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INTRODUCTION

This book describes practical syntheses and applications of those fatty acids that are used by the rubber and synthetic resin industries, and to some lesser extent by manufacturers of paints, printing inks, adhesives, and allied products.

All patents with edible applications have been excluded here, but will be used in a forthcoming new edition of the Noyes Data book on edible oils and fats.

Since the term "fatty acids" means many things to many people, we have tried to adhere to the definitions set forth by Klare S. Markley in his monumental five volume standard work entitled "Fatty Acids, Their Chemistry and Physical Properties" and published during the last decade by Wiley and Sons.

Naturally occurring fatty acids are higher straight chain unsubstituted carboxylic acids containing an even number of carbon atoms. They may be saturated or unsaturated, i.e., they may contain double bonds. Since synthetic modifications are countless, the definition is broadened to include odd- and even-numbered compounds containing six or more carbon atoms in the carbon chain and resembling the natural fatty acids. They may have various substituents along the chain; they may be branched and even contain certain additional short side chains. They may be oxidized to yield dicarboxylic acids and/or aldehyde acids.

Short chain, water-soluble acids, such as maleic acid, do not fall into this definition. Such acids will be covered in separate monographs to be published shortly by Noyes Data Corporation.

PREPARATION BY OXO SYNTHESIS

It has been known for some time that fatty acids can be produced by high pressure synthesis from olefins, carbon monoxide and water in the presence of a variety of catalysts. The patents in this chapter are grouped according to the type of catalyst used.

SULFURIC ACID CATALYST

High Sulfuric Acid Concentration

In a process described by G.A. Kurhajec, D.L. Johnston and K.E. Furman; U.S. Patent 3,047,622; July 31, 1962; assigned to Shell Oil Company an olefinic compound is combined with relatively dilute polybasic inorganic acid, thereby obtaining an olefinic compound-dilute acid admixture, reacting the olefinic compound-dilute acid admixture, while in liquid phase, with carbon monoxide, in the presence of sufficient concentrated sulfuric acid to result in a reaction mixture having a sulfuric acid strength above about 90%, in the absence of any substantial amount of water addition, at a temperature of from -10° to 100°C. and a pressure of from about atmospheric to 1,500 psig.

Thereafter water is added to the resulting reaction mixture in the substantial absence of carbon monoxide addition, and organic acid is separated from the resulting reaction mixture after the water addition. Olefinic compounds employed as charge to the process comprise organic compounds containing an olefinic unsaturation, such as, for example, the monoolefinic hydrocarbons having at least 3 carbon atoms to the molecule. Examples of suitable olefins comprise propylene, butene-1, butene-2, isobutene, the pentenes, hexenes,

etc., and their homologues; olefinic polymers, such as propylene tetramer; the cyclic olefins, such as cyclopentene, cyclohexene, 4-vinylcyclohexene-1, and the like; etc. Olefinic compounds having a carbinol group in addition to olefinic unsaturation, as well as olefinic compounds having substituents, such as halogen, which do not adversely affect the course of the reaction, for example, 4-methyl-4-pentene-2-ol, ricinoleic acid, soya fat acid, methallyl chloride, and the like, are comprised in the suitable unsaturated olefinic compounds which may be reacted in accordance with the process. The olefinic charge to the process may comprise a single one, or a plurality of two or more, of the suitable olefinic compounds; hydrocarbon fractions comprising them; and the like.

Preferred olefinic charge material comprises the monoolefins having up to 20 carbon atoms to the molecule. A particularly preferred charge comprises the tertiary base olefins (that is, those yielding a tertiary alcohol upon hydrolysis). The olefinic charge to the process need not necessarily be in a state of high purity. Impurities generally encountered in the olefinic materials as commercially available do not adversely affect the efficiency of the process to any substantial extent.

Essential to the process is the initial combining of the olefinic charge to the process with a relatively dilute polybasic acid, such as, for example, aqueous sulfuric acid, or aqueous phosphoric acid, etc., aqueous sulfuric acid being preferred. The relatively dilute, or weak, acid thus initially combined with the olefinic charge is preferably of an acid strength not substantially in excess of about 80%. Preferred is the use of aqueous sulfuric acid containing from about 60 to 75%, and still more preferably from about 65 to 70%, by weight of sulfuric acid.

