slightly poorer in color of bodied oil, faster drying, harder, stronger, and perhaps somewhat tougher than the bodied alkali refined oil. In addition, the synthetic oil shows remarkable alkali resistance in varnishes; moreover, the results obtained on film solubility would indicate that the synthetic oil had broken down or decomposed to a much lesser extent on exposure than the alkali refined oil. Table 7 shows significant differences between the two oils. In other respects, the oils can be considered similar. It can easily be seen that the synthetic oil has definite advantages over the natural oil and in this case would be seriously considered for general use.

The evaluation program outlined above is subject to considerable change and modification as our experience and knowledge of oils increase. In addition, it is hoped that it may be expanded to give information to fields other than the protective coating, such as printing inks, patent leather, core binders, linoleum, etc. The value of conducting such a study becomes more apparent after a large number of oils have been so tested and the information collected and examined. It would be extremely useful to the consumer if the industry could standardize on an evaluation program and have available information on the various oils in a standard and uniform manner. Perhaps, this would not be practical at present, but it is presented as an idea for discussion.

Acknowledgment

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REFERENCES

1. West, Hoagland, and Curtis, J. Biol. Chem. *104*, 627 (1934).
2. B. A. Ellis and R. A. Jones, Analyst *61*, 812 (1936).
3. National Paint, Varnish, and Lacquer Association S.S.C. 546, 1937.
4. National Paint, Varnish, and Lacquer Association S.S.C. 520, 1936.

Vapor Phase Dehydrochlorination of Chlorinated Fatty Substances

I. Investigation of Removal of Hydrogen Chloride from Dichlorinated Palmitic Acids*

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Introduction

WARTIME curtailment of imported soap and paint oils prompted this inquiry into possible methods for desaturating long-chain fatty acids. Considerable advance has been made in the past decade in commercial development of derivatives formed by operations on the carboxyl groups (1). Corresponding methods of modifying the comparatively inert alkyl portion of these acids have not been as satisfactorily developed. Among the agents that react with the alkyl chains, the halogens, and more particularly chlorine, appeared to provide the best means for obtaining suitable intermediate derivatives. Partial chlorination of a single saturated fatty acid, such as palmitic, yields a mixture of products of differing degrees of chlorination with chlorine atoms at various chain positions. Subsequent removal of chlorine as hydrogen chloride presents the possibility of forming unsaturated acids that might be commercially useful or could be made so by isomerization.

Reported treatments for removal or replacement of chlorine may be grouped in two classes: a) Hydrolytic processes tending to give differing proportions of hydroxylation and unsaturation in the products, and b) thermal or catalytic dehydrochlorination under acid conditions.

Hydrolytic processes have commonly been utilized at atmospheric or superatmospheric pressures (2, 3, 4, 5, 6) at times in the presence of organic solutions of ammonia (7) or of solutions of sulfides or polysulfides (8). Treatment of salts of chlorinated acids in steam at temperatures above their melting points for formation of soaps of unsaturated acids has been recently patented (9). Thermal dehydrochlorination of chlorinated oils, according to Gardner and Bielous (10, 11) resulted in oils of increased drying properties. Approximately one half of the chlorine was removed by heating chlorinated oils containing between 5 and 12% of chlorine to 220-250° C. at atmospheric pressure in the presence of coppered-zinc. This catalyst was believed to aid in the production of polymerized compounds. Meunier and Wierzchowski (12) commented on the partial loss of hydrogen chloride when chlorinated oils were heated above 100° C. Scheiber (13) added chlorine to unsaturated oils and subsequently desaturated the chlorinated materials by heating in the presence of metallic zinc. Enhanced drying properties were claimed for the products. Vanin and Chernoyarova (14) added hydrogen chloride to oleic and petroselinic acids and obtained isomeric monounsaturated acids as the result of heating the chlorinated materials with nickel carbonate at 190-210° C. for three hours. The passage of chlorinated acids or esters, together with an alcohol or ether, over a heated solid catalyst is reported by Andrussow and Stein (15) to yield unsaturated compounds and alkyl halides.

In many of these earlier investigations a considerable proportion of chlorine remained in the final product. Investigations in this laboratory have shown that hydrogen chloride is readily removed from vaporized chlorinated fatty acids on passage at reduced

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pressure through a catalyst-packed heated reaction tube. The results reported in this paper show some of the effects which catalyst, pressure, temperature, and other factors have upon the extent of desaturation and the type of product obtained from dichlorinated palmitic acid. A second paper will present results obtained from experiments with a limited number of other chlorinated fatty materials and will discuss briefly the possible utility of products of the process.

The use of reduced pressure and maintenance of the vapor phase are factors which minimize side reactions and greatly accelerate dehydrochlorination. Crude desaturated products that are pale in color and contain but little chlorine can be obtained by the vapor-phase treatment.

