

## KINETIC INVESTIGATION OF THE OXIDATION OF BROMIDE IONS BY COBALT(III). REACTION IN THE PRESENCE OF *p*-TOLUIC ACID

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The rate of Co(III) reduction under inert atmosphere in the presence of *p*-toluic acid (PTA) and hydrobromide obeys the rate law  $d[\text{Co(III)}]/dt = k[\text{Co(III)}]^2 [\text{Co(II)}]^{-1} [\text{PTA}] [\text{HBr}]$ . The proposed reaction mechanism involves the reduction of Co(III) by  $\text{Br}^-$  ions and formation of a cation-radical from *p*-toluic acid. *p*-Xylene is attacked by bromine species and not directly by Co(III). The rate constants of Co(III) and  $\text{Br}^-$  consumption as well as apparent activation energies were estimated.

The oxidation of alkyl aromatic hydrocarbons to corresponding aromatic carboxylic acids catalyzed by transition metal salts is markedly enhanced in the presence of bromide ions. The role of these activators has been extensively studied in acetic acid solvent under aerobic and anaerobic conditions<sup>1-3</sup>. In aqueous systems, the effect of bromide ions is observed only in the presence of PTA, pyridine or some lipophilic quaternary onium compounds<sup>4,5</sup>. In such systems the effect of PTA has been studied in the presence and absence of oxygen<sup>6,7</sup>.

In the present paper we show the results obtained by kinetic study of the reaction of Co(III) simultaneously with bromide ions and PTA. This reaction was studied in two solvents, in water and *p*-xylene containing a soluble amount of water.

### EXPERIMENTAL

Apparatus, rate measurement, analysis and reagents were the same as described earlier<sup>3</sup>. Co(III) acetate was used in the form of a concentrated aqueous solution and always contained a certain amount of Co(II). *p*-Toluic acid was prepared by hydrolysis of *p*-methyl toluate (99.1% purity) and was twice crystallized from *p*-xylene.

### RESULTS

In contrast to acetic acid solvent<sup>2</sup>, the reduction of Co(III) alone proceeds at temperature 80°C in an inert atmosphere very slowly in aqueous as well as *p*-xylene solution. Table I reveals that in these systems the influence of HBr and pyridine

is also low. The initial reaction rates of Co(III) reduction and Br<sup>-</sup> oxidation increase in the presence of PTA.

The effect of reactants concentration on the initial reaction rates, estimated from conversion curves of Co(III) and Br<sup>-</sup> ions, was studied in different concentration ranges. In Tables II and III are summarized the values of apparent orders with respect to each component.

From the data given in these tables it was estimated that at 80°C the values of the rate constants of Co(III) reduction are  $(6.8 \pm 0.7) \cdot 10^{-3} \text{ s}^{-1}$  and  $(6.34 \pm 0.16) \text{ dm}^3 \cdot \text{mol}^{-1} \text{ s}^{-1}$  in aqueous system and *p*-xylene solution, respectively. For the same experimental conditions the rate constants of bromide oxidation are  $(5.9 \pm 0.8) \cdot 10^{-3} \text{ s}^{-1}$  in aqueous system and  $(5.69 \pm 0.12) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  in *p*-xylene solution. The apparent activation energies found in the temperature region from 60 to 90°C are  $(72.6 \pm 4.9) \text{ kJ mol}^{-1}$  and  $(69.2 \pm 4.1) \text{ kJ mol}^{-1}$  for aqueous and *p*-xylene system, respectively.

## DISCUSSION

A study of Co(III) reduction in the presence of bromide ions and PTA shows that the overall stoichiometry for the initial stage of the reaction, i.e. the average amount of reduced Co(III) and oxidized Br<sup>-</sup> ions,  $\Delta\text{Co(III)}/\Delta\text{Br}^-$ , change in aqueous system from 1.2 to 1.86 and in *p*-xylene system from 2.0 to 2.3 (Tables II and III). At temperature 60°C this ratio is 1.06 for both systems. The above mentioned results suggest that at higher temperature also PTA and *p*-xylene participate in the oxidation process.