The specific strength of the dilute acid preferably employed will depend to some extent upon the specific olefinic material charged and specific operating conditions employed. Admixture of the relatively dilute acid with the olefinic charge is generally effected at a temperature at which no substantial polymerization of the olefins is encountered. Thus, the dilute acid may be combined with olefinic charge at a temperature in the range of from about 0° to 40°C. The specific temperature employed will depend upon the specific olefinic charge and degree of acid strength used. Higher temperatures may however be employed.

Thus, at times it is desirable to produce reaction mixtures comprising higher boiling organic acids, corresponding approximately to the polymeric compounds of the olefinic charge. In such case initial admixing of dilute acid with olefinic charge may be carried out at a higher temperature, for example, as high as about 100°C., to obtain polymerization of at least a substantial part of the olefinic compounds charged while in contact with the

dilute acid during the initial phase of the process. The resulting admixture obtained by combining dilute acid and olefinic charge in the initial phase of the process is thereupon reacted with carbon monoxide in the presence of sufficient added concentrated sulfuric acid to obtain a reaction mixture having an acid strength of at least 90%. The dilute acid-olefinic charge mixture thus initially formed may comprise at least a part or all of the olefinic constituents in the form of suspension, solution, or reaction product with the acid.

The method of combining the preformed admixture of dilute acid and olefinic charge with the concentrated sulfuric acid may vary. Thus, the admixture of dilute acid and olefinic charge may be introduced into a large body of concentrated sulfuric acid. In such case, the body of concentrated sulfuric acid is preferably under carbon monoxide pressure. In continuous operation it is generally preferred to effect the addition of a continuous stream of the preformed dilute acid-olefinic compound admixture to a body of concentrated sulfuric acid in a reaction zone maintained under a substantial carbon monoxide pressure.

Contact of the fortified acid-olefinic compound admixture with carbon monoxide is carried out at relatively mild conditions. Temperatures of from -10° to 100°C., and preferably in the range of 20° to 60°C. are employed. Carbon monoxide pressures ranging from atmospheric to 1,500 psig and higher may be used. However, pressures higher than 700 psig need generally not be used. A constant carbon monoxide pressure in the range of from 100 to 650 psig is generally preferred. A particularly suitable pressure range is that from 450 to 550 psig. Conditions are controlled so that at least the greater part of the olefinic charge is in the liquid phase throughout the course of the reaction.

Essential to the process is the avoidance of introduction of any substantial amount of water into the reaction zone from an outside source during the course of the reaction with carbon monoxide. Upon completion of the reaction the reaction mixture is brought to substantially atmospheric pressure, and contacted with water. The water so added may be in the form of ice, liquid water or steam. Organic acid is thereupon separated from the reaction mixture resulting from the reaction with the water, by conventional means comprising one or more such steps as, for example, decantation, distillation, extractive distillation, adsorption, solvent extraction, etc.

Example 1: Isobutylene is dissolved in aqueous 65% H_2SO_4 at 30°C. and a pressure of 150 psig. The resulting solution contains a ratio of isobutylene to 65% H_2SO_4 of 1:2 by weight. The solution of isobutylene in 65% H_2SO_4 so obtained is then added to concentrated (92%) H_2SO_4 under a carbon monoxide pressure of 500 psig with vigorous stirring at 20°C. The mol ratio of

isobutylene to total sulfuric acid in the resulting fortified mixture is 3.3:10. The resulting fortified solution is subjected to a constant carbon monoxide pressure of 500 psig at a temperature of 20°C. until no further absorption of carbon monoxide is evident. Pressuring with carbon monoxide is then terminated, and the pressure reduced to substantially atmospheric by venting.

Water is added to the resulting reaction mixture in an amount equal to 400% by volume at a temperature of 0°C. while at atmospheric pressure. Reaction is rapid with the formation of two separate liquid layers; an upper organic layer and a lower aqueous sulfuric acid layer. Analysis of the products thus obtained indicates that substantially all butylene has reacted with the production of 0.9 mol organic acid product per mol isobutylene charged with a yield of trimethylacetic acid of 83%; the rest of the organic acid obtained being polymeric in character.

Example 2: For the purpose of comparison isobutylene is added directly to concentrated sulfuric acid (92%) under a carbon monoxide pressure of 500 psig. The mol ratio of isobutylene to sulfuric acid in the resulting admixture is 3.3:10. The resulting solution is maintained at a constant carbon monoxide pressure of 500 psig at a temperature of 20°C. until no further absorption of carbon monoxide is apparent. Pressuring with carbon monoxide is then stopped and the pressure brought to atmospheric by venting. Water is then added to the resulting reaction mixture in an amount equal to 400% by volume at 0°C.

