

## KINETICS OF ESTERIFICATION OF SODIUM 3,5-DICARBOXYBENZENESULPHONATE WITH ETHYLENE GLYCOL CATALYSED BY TITANIUM(IV) AND TIN(II) IONS\*

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Received December 21st, 1976

Kinetics of esterification of sodium 3,5-dicarboxybenzenesulphonate (A) with twentyfold molar excess of ethylene glycol in the presence of titanium tetra-*n*-butoxide and tin(II) oxalate as catalysts has been investigated in an open system and at temperatures ranging from 162.5 to 190°C. Time-concentration dependences were determined by means of gel permeation chromatography on Sephadex LH-20 gel at pH 8.5 by using  $\text{KH}_2\text{PO}_4$ — $\text{Na}_2\text{HPO}_4$  buffer as eluent. The formation of sodium 3-(2-hydroxyethoxycarbonyl)-5-carboxybenzenesulphonate (C) ( $k_1$ ) is first-order in the carboxylic acid A and the formation of sodium 3,5-bis(2-hydroxyethoxycarbonyl)benzenesulphonate (D) ( $k_2$ ) is first-order in the mono-ester C; both consecutive reactions are one-half order in  $\text{Ti}^{4+}$  and  $\text{Sn}^{2+}$  ions. These kinetic relations describe the reaction course to at least 97% conversion of compounds A and C. In both reactions  $\text{Ti}^{4+}$  ion exhibits 1.6-times higher catalytic activity compared to  $\text{Sn}^{2+}$  ion. The ratio of pseudo-first order rate constants  $k_1/k_2$  equals to approx. 1.9, irrespective of the temperature and of the type of the catalyst. In comparison with the metal ion catalysed conversion of isophthalic acid into 2-hydroxyethyl hydrogen isophthalate and of the latter into bis(2-hydroxyethyl) isophthalate, formation of the mono-ester C and bis-ester D is characterized by about  $21 \text{ J K}^{-1} \text{ mol}^{-1}$  and  $32 \text{ J K}^{-1} \text{ mol}^{-1}$  more positive activation entropy, respectively.

Bis(2-hydroxyethyl) esters of alkali metal 3,5-dicarboxybenzenesulphonates, which are important monomers for the polycondensation with bis(2-hydroxyethyl) terephthalate<sup>1</sup>, can be prepared either by classical transesterification of alkali metal 3,5-bis(carbomethoxy)benzenesulphonates with ethylene glycol<sup>1</sup> or newly by reactions of alkali metal 3,5-dicarboxybenzenesulphonates with ethylene oxide<sup>2</sup> or ethylene glycol<sup>3,4</sup>. No rate data are available on both the latter reactions. In this communication we report the kinetics of catalytic esterification of sodium 3,5-dicarboxybenzenesulphonate with ethylene glycol in excess. The kinetics has been determined in an open system in the range from 162.5 to 190°C and in the presence of titanium(IV) or tin(II) compounds. These substances are known to be the most effective metal catalysts for esterification of aromatic carboxylic acids with aliphatic

\* Part XII in the series Esterification of Benzenecarboxylic Acids with Ethylene Glycol; Part XI: *Makromol. Chem.* 178, 2211 (1977).

diols<sup>5-7</sup>. The only method suitable to follow quantitatively the course of the reaction has turned out to be gel permeation chromatography on Sephadex LH-20 gel at pH 8.5 by using  $\text{KH}_2\text{PO}_4\text{-Na}_2\text{HPO}_4$  buffer as eluent. This method was reported earlier by us for separation of a mixture of alkali metal carboxybenzenesulphonates and their 2-hydroxyethyl esters<sup>8</sup>.

