Chlorinated Long Chain Fatty Acids—Their Properties and Reactions: III. Solvent Effects in the Dehydrohalogenation of Sodium 9,10-Dichlorooctadecanoate in Dilute Alkaline Solutions

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ABSTRACT

The first stage of the alkaline dehydrohalogenation of sodium 9,10-dichlorooctadecanoate (DCO) has been studied in ethylene glycol-water mixtures and in pure water at 90 C. The rate of the reaction was found to decrease rapidly with increasing water concentration. The rate of removal of the first chlorine from sodium 9,10-dichlorooctadecanoate was determined as a function of the water concentration in various ethylene glycol-water mixtures. The rate coefficient (k_{OH}) in pure water solution was $1.4 \cdot 10^{-4}$ kg·mole^{-1}·min^{-1} as compared to the maximum value of $2.7 \cdot 10^{-2}$ kg·mole^{-1}·min^{-1} in 19 wt % solution. The effects of temperature and base concentration on the reaction rate were also investigated.

INTRODUCTION

The base-catalyzed dehydrohalogenation of saturated organic halides in alcohol-water mixtures proceeds rapidly and mostly quantitatively. In water the rate of this reaction is smaller but still easily detectable.

Unsaturated long chain fatty acids (C_{18}) form the main part of the fatty acid fractions in the resins of spruce and pine woods (1-3). During the bleaching process in the pulp industry, these acids may be chlorinated and again dehydrochlorinated. The halogen may also be eliminated in the highly alkaline mercerization in viscose manufacture. The dehydrochlorination is also partly responsible for the decrease in the brightness of bleached pulp under certain conditions (4). However, most of the earlier investigations dealing with the alkaline dehydrohalogenation of the vic-dihalogenated long chain fatty acids are merely semi-qualitative (5-9). Kinetic and mechanistic studies of alkaline dehydrohalogenation are mainly limited to alkyl halides (10) and the results reported for the vic-dihalides of long chain fatty acids are acetylenic derivatives rather than conjugated diolefins (5). Consequently, both technical and basic applications make clarification of the latter reactions very desirable and important.

In a previous paper (11) we described the alkaline dehydrochlorination of sodium 9,10-dichlorooctadecanoate (DCO) in aqueous ethylene glycol. The reaction mechanisms were established with kinetics and product analyses carried out by NMR and IR spectroscopy. The reactions have been found to proceed in two stages, the reaction product after the first stage being a vinyl halide-type intermediate and that after the second stage, an acetylenic acid. We found that the rate ratio of the removal of the first and second chlorines at 90 C is about 350. In this paper, we will present the effects of temperature, solvent composition and sodium hydroxide concentration on the dehydrochlorination rate of DCO in ethylene glycol-water mixtures and the reaction rate in alkaline water solution.

EXPERIMENTAL PROCEDURES

9,10-Dichlorooctadecanoic acid and its sodium salt

(DCO) were prepared as described previously (12).

Kinetic Measurements

The reaction mixture was prepared from two thermostated (30 min) solutions, one composed of DCO in ethylene glycol-water mixture and the other of sodium hydroxide in the similar ethylene glycol-water mixture, by pouring the latter solution into the former. This mixture was kept in the constant temperature oil bath and its temperature was held constant to ± 0.1 C by a Jumo mercury contact thermometer. The reactions were followed by titrating the released chloride ions with 0.01 N $Hg(NO_3)_2$. Two parallel series of samples were titrated after dilution to 100 ml with methanol (12). The samples were taken with a thermostated glass pipette and divided into two parts (about 2.5 g/sample), each of which was discharged into a weighed ice-cooled flask to which about 1 ml of 2.5 N nitric acid had been added to arrest the reaction before weighing. The samples were weighed immediately. Before titration carried out at 23 C, the samples were stored at 0 C.

