but product yield would be less. During solvent recrystallization, *trans* monoene content can be increased to 97.1%, but only with a 23.8% yield from the starting material.

The composition of the original oleic acid has a marked influence on the amt of *trans* bonds introduced and the overall yield of the process. In an ideal isomerization reaction with pure 9-*cis*-octadecenoic acid, 75–80% *trans* bonds could be introduced (31). Subsequent solvent recrystallization should yield pure elaidic acid in 50–65% yield. The technical oleic acid used in these experiments contained numerous components other than 9-*cis*-octadecenoic acid, and these impurities prevented maximum production of *trans* bonds. The 8.4% saturated fatty acids cannot participate in the isomerization. The 3.0% polyunsaturated fatty acids form substantially more nitrogenous reaction by-products than do monoene fatty acids (31,32) and increase losses. The presence of a mixture of monoene fatty acids leads to high crystallization losses. For these reasons, the most feasible way to increase the *trans* content of the product above 60% would be to raise the C-18 monoene content of the starting material.

Several workers (12–14) have shown that a similar 55–65% *trans* content can be achieved by hydrogenating soybean oil to an I.V. of 65–85 using a palladium catalyst under highly selective conditions. Such a

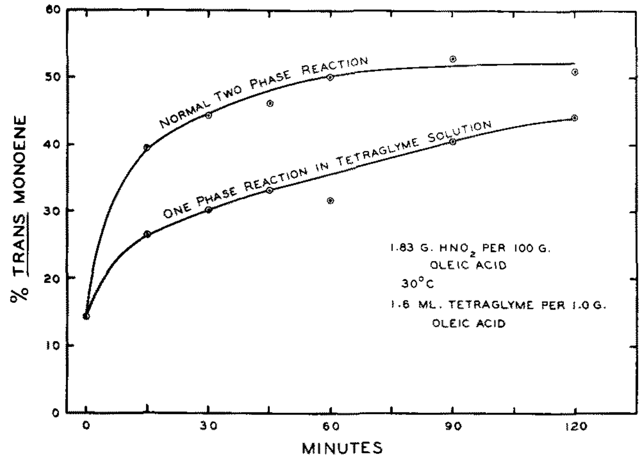


FIG. 3. *Cis-trans* isomerization of technical oleic acid by HNO_2 in one and two phase systems.

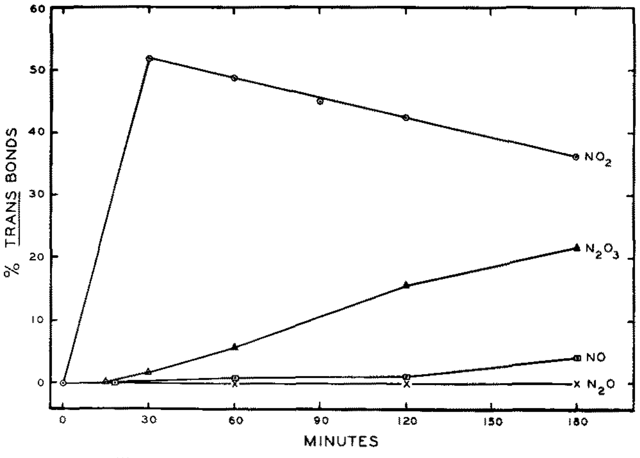


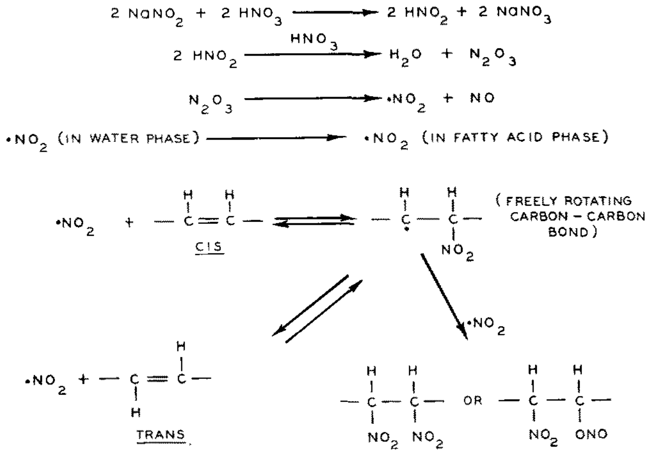
FIG. 4. *Cis-trans* isomerization of cottonseed oil at 60C by pure oxides of nitrogen.

