EFFECT OF TRIETHANOLAMINE ON THE ACTIVITY OF COBALT BROMIDE CATALYSTS AT THE OXIDATION OF MESITYLENE*

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Effect of triethanolamine on the oxidation of mesitylene in acetic acid catalysed by cobalt bromide was studied by measuring the kinetics of the process. Triethanolamine increases initial rates of oxidation and at the initial stage of reaction each bromine atom oxidises in average 33 molecules of mesitylene. Selectivity of the reaction is also increased, and despite the lowered initial concentration of bromine compound from the molar ratio of Co : Br = 1 : 1 to 1 : 0·25, it is possible to prepare trimesic acid in 80 mol% yield by adding triethanolamine. In the absence of the last mentioned compound the yield drops to 34 mol%. Mechanism of activation by triethanolamine is sought in the activation of Co—Br bond in a newly formed complex.

The role of a transition metal and a halogenide in the mechanism of homogeneously catalysed oxidation of alkylaromatic hydrocarbons was studied by a number of authors[1-6]. Toluene — the simplest representative of aromatic hydrocarbons — was the most studied. In this work we have focussed our experiments to study the activity variation of cobalt–bromine catalytic system at the oxidation of trimethylbenzenes to benzenetricarboxylic acids. When solving the problem of activation of homogeneous catalysts of this type, it is important to know the functions of the individual reaction components in the process of oxidation. Our previous studies dealt with this problem; the effect of reaction products and intermediate products of trimethylbenzene oxidation and also the effect of salts of cobalt and bromine on catalytic activity of the cobalt bromide catalyst were studied. From the known results of the effect of bromine compounds on the activity of metal catalysts follows that the coordination of bromine with cobalt salt in acetic acid changes electron distribution of the original complex and localizes catalytic reactivity on bromine atom[6]. Positive effect of bromine compounds on the activity of metal catalysts, however, brings also some difficulties in practice, which are connected with high corrosion of the system at the operation temperatures, which are as high as 200°C. On the other hand the universality of the process by which it should be possible to prepare different aromatic polycarboxylic acids leads to lowering or even to elimination of corrosive components.

In solving the problem of substitution of corrosive bromine component by a non-corrosive but an active one, we have started from the known principles of coordination chemistry, especially from the dependence of reactivity of coordinated ligands on the composition of coordination sphere of the complex. Such a modification

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can finally lead to the change of catalyst activity in the required direction. In order to modify the catalyst structure and the bonds of remaining ligands, specially that of cobalt–bromine, we have tried to coordinate the metal complex by the ligands which have high enough affinity to the central metal atom as to stay more or less permanently bound to the metal atom.

EXPERIMENTAL

Chemicals. Mesitylene (99·3%) was washed with sulphuric acid, dried and distilled. 3,5-Dimethyl benzaldehyde was prepared by oxidation of mesitylene with MnO_2; prior to each experiment the compound was freshly vacuum distilled under nitrogen atmosphere. Triethanolamine was purified by crystallization. Cobalt catalyst was used as tetrahydrate of Co(II) acetate, which was purified by crystallization. Other chemicals were of analytical grade and were not further purified.

Oxidation. The apparatus and the analysis of reaction products were described in our previous paper[7,8]. All experiments were performed at atmospheric pressure.

RESULTS AND DISCUSSION

The presence of triethanolamine increases considerably the activity of cobalt bromide catalysts. The initial rates of oxidation increase by a factor of 3 to 10. This phenomenon makes possible to use lower catalyst concentration, but it is better

TABLE I

Yield of Aromatic Acids from Oxidation of Mesitylene *vs* Concentration of NaBr
100°C; 1 atm; 0·545 mol/l of mesitylene; molar ratio of Co : triethanolamine 1 : 1.

No Exp.	10^2 mol/l			Reaction time h	Yield of acids in mol%		
	Co	NaBr	triethanol-amine		monocarbo-xylic	dicarbo-xylic	trimesic
1	4·04	4·04	4·04	16	0·2	5·8	62·7
2	4·04	2·02	4·04	16		4·1	79·2
3	4·04	1·01	4·04	16	—	4·0	80·2
4	4·04	0·50	4·04	16[a]	7·4	29·1	38·2
5	8·08	0·00	8·08	17[a]	absorption is only 0·3 mol of O_2 per 1 mol of RH		
6	4·04	1·01	0·00	16[a]	2·9	27·1	33·5
7	8·08	0·00	0·00	17[a]	35·1	52·4	3·0
8	4·04	4·04	0·00	16	—	4·7	78·7

[a] Reaction still proceeds.

