

THE CATALYTIC ACTIVITY OF TERTIARY PHOSPHINES, ARSINES, STIBINES, AND QUARTERNARY PHOSPHONIUM SALTS IN REACTION OF TEREPHTHALIC ACID WITH ETHYLENE OXIDE*

J. MÁLEK and P. ŠILHAVÝ

*Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague 6 - Suchbát*

Received December 6th, 1974

Second-order rate constants of the reaction of terephthalic acid with ethylene oxide catalysed by tri-*n*-butylphosphine, triphenylphosphine, triphenylmethylphosphonium bromide, triphenylarsine, tri-*n*-butylstibine and strongly basic quarternary ammonium anion-exchange resin Amberlite IRA-400 have been measured. The reaction was first-order in ethylene oxide and the catalyst and zero-order in the acid. The activity of the catalysts decreased in the order: triphenylmethylphosphonium bromide > triphenylphosphine > tri-*n*-butylphosphine \approx triphenylarsine \approx tri-*n*-butylstibine > Amberlite IRA-400. The activities of tri-*n*-butylphosphine, triphenylarsine and tri-*n*-butylstibine were identical with the activity of pyridine. Characteristic feature of the reactions catalysed with all these catalysts is essentially the same activation energy and activation entropy, whose approximate values are 18.3 kcal mol⁻¹ and -24.2 e.u., respectively. Identical mechanism is assumed for the rate-determining step of the reaction accelerated by these catalysts.

Previous works of this series¹⁻³ and some data available in patent literature⁴⁻¹¹ proved a high selectivity of the reaction of carboxylic acids with 1,2-alkylene oxides in protic and aprotic dipolar solvents when tertiary amines were used as catalysts. The reactions produced corresponding 2-hydroxyalkyl esters as sole products. According to patent literature, also other compounds can be employed as catalysts in this medium, such as mercaptans¹², thioethers¹³, quarternary ammonium salts¹⁴ or hydroxides¹⁵, anion-exchange resins¹⁶, tertiary phosphines^{17,18}, quarternary phosphonium salts or hydroxides¹⁹, tertiary arsines¹⁸, stibines^{18,20}, and bismuthines²⁰. The catalytic effectiveness of stibines in this reaction, found independently by us and Japanese authors, is of special interest in view of the known ability of antimony(III) compounds to catalyse polycondensation reactions of bis(2-hydroxyalkyl) esters^{21,22}, which compounds can be obtained by the reaction of dicarboxylic acids with 1,2-alkylene oxides.

To our knowledge, there are no data which would allow to compare the activity of the above-mentioned catalysts in the reaction of carboxylic acids with 1,2-alkylene oxides, with the exception of tertiary amines¹⁻³ and thioethers²³. In the present work we report on the results of measurements of catalytic activity of tri-*n*-butylphosphine, triphenylphosphine, triphenylarsine, tri-*n*-butylstibine, triphenylmethylphosphonium

* Part IV in the series Reactions of Carboxylic Acids with Ethylene Oxide; Part III: This Journal 41, 84 (1976).

bromide, and strongly basic anion-exchange resin Amberlite IRA-400 in the reaction of terephthalic acid with ethylene oxide in *n*-butanol as a solvent. The measurements were based on the known kinetics of this reaction catalysed with tertiary amines¹, according to which terephthalic acid, due to its sparse solubility in protic solvents and low, essentially constant concentration of transiently formed 2-hydroxyethyl ester in the reaction system, is converted to the bis(2-hydroxyethyl) ester according to zero-order kinetics in the acid. This reaction system, making easier to follow the reaction course, has been chosen to compare catalytic activity of the above catalysts with the known activity of tertiary amines and to ascertain the effect of the catalysts on the selectivity of the reaction.

