THE SIDE REACTIONS IN THE ESTERIFICATION OF PHTHALIC ANHYDRIDE WITH 2-ETHYLHEXANE-1-OL IN THE PRESENCE OF ORGANOTITANATES

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Using synthetic, chromatographic and spectral methods, we studied the side reactions accompanying the preparation of di-2-ethylhexyl phthalate from phthalic anhydride and 2-ethylhexane-1-ol in the presence of catalytic amounts of tetra-n-butyl titanate. The catalyst proper was titanium(IV) mono-2-ethylhexyl phthalate. The possibility of a simultaneous gas-chromatographic quantitative determination of mono-2-ethylhexyl phthalate, di-2-ethylhexyl phthalate, 2-ethylhexane-1-ol and tetra-n-butyl titanate, reported in the literature, has been refuted. In the esterification catalysed by hydrated titanium dioxide homogeneous catalysis by the formed organotitanate was dominating. The dissolving of hydrated titanium dioxide in the esterification of phthalic anhydride with 2-ethylhexane-1-ol was studied polarographically.

Esterification of phthalic anhydride by monohydroxylic alcohols is an important technological route to the phthalate plasticizer. The esterification is catalysed by other compounds. The mechanism of the catalytic action was studied by several workers[1-6]. The side reactions proceeding in the esterification of phthalic anhydride with 2-ethylhexane-1-ol were studied by Angelova and coworkers[7].

The present paper deals with a detailed analysis of products of the possible side reactions of a tetraalkyl titanate with other reaction components, and of the other side reactions accompanying the esterification of phthalic anhydrides with 2-ethylhexane-1-ol. Another objective of the work was a study of the catalytic action of hydrated titanium dioxide in the esterification.

EXPERIMENTAL

Gas-Liquid Chromatography

Analyses in packed columns were performed with apparatuses Chrom 2 (Laboratorní přístroje Prague) and Fractovap Mod. GV (Carlo Erba, Milano), analyses in capillary columns with an apparatus Fractovap 2400 T (Carlo Erba, Milano), all the apparatuses were equipped with a flame-ionization detector. The columns and the chromatographic conditions were (number of column, its length in m, support with a stationary phase, temperature in °C, pressure of argon in kPa and its flow-rate in ml min^{-1}): column 1, 1·0, Chromosorb W + 5% of Carbowax 1500, 90, 68·7, 31; column 2, 2·0, Chromosorb W DMCS + 3% of Apiezon L, 50 at sample injection and elevated by 5°C/min to 250, final isotherm for 20 min, 98, 30; column 3, 2·0, Chromosorb W + 3% of OV-17, 230, 98·1, 32; column 4, 2·0, Chromosorb W + 3% of SE-30, 90, 68·6, 31. The glass capillary columns (number, length in m, stationary phase, temperature in °C, pressure of argon in kPa, its flow-rate in ml min^{-1}, number of theoretical plates, capacity ratio): column 5, 45, Apiezon L, 130, 98·1, 1·0, 70 000, 3·1; column 6, 42, Carbowax 20 M, 70, 63·7, 0·9, 86 000, 3·4. The splitting ratio of the inlet splitter of the capillary columns was always adjusted to 1 : 100; all the capillary columns had an inner diameter of 0·25 mm.