to leave the original metal concentration constant and lower the concentration of bromine compound. The effect of the lowered initial concentration of sodium bromide on the rate of mesitylene oxidation is shown in Fig. 1. At the same NaBr concentration the reaction rate decreases considerably in the absence of triethanolamine (Fig. 1, curves 3 and 5). The effect of lowered bromide concentration on the yield of aromatic tricarboxylic acid can be understood from the results summarised in Table I. At the molar ratio of Co : Br = 1 : 1 the reaction rates are very high due to the addition of triethanolamine, but the oxidation is less selective. Lesser amount of solid oxidation product, aromatic acids, is formed and thus decreases their yield. Moreover, among these acids are also aromatic acids other than those formed as intermediate products of mesitylene oxidation; they probably were formed by decarboxylation of aromatic aldehydes and aldehyde acids or of peroxy compounds formed from them.

The drop of NaBr concentration makes the oxidation more selective and at the molar ratio of Co : Br = 1 : 0·25 the yield of trimesic acids increases to 80·2 mol.%. This shows that under these conditions the addition of triethanolamine saves 75% of bromine and keeps the catalyst activity at the original level. Further lowering of bromide below this ratio increases reaction time and decreases the yield of tri-
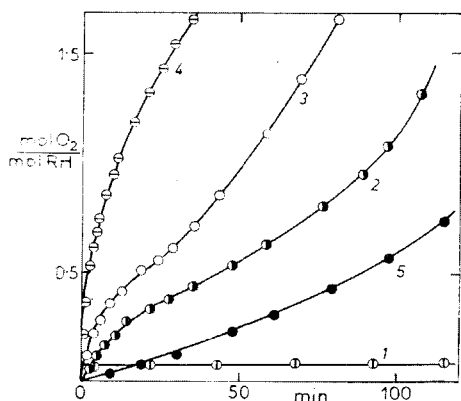

FIG. 1

Influence of NaBr Concentration on Mesitylene Oxidation in Acetic Acid

100°C, 1 atm, 0·545 mol/l of mesitylene, $4·04 . 10^{-2}$ mol/l of Co, $4·04 . 10^{-2}$ mol/l of triethanolamine, NaBr concentration *1* 0, *2* $5 . 10^{-3}$ mol/l, *3* $1·01 . 10^{-2}$ mol/l, *4* $4·04 . 10^{-2}$ mol/l, *5* $1·01 . 10^{-2}$ mol/l without triethanolamine.
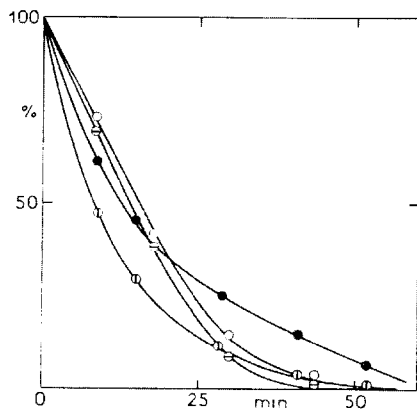
FIG. 2

Consumption of Bromide Anions (⊙, ⊝) and of Hydrocarbon (○, ●) vs Type of Inorganic Bromide

90°C, 0·545 mol/l mesitylene, $4·04 . 10^{-2}$ mol/l Co, $4·04 . 10^{-2}$ mol/l Br⁻; NaBr ●, ○; NH₄Br ○, ⊝.

mesic acid. It is interesting, that in the absence of a bromine compound, Co(II) acetate in equimolar ratio with triethanolamine and in a twice as high concentration gives almost no catalytic activity. If a certain amount of bromide is present, *e.g.* Co : Br = 1 : 0·25, the situation is changed and in the presence of triethanolamine the yield of trimesic acid increases from 33·5 mol.% to 80·2 mol.%

In order to understand the mechanism of triethanolamine action, which is assumed to be in the activation of Co—Br bond of a newly formed complex, the kinetics of mesitylene oxidation catalysed by cobalt bromide catalyst activated by triethanolamine in the molar ratio of Co : triethanolamine = 1 : 1 was studied at first. The activity of cobalt bromide catalyst is mostly determined by bromine compound and its concentration. In case of inorganic bromides, the drop of bromide anion concentration linearly depends on the consumption of an alkylaromatic hydrocarbon[6,8]. The reaction orders with respect to consumption of the efficient catalyst component — bromide anions — as well as of the hydrocarbon are under the same reaction and concentration conditions dependent upon the type of inorganic bromide (Fig. 2).
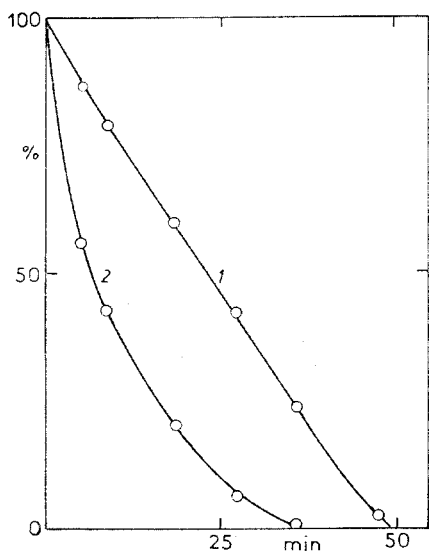