## EXPERIMENTAL.

**Chemicals.** Sodium 3,5-dicarboxybenzenesulphonate (Research Institute of Organic Syntheses, Pardubice) of "fiber grade" quality was dried at 140°C/20 Torr and stored in a desiccator over  $\text{P}_2\text{O}_5$ . For  $\text{C}_8\text{H}_5\text{NaO}_7\text{S}$  (268.2) calculated: 35.83% C, 1.88% H, 8.57% Na, 11.96% S; found 35.75% C, 1.97% H, 8.60% Na, 12.00% S. Ethylene glycol (International Enzymes, Ltd., England) of analytical purity grade (<99% according to gas chromatographic analysis) contained 0.1% of  $\text{H}_2\text{O}$  and <0.05% of diethylene glycol and was used without further purification. Titanium tetra-n-butoxide, b.p. 187.5–188.0°C/11 Torr (ref.<sup>9</sup> records b.p. 185–188°C/11 Torr) was obtained according to the reported procedure<sup>9</sup> and used as a solution in ethylene glycol (0.585 g in 100 ml of  $\text{C}_2\text{H}_6\text{O}_2$ ). Preparation of anhydrous tin(II) oxalate was reported in our previous work<sup>7</sup>. Triethylamine (Fluka A.-G., Switzerland) used as an inhibitor of diethylene glycol formation during esterification reactions<sup>4</sup> was of analytical purity grade and was not further purified. Sodium 3,5-bis(2-hydroxyethoxycarbonyl)benzenesulphonate used as standard for the gel permeation chromatography was obtained by the reaction of ethylene oxide with sodium 3,5-dicarboxybenzenesulphonate in dimethylformamide in the presence of pyridine as the catalyst<sup>10</sup>; after solvent evaporation *in vacuo*, the residue was dissolved in the smallest amount of hot water, mixed with absolute ethanol and cooled to 0°C. The crystalline product was recrystallized repeatedly from water, dried at 50°C/12 Torr and stored in a desiccator over  $\text{P}_2\text{O}_5$ . For  $\text{C}_{12}\text{H}_{13}\cdot\text{NaO}_6\text{S}$  (356.3) calculated: 40.45% C, 3.68% H, 6.45% Na, 9.00% S; found: 40.38% C, 3.74% H, 6.40% Na, 9.05% S.

**Analytical methods.** The apparatus and experimental conditions for the determination of time changes in concentrations of sodium 3,5-dicarboxybenzenesulphonate and its 2-hydroxyethyl esters by means of gel permeation chromatography were reported in a previous work<sup>8</sup>. In the presence of tin(II) oxalate as the catalyst, the chromatograms of esterification mixtures showed three well resolved peaks corresponding, in the order of increasing elution volume, to sodium 3,5-dicarboxybenzenesulphonate, the yet unknown sodium 3-(2-hydroxyethoxycarbonyl)-5-carboxybenzenesulphonate (this peak increased to a maximum with time and disappearance of the peak of the starting acid and then gradually disappeared as the peak of the bis-ester increased) and sodium 3,5-bis(2-hydroxyethoxycarbonyl)benzenesulphonate; the elution volumes of these compounds corresponded to  $38.5 \pm 0.8$ ,  $61.7 \pm 1.2$  and  $95.1 \pm 1.9$  ml, respectively. In the presence of titanium tetra-n-butoxide as the catalyst, an additional peak has appeared in chromatograms which was ascribed to  $\text{Ti}^{4+}$  ion. Its elution volume ( $19.4 \pm 0.4$  ml) was identical both for the solution of the catalyst in ethylene glycol and for the samples of the esterification mixture containing the titanium(IV) catalyst; the area of this peak increased linearly with  $\text{Ti}^{4+}$  concentration in the charged sample. Samples of the esterification mixture (10–30  $\mu\text{l}$ ) were withdrawn from the reactor by a glass pipette, cooled immediately to room temperature and introduced on to the column without further dilution. The analysis took 110 min. Concentrations of the starting carboxylic acid, the mono-ester and the bis-ester were calculated from the areas of the corresponding peaks with the aid of calibration. The method of direct and indirect

