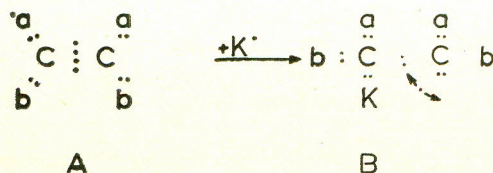


85- SPECTROPHOTOMETRIC STUDIES ON TRANSITION COMPLEXES IN
CIS-TRANS INTERCONVERSION

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It is well known that only paramagnetic substances catalyze the *cis-trans* interconversion, for which the following mechanism has been adopted generally:



Accordingly, it can be expected that all oxides of nitrogen (except nitrous oxide) and oxygen, which have one feature in common, namely an odd number of electrons giving rise to three-electron bonds,¹ as shown in Fig. 1, will catalyze this *cis-trans* conversion. It has been proposed previously by the author^{11,12} that the oxygen molecule may interact with electrons through hydrogen bonding with the formation of a six-membered transition ring. Under such circumstances, the pull of π electrons and their subsequent recovery cause *cis* to *trans* conversion, but the complexing oxygen once changed from its inert structure^{12,19} seems to be highly reactive in getting attached to the carbon chain and shifting the newly generated *trans* double bond to adjacent position. In both nitrogen dioxide and oxygen conversion of *cis* to *trans* form through transition complexes, (as shown at B above), the transitory removal of electrons in a *cis* double bond leaves

a single bond structure for easy change over to *trans* form. This common aspect of the *cis-trans* interconversion has been investigated and confirmed through various experiments, described in the present paper.

All nitrogen oxides were not found to be isomerizing agents. Nitrous oxide did not form any nitrogen derivative with oleic acid, nor did it convert *cis* form to *trans* form. Figure 3 shows the infrared absorption at two regions by the different reaction products from vessel I-III of Fig. 2. Nitrogen derivatives (6.10μ and 6.44μ) were formed in large quantities by all sets of the reactions. However, the amount of *trans* isomer (10.32μ) produced was highest in the case of nitrogen dioxide reactions (III), smaller with the total oxides of nitrogen (I) and none in the case of nitric oxide reactions (II). Moreover, while the reactions were going on, the temperature of the substances in vessels I and III rose to over 80°C . but there was no temperature rise in the reaction vessel II. Such processes of bubbling nitrogen dioxide, when applied to linoleic and linolenic acids, caused instantaneous polymerization.

Dinitrogen trioxide reactions produced

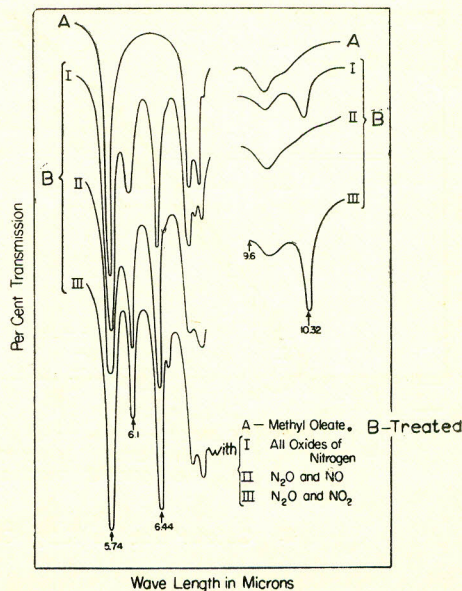
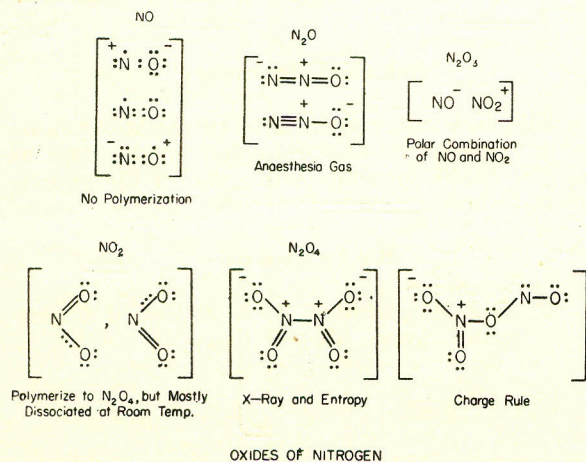


Fig. 3.—Infrared analysis on isomerization products of methyl oleate.

