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UREA ADDUCTS OF THE ESTERS OF STEARIC ACID

A Thesis
Presented to
The Faculty of the Department of Chemistry
College of the Pacific

In Partial Fulfillment
of the Requirements for the Degree
Master of Arts

by
Paul Elliott Greene
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TABLE OF CONTENTS

LIST OF TABLES

FOREWORD

Urea forms crystalline complexes with n-alkanes and their linear derivatives but not with most branched and cyclic hydrocarbons and their derivatives. The compounds are stable enough to be used in separating these types of aliphatic compounds from their branched and cyclic analogs. Linear esters derived from normal saturated acids give adducts as expected. Urea complexation was found to be of great importance in the purification and separation of unsaturated esters of high moleculor weight.

The object of the present research was to investigate the compositions of urea adducts of various long-chain esters, approaching the class of waxes, to test various methods of determining their compositions, and to determine the suitability of the adduct method for purifying such esters.

UREA AND UREA COMPLEXES

Urea, the diamide of carbonic acid, is a colorless, crystalline compound, m.p. 132° C., which was first isolated from human urine in 1773 by H. M. Roulle. Wohler obtained urea in 1828 by heating the isomeric ammonium cyanate. This was one of the earliest preparations of an organic compound from an inorganic source.

The properties of urea, as is often the case with low molecular weight compounds, differ in some respects from those of the higher molecular weight analogs. While other amides are either neutral or weakly acidic, urea is somewhat basic. The single carbonyl group is not able to suppress the basic properties of the two amino groups completely. For this reason, urea will form salts with various acids such as nitric acid and oxalic acid.

Since early times urea has been known to form complexes with certain oxides and salts. The most common complex-forming oxides and salts are those of mercury and silver. Mercuric oxide is known to form three distinct molecular complexes: $CO(NH_2)_2\text{-}HgO$; $CO(NH_2)_2\text{-}2HgO$; and $CO(NH_2)_2 3HgO$; while silver oxide has been found to form only one complex, $CO(NH_2)_2\text{-}3AgO$. Many salts have been found to form these coordination complexes. The most important of these are, as a rule, salts of chromium, silver, and most of the alkaline earths. Silver nitrate, calcium nitrate, and chromium chloride react with aqueous solutions of urea to produce crystalline complexes having the following formulae: $CO(NH_2)_2 \cdot AgNO_3$, $[CO(NH_2)_2]_6 \cdot CrCl_3 \cdot 3H_2O$, and $[CO(NH_2)]_4 \cdot Ca(NO_3)_2$ respectively.

This property has been used in many cases to alter the physical or chemical characteristics of the complexed compounds. If calcium nitrate is complexed with urea, the complex formed is no longer deliquescent and can be used very effectively as a fertilizer (C. Bosch, 1921).

The amino groups seem to play the greatest role in urea's inorganic complexes (Stoltzenberg, 1916). This can be shown from the fact that alkylated or acetylated ureas have very little ability to form such compounds. Urea in an aqueous saline solution reacts with hydrogen peroxide to form $CO(NH_2)_2 \cdot NaCl \cdot \frac{1}{2}H_2O_2$, but parabanic acid and allantoin do not form hydrogen peroxide addition compounds.

Urea has the interesting property of not only forming complex compounds with inorganic materials but also with straight chain organic compounds. Urea-organic complexes were first described in a German patent application by Bengen in 1940. This early work underwent further development at the Oppau Laboratory of the former I. G. Farbenindustrie A. G.. Attention was called to urea complexes or adducts by recent publications (Bengen and Schlenk, 1949)

(Zimmerschied, 1949) in Germany as well as in this country. These authors have confirmed the essential features of Bengen's discovery and have extended his observations in a number of respects.

Bengen claimed that a wide variety of linear compounds with six or more carbons formed adducts with urea. He believed that a small amount of urea solvent such as water, or a low molecular weight alcohol, acted as a catalyst or activator for the reaction. Bengen also found that all of the adducts could be decomposed into their constituents by either heating or treating with large amounts of the urea solvent.

Many materials were investigated (Zimmerschied, 1949) (Schiessler, 1952) to determine the range of linear compounds that form adducts. From these investigations it has been found that only linear hydrocarbons, saturated or unsaturated, formed urea complexes. Typical hydrocarbons of the isoparaffin, cycloalkane, and aromatic classes gave very little evidence of adduct formation. In most of these cases a qualitative precipitation method was used as evidence for adduct formation. This method consisted of adding a few drops of the hydrocarbon to a saturated solution of urea in methanol. If the formation of a voluminous precipitate was observed, a complex was considered to have been formed.