Reaction is rapid with the formation of two separate liquid layers; an upper organic layer and a lower aqueous sulfuric acid layer. Analysis of the products thus obtained indicates that substantially all isobutylene has undergone reaction with the formation of 0.59 mol of organic acid product per mol of isobutylene charged with a yield of 47% of trimethylacetic acid; the rest of the organic acid obtained being polymeric in character.

Spent Alkylation Acid Containing 80 to 90% Sulfuric Acid

C.G. McAlister, R.J. Lee and H.M. Knight; U.S. Patent 3,053,869; September 11, 1962; assigned to Standard Oil Company describe a process for the preparation of fatty acids from carbon monoxide and an olefin of 3 to 20 carbon atoms under mild reaction conditions; i.e., temperatures not exceeding 100°C. and pressures no higher than 100 atmospheres, using as the catalyst spent alkylation acid. Spent alkylation acid is essentially a petroleum refinery waste stream whose principal use is a feed to a system for recovery of sulfuric acid values therefrom by a thermal decomposition process such as heating in admixture with fine coke particles to liberate SO_2 which is dried and charged to a catalytic sulfuric acid process.

Spent alkylation acid is obtained as the result of alkylating olefins with isoparaffins in the presence of concentrated sulfuric acid of no less than 89% H_2SO_4. Such a process is well-known to those skilled in the art. The acid withdrawn from such an alkylation process may have an H_2SO_4 content of from 80 to 95% total titratable acidity as H_2SO_4, more usually it contains not more than about 90% H_2SO_4 on the same basis, and is unsuitable for further use as an alkylation catalyst. Hence, it is known as spent alkylation acid. Although spent alkylation acid may contain 80 to 90% H_2SO_4 on the basis of total titratable acidity, it is recognized by those skilled in the art as being quite different from 80 to 90% fresh sulfuric acid, for such a fresh sulfuric acid contains water as the only other principal ingredient in an amount of from 10 to 20%.

Spent alkylation acid on the other hand, while containing 80 to 90% H_2SO_4 on the above basis, contains only from 1 to 5% water with the remainder being "red oils" which are complex mixtures of polyolefins, organic sulfates and sulfonates. The free H_2SO_4 content of spent alkylation acid as determined by the aniline method will be 5 to 7% below the total titratable acidity concentration. The process is applicable for the preparation of carboxylic acids from such olefins as simple alkenes; i.e., straight and branched chain, terminal and internal unsaturated alkenes, cyclic olefins, diolefins, and unsaturated difunctional compounds such as unsaturated carboxylic acids from which dicarboxylic acids are prepared among others.

The olefin reactant employed may be a single normal olefin, or such branched chain olefins as the liquid polymers of propylene containing 5 to 20 carbon atoms and copolymers of propylene and butylene containing 5 to 20 carbon atoms a mixture of the foregoing olefins, or mixtures of olefins with saturated hydrocarbons or other inert solvents such as in a catalytic gasoline containing 50% olefins. In general, olefins containing 3 to 20 carbon atoms and especially branched chain olefins of 5 to 20 carbon atoms are preferred.

More specifically, the process comprises adding the olefin to stirred, spent alkylation acid at reaction temperature pressurized with CO. The mol ratio of spent alkylation acid employed is at least 1 mol H_2SO_4 per mol of olefin. The reaction mixture is maintained at a temperature in the range of -10° to 100°C. The reaction pressure employed is 10 to 100 atmospheres of carbon monoxide. The mixture resulting is held for 5 to 30 minutes after all the olefin has been added. The resulting mixture is depressurized, and water is added until the titratable acidity of the aqueous layer is between 65 to 75% and preferably 70 to 72% by weight, calculated as H_2SO_4. The temperature during dilution is controlled to not exceed about 60°C. The organic phase is separated from the aqueous phase and the fatty acid is recovered from the organic phase. Recovery of the fatty acid product may be

accomplished by extraction, distillation, converting the fatty acid to a soap and extracting the soap with water or other solvent and springing the acid from its soap, and other methods understood by those skilled in the art. While mol ratios of up to 100 mols of H_2SO_4 per mol of olefin can be employed, little advantage is gained by employing more than 10 mols per mol. Satisfactory yields of fatty acids can be obtained for commercial operation by employing less than 10 mols H_2SO_4 per mol of olefin, and preferably the mol ratio is in the range of 1.5 to 5 mols per mol of olefin.