Fig. 1.—Oxides of nitrogen and probable structures.

considerable amounts of nitrogen derivatives with a minimal conversion of *cis* configuration to *trans*. Nitric oxide and dinitrogen trioxide appeared to be the additive reagents; the minor conver-

sion of *cis* to *trans* form by dinitrogen trioxide might have resulted from some possible contamination of dinitrogen trioxide by free nitrogen dioxide.

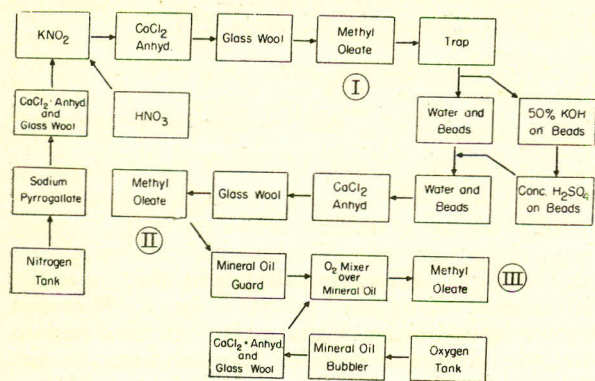


Fig. 2(a).—A scheme for isomerization reaction.

Formation of Labile Species of Products

The foregoing rapid reactions by nitrogen dioxide did not reveal all aspects of fatty acid behaviour. The slow processes of nitrogen dioxide reactions were then arranged by a gaseous atmosphere of nitrogen dioxide in a desiccator that contained fatty acid in thin layers. In the presence of nitrogen dioxide, methyl linoleate gave a definite absorption in the ultraviolet region at $249 \text{ m}\mu$ (Fig. 4), which increased gradually to maximum intensity after 4 hours and then decreased until it disappeared after 8 hours. Methyl linolenate showed absorption at $310 \text{ m}\mu$ (Fig. 4) after 10 minutes which reached its

