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Vapor Phase Dehydrochlorination of Chlorinated Fatty Substances

II. Catalytic Process Applied to Various Chlorinated Fatty Materials*

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Introduction

THE first paper in this series (1) described a method for catalytically dehydrochlorinating chlorinated fatty acids in the vapor phase at low pressures. Therein were presented results of experiments conducted with the mixture of acids that is obtained when palmitic acid is treated with chlorine gas until an average of about two equivalents of chlorine are combined per mole of acid.

The present paper reports work done on a limited number of other chlorinated fatty materials. Further experiments comparing the behavior of chlorinated palmitic acid containing differing amounts of chlorine and prepared in different ways are also reviewed. A brief discussion is included of the possible utility and the limitations of the vapor-phase process as they now appear.

Chlorinated Materials

Chlorinated methyl palmitate was prepared from purified methyl palmitate by direct chlorination at 40-59° C. Before chlorination the ester had an iodine value of less than 0.5 and its saponification equivalent was 270.7; theoretical for methyl palmitate, 270.44. The chlorinated product contained 21.6% of chlorine; theoretical for methyl dichloropalmitate, 20.9%.

Three lots of chlorinated palmitic acid were used. Two lots, those used in Experiments 21 and 44 (See Tables I and II, and following text) were prepared from purified palmitic acid by the method described in the previous paper. The chlorinated acid used in Experiment 21 contained 36.8% of chlorine and that used in Experiment 44 contained 22.1% of chlorine. The chlorine contents of tetrachloro- and di-chloropalmitic acids are 35.98% and 21.80%, respectively.

The third lot of chlorinated palmitic acid, which was used in Experiment 49, was prepared by saponification of the chlorinated methyl ester previously described. During saponification and recovery some of the chlorine was hydrolyzed with the result that the free acid contained 18.1% of chlorine and had an iodine value of 2.2.

Chlorinated stearic acid containing 20.3% of chlorine was prepared by direct chlorination of stearic acid previously purified by fractional crystallization from solvents. The purified stearic acid melted at 68.2 to 69.3° C. and its neutral equivalent was 285.0. Dichlorostearic acid contains 20.07% of chlorine.

Chlorinated oleic acid was prepared from purified oleic acid obtained from olive oil. The oleic acid had an iodine value of 89.6 and its neutral equivalent was 283.6; theoretical values for pure oleic acid, 89.9 and 282.46, respectively. In chlorinating this acid, conditions were chosen which were intended to favor addition of halogen to double bonds and allow a minimum of substitution. Chlorination was effected by slowly pouring a 0.9 *N* solution of chlorine in methylene chloride cooled to —20° C. into a 10% solution of the acid in the same solvent at the same temperature. The temperature of the mixture was not allowed to rise above —8° C. during the addition. The quantity of chlorine added was limited to 95% of the amount required for saturation of the oleic acid. Five minutes after mixing, the solution was put under reduced pressure, and a stream of nitrogen was bubbled through it to assist in removing any unreacted chlorine. After the solution was purged of free chlorine, the solvent was removed by distillation at reduced pressure. The chlorinated product contained 18.0% chlorine and had an iodine value of 9.6. Calculations based on these figures and the iodine value of the original acid indicate little if any chlorination occurred by substitution. Assuming that no substitution did occur, the chlorinated product was comprised

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TABLE I.

Dehydrochlorinations.

Experiment Number	Starting Material	Chlorine in Starting Material	Maximum Pressure in System	Temperature in Reaction Chamber	Chlorine in Desaturated Product	Product Recovered
	Treatments conducted in large dehydrochlorinator [1]	%	*mm. Hg*	°*C.*	%	% *of theory*
20	Chlorinated oleic acid	18.0	1.3	270	3.1	75.5
21	Chlorinated palmitic acid	36.8	1.3	280	8.4	70.4
	Treatments conducted in small dehydrochlorinator [1]					
47	Chlorinated stearic acid	20.1	1.0	240	0.7	≈ 80.0
44	Chlorinated palmitic acid	22.1	1.0	220	1.5	≈ 88.0
45	Chlorinated methyl palmitate	21.6	1.0	220	11.5	≈ 93.0
49	Chlorinated palmitic acid from chlorinated methyl ester	18.1	1.0	220	1.4	≈ 85.0
51	Chlorinated linoleic acid	30.7	1.1	285	2.4	≈ 55.0

[1] Apparatus described in first paper of this series (1).

of about 13.0 mol % of oleic acid and 87.0 mol % of dichlorostearic acid.

