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Models for Polyesterification Kinetics. II. Esterification Kinetics in Nonpolar Medium

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ABSTRACT

In order to examine the influence of the polarity of the reaction medium on the polyesterification mechanism, the kinetics of the reaction of 1-octadecanol with octadecanoic acid in octadecanyl octadecanoate is studied with and without p-toluenesulfonic acid catalyst. Without added catalyst the overall order is 2.5 and the orders in acid and in alcohol are 1.5 and 1, respectively. The mechanism consists of an autocatalysis by the acid and involves a nonnegligible dissociation of ion pairs. This differs from the observation made in more polar media. With added p-toluenesulfonic acid, the reaction is first order in alcohol, acid, and catalyst. Activation entropy is the same both for catalyzed and noncatalyzed reactions. The catalytic effect is due to a large decrease of activation enthalpy.

INTRODUCTION

In his classic work [2-6] Flory gave a 3rd overall order for the last steps of polyesterification. Since then many controversial interpretations have been published. The various interpretations of the results obtained for esterifications and polyesterifications in the bulk can be classified into two categories:

Some authors take into consideration the results obtained during the whole course of the reaction. Most of them find a 2.5 overall order and assume that the order in acid is 1.5. The mechanism involves the existence of dissociated ion pairs.

In agreement with Flory, other authors consider only the ultimate stages of the reaction when the polarity of the medium has stopped changing and when it can be assumed that the reactive groups form a diluted solution in the polyester. A 3rd overall order is found and the mechanism involves the existence of nondissociated ion pairs.

In recent work [1] we studied esterifications carried out with low reactive end group concentrations in relatively polar media: Bulk reaction between monocarboxylic and monohydroxylic polyoxyethylenes ($\overline{M}_n \simeq 1000$), and reaction between 1-octadecanol and octadecanoic acid in benzophenone.

Such reactions are models for the last steps of polyesterifications. Both reactions are 3rd order which fits Flory [4] and Solomon [7]. Moreover, the reaction between oligomers carried out with a nonstoichiometric ratio of reactants clearly shows that the orders in acid and in alcohol are 2 and 1, respectively. This fits the existence of associated ion pairs and of an autocatalysis by the acid in polymeric medium.

From these results it was concluded that the whole course of polyesterification cannot fit a 2.5 order and that conclusions drawn from this value have no meaning.

We previously studied the reaction of 1-octadecanol with octadecanoic acid in the absence of solvent [8]. The results were not univocal since we found the overall order increasing with increasing pressure. This was explained by modifications in dielectric properties with a possible role of water in local modifications of the dielectric constant since the medium could not be regarded as diluted, at least in the early stages of the reaction. The aim of the present work is to examine the influence of the polarity of the reaction medium on the polyesterification mechanism. It consists of the study of a model esterification in nonpolar medium, namely, the reaction of 1-octadecanol with octadecanoic acid in 1-octadecanyl octadecanoate (C36 ester) solution, with or without added p-toluenesulfonic acid.

EXPERIMENTAL

Apparatus

This was described in the first article of the present series [1].

Procedure

This was described in the same article [1].

Reactions under reduced pressure were carried out either in a

50-cm^3 vessel with ~40 g of reaction mixture or under atmospheric pressure in a 500-cm^3 vessel with ~400 g of reaction mixture. The initial concentration of acid was 0.25 eq/kg in the case of an excess of alcohol and 0.5 eq/kg in the other cases.

Reactants

1-Octadecanol and octadecanoic acid (Fluka A.G. puriss grade) were used without further purification.

1-Octadecanyl octadecanoate is synthesized as follows: A mixture of 1-octadecanol (2 mol, 541 g), octadecanoic acid (2.02 mol, 575 g) (both Fluka A.G. puriss grade), and toluene (120 cm^3) is heated to reflux in a flask fitted with a reflux condenser and a Dean-Stark separator. Condensation water is removed by azeotropic distillation for a period of 24 h (temperature must be raised from 170 to 190°C). Toluene is stripped off in vacuo and the resulting ester recrystallized once in absolute ethanol (90 g/L solution) and twice in absolute acetone (100 g/L solution) (both solvents are puriss grade from Prolabo). $T_f = 60.3$ C; (Ref. 16, 60.3°C).

Carboxy content (octadecanoic acid) $< 0.009\%$.

Catalyst

p-Toluenesulfonic acid (PTSA) is recrystallized from its solution in concentrated hydrochloric acid and then vacuum dried over NaOH pellets for a week [17]. Predetermined amounts of concentrated water solution of catalyst are introduced through a calibrated microsyringe into the reaction medium.

Titration

Samples (50 to 100 mg) are dissolved in a toluene/ethanol mixture (1/1 vol) at 35°C and titrated by alcoholic KOH to the potentiometric end point. The titration device is described in Ref. 1.

Treatment of Experimental Data

As previously, these were performed on a Texas Instruments T.I. 980 B computer with a FORTRAN IV program.

RESULTS AND DISCUSSION

The Problem of Side Reactions

As previously mentioned [1], alcoholysis, ester interchange, and acidolysis do not interfere with the main reaction. Hydrolysis can be disregarded as shown in specific experiments. The evaporation of reactants, oxidation, and decarboxylation were found to be negligible under our experimental conditions.

