Hydrochlorination of Oleic Acid: Kinetics and Henry's Constant

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ABSTRACT: The addition reaction of gaseous hydrogen chloride to oleic acid (hydrochlorination) was investigated. Oleic acid was placed in an autoclave chamber, into which gaseous hydrogen chloride was fed, and the reaction was carried out under batch and semiflow conditions. The hydrochlorination of oleic acid by hydrogen cloride is a gas–liquid reaction involving the initial absorption of hydrogen chloride into a quiescent liquid, accompanied by a reaction of the dissolved gas with the liquid to form chlorostearic acid. The course of the reaction was monitored by withdrawing oil samples at 30-min intervals and determining the iodine value, acid value, and chlorine content. The kinetics of hydrochlorination was studied at constant pressure (40 atm). The experimental data were fitted to an irreversible pseudo zero-order rate equation with the reaction constant $k = 2.293 \times 10^{-7}$ mol/cm^3·s. The solubility of HCl (Henry's constant) in chlorostearic acid was estimated from two types of batch experiments, including a single and double feed of HCl. The mean Henry's constant value for physical absorption was 3218 atm cm^3/mol in the pressure range of 11.2–16 atm and at a temperature of 21°C. Similar batch experiments were performed in oleic acid, and the results supported the Henry's constant value determined for chlorostearic acid.

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KEY WORDS: Chlorostearic acid, Henry's constant, hydrochlorination reaction, kinetics, oleic acid, solubility.

Vegetable oils and their component FA represent a significant renewable source for the production of useful chemicals. However, their reactivity must be enhanced by introducing additional functionalities into the FA molecules (1,2). Thus far, a variety of chemical and biochemical reactions have been used for their conversion to value-added products, such as the group of hydroxystearic FA and their derivatives. These compounds are very important materials for use in greases, lubricants, detergents, and chemical additives (3–6). In addition, 9- or 10-monohydroxystearic acids can be used as substitutes for 12-hydroxystearic acid (derived from castor oil), which plays an important role as a chemical intermediate in a variety of final products, such as high-temperature lubricants (7, 8).

The introduction of a polar group, such as a hydroxyl group, into the middle of the hydrocarbon chain of an oleic acid molecule reduces its hydrophobicity and can improve the HLB ratio (hydrophilicity to hydrophobicity) of surfactants based on oleic acid (9). In addition, the synthesis of monohydroxystearic acids from oleic acid has been achieved by different chemical reactions, such as the hydroboration of methyl oleate, formoxylation, and acetoxylation, as well as by enzymatic reactions (2–6,10). We have already studied the kinetics of the chloroacetoxylation of oleic acid (11). At present, kinetic studies on the hydrochlorination of oleic acid or other unsaturated FA have not been conducted.

This work is part of ongoing research aimed at the production of methyl monohydroxystearates and their derivatives from oleic acid through a hydrochlorination reaction followed by saponification or esterification of the addition product. The present work investigated the kinetics of the reaction of oleic acid with gaseous hydrogen chloride under constant pressure (40 atm). The solubility of hydrogen chloride (Henry's constant) in FA (chlorostearic acid and a mixture of oleic and chlorostearic acid) was estimated from two types of batch experiments, including a single and double feed of HCl. These experiments were carried out in an autoclave at an initial pressure of 40 atm and a constant temperature of 21°C.

EXPERIMENTAL PROCEDURES

Materials. Oleic acid (pure, Merck Art 471 with an acid value of 199, an iodine value of 90, a saponification value of 198.5, a mean oleic acid content of 85%, and a density of 0.89 g/mL), hydrogen chloride (gaseous, chemically pure, anhydrous), petroleum ether (Merck, b.p. 40–70°C), sodium sulfate, and sodium hydrogen carbonate (purity grade, for analysis) were obtained from Merck (Darmstadt, Germany).

Apparatus. The reaction was performed in a stainless steel autoclave (468 cm^3; Fig. 1) equipped with a glass cylinder (with a 40 mm o.d., 37 mm i.d., and a conical end 15 mm long), manometer, thermometer, and gas inlet. The cylinder was placed in a water bath of constant temperature (± 0.5°C). A Schoeniger apparatus was used for chlorine analysis (12,13). This is a microanalytical method for the determination of chlorine in organic substances. The sample is burned in a special ashless filter paper in an Erlenmeyer flask filled with O_2 and containing a solution of H_2O_2. After combustion, the product is absorbed into the solution, and an acidimetry method is applied for the determination of chlorine. The density of the fatty mixture was determined using IUPAC Method 2.101 (14). In