Zimmerschied extended the work with n-alkanes by a systematic investigation of the effects upon the yield of adduct with time, temperature, and concentrations. This investigation showed that the yield of adduct increased appreciably with time until the equilibrium yield was obtained. The lowest yields of adduct were obtained at temperatures much above 25° C. due to the high temperature instability of the adducts. The yield of complex was increased considerably if the concentrations of either the urea or the reactant in the activator was increased. The upper limit of yield was limited by the solubilitics of the urea and the hydrocarbon in the activator at 25° C. Under comparable conditions, Bengen (1940) and Zimmerschied (1949) observed that higher molecular weight n-alkanes gave greater yields of adduct than the lower members of the homologous series. This suggests increased stability with chain length. These results indicated clearly that urea adducts are easily dissociated molecular compounds.

Adducts of Hydrocarbon Derivatives: Many derivatives of linear or occasionally non-linear hydrocarbons are known to form crystalline adducts of urea. Among these are linear alkenes, alcohols, amides, amines, nitriles, halides, esters, ethers, and ketones (Bengen, 1949). Neither a terminal double bond nor a terminal monocyclic group on a long chain prevents adduction (Schiessler, 1952). For example 1-phenyl eicosane and 1 cyclohexyl eicosane both form crystalline adducts at 25° C. Derivatives of slightly branched alkanes also form urea adducts if the chain is of sufficient length. The critical lengths, the minimum lengths required for the formation of a stable complex from a branched alkane derivative, have not as yet been determined since many of the key reactants are unobtainable.

The action of urea on hydrocarbon derivatives is less specific than the nearly exclusive removal of n-alkanes from hydrocarbon mixtures. The most significant derivatives are esters since the ester group seems very effective in enabling singly branched chains to form adducts. Urea complexes were obtained from methyl alkanoic acid esters of normal alcohols or from normal acid esters of methyl alkanols. Larger groups (Zimmerschied, 1949) such as a phenyl group in the acid portion of a normal alcohol ester prevented adduct formation.

<u>Similar Molecular Complexes</u>: There is a close resemblance of urea complexes to the "Choleic Acids", the name given to complexes of hydrocarbons with desoxycholic acid by Wieland and Sorge (Zimmerschied, 1949). The compounds formed with the aliphatic, monocarboxyllic acids have received considerable study. Herzog and Kuriyama

studied the x-ray structure of stearic acid-choleic acid, with the result that the crystal cell was found to occupy only one-half of the minimum molecular volume as computed from the molecular weight and the density of stearic acid-octacholeic acid. The eight molecules of bile acid (H. Sobotka, 1934) are suggested to be arranged in two tetrades around the upper and lower half of the stearic acid chain. This type of arrangement will be shown to be analogous to the crystal structure of the urea complexes.

It has been found by Barrer in 1944 (Zimmerschied, 1949) that certain minerals such as chabazite, common zeolite, and analcite allow adsorption of linear alkanes within their crystal lattices while branched alkanes are prevented from adsorption by their protruding methyl groups.

The sulphur analog of urea, thiourea, has also been found to form complexes with a few compact hydrocarbons (Redlich, 1950) (Schiessler, 1952). Linear alkanes or their derivatives do not form stable complexes with thiourea. However, some highly branched alkanes such as 2, 2, 4 trimethyl pentane, isooctane, do adduct with thiourea. The stabilities of thiourea adducts have been found to be lower than most of the adducts of urea. Schiessler determined that the molecular dimensions of the reactant must be smaller than 5.8 X 6.8 Å in order to form a stable thiourea adduct.

Structure of Urea Adducts: Urea adducts cannot be considered saltlike chemical combinations involving the weakly basic properties of urea in molecular combination with the linear reactants behaving as acids, because compounds of widely differing acidity would not be expected to produce a series of such similar complexes.

The inclusion of extraneous molecules in a molecular crystal usually greatly impairs its stability (Redlich, 1950). Strong intermolecular forces, however, furnish a good opportunity for building into the crystal various molecules which by themselves do not appreciably contribute to the stability. The crystal structure of urea has received great attention (W. Schlenk Jr., 1950), and indicates that it may be possible for n-alkyl chains to penetrate the lattice. By x-ray investigation of the crystal structure of urea complexes, sufficient data were obtained to give a good idea of the molecular configuration. Powder patterns were taken of urea complexes of C_{10} - C_{50} hydrocarbons with various straight-chain alcohols, acids and esters (A. E. Smith, 1950). All of these adducts gave essentially the same patterns. By interpretation of these patterns, it was found that the urea molecules form spirals with the hydrocarbon molecules situated at the center. The urea channel in which the hydrocarbon is held has a diameter of about 5.5 to 6Å . Spirals of the hydrogen bonds between the O and the NH_2 groups of adjacent urea molecules account largely for the stability of the structure.

These urea adducts are definitely not adsorption products (W. Schlenk Jr., 1949) since on evacuation of the less stable adducts the vapor pressure remains constant until complete dissociation has occurred.