Analytical Standards

Mono-2-ethylhexyl phthalate was prepared according to a reported procedure[8]. The content of the monoester in the product, determined from the acid value, was 98·5%. n-Butyl-2-ethylhexyl phthalate was prepared as a mixed standard by esterification of phthalic anhydride with an equimolar mixture of 2-ethylhexane-1-ol and n-butanol, catalysed by 0·5% sulphuric acid. By analysis in columns 2 and 3 we found the composition: 15·1% of di-n-butyl phthalate, 41·9% of n-butyl-2-ethylhexyl phthalate and 43·0% of di-2-ethylhexyl phthalate. A complex of mono-2-ethylhexyl phthalate with tetra-n-butyl titanate (Dynamit Nobel, F.R.G.) was obtained by distillation of 1 mol of mono-2-ethylhexyl phthalate with 0·25 mol of tetra-n-butyl titanate at 98·6 kPa, then at 1·33 kPa. The distillate was analysed by GLC in column 1. A complex of phthalic acid with tetra-n-butyl titanate was prepared by dissolving 0·030 mol of phthalic acid in 350 ml of chloroform (freshly redistilled and dried with a molecular sieve), followed by adding 7·55 mol of tetra-n-butyl titanate and removal of chloroform by distillation. In the chloroform that was distilled off and in the weighed distillation residue the contents of n-butanol were determined using column 1 and a weighed amount of 1-pentanol as internal standard. The products from the last two experiments were analysed by IR spectroscopy (apparatus SPG 200, Unicam, Great Britain). To determine the conversion degree in the reaction of tetra-n-butyl titanate with 2-ethylhexane-1-ol, 0·8 mol of the latter was distilled at a pressure of 1·3 kPa of nitrogen (dried by bubbling through concentrated sulphuric acid) with 0·1 mol of tetra-n-butyl titanate in a bath heated to 150°C. The acid value was determined by titration with ethanolic 0·01M-KOH to the phenolphthalein end point and the content of titanium was determined polarographically. The distillation residue was decomposed by adding a 20% excess of 10% aqueous sodium hydroxide. The organic phase was extracted into diethyl ether and dried with anhydrous sodium sulphate. The ether was distilled off and the residue was analysed by GLC in column 1 (1-pentanol as internal standard). Reactions of 2-ethylhexane-1-ol with chlorides of acetic, propanoic, butanoic, 2-methylpropanoic, hexanoic, 2-ethylbutanoic, 3-methylbutanoic and 2-ethylhexanoic acids in equimolar ratios, in the presence of a catalytic amount of pyridine, gave the respective esters. 2-Ethylhexyl formate was obtained by esterification of formic acid with 2-ethylhexane-1-ol. Hemiacetales of butanal, 2-methylpropanal and acetaldehyde with 2-ethylhexane-1-ol were prepared as mixed standards by reactions of the respective aldehydes with equimolar amounts of 2-ethylhexane-1-ol in the presence of the catalyst (5% w/w) used in esterification experiment B (Table II) in sealed ampoules at 80—100°C for 24 h. n-Butyl 2-ethylhexyl ether was prepared by reaction of n-butyl iodide with sodium 2-ethylhexylate in an equimolar ratio. Mixed aldolization of butanal with 2-ethyl-2-hexen-1-al in ethanolic sodium hydroxide, followed by reduction of the formed aldol with sodium borohydride, afforded 2-ethyl-3-propylheptane-1,4-diol, which was dehydrated by a mixture of sodium hydrogen sulphate and anhydrous sodium sulphate at 200 to 230°C for 4 h to 4-ethyl-2,3-di-n-propyltetrahydrofuran.

Reactions of Tetra-n-butyl Titanate

A weighed quantity of tetra-n-butyl titanate (0·60 to 2·62% in the reaction mixture, Table I) was added to the other reaction component (2-ethylhexane-1-ol, or di-n-butyl phthalate, or di-2-ethylhexyl phthalate) and a sample of the mixture was taken for GLC. The rest was transferred into a glass ampoule, sealed and heated in a bath to 190°C for 5 h. The samples for GLC were immediately analysed in columns 1 and 3, the content of the liberated n-butanol was determined using n-pentanol as internal standard; the content of n-butyl 2-ethylhexyl phthalate was determined using an admixture of di-n-pentyl phthalate. The contents of the ampoules after the heating were analysed in the same way. Mono-2-ethylhexyl phthalate, tetra-n-butyl titanate (its 50% solution in di-n-butyl phthalate), n-butyl 2-ethylhexyl phthalate, the recycled 2-ethylhexane-1-ol and the product from esterification A (Table I) were determined by GLC in column 2. The conditions were as described in the literature[7].

Attempted Preparation of an Organotitanium(IV) Complex of Mono-2-ethylhexyl Phthalate

A solution of titanium tetrachloride (0·01 mol) in tetrachloromethane (8 ml) was added dropwise under stirring to a solution of mono-2-ethylhexyl phthalate (0·04 mol) in tetrachloromethane (20 ml). The liberated hydrogen chloride was removed by a stream of bubbling nitrogen (dried by phosphorus pentoxide) and absorbed in 0·5M-NaOH (100 ml). The decrease in alkalinity

TABLE I

Composition of products (%) of the reactions of tetra-n-butyl titanate with 2-ethylhexane-1-ol, mono-2-ethylhexyl phthalate and di-2-ethylhexyl phthalate