process results in lower losses and is less costly than the procedure described here. However, a considerable portion of the *trans* bonds in such a hydrogenated fat are contained in polyunsaturated fatty acids which may affect the ultimate usefulness and stability of the product. In addition, some sautrated fatty acid would inevitably be formed during hydrogenation.

The silicic acid column chromatography conditions used here to remove nitro-fatty acids are essentially those of displacement analysis (36). More fatty acid is applied to the column than the adsorption sites of the silicic acid can hold. Under these conditions, the silicic acid absorbs the more polar nitrogenous by-products in preference to the ordinary fatty acids. The ratio of silicic acid to sample has been chosen so that almost all the nitrogenous by-products are adsorbed, and a minimum amt of non-nitrogenous fatty acid remains on the column. Test experiments have shown that with petroleum ether as an eluting solvent, this loss is ca. 150–200 mg of fatty acid/gram of silicic acid in that portion of the column where no nitrogenous by-products are present.

The reactions of N_2O, NO, NO_2 and N_2O_3 with cottonseed oil indicate that NO_2 is probably the active species in HNO_2-catalyzed *cis-trans* isomerization of unsaturated fatty acids. NO_2 isomerization reached a maximum *trans* content within 30 min while the other nitrogen oxides tested had a much smaller effect. N_2O gave no isomerization. Very little isomerization resulted with NO, and this small amt can probably be attributed to the formation of NO_2 by reaction of NO with the residual oxygen in the system. N_2O_3 gave some isomerization, which is probably due to its rapid breakdown into NO_2 plus NO. The drop in *trans* content with NO_2 after 30 min is undoubtedly due to a decrease in the total unsaturation of the system by formation of olefin addition products. These results agree with the earlier work of Khan (30) who also found NO_2 to be the active species causing *cis-trans* isomerization.

Nitrogen dioxide dimerizes at low temp to form dinitrogen tetroxide. At 30C, the dimer is ca. 25% dissociated into NO_2 (41), which has an odd number of valence electrons and thus can function as a free radical. The ability of nitrogen dioxide free radicals to add to olefins is well known (37–39). On the basis of Schechter and Conrad's work (37) and the review of Gould (40), it appears that *cis-trans* isomerization of oleic acid by HNO_3 plus $NaNO_2$ proceeds via the following free radical mechanism:



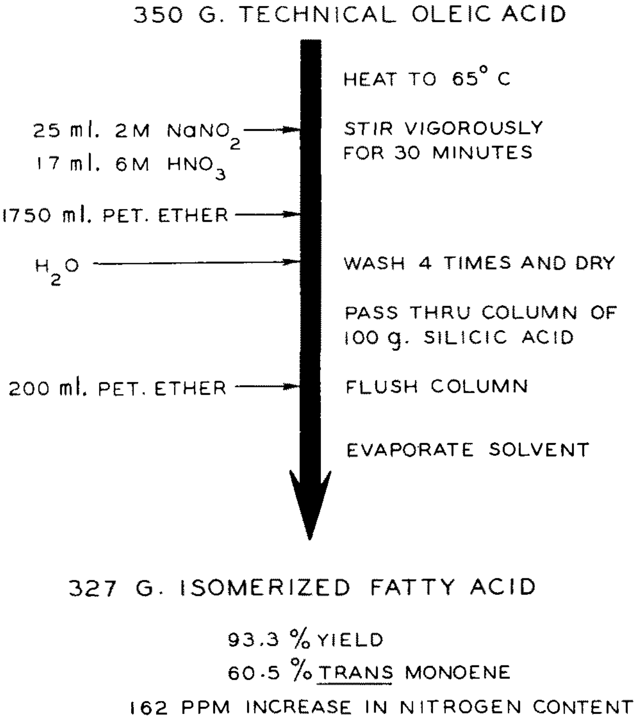


Fig. 5. Flow chart for *cis-trans* isomerization of technical oleic acid and removal of nitrogenous by-products with silicic acid.