The reaction temperature need not exceed 100°C., so temperatures in the range of from -10° to 100°C. will be useful with temperatures in the range of 20° to 45°C. being preferred. As hereinbefore stated, the CO pressure need not exceed 100 atmospheres and pressures in the range of 10 to 50 atmospheres are advantageously employed. To illustrate the mode of operating according to the process, the following example is given. In this example a 316 stainless steel autoclave equipped with an internal cooling coil, baffles, an efficient stirrer and a dip-tube for introducing olefin below the spent alkylation acid surface is employed. Olefin from a weighed reservoir is pumped into the autoclave.

Example 1: Spent alkylation acid containing 83.1 weight percent free H_2SO_4, 4% water, 5% red oil, and having a total titratable acidity of 89.5 weight percent and a specific gravity of 1.7170 at 20°C. is charged to the autoclave in an amount (2,954 g.) to provide 25 gram mols H_2SO_4. The autoclave is closed. The spent alkylation acid is stirred and maintained at a temperature of 20° to 21°C. and pressured with carbon monoxide to 400 psig (about 27 to 28 atmospheres). Pentene-1 is pumped into the autoclave over a 6-hour period until 9.1 mols (635 g.) are added, which is equivalent to a mol ratio of "free H_2SO_4"/pentene-1 of 2.75.

The reaction temperature is maintained in the range of 20° to 21°C. during the olefin addition while the reaction mixture is stirred. Stirring is continued for 15 minutes after all the olefin is added. The recovered reaction mixture weighed 3,589 g. which indicates that approximately 130 g. of CO (plus the amount of handling losses) is taken up by the olefin. The stirred depressurized reaction mixture is cooled to 10°C. and there is added 2,700 grams of water to provide an aqueous phase of about 45% titratable acidity. The mixture is maintained at 30°C. during the addition of water. Heptane in an amount equal to about 1/2 the volume of the olefin charged is added and thoroughly mixed with the diluted reaction mixture.

Stirring is stopped. Two phases form. The lower aqueous phase is withdrawn. The heptane phase, containing the organic acids, is washed with 5 volume percent of water and then 3 times with 5 volume percent of a 10% sodium bicarbonate solution in order to remove the sulfuric acid, sulfur

dioxide, and the like which are present in this phase. The organic acids in the heptane phase are taken up in 3,220 ml. of aqueous sodium hydroxide (7 weight percent NaOH concentration). The sodium hydroxide solution is then extracted several times with 200 ml. quantities of benzene to remove nonacidic organic polymers. The sodium soap solution is next acidified with hydrochloric acid to spring the free aliphatic carboxylic acids. The aqueous phase is extracted with a small amount (5%) of benzene, and the benzene washings are combined with the aliphatic acid phase.

Benzene and a water azeotrope are distilled off. The remaining aliphatic acids weighed 598 g. These are fractionated at atmospheric pressure through a 12" Vigreux column yielding 571 g. of C_6 acid boiling between 180° to 200°C. (largely 185° to 190°C.), and 27 g. of higher boiling acids. The C_6 acid product contained 85 to 90% of 2,2-dimethylbutyric acid as determined by gas chromatographic analysis. The yield of total C_6 acid is 54.3 mol percent or 90.0 weight percent, based on the pentene-1 charged. The yeild of polymer, after correction for the "red oils" present in the spent alkylation acid, amounted to 8.5 weight percent based on the olefin charged.

A similar run was made at a 2.32 mol ratio of "free H_2SO_4"/pentene-1. In this run, 2,490 g. of spent alkylation acid (83 weight percent free H_2SO_4) was charged to the autoclave, and 634 g. of pentene-1 was added over a 6-hour period. A carbon monoxide pressure of 400 psi and a temperature of 20°C. were maintained in identical fashion to the previous run. The total aliphatic acid product amounted to 503 g., of which 473 g. was C_6 acid. The yield of C_6 acid was 45.0 mol percent and the yield of polymer (corrected) was 16 weight percent based on pentene-1 charged.