Dehydrochlorinations at Atmospheric and at 30 mm. Pressures

Exploratory investigations involved removal of hydrogen chloride from liquid samples of mixed acids obtained by directly chlorinating palmitic acid until the resulting product contained about 21% of combined chlorine. This amount of chlorine corresponds to about two equivalents per mole of acid. To avoid confusing it with definite dichloro-compounds such a mixture is designated here as dichlorinated palmitic acid.

The samples were heated to about 200° C. in flasks swept continuously with nitrogen to remove gaseous products. The acids darkened rapidly under these conditions, and the rate of hydrogen chloride evolution decreased progressively to very low values. The charges lost about one-half their combined chlorine as hydrogen chloride in 8 hours and but little more in 15 hours of treatment.

In order to attempt more rapid and complete dehydrochlorination than was possible at atmospheric pressure, experiments were performed in which the chlorinated acids were passed through heated tubes at about 30 mm. pressure. Several arrangements of apparatus were employed for the purpose. In each a straight tube, either inclined or vertical, served as both reaction chamber and cooler. Tubes of glass, porcelain, and stainless-steel were used. The upper sections were heated by tubular furnace elements and the lower sections were cooled either by the atmosphere or by a water jacket. Water-jet aspirators were employed to maintain reduced pressure during operation. Temperatures were measured by means of thermocouples. Chlorinated material was fed at controlled rates into the upper ends of the tubes from whence it passed first through the hot and then through the cold section to a receiver.

At 30 mm. the chlorinated acid used was vaporized completely in the neighborhood of 250° C. Treatment temperatures applied covered the interval from 100-525° C. Duration of heating as governed by feed rate was also varied over a considerable range.

In the earlier experiments at reduced pressure, the feed material at temperatures below its boiling range was allowed to flow in a thin film through an unpacked tube. Very little dehydrochlorination resulted from this type of treatment. It was found, however, that if the temperature of the heated zone was raised enough to cause the chlorinated acid to completely vaporize, the product which was obtained as a condensate was desaturated to a significant degree. Dehydrochlorination was promoted still more if the vaporized material passed through packings of granular charcoal, clay shards, or stainless-steel strips. Thus, when a stainless-steel tube packed with twisted strips of the same metal was used at 275° C., a product resulted which contained 2.8% residual chlorine. When the temperature was raised to 525° C. the product contained only 0.8% of chlorine. In these instances times of treatment calculated from the length of the heated, packed zone and the estimated vapor velocities, were approximately 1 to 2 seconds.

Although vapor-phase treatment at 30 mm. appeared to be satisfactory from the standpoint of speed and completeness of dehydrochlorination, the process possessed serious disadvantages, owing to rapid formation of dark polymers in the liquid product and on all surfaces within the heated section of the tube. At the instant of condensation the products were clear, pale liquids, but immediately thereafter they began to darken with the result that often within a few minutes their color became almost black. Being non-volatile, the polymers that formed on the heated surfaces of the tube and packing accumulated there as a viscous black liquid. With continued heating this changed to a coke-like solid which eventually closed the passages through the packed zone. This severely limited the quantity of chlorinated acid that could be treated before it became necessary to clean the apparatus, and it also prevented comparison of specific catalytic effects of different substances.

By distilling the crude products at pressures of 1-2 mm. it was possible to obtain desaturated materials which were clear, pale, and color stable, but the polymers which remained as distillation residues together with those deposited in the reaction chamber often amounted to as much as 25% of the theoretical yield of product.

It was discovered that polymerization of the desaturated products is catalyzed by aqueous solutions of strong acids as well as by anhydrous hydrogen chloride gas, the apparent speed of the reaction being dependent upon concentration and/or pressure of the acid. This explained the fact that color stable desaturated materials were obtained by distilling the crude products at low pressure. Thus, at hydrogen chloride pressures of about 2 mm. or less polymerization was so slow that perceptible darkening of the distilled products did not occur at room temperature with several hours' exposure to the gas. As the pressure of hydrogen chloride was raised, however, polymerization was accelerated until at 30 mm. it apparently proceeded at the same rate and with the same effect as when the crude product was prepared at that pressure.

Dehydrochlorinations at Pressures Below 5 mm.

It was expected that lowering the hydrogen chloride pressure during dehydrochlorination would retard formation and deposition of polymers in the reaction chamber as well as in the condensed liquid product. Under this circumstance it would be possible to compare catalytic effects of different substances upon the speed and completeness of dehydrochlorination. Accordingly a series of experiments was conducted for the purpose of finding a suitable solid catalyst for vapor-phase dehydrochlorination.

Palmitic acid used for chlorination and subsequent dehydrochlorination was prepared by careful fractionation of the methyl esters of a commercial acid (Neofat No. 1-56). The purified acid had a neutralization equivalent of 256-7 in different preparations (theory 256.4) and a Wijs iodine value of less than one.

Chlorinations were performed on the molten acid at temperatures not over 70° C. Gaseous chlorine was introduced directly into the acid until control analysis showed approximately two equivalents of chlorine had been substituted per equivalent of acid. This degree of chlorination was the lowest that would yield a reasonably small proportion (roughly 10%) of unchanged palmitic acid in the chlorinated product.

