Hyperchlorinated Fatty Acids: I. Tentative Methods of Synthesis

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ABSTRACT

The hyperchlorination of fatty acids was studied by four methods using mainly stearic acid. This acid was first submitted to the action of nascent chlorine from NaCl electrolysis, for which the best results never exceeded 43% of fixed chlorine (about 6 Cl atoms per mole of acid), with a yield of 30% based on the acid. Stearic acid was also submitted to electric discharges in CCl_4, and so transformed into various chlorinated and unsaturated compounds, which indicate a near simultaneity of chlorination and dehydrochlorination. However, when the time of contact of the acid with the reactive solution was reduced, formation of only saturated chlorinated compounds occurred, of which the chlorine content, in the best case, was 54% (9 Cl/mole). Direct photochlorination of acid without solvent gave a product containing a maximum of 8 Cl atoms per mole (about 50%). Finally, direct photochlorination of the fatty acid in CCl_4 led to a hyperchlorinated acid containing 68.3% Cl (16-17 Cl/mole), and minor, more or less polymerized products. Although the second and third methods readily afford stearic acid chlorinated to the extent of about 50%, this value, corresponding to an average of 0.5 Cl/C atom, appears to be a barrier that can only be overcome by employing photochlorination in an inert solvent, such as CCl_4.

INTRODUCTION

Direct substitution of the maximum number of hydrogen atoms of an aliphatic long chain by chlorine atoms is of great interest. It permits the introduction of numerous reaction sites on the chain which should afford access to highly functional compounds.

If chlorinated paraffins and polymers such as polyvinyl chloride are excluded, classical chlorination methods generally lead only to lowly chlorinated products, which are relatively unstable (10). Formation of polychlorinated materials was observed by some authors, but such compounds were always considered as by-products to be systematically avoided (4,6).

In our attempts to hyperchlorinate stearic acid or its methyl ester, we tried various procedures: anodic chlorination, electric discharges in CCl_4 and direct photochlorination by chlorine gas (2,8,10,11).

EXPERIMENTAL PROCEDURES

Pure commercial stearic acid (Dubois and Son, 99.5% pure) was recrystallized in acetone at -20 C; the final purity was checked by gas liquid chromatography (GLC).

Anodic Chlorination

By electrolysis of an aqueous solution of NaCl, it is known that very reactive, nascent chlorine is obtained. The problem was to establish a good contact between fatty material and chlorine. For that, three electrolysis processes were successively explored:

Electrolysis in a U-tube with carbon electrodes and emulsified stearic acid.

Electrolysis with an asbestos plate to separate anodic and cathodic compartments. Various experiments were so realized, using an agitating carbon anode and a stainless steel cathode, or a system for injecting stearic acid through a tubular vertical stationary carbon anode. The lower part of the wall of this anode was grooved and drilled.

Electrolysis according to Castner-Kellner's method (9). The mercury cathode apparatus was fitted with a rotating horizontal carbon anode half immersed in electrolyte solution, and directly submitted to the action of chlorine. In all experiments work-up was performed by dissolution in methylene chloride, washing with water, drying with anhydrous sodium sulfate, evaporation in vacuum and recrystallization in acetone at -20 C to -50 C. The residue not crystallized at -50 C was examined by IR spectrometry, and its chlorine content determined by Schoniger's method. Experimental conditions and results are given in Table I.

TABLE I

Chlorination by Electrolysis of NaCl

Electrolysis methods	Nature of Anode	Nature of Cathode	Electrolyte	Weight of acid, g	Voltage, v	Intensity amps	Time, min	Temperature, C	% Cl fixed	Yields[a], %
U-tube	Carbon	Carbon	300 ml H_2O 9 g NaCl	3	66	0.8	60	80	12	25
Membrane	Carbon	Stainless steel	3000 ml H_2O 45 g NaCl	10	9	4	180	85	43	30
Castner-Kellner	Carbon	Hg	1300 ml H_2O 30 g NaCl	20	6	4	60	75	18	20

[a] Yields indicated are those of chlorine-containing products, related to the weight of fatty acid allowed to react.