Chlorinated linoleic acid was obtained by chlorinating the acid prepared by debrominating linoleic tetrabromide made from sunflower-seed oil fatty acids. The chlorination procedure was the same as that applied to oleic acid. The neutral equivalent of the linoleic acid was 280.6 and its iodine value was 180.5 as compared to 280.44 and 181.04, respectively, for the pure acid. The chlorinated product contained 30.7% of chlorine and its iodine value was 4.6. Tetrachlorostearic acid contains 33.59% of chlorine.

Dehydrochlorinations

Vapor-phase dehydrochlorinations reported here were conducted at pressures of about 1 mm. and temperatures from 220° to 305° C. The experiments were conducted with the aid of the cobalt chloride-pumice catalysts and the two low-pressure dehydrochlorinators described in the first paper of this series(1). As before, bits of stainless-steel screen supplemented the cobalt chloride-pumice catalyst used in the larger apparatus in order to maintain an open channel through the catalyst for as long a time as possible.

Treatment records for the experiments and analyses of the desaturated products are summarized in Tables I, II, and III. Analyses shown were made by methods described in the first paper (loc. cit.). To avoid repetition only one of each type of experiment is reviewed. Separate tests, however, have shown the results recorded to be completely representative for the respective materials, treatments and products concerned.

It was not possible to determine materials balances accurately for Experiments 44, 45, 47, 49, and 51 which were conducted in the small dehydrochlorinator. Product yield figures for these runs may be 5-15% lower than actual values because of hold-up in the equipment.

The results of Experiment 47, when compared with those of Experiment 44, show that dichlorinated stearic and dichlorinated palmitic acids yield closely similar products. The differences in physical properties between these two types of chlorinated acids and between their respective desaturated products are not sufficient for special comment at this time.

It was shown in the preceding paper that yields in excess of 95% of theory were obtained by dehydrochlorination of dichlorinated palmitic acid under conditions comparable to those in Experiment 21 for tetrachlorinated palmitic acid. The greater loss of material sustained in the treatment of tetrachlorinated acid is in harmony with the observation that polymers were deposited on the catalyst far more rapidly in this instance than in comparable trials with the dichlorinated acid.

TABLE III.

Spectrophotometric Analyses of Desaturated Products.[1]

Experiment Number	Conditions	Dienoic	Trienoic	Tetraenoic
20	Conjugated constituents, without alkali isomerization	55.5	.3	≈ .001
51	Conjugated constituents, without alkali isomerization	28.8	6.5	3.4
51	Constituents conjugated by treatment with alkali	—26.4	22.1	—0.9

[1] Results are calculated by method and constants used by Brice *et al.* (2)and are expressed as per cent of C_{18} acids having unsaturation of types indicated.

One of the objectives of Experiment 20 was to find out what effect upon yields might be expected from the presence of oleic acid as an impurity in a saturated acid taken for chlorination and dehydrochlorination. The results of this and other trials of a similar character indicate that under the conditions of these tests product yields from chlorinated oleic acid are lower than those from dichlorinated saturated acids.

If no migration is involved, complete dehydrochlorination of 9,10-dichlorostearic acid could conceivably

TABLE II.

Chemical Analyses of Desaturated Products.

Characteristics	Experiment Number						
	20	21	47	44	45	49	51
Chlorine,%	3.1	8.4	0.7	1.5	11.5	1.4	2.4
Unsaponifiables, %	1.2	6.7	2.6	2.8	....	3.0	....
Neutralization equivalent, unsaponifiable-free fraction	294.0	509.0	342.0	326.2	....	330.7	....
Saponification equivalent, unsaponifiable-free fraction	294.0	311.0	280.0	257.5	....	253.3	....
γ-lactones (by calculation)%	0.0	36.3	17.6	20.4	....	22.7	....
Total free acids (by difference) %	98.8	57.0	79.8	76.8	....	74.3	....
Saturated acids, %	....	≈ 0.2	....	....	....	....	....
Iodine Value (Total unsaturation by H_2)	148.0	222.5	....	....	....	....	244.1
Iodine Value (Wijs)	96.3	157.7	131.6	130.2	81.3	134.6	139.4

result in formation of either or both conjugated and cumulated (allenic) double bonds. Another possible outcome would be formation of an acetylenic linkage.