In a third run in this series, the mol ratio of "free H_2SO_4"/pentene-1 was reduced to 1.85. In this run, 1,985 g. of spent alkylation acid was charged to the autoclave, and 638 g. of pentene-1 was added over a 6-hour period while maintaining 400 psi carbon monoxide pressure in the autoclave. The product was worked up in the same manner as the 2 previous runs, yielding 370 g. of aliphatic acids of which 359 g. was C_6 acid. The yield of C_6 acid was 34.0 mol percent and the yield of polymer (corrected) was 23.5 weight percent based on the olefin charged. Results are summarized below.

Production of Aliphatic Acids from Pentene-1 and CO Using Spent Alkylation Acid as the Condensing Agent

Temperature: 20°C. CO pressure: 400 psi

Mol Ratio "Free H_2SO_4":Olefin	Total Yield of Aliphatic Acids*	Yield of C_6 Acid*	Mol % Yield of C_6 Acid	Weight % Yield of Polymer**
2.75	94.3	90.0	54.3	8.5
2.32	79.4	74.8	45.0	16.0
1.85	58.0	56.3	34.0	23.5

*Weight percent based on pentene-1 charge

**Polymer yield corrected for the polymer (red oil) present in the spent alkylation acid used in the runs.

Use of Isoolefins

J.E. Anderson and N.W. Franke; U.S. Patent 3,167,585; January 26, 1965; assigned to Gulf Research & Development Company have found that optimum amounts of organic acids are formed in the process wherein an olefin which gives tertiary carbonium ions upon proton addition is reacted with carbon monoxide and water when the olefin and carbon monoxide are reacted in the liquid phase in the presence of sulfuric acid having a concentration of about 82 to 88% and the reaction product so produced is thereafter taken up with water. Olefins which give tertiary carbonium ions upon proton addition and which can be employed in this process can be defined by the following structural formula:

$$R_1-\overset{R_2}{\underset{|}{C}}=\overset{R_3}{\underset{|}{C}}-R_4$$

wherein R_1 and R_2, the same or different, can be alkyl radicals having from 1 to 20 carbon atoms, preferably from 1 to 15 carbon atoms, such as methyl, ethyl, propyl, n-butyl, isobutyl, tert-butyl, pentyl, neopentyl, methylbutyl, decyl, eicosyl, ethylmethylpentadecyl, etc.; and R_3 and R_4 can be hydrogen or similar to R_1 or R_2 above. Examples of olefins which can thus be employed are isobutylene, 2-methylbutene-1, 2-methylbutene-2, 2,4-dimethylpentene-2, 2,4,4-trimethylpentene-1, 2,2,4-trimethylpentene-2, 2-methylpentadecene-2, etc.

The reaction requires approximately equal molar amounts of each of the reactants, carbon monoxide, water and olefin, and sulfuric acid. Desirably, it is preferred that the molar ratio of sulfuric acid to olefin be at least 3 to 1. Using the preferred ratios we obtain less polymerization of olefin under the reaction conditions. The sequence in which the reactants and catalyst are brought together is of utmost importance. Sulfuric acid and carbon monoxide, separately or together, are introduced into the reaction zone. Only after the catalyst and reaction zone have been saturated with carbon monoxide is the addition of the defined olefin made. This is done primarily to reduce or inhibit olefin polymerization in the presence of sulfuric acid.

Water is then added to the reaction product obtained from the reaction of carbon monoxide and sulfuric acid with olefin. The desired organic acid is thereafter recovered from the final reaction product. It has been found that in order to obtain optimum yields of organic acids in the above process when the olefin employed is one which will give tertiary carbonium ions upon proton addition it is absolutely imperative that the concentration of the sulfuric acid be between about 82 to 88%, preferably between about 83 to 86%. Carbon monoxide is added to the reaction zone at the beginning of the reaction and by periodic addition or any other suitable means as

required during the course of the reaction to maintain the desired concentration of the same as well as the desired reaction pressure. The reaction of carbon monoxide and sulfuric acid with olefin is extremely fast. Thus, it was found that when 1.5 mols of olefin were added at the rate of 1 ml. per minute to an autoclave containing 4.5 mols of H_2SO_4 having a concentration of 85% under a carbon monoxide pressure of 1,000 pounds per square inch gauge, the reaction was completed in 4 hours without undue polymerization. Under reaction conditions employed, care must be exercised to have only sufficient olefin present to facilitate the desired reaction and not such an excess that will promote the polymerization thereof. The amount of olefin introduced therein must, therefore, correspond approximately to the amount of olefin reacted.