Reaction mixture	n-Butanol			n-Butyl 2-ethylhexyl phthalte		
	theor.[a]	before heating	after heating	theor[a]	before heating	after heating
2-Ethylhexane-1-ol + 0·63% of tetra-n-butyl titanate	0·54	0·53[b]	0·53[b]	—	—	—
Mono-2-ethylhexyl phthalate +2·10% of tetra-n-butyl titanate	1·79	1·47	1·77	—	—	—
Di-2-ethylhexyl phthalate +1·74% of tetra-n-butyl titanate	1·72	1·43	0·00	6·77	0·00	6·51
Di-n-butyl phthalate 2·62% of tetra-n-butyl titanate	2·28	1·93	1·93	—	—	—

[a] Theoretical content of n-butanol or n-butyl 2-ethylhexyl phthalate after 100% conversion of the added tetra-n-butyl titanate; [b] content of n-butanol after subtracting the n-butanol in 2-ethylhexane-1-ol, determined by GLC in column 1 (using n-pentanol as internal standard).

of the hydroxide (titration with 0·5M-HCl to the phenolphthalein end point) showed the quantity of the liberated hydrogen chloride. The tetrachloromethane was removed by distillation under atmospherical pressure, then at 1·3 kPa.

Reaction of titanium tetrachloride (0·10 mol) in tetrachloromethane (35 ml) with ethane-1,2-diol (4·0 mol), which had been dried by distillation with anhydrous sodium sulphate, gave tetra(2-hydroxyethyl) titanate. The unreacted diol was distilled off *in vacuo* under dried nitrogen; yield 97% (based on titanium tetrachloride). A sample of the product (0·05 mol) was mixed with mono-2-ethylhexyl phthalate (0·2 mol) and the mixture was distilled at a pressure of 0·67 kPa on a bath heated to 210°C. The distillate was analysed by GLC in column 2.

General Procedure of the Esterification

Phthalic anhydride (2·5 mol) was esterified with 2-ethylhexane-1-ol (7·26 mol) in the presence of a catalyst (Tables II and III). The reaction water was continuously distilled from the stirred mixture as an azeotrope with 2-ethylhexane-1-ol, which after condensation and separation of water in the Dean-Stark distillation head was returned to the reaction flask. After the esterification, in experiments A, B, D, E, F, G_1, H_1 and H_2, 2-ethylhexane-1-ol was distilled off at 2·70 kPa and the product was stripped for 1·5 h at 170 to 175°C with steam at the same pressure. After experiments G_1, H_1 and H_2 (when all the reaction water had been removed). the catalyst was collected on a filter and used again in the subsequent experiment of the series G or H. Toward the end of an esterification experiment the acid value of the mixture was determined by titration with alcoholic 0·1M-KOH to the phenolphthalein end point. Prior to the titration the weighed sample was always diluted with 20 ml of ethanol, the acidity of which had been neutralized with 0·1M-KOH (phenolphthalein). The catalyst (designated as c_1) in experiment G_1 was an alkaline suspension of hydrated titanium dioxide, containing 13·0% of sodium hydroxide, 11·0% of tita-

TABLE II

Esterification of phthalic anhydride with 2-ethylhexane-1-ol in the presence of various catalysts

Experiment	Catalyst	Time min	Acid value, mg KOH/g after esterification	Acid value, mg KOH/g after stripping
A	38·5 mmol of tetra-n-butyl titanate	150	0·190	1·280
B	9·63 g of a catalyst containing 6·5% of $Al(OH)_3$	360	0·080	0·095
C	134 mmol of 98% H_2SO_4	480	11·830	—
D	11·33 mol of titanium(IV) mono-2-ethylhexyl phthalate	160	0·250	1·830
E	11·33 mmol of tetra-n-butyl titanate	160	0·235	1·260
F	55 mmol of hydrated TiO_2[a]	180	0·260	0·090

[a] Catalyst c_2, see Table III.

TABLE III

Dissolving of hydrated and anhydrous titanium dioxide in esterification of phthalic anhydride with 2-ethylhexane-1-ol

Time, min	t_n, °C	Water, ml	$c_{Ti^{4+}}$, mmol l^{-1}
New catalyst c_1, experiment G_1			
20	85	0	0·150
40	150	12	0·164
60	182	32	1·310
80	197	45	3·940
100	205	55	5·520
120	209	60	6·630
140	212	65	3·870
160	219	67	2·430
180	220	68	3·130
Catalyst c_1, 1st recycle, experiment G_2			
20	87	0	2·610
40	169	0	2·760
60	194	13	4·360
80	201	24	5·470
100	208	31	5·890
120	213	38	4·680
140	215	42	3·060
160	222	43	2·550
180	223	43	3·340
New catalyst c_2, experiment H_1			
20	120	0	0·096
40	176	26	0·471
60	196	39	2·670
80	202	51	3·020
100	211	61	1·860
120	217	66	0·946
140	220	68	0·946
160	222	68	1·430
Catalyst c_2, 1st recycle, experiment H_2			
20	120	0	0·293
40	180	2	0·960
60	198	17	2·080
80	208	30	1·620
100	217	38	1·030
120	222	44	1·031
140	225	46	1·380
160	226	46	1·580

