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Trans-Isomerization of Oleic Acid and Potassium Oleate by Ionizing Radiation[1,2]

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Unsaturated fatty acids *trans*-isomerize upon heating with suitable catalysts (14), upon oxidation (12), or upon catalytic partial hydrogenation (1, 2, 3, 12, 16). The *trans*-isomerization that takes place under these conditions has been intensively investigated. The authors found that oleic acid and potassium oleate also *trans*-isomerize upon irradiation with cathode rays. Oleic acid was chosen for the preliminary study because of its relative simplicity among unsaturated fatty acids in containing only one double bond; potassium oleate was used since its solubility in water permitted the study of irradiation in the presence of water.

Materials and Methods

Oleic acid used in the investigation was obtained from two sources. That obtained from the Hormel Foundation was 99.64% pure (containing 0.27% saturated and 0.05% dienoic fatty acids) with an iodine value (Wijs) of 89.8 (theoretical value 89.87). The other was prepared by fractional crystallization of Eastman U.S.P. oleic acid, followed by distillation (11). The acid had an iodine value of 89.2. Elaidic acid was prepared by heating the oleic acid of IV 89.2 at 225°C. with selenium metal for one hour, followed by repeated fractional crystallization (14). The product was found to have an iodine value of 89.9. Potassium oleate was precipitated by the addition of acetone to the reaction solution. It was purified by reprecipitation from an ethyl alcohol solution with acetone (9).

Two Van de Graaff accelerators (15) were used in this investigation. The oleic acid of IV 89.8 was irradiated with cathode rays from one accelerator, which had an energy level of 2 M.e.v.[3]

The oleic acid of IV 89.2 was irradiated with cathode rays from the other accelerator, which had an energy level of 3 M.e.v.

The conveyor belt carrying the samples to be irradiated was sprinkled with pulverized dry ice to prevent any substantial rise in the temperature of the samples during irradiation. At high dose-levels the samples were cooled with dry ice between successive doses of irradiation.

The degree of *trans*-isomerization of the oleic acid from the irradiation samples was examined by means of infrared spectroscopy (5, 8, 12). Infrared absorption spectrograms of 20% carbon disulfide solutions of irradiated oleic acid (W/V[4]) were obtained with a Perkin Elmer Spectrophotometer Model 21. A sodium chloride cell of 0.104-mm. thickness was used. The speed of recording was 138 cm^{-1} per minute (denoted as 7 on the machine). The amounts of *trans*-isomerized oleic acid were determined quantitatively at 966 cm^{-1} on the infrared spectra.

The absorption spectrum between 1,000 and 900 cm^{-1} was investigated. The spectrum indicated that some unknown chemical changes as well as *trans*-isomerization occurred in the irradiated oleic acid. The decrease in the amount of the carboxyl group, as shown by the decrease of the peak at 933 cm^{-1} (4, 13), and a general change in intensity of the infrared absorption spectra in the region 1,000–900 cm^{-1} indicated that the chemical changes caused a decrease in the total fatty acid concentration in each of the irradiated samples (Figure 1). Both the decrease in the concentration of fatty acids and the