EXPERIMENTAL

Compounds Used

Terephthalic acid, "fiber grade" purity (Mobil Oil Corp., U.S.A.) (particle size 0.005–0.010 mm) was free of isophthalic acid and contained 0.07% phthalic acid and less than 0.005% benzoic acid; the acid was used without further purification. Ethylene oxide, 99% purity (by gas chromatography), contained a total of less than 1% acetaldehyde, acetylene, water, and carbon dioxide. *n*-Butanol (Spolana, Neratovice) was distilled before use through the column filled with an activated A4 molecular sieve and the fraction collected had b.p. 116.4°C/733 Torr. Pyridine, analytical purity grade (Fluka AG.), was purified by the procedure described earlier³ and the fraction used had b.p. 114°C/754 Torr. Triphenylphosphine, purum (Lachema, Brno), was recrystallised from ethanol, m.p. 79.0–79.5°C (ref.²⁴ m.p. 80°C). Triphenylarsine, purum (Fluka AG.), was recrystallised from ethanol, m.p. 59.5–60.0°C (ref.²⁵ m.p. 59–60°C). Tri-*n*-butylstibine, purum (Fluka AG.), was distilled under nitrogen, b.p. 132–134°C/13 Torr (ref.²⁶ b.p. 130°C/12 Torr). Tri-*n*-butylphosphine (Schuchardt AG., München) of 99% purity was used as obtained. Triphenylmethylphosphonium bromide, purum (Lachema, Brno), was recrystallised from ethanol before use. Strongly basic anion-exchange resin Amberlite IRA-400 (12.6 ml, *i.e.* 12.6 meq. of the resin preswollen in water) (Serva-Entwicklungslabor, Heidelberg, GFR) was converted into the OH form by dilute sodium hydroxide, washed with water and brought to the terephthalate cycle in *n*-butanol. Water was removed from the resin as *n*-butanol–water azeotrope, the resin was washed with fivefold volume of dry methanol and dried at 50–55°C/0.5 Torr for 3 h.

Analytical Methods

The total acidity of the reaction mixture was determined by acidimetric titration of the sample (1–2 ml) diluted with 5 ml of ethanol and 3 ml of pyridine in an atmosphere of nitrogen with 0.1M-KOH on phenolphthalein as indicator. The amount of absorbed ethylene oxide or of the oxide consumed during the reaction was determined manometrically on the apparatus used for kinetic measurements. The methods employed in determining the solubility and concentration of ethylene oxide and terephthalic acid in *n*-butanol were described in a previous work¹. The concentration of the "free-carboxyl groups", *i.e.* that of the dissolved and suspended terephthalic acid and 2-hydroxyethyl terephthalate, the concentrations of 2-hydroxyethyl terephthalate and bis(2-hydroxyethyl) terephthalate in the reaction mixture containing the catalyst were determined by combined acidimetric titration and polarographic analysis¹. The purity of isolated bis(2-hydroxyethyl) terephthalate was checked polarographically²⁷. Selectivity of the reaction

of ethylene oxide with terephthalic acid was determined at the end of each kinetic run by comparing the total consumption of ethylene oxide with the "free-carboxyl group" concentration. The absence of side products was verified by gas chromatographic analysis of the reaction mixture which was freed of the undissolved terephthalic acid by filtration. The instrument used was Pye-Argon chromatograph equipped with a column filled with 20% poly(ethylene glycol) on Chromosorb W.

