OXIDATION OF *p*-XYLENE TO TEREPHTHALIC ACID
IN BENZOIC ACID AND METHYL ESTER OF *p*-TOLUIC ACID

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The oxidation of *p*-xylene to terephthalic acid has been studied at 130 to 190°C, using benzoic acid and methyl ester of *p*-toluic acid as the solvent. It was found that the solvent affects strongly the activity of the cobalt catalyst which effect is dependent on the presence of bromide and pyridine ligands. In the methyl ester of *p*-toluic acid as the solvent, cobalt–bromide catalysts induce also hydrolysis of the methyl ester which proceeds parallelly to the oxidation of *p*-xylene. The activating effect of bromide and pyridine ligands results from their effect on the rate of the reaction of peroxy radicals with the catalyst in the propagation step and from their effect on the rate of consecutive oxidation of *p*-toluic acid to terephthalic acid.

Oxidation of *p*-xylene in the liquid phase forms the basis of many commercial processes for production of terephthalic acid[1]. As the products of the oxidation are solids with high melting points, the reaction is performed in a solvent, most frequently in acetic acid or in the methyl ester of *p*-toluic acid (DMT process). The solvent prevents not only solid products to precipitate but influences also the activity of the catalyst[2,3], changes the rate of the oxidation, the yields of terephthalic acid and sometimes leads to the changes in the reaction mechanism[4-6]. Such a behaviour is observed with cobalt and manganese catalysts as well as with complex cobalt–bromide catalysts. The effect of the coordinated nitrogen-containing ligand on the activity of the latter catalysts has been studied in detail in case of the oxidation of mesitylene[7], methylnaphthalene[8], and alkylpyridines[9,10], using acetic acid as the solvent.

In this work we report on the effect of bromide and pyridine ligands on the activity of cobalt catalyst in the oxidation of *p*-xylene to terephthalic acid, using benzoic acid and the methyl ester of *p*-toluic acid as solvents.

EXPERIMENTAL

Materials. *p*-Xylene (99·6%) and the methyl ester of *p*-toluic acid (98·4%) were purified by distillation. Metal complex catalysts were prepared by reported procedures[7]. The other chemicals and catalysts were of analytical grade purity and were used without further purification.

Procedure. Oxidations were carried out in a 250 cm³-titanium reactor equipped with a magnetic stirrer[4]. The gases leaving the reactor were cooled and analyzed for the content of oxygen and carbon dioxide with the use of Permolyt and Infralyt arrangement (Junkalor Dessau, G.D.R.).

Analysis. After completion of the oxidation, the products formed were analysed as corresponding methyl esters by gas chromatography on Hewlett–Packard 5 830 A instrument equipped with flame ionization detector. The internal standard was amyl benzoate. Glass columns, 50 cm long, packed with 15% neopentyl succinate on Chromosorb W (80—100 mesh) impregnated with 1% H_3PO_4, were programmed from 70 to 225°C at 15°C min^{-1}. In some samples, terephthalic acid was determined by weight analysis, as the portion insoluble in acetone.

