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The effects of structural changes on the formation of urea adducts of esters

Gerard Vinton Smith
University of the Pacific

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THE EFFECTS OF STRUCTURAL CHANGES
ON THE FORMATION OF UREA ADDUCTS OF ESTERS

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 Science

by
Gerard Vinton Smith
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TABLE OF CONTENTS

	PAGE
UREA	1
UREA ADDUCTS	2
COMPLEXES	4
CHOICE OF INTERMEDIATES	6
PREPARATION OF INTERMEDIATES	6
Methyl Nonadecanoate	9
n-Propyl Heptadecanoate	10
n-Pentyl Pentadecanoate	10
n-Heptyl Tridecanoate	11
n-Nonyl Undecanoate	11
n-Undecyl Nonanoate	11
n-Tridecyl Heptanoate	12
n-Pentadecyl Pentanoate	12
n-Heptadecyl Propionate	12
n-Nonadecyl Methanoate	13
THE PREPARATION OF THE UREA ADDUCTS	13
THE DECOMPOSITION OF THE UREA ADDUCTS	14
QUALITATIVE OBSERVATIONS	16
CORRELATION OF RESULTS	18
SUMMARY	22
LITERATURE CITED	23

LIST OF TABLES AND FIGURES

TABLE

PAGE

I. The Composition of the Adducts of the Esters	15
--	----

FIGURE

1. Moles of Urea per Chain Atom vs. Position of Carbonyl Group	19
---	----

FORWARD

An unexpected discovery in 1940 revealed that urea has the peculiar property to form crystalline adducts with many straight chain organic compounds. Since the discovery, considerable time and money have been spent on the elucidation of this phenomenon, and the field of urea adducts has now advanced to the stage at which many empirical rules have been observed but, unfortunately, no sound theory has been formulated.

The purpose of this research was to determine the effect, if any, of changes in structure upon the amount of urea required to adduct with esters. The change in structure consisted of changing the position of the carbonyl group in a series of straight chain twenty-carbon esters.

UREA

Urea, $(\text{NH}_2\text{CONH}_2)$, a white crystalline solid is the most interesting and important derivative of carbamic acid. It is the main final product of nitrogen metabolism in man and mammals, and occurs in small quantities in plants.

The discovery of urea as a component of urine in 1773 by Roulle, paved the way for a later full investigation of the compound by Fourcroy, Prout and Vauquelin. In 1828 Wohler synthesized urea from ammonium cyanate and this, with the previously successful synthesis of oxalic acid from cyanogen, was the first indication that the "vital force" theory was not valid.

Urea crystallizes in tetragonal prisms, M.P. 132°C , sublimes, and is readily soluble in alcohol and water. It takes part in reactions which are characteristic of amides, forming addition compounds with mineral acids and salts of certain metals, the mercury salts being the most stable.

While other amides are either neutral or weakly acidic, urea is slightly basic as can be seen from the four most important members of its resonance hybrid.



Since oxygen is more electronegative than carbon, the electrons composing the oxygen-carbon bond can more easily

reside on oxygen than on carbon giving the oxygen a partial negative charge and the carbon a partial positive charge. The partial positive charge on the carbon is stabilized by resonance with the two amino groups and is thus spread over a larger volume of space than is the partial negative charge on oxygen. The overall effect most probably is that of a dipole with a concentrated negative charge and a less concentrated partial positive charge. The effect of the two amino groups in urea tends to put more of a negative charge on the oxygen than does the lone amino in other amides.

UREA ADDUCTS

Among its chemical properties urea has the peculiar ability to form solid crystalline complexes with certain straight chain organic compounds. These complexes are commonly called "urea adducts" and will be referred to as such in this paper.

Bengen, a German chemist, discovered urea adducts and described them in a patent in 1940 (Bengen 1940). Since Bengen's discovery, considerable research has been performed on urea adducts.

The requirements for the formation of urea adducts are simple. Urea is dissolved in a solvent (activator), usually methanol but other activators give satisfactory results (Zimmerschied 1950), and a straight chain compound

is introduced into the solution. The straight chain compound may be any organic compound with a minimum chain length of about six atoms. Certain branched compounds have been reported to form urea adducts (Zimmerschied 1950), and the minimum required chain length varies slightly depending upon the functional group attached to the carbon chain. The minimum chain lengths for several typical functional groups have been determined (Truter 1953). The length for esters is eight atoms; ketones, three atoms (acetone); acids, five atoms (butyric), hydrocarbons, six atoms (hexane); alcohols, seven atoms (hexanol). The adduct precipitates as a white crystalline solid which decomposes upon heating (Francis, 1953) or upon addition of a suitable solvent such as water or methanol.