Kinetic Measurements

Rates of the catalytic reaction of terephthalic acid with ethylene oxide in *n*-butanol were determined by known procedure using the apparatus described in a previous work³. The reaction mixture was prepared in the following way: The acid (10 g) and the catalyst (0.83–3.31 g) weighed in nitrogen atmosphere and 100 ml of *n*-butanol were placed into a 500 ml-glass reaction flask which was purged with nitrogen. The flask was equipped with a jacket connected to Ultrathermostat U 10 and placed on a shaking device. The mixture was warmed up to the reaction temperature in 20 min, then the pressure in the flask was decreased to 250 Torr, the stirrer started, the flask connected to the measuring apparatus which was joined to the ethylene oxide reservoir, and the mixture was saturated with ethylene oxide. After 5 min, the pressure in the reaction flask reached a constant value and this moment was taken as the beginning of the reaction from which the consumption of ethylene oxide by the reaction with terephthalic acid was calculated¹. The pressure in the reaction flask was kept constant throughout the run. The measurements were carried out at a concentration of terephthalic acid corresponding to 0.743 mol kg⁻¹, ethylene oxide concentration being 0.507–1.275 mol kg⁻¹ and that of the catalyst 0.03–0.15 mol kg⁻¹ (the anion-exchange resin concentration was 0.143 mequiv. kg⁻¹); the reaction rates were measured at 70–100 ± 0.1°C and at a total pressure of 855 Torr. The reaction course was followed according to ethylene oxide consumption¹ that in the presence of the above-mentioned catalysts, except triphenylarsine and tri-*n*-butylstibine, increased linearly with time up to 93–95% conversion of the acid. The reactions catalysed with triphenylarsine and tri-*n*-butylstibine showed an induction period which decreased with increasing temperature. This induction period was not observed in experiments in which the mother liquor obtained by reacting terephthalic acid until disappearance of the induction period was used as a reaction medium. Rates of the reactions catalysed with triphenylarsine and tri-*n*-butylstibine were therefore measured in the following way: The reaction mixture obtained in the presence of these catalysts was freed of terephthalic acid by filtration while hot, cooled to room temperature and the dissolved ethylene oxide was desorbed at 100–200 Torr. Then the "free-carboxyl group" content in the mixture was determined, the known amount of the acid was added and rate measurements were performed in the way described above. The "free-carboxyl group" content at the end of the reaction was calculated after allowance being made for the carboxyl content in the starting reaction mixture. Parallel experiments showed that twofold concentration of the bis-ester did not affect the rate of absorption of ethylene oxide in the reaction mixture under given reaction conditions. Also the mother liquor freed of the bis-ester by the procedure described below can be used as a reaction medium. In this case, the analytically determined content of the catalyst in the mother liquor should be readjusted to the original value by addition of that amount of the catalyst which was taken along with the crystals of the separated bis-ester. Owing to sparse solubility of terephthalic acid in *n*-butanol¹, reaction mixtures were heterogeneous in all experiments up to 93–95% conversion of the acid. In agreement with previous measurements¹ it was found that under the given concentration conditions, at a given size of terephthalic acid particles and the frequency of shaking (120 vibrations per min) the reaction rate was not affected by mass transfer on the solid-liquid-gas phase boundaries; the measurements were thus carried out in the kinetic region. The difference

between the total consumption of ethylene oxide and the sum of concentrations of terephthalic acid and the mono-ester was $\pm 1\%$ and varied thus within an analytical error. Also gas chromatographic analysis confirmed that the only final product of the reaction, carried out to a conversion less than 100%, was bis(2-hydroxyethyl) terephthalate. Under the reaction conditions chosen the reaction was accompanied by 3–5% change of the volume of the reaction mixture; this change was not considered in the rate calculations. All concentrations are given in mol per kg of the suspension.

Isolation of Bis(2-hydroxyethyl) Terephthalate

The reaction mixture obtained at 90% conversion of terephthalic acid was freed of the unreacted and undissolved acid by filtration while hot (in the case of Amberlite IRA-400 as catalyst, this was also removed); the mother liquor was cooled to room temperature, freed of the absorbed ethylene oxide by evacuation at 100–200 Torr, extracted twice with 10% aqueous sodium hydrogen carbonate solution and washed with water. After removal of water as a n-butanol-water azeotrope, n-butanol was distilled off *in vacuo* to give a saturated solution of bis(2-hydroxyethyl) terephthalate²⁸. The product precipitated by cooling the solution to 0°C was recrystallised from n-butanol; white needles, m.p. 110.0–110.5°C (ref.²⁹ m.p. 110.0–110.5°C), 75–85% yield. For $C_{12}H_{14}O_6$ (254.2) calculated: 56.69% C, 5.55% H; found: 56.75% C, 5.58% H.

