THE ACTIVITY OF METAL IONS IN CATALYTIC ESTERIFICATION OF AROMATIC CARBOXYLIC ACIDS WITH ALIPHATIC GLYCOLS*

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Received July 21st, 1975

The catalytic activity of seventeen metal compounds in the reaction of benzoic acid with C_2 to C_5 aliphatic glycols was measured under normal pressure and at 167—197 °C. In the absence of catalysts the reaction was first-order in the monocarboxylic acid, while the metal-ion catalysed reaction was half-order in the acid and at catalyst concentrations from $5 \cdot 10^{-4}$ to $3 \cdot 10^{-3}$ mol kg^{-1} also half-order in Ti^{4+}, Sn^{2+} and Pb^{2+} ions. The rates of both the uncatalysed and catalysed reactions decreased with the length and branching of carbon chain of glycols within one order of magnitude. The most active catalysts were titanium tetra-n-butoxide and tin(II) oxide or tin(II) oxalate; the medium effectiveness was shown by di-n-butyltin oxide and bismuth(III) hydroxide. Compounds of Mg(II), Zn(II), Cd(II), Al(III), Pb(II), Sb(III), Mn(II) and Co(II) exhibited only low catalytic activity. Identical increase in the rate of the esterification reaction catalysed by an oxide, acetate, oxalate or benzoate derived from the same metal speaks for decisive role of the metal cation in determining the activity of the catalysts.

Hydrogen ion-catalysed esterification of carboxylic acids with mono- and polyhydric alcohols is one of the most widely investigated reactions and the study of its kinetics and mechanism had been the subject of numerous works which were critically surveyed in monographs[1,2]. Great attention has been paid to the kinetics of esterification of dicarboxylic acids with glycols in the absence and presence of strong acids as catalysts; studies concerning this problem were reviewed in previous communications[3,4]. Aliphatic glycols undergo, however, readily the hydrogen ion-catalysed etherification reaction at elevated temperatures and, therefore, much effort has been made to replace acid catalysts by metal compounds that would exhibit high activity in the esterification but little or no activity in the etherification reactions. Hundreds of patents have appeared in which compounds of nearly all the metals of the periodic system were claimed to catalyse esterification of carboxylic acids with glycols; wide variety of experimental conditions and substrates does not allow, however, to evaluate quantitatively the relative activity of metal ions in these reactions from the available data. So far, only few studies concerned with the kinetics and mechanism of the metal ion-catalysed esterification reactions of this type[3,4].

In an effort to contribute to the elucidation of the catalytic effect of metal ions in esterification reactions we studied kinetics of the esterification of benzoic acid with C_2 to C_5 aliphatic glycols in the absence and presence of various metal catalysts.

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* Part VIII in the series Esterification of Benzenecarboxylic Acids with Ethylene Glycol; the work published in J. Chromatogr. *109*, 101 (1975) is considered as Part VII of this series.

The rate constants obtained for the model reaction carried out under normal pressure and at temperatures from 167 to 197°C were used to express the relative catalytic activity of metal ions in reactions of this type.

EXPERIMENTAL

Chemicals. Benzoic acid (Lachema Brno), *p.a.*, was of 99·5% purity according to the acid number determination; m.p. 122—123°C. Ethylene glycol (Slovnaft, Bratislava) and the other glycols (Fluka A. G.) were commercial products which were purified by fractional distillation *in vacuo* under nitrogen or by crystallisation until they were $\geq$ 99% pure (by gas chromatographic analysis): ethylene glycol, b.p. 94°C/11 Torr (ref.[5] b.p. 197·4°C/760 Torr); propylene glycol, b.p. 87—88°C/12 Torr (ref.[6] b.p. 97°C/20 Torr); trimethylene glycol, b.p. 110—111°C/13 Torr (ref.[7] b.p. 127°C/33 Torr); tetramethylene glycol, b.p. 120—121°C/11 Torr (ref.[6] b.p. 102°C/2 Torr); neopentyl glycol, m.p. 124—125°C (benzene–light petroleum) (ref.[8] m.p. 126—128°C).