An interesting vapor phase decomposition of urea adducts is described in a patent by G. G. Ray (Ray, 1952). The adduct is suspended in a preheated inert carrier gas which passes into a decomposition zone and is heated to a temperature just below its decomposition point. An auxiliary inert carrier gas, which has been preheated to a temperature somewhat above the decomposition point of the adduct, is introduced into a point midway in the decomposition zone to heat the adduct to a temperature above its decomposition point. The organic compound is liberated as a vapor, and it and the suspension of liberated urea in the carrier gas are carried into a solid-gas separation zone, to separate the urea from the gas.

COMPLEXES

Several complexes related to urea adducts are known to exist. They are the "Choleic acids", quinol addition compounds, thiourea adducts, and urea complexes with certain inorganic oxides and salts.

The "Choleic acids", as named by Wieland and Sarge, are addition compounds between desoxycholic acids and paraffins or fatty acids (Zimmerschied, 1949). Similar to urea adducts, the proportion of the components depends upon the straight chain length of the paraffin or fatty acid, but dissimilarly the ratios are always small whole numbers (J. W. Smith, 1950). It has been suggested by Go and Kratky (J. W. Smith, 1950), as a result of x-ray studies, that the fatty acid chains lie parallel to the c-axis of the desoxycholic acid crystals. This type of structure is similar to the urea adduct crystal.

The quinol addition compounds are described by Palin and Powell (Palin, 1950) and called clathrate compounds. They have the general formula $3 \text{C}_6\text{H}_4(\text{OH})_2 : \text{M}$, where M is a small molecule such as methyl alcohol or formic acid.

Quinol crystallizes from a solvent in the presence of large amounts of compound M to form the adduct. Like the urea adduct, the quinol addition compounds have a definite shape and size, but unlike the urea adducts they have a definite formula by which they combine.

Thiourea, which is very similar to urea, in structure,

is known to form complexes or adducts with straight chain compounds in the same manner as urea. (Redlich, 1950) (Francis, 1953). The thiourea adducts are, however, less common and less stable than urea adducts. The hydrocarbons which adduct with thiourea are usually compact and branched. For instance, 2,2,4-trimethyl pentane forms an adduct with thiourea, but it is unreactive towards urea to the extent that it was used as the ester solvent in this research.

The lower stability of the thiourea adducts can be explained by the fact that the partial negative charge on the sulfur is spread over a larger volume of space than the corresponding charge on the oxygen of urea. This leads to a lower stability of the hydrogen bonds necessary to form the adduct.

The carbon sulfur bond in thiourea is 1.64 \AA (Wheland 1949), while the carbon oxygen bond in urea is 1.25 \AA . Evidently, if the thiourea adducts are of a hexagonal crystalline structure similar to those of urea adducts, the inside diameter of the thiourea channel will be correspondingly larger. It would then be expected to enclose branched chain molecules.

The complexes of urea with certain inorganic oxides and salts are coordinate complexes. These complexes unlike urea adducts with hydrocarbons exist in definite molecular ratios. For instance, one of the most common complexes of this type is one in which three moles of silver oxide combine

with one mole of urea, $\text{CO}(\text{NH}_2)_2 \cdot 3 \text{AgO}$.

CHOICE OF INTERMEDIATES

Work in this laboratory has been performed on urea adducts of esters containing twenty carbons prepared from even carbon alcohols and acids (Johnson, 1953). In order to complete the twenty-carbon ester series, this study was conducted on the urea adducts of straight chain twenty-carbon esters prepared from odd-carbon acids and alcohols.

PREPARATION OF INTERMEDIATES

Due to the unavailability of certain of the odd-carbon species of the normal alcohols and acids, it was necessary to prepare them from certain more available even-carbon alcohols. This was done by conversion of the even-carbon n-alcohols into the corresponding n-bromides, preparation of the n-alkyl magnesium bromides, and reaction of the resulting Grignard reagent with either carbon dioxide or formaldehyde.

N-octyl, n-decyl, n-lauryl, n-myristyl, and n-cetyl bromide were prepared by refluxing the corresponding alcohols with a 48% hydrobromic acid-concentrated sulfuric acid mixture for periods ranging from four to twenty hours. N-octadecyl bromide was prepared by bubbling hydrogen bromide gas into n-octadecanol at 100°C .