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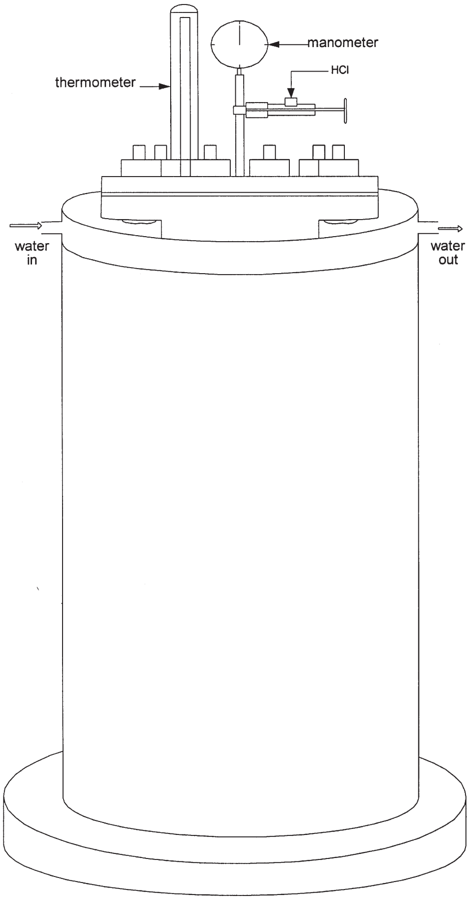

FIG 1. Autoclave of hydrochlorination.

all the experiments, the initial pressure (40 atm) was selected because we observed experimentally that the reaction or physical absorption yield was greatly affected by pressure. The temperature was held constant at 21°C. Since the reaction is exothermic, the cylinder of the autoclave was cooled with water.

Hydrochlorination of oleic acid (semibatch operation). In the first series of experiments, hydrogen chloride was fed continuously into an autoclave containing 0.5 mol of oleic acid while the pressure was held at 40 atm. The reaction time examined was in the range of 1200 to 14400 s.

The course of the reaction was estimated by analyzing samples of the liquid phase after pretreatment. The liquid sample was poured into petroleum ether and washed thoroughly with distilled water to remove the hydrogen chloride (excess) that was absorbed physically. The organic layer was then dried using anhydrous sodium sulfate and distilled to remove the solvent using a flash evaporator. The fatty mixture consisted mainly of oleic and chlorostearic acids.

Hydrochlorination of oleic and chlorostearic acids (batch operation). In the second series of experiments, oleic acid (0.5 mol) was added to the cylinder and gaseous hydrogen chloride was fed once into the cylinder, immediately raising the pressure to 40 atm. As the hydrogen chloride was absorbed in the oleic acid, an addition reaction took place. As the gas was absorbed in the liquid, the pressure gradually decreased, and after several hours, equilibrium was established. The reaction product was treated as described in the previous series of experiments and then analyzed. Similar experiments were carried out in which oleic acid was replaced with chlorostearic acid (152 g, density 0.96 g/cm^3, measured experimentally) in order to calculate the solubility of hydrogen chloride in the saturated FA. In the latter case, only physical absorption occurred. The pressure and temperature were recorded against time until equilibrium was established. In the third series of experiments, the same procedure was followed with one modification. Gaseous hydrogen chloride was fed into the system twice, raising the pressure to 40 atm, at $t = 0$ and $t = 3720$ s for absorption with a chemical reaction, and at $t = 0$ and $t = 6360$ s for physical absorption. These times were selected to accelerate the reaction and to achieve higher yields, because in that range of times, the rate of conversion of oleic acid or the physical absorption of HCl begins to reduce considerably.

Analysis. The total yield of addition product was determined by iodine value (15), acid value (15) and chlorine analysis using the Schoeniger method (12,13). Triplicates of each experiment were performed to check the reproducibility of the results.

RESULTS AND DISCUSSION

Kinetics of the hydrochlorination of oleic acid. The hydrochlorination reaction is oleic acid + HCl → chlorostearic acid (16).

In semibatch hydrochlorination, the progress of converting oleic acid to chlorostearic acid at 21°C and at a constant pressure of 40 atm was based on the analysis of data shown in Table 1 and Figure 1. The iodine value, a measure of the unsaturation of oleic acid, decreased continuously with time and revealed that as the concentration of oleic acid decreased, the product yield increased. The addition to the double bond of oleic acid was also measured by an acid value determination and a chlorine analysis (a direct measure of chlorine added) of the fatty mixture. Similar conversion results with mean deviations of ± 0.1% and ± 2%, respectively, were obtained in comparison to those calculated by the iodine value.