Catalysts. Aluminium acetate, lead(II) acetate trihydrate, zinc acetate dihydrate, bismuth(III) hydroxide, lead(II) oxide (Lachema, Brno), magnesium oxide, antimony(III) oxide (Koch-Light), di-n-butyltin oxide and tetra-n-butyltin (Research Institute of Organic Syntheses, Rybitvi) were of analytical purity and were used without further purification. Cadmium acetate (Koch-Light) was recrystallised from water. Tin(II) oxide[9], tin(II) oxalate[10], titanium tetra-n-butoxide[11] (b.p. 187·5—188 °C/11 Torr; ref.[7] b.p. 185—188°C/11 Torr), manganese(II) acetate tetrahydrate[12] and cobalt(II) acetate tetrahydrate[12] were prepared by reported procedures. Lead(II) benzoate monohydrate was obtained by mixing hot 10% solutions of lead(II) acetate and sodium benzoate, slightly acidified by acetic acid, in the 1 : 4 molar ratio; the mixture was cooled slowly to room temperature, the precipitate formed was separated by filtration, washed several times with cold water and dried *in vacuo* at 40°C. Cadmium(II) oxalate was prepared by adding cadmium(II) carbonate in small portions to a great excess of boiling 10% aqueous solution of oxalic acid; residual carbon dioxide was expelled by prolonged boiling, the mixture was diluted with tenfold volume of hot water and then cooled slowly to room temperature. The precipitate formed was separated by filtration, washed with cold 50% ethanol and dried *in vacuo* at 100°C. According to the metal content, all the catalysts used were of $\geq$ 98·9% purity. Nitrogen used as an inert gas contained 0·1% of oxygen. Melting points were measured with a Kofler hot plate microscope and are uncorrected.

Analytical methods. A decrease in benzoic acid concentration in the esterification mixture with time was determined by acidimetric titration using Acidimeter EK (Druopta, Prague) apparatus equipped with glass and calomel electrodes; samples of the mixture (0·3—0·8 g) withdrawn at fixed time intervals by means of a heated pipette were immediately cooled to room temperature, dissolved in a mixture of pyridine (10 ml) and distilled water (20 ml) and titrated under argon with 0·05M-KOH. The formation of the free and ester-bound dialkylene glycols during the metal ion-catalysed esterification of benzoic acid with glycols was followed by methods reported in the previous work[8]; it varied between 1 to 1·5% (with respect to the charged acid). Material balance of the esterification reaction was determined by gel-permeation chromatography on a column filled with "Kieselgel 60" (0·040—0·063 mm, Merck) with the use of dioxane as an eluent; according to this analysis, the final reaction mixture contained, in addition to 3% of the unreacted benzoic acid, 90% of 2-hydroxyethyl benzoate and about 3% of ethylene glycol dibenzoate.

Kinetic measurements. The apparatus described in the previous work was used[12]. Rate constants of the esterification of benzoic acid with C_2 to C_5 aliphatic glycols in the absence and presence of metal catalysts were determined under normal pressure and at 167—197°C; the acid to glycol initial molar ratio was 1 : 30. The known amount of the glycol (38—45 g) was introduced into a tubular glass 200 ml-reactor equipped with a stirrer, nitrogen inlet and a cooler heated in the jacket to 105°C and the reactor was placed in a thermostated (Ultrathermostat U 10) methyl phenyl silicone bath. The nitrogen flow was adjusted to 3·5 l/h and the glycol was warmed up to the reaction temperature; a thin-walled glass ampoule containing the known amount of benzoic acid (2·5—3·0 g), and eventually a catalyst (18—22 mg), was quickly introduced into the reactor and the ampoule was scattered by starting the stirrer. The reaction temperature that somewhat decreased upon introduction of the acid has attained its original value in 2—4 min and has been then maintained with an accuracy of ±0.5°C. During this period both the acid and catalyst dissolved. The time of the introduction of the ampoule into the reactor was taken as the beginning of the reaction. The water formed during the reaction was removed immediately from the reaction system by a stream of nitrogen. With the given amounts of reacting components, at a nitrogen flow rate of 3·5 l/h and a stirring intensity of 200 rev./min, esterification reactions took place in the kinetic region. Volume changes of the reaction mixture due to evaporation of the reaction water amounted, under the above conditions, to $\leq 1.5\%$ and were not considered in deriving the kinetic equations. Transformation of the acid into the corresponding esters was followed over at least two or mostly three half-times. Each rate constant was an average of at least two, sometimes three or four independent measurements. Values of rate constants, standard deviations and correlation coefficients were obtained by the least squares analysis and are listed in Tables I—V.

Isolation of 2-hydroxyethyl benzoate and ethylene glycol dibenzoate. The reaction mixture resulting from the catalysed esterification of benzoic acid with ethylene glycol was cooled to room temperature, freed of the glass scattering by filtration and of the excess ethylene glycol by distillation under nitrogen *in vacuo*. Fractionation of the residue *in vacuo* afforded 2-hydroxyethyl benzoate boiling at 146—147°C/9 Torr (ref.[13] b.p. 160—162°C/14 Torr). For $C_9H_{10}O_3$ (116·2) calculated: 65·05% C, 6·06% H; found: 65·02% C, 6·19% H. Crystallisation of the distillation residue (that solidified on cooling) from ethanol–light petroleum yielded ethylene glycol dibenzoate, m.p. 71—72°C (ref.[14] m.p. 73°C). For $C_{16}H_{14}O_4$ (270·3) calculated: 71·10% C, 5·22% H; found: 70·92% C, 5·31% H.