Grignard reagents were prepared by the usual method and immediately reacted as indicated below.

The preparation of the odd-carbon acids involved the addition of carbon dioxide to the freshly prepared Grignard reagents under sixty pounds of pressure per square inch in a Parr series 3910 low pressure, shaker type, catalytic hydrogenation apparatus. Carbon dioxide was added until no additional absorption was observed as indicated by the pressure gauge. Acids prepared by this method were n-undecylic, n-tridecylic, n-pentadecylic, n-heptadecylic, and n-nonadecylic acid.

Alcohols were prepared by vigorously stirring from eight to twelve hours the ether solution of freshly prepared Grignard reagent with an excess of paraformaldehyde. These reactions were conducted at room temperature using paraformaldehyde which had been dried over phosphorous pentoxide for several days. The lengthy agitation periods were used in order to more completely depolymerize the paraformaldehyde. Alcohols prepared by this method were n-nonanol, n-undecanol, n-tridecanol, n-pentadecanol, n-heptadecanol, and n-nonadecanol.

All of the esters used in this research were prepared by direct esterification with the use of either acetyl chloride or p-toluenesulfonic acid as sources for the necessary hydrogen-ion catalyst. Since this type of reaction is definitely reversible with a certain percentage

of ester being formed at equilibrium (Groggins, 1947), it was necessary to remove water from the reaction mixture in order to obtain sufficient yield of the ester. This was accomplished by azeotropic distillation.

In the case of the higher boiling alcohols, benzene was added in order to reduce the reflux temperature and to aid in the removal of water.

Sulfuric acid is a common catalyst used in this type of reaction; however, due to the possibility of extensive decomposition, it was decided to use p-toluenesulfonic acid and in the case of the methyl ester, acetyl chloride (Freudenberg, 1941). No acid catalyst was necessary in the case of the ester of formic acid since the acid itself was sufficiently reactive to catalyze the esterification.

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 higher 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 was 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 - 30 mm of Hg using a water aspirator. The remaining 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 temperature up to 250°C. The still head was of the partial reflux variety using external heating to permit variation in take-off rates.

Methyl Nonadecanoate. To 172 grams of methyl alcohol were added 40 grams of crude n-nonadecanoic acid prepared by the aforementioned process. About 2 ml of acetyl chloride (Freudenberg, 1941) were added to the mixture with constant agitation for a period of 60 minutes. The reactants were allowed to stand for a period of twelve hours during which the solid-liquid mixture changed into a liquid-liquid mixture signifying that a reaction had taken place. Agitation was again performed and the reaction mixture was again allowed to stand for approximately 12 hours. This method of preparation was chosen because of high yields without azeotropic distillation and low percentage of decomposition products.

The impure ester obtained after vacuum distillation to remove all of the methyl alcohol was fractionated in the Podbielniak column at a pressure of 3-4 mm of Hg. The methyl nonadecanoate fraction was taken off at a head

temperature of 194-195°C and a mean jacket temperature of 205°C. Since the purity of the ester was considered to be more important than high yields, only the middle fraction was used for the adduction.

n-Propyl heptadecanoate. About 40 grams of crude n-heptadecanoic acid were dissolved in 190 grams of n-propyl alcohol. Approximately .2 grams of p-toluenesulfonic acid were dissolved in the solution and 100 ml of benzene were added. The resulting solution was placed in the still pot of the 120 cm helice-packed column and refluxed totally for a period of five hours. The ternary azeotrope of water, benzene and n-propyl alcohol (B.P. 68.5°C) was taken off at a rate of one to two mls per minute which was slow enough to prevent a disturbance of the equilibrium in the column. When the reaction was complete, the temperature in the still head rose to 77.1°C, the boiling point of the binary azeotrope of benzene and n-propyl alcohol.

The yield was taken at a head temperature of 194-196°C, a jacket temperature of 202°C, and a pressure of 3-4 mm of Hg.

n-Pentyl pentadecanoate. The same method of preparation was used here as in the case of n-propyl heptadecanoate, but no benzene was added to form a ternary azeotrope because the binary azeotrope of n-pentanol and water (B.P. 96.0°C) was entirely satisfactory.

The yield was taken at a head temperature of 192-194°C,

a jacket temperature of 196°C , and a pressure of 2-2.5 mm of Hg.

n-Heptyl tridecanoate. The same method of preparation was used here as in the case of n-pentyl pentadecanoate.