Small quantities of hydrogen chloride remaining in the reaction mixture were removed by repeatedly drawing the warmed chlorinated product through a sintered-glass suction filter. Combined chlorine in different preparations varied from 21-23%. Dichloropalmitic acid contains 21.80% chlorine.

The chlorinated material comprised mono-, di-, and poly-chlorinated acids, together with some unchanged palmitic acid. The latter component tended to crystallize from the mixture at room temperature. A stock lot of chlorinated acid for use in the catalyst trials and later experiments was obtained by combining a number of separate preparations. This stock acid contained 22.6% of combined chlorine.

The dehydrochlorinator used in the catalyst trials is shown in Figure 1. A vacuum pump having a capacity of 19 liters of free air per minute was used with the apparatus. If even small amounts of desaturated product vapors should reach the pump they would be trapped in the lubricating oil where, on the exhaust side, they would be subjected to the influence of hydrogen chloride at atmospheric pressure and be deposited as varnish-like polymers, which would "freeze" the pump. To prevent this the gases leaving the dehydrochlorinator were scrubbed by passing them through pumice-packed sulfuric acid towers before they entered the pump.

Because of the small size of the dehydrochlorinator and the limited capacity of the pump it was possible to feed the chlorinated acid at only about 3 grams per hour. During these trials the oil-bath temperature was maintained at 220° C. and the pressure in the condenser at slightly less than 1 mm. In each experiment the length of the catalyst column was approximately 5.5 cm. Granules of pumice (2-3 mm. in dimensions) were used to support the trial catalysts except in the few instances where a support was unnecessary. Wijs iodine values of the condensed products were taken as comparative measures of desaturation.

Table 1 presents the results of some of the catalyst trials. Substances tried as catalysts but not reported in the table included V_2O_5, ThO_2, Cr_2O_3, TiO_2, CeO_2, WO_3, $AgVO_3$, UO_2, and UO_3. Under the conditions of the experiments none of these materials were as active as the cobalt compounds listed in the table.

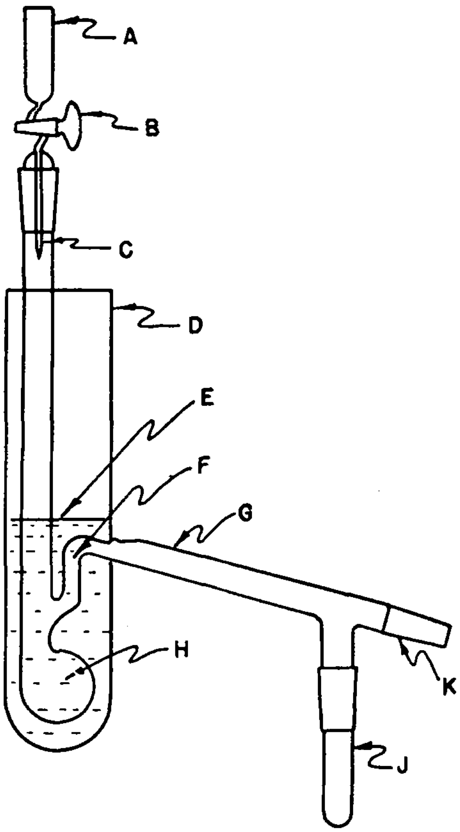

FIG. 1. Diagram of small dehydrochlorinator used in catalyst experiments.

A. Feed reservoir
B. Stopcock with filed plug
C. Capillary tube
D. Oil bath tube 70 mm. O. D. ×30 cm.
E. Oil level
F. Catalyst chamber 12 mm. O. D. × 40 mm.
G. Condenser
H. 50-ml. bulb
J. Product receiver
K. Connection to vacuum system

TABLE I.

Tests of Various Substances as Dehydrochlorination Catalysts for Dichlorinated Palmitic Acid at 220° C. and 1 mm. Pressure.

Trial Catalyst	Support	Wijs Iodine Value of Product
None	None	3.1
Glass wool	None	6.6
Granular Pumice	None	23.6
Carbon-steel Wool	None	44.5
18-8 Stainless-steel Wool	None	81.1
Fe_2O_3	Granular Pumice	56.8
NiO_2	Granular Pumice	61.2
Co_3O_4	Granular Pumice	106.0
$CoCl_2$	Granular Pumice	128.0
$Co_3(PO_4)_2$	Granular Pumice	135.7

The catalyst trials were little more than exploratory, but their outcome afforded a basis for selecting anhydrous cobalt chloride supported on granular pumice for use in further dehydrochlorination experiments. This material had the advantages of simple preparation and fair ruggedness as well as high and reproducible activity. In its preparation screened pumice was immersed for 5 minutes in a stirred, boiling solution made up of 182 grams of $CoCl_2 \cdot 6H_2O$ and 100 ml. of water. Then, after draining, the granules were spread on trays and dried in an oven at 130° C. The finished preparations contained 22-26% of $CoCl_2$ by weight.