Product Analyses

The reaction products of the first and second stages of dehydrochlorination were separated and analyzed (11). The ferric chloride test of the product for the presence of hydroxyl groups after the removal of the first chlorine atom was negative. The final product collected after the removal of both chlorines was purified by crystallization and the melting point of this product was 45.5 C (11). The IR spectrum of the final product was recorded using a potassium bromide pellet technique (11). The NMR spectra of the products of both stages of dehydrochlorination of DCO and those of oleic and dichlorooctadecanoic acids were recorded in deuterochloroform. The characteristic proton chemical shifts downfield from tetramethyl silane (TMS) were 5.24-5.42 ppm for the olefinic hydrogens of oleic acid, 4.09-4.28 ppm for the protons of the grouping -CHCl-CHCl- in 9,10-dichlorooctadecanoic acid and 5.35-5.58 ppm for the proton of the vinylic grouping -CCl=CH- in the product after the first stage of the dehydrochlorination. The results obtained in our previous work (11) are in close agreement with those reported by Rheineck and Sreenivasan (9) and Ucciani (13) and confirm that the dehydrochlorination of DCO proceeds via a vinyl halide-type intermediate and yields 9-octadecynoic acid as the final product.

Calculation of Rate Coefficients

As previously reported, the pseudo first-order rate coefficients for the removal of the first chlorine atom from DCO may be calculated from the expression (11):

$$K = \frac{1}{t} \ln \frac{v_\infty - v_0}{v_\infty - v_t} \quad (\text{min}^{-1}) \qquad [1]$$

TABLE I

Rate Coefficients of the First Stage of Alkaline
Dehydrochlorination of Sodium 9,10-Dichloroctadecanoate

Experiment	Temperature[a] C	Substrate (molality) 10^3	NaOH molality	Water content Mole fraction	Water content Weight percent	$10^3 k$ min⁻¹	$10^3 k_{OH}$ kg·mole⁻¹·min⁻¹
1	90	9.6	0.787	1.000	100.0	0.22 ± 0.01[b]	0.14 ± 0.01[b]
2	90	9.7	0.786	0.952	85.2	0.48 ± 0.02	0.31 ± 0.01
3	90	9.5	0.786	0.890	70.0	1.07 ± 0.01	0.68 ± 0.01
4	90	9.6	0.796	0.737	44.9	8.21 ± 0.10	5.16 ± 0.06
5	90	9.5	0.779	0.652	35.2	16.8 ± 0.2	10.8 ± 0.2
6	90	9.4	0.780	0.360	14.0	40.8 ± 0.5	26.1 ± 0.4
7	90	9.4	0.776	0.262	9.3	36.5 ± 0.5	23.5 ± 0.4
8	90	10.0	0.774	0.165	5.4	31.4 ± 0.4	20.3 ± 0.3
9	80	8.1	0.681	0.837	59.8	0.96 ± 0.03	0.71 ± 0.02
10	90	8.1	0.661	0.837	59.8	3.58 ± 0.05	2.71 ± 0.04
11	100	8.1	0.654	0.837	59.8	10.6 ± 0.2	8.10 ± 0.20
12	70	9.4	0.778	0.536	25.1	3.13 ± 0.05	2.01 ± 0.03
13	70	9.4	0.776	0.536	25.1	3.23 ± 0.03	2.08 ± 0.02
14	80	9.8	0.777	0.536	25.1	11.3 ± 0.3	7.28 ± 0.19
15	80	9.6	0.778	0.536	25.1	11.8 ± 0.2	7.60 ± 0.11
16	90	9.4	0.777	0.536	25.1	33.8 ± 0.3	21.7 ± 0.2
17	70	9.4	0.779	0.447	19.0	4.59 ± 0.06	2.95 ± 0.04
18	80	9.4	0.780	0.447	19.0	15.2 ± 0.1	9.73 ± 0.06
19	90	9.4	0.779	0.447	19.0	42.2 ± 0.4	27.1 ± 0.3
20	60	9.0	0.733	0.165	5.4	1.55 ± 0.02	1.06 ± 0.01
21	70	9.1	0.723	0.163	5.4	4.17 ± 0.04	2.89 ± 0.03
22	80	9.1	0.730	0.165	5.4	11.1 ± 0.2	7.57 ± 0.10
23	90	8.7	0.733	0.167	5.5	27.8 ± 0.3	19.0 ± 0.2
24	70	9.1	0.806	0.007	0.2	4.10 ± 0.04	2.55 ± 0.03
25	80	9.1	0.804	0.007	0.2	11.3 ± 0.1	7.02 ± 0.06
26	90	9.2	0.803	0.007	0.2	27.1 ± 0.3	16.9 ± 0.2
27	90	9.5	0.211	0.167	5.5	(7.16)	17.0 ± 0.3[c]
28	90	10.1	0.413	0.167	5.5	(14.0)	16.8 ± 0.3[c]
29	90	8.0	1.044	0.167	5.5	37.9 ± 0.4	18.1 ± 0.2
30	90	7.9	0.732	0.167	5.5	26.3 ± 0.6	18.0 ± 0.5
31	90	14.2	0.731	0.167	5.5	29.6 ± 0.3	20.2 ± 0.2