Considerable amounts of urea are required for adduct formation. Determinations of the number of urea molecules reacting with n-alkanes have been carried out by several methods. The composition of the complexes as a function of chain length was calculated (A. E. Smith, 1950) making use of x-ray data. The urea-carbon atom ratio is approximately equal to $[0.6925(n-1) + 2.18]/n$ where n is the number of carbon atoms in the straight chain of the adduct-forming alkane.

Zimmerschied used a calorimetric method to determine this urea per carbon atom, ratio. His method involved the addition of successive small portions of hydrocarbon to a mixture of urea and methanol until the temperature ceased to rise. Plotting of the temperature readings against the moles of alkane added gave curves from which the moles of n-alkane reacted could be estimated from the point of intersection of the lines of extrapolation of the initial rate of temperature rise and the final temperature level.

Reliable results were also obtained (Redlich, 1950) by determining the concentration changes in a weighed amount of an unsaturated solution of urea when a weighed amount of reactant was added to the urea solution. From the changes of the concentration of the urea solution, the ratio was determined for a great many linear aliphatic compounds. The greatest disadvantage of this method is that complete reaction is not usually obtained for one or two days at room temperature.

Separation (Redlich, 1950) of the complex from the mother liquor, washing, and analysis was found in many cases to lead to erratic results. Zimmerschied found that good results were obtainable with urea adducts of the longer n-alkanes because of their greater stability.

All of these methods have found that there is no simple molecular ratio of urea to carbon atom. The more precise determination for n-alkanes indicate a value near .75 (Zimmerschied, 1950).

Many of the investigators (Redlich, 1950), (Zimmerschied, 1950), (W. Schlenk, 1949), have noticed that a solution of normal alkane becomes considerably warmer on adding urea. The magnitude of this heat effect has been determined in a number of different ways. Zimmerschied measured the ΔH's calorimetrically in a small adiabatic calorimeter. His reported results were reproducible to ±.5 kg.-cal. The results obtained by this method have been found to be too small in most instances, (Redlich, 1950). This can be explained by the fact that the reaction cannot be expected to go to completion in less than a few hours time which leads to rather serious heat losses. Redlich found that an expression for an equilibrium constant could be set up and used to determine the heats of formation. The equilibrium constant was defined as being equal to the mole fraction of the reactant in a solution which is in equilibrium with the complex and solid urea. This was expressed by $K = a_r a_u^m$ for the reaction;

$$\text{Complex} \rightleftharpoons \text{Reactant} + m.\text{Urea}$$

where a_r is the activity of the reactant and a_u is the activity of the urea. Equilibrium was established between the pure reactant, and aqueous urea solution, and the complex. The concentration of the urea was determined, and the constant was given by the urea activity and the molal ratio m since a_r was equal to one. The heats of formation were then determined by making use of the temperature dependence of the equilibrium constant. The complexes form with the evolution of about 1.6 kg.-cal. per methylene group in the linear hydrocarbon chain.

The heat evolved during adduct formation may be looked upon as the resultant of two separate processes (Zimmerschied, 1950) one large and exothermic, and the other smaller and endothermic. The exothermic process is very similar to a physical adsorption process, although adduction within the urea lattice should be more exothermic than adsorption on a surface. The endothermic process includes the energy necessary to distort the urea lattice. All x-ray evidence indicates that these urea crystals are rather severely distorted. It may be concluded from this that crystals allowing penetration of hydrocarbon molecules with less distortion would allow adduction with other than n-alkane molecules, but crystals more difficult to distort than urea would not permit adduction at all.

Applications of Urea Adducts: Even the earliest reports gave indications of many of the possible applications of urea complexes (Bengen, 1949) (W. Schlenk Jr., 1949). These reports indicated that normal compounds could be separated from branched compounds. This type of separation has wide potentiality especially in petroleum technology. Zimmerschied has shown that urea adduction can be used as a means of not only separating unbranched hydrocarbons from complex petroleum fractions but also as a means of fractionating the n-alkanes by molecular weight. This is possible because of the greater stability of the long-chain hydrocarbon adducts.

More recent work has given many new applications of the urea complexes to organic chemistry. The urea complexes of a series of saturated and unsaturated fatty acids were prepared and studied (H. Schlenk, 1950). By repeated complexations a separation could be achieved between these fatty acids. Schlenk also found that the solid complexes of the unsaturated fatty acids did not develop the characteristic odor of rancidity upon standing in air. This phenomenon was accounted for by the fact that the fatty acid molecules occupy a restricted space within the crystal lattice. The lattice probably offers a barrier against the free penetration of oxygen, and the restricted space within the lattice is too small to permit the formation of a peroxide if the oxygen were to penetrate. Apparently, then, easily oxidized, unsaturated compounds are protected against autoxidation when in the form of the urea complex.

Urea adduct formation was also used to separate monomeric vinyl esters from mixtures containing monomer, polymer, inhibitor, and other unknown impurities (Swern, 1952). This indicates that urea adduction may be useful in a variety of polymerization and preparation investigations involving monomers which contain long chains.