Calculation Methods

The calculation methods relative to the reactions carried out without added catalyst were fully described in the first part of this series [1]. In consequence, in this article we report only the calculation methods relative to the reactions carried out in the presence of added catalyst.

The noncatalyzed side reaction must be taken into account in the study of the reaction with added catalyst in order to determine whether it can be disregarded or not. When in the present work the noncatalyzed reaction was not taken into consideration, the resulting error on k_d was around 2 to 5%, which is very small. However, we took this side reaction into consideration in all cases.

The general rate equation is

$$-\frac{dx}{dt} = k_{d_1} x^{m_1} (x + b)^{n_1} + k_{d_2} x^{m_2} (x + b)^{n_2} \qquad (1)$$

Subindexes 2 and 1 are relative to the noncatalyzed and catalyzed reactions, respectively.

Since k_{d_2}, m_2, and n_2 are known from the noncatalyzed reaction study, Eq. (1) can be solved by the iterative integration method and the correct values of k_{d_1} obtained.

Only integer or half integer orders were tested in the studies on the catalyzed reaction since the maximum extent of reaction, p_{max}, is at least 0.8. The maxima of the curves $I_d = f(d)$ are therefore sharper than those relative to noncatalyzed reactions, and the step $\Delta d = 0.5$ is large enough to allow nonambiguous determinations of reaction orders. (The step $\Delta d = 0.02$ was used for the noncatalyzed stoichiometric reaction in order to improve the accuracy of the determination.)

When the balance of the reactants was nonstoichiometric, the release of water was taken into consideration [18].

On account of the loss of weight of the medium, the catalyst concentration increases with increasing extent of reaction. However, from a computation taking this phenomenon into consideration, it appeared that it can be disregarded.

Activation parameters were obtained as in Ref. 1. However, the rate constant which was taken into consideration for computation was $k_{d_1}^{\circ}$.

Results Obtained for 1-Octadecanol-Octadecanoic Acid Reaction in Octadecanyl Octadecanoate (C36 ester) Solution without Added Catalyst

1. Determination of Overall Order

In all runs which were carried out with a stoichiometric ratio of the reactants, a 2.5 overall order was obtained. Correlation coefficients range from 0.9995 to 0.9999 (for d = 2 or 3 it is never above 0.997). Experimental conditions and results are reported in Table 1.

From these results the following remarks can be made:

The overall order (2.5) differs greatly from that found for the same reaction in benzophenone (3.0).

In this medium the reaction is faster than in benzophenone.

The pressure has only a small influence on the reaction rate.

The pressure-depending order found [8] for the same reaction when carried out in bulk may be due to the nonideal behavior of such a reaction mixture. It is more satisfactory to carry out the reaction in a diluted medium which is the case for the solution of the reactants in their ester.

2. Determination of Orders in Acid and in Alcohol

The following runs were carried out at 181.7°C under 100 torr with an excess of acid (r = 0.5) in Run 9 and an excess of alcohol (r = 4) in Run 10.

The results of calculations for the different pairs (m;n) are reported in Table 2.

Crosschecking of the areas where the correlation coefficient I is above 0.99 shows that the best fitting pairs are (1;1), (3/2;1), and (2;1). However, it can be seen in Fig. 1 (Run 10) that the pair (3/2;1) has the best fit with the experimental data. These values fit perfectly with the overall order found in the stoichiometric study.

Moreover, a comparison of the different values of k_d found when the stoichiometric ratio of the reactants increases from 0.5 to 1 and up to 4 shows clearly that the 2.5 order fits best with experimental data (Table 3) since k_d has only limited variations.

TABLE 1. Noncatalyzed Reaction of 1-Octadecanol with Octadecanoic Acid in C36 Ester and in Stoichiometric Conditions. Values of 2.5th Order Rate Constants

Run	P (torr)	T (°C)	p_{max}	$k_{5/2}$ ($kg^{3/2}eq^{-3/2}s^{-1}$) × 10^4
1	760	165.9	0.76	0.94
2	760	181.7	0.73	1.57
3	100	165.9	0.70	1.06
4	100	171.1	0.53	1.25
5	100	181.7	0.75	1.85
6	100	181.7	0.75	1.83
7	100	192.2	0.54	2.39
8	100	202.8	0.53	3.34

From these results the rate of acid disappearance is

$$v = k_{5/2}[\text{acid}]^{3/2}[\text{alcohol}] \quad (2)$$

3. Determination of Activation Parameters

From Table 1 and Fig. 2 the following values were obtained:

$$\Delta H^{\ddagger} = 50.0 \pm 2.5 \text{ kJ/mol}$$

$$\Delta S^{\ddagger} = -210 \pm 10 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

They are very close to those found for the reaction in benzophenone [1] although the reaction order was 3 instead of 2.5.