RESULTS AND DISCUSSION

Esterification of benzoic acid with ethylene glycol (equation (*I*)) in the absence of a catalyst and under normal pressure proceeded, even with thirthyfold excess of the glycol, at relatively high temperature and on immediate removal of the reaction water from the system, at a slow rate.

$$\mathrm{RCO_2H + HOR'OH \longrightarrow RCO_2R'OH + H_2O} \qquad (I)$$

$$\mathrm{2\,RCO_2R'OH \rightleftharpoons RCO_2R'O_2CR + HOR'OH} \qquad (II)$$

$$\mathrm{R'} = \mathrm{(CH_2)}_n\,,\quad \mathrm{CH_2CHCH_3}\,,\quad \mathrm{CH_2C(CH_3)_2CH_2}\,,\quad n = 2-4$$

In agreement with the results reported by Matsuzaki and Mitani[15], the uncatalysed reaction was first-order in the acid and under the concentration conditions used by us it was zero-order in ethylene glycol. The value of the pseudo-first order rate constant

k_0 for the esterification reaction (187°C) in the absence of metal catalysts, which was determined from the slope of the linear dependence of log $[A]_0/[A]$ on time (A is benzoic acid) (Fig. 1) and refined by least-squares method, was $0{\cdot}197 \pm 0{\cdot}002\ h^{-1}$ ($r = 0{\cdot}9980$). The esterification of benzoic acid could be facilitated by addition of catalytic amounts of some metal compounds (Table I) soluble, even though to a limited extent, in the acid–glycol mixture. According to Hovenkamp, compounds of some heavy metals accelerate also the equilibrium condensation reaction (equation (*II*)) of 2-hydroxyethyl benzoate[16] which may proceed parallelly to the esterification reaction. By gel-permeation chromatographic analysis of the final reaction mixtures it was found, however, that besides 90% of the 2-hydroxyethyl ester only 2·5 to 3% of ethylene glycol dibenzoate were formed. Esterification rate measurements in the presence of lead(II) oxide and at varying initial concentrations of the 2-hydroxyethyl ester showed that the transformation of benzoic acid into 2-hydroxyethyl benzoate does not depend significantly on the product concentration (Fig. 2). When the values

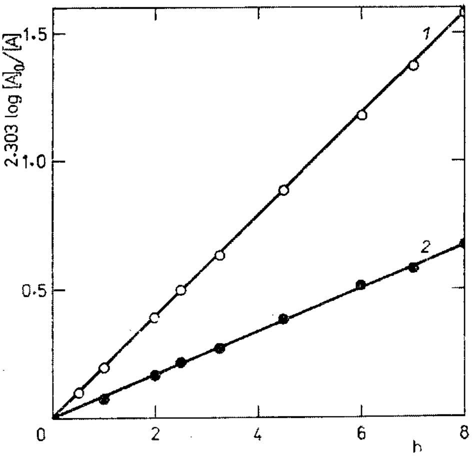

FIG. 1

Pseudo-First Order Esterification of Benzoic Acid (A) with Ethylene Glycol (B) (*1*) and Tetramethylene Glycol (B) (*2*) in the Absence of Metal Catalysts

$[A]_0 = 0{\cdot}5043\ \text{mol kg}^{-1}$, $[B]_0 = 15{\cdot}1290\ \text{mol kg}^{-1}$; temperature 187±0·5°C.

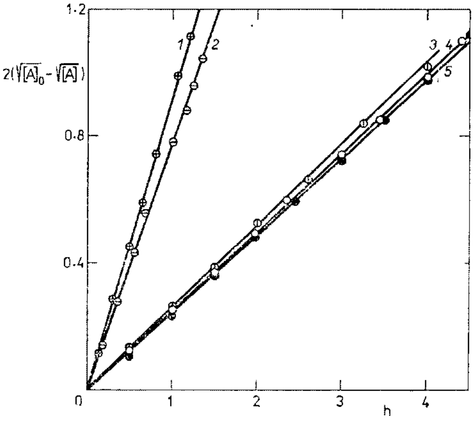

FIG. 2

Pseudo-Half Order Esterification of Benzoic Acid (A) with Ethylene Glycol (B) in the Presence of Titanium Tetra-n-butoxide (*1*) and Tin(II) Oxalate (*2*) as Catalysts (C) and the Esterification Reaction at Varying Initial Concentrations of 2-Hydroxyethyl Benzoate (D) Catalysed by Lead(II) Oxide (C) (*3*, *4*, *5*)