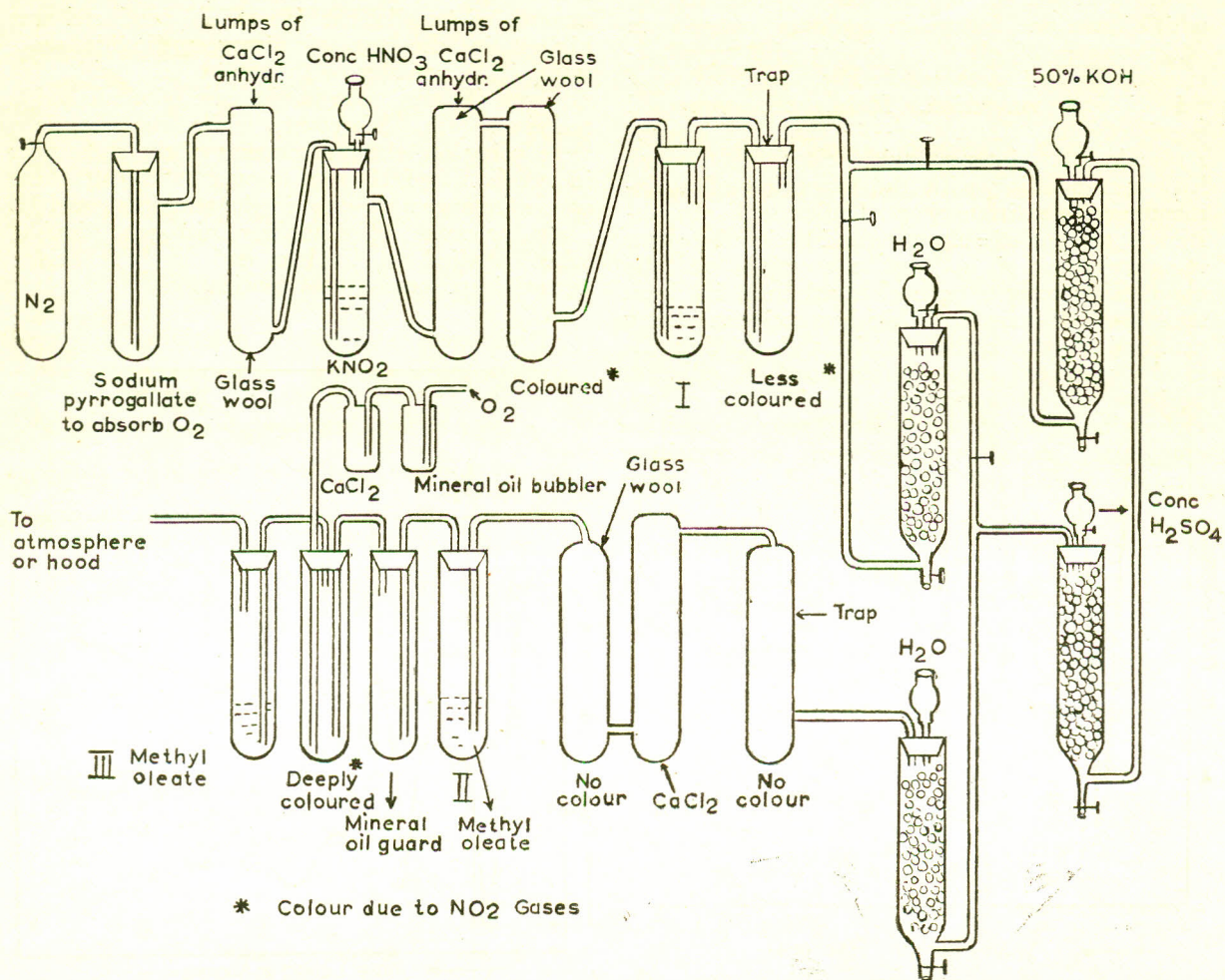


Fig. 2(b).—Reaction systems.

maximum after 30 minutes. Another interesting phenomenon in methyl linolenate isomerization reactions was that it yielded some labile *trans* isomer (absorbing at 10.32μ) that disappeared under

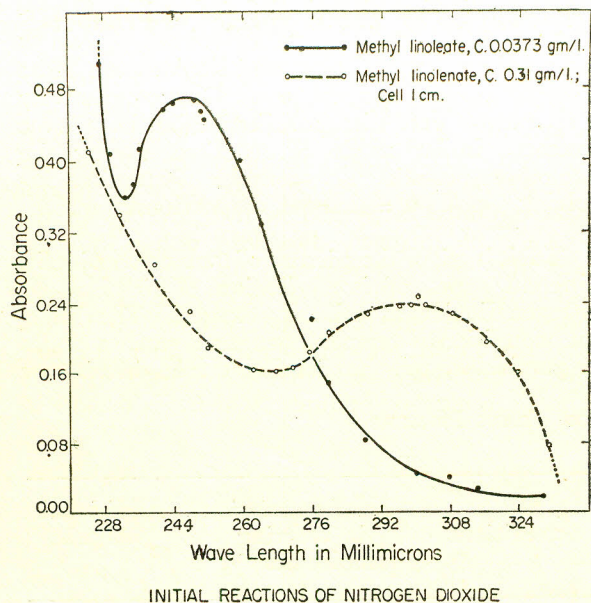


Fig. 4.—Ultraviolet absorption curves of methyl linoleate and linolenate reacting with NO_2 .

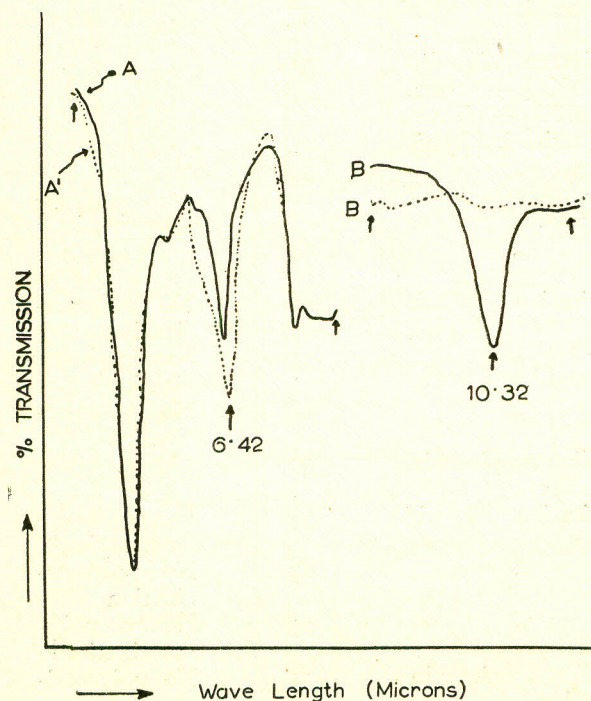


Fig. 5.—Infrared spectra of labile *trans* isomer of methyl linolenate before (A and B) and after (A' and B') evacuation.

vacuum. A portion of methyl linolenate, after reaction with nitrogen dioxide for 15 minutes, was subjected to infrared analysis to obtain the solid line curves (A & B, Fig. 5), and another evacuated portion gave rise to the dotted line curves (A' & B', Fig. 5). These curves show two important regions, $3.5-7.1 \mu$ (nitrogen derivative absorbing at 6.42μ) and $9.6-10.8 \mu$ (*trans* isomer at 10.32μ); methyl linolenate does not have any band at 6.42 , nor any at 10.32 . The application of vacuum increased the amount of nitrogen derivatives (6.42μ , curve A') and eliminated almost all of the *trans* forms (curve B', 10.32μ).