4. Reaction in 1-Octadecanol

Octadecanoic acid (0.5 eq/kg) was reacted in 1-octadecanol (no added solvent, 165.9°C, atmospheric pressure, Run 11). Table 4 shows clearly that the best fits are obtained for a 2nd order in acid. If the order in alcohol is considered to be 1, the rate constant obtained from computation is

$$k_{(2;1)} = 0.779 \times 10^{-4} \text{ kg}^2\cdot\text{eq}^{-2}\cdot\text{s}^{-1} \qquad (p_{max} = 0.65; I_3 = 0.9992)$$

TABLE 2. Noncatalyzed Reaction of 1-Octadecanol with Octadecanoic Acid in C36 Ester and in Nonstoichiometric Conditions; 181.7°C, 100 torr. Variations of the Correlation Coefficient $I_{m;n}$ for the Various (m;n) Pairs of Orders in Acid and in Alcohol Which Are Tested. Underlined Values: $I \geq 0.99$

	n						
m	0	1/2	1	3/2	2	5/2	3
0	0.8503	0.9373	0.9906	0.9884	0.9290	0.8351	0.7350
1/2	0.8744	0.9541	0.9957	0.9812	0.9141	0.8183	
1	0.8966	0.9681	0.9980	0.9722	0.8986		
3/2	0.9169	0.9794	0.9976	0.9616			
2	0.9349	0.9880	0.9949				
5/2	0.9507	0.9940			Run 9:	r = 0.5	
3	0.9642						
0	0.9223	0.9284	0.9343	0.9399	0.9453	0.9505	0.9554
1/2	0.9606	0.9651	0.9693	0.9733	0.9770	0.9804	
1	0.9872	0.9898	0.9920	0.9940	0.9956		
3/2	0.9993	0.9998	0.9999	0.9998			
2	0.9959	0.9943	0.9926				
5/2	0.9779	0.9748			Run 10:	r = 4	
3	0.9483						

5. Reaction in Octadecanoic Acid

1-Octadecanol (0.5 eq/kg) was reacted in octadecanoic acid (no added solvent, 165.9°C, atmospheric pressure, Run 12). In this case, alcohol concentrations are low and acid concentrations are high. However, the first are obtained from the experimental determination of the second, which are measured with a lower degree of accuracy than in Part 4. This explains why the dispersion of data points is wider. From Table 5 the order in alcohol is very probably 1 but the order in acid cannot be obtained.

When the order in acid is 1.5 or 2, the corresponding rate constants are

$$k_{(3/2;1)} = 0.755 \times 10^{-4}\ \mathrm{kg}^{3/2}\cdot\mathrm{eq}^{-3/2}\cdot\mathrm{s}^{-1} \qquad (p_{max} = 0.70;\ I_{5/2} = 0.9958)$$

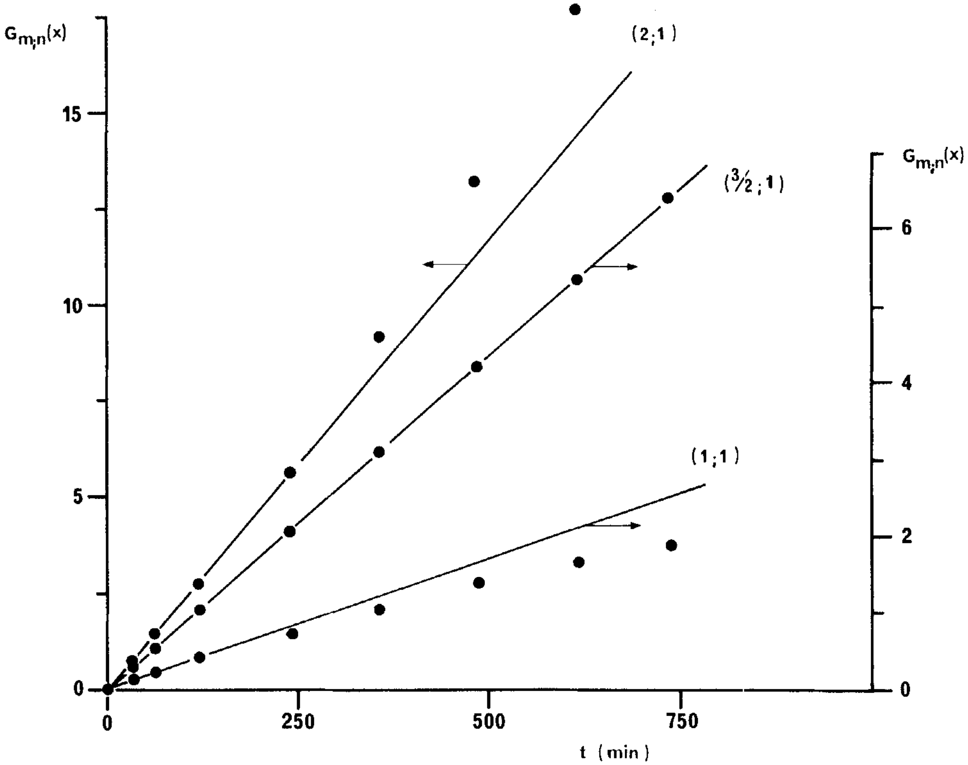


FIG. 1. Noncatalyzed reaction of 1-octadecanol with octadecanoic acid in C36 ester (r = 4, 181.7°C, 100 torr: Run 10). Plots of integrals for the following pairs of orders: (2;1), (3/2;1), (1;1).