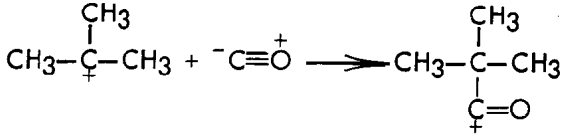
The temperature and pressure required for the reaction of carbon monoxide and sulfuric acic with olefin are moderate. Thus the temperature can be about -20° to 70°C., preferably about 0° to 50°C. and the pressure in excess of about 100, preferably about 800 to 2,000 pounds per square inch gauge. At least one mol of water must be added to the reaction product for each mol of olefin which has reacted in the desired reaction. The temperature employed in this phase of the reaction can be about -10° to 60°C. and the pressure about 1/2 to 10 atmospheres..

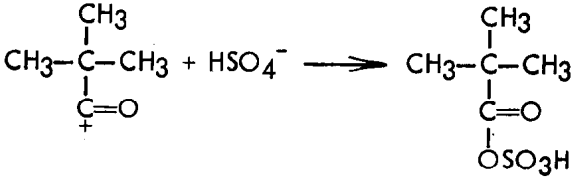
The reaction product obtained upon the addition of water contains the desired organic acid along with some minor amounts of alcohol, esters and polyolefins. If the organic acid has 4 to 6 carbon atoms it will be completely soluble in the sulfuric acid associated therewith. One having 7 to 10 carbon atoms will be extremely soluble in the sulfuric acid. If the organic acid has from 11 to 15 carbon atoms it will be slightly soluble in the sulfuric acid, while one having 16 or more carbon atoms will be insoluble therein.

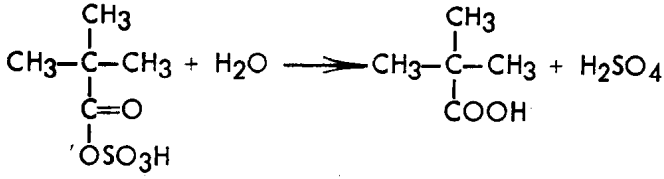
Thus, the separation of the desired organic acid from the sulfuric acid and other constituents associated therewith will depend upon its solubility in the sulfuric acid. With an organic acid having 4 to 6 carbon atoms, the mixture is diluted further with water. The solubility of the organic acid in dilute sulfuric acid being small, ordinary decantation is satisfactory. Organic acids having from 7 to 10 carbon atoms can be extracted with a saturated hydrocarbon such as hexanes, pure or mixed pentanes, heptanes, etc.

The organic acid is then separated from the saturated hydrocarbon by distillation. Since organic acids having 11 or more carbon atoms are slightly soluble or insoluble in sulfuric acid, ordinary separation such as decantation is satisfactory. The sulfuric acid can be recovered and reused. The mechanism of the reaction is believed to be as follows, using isobutylene as the representative olefin.

(1) 

(2) 

(3) 

(4) 

The process is illustrated using sulfuric acid of various concentrations and diisobutylene feed (about 80% by weight of which was 2,4,4-trimethyl pentene-1 and 20% by weight 2,4,4-trimethyl pentene-2).

Example 1: In each run 4 1/2 mols of the sulfuric acid was placed in a container and sufficient carbon monoxide (about 100% carbon monoxide) was introduced therein to saturate the sulfuric acid, obtain a carbon monoxide atmosphere and a pressure of 1,000 pounds per square inch gauge. Periodically during the reaction carbon monoxide was introduced therein to maintain a constant pressure of 1,000 pounds per square inch gauge. In each run after the desired pressure was obtained the olefin was introduced therein at the rate of 1 ml. per minute until 1.5 mols of olefin had been introduced. The temperature during the reaction was maintained at 20°C.

When the reaction was complete the container was depressured and drained. Sufficient water was then added to the container to dilute the acid to a concentration of 75%. This resulted in an almost complete separation of organic product from the sulfuric acid. The sulfuric acid layer, after decantation, was extracted with 500 ml. of n-hexane to recover contained organic acids. The organic product was stirred into 600 g. of a 10% by weight of sodium hydroxide solution, and this basic mixture was shaken in a separatory funnel with the aforementioned hexane extract to recover any organic acid

in the extract. The organic acids are more soluble in a basic solution and, consequently, were removed from the n-hexane phase. The basic layer containing the organic acids was separated from the n-hexane layer by decantation. Then the basic layer was placed into a vessel provided with means for cooling. Sufficient amount of hydrochloric acid (about 20% by weight hydrochloric acid) was added with cooling until the pH of the solution was about 2 and the organic acid layered out from the basic solution.