RESULTS AND DISCUSSION

Reactions of terephthalic acid with ethylene oxide in anhydrous n-butanol catalysed by tri-n-butylphosphine, triphenylphosphine, triphenylarsine, tri-n-butylstibine, triphenylmethylphosphonium bromide, and quarternary ammonium anion-exchange resin Amberlite IRA-400 are highly selective when they are performed up to less than 100% conversion of the acid;* the only final product is bis(2-hydroxyethyl) terephthalate. The rate of ethylene oxide consumption in the reaction with terephthalic acid catalysed by tri-n-butylphosphine, triphenylphosphine, triphenylmethylphosphonium bromide and Amberlite IRA-400 is time-independent (Fig. 1). Similarly to the tertiary amine-catalysed reaction¹, the reaction obeys a zero-order rate law (Eq. (1)). We found that this relation is valid from the very beginning of the reaction up to 93–95% conversion of the acid, the upper limit being connected with disappearance of the solid phase and formation of homogeneous mixture. The reaction catalysed with triphenylarsine and tri-n-butylstibine showed relatively long induction periods (6 and 2 h, respectively, at 90°C) (Fig. 2) which increased with decreasing reaction temperature. These induction periods were eliminated (Fig. 2, line 3) by carrying out the reactions in the prereacted and analytically defined reaction mixtures which exhibited linear dependence of the ethylene oxide consumption on time (see Experimental).

* The removal of the last traces of the acid by the reaction with ethylene oxide is accompanied by instantaneous change of a practically neutral reaction mixture to strongly basic. This change is followed by immediate formation of side products resulting from the fast, base-catalysed reaction of ethylene oxide with n-butanol.

The slopes of the straight lines, determined from the linear dependence of the ethylene oxide consumption on time in reactions accelerated by catalysts of steady activity (Fig. 2, line 3), are identical with the slopes read from the linear part of the curves exhibiting induction period (Fig. 2, curves 1 and 2). These facts as well as the dependence of the induction period on temperature support the assumption that the decrease of the reaction rate in the initial phase of the reaction is caused by the slower formation of presumably tri-*n*-butylstibonium and triphenylarsonium quarternary bases (see later), supposed to be the actual catalysts of the reaction; this contrasts with other compounds used as catalysts.

The values of rate constants k_0 , which were determined from the slopes of the linear plots of the ethylene oxide (A) consumption against time, were in all experiments identical, within the experimental error ($\pm 1\%$), with the values of this constant calculated from the linear plots of the decrease of the "free-carboxyl group" concentration ($[E]$) against time according to Eqs. (2) and (3) where $[B]$ denotes the total concentration of the undissolved and dissolved terephthalic acid and $[C]$ and $[D]$ is the concentration of 2-hydroxyethyl terephthalate and bis(2-hydroxyethyl) terephthalate, respectively. For all the catalysts studied, the values of rate constants k_0 increase

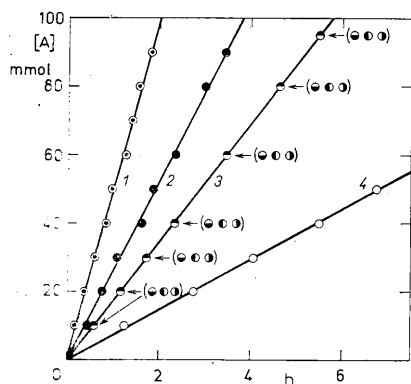


FIG. 1

Time Dependence of Consumption of Ethylene Oxide (A) in the Reaction with Terephthalic Acid in *n*-Butanol in the Presence of Catalysts (F)

$[A] = 1.00 \text{ mol kg}^{-1}$; $[B]_0 = 0.743 \text{ mol} \cdot \text{kg}^{-1}$; $[F] = 0.143 \text{ mol kg}^{-1}$; temperature $80 \pm 0.1^\circ\text{C}$; 1 $(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_3)\text{Br}$, 2 $(\text{C}_6\text{H}_5)_3\text{P}$, 3 $(\text{n-C}_4\text{H}_9)_3\text{Sb}$ \ominus (after steady activity was established), $(\text{n-C}_4\text{H}_9)_3\text{P}$ \ominus , $(\text{C}_6\text{H}_5)_3\text{As}$ \bullet (after steady activity was established), $\text{C}_5\text{H}_5\text{N}$ \bullet , 4 Amberlite IRA-400.

