Hyperchlorinated Fatty Acids: II. Photochlorination of Stearic Acid in Carbon Tetrachloride, Reaction Study

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ABSTRACT

The free radical chlorination of stearic acid in carbon tetrachloride was studied with variation of the chlorine flow rate, the active light intensity and the initial fatty acid concentration. In addition the variation of temperature with time was measured. The chlorine flow rate affects only the reaction time and modifies neither the chlorine content of the products obtained nor the yield, approximating 100%. On the other hand, the initial fatty acid concentration seems to be the prime factor determining the chlorine content of the products. Similarly, the onset of the polymerization of the chlorinated monomers depends essentially on the initial fatty acid concentration. These polymers are probably chlorinated polyesters. This behavior can be explained by the incursion of radical ions $RCOO\cdot^+$ resulting from irradiation of exciplexes formed by interaction between the more or less highly chlorinated fatty acid and the solvent. These interactions take place when the fundamental complex occupies a critical volume, which depends on the acid concentration.

INTRODUCTION

In an earlier paper (1), we showed that the only method by which stearic acid could be hyperchlorinated by gaseous chlorine, without catalyst, to fix more than 8 chlorine atoms per mole of acid, was direct photochlorination in carbon tetrachloride. After measuring the variation of temperature with time, the reaction was studied successively, as a function of the chlorine flow rate, the active light intensity and the fatty acid concentration.

EXPERIMENTAL PROCEDURES

Stearic acid (Dubois and Son, 99.5% pure), recrystallized from acetone at -20 C to a purity higher than 99.9% by gas liquid chromatography, was dissolved in carbon tetrachloride purified by the method of Klein (4). It was then placed in the apparatus described previously. After the careful expulsion of oxygen, dry gaseous chlorine was introduced and the irradiator was turned on. When the solution became once more yellow and turbid, the reaction was stopped. The reaction products were then extracted following the method described earlier.

RESULTS

Variation of Temperature as Function of Time

Whatever the chlorine flow rate, the fatty acid concentration or the irradiator used, the curve $T = f(t)$ was always as in Figure 1.

The origin O corresponds to the lighting of the irradiator. The temperature rose rapidly (OA), reached a plateau (AB) and then decreased slightly (BC). The initially clear and colorless solution yellowed rapidly (OO') and then very abruptly became colorless again near 60 C at O'; at point B the solution once more yellowed and became more and more turbid. The $O'A$ part of the curve was considered the induction period and the $O'B$ part the reaction time. Section OO', which is very short and whose origin O varies from one experiment to another, was neglected. It should be noted that the temperature could not be measured satisfactorily with a mercury thermometer, whose bulb focuses the radiation, leading to temperature indications much higher than reality. A platinum probe connected to a

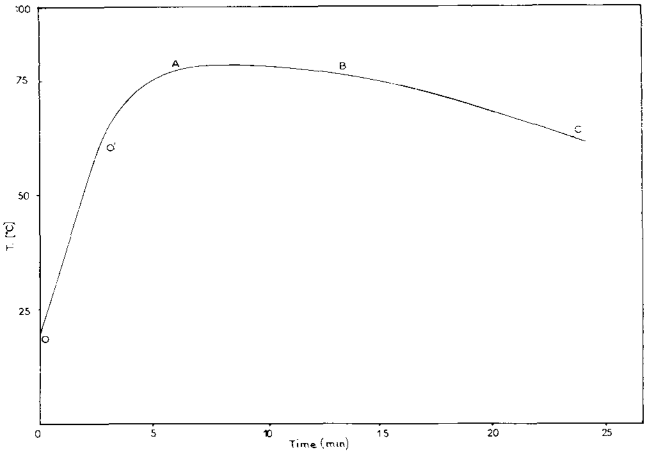

FIG. 1. Variation of temperature as a function of reaction time.