[a]$\pm$ 0.1 C

[b]Standard deviation of the mean of 10 to 15 individual determinations.

[c]Calculated from the second-order rate equation.

and the second-order rate coefficient from the expression:

$$k_{OH} = \frac{k}{2[OH^-]} \quad (kg \cdot mole^{-1} \cdot min^{-1}) \qquad [2]$$

Mean rate coefficients estimated by substituting experimental data in these equations were reproducible in the limits of 5% (entries 12 and 13 in Table I). The rate coefficients of the slow reactions (entries 2, 9 and 14 in Table I) were calculated by the Guggenheim equation:

$$kt + \ln(v' - v) = constant \qquad [3]$$

where v is the consumption of the titrant per gram of reaction mixture at time t and v' the consumption at time t'; t' = t + τ, where τ is a constant. The values of the pseudo first-order rate coefficient k were calculated by the method of least squares. The rate coefficients estimated by this method were in good agreement with those calculated from Equation 1 (entries 14 and 15 in Table I). The decrease in base content due to the formation of sodium chloride during the elimination reactions at low initial base concentrations (entries 27 and 28 in Table I) had to be taken into account. The rate coefficients were then calculated from the common second-order rate equation.

The titrant consumption without substrate at 90 C increased slightly with time, obviously owing to the reaction of the alkali with glass. The consumption (ml/g) was 0.036 and 0.059 at 10 and 2850 min, respectively, after beginning of the reaction. Molality of sodium hydroxide in ethylene glycol-water mixture (16.7 mole % H_2O) was 0.732. The error due to this effect is less than 1-2%. Application of the Guggenheim method in which the final value is unnecessary makes it possible to reduce the error in

the rate coefficients of the slow reaction.

The determination of the rate coefficient in water solution differed slightly from the other measurements. The preexaminations showed that the half-life of the dehydrochlorination reaction of DCO in water was about 40 hr. That is why the pseudo first-order rate coefficient (k) was determined following the reaction during the first half-life and plotting ln(a-x) against reaction time. A good linear dependence was observed and the slope of this line gave the value $2.20 \cdot 10^{-4}$ min⁻¹ for k from which the second-order rate coefficient (k_{OH}) was obtained using Equation 2. The quantity a is the final consumption of the titrant (ml/g) which was obtained by multiplying the calculated final consumption with the factor 1.080 ± 0.005 based on the ratio a_{obs}/a_{calc} of eight earlier kinetic runs in different solvent mixtures, whereas x is the consumption at time t.

RESULTS

Solvent Effect

The second-order rate coefficient depends greatly on the ratio of the components of the solvent mixture. The plot of the second-order rate coefficient (k_{OH}) against mole fraction of water based on the experimental data (Table I) presented in Figure 1 has a maximum when the water content is about 45 mole %. The value of the second-order rate coefficient of the dehydrochlorination of DCO in alkaline (0.787 m NaOH) water solution at 90 C was found to be $1.4 \cdot 10^{-4}$ kg·mole⁻¹·min⁻¹.

Effect of Temperature

Arrhenius plots for the reactions in five ethylene glycol-water mixtures are shown in Figure 2. The values of the Arrhenius parameters and activation entropies at 90 C
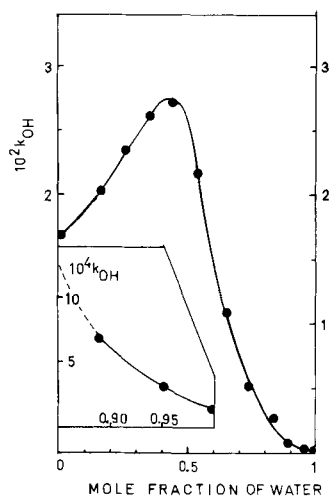
FIG. 1. Dependence of second-order rate coefficient of sodium 9,10-dichlorooctadecanoate in the first stage of the alkaline dehydrochlorination on water content in ethylene glycol-water mixtures at 90 C.