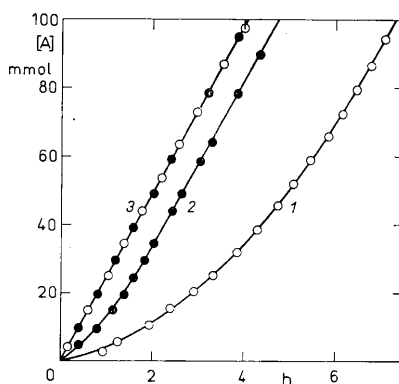


FIG. 2

Time Dependence of Consumption of Ethylene Oxide (A) in the Reaction with Terephthalic Acid in *n*-Butanol Catalysed by $(\text{C}_6\text{H}_5)_3\text{As}$ 1, $(\text{n-C}_4\text{H}_9)_3\text{Sb}$ 2 and Active Forms of These Catalysts 3

$[A] = 0.754 \text{ mol kg}^{-1}$; $[B]_0 = 0.743 \text{ mol} \cdot \text{kg}^{-1}$; $[F] = 0.143 \text{ mol kg}^{-1}$; temperature $90 \pm 0.1^\circ\text{C}$.

linearly with increasing concentrations of ethylene oxide and the catalyst ($[F]$); the reaction is thus first-order in ethylene oxide and the catalyst

$$-[A] = k_0 t \quad (1)$$

$$2[B] + [C] = [E] = [E]_0 - k_0 t \quad (2)$$

$$2[B]_0 - 2[D] - [C] = [E] \quad (3)$$

and the rate of ethylene oxide consumption can be described by Eq. (4), irrespective of the type of the catalyst. The values of second-order rate constants k_2 (Table I) were obtained by dividing k_0 values by the product of ethylene oxide and catalyst concentrations.

$$-d[A]/dt = k_2[A][F]. \quad (4)$$

As follows from Fig. 1 and from the values of constants k_2 , all trisubstituted phosphines, arsines and stibines, but triphenylphosphine, exhibit essentially the same catalytic activity. This activity is identical with that of pyridine; nearly 50% higher activity was found for triphenylphosphine and almost three times higher activity

TABLE I

Second-Order Rate Constants k_2 , Activation Energies (E), Enthalpies (ΔH^\ddagger), Entropies (ΔS^\ddagger) and Preexponential Factors (k_2^0) for the Catalytic Reaction of Terephthalic Acid with Ethylene Oxide in n-Butanol; $[A] = 1.000 \text{ mol kg}^{-1}$, $[B]_0 = 0.743 \text{ mol kg}^{-1}$, $[F] = 0.143 \text{ mol kg}^{-1}$

Catalyst	$k_2 \cdot 10^3$ ^a kg mol ⁻¹ s ⁻¹	E ^b kcal mol ⁻¹	r_E	ΔH^\ddagger kcal mol ⁻¹	k_2^0 kg mol ⁻¹ s ⁻¹	ΔS^\ddagger e.u.
(n-C ₄ H ₉) ₃ P	0.381	18.3 ± 0.8	0.9983	17.4 ± 0.8	1.0 · 10 ⁸	-24.6
(C ₆ H ₅) ₃ As ^c	0.370	17.7 ± 1.2	0.9951	16.8 ± 1.2	3.8 · 10 ⁷	-25.9
(n-C ₄ H ₉) ₃ Sb ^c	0.384	18.6 ± 0.9	0.9976	17.7 ± 0.9	1.3 · 10 ⁸	-23.7
(C ₆ H ₅) ₃ P	0.580	17.6 ± 0.8	0.9981	16.7 ± 0.8	4.9 · 10 ⁷	-25.7
(C ₆ H ₅) ₃ P(CH ₃)Br	1.114	18.3 ± 1.1	0.9948	17.4 ± 1.1	2.1 · 10 ⁸	-22.7
C ₅ H ₅ N	0.390 ^d	18.9 ± 1.1	0.9967	18.0 ± 1.1	1.9 · 10 ⁸	-23.0
Amberlite IRA-400	0.169	19.1 ± 1.1	0.9967	18.2 ± 1.1	1.0 · 10 ⁸	-24.2