A second objective of Experiment 20 was to attempt to determine whether dehydrochlorination of an acid having two chlorine atoms on adjacent carbons would result in exclusive formation of an acid with two conjugated double bonds.

If it is assumed that the various chemical types present in the reaction product contributed equally to the loss sustained in the experiment, and if account is taken of the chlorine content of the product and the composition of the starting material, the total unsaturation in the product expressed in iodine value units should have been 141 as compared to 148, which was the value found by hydrogenation. Upon the same basis it is also possible to show that roughly as much as 59 to 72% of the product could have been made up of acids with diene conjugation. The lower estimate would represent the situation if all residual chlorine in the final product was in the form of monochloroleic acid, but if it existed only as dichlorostearic acid, the higher value would be correct.

The results of the spectrophotometric analysis shown in Table III for the product from Experiment 20 are in tolerable agreement with the lower estimate of possible conjugated unsaturation. These results also support the conclusion that all the residual chlorine in the product occurred as monochloro monounsaturated acids and that no dichlorostearic acid remained.

Experiment 51 was performed with the nearly saturated product obtained by chlorinating linoleic acid. It showed that the dehydrochlorination method at its present development is not suited to treatment of this type of material.

The chlorinated acid was a firm solid at ordinary temperature and did not melt completely below about 90° C. Somewhat before the latter temperature was reached active evolution of hydrogen chloride and immediate polymerization began. Since it was necessary to introduce the material into the dehydrochlorinator as a liquid, a considerable quantity of nonvolatile polymer was formed before evaporation took place. Deposition of polymers on the catalyst was also quite rapid.

Because of the relative positions of the halogen atoms on the carbon chain, the desaturated product from chlorinated linoleic acid would be bound to possess either, and probably both, conjugated and cumulated unsaturation, unless extensive migration occurred. The high reactivity of such multiple unsaturated systems doubtless accounts for the large material loss encountered in this experiment.

When an attempt was made to measure the increase in the proportion of conjugated unsaturation produced by digestion of the product from chlorinated linoleic acid with glycerolic alkali according to the method of Brice *et al.*, the negative values shown in Table III for dienoic and tetraenoic conjugation were obtained. It seems probable that the negative value for dienoic conjugation may be traceable, at least in part, to the presence in the original product of trienoic acids in which two of the three double bonds were conjugated.

Destruction of tetraenes during treatment with alkali may be the explanation for the negative value for tetraenes conjugated by isomerization.

It may be well to point out that the absorptive characteristics of the individual components of dehydrochlorination products have not been determined. Hence, although the alkali-treated product from linoleic acid probably represents a special case, the other estimates based on spectrophotometric measurements may be in some error.

Trials have repeatedly shown that only about half the chlorine is removed in vapor-phase dehydrochlorination of dichlorinated methyl palmitate. This is illustrated by the results shown for Experiment 45. Lengthening the time of contact between vapor and catalyst has little if any effect upon the extent of dehydrochlorination, and only minor quantities of the residual combined chlorine are removed if the treatment is repeated. This behavior of the chlorinated ester is in contrast with that of all the chlorinated acids tested to date. Although most of the desaturated products prepared from chlorinated acids have contained several per cent of residual chlorine there has been no evidence to indicate the remaining chlorine was more strongly held than that which was removed. On the contrary, work with chlorinated acids has consistently appeared to support the conclusion, that under favorable temperature and pressure the completeness of dehydrochlorination of these materials is a function only of catalyst activity and opportunity for contact between chlorinated molecules and catalyst.

Experiment 49 was performed with chlorinated acid regenerated from the chlorinated ester whereas the chlorinated acid used in Experiment 44 was prepared in the usual way from free acid. It is evident from the results of these trials that retention of chlorine by the ester is not due to a special distribution of chlorine in the chain but rather to the presence of the ester group.

Tests of Dehydrochlorinated Products as Soaps and Drying Oils

Extensive investigation of uses to which the dehydrochlorinated products could be put was outside the immediate scope of this study. Consequently, only a few exploratory tests bearing on that subject were undertaken. Solutions of the sodium soap of the products from dichlorinated palmitic acid were compared with those of several other materials for foaming power, wetting power and detergency.