To improve this separation, the entire organic layer was placed into another separatory funnel and 250 ml. of n-hexane was added. In this acidic medium and with proper shaking, the organic acid dissolved into the n-hexane layer. About 300 ml. of water was added to wash out any traces of the mineral acid (hydrochloric acid). The hexane layer was then recovered by decantation. It was passed over Drierite (anhydrous calcium sulfate) to remove any absorbed water and distilled at atmospheric pressure to recover the n-hexane which could be reused. The remaining bottom from this distillation was vacuum distilled at 10 mm. of mercury to recover the carboxylic acid.

Run No.	Sulfuric Acid Concentration % by Wt.	Weight of CO Absorbed, grams	Isononanoic Acid Recovered % by Wt.
1	78.2	14.5	49
2	80.0	24.9	75
3	82.8	34.3	92
4	85.0	38.7	96
5	87.0	38.4	97
6	88.7	36.2	93
7	90.0	38.7	93
8	96.9	26.9	40

Use of Long Chain Olefin

E.T. Roe and D. Swern; U.S. Patent 3,170,939; February 23, 1965; assigned to the U.S. Secretary of Agriculture describe the carboxylation of long carbon chain olefinic compounds with carbon monoxide at atmosphere pressure. Direct carboxylation of long chain olefinic compounds with carbon monoxide can be achieved at atmospheric pressure by employing a narrow range of operating conditions in which the concentration of the sulfuric acid and also the molar ratio of sulfuric acid to the long chain olefinic compound must be regulated.

According to the process carbon monoxide at atmospheric pressure is (a) dispersed in aqueous sulfuric acid having a concentration in the range of about

93 to 98% H_2SO_4, (b) the olefinic compound is combined with this sulfuric acid at about 10° to 20°C. in such proportions that the resulting mixture contains at least about 3 mols water to each mol of olefinic compound, and (c) during the mixing of olefinic compound and sulfuric acid additional carbon monoxide is dispersed in the mixture. The entire operation is conducted at substantially atmospheric pressure, and the new carboxylic acid derivative is recovered from the sulfuric acid by dilution with water and solvent extraction or mechanical separation.

The product is typically recovered from the reaction mixture by pouring the sulfuric acid solution into a mixture of ice and water, followed by extraction of the product with a suitable solvent such as ether. Alternatively, procedures for extracting the product directly from the reaction mixture may be employed. A critical variable in the high yield atmospheric carboxylation of the less reactive, long carbon chain nonterminally unsaturated compounds is the concentration and quality of water. The importance of water is quite evident as shown in the table in which the results of the carboxylation of oleic acid are tabulated. In all of these examples the amount of water does not change during carboxylation, since the carbon monoxide is generated externally. The following equation summarizes the chemistry involved:

$$CH_3-(CH_2)_7-CH=CH-(CH_2)_7-CO_2H + CO + H_2O \longrightarrow$$

$$CH_3-(CH_2)_x-\underset{\displaystyle COOH}{\underset{|}{CH}}-(CH_2)_{15-x}-COOH$$

(wherein x may be 6 to 9)

Commercial oleic acid was purified by crystallization at low temperature followed by fractional distillation to give the oleic acid employed as the starting material in these examples. The process is illustrated with particular reference to Example 6 in the table. Carbon monoxide was passed through 80.4 g. (0.795 mol) of 97.2% sulfuric acid contained in a 500 ml. 3-necked flask, vented to the atmosphere, using a gas dispersion tube with a coarse fritted cylinder. With stirring, 7.1 g. (0.025 mol) of oleic acid was added dropwise in 16 minutes to the sulfuric acid solution which was saturated with carbon monoxide. Carbon monoxide was allowed to pass through the stirred mixture for a total of 2 hours, while the temperature was maintained between 9° and 13°C. with external cooling.

At the end of this time the mixture was poured into approximately 300 ml. of a mixture of ice and water. The product was extracted with ether and washed free of sulfuric acid. The ether solution was dried over anhydrous sodium sulfate, filtered, and the ether was then evaporated, yielding