calibration was used. *a*) Direct calibration comprised *aa*: construction of the calibration graph and experimental determination of factors for the starting carboxylic acid and the bis-ester which were available in the pure state, *ab*: calculation of the factor for the mono-ester. For the given reaction proceeding without change in molecular number, the factor for the mono-ester was calculated on the basis of chromatographic analysis of 8 samples of the reaction mixture which contained different amounts of the carboxylic acid, the mono-ester and the bis-ester. Eqs (1) and (2) were used for the calculation where  $P_i$  are peak areas,  $F_i$  are correction factors,

$$A_0 = P_1/F_1 + P_2/F_2 + P_3/F_3 \quad (1)$$

$$F_i = P_i/n_i \quad (2)$$

$n_i$  is the number of moles of the component  $i$  in the fed sample and  $A_0$  is the initial concentration of the carboxylic acid ( $\text{mol kg}^{-1}$ ) in the sample. Indices 1, 2 and 3 related to the carboxylic acid, the mono-ester and the bis-ester, respectively. *b*) Indirect calibration was based on the calculation performed by using three equations (1) and the data obtained by chromatographic analysis of three samples of the reaction mixture differing in the concentration of the acid, the mono-ester and the bis-ester and relating to reaction times,  $t_1$ ,  $t_2$  and  $t_3$ . Measurements were repeated three times to yield the relation  $(F_1/F_1) : (F_2/F_1) : (F_3/F_1) = 1 : 0.9821 : 0.5720$ , according to which the factors for the carboxylic acid, the mono-ester and the bis-ester correspond to 3.304, 3.245 and 1.890, respectively. Since the sum of concentrations ( $c$ ) (in  $\text{mol kg}^{-1}$ ) of all components 1, 2 and 3 can be expressed as  $\sum c_i = A_0$ , the concentration of a component  $i$  (in  $\text{mol kg}^{-1}$ ) in the sample follows from Eq. (3)

$$c_i = (P_i/F_i) / (\sum P_i/F_i) A_0 \quad (3)$$

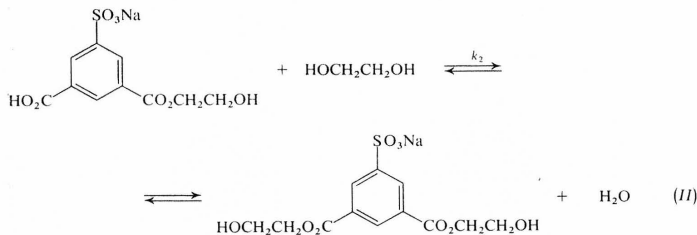
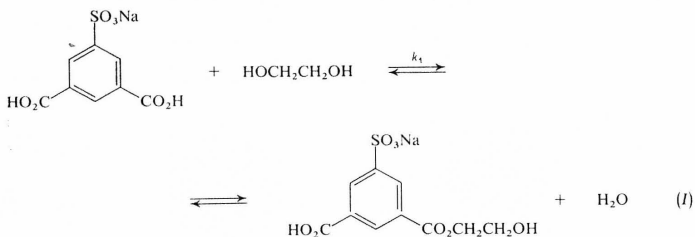
The results obtained by the direct and indirect calibration differed from one another by  $\pm 1\%$  rel. Concentrations of the carboxylic acid, the mono-ester and the bis-ester were determined with an error of 2.5–3.0% rel. Balance of the total carboxyl content was checked by acidimetric titration of samples of the esterification mixture (a solution in dimethylformamide) with 0.1N ethanolic NaOH solution in the presence of thymolphthalein. The sum of concentrations of the carboxylic acid and the mono-ester determined by chromatographic analysis in a series of incidentally chosen samples differed from the values obtained by acidimetric titration by  $\pm 1.5\%$  rel. The content of diethylene glycol was determined according to a reported procedure<sup>11</sup> in samples of the esterification mixture withdrawn at the end of each kinetic run; the content of diethylene glycol varied from 0.9 to 1.5 wt.-%.