The kinetics of the hydrochlorination reaction of oleic acid was investigated. The hydrochlorination of oleic acid by hydrogen chloride is a gas–liquid reaction in which hydrogen chloride initially absorbs into a quiescent liquid (FA) and is accompanied by an addition reaction.

The mass transport of oleic acid (17) can be described by Equation 1:

$$\frac{dC_A}{dt} = -u\nabla C_A + D\nabla^2 C_A - r_A \qquad [1]$$

where C_A is the concentration of oleic acid, u is the flow velocity of oleic acid, D is the diffusivity of oleic acid into the FA, and r_A is the rate of the reaction.

Since the FA is quiescent, u equals zero and Equation 1 can be written as

TABLE 1
Conversion of Oleic Acid During Hydrochlorination with Gaseous Hydrogen Chloride at a Constant Pressure of 40 atm and a Constant Temperature of 21°C

Reaction time (s)	Iodine value	Cl (% w/w)	Acid value	Conversion of oleic acid (%)	Chlorostearic acid (% w/w)
1200	83.8	0.7	196.8	6.9	6.3
1800	78.9	1.3	195.6	12.3	11.7
3600	64.3	3.1	192.1	28.5	27.9
5400	55.5	4.3	189.9	38.3	38.6
7200	42.9	5.7	186.5	52.3	51.2
9000	29.1	7.5	183.2	67.7	67.4
10800	17.6	8.8	180.1	80.4	79.3
12600	9.5	10.1	178.3	89.4	90.1
14400	2.5	10.6	176.4	97.2	95.5

$$\frac{dC_A}{dt} = D\nabla^2 C_A - r_A \qquad [2]$$

The hydrochlorination of oleic acid appears to be an irreversible pseudo zero-order reaction, as verified by the linearity of conversion and the concentration against time (Table 1, Fig. 2).

Thus,

$$\frac{dC_A}{dt} = k_{\text{app}} \qquad [3]$$

where k_{app} is the overall (apparent) reaction rate. A constant value of $k_{\text{app}} = 2.293 \times 10^{-7}$ mol/cm^3·s was calculated from Equation 3 (18).

Equation 3 then becomes

$$k_{\text{app}} = D\nabla^2 C_A - r_A \qquad [4]$$

It is evident that since this process takes place under nonsteady-state conditions, $D\nabla^2 C_A \neq 0$. This means that the overall reaction rate includes both terms, diffusion and reaction phenomena.

The values of the overall rate constant k_{app} were also calculated for a first-, second-, and *n*th-order reaction (18) and are given in Table 2. For a first-order irreversible reaction using the expression for the conversion x_A, the equation is

$$dC_A/dt = k_{\text{app}} C_A \text{ or } -\ln(1 - x_A) = k_{\text{app}} t \qquad [5]$$

where x_A is the conversion of oleic acid. The plot of $-\ln(1 - x_A)$ vs. t did not give a straight line but a curve, meaning that the data did not fit this model. For the second-order reaction,

$$dC_A/dt = kC_A^{\,2} \qquad [6]$$

the plot of $x_A/[C_{A0}(1 - x_A)]$ vs. t gave a curved line.

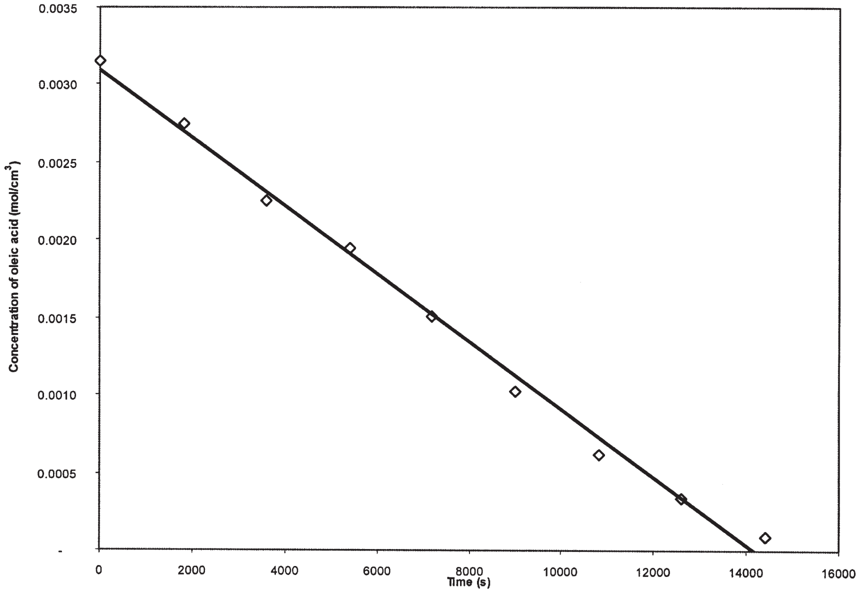

FIG 2. Hydrochlorination of oleic acid at a constant pressure (40 atm) and temperature (21°C). Test for the pseudo zero-order reaction.