$[A]_0 = 0{\cdot}5043\ \text{mol kg}^{-1}$, $[B]_0 = 15{\cdot}1290\ \text{mol kg}^{-1}$, $[C] = 2 \cdot 10^{-3}\ \text{mol kg}^{-1}$, temperature 197±0·5 C; *3* $[D]_0 = 0$, *4* $[D]_0 = 0{\cdot}2522\ \text{mol kg}^{-1}$, *5* $[D]_0 = 0{\cdot}7565\ \text{mol kg}^{-1}$.

TABLE I

Pseudo-Half Order Rate Constants k_{obs} for the Esterification of Benzoic Acid (A) with Ethylene Glycol (B) in the Presence of Various Metal Catalysts (C) and the Relative Activity of the Catalysts

$[A]_0 = 0{\cdot}5042$ mol kg^{-1}, $[B]_0 = 15{\cdot}1290$ mol kg^{-1}, $[C] = 2 . 10^{-3}$ mol kg^{-1}; temperature 197 ± 0·5°C.

Catalyst	$10^3 . k_{obs}$ mol$^{1/2}$ kg$^{-1/2}$ h^{-1}	$r(k_{obs})$	$\frac{k_{obs}[C]^a}{k_{obs}[MgO]}$	$k_{obs}[A]_0^{1/2}$ mol kg^{-1} h^{-1}	$\frac{k_{obs}[A]_0^{1/2}}{k_0[A]_0}$ ^{b}
Magnesium oxide	150 ± 1	0·9981	1·0	0·107	0·92
Zinc acetate dihydrate	278 ± 3	0·9989	1·9	0·197	1·70
Cadmium acetate	181 ± 1	0·9994	1·2	0·129	1·10
Cadmium oxalate	180 ± 1	0·9997	1·2	0·128	1·10
Aluminium acetate	215 ± 3	0·9958	1·4	0·153	1·32
Titanium tetra-n-butoxide	925 ± 11	0·9984	6·2	0·657	5·66
Lead(II) oxide	255 ± 11	0·9998	1·7	0·181	1·56
Lead(II) acetate trihydrate	260 ± 2	0·9996	1·7	0·185	1·59
Lead(II) benzoate monohydrate	255 ± 2	0·9995	1·7	0·181	1·56
Tin(II) oxide	770 ± 18	0·9949	5·1	0·547	4·69
Tin(II) oxalate	767 ± 7	0·9989	5·1	0·545	4·71
Di-n-butyltin oxide	570 ± 4	0·9995	3·8	0·405	3·49
Tetra-n-butyltin	—[c]	—	—	—	—
Antimony(III) oxide	250 ± 2	0·9987	1·7	0·178	1·53
Bismuth(III) hydroxide	515 ± 3	0·9984	3·4	0·368	3·15
Manganese(II) acetate tetrahydrate	214 ± 2	0·9995	1·4	0·152	1·30
Cobalt(II) acetate tetrahydrate	186 ± 1	0·9996	1·2	0·132	1·14

[a] The activity of MgO is taken as equal to 1·0; [b] in comparing the rates of the reactions of different kinetic order, concentrations should be considered; under the given conditions $k_0[A]_0$ has a value of 0·1161 mol kg^{-1}h^{-1}; [c] in comparison with the uncatalysed reaction, tetra-n-butyltin did not show any catalytic activity.

of $2([A]_0^{1/2} - [A]^{1/2})$ determined for acid conversions up to 90% at a constant concentration of titanium tetra-n-butoxide, tin(II) oxalate or lead(II) oxide as catalysts ($2 . 10^{-3}$ mol kg^{-1}) were plotted against time, linear dependences were obtained (Fig. 2). Identical linear relations were found also for the esterification reaction catalysed by the other metal compounds used in this study. The metal ion-catalysed conversion of benzoic acid into 2-hydroxyethyl benzoate was therefore half-order in the acid and at the given molar ratio of the reacting components it was zero-order in ethylene glycol. The reaction could be described by empirical rate equation (*1*) or in an integrated form by Eq. (*2*) where k_{obs} is the experimental pseudo-half order