*Kinetic measurements.* The apparatus used for the rate measurements was described in a previous work<sup>7</sup>. The reaction water was removed by a stream of nitrogen flowing through a condenser heated to 105°C, which prevented the entrainment of ethylene glycol from the reaction system. All the measurements were made at an identical initial molar ratio of sodium 3,5-dicarboxybenzenesulphonate to ethylene glycol corresponding to 1 : 20 and in the presence of 0.4521 g of triethylamine and  $1.1 \cdot 10^{-3}$  to  $3.0 \cdot 10^{-3}$   $\text{mol kg}^{-1}$  of the metal catalysts. The reactor was charged with 10.3732 g (0.03868 mol;  $0.6579 \text{ mol kg}^{-1}$ ) of sodium 3,5-dicarboxybenzenesulphonate, 48.017 g (0.7736 mol;  $13.1580 \text{ mol kg}^{-1}$ ) of ethylene glycol, 0.4521 g (4.3 wt.-% with respect to the carboxylic acid) of triethylamine and 0.0133 g (0.064 mmol;  $1.1 \cdot 10^{-3} \text{ mol kg}^{-1}$ ) to 0.0362 g (0.175 mmol;  $3.0 \cdot 10^{-3} \text{ mol kg}^{-1}$ ) of tin(II) oxalate or 0.02186 g (0.064 mmol;  $1.1 \cdot 10^{-3} \text{ mol kg}^{-1}$ ) to 0.0596 g (0.175 mmol;  $3.0 \cdot 10^{-3} \text{ mol kg}^{-1}$ ) of titanium tetra-*n*-butoxide. The reactor was placed in a thermostatted silicone oil bath and the stirred reaction mixture

was warmed up in a stream of nitrogen to the required temperature within 5 min. The temperature was maintained constant within  $\pm 0.2^\circ\text{C}$ . During this time interval the carboxylic acid and the catalyst completely dissolved; the first minute of this time interval was taken as the beginning of the reaction. At a nitrogen flow rate of 4 l/h and an intensity of stirring of 500 rev./min the reaction proceeded in the kinetic region. Triethylamine reacts with the carboxylic acid and its mono-ester to form triethylammonium salts and inhibits the formation of diethylene glycol whose rate is highest at the beginning of the esterification reaction<sup>4</sup>. These salts are thermally unstable and gradually undergo complete decomposition to the carboxylic acid and the mono-ester with the release of triethylamine; triethylamine is removed from the system by a stream of nitrogen together with water vapours. By analogy to the esterification of ammonium salts of terephthalic acid<sup>12,13</sup>, one can expect that ammonium salts of sodium 3,5-dicarboxybenzenesulphonate and of its mono-ester react with ethylene glycol at the same rate as does the free sodium 3,5-dicarboxybenzenesulphonate and its free mono-ester. Parallel experiments proved that at temperatures from 162.5 to 190.0°C, the given concentrations of reactants and at a nitrogen flow rate of 4 l/h, the reaction mixture contains only traces of water (Fischer method); these conditions exclude practically the reverse reaction. Under the given concentration conditions, the volume changes, which would be caused above all by water release from the reaction mixture, were negligible and were not considered in deriving kinetic equations. Transformations of sodium 3,5-dicarboxybenzenesulphonate and its mono-ester were followed over at least four and mostly five half-lives. The order of the esterification reaction in the carboxylic acid and the orders of both consecutive esterification reactions in the metal catalysts were determined experimentally; the order of the reaction in the mono-ester and the best fit values of the rate constants (95% confidence level) were determined numerically by nonlinear regression analysis by using a program<sup>14</sup> modified for the system of two consecutive reactions which was based on the Marquardt method<sup>15</sup>. The  $S/N$  ratio, where  $S$  is the sum of squared deviations for the values of rate constants and  $N$  is the number of measurements during one kinetic run, varied from  $0.452 \cdot 10^{-3}$  to  $0.199 \cdot 10^{-4}$ .