TABLE 3. Noncatalyzed Reaction of 1-Octadecanol with Octadecanoic Acid in C36 Ester at Various Stoichiometric Ratios: 181.7°C, 100 torr. Rate Constants Obtained for the Pairs (2;1), (3/2;1), (1;1)

	$k_d\ (kg^{d-1} eq^{1-d} s^{-1}) \times 10^4$		
(m;n)	Run 9, r = 1/2	Run 5, r = 1	Run 10 r = 4
(1;1)	1.23	0.791	0.430
(3/2;1)	1.88	1.95	1.44
(2;1)	2.88	4.44	4.96

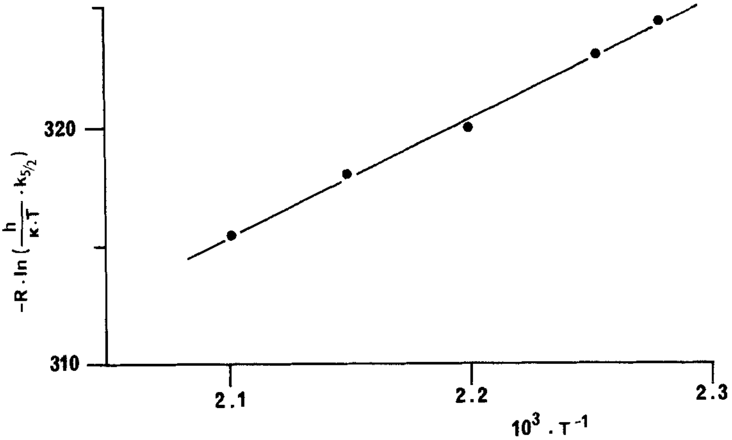


FIG. 2. Noncatalyzed reaction of 1-octadecanol with octadecanoic acid in C36 ester. Determination of activation parameters.

TABLE 4. Noncatalyzed Reaction of Octadecanoic Acid in 1-Octadecanol (Run 11). Variations of the Correlation Coefficient $I_{m;n}$ for the Various (m;n) Pairs of Orders in Acid and in Alcohol Which Are Tested. Underlined Values: I ≥ 0.99

	n						
m	0	1/2	1	3/2	2	5/2	3
0	0.8950	0.8989	0.9027	0.9065	0.9101	0.9137	0.9173
1/2	0.9385	0.9416	0.9447	0.9476	0.9504	0.9532	
1	0.9721	0.9742	0.9762	0.9781	0.9700		
3/2	0.9929	0.9939	0.9948	0.9957			
2	0.9995	0.9994	0.9992				
5/2	0.9919	0.9908				Run 11	
3	0.9717						

TABLE 5. Noncatalyzed Reaction of 1-Octadecanol in Octadecanoic Acid (Run 12). Variations of the Correlation Coefficient $I_{m;n}$ for the Various (m;n) Pairs of Orders in Acid and in Alcohol Which Are Tested. Underlined Values: $I \geq 0.99$

	n						
m	0	1/2	1	3/2	2	5/2	3
0	0.9563	0.9843	0.9958	0.9890	0.9645	0.9248	0.8743
1/2	0.9593	0.9859	0.9959	0.9878	0.9621	0.9216	
1	0.9621	0.9873	0.9959	0.9864	0.9596		
3/2	0.9648	0.9887	0.9958	0.9850			
2	0.9674	0.9899	0.9956				
5/2	0.9699	0.9910				Run 12	
3	0.9722						

$k_{(2;1)} = 0.453 \times 10^{-4}\ \mathrm{kg^2 \cdot eq^{-2} \cdot s^{-1}}$ $\quad (p_{max} = 0.70;\ I_3 = 0.9956)$

6. Reaction in the Mixture of C36 Ester with α,ω-Dimethoxy Polyoxyethylene

Runs 13 and 14 were carried out in a 80/20 (weight) mixture of C36 ester and of α,ω-dimethoxy polyoxyethylene (100 torr, r = 1, 165.9 and 181.7°C, respectively).

The maximum of the curves I = f(d) is at d = 3.15 ± 0.2. Only integer order 3 can be accepted here.

Computed rate constants are reported in Table 6. The reaction rate constants are far lower than those obtained in the case of reactio carried out in C36 ester. The comparison of the values obtained in the two cases is difficult since the orders of reaction are not the same. However $k_{5/2}$ can be estimated, and Table 7 clearly shows a decrease of the rate constant when dimethoxy polyoxyethylene is added.

From these results it would seem that the rather low polar nature of C36 ester is responsible for the increase of the reaction rate and the decrease of the overall order of reaction.

From rate constants at 165.9 and 181.7°C an estimation of activation parameters can be obtained:

$$\Delta H^{\ddagger} \approx 55\ \mathrm{kJ/mol}$$

$$\Delta S^{\ddagger} \approx -200\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$$

These are close to the values obtained in C36 ester.

