

## STUDY OF STRUCTURE AND ACTIVITY OF COBALT BROMIDE COMPLEXES IN THE OXIDATION OF ALKYLAROMATIC HYDROCARBONS\*

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Catalytic activity of tetrabromocobalt(II) complexes and halo complexes of the type  $\text{CoX}_2\text{L}_2$  respectively with ligands involving as donor atom, nitrogen, sulphur, phosphorus, arsenic, or antimony was studied in oxidation of alkylaromatic hydrocarbons. The participation of the nitrogen compounds in the complex formation and in the elementary reaction stages was investigated. Highly catalytically active are tetrahedral complexes of the types  $\text{CoBr}_4^{2-}$  and  $(\text{CoBr}_3\text{OAc})^{2-}$ . Triethanolamine-coordinated cobalt bromide and chloride complexes react in acetic acid or its anhydride with oxygen, the triethanolamine ligand being oxidized as well. In addition to their participation in the cobalt complex formation, nitrogen compounds influence the recovery of the active forms of the catalyst; they do not, however, affect the rate of dehalogenation of organic bromides.

Our previous investigations<sup>1-7</sup> revealed that the activity of cobalt bromide catalysts for oxidation of alkylaromatic hydrocarbons in liquid phase can be increased by coordination of ligands involving nitrogen atom in the molecule. The factors affecting the catalytic activity of such complexes have been discussed. Extension of that study to cobalt complexes with ligands of other types made it possible to examine in detail some of the elementary steps of the radical reaction and participation of the complexes in them. In addition to halide complexes, ligands of the phosphine, arsine, stibine, and sulphide types or their onium compounds were subject to the study. The most active cobalt complexes are formed in the presence of bromide and nitrogen ligands.

### EXPERIMENTAL

*Reagents.*  $\text{CoBr}_2\text{L}_2$  complexes, where L is pyridine (Py), tributylphosphine, ( $\text{PBu}_3$ ), triphenylphosphine ( $\text{PPh}_3$ ), triphenylstibine ( $\text{SbPh}_3$ ), or triphenylarsine ( $\text{AsPh}_3$ ), were synthesized in anhydrous alcohol from anhydrous  $\text{CoBr}_2$  and the corresponding ligands according to<sup>8,9</sup>. The complex  $\text{CoBr}_3[\text{PPh}_3]_2[\text{N}(\text{CH}_3)_4]$  was prepared by reaction of boiling solutions of tetramethylammonium bromide and triphenylphosphine in butanol with cobalt dibromide solution<sup>9</sup>. The

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tetrabromocobalt(II) complexes  $\text{CoBr}_4(\text{PyH})_2$ ,  $\text{CoBr}_4(\text{PBu}_4)_2$ ,  $\text{CoBr}_4(\text{PPh}_3\text{Et})_2$ ,  $\text{CoBr}_4(\text{SbPh}_3\text{Bu})_2$ ,  $\text{CoBr}_2(\text{AsPh}_3\text{Bu})_2$ ,  $\text{CoBr}_4(\text{SPh}_2\text{Bu})_2$ ,  $\text{CoBr}_4(\text{SOct}_2\text{iPr})_2$ ,  $\text{CoBr}_4[\text{S}(\text{PhCH}_2)_2\text{Bu}]_2$ , and  $\text{CoBr}_4\text{Cs}_2$  were prepared by reaction of cobalt dibromide with pyridinium bromide, tetrabutylphosphonium bromide, triphenylethylphosphonium bromide, triphenylbutylstibinium bromide, triphenylbutylarsonium bromide, diphenylbutylsulphonium bromide, dioctylisopropylsulphonium bromide, dibenzylbutylsulphonium bromide, and cesium bromide, respectively, according to <sup>10-12</sup>. The  $\text{Co}[\text{TEA}]_2\text{X}_2$  complexes (TEA is triethanolamine) with  $\text{X} = \text{Cl}, \text{Br}$ , and  $\text{I}$  were prepared according to <sup>13</sup>. The composition of prepared complexes was verified by determination of cobalt and bromide in them. The other chemicals, solvents, and hydrocarbons were the same as in the previous works <sup>7</sup>.

The analyses of the reaction mixtures, determination of bromide ions, spectra measurements, and oxidation procedure were the same as in the previous works.