TABLE III
(*Continued*)

Time, min	t_n, °C	Water, ml	$c_{Ti^{4+}}$, mmol l^{-1}
Catalyst c_2, 2nd recycle, experiment H_3			
20	130	0	1·130
40	185	2	1·040
60	197	17	1·720
80	205	30	1·710
100	212	38	1·460
120	217	43	0·894
140	221	44	1·160
160	222	44	1·680
New anhydrous titanium dioxide, experiment I			
90	197	18	0·044
180	201	26	0·046
270	202	29	0·041
360	204	30	0·046
450	205	31	0·057
540	205	32	0·064
630	206	32	0·065
New catalyst c_2, experiment J^c			
20	170	0	0·010
40	180	20	0·918
60	182	23	1·410
80	182	23	1·910
100	182	23	1·820
120	182	23	2·050
140	182	23	2·110
160	182	23	2·300
New catalyst c_1, experiment K^c			
20	171	3	0·010^d
40	182	30	0·010
60	182	31	0·010
80	182	31	0·010
100	182	31	0·010
120	182	31	0·010
140	182	31	0·010
160	182	31	0·010

TABLE III

(*Continued*)

Time, min	t_n, °C	Water, ml	$c_{Ti^{4+}}$, mmol l^{-1}
	New catalyst c_1, experiment L[e]		
20	180	0	0·422
40	204	0	0·520
60	207	0·1	0·618
80	212	0·1	0·693
100	212	0·1	0·769
120	214	0·2	0·999
140	208	0·2	1·280
160	205	0·2	1·320

[a] Temperature of the reaction mixture in the esterification; [b] total volume of water which was distilled off; [c] the catalyst was heated with 2-ethylhexane-1-ol alone; [d] below the threshold of detection by the polarographic method used; [e] the catalyst was heated with mono-2-ethylhexyl phthalate alone.

nium dioxide and 66% of water. Catalyst c_2 in experiment H_1 was prepared by 2 hours'boiling of the described suspension with 400 ml of water under stirring. It was collected on a filter and washed with water until pH of the filtrate had decreased to 9·5. The filter cake (32·5—33·0 g) was used directly. Phthalic anhydride was also esterified with 2-ethylhexane-1-ol in the presence (0·062%) of tetra-n-butyl titanate. In the course of the experiments (Table III) samples were withdrawn at 20 min intervals for polarographic determination of the dissolved titanium. In experiment B the catalyst was aluminium hydroxide prepared as described[9]. Esterification experiment I was carried out with 4·4 g of titanium dioxide. We also investigated the dissolving of catalysts c_1 and c_2 in boiling 2-ethylhexane-1-ol (experiments J, K; Table III), using the same charges of the two components. The dissolving of c_2 in mono-2-ethylhexyl phthalate was followed in experiment L. A suspension of c_1 (13 g) was freed from the surface water by distillation with benzene (13 g) under stirring. The dehydrated catalyst was immediately treated with mono-2-ethylhexyl phthalate (1 mol), which was pre-heated to 100°C. The mixture was brought to 220°C in the course of 180 min, while nitrogen (dried on a molecular sieve) was bubbled through. Samples were taken at 20 min intervals for polarographic determination of the dissolved organotitanate.

To ascertain the effect of the tetra-n-butyl titanate complex with mono-2-ethylhexyl phthalate on the course of the stripping, 10 g of the complex and 2·56 mol of di-2-ethylhexyl phthalate (acid value 0·09 mg KOH g^{-1}) were stripped under the same conditions as in the esterification experiments. The acid values were determined after 30, 60, 90 and 120 min. The stripped portion was analyzed by GLC in column 3.