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

The yield was taken at a head temperature of $192-194^{\circ}\text{C}$, a jacket temperature of 200°C , and a pressure of 2-2.5 mm of Hg.

n-Nonyl undecanoate. The procedure for preparation in this case was identical to the procedure for the preparation of n-pentyl pentadecanoate.

The azeotrope used in this case was n-nonyl alcohol and water (B.P. 99°C).

The yield was taken at a head temperature of $189-191^{\circ}\text{C}$, a jacket temperature of 196°C , and a pressure of 2-3 mm of Hg.

n-Undecyl nonanoate. In this case the method of preparation was the same as the method used in the preparation of n-pentyl pentadecanoate except that benzene was added to assist in the removal of water and most of the excess alcohol.

The azeotropes used were n-undecyl alcohol, benzene and water (B.P. 79.0°C).

The yield was taken at a head temperature of $191-195^{\circ}\text{C}$, a jacket temperature of 200°C , and a pressure of 2-3 mm of

Hg.

n-Tridecyl heptanoate. The same procedure was used here as described above.

The azeotropes used were n-tridecyl alcohol, benzene and water (B.P. 69.8°C) and n-tridecyl alcohol and benzene (B.P. 79.3°C)

The yield was taken at a head temperature of 195°C , a jacket temperature of 196°C and a pressure of 2-2.5 mm of Hg.

n-Pentadecyl pentanoate. The preparation of n-pentadecyl pentanoate consisted of the same procedure employed in the preparation of n-tridecyl heptanoate.

The azeotropes used were n-pentadecyl alcohol, benzene and water (B.P. 70.9°C) and n-pentyl alcohol and benzene (B.P. 79.0°C).

The yield was taken at a head temperature of $192-195^{\circ}\text{C}$, a jacket temperature of 203°C and a pressure of 2-3 mm of Hg.

n-Heptadecyl propionate. The preparation of n-heptadecyl propionate followed the same procedure employed in the preparation of n-tridecyl heptanoate except that a large excess of propionic acid was used since the boiling point of n-heptadecyl alcohol was near that of the ester.

The azeotropes used were propionic acid, benzene and water (B.P. 70.0°C) and propionic acid and benzene (B.P. 78.8°C).

The yield was taken at a head temperature of 190-193°C, a jacket temperature of 201°C and a pressure of 2-3 mm of Hg.

n-Nonadecyl methanoate. The preparation here was the same as described above except that benzene was added several times in an attempt to remove all of the excess formic acid. No p-toluene sulfonic acid was used in this case since formic acid was reactive enough so as not to require a catalyst for esterification. The main difficulty lay in the absolute removal of excess formic acid.

The azeotropes used were formic acid, benzene and water (B.P. 70.1°C) and formic acid and benzene (B.P. 77.1°C).

The yield was taken at a head temperature of 161-162°C, a jacket temperature of 172°C and a pressure of 3-4 mm of Hg.

THE PREPARATION OF THE UREA ADDUCTS

Approximately 200 ml of a saturated solution of chemically pure grade urea in methanol was pipetted into a two hundred and fifty cubic centimeter florence flask fitted with a ground glass stopper. To this urea solution was added from ten to fifteen grams of an ester dissolved in 10 ml of 2,2,4-trimethylpentane. The resulting mixture was vigorously shaken for ten minutes and placed on a shelf for twelve hours. The white needle-like precipitate was

then filtered and washed with three 25 ml portions of 2,2,4-trimethyl pentane. The precipitate was then transferred to a crystallizing dish and vacuum dried at 2 mm of mercury at room temperature until a constant weight was obtained.

THE DECOMPOSITION OF THE UREA ADDUCTS

The urea adduct precipitate, after being dried to constant weight, was divided into three portions each of which was weighed to the nearest tenth of a milligram. Each of these portions was then transferred into a clean, dry one hundred and twenty-five milliliter separatory funnel free from stop-cock grease. 100 ml of distilled water was added to each adduct with vigorous shaking until the adduct was completely decomposed. Extraction of the ester was accomplished with three 20 ml portions of petroleum ether (B.P. 25-65°C), combined in a crystallizing dish, and dried at 90°C for one hour.

From the weight of the ester recovered and the weight of the adduct decomposed the mole ratios of urea to ester were computed and appear in Table I.