## RESULTS AND DISCUSSION

Gel chromatograms of reaction mixtures from the esterification of sodium 3,5-dicarboxybenzenesulphonate (A) with eighteenfold and higher initial molar excess of ethylene glycol catalysed by titanium tetra-*n*-butoxide or tin(II) oxalate show three well resolved peaks of the carboxylic acid (A), the yet unknown sodium 3-(2-hydroxyethoxycarbonyl)-5-carboxybenzenesulphonate (C) and sodium 3,5-bis(2-hydroxyethoxycarbonyl)benzenesulphonate (D) (ref.<sup>8</sup>). Kinetically significant amount of an oligomer, probably neutral dimer of the bis-ester, is formed only at the lower molar excess of ethylene glycol. According to this finding, the hydroxyethyl esters of the carboxylic acid A, similarly as hydroxyethyl esters of isophthalic acid<sup>7</sup>, are substantially less prone to oligomerisation reactions than are hydroxyethyl esters of terephthalic acid<sup>16-18</sup>. All the rate measurements were performed at an identical initial molar ratio of the acid A to ethylene glycol equaling to 1 : 20. With regard to the absence of oligomers in the reaction mixture, the conversion of carboxylic acid A in the reaction with ethylene glycol can be depicted by two consecutive reactions (I) and (II).



Under the given experimental conditions the esterification mixture contains only traces of water and both reactions (I) and (II) can be considered as irreversible. The reactions catalysed by titanium tetra-*n*-butoxide and tin(II) oxalate proceed in homogeneous system and without significant induction period.

As follows from the dependence of  $\log [A]$  upon time (Fig. 1), the conversion of carboxylic acid A into mono-ester C (Eq. (I)) in the presence of titanium tetra-*n*-butoxide and tin(II) oxalate is first-order in A through at least four half-lives. At present no suitable method for preparing the pure mono-ester C is known; its inaccessibility did not allow us to find experimentally the order of the reaction in this intermediate product. The order of reaction (II) in mono-ester C and best fit values for rate constants  $k_1$  and  $k_2$  were determined numerically by nonlinear regression analysis with the use of a program<sup>14</sup> which was modified for the system of two consecutive reactions and was based on the Marquardt method<sup>15</sup>. From the generated set of concentrations of the reactants and products as a function of time, which was adjusted until a satisfactory fit to experimental data has been obtained, it resulted that the reaction (II) was first-order in the mono-ester C through at least 5 half-lives. The agreement of experimental and calculated time-concentration dependences for carboxylic acid A, mono-ester C and bis-ester D is evident from a typical plot shown in Fig. 2.

Under the given experimental conditions the rates of both consecutive reactions (I) and (II) are not affected by ethylene glycol concentration and the conversion of carboxylic acid A into bis-ester D can be expressed by formal kinetic equations (4) to (6).

$$-d[A]/dt = k_1[A], \quad (4)$$

$$d[C]/dt = k_1[A] + k_2[C], \quad (5)$$

$$d[D]/dt = k_2[C]. \quad (6)$$

Optimum values of the pseudo-first order in solution rate constants  $k_1$  and  $k_2$  for the titanium(IV) ion catalysed esterification reactions determined at temperatures ranging from 162.5 to 190°C are presented in Table I. The least-squares analysis of dependences of  $\log k_{1(\text{Ti})}$  and  $\log k_{2(\text{Ti})}$  upon  $T^{-1}$  yielded activation energies  $E_{I(\text{Ti})}$  and  $E_{II(\text{Ti})}$  equaling to  $96.8 \pm 3.4 \text{ kJ mol}^{-1}$  ( $23.1 \pm 0.8 \text{ kcal mol}^{-1}$ ) ( $r = 0.9988$ )