RESULTS AND DISCUSSION

Oxidation of *p*-xylene to terephthalic acid was studied in benzoic acid and in the methyl ester of *p*-toluic acid as solvents. As the catalysts we used cobalt salts with bromine or the salts activated by pyridine (Py). As it is seen from Fig. 1 the effect of the solvents studied on the formation of terephthalic acid is very different and depends on the temperature of the reaction. In contradistinction to benzoic acid, where the activity of both catalysts $CoBr_2$ and $CoBr_2Py_2$ (estimated from the yields of terephthalic acid) is essentially the same in temperature region 150—190°C (at other *p*-xylene/benzoic acid ratios there are, however, differences[2]), in the methyl ester of *p*-toluic acid the activity gradually increases, that of $CoBr_2Py_2$ complex being always higher. However, in this solvent considerable destruction (de-esterification) of the ester is taking place at higher temperatures, which is indicated by the very high yields of terephthalic acid. The activity of the cobalt catalyst is markedly influenced by the type of the ligand used (Table I). Under the reaction conditions used, the positive effect of pyridine on the activity of $CoBr_2$ catalyst in the methyl ester of *p*-toluic acid as the solvent manifests itself most pronouncedly at the Py/Co molar ratios = 1—2 : 1 (Fig. 2). The greater pyridine concentrations show negative effect on the catalyst activity in both solvents. Similarly as pyridine, also bromide ion effect on the catalytic activity is dependent on bromide ion concentration and the solvent used (Fig. 3). In the methyl ester of *p*-toluic acid, HBr and NaBr exert different effects. While in the range of Br/Co ratios = 1—4 : 1 essentially identical yields of terephthalic acid are obtained with HBr, the catalytic effect of NaBr at these ratios is more pronounced. When compared to $CoBr_2$ or $CoBr_2Py_2$ catalysts (Fig. 1), the latter catalyst produces at the same concentration and reaction temperature terephthalic acid in very high yields. This can be accounted for by oxidation of the ester group by the highly efficient catalyst formed, as at this temperature, the more pronounced effect of sodium acetate on deesterification of the methyl ester of *p*-toluic acid has not been observed.

In the case of the oxidation of *p*-xylene in the methyl ester of *p*-toluic acid, the methyl groups of both compounds are oxidized simultaneously. As seen in Figs 4—6, the rates of formation of the corresponding oxidation products are substantially higher in the presence of bromides or their combination with pyridine. The effect of these activators is also responsible for the change in the distribution of oxidation products.

TABLE I

Effect of catalyst on the oxidation of a mixture of *p*-xylene (35 g) and the methyl ester of *p*-toluic acid (80 g). Conditions: 150°C, 2·0 MPa, air flow rate 60 dm^3 h^{-1}, catalyst concn. $1·89 . 10^{-2}$ mol. . kg^{-1}, reaction time 4 h

Catalyst[a]	Yield of products, mole %		
	PTA[b]	MMET[b]	TA
$CoBr_2.6 H_2O$	38·2	70·9	52·9
$CoBr_2 Py_2$	22·4	71·4	69·9
$CoCl_2 Py_2$	28·7	69·5	13·6
$CoBr_3[P(C_6H_5)_3] [N(CH_3)_4]$	21·2	66·9	47·8

[a] The oxidation did not proceed even at 190°C in the presence of $Cs_2 CoBr_4$, $[(n-C_4H_9)_4 P]CoBr_4$, and $[P(C_6H_5)_3]CoBr_2$. [b] PTA *p*-toluic acid, MMET the monomethyl ester of terephthalic acid.
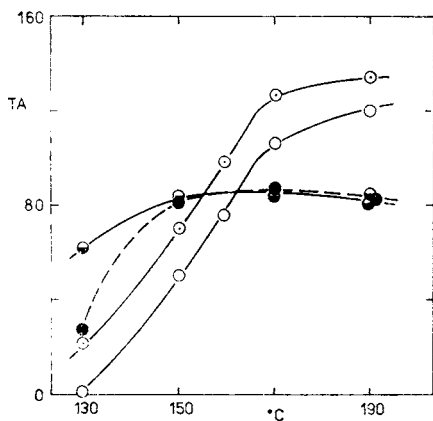

FIG. 1

Effect of temperature and catalyst on the yield of terephthalic acid (TA, mole %) using benzoic acid (● $CoBr_2.6 H_2O$, ◓ $CoBr_2 Py_2$) and the methyl ester of *p*-toluic acid (○ $CoBr_2.6 H_2O$, ⊙ $CoBr_2 Py_2$) as solvents. Conditions: pressure 2·0 MPa, air flow rate 520 dm^3 h^{-1} kg^{-1}; [*p*-xylene] = 2·54 mol . . kg^{-1}, [catalyst] = $1·89 10^{-2}$ mol kg^{-1}
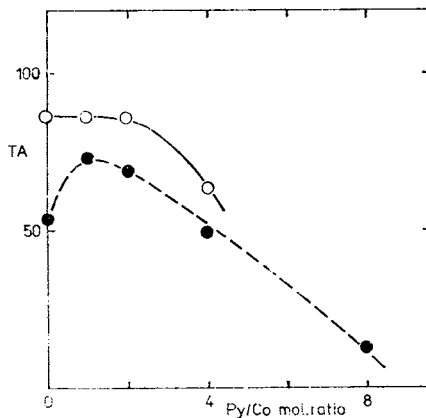
FIG. 2