FIG. 3

Consumption of Bromide Anions *1* and of Hydrocarbon *2* in the Presence of Triethanolamine

75°C, 0·545 mol/l mesitylene, 4·04 . 10⁻² mol/l Co, 4·04 . 10⁻² mol/l NaBr, 4·04 . 10⁻² mol/l triethanolamine.
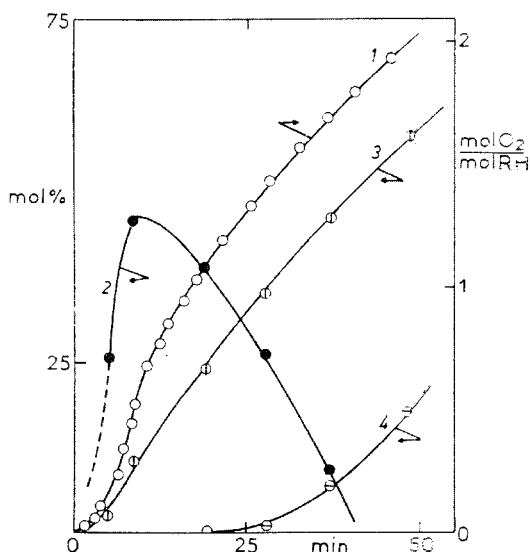
FIG. 4

Yields of 3,5-Dimethylbenzaldehyde *2*, 3,5--Dimethylbenzoic Acid *3* and of 5-Methylisophthalic Acid *4* at Mesitylene Oxidation

75°C, 0·545 mol/l mesitylene, 4·04 . 10⁻² mol/l Co, NaBr and of triethanolamine, resp.; *1* oxygen absorption.

Further change is caused by the addition of triethanolamine. At 75°C mesitylene is oxidised faster but the bromide concentration decreases with time considerably slowly (Fig. 3). At the initial reaction stage each bromine atom oxidises in average 33 molecules of mesitylene. Considerable difference is also in the selectivity of subsequent reactions. In the absence of triethanolamine, at maximum concentration of 3,5-dimethyl benzaldehyde, which is around 26 mol.%, 3,5-dimethylbenzoic acid is present in the concentration higher than 30 mol.%, *i.e.* the subsequent products were also formed. Under the same concentration conditions and in the presence of triethanolamine 3,5-dimethylbenzaldehyde is formed in the maximum concentration of about 45 mol.%, while the concentration of the subsequent product — 3,5-dimethylbenzoic acid — at the same reaction time is only about 10 mol.% (Fig. 4). The increased selectivity is observed also in further subsequent reactions involving 3,5-dimethylbenzoic acid and 5-methylisophthalic acid.

The high catalytic activity and an inadequately low decrease of bromide concentration with respect to the amount of consumed mesitylene enables, in the catalytic system which includes triethanolamine, considerably lower the initial bromine compound concentration and preserve other reaction parameters. As it is seen in Fig. 5,
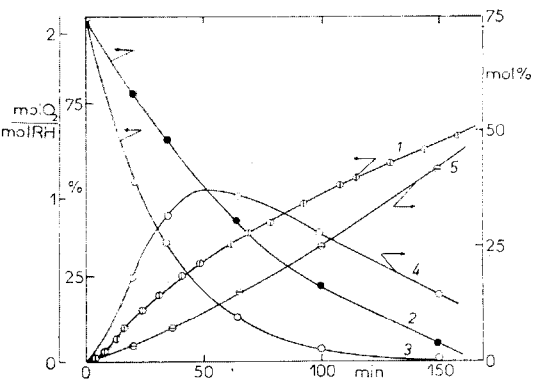