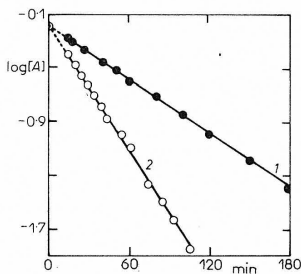


FIG. 1

Pseudo-First Order Dependence for Esterification of Sodium 3,5-Dicarboxybenzenesulphonate (A) with Ethylene Glycol (B) in the Presence of Tin(II) Oxalate (1) and Titanium Tetra-*n*-butoxide (2) as Catalysts

$[A]_0 = 0.6579 \text{ mol kg}^{-1}$ ,  $[B]_0 = 13.1580 \text{ mol kg}^{-1}$ ,  $[\text{SnC}_2\text{O}_4] = 1.6 \cdot 10^{-3} \text{ mol kg}^{-1}$   
 $[\text{Ti}(\text{OC}_4\text{H}_9\text{-}n)_4] = 3.0 \cdot 10^{-3} \text{ mol kg}^{-1}$ ,  
 temperature =  $180 \pm 0.2^\circ\text{C}$ .

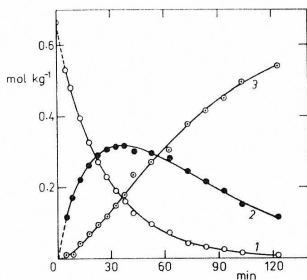


FIG. 2

Experimental (points) and Calculated (lines) Rate Curves for Conversion of 1 Sodium 3,5-Dicarboxybenzenesulphonate (A) into 2 Sodium 3-(2-Hydroxyethoxycarbonyl)-5-carboxybenzenesulphonate (C) and of the Latter Compound into 3 Sodium 3,5-Bis(2-hydroxyethoxycarbonyl)benzenesulphonate in the Reaction with Ethylene Glycol (B) Catalysed by Titanium Tetra-*n*-butoxide

$[A]_0 = 0.6579 \text{ mol kg}^{-1}$ ,  $[B]_0 = 13.1580 \text{ mol kg}^{-1}$ ,  $[\text{Ti}(\text{OC}_4\text{H}_9\text{-}n)_4] = 3.0 \cdot 10^{-3} \text{ mol kg}^{-1}$ ,  
 temperature =  $180 \pm 0.2^\circ\text{C}$ .

and  $97.6 \pm 3.4 \text{ kJ mol}^{-1}$  ( $23.3 \pm 0.8 \text{ kcal mol}^{-1}$ ) ( $r = 0.9988$ ), respectively. Pseudo-first order rate constants for reactions (I) and (II) catalysed by titanium(IV) ion can be thus expressed by general equations (7) and (8).

$$k_{1(\text{Ti})} = (8.3 \pm 2.6) \cdot 10^7 \exp(-96800 \pm 3400/RT) \text{ s}^{-1}, \quad (7)$$

$$k_{2(\text{Ti})} = (5.5 \pm 2.6) \cdot 10^7 \exp(-97600 \pm 3400/RT) \text{ s}^{-1}. \quad (8)$$

TABLE I

Temperature Dependence of Pseudo-First Order Rate Constants  $k_1$  and  $k_2$  for Esterification of Sodium 3,5-Dicarboxybenzenesulphonate (A) with Ethylene Glycol (B) Catalysed by Titanium Tetra-n-butoxide

$$[A]_0 = 0.6579 \text{ mol kg}^{-1}, [B]_0 = 13.1580 \text{ mol kg}^{-1}, [\text{Ti}(\text{OC}_4\text{H}_9\text{-n})_4] = 3.0 \cdot 10^{-3} \text{ mol kg}^{-1}.$$

Temperature K	$10^4 \cdot k_1$ $\text{s}^{-1}$	$10^4 \cdot k_2$ $\text{s}^{-1}$
435.6	1.99	1.05
443.1	3.31	1.71
453.1	5.96	3.19
463.1	9.74	5.16