All of these newer developments using urea as a separating device have dealt mainly with fatty acids or their esters. These investigators have been satisfied to deal with only the fatty esters having an alcoholic portion shorter than three carbons in length. This fact brings about the question as to whether all the properties of the long chain, C_{18} to C_{50}, hydrocarbon adducts are analogous in all respects to those of esters approaching the class of waxes. Since there was such meager information available concerning the nature and composition of the urea complexes of fatty esters, the major portion of this research was to determine the compositions of the adducts of the esters of a typical fatty acid, namely stearic acid. This information may provide some insight into the applicability of urea adduction to esters of high molecular weight.

PREPARATION OF INTERMEDIATES

Purification of stearic acid. In the preparation of a series of esters of a typical fatty acid, it is desirable to choose an acid which is readily available and easy to purify. Because stearic acid meets these requirements, it was chosen for use in this research.

The purification of U.S.P. grade stearic acid was found to be necessary because of the presence of some unsaturated substances such as oleic acid. Purification was carried out by repeated crystallizations from benzene using the following procedure. About 400 grams of the U.S.P. acid were placed in a one liter beaker and heated gradually to 150°C., at which temperature most of the volatile impurities had vaporized. The melt was cooled to 75°C. and 500 mls. of benzene were added. The solution was heated to boiling and 20 grams of decolorizing charcoal were added to remove the brownish-yellow color of the solution. While still hot, the solution was filtered through a heated Büchner funnel. White platelets of stearic acid crystallized upon slow cooling to room temperature. These crystals were separated from the mother liquor by filtration and allowed to dry in the air. This procedure was repeated until a solution of the recrystallized acid in carbon tetrachloride did not give a reaction with a solution of bromine in carbon tetrachloride. The observed melting point of the recrystallized acid was 68°C.

THE PREPARATION OF ESTERS BY DIRECT ESTERIFICATION

Nearly all of the stearic acid esters used were prepared by direct esterification, i.e. the reaction of an alcohol with an acid at various temperatures and pressures, employing various catalysts. Various considerations had to be given to these esterifications in order that an ester relatively free from unchanged acid would be obtained before high-vacuum, fractional distillation was carried out. Esterification reactions of this type are definitely reversible and reach equilibrium when a certain percentage of ester has been produced (Groggins, 1947). To complete an esterification, the water is removed as fast as it is formed in order to remove one of the reactants involved in the reverse reaction. To esterify a relatively non-volatile acid, such as stearic acid, with an alcohol of low moleculor weight, a large excess of the alcohol can be used and is distilled off during the process. This carries the water over as it is formed allowing the reaction to go to completion. Most of the alcohols above methanol in the aliphatic series form binary azeotropes with water, allowing these alcohols to be used very efficiently in this type of esterification.

In many instances continued high-temperature refluxing causes considerable decomposition of the reacting substances.

In such cases the addition of a liquid such as benzene, toluene, chloroform, or carbon tetrachloride assists in the removal of the water from the reaction by forming azeotropes of relatively low boiling point; thus lowering the temperature at which the reflux action takes place preventing serious decomposition. Since the rate of the reaction is slower at this lower temperature, the reaction time must be increased accordingly.

The rate of esterification may be considerably increased by the addition of a strong acid, such as sulphuric acid or hydrochloric acid. The acceleration is due to the hydrogen ions present in the reacting mixture. The esterifications carried out in this research indicated that sulphuric acid was not satisfactory as a catalyst because of the large amount of decomposition products and sulphur compounds that were present to contaminate the product. These difficulties were overcome by the use of a solution of anhydrous hydrogen chloride in benzene, acetyl chloride, or p-toluensulphonic acid as catalysts in these reactions.

The azeotropic distillations were carried out at atmospheric pressure using appropriate fractionating columns (Todd, 1945) for higher efficiency. For low-boiling azeotropes a 120 cm. X 20 mm. column was employed; for high-boiling azeotropes a 50 cm. X 20 mm. Vigreux column was used. All of the column heads were of the total reflux, variable take-off variety. The packing of the 120 cm. column consisted of a mixture of one, two, and three-turn glass helices and were rated at about three centimeters per theoretical plate at total reflux.

The esters obtained after azeotropic distillation were distilled to remove the excess alcohols present, at a pressure of about 20 mm. to 40 mm. of Hg, obtained with an ordinary water aspirator. The resulting impure esters were transferred to the still pot of a 100 cm. X 12 mm. high-vacuum fractionation column (Podbielniak, 1931). The column packing consisted of a nichrome wire spiral with an open core, and was externally heated to permit adiabatic operation ranging from room temperatures up to 250°C. The still head was of the partial reflux variety using external heating to permit variations in the rate of take off.