TABLE I
THE COMPOSITION OF THE ADDUCTS OF THE ESTERS

	Mean Mole- ratios ¹	Estimated limits of error	Moles urea/atom in chain A ³ B ⁴	
methyl nonadecanoate	16.52	— 0.1	.826	.786
n-propyl heptadecanoate	17.00	— 0.1	.850	.809
n-amyl pentadecanoate	16.33	— 0.1	.816	.777
n-heptyl tridecanoate	16.06	— 0.1	.803	.765
n-nonyl undecanoate	16.44	— 0.1	.822	.783
n-undecyl pelargonate	16.28	— 0.1	.814	.775
n-tridecyl heptanoate	15.87	— 0.1	.793	.756
n-pentadecyl valerate	16.92	— 0.1	.846	.806
n-heptadecyl propionate	16.18	— 0.1	.809	.770
n-nonadecyl formate	15.87	— 0.1	.793	.756
Mean	16.34	— 0.12 ²	.817	.778

¹Mole-ratio of urea to ester in the complex.

²Standard deviation of individual esters from the mean of all.

³Using the chain length as twenty atoms.

⁴Using the chain length as twenty-one atoms.

QUALITATIVE OBSERVATIONS

The intermediates were prepared in a straight forward manner and only mechanical difficulties were encountered. In the case of the long chain bromides, troublesome emulsions formed while washing the bromides with sulfuric acid. These, however, separated upon heating. The acids and alcohols were prepared but not separated as such. The crude acids and alcohols were converted into their corresponding twenty-carbon esters which were then purified by fractional distillation. The esters had small boiling point ranges which indicated high purity. All esters were colorless and odorless except n-nonadecyl methanoate which had the odor of formic acid. The n-nonadecyl methanoate recovered from the urea adduct, however, was also colorless and odorless.

The adducts formed immediately upon addition of the esters to the saturated solution of urea in methanol, and decomposed readily with the addition of water to the isolated solids. They were white crystals, showing typical hexagonal characteristics when observed through a microscope.

It was noticed that only about 80 percent of each ester was recovered after decomposition of the adduct, indicating incomplete adduction of the esters. No significant difference in either the formation or decomposition

of the adduct, indicating incomplete adduction of the esters. No significant difference in either the formation or decomposition of the adducts was observed, an indication of relatively equal ability to form adducts and relatively equal stability of the adducts towards hydrolytic decomposition.