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TABLE II

Chlorination by Electric Discharges in CCl_4

Experiments	Concentration in CCl_4, g/l	Reaction time, min	Average current intensity, amps	Voltage, v	Average electric power, w	Average content of chlorine fixed, %	Character of unsaturation[a]
Stearic acid							
A	50	150	2	10 to 20	30	29.6	Strong
B	50	240	2	10 to 20	30	26	Strong
C_1	20	20	4	3 to 12	30	17.5	Zero
C_2	5	30	4	3 to 12	30	39	Weak
C_3	5	60	4	3 to 12	30	18	Strong
Methyl ester							
D_1	30	15	4	7 to 11	36	7	Zero
D_2	15	15	4	10 to 15	50	23	Very weak
D_3	7.5	15	4	12 to 18	60	40	Weak
E	50	-----	2	60 to 80	140	42.5	Medium
F	50	-----	4	20 to 60	160	43	Medium

[a] Character of unsaturation was evaluated from UV spectra of products obtained, according to the E_1^1 and the wave lengths (number of absorption bands of each spectrum).

Electric Discharges in CCl_4

Menzel et al. (5) indicated formation of unsaturated compounds from fatty acids submitted to electric discharges, and Kantsky (3) noted the production of chlorine when electric sparks were generated in CCl_4. In our experiments, sparking was realized between two copper pieces coming periodically in contact, the energy being furnished by a direct current generator.

In every case, the final product was obtained by filtering to eliminate carbon, washing with water to neutrality, drying over sodium sulfate, evaporating in vacuum and dissolving in acetone. After recrystallization at -20 C and washing the residue with a 3N sodium thiosulfate solution to remove the dissolved chlorine, its chlorine content was determined. Table II summarizes the results obtained under various experimental conditions.

Experiment groups C (stearic acid) and D (methyl stearate) correspond to a study of the influence of dilution and reaction time. After reaction, 250 ml of solution C_1 were diluted to 1000 ml with CCl_4. Half of this volume was allowed to react again for 30 min (C_2) and the other part for 60 min (C_3). Similarly, 500 ml of solution D_1 were diluted after reaction to 1000 ml with CCl_4 and allowed to react for an additional 15 min (D_2). After completion of reaction period D_2, the solution was again diluted and reacted for 15 min more (D_3). In.thie case, the product obtained was fractionated by thin layer chromatography (TLC) (eluent: hexane-acetic acid 8/2, v/v). Each fraction was extracted by CS_2 in a Soxhlet apparatus and then examined by UV and IR spectrometry. The chlorine content was also determined.

In experiments E and F, a CCl_4 solution of methyl stearate was allowed to fall drop by drop on copper