Effect of the pyridine to cobalt molar ratio (Py/Co) on yield of terephthalic acid (TA, mole %) in the oxidation of *p*-xylene in benzoic acid (○) and in the methyl ester of *p*-toluic acid (●). Conditions: 150°C, 2·0 MPa; air flow rate 520 dm^3 h^{-1} kg^{-1}; [*p*-xylene] = 2·54 mol kg^{-1}, [$CoBr_2.6 H_2O$] = $1·89 . 10^{-2}$ mol kg^{-1}

In benzoic acid as the solvent, the rates of the oxidation of p-xylene in the presence of $CoBr_2Py_2$ catalyst are higher and oxidation products are formed in very high yields (Fig. 7).

The results discussed thus show that the oxidation of p-xylene to terephthalic acid is in addition to the reaction conditions also markedly influenced by the solvent used and by ligands of the homogeneous catalyst. As found earlier[2], under the above reaction conditions, the oxidation proceeds via free radical mechanism. This is indicated by the sequence of the reactivity of toluene, ethylbenzene, and cumene, equaling to 1 : 2·3 : 2·7 for the $CoBr_2Py_2$ catalyst in benzoic acid at a temperature of 150°C. On the basis of the kinetic study of the effect of solvent and of the type of homogeneous catalyst on the oxidation of p-xylene[5,11,12] it was concluded that at the temperature above 100°C, the rate of the reaction is second order with respect to p-xylene in different solvents, but the reaction order with respect to the catalyst varies in dependence on the solvent used. In acetic and benzoic acids, the reaction order with respect to the $CoBr_2Py_2$ catalyst equals to two. It is assumed that the metal complex participates in the initiation and propagation steps according to the following scheme
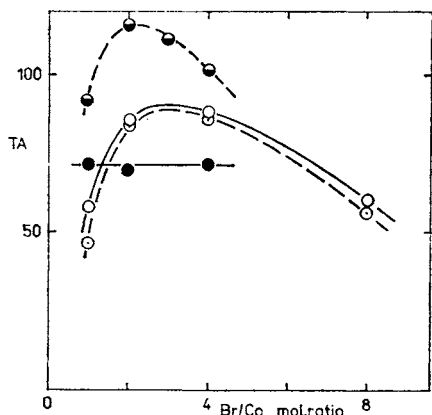
$$RCH_2OOH + Co(II/III) BrPy \rightarrow radicals \qquad (A)$$

FIG. 3

Effect of the Br/Co molar ratio on yield of terephthalic acid (TA, mole %) using benzoic acid (● HBr, ◕ NaBr) and the methyl ester of p-toluic acid (○ HBr, ⊙ NaBr). [Co(OAc)$_2$ . .4 H$_2$O] = 1·89 10^{-2} mol kg^{-1}; HBr used as 47% aqueous solution
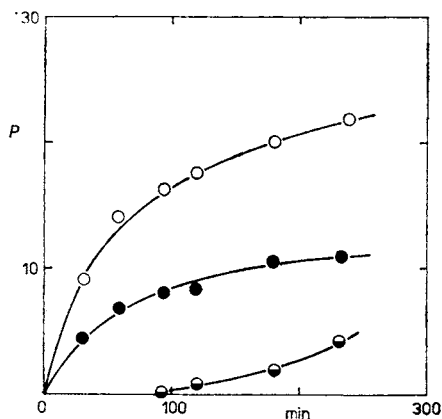
FIG. 4