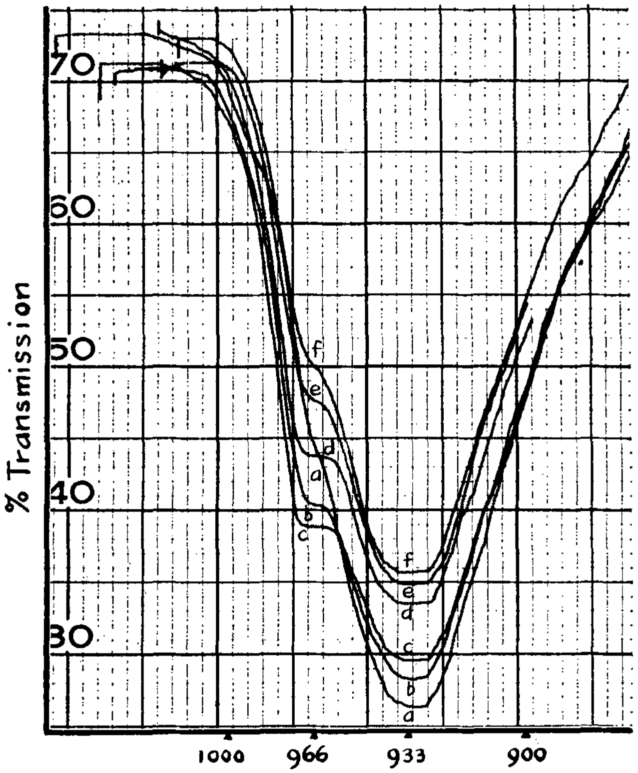

FIG. 1. Infrared spectrograms, 1,000–900 cm^{-1}, of oleic acid recovered from 2.5% aqueous solutions of potassium oleate irradiated with cathode rays at various dose-levels (the recovered oleic acid in CS_2, 20% W/V). Spectrogram a, unirradiated; b, 5 x 10^6 rep; c, 10 x 10^6 rep; d, 15 x 10^6 rep; e, 20 x 10^6 rep; and f, 25 x 10^6 rep.

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[2] Contribution No. 305 from the Department of Food Technology, Massachusetts Institute of Technology.

[3] Million electron volt.

[4] Weight to volume.

change in intensity of the absorption peak at 966 cm^{-1} made it impossible to measure, by the conventional "baseline" technique, the values of I_0 and I (the intensity of the light entering and leaving the carbon disulfide solution of the irradiated oleic acid) on the spectrum of one sample of irradiated oleic acid relative to the values on the spectrum of another. Thus the conventional "baseline" technique (7, 17), which has proved useful in infrared spectrophotometric analysis of *trans*-isomerization in hydrogenated fats and oils, fails to be applicable to the quantitative determination of the degree of *trans*-isomerization of oleic acid irradiated with cathode rays. However a modified method (Figure 2) was used to determine quantitatively the degree of *trans*-isomerization of the oleic acid irradiated with cathode rays.

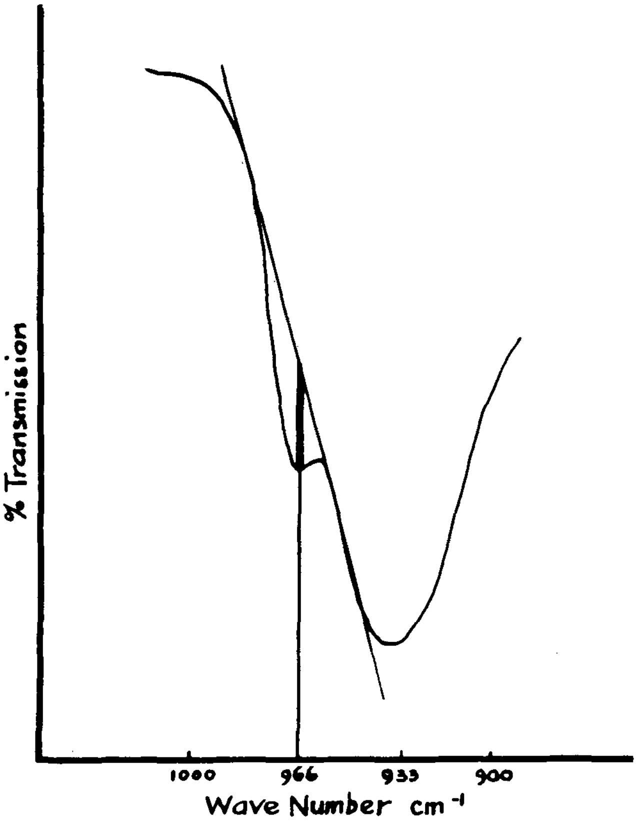

FIG. 2. Determination of the degree of *trans*-isomerization of oleic acid irradiated with cathode rays by measuring the length of the vertical bold straight line between the infrared absorption peak at 966 cm^{-1} and the slant straight line (irradiated oleic acid in CS_2, 20%W/V).