^a Measured at 80 ± 0.1°C; ^b determined at temperatures from 70 to 100 ± 0.1°C; ^c after steady activity of the catalyst was established; ^d at the pyridine concentration 0.156 mol kg⁻¹, the value of k_2 equals to 1.43 kg mol⁻¹ h⁻¹; incorrect value of $k_2 = 1.76 \text{ kg mol}^{-1} \text{ h}^{-1}$, reported by Mareš and coworkers¹ for this pyridine concentration on the basis of erroneous solubility value of ethylene oxide in n-butanol at 80°C (0.841 mol kg⁻¹), corresponds after recalculation to a value of 1.48 kg mol⁻¹ h⁻¹.

was observed for triphenylmethylphosphonium bromide. The activity of the anion exchange resin Amberlite IRA-400, used in an equivalent concentration, was 6.5-times lower than that of triphenylmethylphosphonium bromide.

In a series of tertiary phosphines, arsines, and stibines under study, pK_a values are known only for tri-*n*-butylphosphine (pK_a 8.43, determined in nitromethane^{30,31} and recalculated for an aqueous medium^{30,32,33}; pK_a 6.00 in an ethanol-water mixture³⁴) and triphenylphosphine (pK_a 2.73 in nitromethane³⁰⁻³³; pK_a < 2.60 in an ethanol-water mixture³⁴). These values cannot be directly compared and are defined only by the method of the measurement. This circumstance makes it difficult to correlate the activity of the catalysts with their basicity, nevertheless, the known chemical behaviour and pK_a values of some other compounds of this series allow at least qualitatively to estimate the validity of such a correlation. The pK_a values of triethylamine, triethylphosphine and triethylarsine decrease in aqueous ethanolic medium in the given order³⁴ (pK_a 9.71, 6.68, and < 2.6, respectively). As the basicity of trialkylphosphines in the same medium decreases also with lengthening of the alkyl chain, it may be assumed that the same relation holds also for trialkylstibines, and the pK_a of tri-*n*-butylstibine should be well below a value of 2.6. This assumption is not affected by the fact that in nitromethane the basicity in the series of trialkylphosphines was observed to decrease already from tributylphosphine³⁴. On the basis of conductivity titrations of triarylamines, -phosphines, and -arsines with boron trichloride in liquid hydrogen chloride as ionizing solvent Peach and Waddington³⁵ have concluded that the basicity of these compounds increases in the order $(C_6H_5)_3N < (C_6H_5)_3P < (C_6H_5)_3As$.

A similar conclusion was also drawn by Issleib and Bruchlos³⁴ from the lower stability of triarylammonium salts³⁶ in aqueous medium compared to triarylphosphonium salts. Triarylamines and triarylphosphines are generally so weak bases that their dissociation constants could be determined in aqueous alcohol only with high inaccuracy³⁴. It can be therefore assumed that triphenylarsine would be the weakest base in the series of the catalysts studied. These conclusions are consistent with a long induction period observed by us in the reactions catalysed with triphenylarsine and a somewhat shorter induction period in the reactions conducted in the presence of tri-*n*-butylstibine. If the identical catalytic activities of tri-*n*-butylphosphine and triphenylarsine, differing in basicity by 4–6 pK_a units, are taken into account, then it can be concluded that the rate of the reaction of terephthalic acid with ethylene oxide is in the rate-determining step essentially independent on the nucleophilicity of the tertiary phosphines, arsines and stibines used as catalysts. This also means that these compounds do not participate as such in the rate-determining step. A somewhat higher activity of triphenylphosphine, whose basicity is substantially lower than that of tri-*n*-butylphosphine, indicates that also other factors affect the activity of the catalyst. Relatively low activity of Amberlite IRA-400 is obviously influenced by transport phenomena depending on the cross-linking and swelling properties of the