Methyl stearate. About 500 mls. of methyl alcohol were mixed with 150 gms. of recrystallized stearic acid in a liter Erlenmeyer flask. About 2 mls. of acetyl chloride (Freudenberg, 1941) were added to the mixture with constant agitation for a period of 30 minutes. The reactants were allowed to stand at room temperature for at least 24 hours. During this time the mixture of solid and liquid changed to a liquid-liquid mixture signifying that a reaction had taken place. This method of preparation was chosen since very little decomposition was noticed and because of the high yields obtainable without azeotropic distillation, due to the high reactivity of the methanol.

The impure ester obtained after vacuum distillation to remove all of the methyl alcohol was fractionated twice in the Podbielniak column at a pressure of 2 mm. of Hg. The methyl stearate fraction was taken off at a head temperature of 174°C. and a mean jacket temperature of 180°C. Since the purity of the ester was considered to be more important than high yields, only the middle fraction was retained for adduction.

The preparation of methyl stearate by the reaction of steroyl chloride and methanol was considered because of the high yields obtainable, but this method was discarded due to the possibility of introducing impurities in the form of sulphur compounds resulting from the use of thionyl chloride in the preparation of the acid chloride.

Ethyl stearate. Due to the decreased rate and the decreased yield in the esterification of stearic acid with alcohols above methanol in the aliphatic series, a long period of refluxing and a similar long period of azeotropic distillation must be used to insure a satisfactory yield of pure ester. For the preparation of ethyl stearate 150 gms. of stearic acid was dissolved in 500 mls. of absolute ethanol, and 20 mls. of benzene saturated with hydrogen chloride were added to the resulting solution in the still pot of the 120 cm. helix-packed column and refluxed totally for a period of five hours. The ternary azeotrope of water, benzene, and ethanol, B.P. 64.4°C., was then taken off at a rate of one to two mls. per minute, which is slow enough to prevent a disturbance of the equilibrium in the column. During this distillation it was necessary to add sufficient dry benzene to allow complete removal of the water. When all of the stearic acid had been esterified, the temperature of the still head rose to 67.8°C., the boiling point of the binary azeotrope of benzene and ethanol. The distillation was continued until most of the remaining ethanol was removed. The remaining ethanol was completely removed by distillation at 20 mm. to 30 mm. of Hg. The impure ester was then fractionated in the Podbielniak column for purity rather than for yield as in the case of all the esters used in this research. The yield was taken off at a head temperature of 161°C., a jacket temperature of 176°C., and a pressure of 2 mm. of Hg.

n-Propyl stearate. This ester was prepared by the same method and technique as used in the preparation of the ethyl ester.

The azeotropes used were n-propyl alcohol, benzene, and water (B.P. 68.5°C.); n-propyl alcohol and benzene (B.P. 77.1°C.).

The yield was taken at a head temperature of 161°C., a jacket temperature of 176°C., and a pressure of 2 mm. of Hg.

<u>Isopropyl stearate.</u> Isopropyl stearate was prepared using the process described in the preparation of ethyl stearate, but the period of refluxation was increased to allow for the decreased reactivity of the alcohol.

The azeotropes used were isopropyl alcohol, benzene, and water (B.P. 66.5°C.); isopropyl alcohol, and benzene (B.P. 71.9°C.).

The yield was taken at a head temperature of 155°C., a jacket temperature of 166°C., and a pressure of 2 mm. of Hg.

<u>n-Butyl stearate.</u> The same method of preparation was used here as in the case of ethyl stearate, but no benzene, other than the catalyst solution, was added to form a ternary azeotrope because the binary azeotrope of n-butyl alcohol and water, B.P. 92.4°C., was entirely satisfactory.

The yield was taken at a head temperature of 165°C., a jacket temperature of 172°C., and a pressure of 2 mm. of Hg.

Isobutyl stearate. This preparation was identical with that of n-butyl stearate.

The azeotrope used was isobutyl alcohol and water (B.P. 90.0°C.).

The yield was taken at a head temperature of 170°C., a jacket temperature of 181°C., and a pressure of 2 mm. of Hg.

n-Amyl stearate. This esterification was carried out as described above except that it was necessary to use .2 gm. of p-toluenesulphonic acid instead of the hydrogen chloride as a catalyst because of the volatility of the hydrogen chloride at the reflux temperature used.

The azeotrope used was n-amyl alcohol and water (B.P. 96.0°C.).

The yield was taken at a head temperature of 175°C., a jacket temperature of 190°C., and a pressure of 1 mm. to 2 mm. of Hg.

n-Hexyl stearate. The preparation of n-hexyl stearate used the same procedure employed in the preparation of n-amyl stearate.

The azeotrope used was n-hexyl alcohol and water (B.P. 97.8°C.).

The yield was taken at a head temperature of 185°C., a jacket temperature of 200°C., and a pressure of 1.0 mm. to 1.5 mm. of Hg.

n-Heptyl stearate. The preparation of n-heptyl stearate used the procedure employed in the preparation of n-amyl stearate.