Combined absorption studies at $301 \text{ m}\mu$ in the ultraviolet region and 10.32μ in the infrared region during the reactions of nitrogen dioxide with methyl linolenate showed that as long as the absorption at $301 \text{ m}\mu$ persisted, *trans* isomer (10.32μ) was not observed (Figs. 6 and 7) but

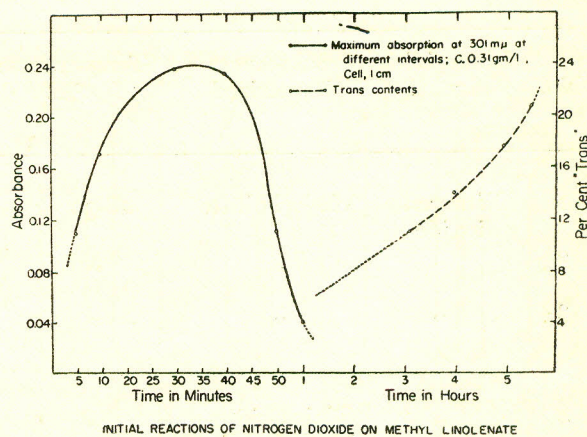


Fig. 6.—Transition complex and *trans* isomer during the reactions of NO_2 .

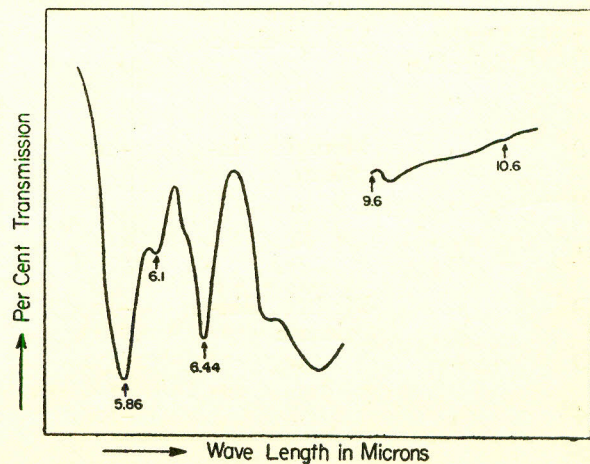


Fig. 7.—Infrared adsorption bands for nitrogen derivatives.

nitrogen derivatives were formed (6.44 μ). Methyl linoleate exhibited the same phenomena with its analogous absorption at 249 m μ during the reactions with nitrogen dioxide. Under similar conditions, methyl oleate did not absorb in the ultraviolet region investigated, and the *trans* isomer was found to be formed from methyl oleate, but only after 8-hour exposure to the atmosphere of nitrogen dioxide giving initially a blue transient colouration²⁵ indicating an unstable complex. Hence, one or more unstable species appeared to be formed prior to *cis-trans* conversion. These probably resulted in unstable complexes, which gave rise to either *trans* isomer free of nitrogen derivatives or stable nitrogen derivatives found in the experiments. Each fatty acid ester thus required certain periods of time to initiate *cis* to *trans* conversion by nitrogen dioxide:

methyl oleate, 8 hours; methyl linoleate 1/4 hour; and methyl linolenate, 1/6 hour.

In the same way, oxygen conversion of *cis* to *trans* form indicated such definite and characteristic induction periods: methyl oleate, 45 days; methyl linoleate, 16 hours; and linolenate, 4 hours only (all at room temperatures). Oxygen reactivity is thus lower than nitrogen dioxide but both have possibly similar mode of reactions during the induction periods, i.e. complex formation involving a pull on π electrons, as previously noted.

Table I gives the picture of *trans* conversion in different types of isomerization of *cis* form by nitrogen dioxide, as well as by oxygen. The different conditions, temperature and gaseous states in particular, play predominant roles in *cis-trans*

TABLE I.—FORMATION OF TRANS ISOMERS.