## RESULTS AND DISCUSSION

The effect of the donor atoms as well as of the ligand type in cobalt bromide complexes  $\text{CoBr}_2\text{L}_2$  on their catalytic activity for oxidation of mesitylene is seen in Fig. 1. The tributylphosphine, triphenylphosphine, triphenylstibine, and particularly pyridine coordinated cobalt complexes are more active than cobalt bromide at the same reac-

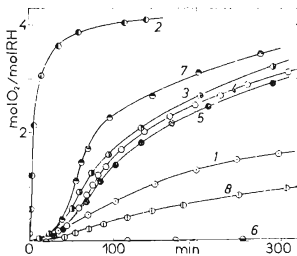


FIG. 1

Oxidation of Mesitylene in Acetic Acid Catalyzed by  $\text{CoBr}_2\text{L}_2$  Complexes

$c_{\text{mesitylene}} = 1.23 \text{ mol l}^{-1}$ ,  $c_{\text{CoBr}_2\text{L}_2} = 1.82 \cdot 10^{-2} \text{ mol l}^{-1}$ ,  $t = 140^\circ\text{C}$ ,  $p = 1.0 \text{ MPa}$ ;  
 1  $\text{CoBr}_2$  alone; 2  $\text{CoBr}_2\text{Py}_2$ ; 3  $\text{CoBr}_2(\text{PBu}_3)_2$ ; 4  $\text{CoBr}_2(\text{PPh}_3)_2$ ; 5  $\text{CoBr}_2 + 3.65 \cdot 10^{-2} \text{ M-PPh}_3$ ; 6  $\text{CoBr}_2(\text{AsPh}_3)_2$ ; 7  $\text{CoBr}_2(\text{SbPh}_3)_2$ ; 8  $\text{CoBr}_2 + 3.65 \cdot 10^{-2} \text{ M}$  dibenzyl sulphide.

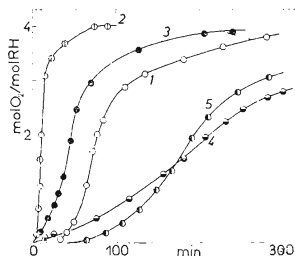


FIG. 2

Activity of Tetrabromocobalt(II) Complexes for Oxidation of Mesitylene

For conditions see Fig. 1; 1  $\text{CoBr}_4\text{Cs}_2$ ; 2  $\text{CoBr}_4(\text{PyH})_2$ ; 3  $\text{CoBr}_4(\text{PBu}_4)_2$ ; 4  $\text{CoBr}_4(\text{PPh}_3\text{Et})_2$ ; 5  $\text{CoBr}_3[\text{PPh}_3]_2[\text{N}(\text{CH}_3)_4]$ .

tion conditions, triphenylarsine and sulphur-containing ligands exert a negative effect. Complexes coordinated by two different ligands do not exhibit a substantial effect. Ionic tetrabromocobalt(II) complexes were expected to be more active, owing to the high amount of bromine involved; however, as Figs 2 and 3 demonstrate, they are relatively less active, except for the pyridinium and tetrabutylphosphonium complexes. An overall comparison of the catalytic activity of the complexes for the mesitylene oxidation is given in Table I.

Cobalt complexes coordinated by nitrogen-containing ligands and involving halides other than bromide are essentially less active or even inactive (Fig. 4, Table II). An analogous relation for the halides has been observed also in the absence of nitrogen ligands<sup>14</sup>.

TABLE I

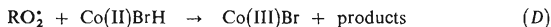
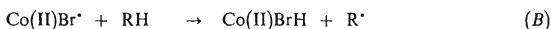
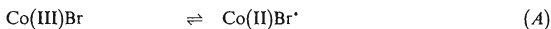
Dependence of Yields of Aromatic Acids on the Catalyst Composition

$c_{\text{mesitylene}} = 1.23 \text{ mol l}^{-1}$  in acetic acid,  $c_{\text{Co}} = 1.82 \cdot 10^{-2} \text{ mol l}^{-1}$ , pressure 1.0 MPa; temperature 140°C.