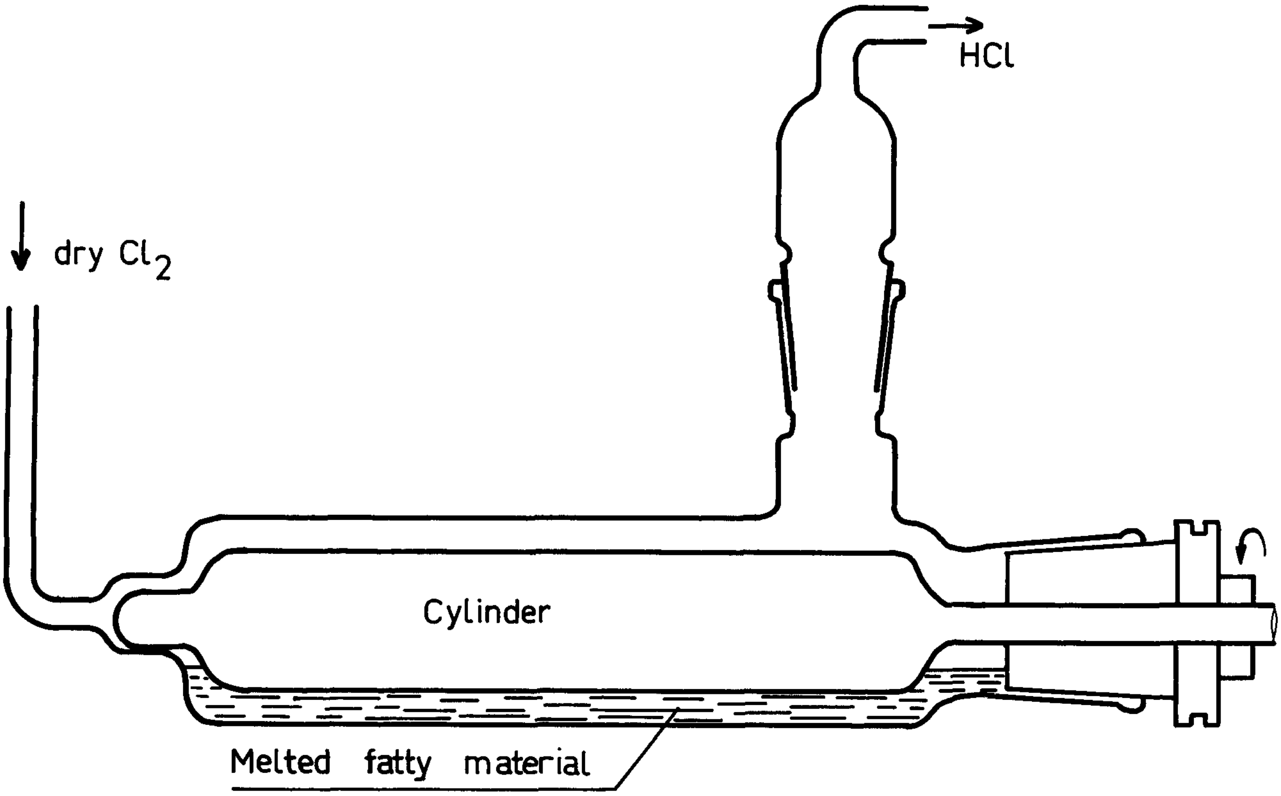

FIG. 1. Apparatus used for direct chlorination without solvent.

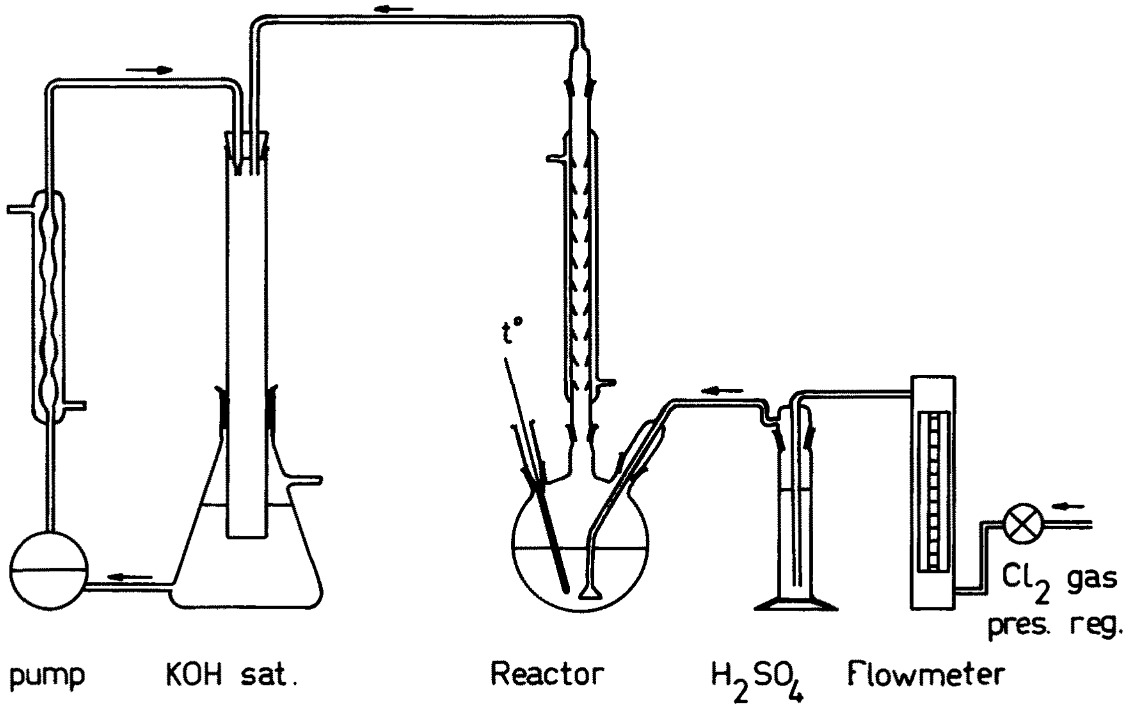

FIG. 2. Apparatus used for direct chlorination of stearic acid in CCl_4.

electrodes and was immediately collected in a flask situated beneath, in order to limit the time of contact. Under these conditions, we got complex mixtures, of which the most chlorinated product, fractionated by TLC, contained 54% Cl corresponding to 9 Cl atoms per mole.

In any case, the UV spectra (Cary Model 15 Special, nitrogen-purged) indicated no double bond. For stearic acid, the IR spectra (on salt plates) were normal, except that the νC=O band was shifted from 1695 to 1715 cm^{-1}. OH bands in the 2800 to 3400 cm^{-1} region, and at 939 cm^{-1}, were not affected. After action of glycolic potassium hydroxide on this product, the UV spectrum showed an absorption (multiplet) centered on 348 mμ, denoting the presence of about five conjugated double bonds.