TABLE 6. Noncatalyzed Reaction of 1-Octadecanol with Octadecanoic Acid in 80/20 (weight) C36 Ester + CH_3O–POE–OCH_3 Mixture (100 torr, r = 1). Values of Third-Order Rate Constants

Run	T (°C)	k_3 ($kg^2 eq^{-2} s^{-1}$) × 10^4	p_{max}	I_3
13	165.9	0.843	0.65	0.9991
14	181.7	1.47	0.60	0.9993

TABLE 7. Noncatalyzed Reaction of 1-Octadecanol with Octadecanoic Acid. Comparison of 2.5th Order Rate Constants for the Reactions in C36 Ester and in the Mixture C36 Ester + CH_3O–POE–OCH_3. (Values for the second reaction are least squares estimates of slopes of nonlinear plots since the reaction is of 3rd order and not of 2.5th order)

T (°C)	Reaction in pure C36 ester $k_{2.5}$ ($kg^{3/2} eq^{-3/2} s^{-1}$) × 10^4	Reaction in mixture C36 ester + CH_3O–POE–OCH_3 $k_{2.5}$ estimated ($kg^{3/2} eq^{-3/2} s^{-1}$) × 10^4
165.9	1.06	0.485
181.7	1.85	0.771

7. Discussion

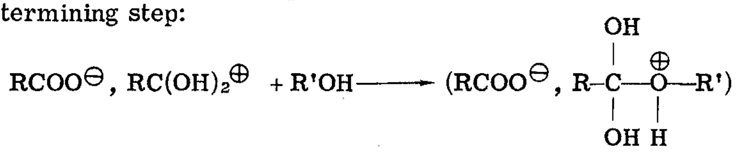
The reaction of 1-octadecanol and octadecanoic acid in octadecanyl octadecanoate shows great differences from the same reaction carried out in a more polar medium:

The reaction rate is higher.

The order in acid is 1.5 instead of 2. However, when the reaction medium becomes more polar, i.e., when α,ω-dimethoxy polyoxyethylene is added, or when the reaction takes place in pure octadecanol, the order in acid increases to 2.

When the ratio of reactants increases from 0.5 to 4, the rate constant slightly decreases. The contrary has been observed in the polar medium reaction.

All these experimental observations are surprising and hard to explain fully. The third overall order (second order with respect to the acid) was interpreted [1] by a mechanism involving the following determining step:



$$\mathrm{RCOO^{\ominus}, RC(OH)_2^{\oplus} + R'OH \longrightarrow (RCOO^{\ominus}, R{-}\overset{\displaystyle OH}{\underset{\displaystyle OH}{C}}{-}\underset{\displaystyle H}{\overset{\oplus}{O}}{-}R')} \qquad \text{(I)}$$

Among the possible explanations of the lowering of the order in acid we analyzed the following:

(a) Superposition of a second-order reaction to the normal third-order reaction. In this case the reaction rate is as follows:

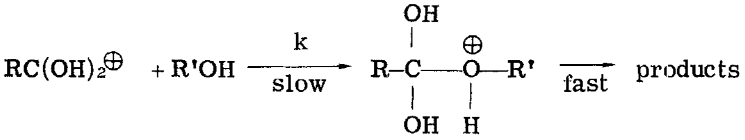
$$v = k_3[\mathrm{COOH}]^2[\mathrm{OH}] + k_2[\mathrm{COOH}][\mathrm{OH}] \tag{3}$$

All attempts to fit experimental data with such a rate equation failed completely. When the stoichiometric ratio of the reactants increases from 0.5 to 4, it is not possible to approximate the rate constants k_2 and k_3. Moreover, with such a change in r, it would be unlikely that $k_{5/2}$ would remain almost unchanged. However, experimental observations show that it does not vary. After due consideration, we discarded this explanation.

(b) Nonnegligible dissociation of ion pairs involved in a rate-determining step. Let S be the solvent. When the protonated solvent is the predominant species:

$$\mathrm{S} + \mathrm{RCOOH} \xrightleftharpoons{K_a} \mathrm{SH}^{\oplus} + \mathrm{RCOO}^{\ominus} \tag{II}$$

$$\mathrm{SH}^{\oplus} + \mathrm{RCOOH} \xrightleftharpoons{K} \mathrm{S} + \mathrm{RC(OH)_2}^{\oplus} \tag{III}$$



$$\mathrm{RC(OH)_2}^{\oplus} + \mathrm{R'OH} \xrightarrow[\text{slow}]{k} \mathrm{R{-}\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}{-}\overset{\oplus}{\underset{\underset{\displaystyle H}{|}}{O}}{-}R'} \xrightarrow[\text{fast}]{} \text{products} \tag{IV}$$

and rate equation is

$$v = k[\mathrm{R'OH}][\mathrm{RC(OH)_2}^{\oplus}] \tag{4}$$

$$v = \frac{kK}{[\mathrm{S}]}[\mathrm{RCOOH}][\mathrm{SH}^{\oplus}][\mathrm{R'OH}] \tag{5}$$

$$v = \frac{kK(K_a)^{1/2}}{[\mathrm{S}]}[\mathrm{S}]^{1/2}[\mathrm{RCOOH}]^{3/2}[\mathrm{R'OH}] \tag{6}$$

Lastly:

$$v = k_{5/2}[\mathrm{RCOOH}]^{3/2}[\mathrm{R'OH}] \tag{7}$$

with

$$k_{5/2} = kK_a^{1/2}[S]^{-1/2} \tag{8}$$

It is surprising to observe that this explanation involves a dissociation of the carboxylic acid, while this assumption was not necessary in more polar medium [1]. However, it can be imagined that all reactive groups assemble in certain areas where they create a more polar medium and where the condensation water tends to be retained. Inside such areas the dissociation of ion pairs would be easier and, in consequence, the overall order would decrease and the reaction rate increase.