TABLE 2
Hydrochlorination of Oleic Acid with Gaseous Hydrogen Chloride at a Constant Pressure of 40 atm and a Constant Temperature of 21°C[a]

Time (s)	Zero $k_{app} \times 10^{-7}$ (mol/cm^3·s)	First $k_{app} \times 10^{-5}$ (s^{-1})	Second $k_{app} \times 10^{-2}$ (cm^3/mol·s)	$n = 0.5$ $k_{app} \times 10^{-6}$ [(mol/cm^3)$^{0.5}$/s]	$n = 0.8$ $k_{app} \times 10^{-5}$ [(mol/cm^3)$^{0.2}$/s]
1800	2.258	7.673	2.612	4.161	2.391
3600	2.494	9.319	3.515	4.815	2.848
5400	2.234	8.942	3.649	4.459	2.693
7200	2.288	10.281	4.834	4.823	3.020
9000	2.366	12.522	7.359	5.373	3.543
10800	2.348	15.137	12.135	5.804	4.080
12600	2.235	17.812	21.250	6.008	4.535
14400	2.126	24.830	76.531	6.491	5.605
Mean	2.293	13.315	16.485	5.242	3.590
SD	0.1099	5.768	25.047	0.881	1.090

[a] Values of the rate constant for a zero-, first-, second-, and *n*th-order reaction. k_{app} = overall (apparent) reaction rate constant.

For the *n*th-order reaction ($n = 0.05, 0.1, 0.2, 0.3, \ldots, 0.9$),

$$dC_A/dt = kC_A^{\,n} \qquad [7]$$

a trial-and-error solution was applied by selecting a value for n and calculating k. All these models failed to describe the apparent kinetics of the reaction because of the variation in k. However, we observed that the variation in k_{app} values was reduced as n approached zero ($n = 0.05$).

Thus, the overall rate of the reaction was independent of the concentration of the reactants and the reaction product. The hydrochlorination of oleic acid could be fitted to a zero-order kinetic model. This means that the reaction rate is determined by some factor other than the concentration of the reacting material. A zero-order reaction is generally observed in higher concentration ranges, as was our case.

The calculation of Henry's constant for HCl in FA. In Figure 3 the number of moles of hydrogen chloride, $n_l^{\,a}$ and $n_l^{\,r}$, in the liquid phase against time is depicted for physical absorption (chlorostearic acid) and for absorption with a chemical reaction (oleic acid), respectively. The curves increase because as pressure drops (fewer moles of gaseous HCl) against time, more moles of gaseous HCl enter the liquid phase. In the beginning, the slope is higher since only a few moles of HCl are dissolved in the liquid; therefore, the driving force of diffusion is higher. However, as time passes, HCl enters the liquid and the slope of the curve decreases and eventually reaches a plateau. For hydrochlorination, the slope of the curve is more enhanced than for physical absorption because the concentration difference of

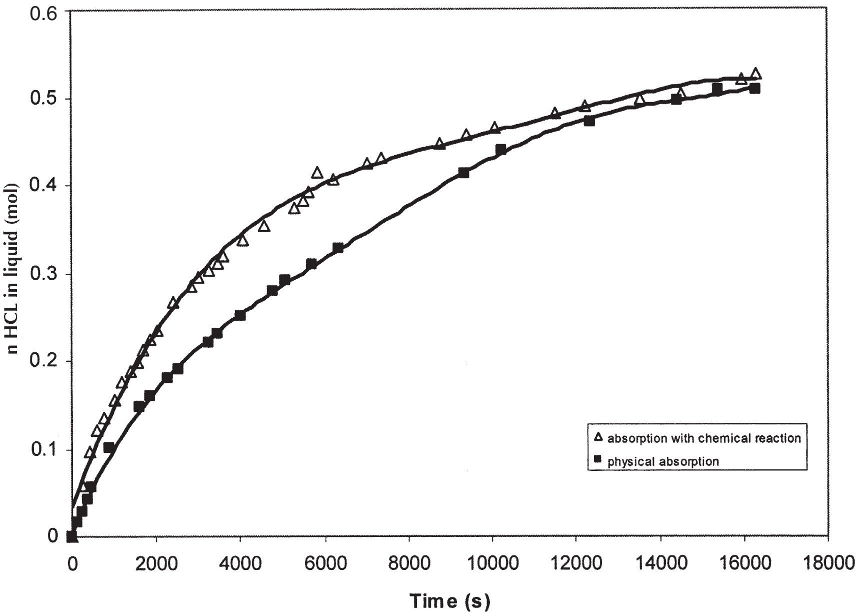

FIG 3. Hydrogen chloride in the liquid phase vs. time. Hydrochlorination of oleic acid and chlorostearic acid (batch operation, single feed) at 21°C.