TABLE II

Dependence of Pseudo-First Order Rate Constants  $k_{1(\text{Ti})}$ ,  $k_{1(\text{Sn})}$ ,  $k_{2(\text{Ti})}$  and  $k_{2(\text{Sn})}$  for Esterification of Sodium 3,5-Dicarboxybenzenesulphonate (A) with Ethylene Glycol (B) upon Concentration of Titanium Tetra-n-butoxide and Tin(II) Oxalate as Catalysts (F)

$$[A] = 0.6579 \text{ mol kg}^{-1}, [B]_0 = 13.1580 \text{ mol kg}^{-1}, \text{ temperature} = 180 \pm 0.2^\circ\text{C}.$$

Catalyst concentration $10^3 \cdot \text{mol kg}^{-1}$	$10^4 \cdot k_{i(\text{F})}, \text{ s}^{-1}$			
	$k_{1(\text{Ti})}$	$k_{1(\text{Sn})}$	$k_{2(\text{Ti})}$	$k_{2(\text{Sn})}$
1.1	3.51	2.15	1.79	1.10
1.5	4.17	—	2.18	—
1.6	—	2.76	—	1.37
2.1	4.77	—	2.35	—
2.4	—	3.19	—	1.66
3.0	5.96	3.73	3.19	1.85

The value of the activation entropy  $\Delta S_{I(Ti)}^\ddagger$  calculated from Eyring equation for the titanium(IV) ion catalysed esterification of carboxylic acid A corresponds to  $-113.5 \pm 7.8 \text{ J K}^{-1} \text{ mol}^{-1}$  ( $-27.1 \pm 1.9 \text{ cal K}^{-1} \text{ mol}^{-1}$ ) and the value of  $\Delta S_{II(Ti)}^\ddagger$  for the esterification of the mono-ester C catalysed by the same ion equals to  $-117.0 \pm 7.8 \text{ J K}^{-1} \text{ mol}^{-1}$  ( $-27.9 \pm 1.9 \text{ cal K}^{-1} \text{ mol}^{-1}$ ).  $E_{I(Ti)}$  and  $E_{II(Ti)}$  values do not differ too much from the activation energies found earlier for the tin(II) ion catalysed esterification of isophthalic acid ( $85.1 \pm 4.9 \text{ kJ mol}^{-1}$ ;  $20.3 \pm 1.2 \text{ kcal mol}^{-1}$ ) and of 2-hydroxyethyl hydrogen isophthalate ( $83.1 \pm 4.2 \text{ kJ mol}^{-1}$ ;  $19.9 \pm 1.0 \text{ kcal mol}^{-1}$ ) with ethylene glycol and for the titanium(IV) ion catalysed esterification of benzoic acid ( $85.8 \pm 2.5 \text{ kJ mol}^{-1}$ ;  $20.5 \pm 0.6 \text{ kcal mol}^{-1}$ ) with the same diol<sup>6</sup>. On the other hand, when compared to metal ion catalysed conversion of isophthalic acid into 2-hydroxyethyl hydrogen isophthalate and of the latter into bis(2-hydroxyethyl) isophthalate<sup>7</sup>, the formation of the mono-ester C is characterized by about  $21 \text{ J K}^{-1} \text{ mol}^{-1}$  and that of the bis-ester D by about  $32 \text{ J K}^{-1} \text{ mol}^{-1}$  more positive activation entropy. Also in comparison with the activation entropy found for the titanium(IV) ion catalysed esterification of benzoic acid with ethylene glycol ( $-143.2 \pm 8.0 \text{ J K}^{-1} \text{ mol}^{-1}$ ;  $-34.2 \pm 1.9 \text{ cal K}^{-1} \text{ mol}^{-1}$ ) (ref.<sup>6</sup>),  $\Delta S_{II(Ti)}^\ddagger$  is less negative by about  $26 \text{ J K}^{-1} \text{ mol}^{-1}$ .