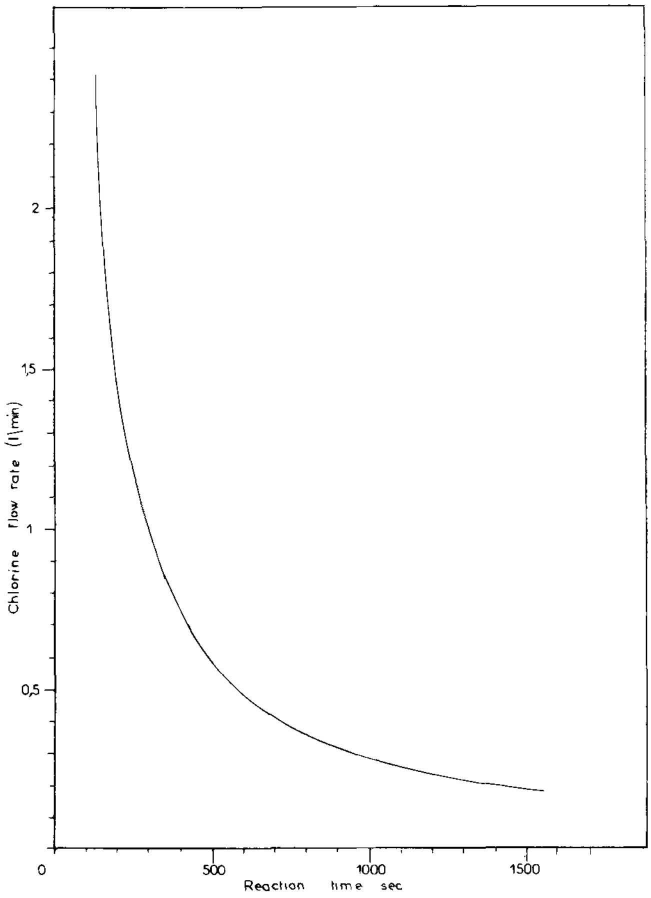

FIG. 2. Influence of chlorine flow rate on reaction time.

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TABLE I

Influence of Chlorine Flow Rate on Quantity of Chlorine Fixed per Mole of Stearic Acid

Experiment	Chlorine flow, liter/min	Induction time, sec	Reaction time, sec	Chlorine used,[a] mol	Chlorine fixed per mol acid, %	Number of Cl atoms fixed per mol acid	Yields (based on Cl used), %
1	0.24	90	1200	0.214	60.51	12.32	99
2	0.40	90	730	0.217	59.85	11.46	93
3	0.66	80	440	0.216	60.05	11.55	98
4	0.785	90	375	0.219	61.15	12.06	97
5	1.95	90	150	0.217	60.60	11.80	96

[a] Quantity of chlorine introduced into reactor during period defined as reaction time.

Wheatstone bridge was satisfactory.

Influence of Chlorine Flow Rate

After establishing the stearic acid content of the carbon tetrachloride at 50 g/liter and choosing the irradiator (Philips lamp SP 371, 3,500-40,000 Å), studies were made successively of the influence of the chlorine flow rate, as follows: (a) on the quantity of chlorine fixed per mole of stearic acid: The results are given in Table I; (b) on the reaction time: The plot of reaction time as a function of the chlorine flow rate was a hyperbola (Fig. 2); (c) on reaction yield in relation to the amount of chlorine introduced. The average amount of gaseous chlorine brought into reaction in each experiment was 0.212 mol or 4.85 liters under standard conditions. But the quantity of gaseous chlorine fixed by the weight of stearic acid treated was an average of 4.65 liters (corresponding to 11.78 Cl/mol fatty acid). The average yield was 96.6%; (d) on the yield in relation to the quantity of acid introduced. Holding an acetone solution of the reaction products at -20 to -70 C caused no precipitation. In addition the molecular weights measured by isopiestic distillation (Mechrolab apparatus), corresponded to the percentages of chlorine measured. This led to the conclusion that yields were very close to 100%.

Influence of Irradiator

With the chlorine flow rate fixed at 0.785 liter/min and the stearic acid content of the carbon tetrachloride at 50 g/liter, the use of two irradiators of different light intensities gave the results shown in Table II.

Care was exercised that the two irradiators should not permit the homolytic rupture of the C-Cl bonds (labile at 2130 Å). The irradiator intensity determines the temperature of the plateau *AB* and seems to have only a small effect on the degree of chlorination.

Influence of Fatty Acid Concentration

With the chlorine flow rate set at 0.785 liter/min and with constant radiation intensity (Philips SP 371), the concentration of fatty acid dissolved in the carbon tetrachloride was varied. The results are given in Table III.