This 2.5 overall order was postulated by Tang and Yao [19] and many other authors for the whole course of polyesterifications. Although this is not true for the end of reactions [1], it is not impossible that it could play an important role in the earlier stages of polyesterifications where an excess of glycol is present, and therefore where polarity is high.

Results Obtained for 1-Octadecanol-Octadecanoic Acid Reaction in Octadecanyl Octadecanoate (C36 ester) with Added p-Toluene Sulfonic Acid (PTSA) as Catalyst

The catalysis of esterification of p-toluenesulfonic acid (PTSA) or by other strong protonic acids has been widely studied. In opposition to the case of noncatalyzed polyesterification, almost all published works in the field of acid-catalyzed polyesterification fit together.

A second overall order and a first order in catalyst are found in most cases. However, orders in reactants are rarely taken into consideration. When they are determined, these are both first order in acid and alcohol [9-12]. However, Lin [13-15] reported a second order in acid and a zero order in alcohol for the reaction carried out in an excess of diol.

The inconsistency of some of the results which have been published led us to completely analyze the system 1-octadecanol/octadecanoic acid with added p-toluenesulfonic acid.

TABLE 8. Reaction of 1-Octadecanol with Octadecanoic Acid in C36 Ester in the Presence of Added PTSA (165.9°C). Values of 2nd Order Rate Constants

Run	P (torr)	[PTSA] (eq·kg^{-1}] × 10^3	p_{max}	k_2 (kg·eq^{-1} s^{-1}) × 10^3	I_2
15	760	2.63	0.84	1.56	0.9998
16	100	2.63	0.85	2.12	0.9985
17	100	1.15	0.86	0.898	0.9999
18	100	1.31	0.84	1.09	0.9998
19	100	5.26	0.89	4.43	0.9998
20	100	10.5	0.88	8.41	0.9988

1. Determination of Overall Order. Influence of Pressure

Two runs were carried out at 165.9°C with the same catalyst concentration, under atmospheric pressure (Run 15) and under 100 torr (Run 16) with a stoichiometric balance of reactants.

Only overall order 2 fits the experimental results (Table 8). The rate constant obtained under reduced pressure is slightly above those obtained under atmospheric pressure, but the overall orders are the same. The same reaction carried out in the absence of solvent was also found to be 2nd order [8].

In contrast with the noncatalyzed reaction (see above), it seems that the results do not depend on the reaction medium. The slight difference between rate constants can be easily explained since the reactions were not carried out in the same apparatus (40 g reaction mixture for reduced pressure reaction, 400 g in the other case).

All the following runs were carried out under 100 torr.

2. Determination of Overall Order and of Order in Catalyst

A set of runs was carried out with different catalyst concentrations (Runs 17 to 20, 165.9°C, 100 torr, $r = 1$). For each run only a second overall order fits the experimental data. Rate constants and correlation coefficients are reported in Table 8.

For high catalyst concentrations the plots curve down at high extents of reaction. This phenomenon seems to be due to the esterification of PTSA acid groups by residual hydroxyl groups, and has often been reported in literature [4, 20, 21].

The variations of ln k_2 versus ln [PTSA] (Fig. 3) are linear. The least-squares estimate of the slope is 1.01. In consequence, the reaction is first order in catalyst and

$$k_2 = k_2^* [\mathrm{PTSA}] \qquad (9)$$

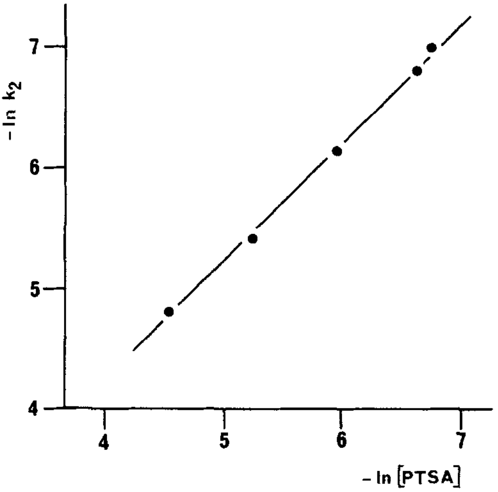


FIG. 3. Reaction of 1-octadecanol with octadecanoic acid in C36 ester. PTSA as catalyst (eq/kg), 165.9°C, 100 torr. Determination of order in catalyst.

3. Determination of Orders in Each Reactant

The values used were 165.9°C, 100 torr, [PTSA] = 1.31×10^{-3} eq/kg.

Run 21 was carried out with an excess of acid (r = 0.5, p_{max} = 0.88) and Run 22 with an excess of alcohol (r = 2, p_{max} = 0.94). Computation of the correlation coefficients for the different (m;n) pairs is reported in Table 9. Crosschecking of the areas where I $\geq$ 0.99 for the two runs shows that only pair (1;1) fits the experimental data. Furthermore, this pair gives by far the best fit in each case. Overall order 2 is thus confirmed. k_2* does not vary very much when r increases from 0.5 to 2 since it increases from 0.706 to 0.989 $eq^{-2} \cdot kg^{2} \cdot s^{-1}$. Therefore it can be assumed that the medium behaves as diluted.