A straight line was drawn on the absorption spectrum in such a way that it coincided with the curve on the right side of the absorption maximum at 966 cm^{-1} and was tangent to the curve on the left side of the maximum. A vertical line was drawn to pass through the absorption curve at 966 cm^{-1} and to intersect the straight line. The distance between the tip of the maximum and the intersection point of the vertical line and the straight line indicated the amount of decrease in percentage transmission of infrared light because of the increase in the concentration of elaidic acid. It was measured accurately with a divider. Since on Perkin Elmer chart paper No. 021-6312 each percentage of transmission is indicated by a length of 2 mm., the equivalent value of the apparent decrease in percentage of transmission of the solution is equal to half the numerical value of the measured length in millimeters. The actual decrease in percentage of transmission was obtained by multiplying the apparent value by a factor that is acquired by dividing the numerical value of 100% transmission with the numerical value of the actual total percentage of transmission as measured between the recorded 0% line and the recorded 100% line at 966 cm^{-1}.

A standard curve was prepared from a series of carbon disulfide solutions containing known concentrations of elaidic and oleic acids by plotting the decrease in percentage transmission of each solution against the respective percentage of elaidic acid in the mixture of fatty acids of known composition (Figure 3). The total concentration of oleic and elaidic acids in each carbon disulfide solution was 20% (W/V). The intensity of the absorption peak at 966 cm^{-1} increases with the increase of the concentration of elaidic acid in the carbon disulfide solution whereas the intensity of the absorption peak at 933 cm^{-1} remains the same at each composition of elaidic acid and oleic acid in the solutions (Figure 4).

By this method a slight decrease in the concentration of the total fatty acids as well as a slight change in the intensity of the absorption spectrum does not significantly affect the quantitative determination of the amount of *trans*-isomer present in the carbon disulfide solution of irradiated oleic acid since the increase in concentration of *trans*-isomer is nearly directly proportional to the decrease in percentage transmission at 966 cm^{-1}. However the slope of the straight line which cuts the absorption curve becomes steeper as the concentration of elaidic acid in the carbon disulfide solution decreases. A large percentage of error would be expected in the results of the quantitative analyses of those samples that contained less than 5% elaidic acid.

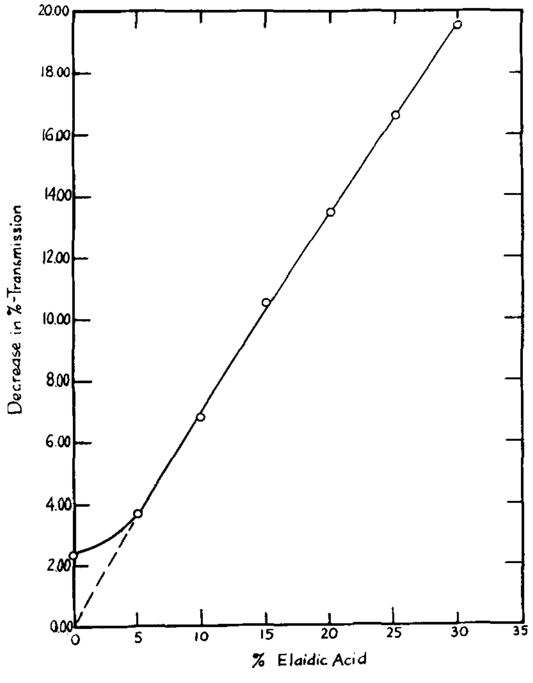

FIG. 3. Decrease in transmission with the increase in amount of elaidic acid (total fatty acids in CS_2, 20% W/V).