No.	Isomerizing agents	Substances isomerized	Temperature o°C.	Other conditions	<i>Trans</i> conversion in reacting molecules %	Additional remarks
1	Nitrogen dioxide	Methyl oleate	28-30	Bubbling gases	46	Some polymerization ^a
2	"	"	"	Atmosphere of gases	57	"
3	"	"	"	Mixture of solid KNO ₂ + conc. HNO ₃ + oleate + agitation by air	51	"
4	"	Oleic acid	"	"	54	"
5	"	Methyl linoleate	"	Atmosphere of gases	21	Heavy polymerization ^a
6	"	Methyl linolenate	"	"	14	"
7	Oxygen molecules	Methyl oleate	"	Agitation by air	66	No polymerization
8	"	"	45	"	77	Some polymerization ^b
9	"	Methyl linoleate	-10	"	88	No polymerization
10	"	"	0	Still atmosphere in cooler	90	"
11	"	"	28-30	Agitation by air	54	Heavy polymerization ^b
12	"	Methyl linolenate	-10	"	87	No polymerization
13	"	"	28-30	"	44	Heavy polymerization ^b
14	"	"	-10	Still atmosphere in cooler	90	No polymerization

^aPolymers as nitrogen derivatives. ^bPolymers as oxygenated compound.

isomerization. The conversions in both types are systematic and start after definite induction periods and consequently quite similar in nature. The slow rate of oxygen favours conversion to *trans* rather than that to polymers. The faster rate of nitrogen dioxide facilitates the reverse processes and consequently *trans* contents are lower in 1-6 items (Table 1). Furthermore, cooler temperature still cuts down the reactivity of oxygen and causes better conversion to *trans* (cf. items, 9, 10, 12 and 14 in Table 1). In the same way, lower reactivity of nitrogen dioxide in gaseous atmosphere (cf. previous desiccator reactions and items 2 and 4 of Table 1) increases the yield of *trans* isomer.

Ultimate Products of Isomerization

There is another phase of *cis-trans* interconversion, in which the recovery of π electrons is not possible, and either the simple or polymeric derivatives are formed. Both nitrogen dioxide and oxygen yield polymeric derivatives with the advance of reactions, nitrogen dioxide (being a stronger reagent) producing a greater degree of polymerization than oxygen which produces no polymer at the start. Furthermore, long-term reactions of nitrogen dioxide and oxygen with methyl oleate, linoleate and linolenate resulted in complete polymerization. This has been shown through urea complex formation, petroleum ether treatment and time-isomerization, discussed below.

The nitrogen dioxide polymers showed identical nitrogen analysis through Dumas and Kjeldahl methods: oleate polymers, 4.5%; linoleate polymers, 5.1%; and linolenate polymers, 5.9% nitrogen. These correspond to one N-atom (i.e. one NO_2) per fatty acid chain, indicating addition reactions.

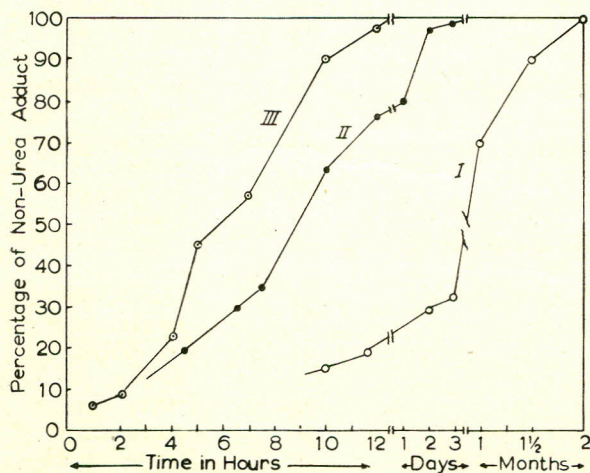


Fig. 8.—Formation of non-urea adducts during the reaction of NO_2 with: I, methyl oleate; II, methyl linoleate; and III, methyl linolenate.