The azeotrope used was n-heptyl alcohol and water (B.P. 98.7°C.).

The yield was taken at a head temperature of 194°C., a jacket temperature of 205°C., and a pressure of 1.0 mm. to 1.5 mm. of Hg.

n-Octyl stearate. The preparation of n-octyl stearate used the procedure employed in the preparation of n-amyl stearate.

The azeotrope used was n-octyl alcohol and water (B.P. 99.4°C.).

The yield was taken at a head temperature of 197°C., a jacket temperature of 214°C., and a pressure of 1.0 mm. to .5 mm. of Hg.

Sec. Octyl stearate. The preparation of sec. octyl stearate used the same procedure employed in the preparation of n-amyl stearate.

The yield was taken at a head temperature of 198-201°C., a jacket temperature of 216°C., and a pressure of 1.5 mm. to 1 mm. of Hg.

<u>Octadecyl stearate.</u> Octadecyl stearate was prepared by the procedure employed in the preparation of n-amyl stearate, but the refluxing was replaced by a 100-hour heating period in a 120°C. oil bath. After 48 hours of heating, water droplets accumulated on the bottom of the reaction flask and gradually formed a distinct, thin layer. This water was removed by azeotropic distillation using benzene. The excess octadecyl alcohol and stearic acid was removed by distillation in the Podbielniak column until the head temperature was at least 210°C. The impure octadecyl stearate remaining in the still pot was purified by decolorizing charcoal in a hot, benzene solution. After allowing the hot solution to cool slowly, platelets of the ester, M.P. 62°C. were found in quantity.

THE PREPARATION OF ESTERS FROM A METAL SALT AND AN ALKYL HALIDE

If a metal salt of a carboxylic acid is heated with an alkyl halide, the alkyl group substitutes for the metal thus forming an ester. The formation of the metal halide by-product is very important from the energy standpoint. Thermodynamically this type of reaction may be regarded as a synthesis of the metal halide, since the intense affinity of the metal and the halide for each other is the driving force that causes the reactions to go to completion. The yield of the metal salt is quantitatively complete; the other parts of the original molecules may combine to form the ester, or they may not. This type of reaction is useful when the alkyl halide is more readily available than the corresponding alcohol or when the ester is difficult to obtain by direct esterification.

Benzyl stearate. About 150 gms. of sodium stearate and 200 mls. of benzyl chloride were placed in a Erlenmeyer flask ground to fit an appropriate condenser. The reactants were heated in an oil bath at 120°C. for at least 100 hours. During this time what appeared to be sodium chloride deposited on the bottom of the flask. The crude benzyl stearate and excess benzyl chloride were decanted from the salt cake into a 500 ml. Claisen flask. The ester was purified by vacuum distillation at a pressure of 20 mm. of Hg. The residue was then fractionated in the Podbielniak column at a pressure of .5 mm. to 1 mm. of Hg. The yield was taken at a head temperature of 205°C. and a jacket temperature of 233°C.

Ethylene glycol distearate. For the preparation of ethylene glycol distearate 250 mls. of ethylene dibromide were refluxed with 100 gms. of sodium stearate for at least 100 hours. The mixture of ethylene glycol monostearate, ethylene glycol distearate, and ethylene dibromide was first fractionally distilled to remove the ethylene dibromide, B.P. 132°C., and further fractionated in the Podbielniak column to remove any ethylene glycol, ethylene glycol monostearate, and stearic acid which might be present. The resulting residue was dissolved in hot benzene and treated twice with decolorizing charcoal. White platelets having the M.P. 77°C. were formed upon cooling.

Cyclohexyl stearate. Cyclohexyl stearate was found to be extremely difficult to prepare by direct esterification. In the presence of sulphuric acid or p-toluenesulphonic acid, cyclohexanol dehydrates easily to yield cyclohexene, but in the presence of hydrogen chloride cyclohexyl chloride is formed. The best yield of cyclohexyl stearate was obtained by the reaction of sodium stearate with cyclohexyl bromide. This preparation was carried out in the same manner as in the preparation of benzyl stearate. The yield was taken at .5 mm. to 1.0 mm. of Hg, head temperature of 192°C., and a jacket temperature of 205°C.

THE PREPARATION OF UREA ADDUCTS OF THE STEARATES

About 200 mls. of a saturated solution of C.P. urea in methanol were pipetted into a 250 cc. Erlenmeyer flask fitted with a ground-glass stopper. A solution of at least

20 gms. of the ester in 2,2,4 trimethyl pentane, isooctane, was added to the urea solution. The resulting mixture was shaken vigorously for about 10 minutes and the stoppered flask was allowed to stand for at least 12 hours. After this reaction period, the voluminous, white precipitate of the urea adduct was removed from the mother liquor by suction filtration in a very dry Büchner funnel. The adduct was washed with three to four 25 ml. portions of anhydrous isooctane to remove any occluded reactant. The fine, crystalline adduct was transferred to a pyrex crystallization dish and vacuum dried at room temperature to remove the remaining isooctane.