Product distribution (P, mole %) in the oxidation of p-xylene in the methyl ester of p-toluic acid catalysed by Co(OAc)$_2$. .4 H$_2$O (concn. 1·89 10^{-2} mol kg^{-1}); for other conditions see Fig. 2; ○ p-toluic acid, ● monomethyl terephthalate, ◕ terephthalic acid

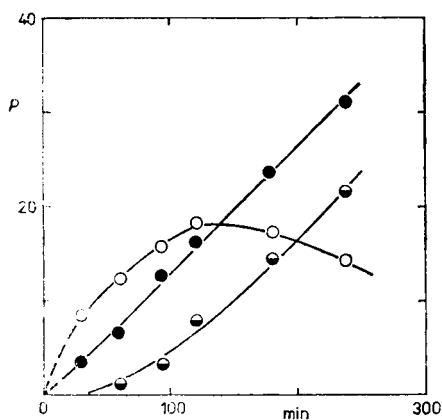$$RCH_3 + Co(III)BrPy \rightarrow RCH_2^{\cdot} + Co(II)PyBrH \tag{B}$$

$$RCH_2^{\cdot} + O_2 \rightarrow RCH_2OO^{\cdot} \tag{C}$$

$$RCH_2OO^{\cdot} + Co(II)BrPy \rightleftharpoons [RCH_2OO^{\cdot}\cdots Co(II)BrPy] \tag{D}$$

FIG. 5

Product distribution (*P*, mole %) in *p*-xylene oxidation catalysed by $CoBr_2.6\,H_2O$ (concn. $1\cdot89\,.\,10^{-2}$ mol kg^{-1}). For conditions and designation see Fig. 4
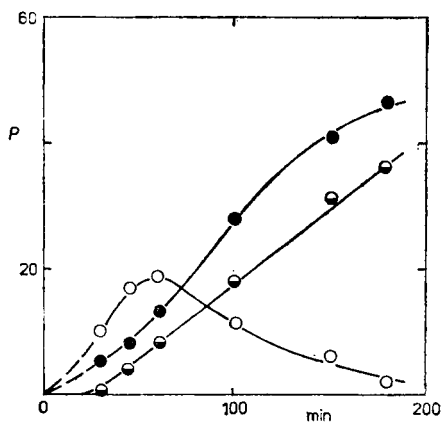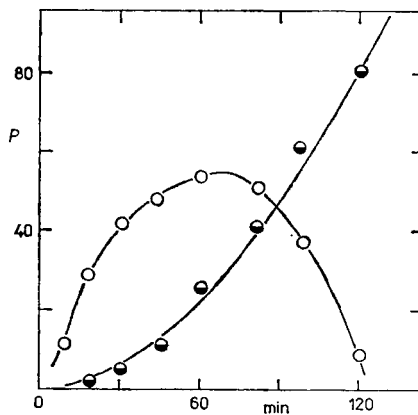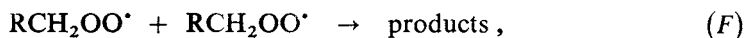
FIG. 6
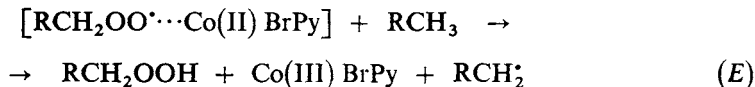
Distribution of reaction products (*P*, mole %) with the use of the catalyst $[CoBr_2Py_2] = 1\cdot89\,.\,10^{-2}$ mol kg^{-1}. The other conditions and designation are the same as in Fig. 4

FIG. 7

Distribution of products (*P*, mole %) of *p*-xylene oxidation in benzoic acid in the presence of the $CoBr_2Py_2$ catalyst (concn. $1\cdot89\,.\,10^{-2}$ mol kg^{-1}). Conditions: 150°C, 2·0 MPa; air flow rate 520 dm^3 h^{-1} kg^{-1}; [*p*-xylene] = 2·54 mol kg^{-1}; ○ *p*-toluic acid; ◓ terephthalic acid

$$\left[\text{RCH}_2\text{OO}^\cdot \cdots \text{Co(II) BrPy}\right] + \text{RCH}_3 \rightarrow$$

$$\rightarrow \text{RCH}_2\text{OOH} + \text{Co(III) BrPy} + \text{RCH}_2^\cdot \qquad (E)$$

$$\text{RCH}_2\text{OO}^\cdot + \text{RCH}_2\text{OO}^\cdot \rightarrow \text{products}, \qquad (F)$$

where RCH_3 is p-xylene and Co(II/III) BrPy is the catalyst.