TABLE I

Initial rates  $r_0$  ( $\text{mol dm}^{-3} \text{ s}^{-1}$ ) of Co(III) reduction at 80°C in water and *p*-xylene ( $[\text{Co(III)}]_0 = 2.78 \cdot 10^{-2} \text{ mol dm}^{-3}$ ,  $[\text{Co(II)}]_0 = 1.67 \cdot 10^{-2} \text{ mol dm}^{-3}$ )

System	Mol. ratio	$r_0 \cdot 10^4$ in	
		water	<i>p</i> -xylene <sup>a</sup>
Co(III)-HBr	1 : 2	0.08	0.09
Co(III)-HBr-Py	1 : 2 : 4	0.06	0.06
Co(III)-PTA	1 : 3	1.28	0.21
Co(III)-PTA-HBr	1 : 3 : 2	3.64	1.63
		(2.96) <sup>b</sup>	(0.92) <sup>b</sup>
Co(III)-PTA-Py	1 : 3 : 4	4.73	0.07
Co(III)-PTA-HBr-Py	1 : 3 : 2 : 4	1.33	1.03
		(1.01) <sup>b</sup>	(0.69) <sup>b</sup>

<sup>a</sup> 0.9 wt. % H<sub>2</sub>O; <sup>b</sup> initial rate of Br<sup>-</sup> oxidation.

Analysis of the reaction products under comparable conditions confirmed this assumptions<sup>8</sup>. On the basis of the above mentioned results the following reaction scheme is proposed:

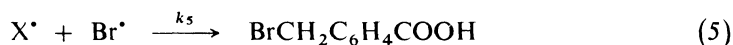
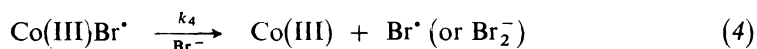
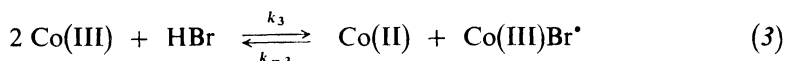
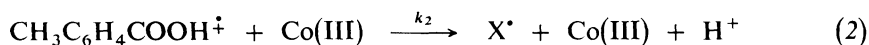
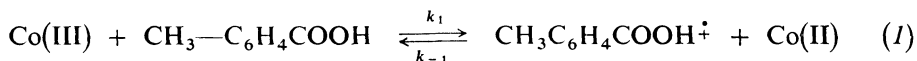


TABLE II

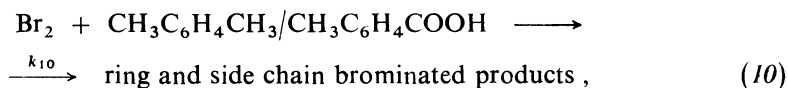
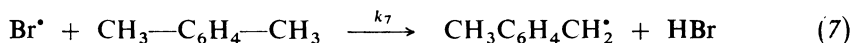
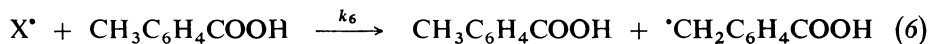
Apparent reaction orders for the rate of Co(III) ( $n_{\text{Co}}$ ) and Br<sup>-</sup> ( $n_{\text{Br}}$ ) consumption and stoichiometry of the overall reaction  $\Delta\text{Co(III)}/\Delta\text{Br}^-$  in aqueous solution

Reactant	Conc. $10^2$ mol dm <sup>-3</sup>	$n_{\text{Co}}$	$n_{\text{Br}}$	$\Delta\text{Co(III)}/\Delta\text{Br}^-$
Co(III)	1.39—5.56	$1.95 \pm 0.09$	$1.85 \pm 0.11$	1.34—1.75
Co(II)	1.67—8.34	$-0.89 \pm 0.11$	$-0.87 \pm 0.13$	1.34—1.70
HBr	1.39—11.12	$0.79 \pm 0.14$	$0.76 \pm 0.09$	1.34—1.86
PTA	1.39—13.90	$0.93 \pm 0.08$	$0.85 \pm 0.07$	1.29—1.50
Py	10.54—22.24	$-1.89 \pm 0.11$	$-1.61 \pm 0.08$	1.20—1.56

TABLE III

Apparent reaction orders  $n_{\text{Co}}$  and  $n_{\text{Br}}$  and stoichiometry in *p*-xylene solution