TABLE 3
Physical Absorption of Gaseous HCl in Chlorostearic Acid in Batch Experiments[a]

Pressure (atm)	Temperature (K)	Compression factor	Volume (cm^3)	HCL (mol)	HCL concentration (mol/cm^3)	Henry's constant ($atm\ cm^3/mol$)
P_o	T_o		V_l^a	N^a		
40	293		158.3	0.476		
P_{ro}	T_{ro}	z_o	$V_g{}^a$	$n_{go}{}^a$		
0.490	0.903	0.730	309.7	0.706		
$P_e{}^a$	$T_e{}^a$			$n_{ge}{}^a$		
11.2	293			0.154		
$P_{re}{}^a$	$T_{re}{}^a$	$z_e{}^a$		$n_{le}{}^a$	$C_{Be}{}^a$	$H_e{}^a$
0.137	0.903	0.935		0.552	3.49×10^{-3}	3212

[a] Conditions (initial, equilibrium), moles HCl (gaseous, liquid phase), and Henry's constant. P_o = initial pressure in absorption, P_{ro} = initial reduced pressure in absorption, $P_e{}^a$ = equilibrium pressure in absorption, $P_{re}{}^a$ = reduced pressure at equilibrium in absorption, T_o = initial temperature in absorption, T_{ro} = initial reduced temperature in absorption, $T_e{}^a$ = temperature at equilibrium in absorption, $T_{re}{}^a$ = reduced temperature at equilibrium in absorption, z_o initial compressibility factor, $z_e{}^a$ = compressibility factor at equilibrium in absorption, V_l^a = constant volume of chlorostearic acid, $V_g{}^a$ = constant volume of gaseous HCl in absorption, N^a = moles of chlorostearic acid in absorption, $n_{go}{}^a$ = initial moles of gaseous HCl in absorption, $n_{ge}{}^a$ = moles of gaseous HCl at equilibrium in absorption, $n_{le}{}^a$ = moles of HCl in liquid phase at equilibrium in absorption, $C_{Be}{}^a$ = concentration of HCl in liquid phase at equilibrium in absorption, $H_e{}^a$ = Henry's constant in absorption.

HCl in the liquid is greater because of the reaction that takes place. The modified ideal gas law, expressed by the compressibility factor z, was used, which is correlated with the reduced temperature ($T_r = T/T_c$) and pressure ($P_r = P/P_c$). The compressibility factor was obtained from corresponding generalized compressibility charts (19).

To estimate the eventual solubility of gaseous HCl in chlorostearic acid (physical absorption), it was necessary to apply the modified gas law (Eq. 8), the HCl mass balance equation (Eq. 9), and Henry's law (Eq. 10) for the calculation of

- The initial total moles of HCl fed into the autoclave under the applied conditions of pressure, temperature, and volume (Eq. 8). It was assumed that the volume of chlorostearic acid remained constant during absorption.
- The moles of gaseous HCl (Eq. 8) and the moles of HCl that entered the liquid phase at equilibrium (Eq. 9).
- The concentration of dissolved HCl in the liquid at equilibrium ($C_{Be}{}^a$).
- Henry's constant (Eq. 10).

$$PV = n_g zRT \qquad [8]$$

where n_g is moles of gaseous HCl, and

$$n_{go} = n_g + n_l \qquad [9]$$

where n_{go} is initial moles of gaseous HCl and n_l is moles of HCl in the liquid phase, and

$$P_e = H_e \times C_{Be} \qquad [10]$$

where P_c is the critical pressure, H_e is Henry's constant, and C_{Be} is the concentration of HCl in the liquid phase at equilibrium.

The experimental conditions (initial and equilibrium), the calculated values of HCl in both phases, and Henry's constant are given in Table 3.