In order to conduct dehydrochlorinations on a scale larger than was possible with the equipment used in the catalyst trials the larger apparatus shown in Figures 2 and 3 was constructed.

The feed device, details of which could not be shown clearly in the figures, included a pair of 10 ml. hypodermic syringes driven from heart-shaped cams for uniform speed of fill and delivery, two consecutive speed reducing gears connected by suitable pulleys and belts, a variable-speed friction drive, and an electric motor. A 4-way stopcock permitted alternate delivery from the syringes which were connected so that one filled while the other emptied. Electric heat-

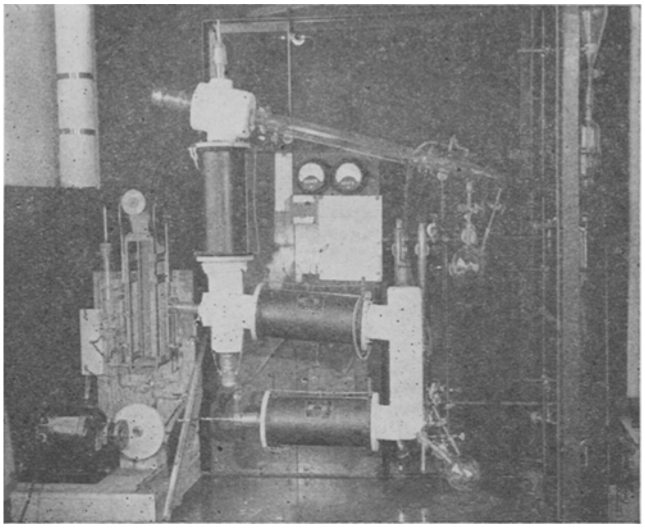

FIG. 2. Large dehydrochlorinator.

ing elements wound on the feed reservoir and connecting tubes warmed the feed material slightly and prevented partial crystallization.

All electric heating elements were controlled by variable voltage autotransformers. Thermocouple wells in all heated tube sections permitted temperature measurements throughout their length.

A vacuum pump having a displacement of 26.2 cu. ft. per minute was used to maintain the desired pressures. Two Dubrovin-type gauges (16) connected to the evaporator and condenser sections continuously indicated pressures within these parts.

The capacity of this dehydrochlorinator was about 0.5 g. of dichlorinated palmitic acid per minute. The explanation for what might appear to be the small capacity of the apparatus relative to its size is found in the velocities attained by the attenuated vapors in the system during operation. The following data from a typical run in which dichlorinated palmitic acid was fed at the rate of 0.5 g. per minute will illustrate this point. During the run the temperature in the catalyst chamber was 250° C. while the pressure was 0.25 mm. in the condenser and 1.15 mm. in the evaporator. The estimated linear velocity of the feed vapor just entering the catalyst packed zone was about 200 cm. per second while that of the product vapors just before leaving the catalyst was about 2700 cm. per second. The pressure differential due to frictional resistance rises with vapor velocity and reaches a practical limit at only a few millimeters since at higher pressures polymer depostion in the evaporator and catalyst chamber becomes excessive. The mixed vapors of condensable fatty acid and noncondensable hydrogen chloride entering the condenser lose velocity as they are cooled, and the former becomes liquid, but if the issuing hydrogen chloride is moving at too high a speed the organic product tends to form a fog which is carried out of the system with the gas. Losses due to this cause began to be detectable when dichlorinated acid was fed at rates greater than 0.5 g. per minute.

The first trials with the larger dehydrochlorinator disclosed that although pale, clear desaturated products could be readily obtained polymers tended to form on the catalyst surfaces even at pressures as low as 1 mm. This tendency had escaped detection during the catalyst trials possibly because those experiments were of relatively short duration and polymer formation was much less rapid than it had been in the previous experiments at 30 mm.

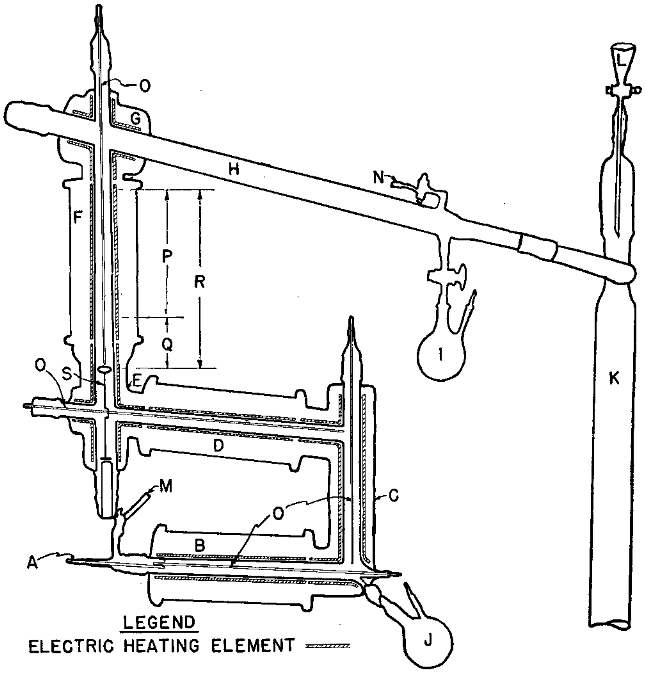

FIG. 3. Diagram showing construction of large dehydrochlorinator.