Foaming powers were compared and ability of the soap solution to remove soil was examined by slight modifications of two procedures used in testing salt-water soaps purchased by the Federal Government during the war.[2] Wetting power was examined according to the Official Method of The American Association of Textile Chemists and Colorists (3).

The foaming power of the soap derived from the desaturated product was distinctly superior to that of soaps of technical oleic acid and coconut-oil acids. Expressing the volume of foam produced by coconut-oil soap as unity, the volumes of foam from oleic acid and product soaps were respectively 1.08 and greater than 1.3.

The relative concentrations of wetting agents in solution required to cause skeins of cotton yarn to sink within a definite time under set conditions were:

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[2] Bureau of Ships ad interim specifications 51 S 46 (I.N.T.) 1 Dec. 1943 and 51 D 7 (I.N.T.) 1 Nov. 1942.

oleic acid, 1:00; Nacconol N R S F,[3] 1.03. Swatches of Soap of desaturated product, 0.81; soap of technical white woolen flannel were soiled and washed according to standard procedures (loc. cit.). Relative efficiencies of the detergents used were indicated by reflectance measurements made on the swatches in the various conditions. Average reflectances found were:

Unsoiled washed cloth	0.697
Soiled cloth	0.258
Soiled cloth washed with soap of coconut-oil acids	0.583
Soiled cloth washed with soap of desaturated product	0.629

The desaturated product from dichlorinated oleic acid was esterified with pentaerythritol and with Pentek 43.[4] Films cast on glass from mixtures of thinner, Japan drier, and these esters dried hard overnight.

Summary

Catalytic vapor-phase dehydrochlorination at pressures below 1.5 mm. and at temperatures from 220° to 350° C. was applied to chlorination products of methyl palmitate, palmitic, stearic, oleic, and linoleic acids. Clear, pale desaturated products were recovered from each material.

About half the combined chlorine was readily removed from chlorinated methyl palmitate containing an average of two atoms of chlorine per molecule. The halogen that remained was strongly held by the ester but was easily removed from the chlorinated free acid regenerated from the ester by saponification.

Product recovery from chlorinated palmitic acid became less as the degree of chlorination was increased from an average of two to an average of four atoms of halogen per molecule of acid.

Oleic acid saturated with chlorine by addition gave lower yields of recovered product than did either palmitic or stearic acid chlorinated to a comparable degree. Still greater product losses were encountered in processing linoleic acid chlorinated by addition.

Losses occurring in the process were traceable almost entirely to the tendency of the desaturated products to polymerize in contact with the solid catalyst. Besides lowering the yields of recoverable product, the accumulation of non-volatile polymers on the catalyst surfaces lowers the activity of the catalyst and shortens its period of usefulness.

Tests of the desaturated product from dichlorinated palmitic acid indicated that solutions of its sodium soap are good detergents, having better than average wetting and foaming powers.

A product having considerable conjugated unsaturation was obtained from chlorinated oleic acid. When esterified with polyhydric alcohols, this material was capable of forming drying films.

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[3] Trade name for a commercial product reported to consist essentially of sodium dodecyl and tetradecyl benzene sulfonate.

[4] Trade name for a commercial product reported to contain about 50% pentaerythritol and 50% dipentaerythritol.

The Spectrophotometric Determination of the Alpha and Beta Isomers of Eleostearic Acid In Tung Oil*

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STUDIES widely reported in the literature have indicated that only the *alpha* isomer of eleostearic acid is elaborated in the tung oil of the common species (1). The *beta* isomer occurs later as a result of isomerization of the *alpha* form. Many lots of commercial tung oil are subjected in storage and handling to conditions which promote this isomerization. A method for the determination of the *alpha* form of the acid in freshly extracted tung oil by use of spectrophotometric principles has been described recently (2). But as the *beta* form of the acid has a somewhat different absorption spectrum from the *alpha,* the presence of the *beta* eleostearic acid in most samples interferes with the determination of the *alpha* by this method. Hence, a procedure is desired that will permit the quantitative determination of both the *alpha* and *beta* isomers in the presence of each other and at the same time permit the determination of the total amount of eleostearic acid present.

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[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

[2] One of the field laboratories under the direction of the Agricultural Chemical Research Division of the Bureau of Agricultural and Industrial Chemistry.