Hence *cis-trans* interconversions may be taken as the processes preceding the addition reactions, substantiating the mechanism in this paper and concepts proposed by Marvel.¹⁰ Such polymer formations with one O_2 per chain have been formulated by various investigators.³⁰

Since urea forms complexes with monomers and not with polymers, nitrogen dioxide isomerization products have been systematically analyzed through urea complexes. The nitrogen derivatives were found to be mostly polymers as non-urea adducts (Fig. 8), while the urea adducts (complexes) were almost free from nitrogen. Such urea complex formation conducted for each batch of reaction products established the trends of polymer formation (Fig. 8), the degree of which in relation to nitrogen derivatives and *trans* isomers was also measured. Under the conditions of isomerization, the periods of time manifesting the peak formation of *trans* isomer were noted as follows: 14-20 hours for oleate; 7½-9 hours for linoleate, and 2-3 hours for linolenate. With longer periods of isomerization, the *trans* isomer in each case was found to disappear entirely (methyl oleate, 1½ months; linoleate, 27 hours; linolenate, 8 hours). Similar trends of reactions are also followed by oxygen isomerization. Some authors³¹ have investigated *trans*- and polymer-formation by oxygen on different fatty substances. Since the reactions are slow, the systematic studies could not be arranged in the present investigation, but in our open shelf experiments (without much attention) complete polymerization occurred in approximately 2¼ years for methyl oleate, 7 months for the linoleate and 2½ months for the linolenate. *Trans* conversion is caused^{11,32,33} by oxygen up to a maximum limit, as with nitrogen dioxide noted above and then *trans* isomer also disappears entirely, yielding only polymers.

During the processes of the determinations of polymers, it was noted in the case of oleic acid isomerized by nitrogen dioxide that, when elaidic and unisomerized oleic acid were obtained as urea complex crystals, elaidic acid always precipitated out first (as urea complexes) and oleic acid after a considerable time lag. This preferential urea complex formation by elaidic acid over oleic acid probably relates to their physical structures. Figure 9 shows schematically the structures of elaidic and oleic in plane projection of the skeleton C-chain. *cis*-Oleic is seen to be folded, which makes it difficult for oleic acid molecule to slide into the hexagonal urea cylinder,⁹ whereas the straight chain character of elaidic acid offers easy access to the same. The easy urea complex formation by stearic acid³⁴ as against *cis*-oleic acid also confirms these ideas on

Experimental

Preparation of Different Materials.—The low-grade samples of the acids (oleic (95-97%), linoleic (85-90%), and linolenic (80-85%)) and their methyl esters were obtained by fractionation of cottonseed and linseed oil acids and esters through urea complex formations.² The pure methyl oleate (I. N. = iodine number, 86.2) was prepared by the method of Khan.³ Methyl linoleate (I.N., 172.4) and linolenate (I.N., 259.6) were prepared by the usual bromination and debromination procedures.⁴

Nitric oxide was prepared by the second method described by Farkas and Melville.⁵ Nitrogen dioxide was obtained by mixing pure nitric oxide with oxygen.

Determination of Unsaturation and the Contents of Nitrogen and Polymer.—The iodine number was determined by the Wijs' half-an-hour method. The quantitative determination of nitrogen was made by micro Kjeldahl²⁶ and Dumas' methods.²⁷ The polymer formation was estimated by: (a) insolubility of the products in petroleum ether, b.p. 30-60°C. and free from the unsaturates;⁶ (b) the products not forming urea complexes.^{7,9} For (a), the crude reaction mixtures were shaken with any amount of petroleum ether, as many times as possible to remove the soluble materials completely. The residue was noted as polymer, as the monomers used were soluble in petroleum ether. In the second case, Swern, Schlenk and Holman have put forward the usually employed "solution method" for urea complex formation. The only important thing to be noted was to remove all materials forming urea crystals by using any amount of methyl alcohol or urea, as necessary. The filtrate contains non-urea complex substances that can be easily measured.

Spectrophotometric Analyses.—The degrees of *cis-trans* interconversion and of formation of the nitrogen derivatives in all materials and in the reaction products were determined by comparative studies of infrared absorption by the Perkin Elmer Instrument, Model 21. The base line technique in conjunction with the absorption of pure elaidic acid and methyl elaidate were used to determine the percentage of *trans* contents.^{22,23} The tested wave lengths were 9.0-12.0 μ (particularly, 10.32 μ) for the isolated *trans* double bond and 5.0-7.5 μ for the nitrogen derivatives. Swern and Wheeler²² have dealt with these analytical methods in enough details.

The Beckman DU model spectrophotometer was employed for the ultraviolet absorption anal-

ysis. The procedures involve common experiments using absolute alcohol (distilled over zinc powder and potassium hydroxide pellets) as 1% solution with the substances for analysis in the range, 222 m μ to 350 m μ recording diverse aspects of interest²⁴ in fat chemistry. Multiple dilution method was employed, if the density of absorption is very intense.