A. Capillary feed inlet
B. Evaporator
C, D, and E. Heated sections for evaporation of entrained spray
F. Reaction section
G. Product vapor heater
H. Condenser
I. Product receiver
J. Drainage trap
K. Scrubber packed with pumice
L. Sulfuric acid supply
M and N. Connections to low-pressure manometers
O. Thermocouple wells
P. Section of reaction chamber packed with $CoCl_2$-pumice catalyst (26.5 cm.)
Q. Section packed with stainless-steel screen (10.5 cm.)
R. Total length of catalyst column (37 cm.)
S. Catalyst rest

Soon after a run was started in the large apparatus, dark-colored polymers would begin to appear on the surface of the catalyst at the bottom of the column. As the run continued, the layer of polymer thickened and its boundary slowly moved upward until after about 4 hours of use the surface of the catalyst was discolored for a distance of about 11 cm. By this time the catalyst pieces in the bottom 3 cm. of the column would be cemented together with a thin hard layer of coke which noticeably impeded gas flow. The freshly deposited polymer appeared to be a liquid which hardened with continued heating. Appearances suggested that local cooling and condensation may take place at the catalyst surface because of the endothermic nature of the dehydrochlorination reaction and poor transfer of heat through the catalyst. Evidently, even at very low pressures, hydrogen chloride can cause the liquefied desaturated materials to polymerize almost instantaneously at the temperatures prevailing in the reaction chamber.

An expedient was adopted, which, while it did not eliminate polymer formation in the reaction chamber, somewhat lessened the problem it presented and enabled completion of the remainder of the dehydrochlorination experiments. U-shaped bits of punched stainless-steel screen were substituted for $CoCl_2$-pumice catalyst in the lower 10.5 cm. of the reaction chamber as indicated in Figure 3. The open structure

TABLE II.

Low-Pressure Dehydrochlorinations of Dichlorinated Palmitic Acid.

Experiment Number	Feed Rate	Pressure		Temperature		Chlorine in Product	Feed Weight	Product Weight	Product Recovered
		Evaporator	Condenser	Evaporator	Reaction Chamber				
	(*g./min.*)	(*mm. Hg*)	(*mm. Hg*)	(°*C.*)	(°*C.*)	(%)	(*g.*)	(*g.*)	(*% of Theory*)
7[1]	0.5	2.4	0.7	350	315	2.87	177.8	119.2	84.75
8	0.5	1.6	0.9	300	295	3.03	71.9	55.6	97.6
9	0.5	1.7	1.3	230	290	3.80	32.5	25.7	99.2
10	0.5	4.0	3.2	280	270	3.30	142.6	108.0	96.7
11(a)[2]	0.5	1.15	0.25	270	250	2.90	....	14.7	....
11(b)[2]	0.9	1.6	0.9	270	250	4.70	....	104.4	....
11(a)+(b)	....	....	....	....	....	4.45	150.7	119.1	98.4
12	0.5	1.15	0.25	285	260	3.80	145.4	114.6	98.6
13[3]	0.5	1.15	0.5	285	275	7.03	183.8	148.6	98.0
14	0.5	1.5	0.5	284	275	3.15	178.4	138.3	97.8
16[4]	0.5	1.8	0.3	275	275	2.40	141.7	108.5	97.2

[1] $CoCl_2$-pumice catalyst used alone in this run. Length of catalyst column was 26 cm. In other experiments recorded catalyst columns were comprised of 10.5 cm. of stainless-steel screen packing surmounted by 26.5 cm. of $CoCl_2$-pumice.

[2] Products from different feed rates collected separately.

[3] Catalyst used in this run had been used previously in Experiment 12.

[4] Pumice used for preparing catalyst was digested in HCl, washed free of acid and dried before impregnation with $CoCl_2$.

of this weak catalyst permitted runs of reasonable duration without excessive accumulation of polymers. The dimensions of the granules of $CoCl_2$-pumice catalyst used to fill the upper 26.5 cm. of the reaction chamber were 9-11 mm. Records of some of the experiments with dichlorinated palmitic acid conducted with the large dehydrochlorinator are summarized in Table II.

Interdependence of such factors as pressure, temperature, polymer formation, age and activity of catalyst prevented conduct of ideal experiments in which influences of single variables could be compared at will. Thus, in Experiment 11 two feed rates were employed with the result that the product obtained at the higher rate contained the most chlorine. How much of this difference is due to difference in contact time and how much to loss of catalyst activity with use (polymer accumulation) is uncertain. The pertinence of this question is brought out by the results of Experiments 12 and 13 in which one catalyst charge was used for two trials. Here the loss of catalyst activity with use is plainly indicated.