Direct Chlorination Without Solvent

Stearic acid or its methyl ester was directly chlorinated by dry chlorine gas in presence of active light (Philips lamp SP 371, 3,500-40,000 Å) in the apparatus schematically shown in Figure 1. In this apparatus, a motor slowly propelled a glass or graphite cylinder rolling in a reactor containing the melted fatty material. A stream of chlorine gas swept the cylinder surface exposed to the lamp. By this method, there were obtained only liquids, which became more and more viscous as the percentage of chlorine increased. With a graphite cylinder, 90 g of stearic acid or its methyl ester were allowed to react for 180 min (chlorine flow: 0.8 l/min); black, viscous and odorless oils resulted. The percentage of chlorine in the products was 38.8% from the acid and 38% from the ester (corresponding to 5 Cl per mole in each case).

With a glass cylinder and the same chlorine flow, 60 g of stearic acid after 150 min yielded a highly viscous and odorless product, which contained 49.9% chlorine (7.75 chlorine atoms per mole). The molecular weight, determined by the isopiestic method (Mechrolab 301 A apparatus) was 556. For 8.0 Cl/mole, the theoretical molecular weight is 560.

In all experiments, yields based on initial fatty compound averaged 100%.

Direct Chlorination Into CCl_4

Prior to this work, Frilette (2) and Ridbo Lab (7) were the only ones to report a procedure for hyperchlorination of fatty materials. But they did not study isolation conditions, structure of synthesized products and reaction mechanism. Using the apparatus schematically shown in Figure 2, we realized hyperchlorination of stearic acid as follows.

Typical Procedure. A 250 ml flattened three-necked flask was fitted with a gas dispersion tube, a thermometer and a gas absorption device. In this flask, solvent (100 ml) and stearic acid were exposed to active light. At first, the solution was yellow, then suddenly became colorless. In a second stage, the colorless solution became again yellow and more and more turbid. Normally, the reaction was stopped at the end of the first stage.

Work-Up. After decolorization by dry nitrogen, the solution was filtered on Millipore (8μ). An insoluble product, which was responsible for the turbidity, was separated and washed with acetone. The insolubility of this product in typical organic solvents suggests a polymeric character.

The clarified solution was then evaporated; the residue was three times dissolved in acetone and the solvent evaporated to eliminate the last traces of CCl_4. By this treatment, an organic glass was obtained.

The chlorine content per mole of the "glass" varied from 58% to about 68% according to the variations of different parameters, chlorine flow, concentration of fatty material in CCl_4, type of active light emitter, etc. But, in each case, the measurement of molecular weight by the isopiestic method was in agreement with the chlorine content determined by Schoniger's method. For example, one glass-like product had a molecular weight of 792, and a chlorine content of 65.72%, whereas for chlorine contents of 64.79% and 66.43% (corresponding respectively to 14 and 15 Cl atoms per mole), molecular weights of 767 and 801.5 are calculated.

DISCUSSION

From the results obtained above, it appears that only photochlorination in presence of solvent gives high chlorine contents. In fact, this method leads to an average of one chlorine atom fixed per carbon atom. Moreover, it gives two types of products, a vitreous product, soluble in most organic solvents, and an insoluble product.

Results from chlorination without solvent suggest the existence of a barrier corresponding to about one chlorine atom fixed for every two carbon atoms. Above this limit, the aliphatic chain is cracked and burned.

Anodic chlorination, as it was applied, does not appear powerful enough to hyperchlorinate fatty acids. In the best case, the extent of chlorination seemed to reach the barrier encountered in the direct photochlorination without solvent.

Finally, experiments with electric discharges in CCl_4 containing stearic acid revealed a very rapid process of chlorination. This is accompanied by dehydrochlorination, leading to lowly chlorinated but strongly unsaturated compounds. This type of experiment offers, however, an interesting route to hyperunsaturated, more or less halogenated products. When the time of contact of the acid with the reactive solution is limited, there is formation of a thoroughly saturated chlorinated acid, containing 54% chlorine.

In papers in preparation, the structure of products from photochlorination in CCl_4 will be examined, and the reaction mechanism discussed.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Agriculture (Contract No. FG-FR-124). Gerhard Maerker and A.N. Wrigley (EURDD) aided by discussion and assistance in translation.

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[Received December 14, 1970]