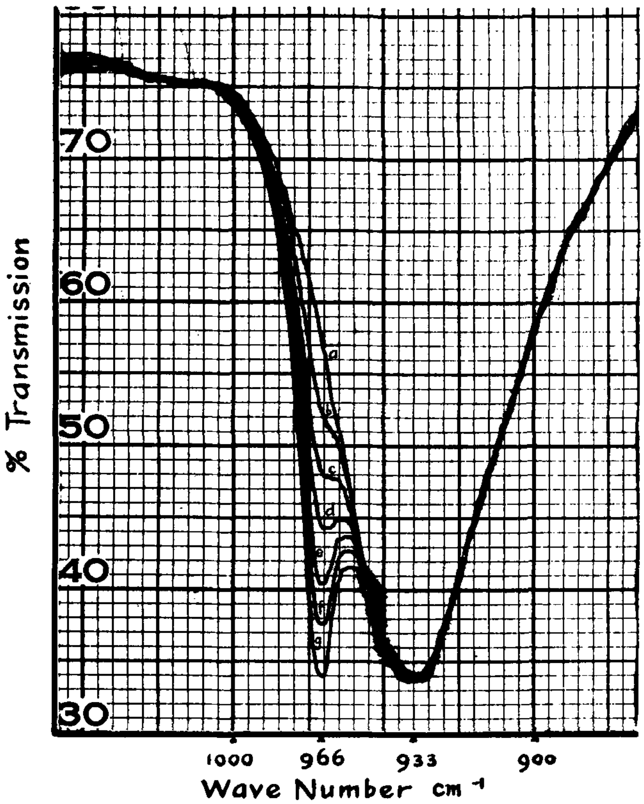

FIG. 4. Infrared spectrograms, 1,000–900 cm^{-1} of mixture of unirradiated pure oleic acid and elaidic acid of known composition. Absorption at 966 cm^{-1} increases with the content of elaidic acid in the mixture (total fatty acids in CS_2, 20% W/V). % elaidic acid in the mixtures: spectrogram a, 0; b, 5; c, 10; d, 15; e, 20; f, 25; g, 30.

Experimental and Results

The oleic acid of IV 89.2 was irradiated with 3 M.e.v. cathode rays with doses of from 15 x 10^6 to 70 x 10^6 rep[5] at dose intervals of 5 x 10^6 rep, in vacuum-sealed, 5-ml. ampoules. *Trans*-isomerization occurred in those samples that received more than 40 x 10^6 rep. The analytical data are shown in Figure 5.

Further investigation was carried out with oleic acid of IV 89.8 irradiated with 2 M.e.v. cathode rays in two ways. One ml. of the acid was pipetted into a series of 5-ml. ampoules. The ampoules were flushed with oxygen-free nitrogen and then evacuated at 0.3 micron mercury pressure and flame-sealed. Another series of 5-ml. ampoules containing the same amount of oleic acid was not sealed so that the oleic acid in the ampoules was exposed to the atmosphere. In both series of ampoules *trans*-isomerization of the acid occurred at doses above 133.8 x 10^6 rep (Figure 6).

For the study with water as the irradiation medium, potassium oleate was used. Aqueous solutions of potassium oleate of two different concentrations, 2.5% and 1%, were made immediately before irradiation. The water used in the experiments was prepared by redistilling distilled water after treatment with potassium permanganate. Seventy-five ml. of the solution were placed in a series of crystallizing dishes 10 cm. O.D. The irradiated solution was acidified with dilute HCl and then extracted with petroleum ether.

The 2.5% solution of potassium oleate was irradiated at dose levels ranging from 5 x 10^6 to 30 x 10^6 rep. A gummy irradiation product formed. This product was insoluble in petroleum ether but readily soluble in acetone; it remained floating on the aqueous layer. The extracts were washed with water to remove HCl and then dried by being dripped through anhydrous sodium sulfate. The petroleum ether was eventually removed under vacuum. The product was kept at 0.1 mm. of mercury pressure over-night. The percentage of *trans*-isomerization in the product was afterwards determined.

Because of the occurrence of compounds that were insoluble in petroleum ether, the determination of the amount of *trans*-isomerized oleic acid with reference to the total original sample was calculated indirectly by multiplying the percentage of *trans*-isomerization of the product soluble in petroleum ether with a factor obtained by dividing the weight of the irradiation product soluble in petroleum ether by the weight of the total irradiation products. The analytical data are shown in Figure 7.

The 1% aqueous solution of potassium oleate was irradiated at dose levels ranging from 1 x 10^6 to 5 x 10^6 rep. In one run the irradiated solution was kept over-night at 0°C. under a nitrogen atmosphere before it was acidified and extracted with petroleum ether. In another run the irradiated solution was immediately acidified and extracted after irradiation. There was no substantial difference between the percentage of *trans*-isomerization of the first run and the second.