It is interesting to note that overall reaction or "contact" time was about 0.11 second if calculated from the estimated linear velocity of the gas entering the catalyst zone in a typical experiment and only about 0.01 second if calculated from the exit velocity of the product gases.

From a general standpoint best results were obtained when the operating pressure was not above about 2 mm. and the temperature was between 250 and 300° C. Some experiments (results of which are not included in the tables) had to be stopped because liquid polymers were deposited on the catalyst at excessive rates when the reaction temperatures were below 250° C.

All of the desaturated products obtained from the low pressure treatments were clear, pale orange-colored liquids at slightly above room temperature. At room temperature they partially crystallized. They showed no tendency to discolor with age when protected from oxygen and mineral acids.

Composition of Dehydrochlorination Products

The dehydrochlorinated products from these experiments would be expected to contain acids of various degrees of unsaturation, isomeric unsaturated acids and some palmitic acid that had escaped chlorination. Any residual combined chlorine present would further increase the variety of substances in the products. Upon examination the products were found to contain small quantities of unsaponifiables and somewhat larger amounts of neutral but saponifiable materials. These latter were subsequently identified as γ-lactones. Because of their complexity, complete resolution of the products into individual components was not attempted. Results of quantitative analyses performed on several representative products are shown in Table III.

TABLE III.

Analyses of Dehydrochlorinated Products Obtained by Low-pressure Treatment of Dichlorinated Palmitic Acid.

Characteristics	Experiment Number			
	10	12	14	16
Chlorine, %	3.3	3.8	3.1	2.4
Unsaponifiable, %	2.7	2.2	2.0	1.7
Neutralization equivalent, unsaponifiable-free fraction	323.9	333.0	336.2	329.0
Saponification equivalent, unsaponifiable-free fraction	260.9	268.0	267.6	260.5
γ-lactones (by calculation), %	19.4	19.1	20.0	20.5
γ-lactones (by recovery), %	20.0	......	......	......
Total free acids (by difference), %	77.9	78.7	78.0	77.8
Total free acids (by recovery), %	75.9	......	......	......
Saturated acid (palmitic), %	8.0	......	......	6.1
Iodine Value (Total unsaturation by H_2)[1]	......	......	......	179.2
Iodine Value (Wijs)	138.8	120.0	124.5	132.9
Iodine Value, recovered free acids (Wijs)	142.8	......	......	......
Iodine Value, recovered γ-lactones (Wijs)	115.6	......	......	......
Iodine Value, recovered unsaponifiables (Wijs)	148.5	......	......	......
Spectrophotometric Determinations				
(Conjugated unsaturation expressed as C_{16} acids)[2]				
Dienoic acids, %	......	......	......	16.1
Trienoic acids, %	......	......	......	1.3
Tetraenoic acids, %	......	......	......	.2

[1] With complete dehydrochlorination and formation of no lactones the total unsaturation possible in these products would have equalled an iodine value of 210.8.

[2] Calculations were based on constants given by Brice *et al.* (21).

The method used for determining chlorine was substantially the same as that described by Baubigny and Chavanne (17).

Determination of equivalent weight by saponification required a correction for chlorine hydrolyzed during treatment with alkali. The correction was determined by acidifying the saponification mixture after titration, extracting the organic material with a mixture of diethyl and petroleum ethers, and determining chloride in the aqueous solution argentometrically.

Neutral and saponification equivalents of the unsaponifiable-free portions of the products were calculated by applying corrections for the amounts of unsaponifiables present. From the values corrected for unsaponifiables and hydrolyzed chlorine the quantities of free acids and γ-lactones (neutral saponifiables) were calculated. These calculations are doubtless in slight error since they assume that the free acids and γ-lactones concerned have the same equivalent weight.

Separation and recovery of γ-lactones for examination was accomplished by extracting them with organic solvents from soap solutions formed by carefully neutralizing the free acids in the unsaponifiable-free materials. Bertram's method (18) was used for determining saturated (palmitic) acid. These results are probably in slight error since trial has shown that high values are obtained when chlorinated acids are present.

Total unsaturation expressed in iodine value units was measured by hydrogenation using the apparatus described by Noller and Barusch (19).

Wijs iodine values were determined by the regular 30 minute procedure. The differences between these values and those given by hydrogenation reflected the presence of conjugated double bonds and possibly unsaturation too close to the carboxyl group to be fully saturated by the Wijs reagent. Qualitative tests with tetranitromethane indicated presence of conjugated unsaturation in the products and this was supported by spectrophotometric analysis. The proportions of conjugated unsaturation in the product from Experiment 16, shown in Table III, were calculated with the aid of the constants and by the method of Brice *et al.* (21). It is believed desirable, for the present, to regard these results as no more than approximations, for the reason that the absorptive characteristics of the particular substances present in dehydrochlorinated products are not fully known.