In the case of gas absorption followed by the hydrochlorination reaction, the same procedure was applied to calculate Henry's constant (Table 4). In addition, Equation 11 was used, as well as Equations 8–10, since the moles of HCl that passed into the liquid (n_l) were equal to the moles of dissolved and reacted gas, namely,

$$n_l{}^r = n_{la}{}^r + n_{lr}{}^r \qquad [11]$$

where $n_l{}^r$ is the moles of HCl in the liquid phase in the reaction, $n_{la}{}^r$ is the moles of HCl absorbed in the liquid phase in the reaction, and $n_{lr}{}^r$ is the moles of reacted HCl.

At equilibrium, the FA mixture consisted of unreacted oleic acid (0.17 mol) and chlorostearic acid (0.33 mol). (This calculation was based on the iodine value 30.8, i.e., $n_{lre}{}^r$ = moles of reacted oleic acid = 0.5 × [(90 – 30.8)/90] = 0.33 = moles of chlorostearic acid produced.) To calculate the volume of FA at equilibrium, a density value of 0.94 g/cm^3 (measured experimentally) was used. We assumed that the liquid volume was incompressible and remained constant even though HCl was absorbed in it.

For batch experiments with a double feed of hydrogen chloride, the pressure decrease against time for physical absorption and absorption with a chemical reaction are given in Figure 4. The pressure profiles were similar to those obtained in the corresponding cases of the single feed. The slope of the curves was higher at high pressures, leading to greater overall yields of dissolved HCl and chlorostearic acid in comparison with the single feed. These experiments were carried out to provide complementary data that supported the basic experimental results. Both curves reached an equilibrium pressure and, following the same algorithm in calculations, Henry's constant values were

TABLE 4
Hydrochlorination of Oleic Acid in Batch Experiments[a]

Pressure (atm)	Temperature (K)	Compression factor	Volume (cm^3)	HCL (mol)	HCL concentration (mol/cm^3)	Henry's constant (atm cm^3/mol)
P_o	T_o		V_{lo}^r	N^r		
40	293		158.7	0.5		
P_{ro}	T_{ro}	z_o	V_{go}^r	n_{go}^r		
0.490	0.903	0.730	309.3	0.705		
P_e^r	T_e^r		V_{le}^r	n_{ge}^r		
5.5	295		163	0.071		
P_{re}^r	T_{re}^r	z_e^r	V_{ge}^r	n_{le}^r		
0.067	0.900	0.970	305	0.634		
				n_{lre}^r		
				0.330		
				n_{lae}^r	C_{Be}^r	H_e^r
				0.304	1.86×10^{-3}	2957

[a] Conditions (initial, equilibrium), moles HCl (gaseous, liquid phase), and Henry's constant. P_o = initial pressure in reaction, P_{ro} = initial reduced pressure in reaction, P_e^r = equilibrium pressure in reaction, P_{re}^r = reduced pressure at equilibrium in reaction, T_o = initial temperature in reaction, T_{ro} = initial reduced temperature in reaction, T_e^r = temperature at equilibrium in reaction, T_{re}^r = reduced temperature at equilibrium in reaction, z_o = initial compressibility factor, z_e^r = compressibility factor at equilibrium in reaction, V_{lo}^r = volume of oleic acid, V_{le}^r = volume of fatty mixture at equilibrium in reaction, V_{go}^r = initial volume of gaseous HCl in reaction, V_{ge}^r = volume of gaseous HCl at equilibrium in reaction, N^r = initial moles of oleic acid or moles of fatty mixture in reaction, n_{go}^r = initial moles of gaseous HCl in reaction, n_{ge}^r = moles of gaseous HCl at equilibrium in reaction, n_{le}^r = moles of HCl in liquid at equilibrium in reaction, n_{lre}^r = moles of reacted oleic acid or HCl at equilibrium, n_{lae}^r = moles of HCl absorbed in liquid at equilibrium in reaction, C_{Be}^r = concentration of HCl in liquid phase at equilibrium in reaction, H_e^r = Henry's constant in reaction.

derived. The experimental conditions (initial, intermediate, and equilibrium), the calculated values of HCl in both phases, and Henry's constant are given in Tables 5 and 6 for physical absorption and for the chemical reaction, respectively.

Consequently, the value of Henry's constant for physical absorption remained almost the same (mean value, 3218 atm·cm^3/mol) in the pressure range of 11.2 to 16 atm. The data obtained for physical absorption (chlorostearic acid) were considered more reliable since true equilibrium was established, whereas the data for the chemical reaction (oleic acid) gave an approximation that supported the value for Henry's constant determined for chlorostearic acid.