When the acid concentration *n* was increased, the quantity of chlorine fixed *x* decreased, approaching a limit near 9-10 chlorine atoms per molecule of chlorinated acid. The study of concentrations above 25% poses difficulties, since stearic acid is only moderately soluble in carbon tetrachloride.

DISCUSSION

Taken together, the experiments described make it evident that: (a) The chlorine flow rate affects only the reaction time, following a hyperbolic relation expressable as $d = k/t$, in which d represents the chlorine flow rate, t the reaction time and k a constant depending on the acid concentration and the irradiator used. In our series of experiments, k = 291 liters sec/min (Fig. 2). (b) The flow rate does not influence the amount of chlorine fixed per molecule of fatty acid, or the average yield in relation to the amount of chlorine introduced (for the range of flow rates studied). (c) The choice of emission spectrum of the irradiator seems to have little effect on the reaction. At most a raising of the temperature plateau attained is noted, which probably explains the slightly higher quantity of chlorine fixed in the case of irradiator SP 371 VD. (d) When the reaction starts (at O' of Fig. 1), the solution remains clear. All the chlorine introduced into the reaction medium is immediately consumed. On several occasions, we halted an experiment in progress before the onset of turbidity (at *B* of Fig. 1). All efforts to separate (by thin layer chromatography or recrystallization from acetone at -20 to -70 C) more highly or less highly chlorinated products failed, indicating that the chlorination of the acid was normal. On the other hand, whatever the concentration chosen, there is always a point beyond which the quantity of chlorine fixed per molecule of fatty acid no longer increases. The introduction of additional chlorine into the flask then leads to polymerization of the chlorinated acid, without further fixation of chlorine. This polymerization was established by isolation of dimers and trimers by thin layer chromatography (Alumina G, Merck, benzene-ether-acetonitrile 75:24.5:0.5 v/v).

The influence of the fatty acid concentration on the quantity of chlorine fixed therefore appears of cardinal importance. If x designates the maximum number of chlorine atoms fixed per molecule of fatty acid in each case, and n the amount of this acid (in g/100 ml) brought into reaction (n being directly proportional to the number of moles), it is evident that: if n increases, x decreases; if n becomes very great, x tends toward a limit, which we will call x_o; if n were zero, x would have a theoretical value, which we will call X, corresponding to the theoretical maximum of chlorine that one can fix on a molecule of stearic acid. The curve representing the influence of the initial fatty acid concentration on the quantity of chlorine

TABLE II

Influence of Irradiator Intensity on Degree of Chlorination

Experiment	Irradiators	Irradiator spectra, Å	Irradiation time, sec	Reaction time, sec	Chlorine used, mol	Number of Cl atoms fixed per mol acid	Maximum temperature,[a] C
4	Philips SP 371	3,500 to 40,000	90	375	0.219	12.06	69
9	Philips SP 371 VD	2,200 to 30,000	105	390	0.232	12.88	74

[a] Plateau *AB* of Figure 1.

TABLE III

Influence of Concentration of Fatty Acid on Quantity of Chlorine Fixed per Mole-Calculation of Best Value of x_o[a]

n,[b] g/100 ml	K[c]							x,[d] experimental	x, theoretical with $K = 2.5$	x, theoretical with $K = 3.4$
	$x_o = 7$	$x_o = 8$	$x_o = 9$	$x_o = 10$	$x_o = 11$	$x_o = 12$	$x_o = 13$			
1	4.20	3.72	3.21	2.68	2.16	1.63	1.10	15.10	15.00	15.18
2	5.10	4.40	3.71	3.00	2.29	1.57	0.85	14.20	13.88	14.03
3	5.10	4.30	3.48	2.67	1.86	1.05	0.24	13.30	13.18	13.25
4	4.50	3.65	2.80	1.96	1.10	0.25	−0.49	12.30	12.69	12.67
5	5.10	4.10	3.09	2.08	1.68	0.06	−0.40	12.06	12.33	12.23
7	5.90	4.66	3.37	2.07	0.77	−0.50	−1.81	11.60	11.84	11.61
8	6.90	5.33	3.85	2.37	0.88	−0.59	−2.07	11.60	11.66	11.38
10	7.20	5.50	3.79	2.06	0.34	−1.37	−3.10	11.20	11.40	11.02
15	10.00	7.50	5.00	2.50	0.00	−2.50	−5.00	11.00	11.00	—
20	13.90	10.50	7.10	3.72	0.34	−3.00	−6.40	11.10	10.77	—
Average K	6.79	5.36	3.94	2.51	1.14	−0.34	−1.02			
K max	7.11	5.14	3.16	1.21	1.15	2.66	5.38			

[a] x_o = lower limit of chlorination when $n \rightarrow \infty$ (number of Cl atoms per mol acid).