4. Determination of Activation Parameters

Great care must be taken when studying high temperature reactions since PTSA stability decreases with increasing temperature. In consequence, the last data points must not be taken into consideration. Four further runs (Runs 23 to 26) were carried out at temperatures ranging from 170 to 200°C. All results fit with a 2nd order rate equation. They are reported in Table 10. From Fig. 4 the following values are computed:

TABLE 9. Reaction of 1-Octadecanol with Octadecanoic Acid in C36 Ester. PTSA as Catalyst, 165.9°C, 100 torr. Values of Correlation Coefficients for the Various (m;n) Pairs of Orders in Acid and in Alcohol Which Are Tested. Underlined Values: I ≥ 0.99

	n						
m	0	1/2	1	3/2	2	5/2	3
0	0.8559	0.9376	0.9892	0.9978	0.9660	0.9092	0.8438
1/2	0.8793	0.9540	0.9952	0.9937	0.9556	0.8966	
1	0.9010	0.9678	0.9986	0.9879	0.9446		
3/2	0.9207	0.9789	0.9995	0.9807			
2	0.9382	0.9873	0.9982				
5/2	0.9534	0.9932				Run 21: r = 0.5	
3	0.9662						
0	0.7908	0.8237	0.8543	0.8821	0.9067	0.9279	0.9457
1/2	0.9171	0.9397	0.9582	0.9726	0.9832	0.9903	
1	0.9926	0.9976	0.9991	0.9976	0.9937		
3/2	0.9849	0.9756	0.9651	0.9536			
2	0.9105	0.8972	0.8832				
5/2	0.8147	0.8018				Run 22: r = 2	
3	0.7243						

TABLE 10. Reaction of 1-Octadecanol with Octadecanoic Acid in C36 Ester. PTSA as Catalyst (1.31 × 10^{-3} eq·kg^{-1}), 100 torr. Influence of Temperature

Run	T (°C)	k_2^* (kg^{2}eq^{-2}s^{-1})
18	165.9	0.829
23	171.1	0.874
24	181.7	1.05
25	191.2	1.14
26	202.8	1.33

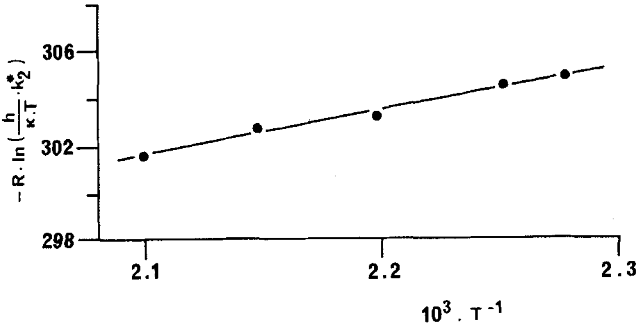


FIG. 4. Reaction of 1-octadecanol with octadecanoic acid in C36 ester. PTSA as catalyst (1.31×10^{-3} eq/kg), 100 torr. Determination of activation parameters.

$$\Delta H^{\ddagger} = 18.5 \pm 5 \text{ kJ/mol}$$

$$\Delta S^{\ddagger} = -210 \pm 10 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

The catalytic effect is due to a net decrease of activation enthalpy. The formation of the activated complex is easier. Activation entropy is the same as for the noncatalyzed reaction. Thus it can be assumed that the mechanisms of the proton-catalyzed esterification and of the esterification without added catalyst are very similar. In fact, the reaction rate is again described by an equation involving three molecules:

$$v = k_2^*[\text{PTSA}][\text{acid}][\text{alcohol}] \tag{10}$$

5. Discussion

As for esterification without added catalyst (Part III of this article), two mechanisms can take place depending on whether ion pairs are dissociated or not.

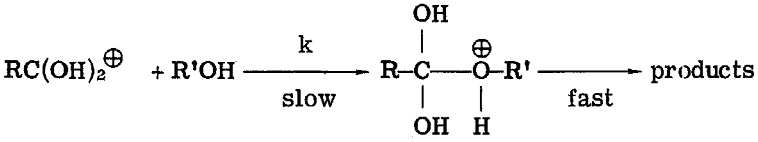
(a) When ion pairs are dissociated and if the acid-base equilibrium relative to the strong acid PTSA is shifted to the right, the following reactions can be suggested (S being the "solvent" providing the proton transfer):

$$S + HA \longrightarrow HS^{\oplus} + A^{\ominus} \qquad (V)$$

$$RCOOH + S \xrightleftharpoons{K_1} RCOO^{\ominus} + HS^{\oplus} \qquad (VI)$$

$$RCOOH + HS^{\oplus} \xrightleftharpoons{K_2} RC(OH)_2^{\oplus} + S \qquad (VII)$$

$$R'OH + HS^{\oplus} \xrightleftharpoons{K_3} R'OH_2^{\oplus} + S \qquad (VIII)$$



$$RC(OH)_2^{\oplus} + R'OH \xrightarrow[\text{slow}]{k} R-\overset{OH}{\underset{OH}{C}}-\underset{H}{\overset{\oplus}{O}}-R' \xrightarrow[\text{fast}]{} \text{products}$$