CORRELATION OF RESULTS

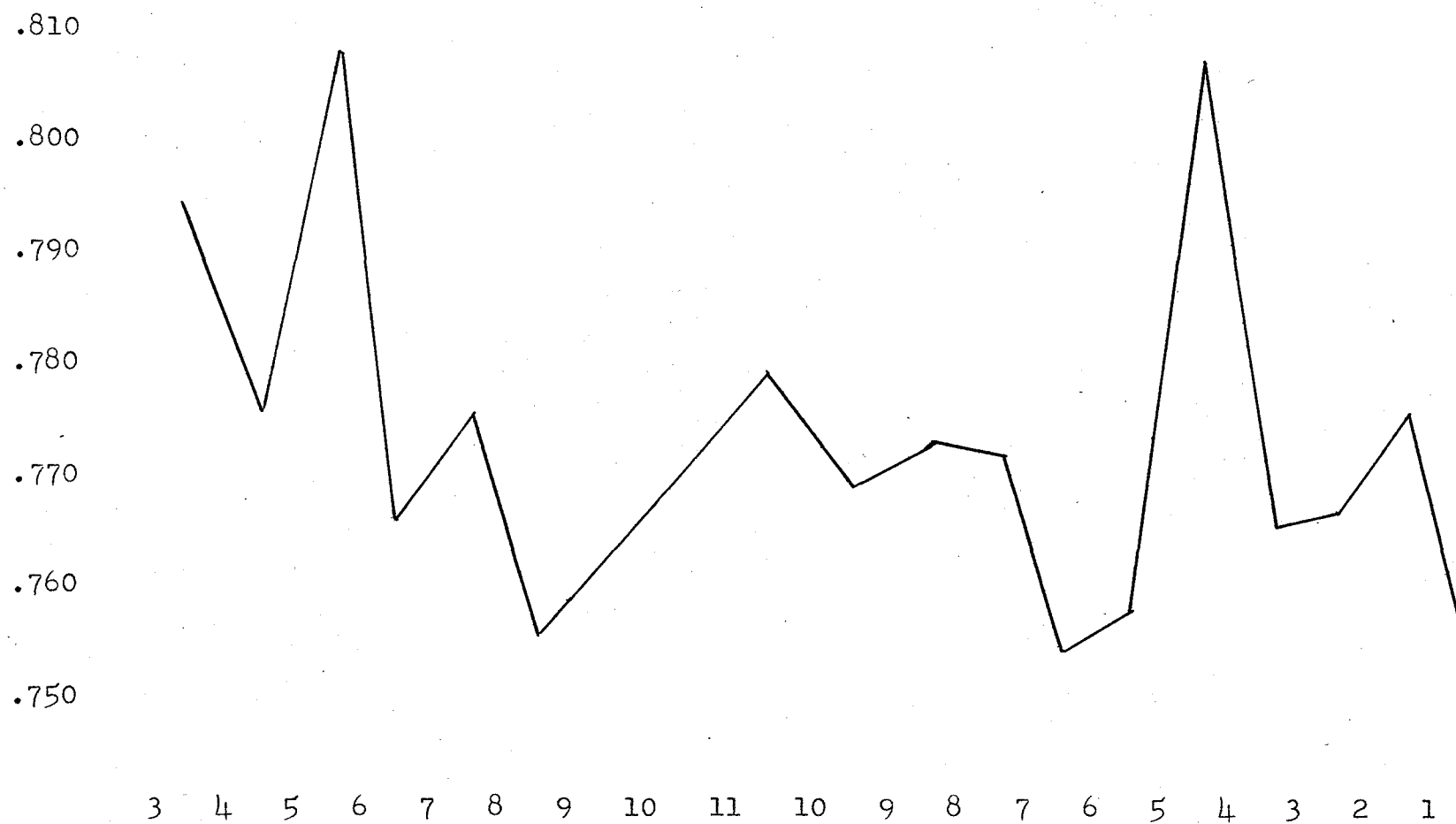
The results of this research show a mean ratio of 0.778 moles of urea per chain atom of ester if the ester chain length is taken as twenty-one atoms. This value, calculated using twenty-one atoms as the chain length, should be preferred over the value calculated using twenty atoms as pointed out by Johnson (Johnson, 1953). Calculations performed by Johnson show that the average value of this research and the average value of Johnson's research (0.770 moles of urea per chain atom of ester) agree very well with values recorded in the literature for similar compounds.

The values for the complete series are plotted in Figure 1 against the position of the carbonyl oxygen. The numbers along the abscissa represent the number of atoms from the end of the chain to the carbon containing the carbonyl oxygen. This plot shows a "W" shaped curve with peaks at points at which the carbonyl group is at the center of the chain and five atoms removed from the end.

This curve is similar to curves obtained from plotting melting points of an ester series against the position of the carbonyl group (Ralston, 1948). A high melting point is evident when the carbonyl group is in the center of the chain and at the ends of the chain. The wide range of melting points illustrates the effect of a small change of

FIGURE 1

MOLES OF UREA PER CHAIN ATOM VS. POSITION OF CARBONYL GROUP



structure. Certainly those esters which are most symmetrical will have a close packed crystal structure and therefore a higher melting point than those esters which are not symmetrical.

As can be seen from Figure 1, a small change in the structure of the ester gives a fairly large change in the number of moles of urea which combine with the ester to form the adduct. The largest difference amounts to 1.13 moles of urea to one mole of ester (Table I). This difference is outside the limits of error and appears to indicate that each ester combines with its own characteristic number of moles of urea in the adducts as each ester has its own characteristic melting point.

Since the structure of the ester appears to influence the number of moles of urea (adduct value) with which it can combine to form the adduct, then the adduct value of each ester is unique and the average adduct value for the series has no meaning except for comparison with average adduct values of other series. An average of melting points of a series of esters has no meaning except for comparison with the average melting point of another series of esters, so possibly esters can be identified not only by their melting points but also by their adduct values.

If more information were available on the urea adducts of ester series it would be possible to determine the validity of the last two paragraphs, and possibly other

series of compounds such as ketones or ethers might show the same sort of variance of adduct value with change in structure.

SUMMARY

A series of normal twenty-carbon esters was prepared from odd carbon alcohols and odd carbon acids. An urea adduct of each ester was prepared, isolated, and separated into three approximately equal weighed portions. Each portion was decomposed and the liberated esters were isolated and weighed.

From the weight of the urea adduct and the weight of the isolated ester in each case the mole ratio of urea to ester was calculated. The ratio of urea to carbon atom was determined and compared with previously determined values for similar compounds.

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