[b] n = concentration of fatty acid in CCl_4 (g/100 ml).

[c] K = concentration constant of equation (2) (g/ml).

[d] x = number of Cl atoms fixed per mol acid.

fixed per mole, is thus of the form:

$$x = (an + b)/(cn + d) \qquad [1]$$

in which a, b, c and d are constants; if $n \rightarrow \infty$, $x \rightarrow a/c$, hence, $x \rightarrow x_o$; and if $n = o$, $x = b/d$, hence, $x = X$ and equation 1 becomes

$$x = (nx_o + KX)/(n + K) \qquad [2]$$

in which K is a constant equal to d/c. The quantity x_o represents the lower limit of chlorination when the concentration n becomes indefinitely large, and X is the upper limit of chlorination when the concentration n tends toward zero. The experiment results lead us semiempirically to set the value of X at 17, as was indicated in the previous paper.

Using the experimental values of n and of x associated with the value adopted for X, one can seek the best value of x_o for which K is constant. To do this, x_o was varied between 7 and 13, and calculations were made of each value of K corresponding to n and the average value of K and that of ΔK for each value of x_o. The best result, for which ΔK is least, corresponds to $11 > x_o > 10$ (Table III).

But the difficulty of dissolving stearic acid in the carbon tetrachloride must be taken into consideration; for substantial concentration ($n \geqslant 15$), the risks of experimental error due to imperfect solution are no longer negligible. For this reason only those values of K were retained corresponding to values of n between 1 and 10. Under these conditions the best value of x_o is 9 (K = 3.4 and ΔK = 0.6). It is interesting to note that this value is close to the limiting degree of chlorination proposed in our previous article, with reference to direct chlorination without solvent (1 atom of chlorine for each 2 atoms of carbon, or 8 Cl for stearic acid).

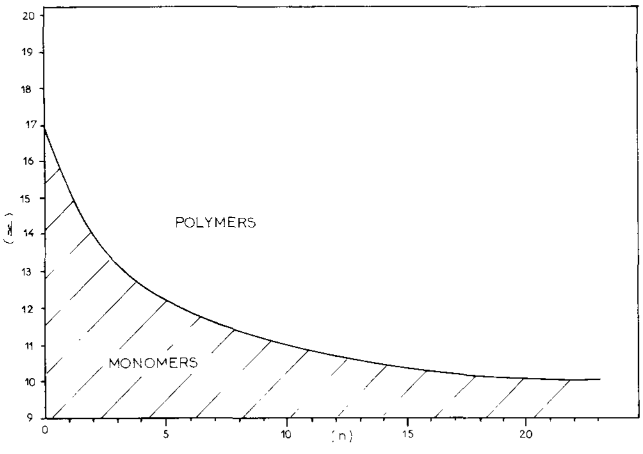

FIG. 3. Maximum of chlorine atoms fixed x per mole of stearic acid as a function of initial acid concentration n.

With the adoption, then, of the value x_o = 9, equation 2 becomes

$$x = (9n + 57.8)/(n + 3.4) \qquad [3]$$

This equation, which is plotted in Figure 3, permits the predetermination of the maximum quantity of chlorine fixable per molecule of stearic acid, as a function of the initial acid concentration. Beyond this quantity, if there is continued introduction of chlorine radicals into the reaction medium, polymerization takes place.

Let m be the number of moles of fatty acid, V the total volume available to them, v the volume available for 1 mol and v' the volume actually occupied by 1 mol in the course of the reaction.