$$-d[A]/dt = k_{obs}[A]^{1/2} \tag{1}$$

$$k_{obs} = 2([A]_0^{1/2} - [A]^{1/2})/t \tag{2}$$

rate constant for the metal ion-catalysed esterification of benzoic acid with ethylene glycol. The independently determined value of k_0 for the esterification reaction in the absence of metal catalysts is not negligible; it might be therefore assumed that the acid is transformed into its monoester by parallel uncatalysed and catalysed reactions. The experimental rate constant k_{obs} would be thus the sum of the constant for the uncatalysed reaction and the "actual" constant for the metal ion-catalysed reaction. Kinetic laws for systems of parallel reactions[17] were tried to apply to the "actual" rate constant and order determination for the metal ion-catalysed reaction using the method of successive approximations. The best agreement between the calculated and experimental data has been, however, obtained when the uncatalysed reaction was neglected. It seems therefore as if the uncatalysed trans-

TABLE II

Dependence of Pseudo-Half Order Rate Constants k_{obs} for Esterification of Benzoic Acid (A) with Ethylene Glycol (B) on Concentration of Lead(II) Oxide, Tin(II) Oxalate and Titanium Tetra-n-butoxide as Catalysts

$[A]_0 = 0.5043$ mol kg^{-1}, $[B]_0 = 15.1290$ mol kg^{-1}; temperature 197 ± 0·5°C.

Catalyst concn., mol kg^{-1}	$10^3 . k_{obs}$, mol$^{1/2}$ kg$^{-1/2}$ h^{-1}					
	PbO	r(Pb)	$Sn(CO_2)_2$	r(Sn)	$Ti(OC_4H_9\text{-}n)_4$	r(Ti)
$5 . 10^{-4}$	137 ± 1	0·9993	417 ± 8	0·9986	410 ± 3	0·9993
$1 . 10^{-3}$	179 ± 1	0·9999	589 ± 4	0·9991	640 ± 4	0·9994
$1·26 . 10^{-3}$	200 ± 1	0·9999	684 ± 7	0·9989	720 ± 6	0·9993
$2 . 10^{-3}$	255 ± 1	0·9998	767 ± 7	0.9989	925 ± 12	0·9984
$3 . 10^{-3}$	290 ± 3	0·9988	—	—	—	—

formation of benzoic acid is suppressed in the presence of metal ions and the acid is esterified to the 2-hydroxyethyl ester only by the metal ion-catalysed reaction. This assumption is based on an indirect evidence and may not be valid for stronger carboxylic acids.

The rate of the esterification reaction was measured in the presence of $5 . 10^{-4}$ to $3 . 10^{-3}$ mol kg^{-1} of titanium tetra-n-butoxide, tin(II) oxalate or lead(II) oxide. The values of the corresponding pseudo-half order rate constants k_{obs} are summarized in Table II. When the logarithms of these constants were plotted against the logarithms of catalyst concentrations, linear dependences were obtained in all cases (Fig. 3). The values of the slopes confirm that the esterification of benzoic acid with ethylene glycol is half-order in Ti^{4+}, Sn^{2+} and Pb^{2+} ions and that in the given region of catalyst concentrations homogeneous catalysis is operative. The pseudo-half order rate constant k_{obs} for the reactions accelerated by the above catalysts can be therefore expressed by Eq. (*3*) where k is the pseudo-first order rate constant for the metal-ion catalysed reaction and [C] is the concentration of Ti^{4+}, Sn^{2+} and Pb^{2+} ions.

$$k_{obs} = k[C]^{1/2} \qquad (3)$$

In order to determine the activation parameters, the rate of the esterification of benzoic acid with ethylene glycol in the presence of titanium(IV), tin(II) and lead(II) catalysts was measured over the temperature range of 167 – 197°C. The values of the corresponding rate constants k_{obs} are presented in Table III. The plots of log k_{obs} against the reciprocal values of absolute temperature were straight lines for all catalysts; the activation energies, enthalpies, entropies and preexponential factors calculated from these dependences are listed in Table IV. The values of activation