FIG. 2. Plots of log k_{OH} against $1/T$ for the first stage of the alkaline dehydrochlorination of sodium 9,10-dichlorooctadecanoate in ethylene glycol-water mixtures. Mole fraction of water: A, 0.837; B, 0.536; C, 0.447; D, 0.165; E, 0.007.

calculated by the method of least squares are presented in Table II.

Effects of Base and Substrate Concentration

The linear dependence of the pseudo first-order rate coefficient on molality of sodium hydroxide indicates that the OH-effect does not play any significant role at the used base concentrations.

Variation of the substrate concentration alters the reaction rate only slightly (entries 23, 30 and 31 in Table I).

DISCUSSION

The dehydrochlorination of DCO in aqueous ethylene glycol promoted by sodium hydroxide occurs in two stages. In the first stage a double bond with a chlorine atom attached to one of the carbon atoms is formed and the reaction product after the second stage contains a triple bond (11). In the conditions used in this work, a bimolecular 1,2- or beta-elimination (E2) which proceeds according to the Saytzeff rule is often accompanied by a bimolecular substitution (S_N2). It is known that the following factors promote the E2 elimination: strong base (OH-, RO-), and a halogen at β-carbon (the halogen in α-position removed).

Moreover, when the halogen is the leaving group, the elimination usually proceeds by the E2 mechanism (14). The possible paths of the elimination and substitution reactions in the dehydrochlorination of DCO in an alkaline aqueous medium are shown in Figure 3. Because both chlorine atoms of DCO are located in the middle of a long carbon chain, both have an equal chance of being removed.
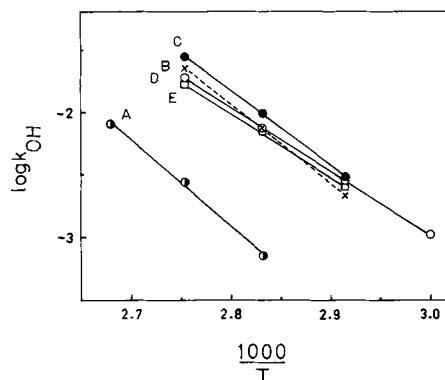
Consequently, sodium 9(10)-monochloro-9-octadecenoates can be produced by elimination and sodium 9(10)-hydroxy-10(9)-chlorooctadecanoates by substitution in the first stage of the reaction. It is unlikely that one of the final products is sodium 9(10)-hydroxy-9-octadecenoate (reaction A2 in Figure 3) because the vinyl carbon is very resistant to nucleophilic substitution (14). Moreover, in an earlier study the product after the first stage of dehydrochlorination of DCO was separated and consisted only the vinylic monochloro derivative (11).

Ratio of the Rates of the Elimination and Substitution Reactions

The kinetic measurements give the sum of the rate coefficients of two different reactions, namely, elimination and substitution (15,16): $k_{OH} = k_{E2} + k_{S_N2}$. The over-all reaction rate depends on temperature, the solvent, the ionic strength and the concentration and strength of the base, but these effects cannot be completely separated (15). The following factors favor the E2 reaction more than the S_N2 reaction (14,17,18): strong base at high concentration, low polarity of solvent, high temperature, and α- and β-branching. The halide-leaving group, however, does not greatly affect the $E2/S_N2$ rate ratio (14).

Chlorinated fatty acids in the alkaline stage of pulp bleaching are in water solution. Because increasing polarity of the solvent decreases the velocity of elimination (E2) more than that of substitution (S_N2) (17,18), the decrease in the over-all reaction rate may be due mainly to a decrease in the elimination rate. On the other hand, the high temperatures (40-140 C) prevailing in the alkaline stage, particularly in the manufacture of dissolving pulp, and the presence of strong base (NaOH) favor elimination.