It may be granted that v', as a first approximation, increases with the number of chlorine atoms fixed until it reaches a limit at which polymerization begins. Experiment shows that if v increases, v' increases, attaining a limit v_x for $v = \infty$. Similarly if v tends toward zero, v' tends toward a lower limit v_o, which corresponds to the limit in the case of chlorination without solvent. There is therefore a relation between v and v' of the form $v' = (ev + f)/(gv + h)$, in which e, f, g and h are constants such that $e/g = v_x$ and $f/h = v_o$. Setting $h/g = k$, there results:

$$v = k\ (v' - v_o/(v_x - v') \qquad [4]$$

an expression in which k is a volume.

By definition, $v = V/m$ and $m = nV/M$, in which M is the molecular weight of the fatty acid under consideration; hence:

$$v = M/n \qquad [5]$$

Combining equations 4 and 5, it follows that:

$$n = M/k\ ([v_x - v']/[v' - v_o]) \qquad [6]$$

Now if we call v_i the initial volume of a mole of fatty acid, and v_{Cl} the increase in volume of this mole corresponding to the fixation of an atom of chlorine (we will suppose that ν_{Cl} is constant whatever the number of chlorine atoms fixed), then at each instant $\nu' = \nu_i + x\nu_{\mathrm{Cl}}$, x being the number of chlorine atoms fixed at that instant. From this, $x = (\nu' - \nu_i)/\nu_{\mathrm{Cl}}$.

One would define in the same way the two limits: $X = (\nu_x - \nu_i)/\nu_{\mathrm{Cl}}$ and $x_o = (\nu_o - \nu_i)/\nu_{\mathrm{Cl}}$. Replacing x, X and x_o by their values, equation 2 becomes

$$n = K\ (\nu_x - \nu')/\nu' - \nu_o) \qquad [7]$$

On comparison of equations 6 and 7, it is deduced that

$$K = M/k \qquad [8]$$

For stearic acid ($M = 284$), the experimental measurements (Table III) give for K a value between 2.5 and 3.4; hence $83.5 < k < 113$.

Thus it appears that k is in fact the simple expression of the reaction volume (100 ml in our experiments). One can therefore write $K = M/V$, indicating that K is a specific constant of the fatty acid considered and of the reaction volume.

The notion of the available volume ν and of the volume ν' actually occupied by a chlorinated molecule permits an attempt to explain the phenomenon of polymerization. One can, in fact, propose the following hypotheses: (a) The acid RCOOH and the carbon tetrachloride interact to form a donor-acceptor complex of the type (RCOOH; CCl_4), stable in its ground state. (b) In a first stage (at least up to the fixation of x_o atoms of chlorine), the process of radical chlorination is of the classical type.(c) After the fixation of x_o atoms of chlorine, the size of the chlorinated molecules and the interactions between these molecules cause the onset in the solution of intermolecular geometric arrangement. This phenomenon depends particularly on the initial fatty acid concentration. This geometric arrangement and the presence of (RCOOH; CCl_4) complexes favor the formation of exciplexes of the type ($RCOOH^{+\cdot}$; $CCl_4^{-\cdot}$) (2,5).(d) Under the continuing action of the irradiator, the exciplex can give rise to a radical-cation $RCOOH^{+\cdot}$ (5). This type of very short-lived radical is extremely reactive (6). (e) Now the normal chlorination of the hydrocarbon chain of the acid leads to the species $R\cdot Cl_xCOOH$, which should, in that process, act on a molecule of chlorine to give $RCl_{x+1}COOH + Cl^{\bullet}$, thus maintaining the reaction, (f) But it is logical to suppose that $RCOOH^{+\cdot}$ will react faster and more selectively on $R^{\bullet}Cl_xCOOH$ than the latter does on Cl_2, to give $RCOO{-}RCl_xCOOH$.

It is found experimentally that the polymerization does not take place if the supply of chlorine is discontinued (suppression of phase e); if the irradiator is extinguished (suppression of phases b, d, and e); if one operates without solvent (suppression of phases a and c); or if one treats a hydrocarbon (suppression of phases a, c and f), for which forced chlorination brings about the destruction of the molecules with liberation of carbon (experiment realized on *n*-octadecane).

Moreover, as we shall show in a subsequent paper, the study of the polymers by IR spectrophotometry clearly indicates the presence of ester groups. It will be noted that Grimm et al. (3) have already shown the occurrence of analogous compounds arising from the chlorination of oleic acid.

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