In contradistinction to p-xylene oxidation in aqueous systems[5,11], where the rate determining step is the propagation reaction

$$\text{RCH}_2\text{OO}^\cdot + \text{RCH}_3 \rightarrow \text{RCH}_2\text{OOH} + \text{RCH}_2^\cdot \qquad (G)$$
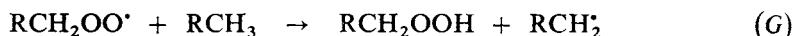
and the catalyst is involved only in the initiation step, in acetic acid, benzoic acid or esters of aromatic acids, this step is not important and is substituted[13] by the faster reaction steps (D) and (E). Therefore, it seems very likely that the effect of bromide and especially pyridine ligands on the activity of the cobalt catalyst in such systems is the result of the effect of these ligands on the rate of the reaction of the cobalt complex with peroxy radicals (reactions (D) and (E)). Apart from the effect of bromide and pyridine ligands on the reactivity of the transition metal complex with peroxy radicals, also the nature of solvent and especially its ability of coordination to the catalyst will play a significant role, too. If the solvent effect is such that it prevents coordination of peroxy radicals to the metal complex, then the propagation reactions (E) and (D) are replaced by the slower step (G) which becomes rate determining. This is confirmed by the results of kinetic study of the oxidation of p-xylene catalysed by the CoBr_2Py_2 complex in the solvents of varying coordination ability[11].

However, the bromide ligands undergo easily oxidation with Co(III) ions[13-16] in the course of the oxidation process, and the bromide radicals function as the initiators of the oxidation. The initiation effect of bromide radicals is not, however, so important in the case of hydrogen atom abstraction from the methyl group of p-xylene, since this role is also played here by the radical intermediates derived from the hydrocarbon. On the other hand, the initiation effect of bromide radicals is significant in the subsequent oxidation of p-toluic acid or of its methyl ester, since -except RCOO$^\cdot$ and RCOOO$^\cdot$ radicals — the other radical intermediates are little effective[5] in the initiation reaction (H).

$$\text{CH}_3\text{C}_6\text{H}_5\text{COOH} + \text{X}^\cdot \rightarrow {}^\cdot\text{CH}_2\text{C}_6\text{H}_5\text{COOH} + \text{HX} \qquad (H)$$
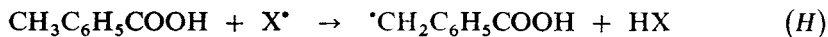
The results of the p-xylene oxidation summarized in Figs 4—6 confirm this assumption. They show that the ratio of the rate of formation of terephthalic acid to that of p-toluic acid, $i.e.$, of the subsequent oxidation of p-toluic acid, is substantially greater with cobalt–bromide catalysts than with cobalt(II) acetate.

Besides the influence of pyridine on the catalytic properties of the metal complex in the processes of initiation of bromide radicals[15] and propagation, pyridine may affect also the oxidation by the direct reaction with molecular bromine which is always formed by the reaction of bromide ions with Co(III) ions[17]. Bonding of molecular bromine into charge-transfer complex PyBr$_2$ prevents the loss of bromine by stripping with released gas from the reaction system as well as its transformation into the catalytically inactive forms by side reactions leading to bromination of aromatic compounds. The formation of the PyBr$_2$ adduct thus ensures the regeneration of bromide ions during oxidation as well as their subsequent reaction with Co(III) ions[17]. By this, the formation of bromide ions is supported, having rate-accelerating effect on the initiation step of the reaction.

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