Pseudo-first order rate constants  $k_1$  and  $k_2$  for homogeneously catalysed esterification of compounds A and C may include, in addition to salt effect caused above all by the presence of  $\text{NaO}_3\text{S}$  group in the molecule, autocatalytic effect of the carboxyl group<sup>7,19</sup> and the rate-accelerating effect of the metal catalyst. To separate the rate-accelerating effect of  $\text{Ti}^{4+}$  and  $\text{Sn}^{2+}$  ions, logarithms of rate constants  $k_{1(Ti)}$  and  $k_{2(Ti)}$  for titanium tetra-*n*-butoxide catalysed reactions (I) and (II) and logarithms of rate constants  $k_{1(Sn)}$  and  $k_{2(Sn)}$  for the same reactions catalysed by tin(II) oxalate were plotted against logarithms of catalyst concentrations (Fig. 3). Linear dependences obtained in both cases confirm homogeneous catalysis to be operative in these

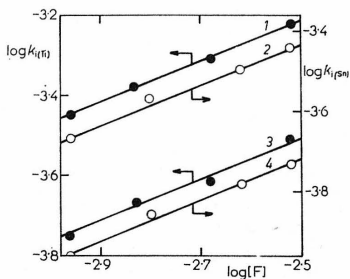


FIG. 3

Linear Dependence of Logarithms of Pseudo-First Order Rate Constants  $k_{1(Ti)}$  (1),  $k_{1(Sn)}$  (2),  $k_{2(Ti)}$  (3) and  $k_{2(Sn)}$  (4) upon Logarithms of Concentrations of Titanium Tetra-*n*-butoxide and Tin(II) Oxalate as Catalysts (F)



reactions. The slopes of straight lines in Fig. 3 confirm further that at catalyst concentrations varying from  $1 \cdot 1 \cdot 10^{-3}$  to  $3 \cdot 0 \cdot 10^{-3}$  mol kg $^{-1}$ , reactions (I) and (II) are one-half order in Ti $^{4+}$  and Sn $^{2+}$  ions. Equations (4)–(6) may be thus re-written to the relations (9)–(11)

$$-d[A]/dt = k_1^c[A][F]^{1/2}, \quad (9)$$

$$d[C]/dt = k_1^c[A][F]^{1/2} + k_2^c[C][F]^{1/2}, \quad (10)$$

$$d[D]/dt = k_2^c[C][F]^{1/2}, \quad (11)$$

where  $k_1^c = k_1/[F]^{1/2}$ ,  $k_2^c = k_2/[F]^{1/2}$  and  $[F]$  is the concentration of Ti $^{4+}$  or Sn $^{2+}$  ions. Empirical equations (9)–(11) hold for esterification reactions with ethylene glycol in at least eighteenfold initial molar excess with respect to carboxylic acid A, in the mentioned region of catalysts concentrations and at least to 97% conversion of the carboxylic acid A and the mono-ester C. First-order dependence on the concentration of reaction components A and C and one-half order dependence upon metal catalyst concentration can be explained by the existence of a fast pre-equilibrium established between components A or C and catalyst F (or rather the glycolate of the corresponding metal) to form a complex which participates in the rate-determining step of the esterification reaction.

The order of reactions (I) and (II) in carboxylic acid A or in mono-ester C and the metal catalyst contrasts with the one-half order of the catalytic esterification of benzoic acid with ethylene glycol with respect to the acid and Sn $^{2+}$  or Ti $^{4+}$  ions<sup>6</sup>; it differs also from the first order of the catalytic esterification of isophthalic acid and its mono-ester with ethylene glycol with respect to Sn $^{2+}$  and Ti $^{4+}$  ions and from the one-half order of the catalytic esterification of 2-hydroxyethyl hydrogen isophthalate with the same diol with respect to this mono-ester<sup>7</sup>. We presume that these kinetic relations are connected with the different composition of the above mentioned pre-equilibrium complexes. The so far unsuccessful attempts at the isolation of these complexes, which exhibit only limited solubility, and determination of their structure do not allow to provide evidence in support of these assumptions.

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Translated by J. Hetflejš.