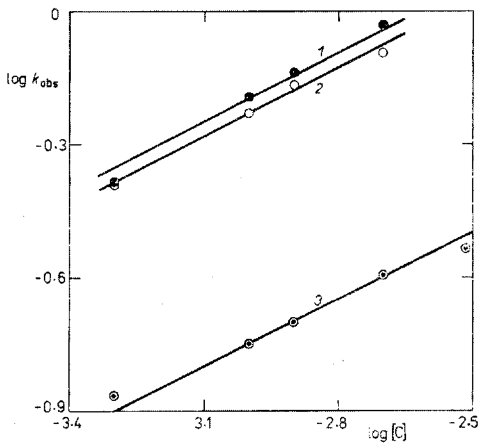

FIG. 3

Dependence of Logarithm of Pseudo-Half Order Rate Constant k_{obs} for Esterification of Benzoic Acid with Ethylene Glycol on Logarithm of the Concentration of Titanium Tetra-n-butoxide (*1*), Tin(II) Oxalate (*2*) and Lead(II) Oxide (*3*) energies for the esterification reaction in the presence of Ti^{4+}, Sn^{2+} and Pb^{2+} ions lie very closely to those reported by Hartman and coworkers[18,19] for an acid-catalysed esterification of benzoic acid and substituted benzoic acids with cyclohexanol (19·3 to 20·2 kcal mol^{-1}) as well as to the activation energy determined by Matsuzaki and Mitani[15] for the esterification of benzoic acid with ethylene glycol in the absence of acidic or metal catalysts (21·2 kcal mol^{-1}). A more distinct difference exists, however, between the values of the activation entropy determined for the esterification of benzoic acid with ethylene glycol catalysed by Ti^{4+}, Sn^{2+} and Pb^{2+} ions ($-34{\cdot}2 \pm 1{\cdot}9$ to $-36{\cdot}8 \pm 1{\cdot}2$ e.u.) and the value of activation entropy for the uncatalysed reaction (−20·5 e.u.)[15]. Hence, the action of a metal ion results in a decrease in ΔS^{+} of

TABLE III

Temperature Dependence of Pseudo-Half Order Rate Constants k_{obs} for Esterification of Benzoic Acid (A) with Ethylene Glycol (B) in the Presence of Lead(II) Oxide, Tin(II) Oxalate and Titanium Tetra-n-butoxide as Catalysts (C)

$[A]_0 = 0{\cdot}5043$ mol kg^{-1}, $[B]_0 = 15{\cdot}1290$ mol kg^{-1}, $[C] = 2 \,.\, 10^{-3}$ mol kg^{-1}.

Temperature K	$10^3 \,.\, k_{obs}$, $mol^{1/2}\, kg^{-1/2}\, h^{-1}$					
	PbO	r(Pb)	$Sn(CO_2)_2$	r(Sn)	$Ti(OC_4H_9\text{-}n)_4$	r(Ti)
470	255 ± 1	0·9998	767 ± 7	0·9989	925 ± 11	0·9984
460	160 ± 1	0·9995	502 ± 9	0·9985	582 ± 9	0·9990
450	93 ± 1	0·9996	309 ± 5	0·9990	365 ± 6	0·9993
440	58 ± 1	0·9942	178 ± 6	0·9987	202 ± 3	0·9995

TABLE IV

Values of the Activation Energies (ΔE), Enthalpies ($\Delta H^{\neq}$), Entropies ($\Delta S^{\neq}$) and Preexponential Factors (k°) for Esterification of Benzoic Acid with Ethylene Glycol in the Presence of Lead(II) Oxide, Tin(II) Oxalate and Titanium Tetra-n-butoxide as Catalysts (C)

$[C] = 2 \,.\, 10^{-3}$ mol kg^{-1}.

Catalyst	ΔE kcal mol^{-1}	r(E)	$\Delta H^{\neq}$ kcal mol^{-1}	$\Delta S^{\neq}$ e.u.	k° $mol^{1/2}$ . . $kg^{-1/2} s^{-1}$
Lead(II) Oxide	20·5 ± 0·6	0·9993	19·6 ± 0·6	−36·8 ± 1·2	$2{\cdot}3 \,.\, 10^5$
Tin(II) Oxalate	19·4 ± 0·6	0·9991	18·5 ± 0·6	−36·6 ± 1·9	$2{\cdot}4 \,.\, 10^5$
Titanium Tetra-n-butoxide	20·5 ± 0·6	0·9990	19·5 ± 0·6	−34·2 ± 1·9	$8{\cdot}4 \,.\, 10^5$

about 16 e.u. with activation energy remaining essentially unchanged. An opposite change in $\Delta S^{\neq}$ was observed for a base-catalysed hydrolysis of potassium ethyl oxalate[20] and ethyl glycinate-N,N-diacetic acid[21], as compared to hydrolytic reactions catalysed by metal ions that formed ion-ester complexes with the substrate. The large negative value of $\Delta S^{\neq}$ found by us in the metal ion-catalysed esterification reaction is typical of bimolecular displacement (S_N2) reactions, where the formation of the transition state is accompanied by a net increase in bonding[22].