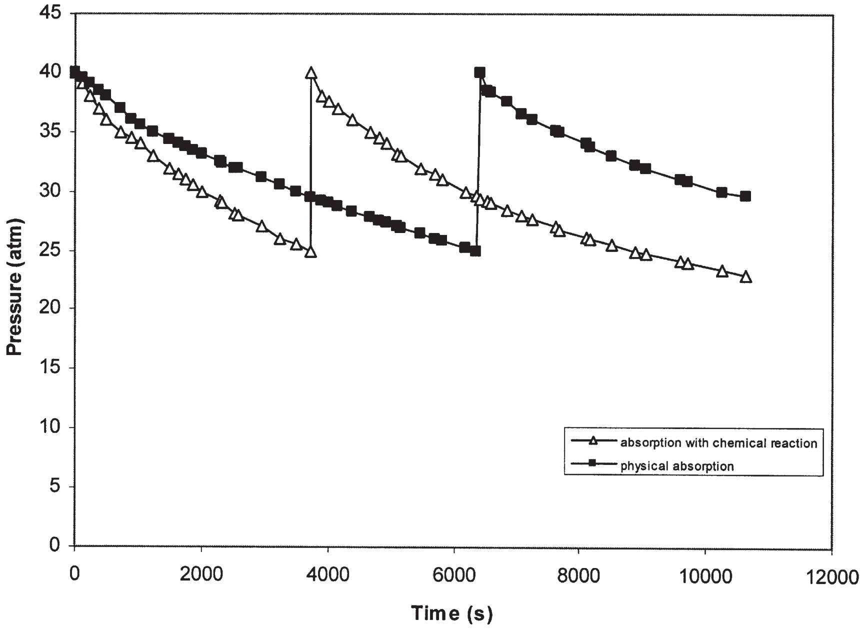

FIG 4. Pressure of gaseous hydrogen chloride vs. time. Hydrochlorination of oleic acid and chlorostearic acid at 21°C (batch operation with a double feed of gaseous hydrogen chloride).

TABLE 5
Physical Absorption of Gaseous HCl in Chlorostearic Acid in Double-Feed Batch Experiments[a]

Pressure (atm)	Temperature (K)	Compression factor	Volume (cm^3)	HCL (mol)	HCL concentration (mol/cm^3)	Henry's constant ($atm\ cm^3/mol$)
P_o	T_o		V_l^a	N^a		
40	293		158.3	0.476		
P_{ro}	T_{ro}	z_o	$V_g{}^a$	$n_{go}{}^a$		
0.490	0.903	0.730	309.7	0.706		
P_t^a	T_t^a					
40	293					
$P_{rt}{}^a$	$T_{rt}{}^a$	$z_t{}^a$		$n_{gt}{}^a$		
0.490	0.903	0.730		0.314		
$P_e{}^a$	$T_e{}^a$			$n_{ge}{}^a$		
16	292			0.238		
$P_{re}{}^a$	$T_{re}{}^a$	$z_e{}^a$		$n_{le}{}^a$	$C_{Be}{}^a$	$H_e{}^a$
0.196	0.900	0.900		0.786	4.97×10^{-3}	3222

[a] Conditions (initial, intermediate, equilibrium), moles HCl (gaseous, liquid phase), and Henry's constant. P_t^a = pressure at time *t* in double-feed absorption, $P_{rt}{}^a$ = reduced pressure at time *t* in double-feed absorption, T_t^a = temperature at time *t* in double-feed absorption, $T_{rt}{}^a$ = reduced temperature at time *t* in double-feed absorption, z_t^a = compressibility factor at time *t* in double-feed absorption, $V_g{}^a$ = constant volume of gaseous HCl in absorption, $n_{gt}{}^a$ = moles of gaseous HCl at time *t* in double-feed absorption. For other abbreviations see Table 3.

TABLE 6
Hydrochlorination of Oleic Acid in Double-Feed Batch Experiments[a]

Pressure (atm)	Temperature (K)	Compression factor	Volume (cm^3)	HCL (mol)	HCL concentration (mol/cm^3)	Henry's constant ($atm\ cm^3/mol$)
P_o	T_o		$V_{lo}{}^r$	N^r		
40	293		158.7	0.5		
P_{ro}	T_{ro}	z_o	$V_{go}{}^r$	$n_{go}{}^r$		
0.490	0.903	0.730	309.3	0.705		
P_t^r	$T_t{}^r$					
40	295					
$P_{rt}{}^r$	$T_{rt}{}^r$	$z_t{}^r$		$n_{gt}{}^r$		
0.490	0.909	0.730		0.365		
$P_e{}^r$	$T_e{}^r$		$V_{lc}{}^r$	$n_{ge}{}^r$		
9	292		168	0.120		
$P_{re}{}^r$	$T_{re}{}^r$	$z_e{}^r$	$V_{ge}{}^r$	$n_{le}{}^r$		
0.111	0.900	0.945	305	0.95		
				$n_{lre}{}^r$		
				0.417		
				$n_{lae}{}^r$	$C_{Be}{}^r$	$H_e{}^r$
				0.533	3.17×10^{-3}	2837