THE COMPOSITION OF THE ADDUCTS

Hydrolytic decomposition. The adduct obtained in the above procedure was dried to constant weight at a pressure of 2 mm. of Hg to assure complete removal of the isooctane wash liquid. Three nearly equal amounts of the adduct were weighed into dry, 125 ml. separatory funnels, free of stopcock grease. These samples were then decomposed by the addition of 100 ml. of distilled water which was at room temperature. The time required for this decomposition varied from 15 minutes to an hour, depending on the character of the adduct. Extraction of the stearates from the aqueous urea solution was carried out using at least three

20 ml. portions of petroleum ether. These combined extractions were evaporated in weighed crystallization dishes on a 90°C. hot plate. The crystallization dishes and contents were then vacuum dried at 2 mm. of Hg pressure to remove any remaining petroleum ether until constant weight was obtained. In the case of the higher molecular weight esters, octadecyl and ethylene glycol stearates, benzene was used as the extracting medium. This change was necessary because of the low solubility of the esters in a low-boiling, non-aromatic solvent like petroleum ether.

From the weight of the ester and the weight of the adduct the mole ratios of urea to ester were computed and appear in table I, (page 28).

Calorimetric determination of the composition of the adducts. To serve as a check on the composition of the adducts as determined by hydrolytic decomposition, the calorimetric titration (Zimmerschied, 1949) of reactant with a urea solution was attempted. A weighed sample of urea dissolved in methanol was placed in the calorimeter cup of a Cenco calorimeter, Cat. No. 78044. A weighed sample of the stearate was dissolved and made up to volume in a 50 ml. volumetric flask using anhydrous isooctane as the diluent. The calorimeter cup was equipped with a mechanical stirrer and a Beckman thermometer. After the

TABLE I

COMPOSITIONS OF THE ADDUCTS OF THE ESTERS OF STEARIC ACID

Stearates	Mean mole-ratios[1]	Standard Deviation[2]	Number carbons in ester	Mole-ratio / Number of carbons[3]
Methyl	15.17	± .1	19	.798
Ethyl	15.92	± .1	20	.796
n-Propyl	16.73	± .1	21	.796
n-Butyl	17.45	± .1	22	.793
n-Amyl	18.10	± .1	23	.787
n-Hexyl	18.85	± .1	24	.785
n-Heptyl	19.60	± .1	25	.784
n-Octyl	20.61	± .1	26	.791
Isopropyl	16.01	± .2	21	.761
Isobutyl	16.60	± .2	22	.754
Sec-Octyl	20.30	± .2	26	.780
Benzyl	19.25	± .1	25	.770
Cyclohexyl	18.97	± .1	24	.791

[1] Mole ratio of urea to ester in the urea complex.

[2] Approximate standard deviation of four results.

[3] Mole-ratio divided by the number of carbons in the ester.

calorimeter and its contents came to thermal equilibrium, the stearate solution was added in .5 ml. portions. The equilibrium temperatures were noted after each addition and were plotted against the volume of stearate solution added. A maximum temperature was reached as the reaction came to an end. On extrapolation of the linear rise and the plateau obtained on completion of the titration, the mole ratios of urea to ester were computed. These titrations were performed using n-propyl stearate, n-butyl stearate, and n-hexyl stearate as reactants. The precision of the measurements of the mole ratios obtained by this method was so poor that the results were meaningless. The slowness of the reaction, heat loses, and insufficient stirring were the major reasons for the failure of this calorimetric determination.

Decomposition by molecular distillation. Bengen (1940) reported that urea adducts could be decomposed by destructive distillation, but he gave no specific directions for this method of decomposition. Since the calorimetric titration failed to give any added information, it was decided to attempt to determine the composition of the adducts by separation of the stearate and urea by destructive distillation. This distillation was performed in a molecular, pot still (Weissberger, 1951) of the Lanzl variety, which was constructed in the laboratory for this specific purpose.

The decompositions of the complexes of isopropyl stearate, n-propyl stearate, and n-octyl stearate were carried out in the following manner. A weighed 5 to 7 gram sample of the complex was placed in the Lanzl still and evacuated to a pressure of 10^{-3} mm. of Hg with no refrigerant in the condenser. This outgassing period required about two to three hours. A mixture of dry ice and acetone was placed in the cold-finger condenser of the still, and evacuation was continued until a pressure of 10^{-5} mm. of Hg was attained, the process requiring approximately two hours. An oil bath at 100°C. was raised under the still until the oil covered about an inch of the still pot. After molecular distillation for four to five hours at 5×10^{-5} mm. of Hg, the still was opened and an analysis of the distillate and still pot residue showed that the condensate consisted of a urea-ester mixture, 5 to 20% urea and 80 to 95% ester, while the still pot contained some unchanged adduct, urea, and traces of biuret. These results testify as to the stability of these adducts under the above conditions, which makes molecular distillation unsatisfactory as a method of analyzing their composition.