FIG. 5

Changes of Reaction Components with Reaction Time

75°C, $4.04 . 10^{-2}$ mol/l Co, $1.01 . 10^{-2}$ mol/l NaBr, $4.04 . 10^{-2}$ mol/l triethanolamine, 0.545 mol/l mesitylene; *1* oxygen absorption; *2* % of unreacted mesitylene; *3* % of Br⁻; *4* 3,5-dimethylbenzaldehyde; *5* 3,5--dimethylbenzoic acid.
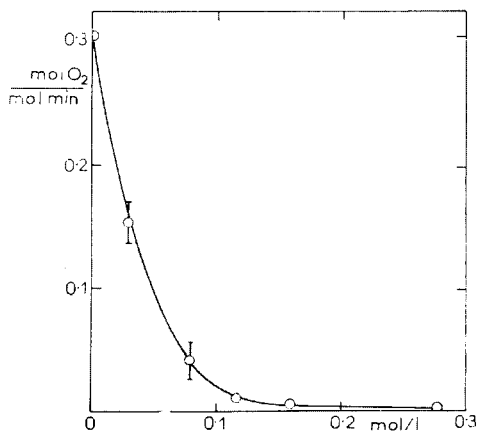
FIG. 6

Rate of Oxidation of 3,5-Dimethylbenzaldehyde in Acetic Acid *vs* Concentration of Mesitylene at 90°C

Initial concentration of 3,5-dimethylbenzaldehyde was 0.537 mol/l.

after four-time decrease of the initial sodium bromide concentration, the consumption of bromide anions is higher than oxidation of the hydrocarbon and also the reaction time is increasing. In spite of this, each bromine atom oxidises in average about 31 molecules of mesitylene. The selectivity of subsequent reactions is impaired by the decrease of NaBr concentration, however, it is still considerably higher than that of the reaction catalysed by cobalt bromide catalyst alone.

It is also worth to note, that with the decrease of the oxygen absorption rate, the concentration of 3,5-dimethylbenzaldehyde begins also to fall down. Oxidation of this aldehyde is, beside other factors, considerably influenced by an instant concentration of mesitylene in the reaction mixture. Fig. 6 shows that mesitylene, in the absence of catalyst, even at low concentrations, considerably decreases the rate of 3,5-dimethylbenzaldehyde oxidation in acetic acid. Similar dependence was observed for the oxidation of binary mixture: benzaldehyde–toluene. Retardation effect of methylbenzenes on the oxidation of corresponding aromatic aldehydes is due to different reactivities of peroxy radicals formed from the corresponding aldehydes and hydrocarbons with respect to hydrogen splitting. Problems of cooxidation of aldehydes with different hydrocarbons were studied in detail by Zaikov[9]. Retardation of 3,5-dimethylbenzaldehyde oxidation by mesitylene has also been observed in the oxidation of mesitylene catalysed by cobalt-bromide catalyst itself[8]. Several-time increase of the rate of oxygen absorption which took place during the reaction was connected with severe fall of 3,5-dimethylbenzaldehyde concentration. Figs 4 and 5 show that in the presence of triethanolamine the situation is quite different. Despite of the high mesitylene concentration at the time of maximum 3,5-dimethylbenzaldehyde concentration, this aldehyde is in a further course of reaction relatively quickly oxidised and simultaneously the fall of the oxygen absorption rate is observed. This suggests that in the mechanism of cooxidation reactions, besides intermediate products, participates also catalyst or at least some of its components.

It has already been mentioned that the shape of oxygen absorption curves of oxidation of trimethylbenzenes is not very often a simple one. Depending upon reaction and concentration conditions the oxidation proceeds *via* several stages, which manifest themselves by different reaction rates seen on oxygen absorption curves. Reaction orders with respect to initial concentration of mesitylene or pseudocumene and cobalt and bromine determined at the initial stage of reaction are identical with those of the prototype oxidation of toluene[6]. In the case that the reaction is autocatalytic and the dependence is followed in the region of maximum rates then different values are obtained[7]. This is caused by the participation of intermediate products in the oxidation reaction as well as on the composition of the homogeneous metal catalyst in different reaction stages. At the stage of maximum rates other intermediates, besides dimethylbenzaldehydes are, also present and they can influence the reaction kinetics and make the kinetic analysis more complicated. The detailed mechanism of catalysed oxidation of alkylbenzenes is under these conditions difficult to define.