[a] Conditions (initial, intermediate, equilibrium), moles HCl (gaseous, liquid phase), and Henry's constant. P_t^r = pressure at time *t* in double-feed reaction, $P_{rt}{}^r$ = reduced pressure at time *t* in double-feed reaction, $T_t{}^r$ = temperature at time *t* in double-feed in reaction, $T_{rt}{}^r$ = reduced temperature at time *t* in double-feed reaction, z_t^r = compressibility factor at time *t* in double-feed reaction, $n_{gt}{}^r$ = moles of gaseous HCl at time *t* in double-feed reaction. For other abbreviations see Table 4.

REFERENCES

1. Gunstone, F.D., *The Lipid Handbook*, Chapman & Hall, London, 1986, pp. 19, 572.
2. Pryce, E.H., *Fatty Acids*, AOCS, Champaign, IL, 1979.
3. Black, L.T., and R.E. Beal, Acetoxylation of Methyl Oleate with Resin Catalyst, *J. Am. Oil Chem. Soc. 44*:310–312 (1967).
4. Koritala, S., and M.O. Bagby, Microbial Conversion of Linoleic and Linolenic Acids to Unsaturated Hydroxy Fatty Acids, *J. Am. Oil Chem. Soc. 69*:575–578 (1992).
5. Lancer, A.C., R.D. Platner, and M.O. Bagby, Production of 15-, 16- and 17-Hydroxy-9-octa-decenoic Acids by Bioconversion of Oleic Acid with *Bacillus pumilus*, *J. Am. Oil Chem. Soc. 69*:363–366 (1992).
6. Derksen, J.T.P., and F.P. Cuperus, Processing of Oil Seeds Constituents for Nonfood Applications, in *Proceedings of the World Conference on Oilseed and Edible Oils Processing*: *Emerging Technologies, Current Practices, Quality Control, Technology Transfer and Enviromental Issues*, Vol. 1, edited by S.S. Koseoglu, K.C. Rhee, and R.F. Wilson, AOCS Press, Champaign, IL, 1998, pp. 113–120.
7. Ikan, R., *Natural Products, a Laboratory Guide*, Academic Press, New York, 1991, pp. 32–33.
8. Naughton, F.C., Production, Chemistry, and Commercial Applications of Various Chemicals from Castor Oil, *J. Am. Oil Chem. Soc. 51*:65–67 (1974).
9. Rosen, M.J., *Surfactants and Interfacial Phenomena*, 2nd edn., John Wiley & Sons, New York, 1989, pp. 323–329.

10. Munns, W.O., S. Kairys, and D.A. Manion, The Preparation of Hydroxystearic Acids from Red Oil (commercial oleic acid), *J. Am. Oil Chem. Soc. 40*:22–24 (1963).
11. Doulia, D., F. Rigas, and C. Gimouhopoulos, Chloroacetoxylation of Oleic Acid—A Kinetic Study, *J. Am. Oil Chem. Soc. 77*:239–242 (2000).
12. Schoeniger, W., The Rapid Microanalytical Determination of Sulfur in Organic Compounds, *Microchim. Acta 1*:123 (1955).
13. Schoeniger, W., The Rapid Microanalytical Determination of Halogens in Organic Substances, *Ibid. 6*:869 (1956).
14. Tsimidou, M., and D. Boskou, *Olive Oil Chemistry and Technology,* AOCS Press, Champaign, 1999, pp. 134.
15. AOAC, *Official Methods of Analysis of the Association of Official Analytical Chemists*, 14th edn., edited by S. William, Association of Official Analytical Chemists, Washington, DC, 1984.
16. March, J., *Advanced Organic Chemistry: Reactions, Mechanisms and Structure*, John Wiley & Sons, New York, 1992, pp. 750–759.
17. Gekas, V., *Transport Phenomena of Foods and Biological Materials,* CRC Press, Boca Raton, FL, 1992, pp. 9–22.
18. Levenspiel, O., *Chemical Reaction Engineering,* John Wiley & Sons, New York, 1972, pp. 409–419.
19. Coulson, J.M., J.F. Richardson, and R.K. Sinnott, *Chemical Engineering: Design*, Vol. 6, Pergamon Press, Oxford, 1991, pp. 72–79.

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