To evaluate the dependence of the reaction rate on the structure of glycols, we have measured the rate of esterification of benzoic acid also with propylene glycol, trimethylene glycol, tetramethylene glycol and neopentyl glycol (the acid to glycol initial molar ratio = 1 : 30). Similarly to ethylene glycol, the reactions followed up to 90% acid conversion were first-order in the acid in the absence of a metal catalyst and half-order in the acid in the presence of lead(II) oxide as catalyst. The values of the corresponding pseudo-first order rate constants k_0 and pseudo-half order rate constants k_{obs} are summarized in Table V. From these data it follows that the rates of both uncatalysed and metal ion-catalysed esterification reactions decrease within one order of magnitude with increasing carbon chain length of the glycol and especially with its branching. The decrease in the rate with branching of the glycol carbon chain in these reactions is in good agreement with an analogous observation resulting from the kinetics of uncatalysed polyesterification of dicarboxylic acids with glycols[23]. On the other hand, an increase in the raction rate with increasing length of the glycol carbon chain has been established for the uncatalysed esterification of adipic acid with aliphatic glycols[24,25]. This difference in the reactivity is at present

TABLE V

Rate Constants for Esterification of Benzoic Acid (A) with Aliphatic Glycols (B) in the Absence and Presence of Lead(II) Oxide as Catalyst

$[A]_0 = 0{\cdot}5043$ mol kg^{-1}, $[B]_0 = 15{\cdot}1290$ mol kg^{-1}, $[PbO] = 2 \,.\, 10^{-3}$ mol kg^{-1}; temperature 187 ± 0·5°C.

Glycol	Uncatalysed reaction		Catalysed reaction	
	$10^3 \,.\, k_0$, h^{-1}	$r(k_0)$	$10^3 \,.\, k_{obs}$ [a]	$r(k_{obs})$
Ethylene glycol	197 ± 2	0·9980	160 ± 1	0·9995
Trimethylene glycol	166 ± 1	0·9997	155 ± 1	0·9990
Tetramethylene glycol	84 ± 1	0·9992	97 ± 1	0·9996
Propylene glycol	66 ± 1	0·9998	72 ± 1	0·9991
Neopentyl glycol	56 ± 1	0·9994	43 ± 1	0·9986

[a] mol$^{1/2}$ kg$^{-1/2}$ h^{-1}.

difficult to explain from the data available so far. The above-mentioned noninhibiting effect of the esterification product (Fig. 2) and a decrease in the rate with increasing carbon chain length of the glycol by a factor of ten in the metal ion-catalysed esterification of benzoic acid with aliphatic glycols differentiates this reaction markedly from the metal ion-catalysed glycolysis of benzonitrile[26], which leads also to ω-hydroxyalkyl benzoates. The rate of the latter glycolytic reaction decreases significantly with increasing concentration of the ester and falls down by a factor of twenty with increasing carbon chain length of the glycol[26]. This fact is accounted for by coordination of one hydroxyl group of the glycol to the nitrogen atom of the transiently formed imino ether and of another hydroxyl group to the metal ion to form a cyclic complex intermediate[26]. It seems likely that an analogous cyclic activated complex is not formed in the metal ion-catalysed esterification of aromatic carboxylic acids with aliphatic glycols.