ion exchange resin in a given reaction medium^{37,38}. Independence of the reaction rate on the basicity of the catalyst was found also in the reaction catalysed with tertiary amines¹⁻³. Similarity of the kinetic dependences derived from our measurements and the kinetics of the reactions effected in the presence of tertiary amines¹ supports the assumption that the conversion of terephthalic acid catalysed with tertiary phosphines, arsines and stibines proceeds by the same reaction mechanism¹. In terms of this mechanism, the initial step would be the formation of the quarternary base $R_3M^{(+)}CH_2CH_2O^{(-)}$ ($M = P, As, Sb$) that by a fast reaction with a terephthalic acid molecule yields terephthalate ion. The rate-determining step would be the interaction of this anion with ethylene oxide molecule to give the anion of 2-hydroxyethyl ester, $HO_2CC_6H_4CO_2CH_2CH_2O^{-}$, which in the next fast step is protonated to form 2-hydroxyethyl terephthalate; the bis(2-hydroxyethyl) ester is produced in a similar way. As we found with triphenylarsine and tri-*n*-butylstibine, the rate of formation of quarternary phosphonium, arsonium, and stibonium bases can be affected by the nucleophilicity of the catalyst. These bases seem to be also responsible for the high basicity of the reaction mixture (pH 10–11) after last traces of the acid had reacted in the reactions catalysed with triphenylarsine or tri-*n*-butylstibine; the quarternary base of a similar type, *i.e.* $R_3N^{(+)}CH_2CH_2O^{(-)}$, was evidenced by Hetflejš and co-workers² in tertiary amine-catalysed reactions of acetic acid with ethylene oxide in *n*-butanol. Formation of quarternary salts derived from the bases of this type was observed in the reactions of ethylene oxide with tertiary amines and strong organic and inorganic acids^{39,40}. Quarternary salts of low thermal stability isolated by Ueshima and Munakata²³ from the products of the reaction of carboxylic acids with ethylene oxide catalysed with thioethers were assigned the structure of dialkyl- β -hydroxyethylsulphoniumcarboxylates, $R_2S^{(+)}(CH_2CH_2O)^{(-)}O_2CR'$. A somewhat different initial reaction step has to be expected in the reaction of terephthalic acid with ethylene oxide catalysed with triphenylmethylphosphonium bromide. Amberlite IRA-400, used in the OH form, is a strong quarternary ammonium base that is rapidly neutralized with terephthalic acid to give the corresponding quarternary salt. Nevertheless, essentially identical values of the activation energy (c. 18.3 kcal mol⁻¹) and entropy (c. -24.2 e.u.) (Table I) for the reaction of terephthalic acid with ethylene oxide, irrespective of type of the catalysts used in this work, seem to indicate an identical mechanism in the rate-determining step. The high negative value of ΔS^\ddagger is consistent with the high degree of formation of a new bond, *i.e.* transition states resemble σ complexes⁴¹. The activation energy determined by us does not differ too much from the activation energy (19.1 kcal mol⁻¹) reported by Mareš and coworkers¹ for the reaction catalysed with pyridine.

REFERENCES

1. Mareš F., Hetflejš J., Bažant V.: This Journal 34, 3086 (1969).
2. Hetflejš J., Mareš F., Bažant V.: This Journal 34, 3098 (1969).