Oxidation of alkylaromatic hydrocarbons in acetic acid catalysed by Co(III) acetate at temperatures below 100°C proceeds *via* an electron-transfer mechanism[3,4] (reaction (*1*)).

$$RH + Co^{3+} \rightleftharpoons RH^{\ddot{+}} + Co^{2+}, \qquad (1a)$$

$$RH^{\ddot{+}} \rightarrow R + H^{+}. \qquad (1b)$$
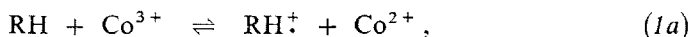
If in such a system a bromine compound is also present, then electron-transfer can proceed through the bond being formed between π-orbitals of an aromatic hydrocarbon and d-orbitals of bromide (reaction (*2*)).

$$RH + Co^{3+}Br \rightarrow Co^{2+}BrH + R^{\cdot}. \qquad (2)$$

Holtz[10] does not rule out the electron-transfer mechanism, but assumes that at temperatures above 100°C the oxidation of alkylaromatic hydrocarbons proceeds *via* a free radical mechanism. Initiation step includes abstraction of hydrogen from an alkylaromatic hydrocarbon by halide radicals or by cobalt complexes containing Br$^{\cdot}$ and Cl$^{\cdot}$ (reaction (*3*)).

$$RH + X^{\cdot} \rightarrow R^{\cdot} + XH. \qquad (3)$$
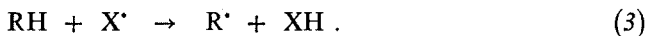
As we have already shown the reactivity of cobalt–bromide complex is influenced by the presence of triethanolamine. The cobalt(II) acetate in acetic acid as such and in the presence of an equimolar amount of triethanolamine acts as a very little efficient catalyst, whereas in the presence of bromides its efficiency increases several
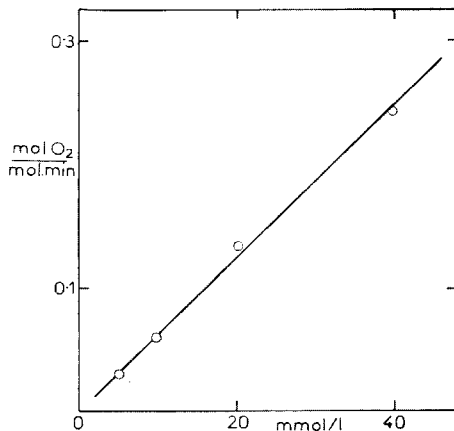

Fig. 7

Rate of Oxidation of Mesitylene *vs* NaBr Concentration 100°C, 0·545 mol/l mesitylene, $4·04 . 10^{-2}$ mol/l Co andtriethanolamine, respectively.

times; there is therefore a high probability that the catalyst reactivity is localised along the bromine bond. As we shall show later, the coordination of suitable ligands can substantially and in a defined way affect the reactivity, therefore we can deduce that bromide ligand will react in a bonded state and not after the cleavage. As it is seen in Fig. 7, the reaction is of first order with respect to NaBr concentration. The same dependence is valid for oxidation of mesitylene in the absence of tri-ethanolamine. This shows that the function of bromide ligands will be in both cases the same and the initiation will take place according to reaction (2). In addition, the activity of the catalytic system cobalt–bromine is, however, in the presence of tri-ethanolamine, increased. The difference between the activities of such catalysts can be evaluated by calculating the number of mesitylene molecules oxidised by one bromine atom, or by the amount of bromide anions which are consumed per one mole of oxygen absorbed and expressed in moles of mesitylene. At 75°C the cobalt bromide catalyst activated by triethanolamine needs for the absorption of this amount of oxygen about 35% of the initial concentration of Br^- (Figs 3, 4); non-activated catalyst[8] at 90°C even more than 95% of Br^-.

REFERENCES

1. Sakota K., Kamiya Y., Ohta N.: Can. J. Chem. *47*, 387 (1969).
2. Heiba E. I., Dessau R. M., Koehl W. J. jr: J. Amer. Chem. Soc. *91*, 6830 (1969).
3. Scott E. J. Y., Chester A. W.: J. Phys. Chem. *76*, 1520 (1972).
4. Kamiya Y., Kashima M.: J. Catal. *25*, 326 (1972).
5. Onopchenko A., Schulz J. G. D., Seekircher R.: J. Org. Chem. *37*, 1414 (1972); *37*, 2950 (1972).
6. Sakota K., Kamiya Y., Ohta N.: Bull. Chem. Soc. Japan *41*, 641 (1968).
7. Hronec M;, Vesely V.: This Journal *38*, 1095 (1973).
8. Hronec M., Vesely V.: Chem. zvesti *27*, 94 (1973).
9. Zajkov G. E., Howard J. A., Ingold K. U.: Can. J. Chem. *47*, 3017 (1969).
10. Holtz H. D.: J. Org. Chem. *37*, 2069 (1972).

Translated by J. Pác.