Reactions of Nitrogen Oxides on Oleic Acid and Methyl Oleate.—Fifty grams of oleic acid (95-97%) was treated with nitrous oxide for several days without any isomerization (analysis: nitrogen, 0.0; *trans*, 0.0). The train of gas reaction was set up as in the flow sheet shown in Fig. 2 and reaction systems in Fig. 2(a), to study individually the effects of other nitrogen oxides. All nitrogen oxides, generated (N₂O, NO, NO₂, N₂O₃, etc.) by nitric acid and nitrite, were allowed to react with 50 g. of crude methyl oleate (reaction vessel, I). After nitrogen dioxide and dinitrogen trioxide were washed off by (a) water or by (b) 50% potassium hydroxide, concentrated sulphuric acid and water, the remaining nitrogen dioxide and nitric oxide were dried by anhydrous calcium chloride and caused to react with another 50 g. of methyl oleate (reaction vessel II). The oxygen was mixed through a proper device with the out-going gases changing the nitric oxide to nitrogen dioxide. Thus, nitrous oxide and nitrogen dioxide passed through the third sample containing 50 g. of methyl oleate (reaction vessel III). Since nitrous oxide was inactive, the degrees of isomerization and addition reactions by all nitrogen oxides in vessel I, by nitric oxide in vessel II, and by nitrogen dioxide in III, were determined by chemical and physical analyses (Fig. 3). The flow-sheet description (Fig. 2) should help workers using their own devices and other details and make the materials clear at a glance. The processes of washing by potassium hydroxide and sulphuric acid assured the absence of nitrogen dioxide and dinitrogen trioxide according to the previous workers. The reactions of methyl oleate, by all oxides of nitrogen (vessel I, analysis *trans*, 31.0%; polymers, 27.0% containing 4.9% nitrogen; *cis* unchanged oleate, 36.0% and unaccounted, 6.0%), by nitric oxide only (vessel II, analysis: *trans*, 0.0; polymer, 54.0%; *cis* unchanged oleate, 38.0%; unaccounted, 8.0%), by nitrogen dioxide (vessel III, analysis: *trans* 33.0% polymer, 34.0% containing 5.3% nitrogen; *cis* unchanged oleate, 29.0%; unaccounted, 4.0%), were, thus, performed.

Dinitrogen Trioxide.—In the case of dinitrogen trioxide reactions, equivalent amounts of nitric oxide and nitrogen dioxide were mixed in a tube containing glass wool. This tube was slightly warmed⁸ by a heating coil. The effluent gas was

allowed to pass through a coil immersed in chipped ice and was then allowed to bubble through pure methyl oleate (10 g., I.N., 84.8) in a closed test tube, precooled to 0°-3° C. by chipped ice plus salt. Both the reaction systems were freed of oxygen at the beginning and of nitrogen oxides at the end of the reactions by flushing with oxygen-free nitrogen gas. The analysis of reacted oleate gave: *trans*, 4.0%; polymer, 61.0% containing 5.1% nitrogen; unchanged, 29.0%; and unaccounted, 6.0%.

Reactions of Nitrogen Dioxide on Linoleic and Linolenic Acids.—The nitrogen dioxide gas was bubbled through linoleic and linolenic acids (30. g. each) in tubes for only 15 minutes, until thick polymers (100.0%) were obtained. Analysis of both samples gave: *trans*, 0.0; unchanged monomer, 0.0 soluble in petroleum ether, or giving urea complexes.

Milder Processes of Nitrogen Dioxide Reactions on Methyl Ester of Linoleic and Linolenic Acids.—The bubbling processes of isomerizations, so far employed in the investigations, were drastic and the reactions (those of linolenate in particular) could not be controlled properly. An attempt was then made to use milder conditions. Furthermore, nitrogen dioxide gas being the only effective isomerizing agent, was used in all the other subsequent experiments. Thin layers (1.0-2.0 mm. thickness) of methyl linoleate (10.0 g.) or of linolenate (10.0 g.) in a crystallizing dish was placed inside a dessicator that was filled with nitrogen dioxide. The course of reaction was followed by infrared and ultraviolet absorption analysis at 5, 10, 15 and 30 minutes, and a 1, 2, 4, 6, and 10 hours after the onset of reactions. The absorption maxima were detected at 249 $m\mu$ for linoleate and at 301 $m\mu$ for linolenate due to some labile transition complexes that disappeared with time (Fig. 4). Even the indication of labile *trans* isomer in the linolenate reactions led to the following experiments.