(IX)

Assuming that protonated hydroxyl and carboxyl group concentrations are negligible compared to $HS^{\oplus}$ concentration:.

$$[HS^{\oplus}] = [A^{\ominus}] = [PTSA] \qquad (11)$$

$$[RC(OH)_2^{\oplus}] = K_2 \frac{[HS^{\oplus}][RCOOH]}{[S]} \qquad (12)$$

since $[S] = C^t$,

$$[RC(OH)_2^{\oplus}] = K'[PTSA][RCOOH] \qquad (13)$$

where

$$K' = K_2[S] \qquad (14)$$

and reaction rate is

$$v = k_2{}^*[PTSA][RCOOH][R'OH] \qquad (15)$$

with

$$k_2^* = kK' \tag{16}$$

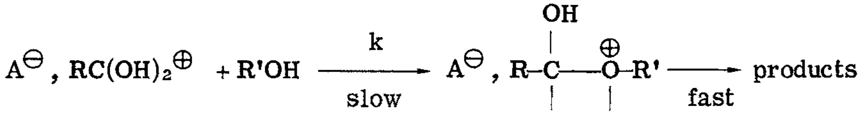
It is worth mentioning that if PTSA dissociation were incomplete, the catalyst order would be 0.5 and not 1.

A mechanism of this type has been already assumed for the reaction without added catalyst carried out in the same solvent (see above). It would be logical to consider that the reaction proceeds in the same way when a catalyst is present. However, a difference can be pointed out: When the molar ratio of the reactants changes, slight opposite variations of the rate constants take place. This would suggest that the mechanisms are not as similar as they would appear at first sight.

(b) When ion pairs association is assumed, Eqs. (X) to (XII) follow:

$$AH \overset{K}{\rightleftharpoons} A^{\ominus}, H^{\oplus} \tag{X}$$

$$RCOOH + A^{\ominus}, H^{\oplus} \overset{K_2}{\rightleftharpoons} A^{\ominus}, RC(OH)_2^{\oplus} \tag{XI}$$



$$A^{\ominus}, RC(OH)_2^{\oplus} + R'OH \xrightarrow[\text{slow}]{k} A^{\ominus}, R-\underset{OH}{\overset{OH}{C}}-\underset{H}{\overset{\oplus}{O}}-R' \xrightarrow[\text{fast}]{} \text{products} \tag{XII}$$

From (XII), Relation (17) can be obtained:

$$[A^{\ominus}, RC(OH)_2^{\oplus}] = K_2[RCOOH][A^{\ominus}, H^{\oplus}] \tag{17}$$

$$[A^{\ominus}, RC(OH)_2^{\oplus}] = K_2K[RCOOH][AH] \tag{18}$$

and

$$v = k_2^*[PTSA][RCOOH][R'OH] \tag{19}$$

with

$$k_2^* = K_2Kk \tag{20}$$

Note that shifting or not of Equilibrium (X) makes no difference.

This mechanism is the same as that relative to the reactions without added catalyst and carried out in a polar medium such as benzophenone or polyoxyethylene [1].

The question as to whether the mechanism involves associated or nonassociated ion pairs cannot be answered since the rate equations are the same. When the reaction takes place in the polar zones of the reaction medium (as in a noncatalyzed reaction), and if PTSA acid-base equilibrium is shifted to the right, the Mechanism (a) should be retained. On the other hand, when the reaction takes place anywhere in the medium and if PTSA acid base equilibrium is not shifted to the right, we must retain mechanism (b).

SYMBOLS

x, x_0	carboxyl content at times t (s) and 0
m, n	orders in carboxyl and hydroxyl groups, respectively
d	overall order ($d = m + n$)
c	order in catalyst
b	algebraic value of the excess of hydroxyl group concentration at time t
r	initial ratio of hydroxyl group concentration to carboxyl group concentration
k_d, $k_{m;n}$	rate constants for d-th or (m;n) orders ($kg^{d-1} \cdot eq^{1-d} \cdot s^{-1}$)
k_d*	rate constant taking catalyst order into account: $k_d{*} = k_d[\text{catalyst}]^{-c}$ ($kg^{d+c-1} \cdot eq^{1-d-c} \cdot s^{-1}$)
$F_d(x)$ $F_{m;n}(x)$	indefinite integral corresponding to a d-th or (m;n) order rate equations
$G_d(x) =$	$F_d(x) - F_d(x_0)$, $G_{m;n}(x) = F_{m;n}(x) - F_{m;n}(x_0)$
I_d, $I_{m;n}$	correlation coefficient for a d-th or a (m;n) order test
T	temperature (K, unless °C is specified)
κ, h, R	Boltzman's, Planck's, and ideal gas constants (in S.I. units)
$\Delta S^{\ddagger}$, $\Delta H^{\ddagger}$	entropy and enthalpy of activation
p_{max}	maximum extents of reaction reached in the different runs

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