Identification of the main constituents of the neutral saponifiable fraction in the products as a mixture of saturated and unsaturated sixteen carbon γ-lactones was accomplished as follows:

A sample of the neutral saponifiable material having an iodine value of 116 was catalytically reduced with hydrogen to give a product having an iodine value of 3.4. A 4.8 g. portion of the reduced material was separated into four composite fractions by saponification, extraction, and acidification, followed by fractional crystallization. In the light of subsequent identification of the principal constituents the fractions were classified as:

1. Neutral material	0.35 g.
2. γ-lactone	1.7 g.
3. Hydroxy acid	1.75 g.
4. Mixtures of 2 and 3	0.45 g.
Total	4.25 or 88.5% recovery

Fraction 3 melting at 77.6-77.8° C. gave a melting point of 78.8-79.1° C. when mixed with synthetic γ-hydroxypalmitic acid (22) melting at 79.0-79.6° C. The neutralization equivalent of the fraction was 273.0; calculated for hydroxypalmitic acid, 272.4.

Conversion of the material to γ-palmitolactone was effected by refluxing with 15% HCl (23) and crystallizing from acetone. The resulting lactone melted at 41.2-41.7° C. alone and at 41.1-41.5° C. when mixed with synthetic lactone melting at the latter temperature.

Transformation of a portion of fraction 2 into the hydroxy acid by Clutterbuck's method (23) gave a product melting at 80.2-80.7° C. Mixed with synthetic γ-hydroxypalmitic acid it showed no depression in melting point.

The ready interconversion of the lactone and the corresponding acid, together with their individual stabilities under usual laboratory conditions, explains the occurrence of both products in the fraction separated after saponification and acidification.

Investigation of the positions of unsaturation in the dehydrochlorination products was limited to a qualitative study of the monounsaturated acids.

The materials examined were three composite fractions of saturated and monounsaturated acids obtained by fractional distillation and crystallization from a dehydrochlorination product previously freed of unsaponifiables and lactones. After conversion to methyl esters, the fractions had iodine values of 12.1, 57.5, and 95.5. The last, which under the conditions of separation could have contained no saturated acid, contained a very minor amount of diunsaturates (theoretical iodine value for methyl hexadecenoate is 94.6).

The method employed was based on the procedure developed by Armstrong and Hilditch (24) which involves oxidation of the esters with potassium permanganate and segregation of the oxidation products. Location of the double bonds was by identification of the dibasic acids produced. When applied to pure acids the method, as modified for the present study, is capable of yielding dibasic products of 6 or more carbon atoms which were recovered in 80% or more of theoretical amounts (25). For dibasic oxidation fragments of lower molecular weight the yields are less, and under the conditions employed, oxalic and probably malonic acids, if produced, would be destroyed.

Identification of the dibasic acids was by melting points and equivalent weights. In most instances findings were verified by melting points of mixtures with authentic samples of the acids.

Dibasic acids containing 6, 7, 8, 9, 10, 12, 13, and 14 carbon atoms were identified in the oxidation products. The presence of C_{11} and C_{15} acids was indicated but not proven. Evidence concerning the presence of glutaric (C_5) acid was inconclusive. These results are taken to indicate that unsaturation occurs at essentially all possible positions in the monounsaturated acid fraction of the products.

Summary

Dichlorinated palmitic acid was catalytically dehydrochlorinated rapidly and nearly completely in the vapor phase at low pressures and at temperatures of 220-315° C. Polymerization of the liquid desaturated material is catalyzed by strong acids. This was prevented from occurring in the recovered products, which were clear and pale in color, by maintaining the pressure of hydrogen chloride liberated in the reaction at less than 2 mm. However, some non-volatile polymers were formed in the process and deposited on the surface of the solid catalyst, thus lowering its activity and shortening its period of usefulness.

The desaturated products of the process contained about 20 per cent of γ-lactones and some conjugated unsaturation.