Preparation of Labile *Trans* Isomer.—Methyl linolenate (50 g.) was kept in the atmosphere of nitrogen dioxide for 20 minutes. One portion of the sample was subjected to high vacuum. Both the nitrogen dioxide and the vacuum treated samples were subjected to infrared absorption analyses (Fig. 5) in the ranges 5.0-7.0 μ and 9.0-11.0 μ . The absorptions due to nitrogen and *trans* isomer were carefully noted. Methyl linolenate used were analyzed (absorption at 6.42 μ , 0.0; N₂, 0.0; *trans*, 0.0). Nitrogen dioxide treated methyl linolenate after being subjected to vacuum showed characteristics (absorption at 6.42 μ ; still stronger band; N₂, 5.9%, *trans*, 0.0).

Detection of Transition Complex and Formation of *Trans* Isomer.—The above experiments aroused our interest in following variations with time in the amounts of absorption at both 301 $m\mu$ in the ultraviolet region and 10.32 μ in the infrared region during the reactions of methyl linolenate with nitrogen dioxide. The nitrogen dioxide reactions on linolenate were checked from the very onset for absorption at 301 $m\mu$ and 10.32 μ . The suitable intervals for the readings were chosen so as to indicate initiation, maximum formation and disappearance of the transition complexes and *trans* isomer. Figures 6 and 7 show the results.

Detection of Polymers through Urea Complex Formation.—The different fatty materials (50 g. each) reacting were exhaustively freed of the urea complex forming substances through solution method of urea complex formation.^{2,43} The polymers were measured from the final filtrate, as they do not form urea complexes. Figure 8 records the trends of polymer formation.

***Trans* Isomers and Urea Complex Formation.**—The solution method^{2,43} was again followed with 50 g. of each material. The *trans* isomers were always isolated ahead of the *cis* isomers. Elaidic acid got precipitated faster than oleic acid. Figure 9 establishes the differences of the acids. Table 1 indicates the degree of *trans* isomer formation.

Oxygen Reactions on Fatty Acid Esters.—Methyl oleate, linoleate and linolenate were oxidized by bubbling oxygen gas at room temperatures (28-30°C.). Due to the slow rate of reactions, oxidation took 6 months for oleate, 16 days for linoleate and 5 days for linolenate in order to attain the desired degree of oxidation and *trans* conversion. The samples from each substance were analyzed for *trans* and peroxide contents^{28,22} at suitable intervals. Autoxidation was continued until peroxide contents reached 10% level (ca., 625 - 700 m.e./Kg. of peroxide value in these instances). The peroxide formation and appearance of *trans* isomers were almost co-incident as far as time is concerned in all the above substances. Such infrared absorption studies together with ultraviolet analyses at different intervals could not establish the presence of any unstable intermediates formed during autoxidation between oxygen and these fatty substances. The other autoxidation reactions were carried out with the different substances as: (a) methyl oleate at 45°C., (b) linoleate at 0°C. and linolenate at -10°C. in the open Erlenmeyer flasks in the coolers without any agitation. The substances autoxidized to the level of 10% peroxides gave analysis for *trans*

contents (methyl oleate, in the range, 6.0-7.0%; methyl linoleate, in the range, 8.5-9.0%; methyl linolenate, in the range, 7.0-8.0%). The oxygenated products were isolated by the following experiments.

Isolation of Trans Isomers from Oxygen Reaction Products.—Since the slowness in oxygen reactions causes loss of time, the reaction products were isolated from the partially oxidized substances (cf. 10%, foregoing section) by counter-current extraction, according to the methods already described,^{1,2} between pairs of solvents (89% alcohol and petroleum ether, 30-60°C. b.p.). The peroxide concentrates thus quantitatively isolated from different sources almost equal to 10% of the original material taken, were subjected to infrared analyses for determining the contents of *trans* isomer in each sample. The *trans* isomers were usually found to be formed without any side reactions in oxygen processes at the initial stages. Table 1 shows the results.

Oxygen Reactions and Time Effects.—The samples of methyl oleate, linoleate and linolenate were left open to air at room temperatures for occasional analyses of *trans* isomer and polymer contents. Solution method of urea complex formation^{2,4,3} was used for the purpose. *Trans* contents disappeared with total conversion to polymers in time (methyl oleate 2½ years; linoleate, 7 months; linolenate, 2½ months).

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