Determination of Dissolved Titanium

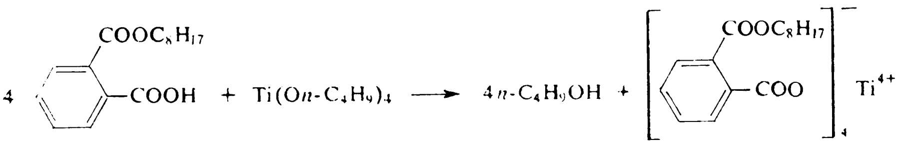
The content of the dissolved titanium was determined polarographically[10] in filtered samples taken from the reaction mixtures and mineralized by 1 h heating with 85% phosphoric acid on a boiling water bath, with occasional stirring. Using a polarograph LP-7 (Laboratorní přístroje Prague), we recorded the polarographic wave with the half-wave potential for the reduction of Ti^{4+} to Ti^{3+}. The content of titanium was determined by the direct calibration method, using a $3{\cdot}6 \,.\, 10^{-2}$ mol l^{-1} solution of tetra-2-ethylhexyl titanate (Dynamit Nobel, F.R.G.) in 2-ethylhexane-1-ol, after its mineralization as described above. Similarly we determined titanium in the stripped ester from experiment H_2 and in the complex of tetra-n-butyl titanate with mono-2-ethylhexyl phthalate.

Identification of Impurities in the Recycled 2-Ethylhexane-1-ol

The 2-ethylhexane-1-ol used had been recovered in the preparation of di-2-ethylhexyl phthalate catalysed by hydrated titanium dioxide; after four reaction cycles its final concentration (determined by GLC in columns 5 and 6, 2-ethylhexyl isobutyrate as internal standard) was 90,3%. The impurities present in it were concentrated into 6 fractions (boiling in the range 190 to 233°C) by distillation over a column with a rotating teflon spiral (Büchi, Switzerland), having 30 TP. According to their IR spectra, all the fractions were both reesterified (as described in ref.[11]) and hydrogenated in methanol on a Pd/C catalyst (hydrogen pressure 980·6 kPa, temperature 40–45°C, time 8 h). The products of the two reactions were analysed by capillary GLC in columns 5 and 6. In the same way we chromatographed the original fractions from the rectification, 4-ethyl-2,3-di-n-propyltetrahydrofuran and hemiacetals of 2-ethylhexane-1-ol with iso- and n-butyraldehyde. One of the components in the fraction boiling at 231–233°C was isolated by chromatography on a 15 cm column of silica gel, with distilled n-hexane as eluent. This component was identified by NMR spectroscopy in an apparatus Jeol JNM-FX 100 (Japan). The components present in the fraction 217–219°C were identified by capillary GLC-MS, using an apparatus Varian MAT 44S (F.R.G.) under the following conditions: glass capillary column 25 m, I.D. 0·25 mm,, coated with SE-54, the starting temperature of the column 80°C was increased by 8°C/min to 190°C, argon pressure 66 kPa, its flow rate 2 ml/min. The column was connected through a direct interface (240°C) with the mass spectrometer, source temperature 200°C, emission current 0·3 mA, energy of electrons on ionization by impact 70 eV, on chemical ionization (the reaction gas methane) 150 eV, the total flow of ions was recorded in the range $m/z = 100$ to 450, the spectra in the range 45 to 450, the time of recording a spectrum was 1 s.

RESULTS AND DISCUSSION

GLC of di-2-ethylhexyl phthalate from experiment A (Table II) and other standards under the described conditions[7] rules out the possibility of a simultaneous quantitative determination of mono- and di-2-ethylhexyl phthalates and of 2-ethylhexane-1-ol by GLC under the given conditions. The peak 1 in ref.[7] cannot be tetra-n-butyl titanate, which under the given conditions remains in the column owing to the high boiling point (185–188°C/1·47 kPa) and its elution cannot be close to that of 2-ethylhexane-1-ol. Mono-2-ethylhexyl phthalate is also partly retained under the given chromatographic conditions and partly decomposes in the injection end of the column to phthalic anhydride and 2-ethylhexane-1-ol (*cf.*[12]). By comparing the chromatographic records with the elution time of n-butyl-2-ethylhexyl phthalate it can be judged that the concentration of this ester in our product was 2·3%, which corresponds to a 44·7% conversion of tetra-n-butyl titanate. Tetra-n-butyl titanate at least partly decomposed in the esterification to n-butyl 2-ethylhexyl phthalate. Heating of tetra-n-butyl titanate with the individual reaction components and esterification products (Table I) have shown that the organotitanate on mere mixing with an excess of 2-ethyl-hexane-1-ol gets 99% converted to tetra-2-ethylhexyl titanate (on mixing 4 mol of 2-ethylhexane-1-ol with 1 mol of tetra-n-butyl titanate the conversion degree was 88%), with the simultaneous liberation of n-butanol. Silanization of the chromatographic support did not affect the content of n-butanol determined by GLC. Consequently, this alcohol is not liberated by reaction of tetra-n-butyl titanate with the terminal silanol groups of the support. Heating of the mixture did not influence the conversion of tetra-n-butyl titanate either. Heating of a mixture of di-2-ethylhexyl phthalate and tetra-n-butyl titanate gave a 96·2% conversion to n-butyl 2-ethylhexyl phthalate. Heating of tetra-n-butyl titanate with mono-2-ethylhexyl phthalate converted 98·9% of the former. The presence of n-butanol in the mixture prior to the heating can be accounted for as due to a decomposition of tetra-n-butyl titanate in the chromatographic column. The amount of n-butanol that was distilled off, referred to the charge of tetra-n-butyl titanate (94% of the theoretical amount of n-butanol was distilled off; the distillate containate 98·0% of n-butanol and 1·5% of 2-ethylhexane-1-ol), suggests that reaction (*A*) occurred:



(*A*)

The structure of the product was confirmed by its acid value (calculated: 193·9 mg KOH h^{-1}, found: 184·1 mg KOH g^{-1}) and the content of titanium (calculated 4·14%, found: 4·10%). The IR spectroscopy also confirmed it as titanium(IV) salt of mono-2-ethylhexyl phthalate (disappearance of vibration bands of the carboxyl group in mono-2-ethylhexyl phthalate at 2 530 and 2 650 cm^{-1}, presence of the carboxylate band at 1 720 cm^{-1}, vibrations at 1 035, 1 070, 1 125, 1 290, 2 925, 2 835, 2 910 and 2 930 cm^{-1}, confirming the presence of a 2-ethylhexyl group). A similar reaction with phthalic acid probably leads to titanium(IV) phthalate (balance for the released n-butanol). The catalyst of the esterification was not tetra-n-butyl titanate (contrary to what is stated in the literature[7]), but titanium(IV) salt of mono-2-ethylhexyl phthalate, or titanium(IV) salt of phthalic acid. The titanium salt of the monoester cannot be obtained by direct reaction of titanium tetrachloride with the monoester, since no decrease in alkalinity of KOH, to be ascribed to evolution of HCl, was observed. Owing to the resistance of tetra(2-hydroxyethyl)-titanate to hydrolysis by water[13], this titanate did not undergo reaction (*A*) (GLC of the distilling fractions found 98·5% of 2-ethylhexane-1-ol and 1·5% of ethylene glycol).

The results of the experiments in Table II confirm the fact that the most active catalysts of esterification are titanium(IV) compounds. Titanium(IV) salt of mono-2-ethylhexylphthalate was as efficient a catalyst as an equivalent amount of tetra-n-butyl titanate (experiments D and E, Table II). The two catalysts behaved equally even in stripping the ester, without the organotitanate having been removed by precipitation with an aqueous hydroxide and filtering off the hydrated titanium dioxide. The titanium dioxide formed in this way catalysed hydrolysis of the diester in the stripping with steam at 170–180°C, in contrast to catalyst c_2. GLC of the products from experiment A revealed again that the reaction was accompanied by decomposition of tetra-n-butyl titanate (the ester contained 2·3% of n-butyl 2-ethylhexyl phthalate, which corresponds to a 44·7%-conversion of the n-butanol released from tetra-n-butyl titanate; the remaining n-butanol had a concentration of 2·1% in 288 g of the distilled 2-ethylhexane-1-ol).

Catalysts c_1 and c_2, containing hydrated titanium dioxide, partly dissolved in the course of the esterification (Table III, Figs 1 to 3), whereas non-hydrated titanium dioxide did not. Depending on the number of recycles at temperatures 195–205°C, as much as 14% of catalyst c_1 and 4 to 6·5% of catalyst c_2 dissolved. At a higher concentration of sodium hydroxide (enhancing the solubility of the catalysts) a greater part of hydrated titanium dioxide is probably converted into sodium titanate, which reacts faster with mono-2-ethylhexyl phthalate than the hydrated titanium dioxide. The fact that hydrated titanium dioxide reacts with the monoester was demonstrated by experiment L. By contrast, a weakly alkaline hydrated titanium dioxide reacted with 2-ethylhexane-1-ol about a hundred times faster than the strongly alkaline catalyst c_1 (experiments J and K, Fig. 3). A prerequisite for good activity of a catalyst was the presence of titanium dioxide in the form of a hydrated gel, which determined even the surface structure of the catalyst. Titanium dioxide itself exhibited no catalytic activity, which may also be due to the concentration of the dissolved organotitanate being 50 to 100 times lower than in the other catalysts.