Nitric acid reacts with sodium nitrite to produce nitrous acid, which decomposes in the presence of the stronger nitric acid. N_2O_3 (nitrous acid anhydride) then decomposes to give the free radical $\cdot NO_2$. After passage from the aqueous phase to the fatty acid phase, the $\cdot NO_2$ adds to a double bond of the oleic acid, producing a freely rotating carbon-carbon single bond. The addition of the $\cdot NO_2$ is reversible, and either a *cis* or *trans* double bond can be formed when the nitrogen dioxide moiety leaves. The addition of a second $\cdot NO_2$ molecule produces either 9,10-dinitro-

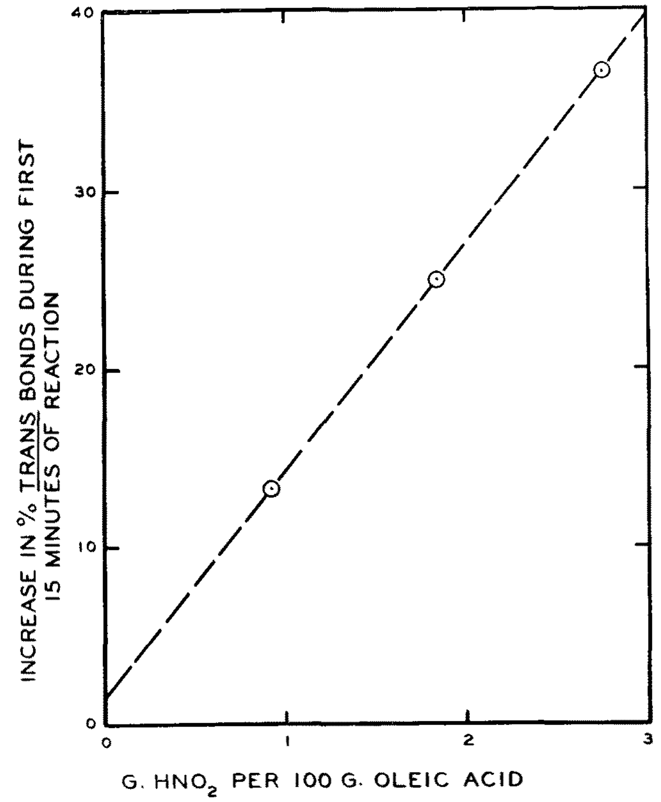


Fig. 6. Dependence of *cis-trans* isomerization rate at 30C on concn of HNO_2.

stearic acid or the analogous nitro-nitrite compound. Undoubtedly other side reactions take place concurrently with those shown above, but reversible free radical $\cdot NO_2$ addition to the double bond probably produces the *cis-trans* isomerization observed.

The rate of isomerization at 30C is sufficiently slow (Fig. 1, top) that a simplified kinetic analysis of the reaction can be made. If one assumes that during the initial stages only *cis* to *trans* isomerization occurs and the reverse reaction can be neglected, then the effect of catalyst concn on the reaction rate can be determined. The increase in *trans* content during the first 15 min of the reaction is plotted against the amt of catalyst used (expressed as the theoretical g HNO_2/100 g oleic acid) in Figure 6. A straight line is obtained passing close to the origin, indicating that reaction rate is directly proportional to catalyst concn (first order reaction).

If the isomerization rate has a first order dependence on catalyst concentration, this must mean that the transfer of $\cdot NO_2$ from the water phase to the fatty phase is not the rate determining step. This agrees with our experimental results showing the rate of isomerization is not a function of agitation.