To determine the relative catalytic activity of metal compounds, the esterification rates were measured at the same concentration of various catalysts ($2 \cdot 10^{-3}$ mol kg^{-1}); the values of the corresponding pseudo-half order rate constants k_{obs}, which were determined from the slopes of the linear dependences $2([A]_0^{1/2} - [A]^{1/2})$ upon time and refined by the least-squares method, are presented in Table I. The relative catalytic activity of metal compounds was expressed both by the ratio of the rate constant k_{obs} to the constant k_{obs} for the reaction catalysed by magnesium oxide, that was the least active catalyst, and by the $k_{obs}[A]_0^{1/2}/k_0[A]_0'$ ratio (Table I). From these relations it follows that the most efficient esterification catalyst is titanium tetra-n-butoxide; the reaction rate is enhanced more than five times at the titanium(IV) ion concentration of $2 \cdot 10^{-3}$ mol kg^{-1}. Somewhat lower activity was observed with tin(II) oxide and tin(II) oxalate; both di-n-butyltin oxide and bismuth(III) hydroxide were of medium activity. On the other hand, magnesium(II), cobalt(II), cadmium(II), zinc(II), lead(II), aluminium(III), manganese(II) and antimony(III) compounds showed relatively low catalytic activity. Similarly low activity exhibited also Pb^{2+}, Zn^{2+}, Mn^{2+} and Co^{2+} ions in the catalytic esterification of potassium 2,4-dicarboxybenzenesulphonate with ethylene glycol reported in a previous work of this series[10]. Essentially the same value of the rate constant k_{obs} was found for the esterification of benzoic acid with ethylene glycol catalysed by lead(II) compounds, irrespective of the type of an anion. This holds also for the group of cadmium(II) and tin(II) compounds (Table I). These findings lead to the conclusion that the catalytic activity of a metal ion plays a decisive role in the rate enhancement of esterification of aromatic carboxylic acids with glycols and that metal oxides, acetates, oxalates or benzoates are transformed under esterification conditions by an equilibrium reaction with the aromatic carboxylic acid or glycol into a complex, presumably that of the metal compound with the acid or more likely a complex of the acid with the metal glycolate, for example $(RCOO)_xM[O(CH_2)_nOH]_y$. This complex reacts in the rate-determining step with another glycol molecule to form the corresponding ester under regeneration of the catalyst. In none of the catalysed reactions, an induction period has been observed; this indicates that the formation of the activated complex is a fast reaction taking place already at the very beginning of the esterification reaction. The rate enhancement of esterification of benzoic acid with ethylene glycol has not been observed with tetra-n-butyltin (Table I) that is otherwise well soluble in the reaction mixture. Tetra-n-butyltin does not react with ethylene glycol even at elevated temperatures to give a glycolate of tetravalent tin and lacks likely also the ability to form an activated complex with benzoic acid. By this it differs significantly from *e.g.* lead(II) oxide, which yields readily lead(II) glycol oxide[27], or from di-n-butyltin oxide[28] and titanium tetraalkoxides[29] which are known to react with ethylene glycol to form the corresponding glycol oxides of complex structure. As it is seen from Table I, titanium tetra-n-butoxide and di-n-butyltin oxide are efficient esterification catalysts. It seems therefore likely that the ability to form an activated complex with glycol or, most likely, with carboxylic acid is a further prerequisite for the catalytic activity of metal compounds in the esterification reaction of this type. As can be judged from the above-mentioned facts, this complex should not be too stable. It was found that the catalytic activity of Sb^{3+} ions in condensation of 2-hydroxyethyl benzoate[16] and in polycondensation of bis(2-hydroxyethyl) terephthalate[30,31] decreases with increasing concentration of hydroxyl groups in the reacting system. This effect was explained by formation of stable complexes of Sb^{3+} ions with hydroxyl ligands. A similar effect is likely the reason why Sb^{3+} ions, although resistant to the poisoning by carboxylic derivatives[16], show also low activity in the esterification of benzoic acid carried out in a great excess of glycols. On the other hand, a decrease in the catalytic activity of Mn^{2+}, Pb^{2+} and Zn^{2+} ions in condensation of 2-hydroxyethyl benzoate[16] and of the same ions as well as Ca^{2+} and Co^{2+} ions in the transesterification of dimethyl terephthalate with ethylene glycol[32] which is caused by the addition of catalytic amounts of carboxylic acids was ascribed to the poisoning of the metal catalysts by carboxylic groups. The low activity of Zn^{2+} ions in the esterification of benzoic acid with ethylene glycol is analogous to the activity of this ion in the esterification of carboxyl groups during the initial stage of polyesterification of terephthalic acid[4] and of 2-hydroxyethyl hydrogen terephthalate[3] with ethylene glycol catalysed by zinc oxide. These "poisoning effects" of hydroxyl and carboxyl groups upon some catalysts are likely the reason why the correlation of pseudo-half order rate constant k_{obs} (Table I) with Pauling's metal ion electronegativities[33,34] has failed for the esterification of benzoic acid with ethylene glycol. An analogous correlation has been employed with success for the metal ion-catalysed transesterification of aromatic alkyl esters with ethylene glycol[35] and for the metal-ion catalysed glycolysis of aromatic amides[12]. The catalytic effectiveness of a series of metal ions often parallels their formation constants for complexation with the same or related chelating agent[36]. In the case of the esterification reaction under study, the more successful correlation would be presumably that of the rate constants k_{obs} (Table I) with formation constants for complexation of the above metal ions with benzoic acid. Unfortunately, these data are quite limited and do not provide sufficient examples to attempt at such a correlation. It is remarkable that Ti^{4+}, Sn^{2+}, Sn^{4+} and Bi^{3+} ions which were found to be active in the studied esterification reaction exert low activity in the mentioned glycolysis of amides[12] or in transesterification of alkyl esters[35] where in turn Cd^{2+}, Mn^{2+} and Pb^{2+} ions are the most effective. The too high stabilization of the ground state of the esterification reaction by the latter ions could account for their reverse effectiveness in this reaction.

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Translated by J. Hetflejš.