Esterification in the presence of 0·062% of tetra-n-butyl titanate (the amount of titanium corresponds to the concentration maximum of the dissolved organotitanate in experiment H_2) was terminated after 170 min, the acid value being 0·198 mg KOH g^{-1}. Consequently, in the esterification with hydrated titanium dioxide the soluble organotitanate was formed in a concentration that was sufficient for an efficient homogeneous catalysis of the esterification. What obviously is most important is the concentration of the soluble organotitanate in the temperature range 180 to 220°C, at which the reaction water distills off. In the use of tetra-n-butyl titanate in an amount equivalent to the concentration maximum of the dissolved organotitanate from the very start of experiment H_2 the esterification rate did not seem to be increased. The fact that in the beginning stage of the esterification the reaction water was not removed obviously had an adverse effect on the solubility of hydrated titanium dioxide, which may be controlled by an equilibrium in which water, in addition to the organotitanate, operates as a reaction product. Fig. 3 shows that at 182°C the concentration of the dissolved organotitanate reached the same value, and with further increasing the temperature the concentration of the organotitanate markedly rose as a result of intense dehydration of the system. The concentration maximum of the dissolved organotitanate was attained after 60 to 80 min (approximately half of the reaction time) at temperatures between 195 and 205°C. The decrease in the concentration of the dissolved organotitanate in the temperature range 205 to 218°C may be due to its pyrolysis, or hydrolysis by the reaction water, or to both. The

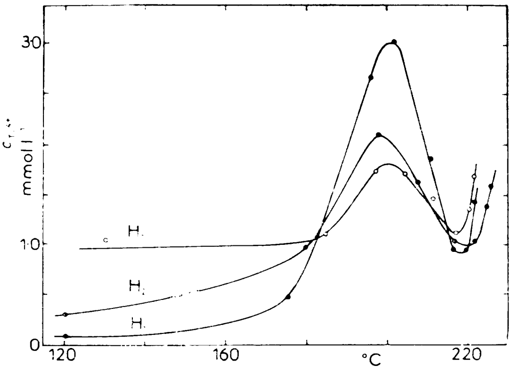


FIG. 1

Temperature dependence of titianum dioxide (catalyst c_2) dissolution during the esterification of 2-ethylhexane-1-ol by phthalanhydride. H_1 fresh catalyst; H_2 first recycle of catalyst; H_3 second recycle of catalyst

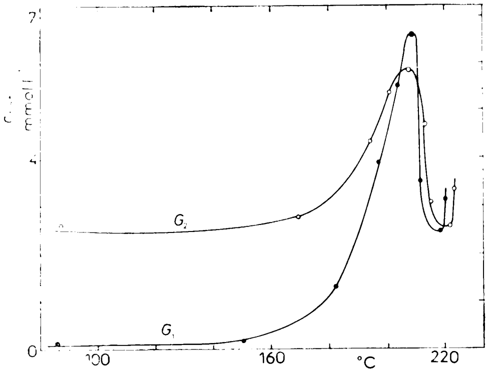


FIG. 2

Temperature dependence of hydrated titanium dioxide (catalyst c_1) during the esterification of 2-ethylhexane-1-ol by phthalanhydride G_1 fresh catalyst; G_2 first recycle of catalyst

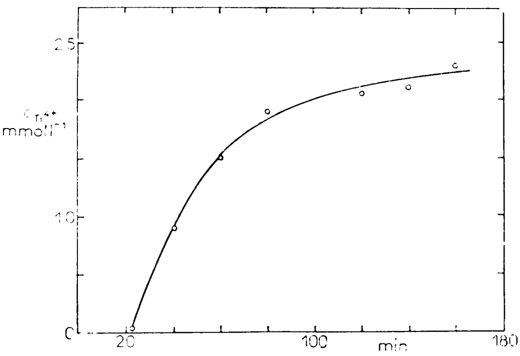


FIG. 3

Time dependence of hydrated titanium dioxide (catalyst c_2) dissolution in 2-ethylhexane-1-ol subsequent rapid increase in concentration of the dissolved organotitanate might be explained by the formation of a new organotitanate, more resistent to pyrolysis or hydrolysis.