The use of HNO_3 for *in situ* generation of HNO_2 gave faster isomerization rates than H_2SO_4, HCl, H_3PO_4 or CH_3COOH. The superiority of HNO_3 might possibly be due to its ability to convert the byproduct NO into additional NO_2 by the reaction:

$$2\,NO + H_2O + HNO_3 \rightleftarrows 3\,HNO_2$$

Abel et al. (43) and Klemanc and Klima (44) have shown that this equilibrium reaction takes place at room temp. H_3PO_4 and CH_3COOH were probably less effective than the strong acids because of their lower pK_a values.

ACKNOWLEDGMENTS

Taken in part from a dissertation to be submitted by the senior author to Texas A&M University in partial fulfillment of the requirement for the degree of Doctor of Philosophy. This investigation supported in part by grants from the Corn Products Institute of Nutrition and Cargill, Inc. Technical assistance by Hugo Gopffarth. Cottonseed oil supplied by The Procter & Gamble Co.

REFERENCES

1. Poutet, Ann. chim. et phys. (2) *12*, 58 (1819). English translation available from Carter Litchfield, Dept. of Biochemistry & Nutrition, Texas Agricultural Experiment Station, College Station, Texas.
2. Griffiths, H. N., and T. P. Hilditch, J. Chem. Soc. —, 2315 (1932).
3. McCutchon, M. A., R. T. O'Connor, E. F. DuPre, L. A. Goldblatt and W. G. Bickford, JAOCS *36*, 115 (1959).
4. Holde, D., and K. Rietz, Ber. *57*, 99 (1924).
5. Kass, J. P., and G. O. Burr, J. Am. Chem. Soc. *61*, 1062 (1939).
6. Bertram, S. H., Chem. Weekbald *33*, 3 (1936); Olele, Fette, Wachse (7), 1 (1938).
7. Fitzpatrick, J. D., and M. Orchin, J. Am. Chem. Soc. *79*, 4765 (1957).
8. Bertram, S. H. (Industrieele Exploitatie Maatschappij), U.S. 2,165,530 (1939).
9. Waterman, H. I., C. Van Vlodrop and W. J. Taat, Chimie Industrie *44*, 285 (1940).
10. Rankoff, G., Ber. *69*, 1231 (1936).
11. Dutton, H. J., JAOCS *40*, 35 (1963).
12. Sims, R. J., and L. Hilfman, *Ibid. 30*, 410 (1953).
13. Cousins, E. R., W. A. Guice and R. O. Feuge, *Ibid. 36*, 24 (1959).
14. Zajcew, M., *Ibid. 39*, 301 (1962).
15. Kircher, H. W., *Ibid. 41*, 351 (1964).
16. Tyutyunnikov, B. N., and I. V. Bogdan, USSR. 123, 648 (1959); Maslob. Zhir. Prom. *26* (9), 20 (1960). English translations available from Associated Technical Services, P.O. Box 271, East Orange, N.J.
17. Brown, L. H., and R. Swidler (Tallow Research), U.S. 3,065,248 (1962).
18. Back, M. H., and R. J. Cvetanovic, Can. J. Chem. *41*, 1396 (1963).
19. Chipault, J. R., and J. M. Hawkins, JAOCS *37*, 176 (1960).
20. Kuhn, H., H. Luck, Z. Lebensm. Untersuch. u. Forsch. *109*, 306 (1959).
21. Pan, H., S. A. Goldblith and B. E. Procter, JAOCS *35*, 1 (1958).
22. Straub, J., and R. N. M. A. Malotaux, Rec. trav. chim. *57*, 789 (1938).
23. Bertram, S. H., JAOCS *26*, 83 (1949).
24. Taufel, K., and E. Spiegelberg, Chemische Umschau, Fette, Oele, Wachse, u. Harze, *37*, 281 (1930).
25. Bertram, S. H., and E. C. S. Kipperman, Chem. Weekbald *32*, 624 (1935); Oele, Fette, Wachse (6), 1 (1936).
26. Schulman, J. H., and E. G. Cockbain, Trans. Faraday Soc. *36*, 651 (1940).
27. Cook, L. R., and J. H Light (Wilbur-Suchard Chocolate Co.), U.S. 2,216,660 (1940).
28. Fieser, L. F., and M. Fieser, "Organic Chemistry," 3rd ed., D. C. Heath, Boston, 1956, pp. 610–611.
29. Eipper, W. R., U.S. 2,310,225 (1943); U.S. 2,456,691 (1948).
30. Khan, N. A., J. Chem. Phys. *23*, 2447 (1955).
31. Litchfield, C., J. E. Lord, A. F. Isbell and R. Reiser, JAOCS *40*, 553 (1963).
32. Harlow, R. D., C. Litchfield and R. Reiser, *Ibid. 40*, 505 (1963).
33. Metcalfe, L. D., and A. A. Schmitz, Anal. Chem. *33*, 363 (1961).
34. Litchfield, C., R. Reiser and A. F. Isbell, JAOCS *40*, 302 (1963).
35. Official and Tentative Methods of the AOCS, Chicago, 1962.
36. Holman, R. T., Progress in the Chemistry of Fats and Other Lipids, *1*, 104 (1952).
37. Schechter, H., and F. Conrad, J. Am. Chem. Soc. *75*, 5610 (1953).
38. Levy, N., and C. W. Scaife, J. Chem. Soc. —, 1093 (1946).
39. Riebsomer, J. L., Chem. Rev. *36*, 157 (1945).
40. Gould, E. S., "Mechanism and Structure in Organic Chemistry," Holt, Rinehart & Winston, New York, 1959, pp. 739–740.
41. "Matheson Gas Data Handbook," Matheson Co., East Rutherford, N.J., 1961, p. 327.
42. Litchfield, C., M. Farquhar and R. Reiser, JAOCS *41*, 588–592 (1964).
43. Abel, E., H. Schmidt and S. Babad, Z. physik. Chem. *136*, 419 (1928); *Ibid. 136*, 430 (1928).
44. Klemenc, A., and L. Klima, Z. anorg. allgem. Chem. *179*, 379 (1929).