Reactant	Conc. $10^2$ mol dm <sup>-3</sup>	$n_{\text{Co}}$	$n_{\text{Br}}$	$\Delta\text{Co(III)}/\Delta\text{Br}^-$
Co(III)	1.39—8.34	$2.22 \pm 0.12$	$1.83 \pm 0.08$	2.00—2.22
Co(II)	1.67—8.34	$-0.83 \pm 0.11$	$-0.91 \pm 0.09$	2.09—2.21
HBr	1.39—11.12	$0.97 \pm 0.13$	$1.08 \pm 0.10$	2.00—2.30
PTA	1.39—13.90	$0.89 \pm 0.12$	$0.90 \pm 0.14$	2.00—2.25
Py	2.78—12.12	$-0.94 \pm 0.11$	$-0.89 \pm 0.09$	2.12—2.21



where Co(III) are cobalt(III) species with at least one toluate ligand and  $X^*$  is  $\text{CH}_3\text{C}_6\text{H}_4\text{COO}^*$  or  $\cdot\text{CH}_2\text{C}_6\text{H}_4\text{COOH}$ . It is assumed that reactions (1), (2) and (3) proceed in the coordination sphere of Co(III) via intermediate complex formation. However, such complexes are hard to define but they are formed in rapid pre-equilibria. The formation of cation-radicals in this mechanism through reversible reaction (1) is supposed on the basis of kinetic measurements in the absence of bromide ions<sup>7</sup>.

Using the steady-state approximation for the intermediate products and assuming that  $k_{-1} \gg k_2$  and  $k_{-3} \gg k_4$ , the initial rate of Co(III) reduction for the mechanism presented above leads to the expression (11) which is valid at the ratio  $[\text{PTA}]/[\text{Co(III)}] > 1$ .

$$-\left(\frac{d[\text{Co(III)}]}{dt}\right)_0 = K_1 K_3 k_2 k_4 \frac{[\text{Co(III)}]^2}{[\text{Co(II)}]} \{[\text{PTA}] + [\text{HBr}]\} \quad (11)$$

The same rate expression and apparent activation energies estimated in both aqueous and *p*-xylene system suggest that in the presence of bromide ions the preferential reaction is the reduction of Co(III) by bromide ions, whereas *p*-xylene is attacked by intermediately formed bromine species and molecular bromine (reactions (7)–(10)). The role of PTA and HBr is to increase the acidity of the reaction system and thus to favour the equilibrium shift between monomeric and dimeric Co(III) species towards active monomeric one<sup>7</sup>. Moreover, the dissociation of acids influences the exchange of acetate ligands with toluate ones in the Co(III) complex. These effects are probably responsible for higher reaction rates in aqueous than *p*-xylene system (Table I).

All the above mentioned kinetic data were obtained in the presence of pyridine. It was found that at concentration of pyridine above  $0.1 \text{ mol dm}^{-3}$  the redox process is in both systems minus second-order with respect to pyridine concentration. This

retardation effect is explainable, assuming that similarly as in acetic acid<sup>3</sup>, pyridine (Py) (i) decreases the concentration of bromide anions through the formation of less dissociated pyridinium hydrobromide



(ii) decreases the acidity of the system, (iii) forms complexes with Co(III) species which possess lower activity<sup>9</sup>.

In accordance with the presented results and previous observation that in the presence of oxygen pyridine enhances the activity of cobalt bromide catalysts we propose that in both systems different rate-determining steps operate. Namely, in the presence of oxygen, regeneration of Co(II) ions proceeds and peroxy radicals play a significant role in the reaction mechanism<sup>4,6</sup>. Kinetic data and product analysis confirm that under aerobic as well as anaerobic conditions *p*-xylene is attacked by bromine species and not directly by Co(III) complexes.

#### REFERENCES

1. Sheldon R. A., Kochi J. K.: *Metal Catalyzed Oxidation of Organic Compounds*. Academic Press, New York 1981.
2. Hendriks Ch. F., van Beek H. C. A., Heertjes P. M.: *Ind. Eng. Chem., Prod. Res. Dev.* **17**, 256 (1978).
3. Schlosserová J., Hronec M., Veselý V.: *J. Chem. Soc., Faraday Trans. 1*, **1986**, **82**, 1405.
4. Hronec M., Ilavský J.: *Oxidn. Commun.* **3**, 303 (1983).
5. Hronec M., Haruštiak M., Ilavský J.: *React. Kinet. Catal. Lett.* **27**, 231 (1985).
6. Hronec M., Cvengrošová Z., Ilavský J.: *Ind. Eng. Chem., Proc. Des. Dev.* **25**, 787 (1985).
7. Novotný J., Hronec M., Ilavský J.: *Ind. Eng. Chem. Res.* **28**, 1471 (1989).
8. Cvengrošová Z., Hronec M., Kizlink J., Malík L., Ilavský J.: *J. Mol. Catal.* **40**, 235 (1987).
9. Steinmetz G. R., Sumner C. E.: *J. Catal.* **100**, 549 (1986).

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