Since the petroleum ether extract of the irradiated oleic acid had to be dehydrated by being passed through anhydrous sodium sulfate and because only small amounts of oleic acid were available in 1% solution, considerable losses were inevitable; and the correction factor, as used in the study of 2.5% solutions, could not be obtained.

The analytical data of the percentage of *trans*-

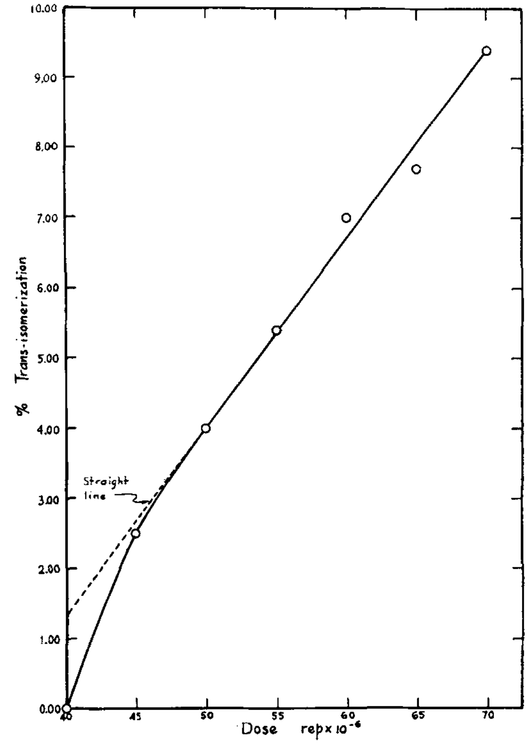

FIG. 5. Degree of *trans*-isomerization occurring in samples of oleic acid of IV 89.2 irradiated with cathode rays (3 M.e.v.) in vacuum-sealed ampoules.

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[5] Roentgen equivalent physical. It is defined as the amount of radiation of any type which imparts 93 ergs per gram of animal tissue.

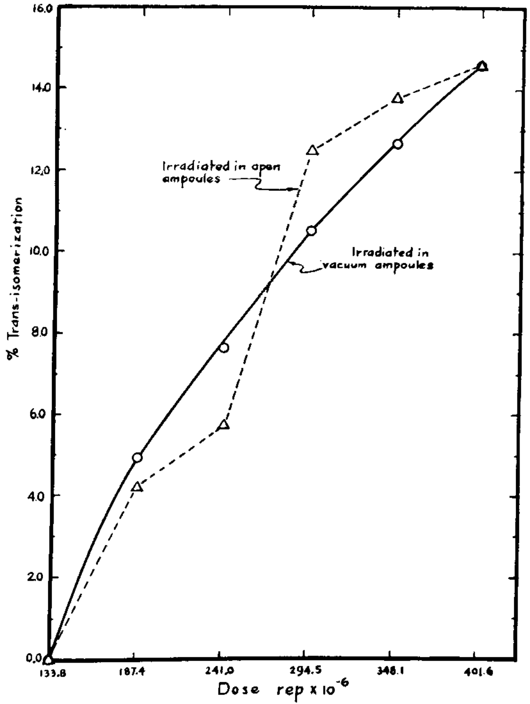

FIG. 6. Degree of *trans*-isomerization occurring in samples of oleic acid of IV 89.8 irradiated with cathode rays (2 M.e.v.) in vacuum-sealed ampoules and in open ampoules.

isomerization that occurred in the petroleum ether fraction are shown in Figure 8.

Discussion

The *trans*-isomerization of oleic acid which occurred in those samples irradiated under vacuum indicated that the *trans*-isomerization of oleic acid induced by high energy ionizing radiation is independent of oxygen. Knight *et al.* (10) found that methyl oleate would *trans*-isomerize only if oxygen were allowed to bubble through it during irradiation with ultraviolet light.

The oleic acid of IV 89.2 *trans*-isomerized to the same extent at a much lower dose-level (cathode rays) than did the oleic acid of IV 89.8. The impurity in the former might have served as a catalyst in the *trans*-isomerization.