The asymptotic course of the concentration of organotitanate in relation to time (Fig. 3) in experiment J suggests that the dissolving of catalyst c_2 in boiling 2-ethylhexane-1-ol proceeded in some other way than in the esterification mixture, because in experiment J the temperature of the reaction mixture could not exceed the boiling point of 2-ethylhexane-1-ol and mono-2-ethylhexyl phthalate was not present in the reaction mixture. Consequently, an equilibrium is established between the dissolved organotitanate and the heterogenous catalyst. The concentration of the dissolved organotitanate in this experiment after 40 min of the reaction (the temperature reachched was 182°C and most of the water brought in with the catalyst was distilled off) is comparable with the concentrations at the same temperature in experiments H_1 to H_3.

The fact that in experiment K the organotitanate was not formed in a concentration measurable by the method used may have been due to the 18% molar excess of sodium hydroxide over titanium dioxide in catalyst c_1, if we postulate the reaction:

$$H_2TiO_3 + 2\,NaOH \rightleftharpoons Na_2TiO_3 + 2\,H_2O \qquad (B)$$

Intense dehydration of the system shifts the equilibrium to the right-hand side, so that the formed sodium titanate cannot react with 2-ethylhexane-1-ol. The content of the organotitanate in the ester after the stripping with steam was 0·0125 mmol l^{-1}, which corresponds to 0·60 ppm of the dissolved titanium. This concentration is comparable by the order of magnitude to the organotitanate concentration reached in experiment I, where anhydrous commercial titanium dioxide was employed (0·044 to 0·065 mmol l^{-1}).

It has been found that in the esterification catalysed by catalyst c_1 the hydrated titanium dioxide reacts with mono-2-ethylhexyl phthalate, the concentration of the dissolved organotitanate having the same order of magnitude as in the esterification experiments. The temperature of the charge could not be elevated up to 225°C, since at a temperature of 212–214°C the monoester rapidly decomposed to 2-ethylhexane-1-ol. Still, it can be said that the hydrated titanium dioxide may, in the course of the esterification, react with the two main reaction components, with the formation of the organotitanate.

During the esterification of phthalic anhydride with 2-ethylhexane-1-ol some products of the side reactions accumulated in the recycled 2-ethylhexane-1-ol. By re-esterification and addition of chromatographic standards it was ascertained that recycled 2-ethylhexane-1-ol contained 2-ethylhexyl formate, 2-ethylhexyl acetate, 2-ethylhexyl propanoate and 2-ethylhexyl butanoate. The presence of 2-ethylhexyl butanoate can be explained by oxidation of the traces of butanol present in the alcohol to butanoic acid, followed by its esterification. It is possible that even the other 2-ethylhexyl esters arise from butanol after its oxidation and degradation to lower acids. Acetalization of butanol catalysed by the esterification catalyst gave rise to its 2-ethylhexyl acetal. Acetals of acetaldehyde and 2-methylpropanal were not detected. Hydrogenation of the isolated impurities on the palladium catalyst did not demonstrate any unsaturated compounds in the recycled 2-ethylhexane-1-ol. The nature and proportion of the impurities in the returned 2-ethylhexane-1-ol were independent of the type of the esterification catalyst; an exception was sulphuric acid, in the use of which the main by-product was 2-ethylhexene-1. The etherification side reactions produced n-butyl 2-ethylhexyl ether (n-butanol was present in the starting 2-ethylhexane-1-ol) and 4-ethyl-2,3-di-n-propyltetrahydrofuran, the latter arising from internal etherification of 2-ethyl-3-n-propylheptane-1,4-diol. In all probability, this diol was present as a trace impurity in the starting 2-ethylhexane-1-ol, as a result of aldolization of n-butanol with 2-ethyl-2-hexenal-1 and hydrogenation of the aldol in the industrial production of 2-ethylhexane-1-ol. The presence of at least three *cis-trans* isomers of 4-ethyl-2,3-di-n-propyltetrahydrofuran was demonstrated by capillary GLC-MS, since fragmentation of chromatographic peaks of three components gave quite identical spectra at a molecular mass of 184, which corresponds to the molecular formula $C_{12}H_{24}O$. Interpretation of the mass spectra testifies to the *cis-trans* isomers of either 3,5-diethyl-2-n-propyltetrahydropyran or 4-ethyl-2,3-di-n-propyltetrahydrofuran. An independent synthesis proved the presence of the latter. NMR spectroscopy and capillary GLC of the component isolated from the fraction boiling at 231 – 233°C identified n-tridecane. The fraction containing n-butyl 2-ethylhexyl ether (b.p. 212 – 214°C) analogously proved to contain n-dodecacane.

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