Moreover, α- and β-branching generally retards the S_N2 reaction but influences only slightly to the rate of the E2 reaction. DCO is a secondary halide in which the α-carbon atom carries the removable chlorine atom. When the

TABLE II

Values of Arrhenius Parameters and Activation Entropies at 90 C for the First Stage of Alkaline Dehydrochlorination of Sodium 9,10-Dichlorooctadecanoate in Ethylene Glycol-Water Mixtures

Water content		E, kcal·mole^{-1}	logA	ΔS, entropy unit
Mole fraction	Weight percent			
0.007	0.2	23.52 ± 0.75[a]	12.39 ± 0.47[a]	- 4.2 ± 2.2[a]
0.165	5.4	23.15 ± 0.12	12.21 ± 0.08	- 5.1 ± 0.4
0.447	19.0	27.55 ± 0.84	15.03 ± 0.52	+ 7.9 ± 2.4
0.536	25.1	28.80 ± 1.64	15.67 ± 1.02	+ 10.8 ± 4.7
0.837	59.8	31.88 ± 1.63	16.60 ± 0.98	+ 15.1 ± 4.5

[a]Standard deviation.

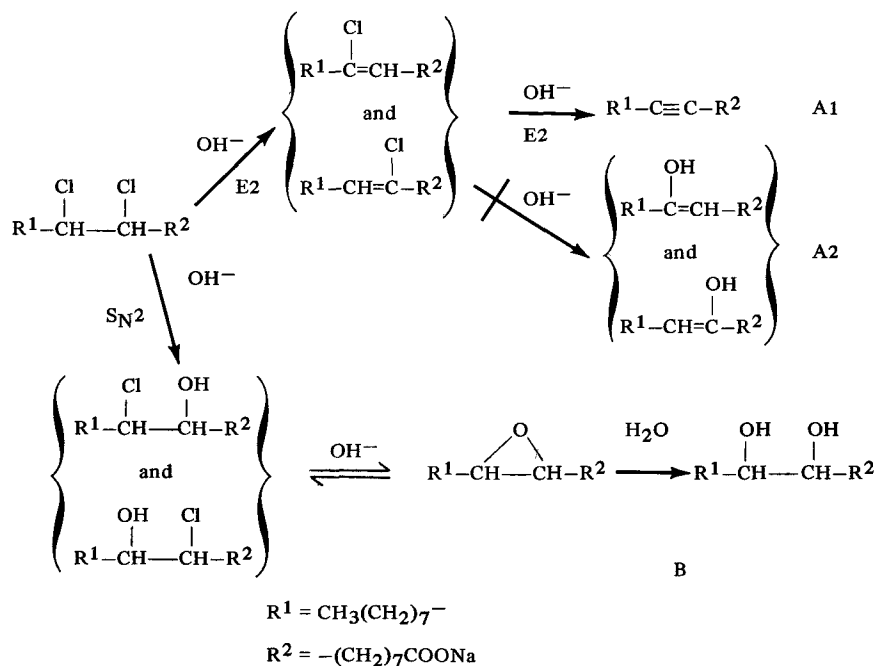R^1 = CH$_3$(CH$_2$)$_7$$^-$

R^2 = -(CH$_2$)$_7$COONa

FIG. 3. Possible reaction paths in the alkaline dehydrochlorination of sodium 9,10-dichlorooctadecanoate in studied conditions.

bimolecular elimination and substitution reactions proceed concurrently, the E2/S$_N$2 rate ratio does not depend on the base concentration (17). On the basis of an earlier study, this ratio is very much greater than unity in aqueous ethylene glycol containing 5.4% water (11). Consequently, it can be assumed that the dehydrochlorination in alkaline water solution promoted by sodium hydroxide occurs principally by the E2 mechanism (reaction A1 in Figure 3).

King (7) obtained a product which contained some potassium 9,10-dihidroxyoctadecanoate by boiling 9,10-dichlorooctadecanoic acid with 2 N potassium hydroxide at 100 C for 30 hr. The liberated acid melted at 95 C (reaction B in Figure 3). The ratio of the elimination and substitution rates may often be determined from the measured over-all rate coefficient and the ratio of products (15). In this work this ratio could not, however, be determined because of the great predominance of the elimination reaction.