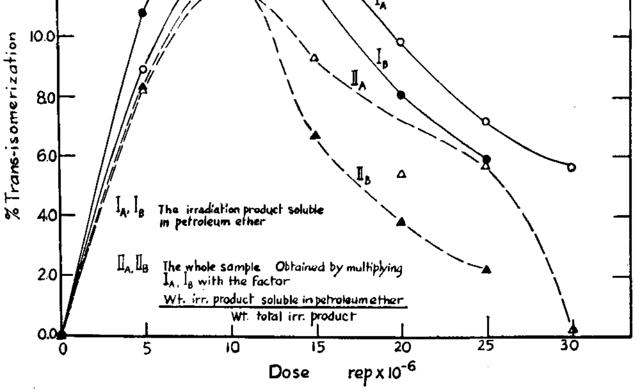

FIG. 7. Degree of *trans*-isomerization of oleic acid recovered from 2.5% aqueous solution of potassium oleate irradiated with cathode rays (3 M.e.v.).

Oleic acid remained as a clear liquid after irradiation with the exception of those samples irradiated at 401.6 x 10^6 rep, in which slight turbidity was present. The turbidity was probably caused by a polymerization product of oleic acid (6).

The irradiation product, soluble in petroleum ether, from the 2.5% potassium oleate solution was a liquid, a semi-solid, or a solid, depending on the amount of irradiation received by the solution. At higher dose levels, a gummy material, which was insoluble in petroleum ether but readily soluble in acetone, was formed. This was probably a polymerization product of oleic acid. The radiation products from the 1% potassium oleate solution were soluble in petroleum ether, but they were also liquid, semi-solid, or solid, according to dose received by the solution. This change of the physical state of oleic acid upon irradiation was not caused by the occurrence of elaidic acid, which has a melting point of 44°C., but to some chemical changes, such as oxidation, hydrogenation, and possibly polymerization, for oleic acid with 15% elaidic acid remains a liquid at room temperature.

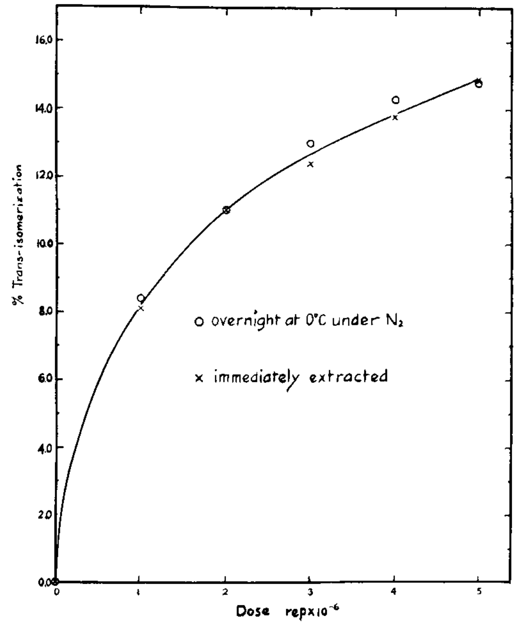

FIG. 8. Degree of *trans*-isomerization of oleic acid recovered from 1% aqueous solution of potassium oleate irradiated with cathode rays (3 M.e.v.).

In the 2.5% potassium oleate solution irradiated with from 5 x 10^6 to 30 x 10^6 rep, the maximum *trans*-isomerization occurred in those solutions irradiated at a dose level of 10 x 10^6 rep. In the irradiated 1% potassium oleate solution the yield of *trans*-isomers was found to decrease gradually with the increase of the irradiation dose. A maximum percentage of *trans*-isomerization would have been expected to occur at a dose above 5 x 10^6 rep. After a maximum yield had been reached, the *trans*-isomers would undergo some chemical changes and gradually disappear.

Although the aqueous solutions of potassium oleate were clear immediately after irradiation, they became turbid upon standing. This indicated that certain chemical changes might have occurred during this time. However the analytical data (Figure 7) showed that the percentage of *trans*-isomerization was practically the same in the irradiated solutions that were acidified and extracted after standing for a period of time. Evidently the process of *trans*-isomerization did not continue in the irradiated solutions.