[Received May 27, 1964—Accepted September 29, 1964]

Characterization and Evaluation of Some Rapeseed Oils[1]

S. A. TREMAZI,[2] N. V. LOVEGREN and R. O. FEUGE, Southern Regional Research Laboratory,[3] New Orleans, Louisiana

Abstract

Rapeseed oil is used mostly in edible products. Four rapeseed oils, brown sarson and toria oils from West Pakistan, a Swedish oil and a Canadian oil, were characterized and examined relative to their suitability as edible oils. The various analytical data obtained are reported. The hydrogenated oils have consistency characteristics and plastic ranges which make them suitable for use as plastic fats.

Introduction

MOST OF THE WORLD PRODUCTION of rapeseed oil is consumed as an edible oil in the countries in which it is produced, principally China and India. Of the total area in West Pakistan devoted to growing oilseeds (not including cottonseed), 80% is occupied by the *Brassica oleiferous* group. Rapeseed oil is a fairly important food oil in Europe. In the U.S. only relatively small amt of the oil have been used, mostly in nonedible products. However, in Canada there is an increasing production of rape to obtain an edible vegetable oil and a replacement crop for wheat. This effort to establish rape in Canada is supported by an extensive research program (2,3,5,9–16).

The objective of the present investigation was to examine and characterize two samples of rapeseed oil produced from the major varieties of rape grown in West Pakistan and to obtain additional data on these and other rapeseed oils relative to their suitability as edible oils.

---

[1] This work supported by a fellowship grant awarded by South East Asia Treaty Organization, Bangkok, Thailand.

[2] Present address: Officer in Charge, Dept. of Food Technology, West Pakistan Agricultural University, Lyallpur, West Pakistan.

[3] A laboratory of the So. Utiliz. Res. & Dev. Div., ARS, USDA.