Effect of Solvent on Rate

The solvent can change the rate and mechanism of elimination reactions. These complicated effects are interpreted, e.g., with the aid of the solvent dielectric constant or different solvation models for the initial and transition states of the reactants. Many other properties of the solvent in the elimination reactions may be also reflected, e.g., hydrogen bonding, cohesion, nucleophilicity and electrophilicity (19). The solvent has also been found to influence the rate of the dehydrohalogenation. This effect is usually greater in the elimination (E2) than in the substitution (S$_N$2) reactions (18). Accordingly, the dehydrochlorination of DCO in alkaline ethylene glycol-water mixtures occurs predominantly by the E2 mechanism. Very likely the solvent does not alter the mechanism of this reaction, even when the composition of the solvent mixture approaches pure water. It is known that a decrease in dielectric constant tends to increase the rate of base-promoted dehydrohalogenation (20). However, the change in the reaction rate cannot be sufficiently explained by the variation of the solvent dielectric constant. The solvation theory of Hughes and Ingold (21,22) is valid for alkyl halides in protic solvents, but the distribution of charge in

the initial reactants and the transition state explains only partially the variation of rates in alcoholic water solutions containing alkali metal hydroxides (14). When water and alcohol are solvent components, hydroxide ion is in equilibrium with alkoxide ion (15,18,23):

$$ROH + OH^- \rightleftharpoons RO^- + H_2O \qquad [4]$$
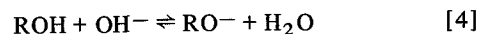
Addition of alkali metal hydroxide shifts the equilibrium to the right and almost completely in dry alcohol (24). The anion of ethylene glycol is a weaker base than the hydroxide ion in aqueous ethylene glycol. The change in the reaction rate may be due to the variation of the concentration ratio of these ions. The plot of the rate coefficient against the mole fraction of water presented in Figure 1 has a maximum when the mole fraction of water is about 0.45. This may be explained by assuming that the addition of water to pure ethylene glycol shifts equilibrium (Equation 4) to the left and thus increases the concentration of the stronger base, the hydroxide ion. Hence the reaction rate increases, but after the maximum, solvation phenomena become predominating and the rate decreases rapidly, mainly as a consequence of increasing selective solvation of the hydroxide ions by water. According to Banthorpe (15), the variation of the elimination rate in aqueous alcohol containing an alkali metal hydroxide is more dependent on the change in the basicity of the reagent than on solvation. On the basis of the above discussion, the rate of dehydrochlorination of DCO in alkaline ethylene glycol-water mixtures depends mainly on two factors: the equilibrium between hydroxide and alkoxide ions, and the changes in solvation associated with changes in solvent composition.

Effect of Temperature

The rates of the dehydrochlorination of DCO in alkaline ethylene glycol-water mixtures at various temperatures follow the Arrhenius equation in the chosen temperature ranges (Fig. 2). Because the dehydrochlorination of DCO resembles closely the dehydrohalogenation of simple alkyl halides in nearly identical conditions, the data obtained in this work may be compared with the results presented by Hughes et al. (22). They found that solvation in aqueous

and alcoholic solvents caused the activation energy to be greater (1-2 kcal/mole) for the E2 elimination than for the S_N2 substitution. Consequently, the elimination is favored by increasing of temperature. The activation energies for simple alkyl halides have been found to be in the range 20-25 kcal per mole (22). Moreover, according to Banthorpe (15), "normal bimolecular" activation entropies vary from -10 to -6 entropy unit. The experimental data in Table II show that the activation energy and entropy for the removal of the first chlorine atom of DCO are of the same order and "normal" only when the content of ethylene glycol in the solvent mixture is very high ($\geqslant 94.5$ wt %). The values of the activation energy and entropy are considerably higher when the solvent contains 81 wt % ethylene glycol and differ clearly from those reported by Hughes et al. (22) who obtained "normal" values for reactions in an ethyl alcohol-water mixture containing only 55 wt % alcohol. This is obviously due to the different solvations by water in ethylene glycol-water and in ethanol-water mixtures. Consequently, it is most likely that in this work the high activation energies and the large positive activation entropies in solvent mixtures containing more than 20 wt % water result from changes in solvation but not from a change in reaction mechanism.

ACKNOWLEDGMENTS

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