Summary

The oleic acid of IV 89.2 was irradiated with cathode rays at doses of 15 x 10^6 to 70 x 10^6 rep and was found to have been *trans*-isomerized from 2.5% at 45 x 10^6 rep to 9.4% at 70 x 10^6 rep; the oleic acid of IV 89.8 irradiated at doses of 13.4 x 10^6 to 401.6 x 10^6 rep and was found to have been *trans*-isomerized to 4.9% at 187.4 x 10^6 rep and to 14.6% at 401.6%.

The *trans*-isomerization was independent of oxygen.

Aqueous solutions of potassium oleate at 1% concentration were irradiated with doses from 1 x 10^6 rep to 5 x 10^6 rep. The oleic acid recovered from the irradiated solutions was found to have been *trans*-isomerized from 8.1% at 1 x 10^6 rep to 1.9% at 5 x 10^6 rep; the oleic acid recovered from the 2.5% solutions was found to have been *trans*-isomerized to 8.3% at 5 x 10^6 rep, 11.9% at 10 x 10^6 rep, and 0.1% at 30 x 10^6 rep.

A modified "baseline" technique in infrared spectrophotometric analysis is described.

Acknowledgments

Appreciation is expressed to J. G. Trump and K. A. Wright of the Electrical Engineering Department, M.I.T. for the irradiation of samples with cathode rays from the 3 M.e.v. Van de Graaff accelerator.

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An Evaluation of the Detergency Value of a Series of Alkylbenzene Sulfonates by Ultrasonic Technique

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IN THIS STUDY ultrasonic energy has been used in the direct evaluation of the detergent characteristics of a series of highly purified sodium alkylbenzene sulfonates which have been synthesized in these laboratories. In a previous paper Sherrill and White (3) presented preliminary results on studies of the magnitude of forces binding soils to textile surfaces. In these studies an ultrasonic cone transducer was used as a means of providing mechanical action of a precisely controlled magnitude. It was demonstrated that specific energy requirements prevail for any given level of soil removal. It also was pointed out that greater precision and reduced test-time was possible through the use of this technique.

The use of synthetic detergents in this country has grown remarkably over the past 30 years. The sodium alkylbenzene sulfonates have played an important role in the development of synthetic detergents. Currently the higher alkylaryl sulfonates account for the largest tonnage of synthetic surface-active agents in this country (2). Accordingly a study of the relationships of the structure of the molecule to detergency should be of interest and value to the industry.

One extensive study in this field has been made by Kourtz (1), in which the relationship of the surface activity and number of carbon atoms in the alkyl group of certain alkylbenzene sulfonates was reported. This investigator found from surface and interfacial tension measurements that, in general, the surface activity increased with an increase in the length of the alkyl chain in the alkylbenzene sulfonate.

In this study 17 alkylbenzene sulfonates were prepared, containing six to 18 carbon atoms. Compounds containing 13, 15, and 17 carbons in the alkyl group were not synthesized. These syntheses made it possible to compare straight-chain, branch-chain, and cyclic compounds as regards detergency efficiency.

Experimental Procedure

Preparation of Alkylbenzene Sulfonates. The 17 alkylbenzene sulfonates synthesized included four compounds containing six carbon atoms in the alkyl radical, one with seven carbons, two with eight carbons, one with nine carbons, two with 10 carbons, one with 11 carbons. two with 12 carbons, two with 14 carbons, one with 16, and one with 18 carbons in the alkyl radical.

In general, the preparation of the alkylbenzene sulfonates included the following series of conversions: acid to acid chloride, to alkylaryl ketone, to hydrazone of the ketone, to alkylbenzene, to sodium alkylbenzene sulfonate.

A total of 10 of the 17 sodium alkylbenzene sulfonates had straight-chain alkyl groups. The alkylbenzenes were not synthesized directly by the Friedel-Crafts reaction since the reaction product would undoubtedly have contained a mixture of straight- and branch-chain alkyl groups which are not readily sep-

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