REFERENCES

1. Ralston, A. W., Chemical & Engineering News *21*, 3 (1943).
2. Colbeth, I. M., U. S. Patent 2,270,856 (1942).
3. I. G. Farbenindustrie, Akt. Ges., British Patent 340,011 (1929), French Patent 687,752 (1930).
4. Prutton, C. F., U. S. Patent 2,272,923 (1942).
5. Stiepel, C., British Patent 272,198 (1926).
6. Tanaka, Yoshio, and Nakana, Yunei, Japanese Patent 111,210 (1935) from Chem. Absts. *30*, 2146 (1936).
7. I. G. Farbenindustrie, Akt. Ges., British Patent 339,675 (1929), German Patent 539,180 (1929), French Patent 687,865 (1930).
8. I. G. Farbenindustrie, Akt. Ges., German Patent 539,449 (1929), British Patent 340,012 (1929), French Patent 696,560 (1930).
9. Dreger, E. E., Ross, J., and Kirschenbauer, H. G., U. S. Patent 2,279,943 (1942).
10. Gardner, H. A., U. S. Patent 1,452,553 (1923).
11. Gardner, H. A., and Bielous, E., Ind. Eng. Chem. *14*, 619 (1922).
12. Meunier, L., and Wierzchowski, Z., Collegium, 610 (1914).
13. Scheiber, J., British Patent 316,872 (1930).
14. Vanin, I. I., and Chernoyarova, A. A., J. Gen. Chem. U.S.S.R., *5*, 1537 (1935), from Chem. Absts., *30*, 2173 (1936).
15. Andrussow, L., and Stein, G., U. S. Patent 2,210,564 (1940).
16. Germann, F. E. E., and Gagos, K. A., Ind. Eng. Chem., Anal. Ed., *15*, 285 (1943).
17. Baubigny, H., and Chavanne, G., Compt. rend., *136*, 1197 (1903).
18. Bertram, S. H., Zeit. f. Untersuch, Lebensm. *55*, 179 (1928).
19. Noller, C. R., and Barusch, M. R., Ind. Eng. Chem., Anal. Ed., *14*, 907 (1942).
20. Kaufmann, H. P., and Kirsch, P., Fette u. Seifen *50*, 314 (1943).
21. Brice, B. A., Swain, M. L., Schaefer, B. B., and Ault, W. C., Oil and Soap, *22*, 219 (1945).
22. Houston, D. F., Material prepared for publication in Jour. Amer. Chem. Soc.
23. Clutterbuck, P. W., J. Chem. Soc., 2330 (1924).
24. Armstrong, E. F., and Hilditch, T. P., J. Soc. Chem. Ind. *44*, 43T (1925).
25. Houston, D. F. Manuscript in preparation.

Analysis of Mixtures of Glycerol, Propylene Glycol, and Trimethylene Glycol*

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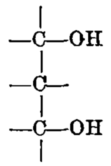
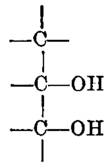
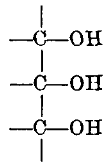
THE analysis of mixtures of glycerol, propylene glycol, and trimethylene glycol is difficult because of the close similarity between these compounds, the structures of which are indicated below:


Trimethylene Glycol


Propylene Glycol


Glycerol

These compounds may be found together in certain fractions from glycerin refining such as sweet water concentrate. Sweet water concentrate is an important source of trimethylene glycol. Neither the dichromate method (1), which oxidizes all organic compounds, nor the acetin method (2), in which acetic anhydride reacts with the hydroxyl group, nor a combination of these will give much information about the composition. However, there are now available other methods in which the reactions are more specific than those formerly used. These reactions were utilized in this study.

Glycerol can be determined by the periodic acid method (3) and this method in combination with the dichromate or acetin methods will give an approximation of the total trimethylene glycol and propylene glycol. A more exact evaluation can be obtained by taking advantage of the specific and selective action of periodic acid on polyhydric alcohols and using this in combination with an accurate method for the determination of total acetylatable material which is described herein.

Procedures making use of the special properties of periodic acid have been applied to mixtures of glycerol, ethylene glycol, and diethylene glycol (6), glycerol, ethylene glycol, and propylene glycol (7, 8).

Periodic acid oxidizes glycerol to formic acid and aldehydes, and propylene glycol only to aldehydes. It does not react with trimethylene glycol. The glycerol is thus determined by titration of the formic acid obtained from such an oxidation. Propylene glycol may then be calculated from the total periodic acid consumed in the reaction less that required to oxidize the glycerol.

$$CH_2OH{-}CHOH{-}CH_2OH + 2H_5IO_6 \rightarrow 2HCHO + HCOOH + 2HIO_3 + 5H_2O$$

$$CH_2OH{-}CHOH{-}CH_3 + H_5IO_6 \rightarrow HCHO + CH_3{-}CHO + HIO_3 + 3H_2O$$

Knowing the percentages of glycerol and propylene glycol, the trimethylene glycol can be calculated after determining the total acetylatable material. A series of analyses were performed on samples of known composition using these reactions with modifications of previous procedures for glycerol (3), monoglycerides (4), and glycerol by acetylation (5).

Experimental

C. P. grade glycerol (95.4% by sp. gr. and 95.5% by periodic acid method) and propylene glycol (Eastman Kodak Co., 1321 b.p. 85-86°/10 mm.) were obtained in a pure state. Some difficulty was encountered in obtaining pure trimethylene glycol. Analysis of a sample (Eastman Kodak Co., P. 264 b.p. 123-125°/30 mm.) showed the presence of 0.9% glycerol, 2.2% propylene glycol and 91.7% trimethylene glycol. We then tried to prepare pure trimethylene glycol by distilling a sweet water concentrate from a Podbielniak Column, collecting the fraction that distilled between 107° and 108°C. under a pressure of 13 mm. mercury. Analysis of the fraction indicated the presence of 0% glycerol, 1.2% propylene glycol, and 97.1% trimethylene glycol. These data indicated that either the trimethylene glycol is very difficult to purify or the methods of analysis under consideration were not entirely reliable when applied to this compound. To obtain more information on this point the Eastman Kodak Co. product was distilled from the Podbielniak Column and the portion distilling within a narrow range was collected in numerous fractions. The analyses of these fractions are given in Table I.

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