QUALITATIVE OBSERVATIONS

It was observed in the case of isopropyl stearate, as well as a few other stearates, that the cake of adduct obtained from the filtration and washing procedure was not a compact mass of crystals but was filled with minute holes that had contained droplets of unreacted ester. This occlusion of ester in the adduct made the precision of the ratios of ester to urea quite low. It was found necessary to increase the reaction time to about 48 hours to give more opportunity for reaction of the occluded reactants. This gave a better crystalline adduct and aided in the removal of the excess reactant.

The use of various alcohols as activators such as ethanol, n-propanol, isopropanol, and isobutanol gave good results for all of the esters, but due to the low solubility of urea in these alcohols, the yields of the adducts were much smaller. The mole-ratios of the adducts obtained by the use of activators other than methanol were in complete agreement with those appearing in table I.

The adducts of n-octadecyl stearate and ethylene glycol distearate were found to be contaminated with varying amounts of urea giving results between 80 and 110 moles of urea per mole of ester. The values should be between 28 and 30 moles of urea per mole of ester as calculated using the value of .79 moles of urea per carbon atom in the ester. These results indicate that a different method of preparation of the pure adducts is necessary in the case of the longer chain esters, 36 carbons in this case.

All of the esters recovered from the adducts after decomposition showed a high degree of purity. The recovered esters crystallized very readily, had good crystal form, and also had good boiling ranges, which are indicative of pure compounds. To show that impure esters could be somewhat purified by the urea process, n-heptyl stearate was heated until slight decomposition occurred as shown by the dark color that developed in the ester. The impure ester was adducted in the normal manner and upon decomposition of the adduct gave a colorless yield of n-heptyl stearate of high purity as evidenced by crystal structure and boiling range.

The rates of hydrolytic decomposition of the adducts were not accurately determined because of the difficulty in determining the completeness of the hydrolysis. Nearly all of the adducts required about 20 minutes for complete hydrolysis, but isopropyl stearate and benzyl stearate required only about 5 minutes for complete hydrolysis indicating a lower degree of stability.

DISCUSSION OF RESULTS

The linear esters of stearic acid from methyl to n-octyl gave a mean value of .791 moles of urea per carbon atom which was in close agreement with Zimmerschied's (1950) value of .75 moles of urea per carbon atom in the case of linear hydrocarbons. The difference between the two values can be explained by the fact that the ester chain is actually one oxygen atom longer than the corresponding hydrocarbon with the same number of carbons. This oxygen atom does not contribute the same adduction value as the methylene groups on the chain, perhaps due to the effect of the adjacent carbonyl group. The effect of the non-carbonyl oxygen seems to be somewhat nullified by any methyl side chains present on the ester as is shown by the mean value of .765 moles of urea per carbon for all of the iso-esters having one methyl side chain.

The formation of stable adducts of benzyl stearate and cyclohexyl stearate indicate that linear substitutions on the alcoholic portion of the esters by cyclic or arammatic residues having less than the maximum allowable diameter, 6Å, do not interfere with the formation of the urea complexes.

In the ease of substituted phenyl or cyclohexyl compounds the length of the side chain is evidently important. Benzene and cyclohexane do not form adducts, but 1-phenyl eicosane and 1-cyclohexyl eicosane give good qualitative adduction tests (Schiessler, 1952). The minimum side-chain length required for adduction has as yet not been determined, but this research shows that a side-chain length of 18 carbons is definitely above the minimum carbons required.

The formation of urea complexes of esters of high molecular weight is complicated by several unavoidable difficulties. Due to the low solubility of the esters in the activators used, the reaction occurred chiefly between the components in the two liquid phases and consequently was very slow. The esters were occluded in a few of the adducts to such a high degree that even with repeated extractive washings the mole ratios obtained upon decomposition did not have good precision.

SUMMARY

A series of esters of stearic acid were prepared and were subjected to urea adduction. In every case a solid complex was formed whose composition was determined by hydrolytic decomposition and subsequent analysis. A colorimetric titration was tried but did not give valid results. The adducts could not be quantitatively decomposed by molecular distillation at a pressure of 10^{-5} mm. of Hg. The mole ratios found in this laboratory follow closely the values given by Zimmerschied for linear hydrocarbons.

Aromatically substituted linear esters give stable adducts, but appear to be more readily hydrolyzed than the other adducts prepared. The mole ratios of the high molecular weight ester adducts, the adducts of octadecyl stearate and ethylene glycol distearate, were not attainable due to the lack of a proper activator or diluent for use in the complexation reaction.

The preparation of quite pure stearates by hydrolysis of the ester adducts suggests that the formation of adducts might be used for the separation of the esters of the higher-molecular weight aliphatic acids from other materials which would not form adducts.

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