3. Málek J., Šilhavý P.: This Journal *41*, 84 (1976).
4. Mareš F., Šilhavý P., Málek J., Bažant V.: Brit. 1 074 274 (1967); Chem. Abstr. *68*, 59 320 (1968).
5. Málek J., Šilhavý P., Bažant V.: Czech. 136 050 (1970); Chem. Abstr. *75*, 21 439 (1971).
6. Málek J., Šilhavý P., Bažant V.: Czech. 136 196 (1970); Chem. Abstr. *75*, 21 418 (1971).
7. Ringwald E. L.: U.S. 2 932 662 (1960); Chem. Abstr. *64*, 16 431 (1960).
8. Bataafse Petroleum Maatschappij N. V.: Brit. 851 029 (1960); Chem. Abstr. *55*, 11 369 (1961).
9. Herzberg S., Sodenkamp T. J.: Neth. 96 444 (1960); Chem. Abstr. *57*, 3366 (1962).
10. Vaitekunas A. A.: U.S. 3 037 049 (1962); Chem. Abstr. *57*, 12 390 (1962).
11. Olin Mathieson Chemical Corp.: Brit. 915 891 (1963); Chem. Abstr. *58*, 13 854 (1963).
12. Celanese Coatings Co.: S. African 68 01 333 (1968); Chem. Abstr. *70*, 77 347 (1969).
13. Badische Anilin & Soda-Fabrik A.-G.: Ger. 1 248 660 (1967); Chem. Abstr. *67*, 108 456 (1967).
14. Enoki Y., Takahashi S., Nagai A.: Japan 69 04 969 (1969); Chem. Abstr. *71*, 112 648 (1969).
15. Toyo Rayon Co.: Japan 65 26 341 (1965); Chem. Abstr. *64*, 8097 (1966).
16. Sumitomo Chemical Co.: Japan 68 19 537 (1968); Chem. Abstr. *70*, 114 846 (1970).
17. Rhone-Poulenc S. A.: Fr. 1 408 874 (1965); Chem. Abstr. *63*, 16 266 (1965).
18. Fujita Y.: Japan 69 09 365 (1969); Chem. Abstr. *71*, 30 253 (1969).
19. Munekata H., Ueshima A., Ugai T.: Japan 70 17 429 (1970); Chem. Abstr. *73*, 77 812 (1970).
20. Málek J., Šilhavý P., Čefelín P., Bažant V.: Czech. 133 579 (1969); Chem. Abstr. *73*, 109 518 (1970).
21. Stevenson R. W.: J. Polym. Sci., Vol. A—1, *7*, 395 (1969).
22. Schnegg R., Pelousek H., Dippelhofer R., Nordt H., Dortmann H. A.: U.S. 3 412 066 (1968); Chem. Abstr. *70*, 29 548 (1969).
23. Ueshima A., Munakata H.: Kogyo Kagaku Zasshi *71*, 990 (1968).
24. Hodgman Ch. J.: *Handbook of Chemistry and Physics*, 47. Edition, p. C-473. Chemical Rubber Publishing Co., Cleveland 1965—1967.
25. Ref. 24, p. C-131.
26. Zacharkin L. I., Ochlobystin O. Ju., Strunin B. N.: Dokl. Akad. Nauk SSSR, *144*, 1299 (1962).
27. Krumpolc M., Málek J.: Makromol. Chem. *171*, 69 (1973).
28. Hradil J., Málek J., Bažant V.: Chem. Prům. *20*, 117 (1970).
29. Krumpolc M., Málek J.: Makromol. Chem. *168*, 119 (1973).
30. Streuli C. A.: Anal. Chem. *32*, 985 (1960).
31. Henderson W. A., Streuli C. A.: J. Amer. Chem. Soc. *82*, 5791 (1960).
32. Hall H. K.: J. Phys. Chem. *60*, 63 (1956).
33. Streuli C. A.: Anal. Chem. *31*, 1652 (1959).
34. Issleib K., Bruchlos H.: Z. Anorg. Allg. Chem. *316*, 1 (1962).
35. Peach M. E., Waddington T. C.: J. Chem. Soc. *1961*, 1238.
36. Becker F. C.: Chem. Ber. *86*, 1150 (1953).
37. Rodriguez O., Setínek K.: J. Catal. *39*, 449 (1975).
38. Setínek K., Rodriguez O.: *Materiali Vsesoiuznoi Konferentsii po Mekhanisme Geterogenno-Katalyticheskikh Reaktsii*, Moscow 1974.
39. Eastham A. M., Darwent B., deB., Beaubien P. A.: Can. J. Chem. *29*, 575 (1951).
40. Eastham A. M., Darwent B. deB.: Can. J. Chem. *29*, 585 (1951).
41. Taylor R.: *Reactions of Aromatic Compounds* (C. M. Banford, C. F. H. Tipper, Eds), p. 174. Elsevier, Amsterdam 1972.

Translated by J. Hetflejš.