Catalyst	Reaction time min	Yield of aromatic acids, mol %		
		3,5-DMB <sup>a</sup>	5-MIP <sup>b</sup>	trimesic acid
CoBr <sub>2</sub>	210 <sup>c</sup>	53.3	8.4	1.2
CoBr <sub>2</sub> Py <sub>2</sub>	140	0	5.9	83.8
CoBr <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	310 <sup>c</sup>	7.2	59.6	6.7
CoBr <sub>2</sub> + PPh <sub>3</sub>	310 <sup>c,d</sup>	9.3	57.7	6.2
CoBr <sub>2</sub> (PBU <sub>3</sub> ) <sub>2</sub>	480	2.1	61.1	10.4
CoBr <sub>2</sub> (AsPh <sub>3</sub> ) <sub>2</sub>	270 <sup>c</sup>	0	0	0
CoBr <sub>2</sub> (SbPh <sub>3</sub> ) <sub>2</sub>	340 <sup>c</sup>	0.9	37.9	48.9
CoBr <sub>2</sub> + dibenzyl sulphide	240 <sup>c,d</sup>	24.6	2.1	—
CoBr <sub>2</sub> + HBr	250 <sup>c,d,e</sup>	0.1	18.6	65.8
CoBr <sub>4</sub> Cs <sub>2</sub>	360	0	3.1	77.4
CoBr <sub>4</sub> (PyH) <sub>2</sub>	90	0	3.4	79.1
CoBr <sub>4</sub> (PBU <sub>4</sub> ) <sub>2</sub>	250 <sup>c</sup>	0	4.7	78.8
CoBr <sub>4</sub> (PEtPh <sub>3</sub> ) <sub>2</sub>	480 <sup>c</sup>	0.7	48.2	31.4
CoBr <sub>3</sub> (PPh <sub>3</sub> ) <sub>2</sub> N(CH <sub>3</sub> ) <sub>4</sub>	405 <sup>c</sup>	1.9	43.2	35.9
CoBr <sub>4</sub> (AsBuPh <sub>3</sub> ) <sub>2</sub>	390 <sup>c</sup>	20.9	50.2	3.1
CoBr <sub>4</sub> (SbBuPh <sub>3</sub> ) <sub>2</sub>	390	1.9	59.7	25.5
CoBr <sub>4</sub> (SBU <sub>4</sub> ) <sub>2</sub>	415 <sup>c</sup>	3.7	63.9	4.6
CoBr <sub>4</sub> (SOct <sub>2</sub> iPr) <sub>2</sub>	480	0.5	20.3	63.4
CoBr <sub>4</sub> [S(PhCH <sub>2</sub> ) <sub>2</sub> Bu] <sub>2</sub>	295 <sup>c</sup>	14.6	0.8	—

<sup>a</sup> 3,5-Dimethylbenzoic acid; <sup>b</sup> 5-methylisophthalic acid; <sup>c</sup> oxidation continued; <sup>d</sup> cobalt-to-activator molar ratio 1 : 2; <sup>e</sup> HBr as 47% aqueous solutions.

The pronounced effect of bromide ions during the metal-catalyzed oxidation of hydrocarbons in acetic acid has been extensively studied by a number of authors. Their effect is not in increase of the initial rate, but in a rise of the propagation stage, which has been explained in terms of the scheme<sup>15</sup>



Cobalt acetate monobromide is assumed to be the active species. The oxidation mechanism involves attack of the alkylaromatic hydrocarbon by the active species

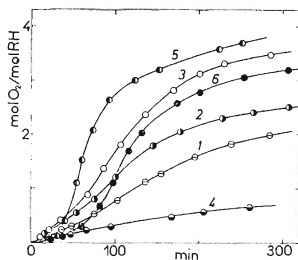


FIG. 3

Activity of Tetrabromocobalt(II) Complexes for Oxidation of Mesitylene

For conditions see Fig. 1; 1  $\text{CoBr}_4(\text{AsPh}_3 \cdot \text{Bu})_2$ ; 2  $\text{CoBr}_4(\text{SPh}_2\text{Bu})_2$ ; 3  $\text{CoBr}_4(\text{Oct}_2\text{iPr})_2$ ; 4  $\text{CoBr}_4[\text{S}(\text{PhCH}_2)_2\text{Bu}]_2$ ; 5  $\text{CoBr}_2 + 3 \cdot 65 \cdot 10^{-2} \text{M-HBr}$ ; 6  $\text{CoBr}_4(\text{SbPh}_3\text{Bu})_2$ .

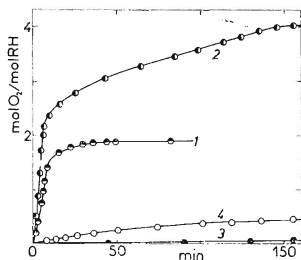
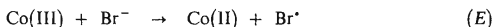


FIG. 4

Effect of Halide Ligands on the Activity of  $\text{Co(TEA)}_2\text{X}_2$  Complexes for Oxidation of Mesitylene in Acetic Acid

$c_{\text{mesitylene}} = 1 \cdot 23 \text{ mol l}^{-1}$ ,  $p = 1 \cdot 1 \text{ MPa}$ ;  
1  $3 \cdot 65 \cdot 10^{-2} \text{M-Co(TEA)}_2\text{Cl}_2$ ,  $150^\circ\text{C}$ ; 2  $1 \cdot 82 \cdot 10^{-2} \text{M-Co(TEA)}_2\text{Br}_2$ ,  $140^\circ\text{C}$ ; 3  $2 \cdot 5 \cdot 10^{-2} \text{M-Co(TEA)}_2\text{I}_2$ ,  $140^\circ\text{C}$ ; 4  $3 \cdot 65 \cdot 10^{-2} \text{M-Co(TEA)}_2\text{OAc}_2$ ,  $150^\circ\text{C}$ .

according to reaction (B) or by the bromide radical<sup>15-19</sup> formed *via* the reaction (E),



Thus a certain number of the alkylaromatic hydrocarbon molecules are oxidized, and gradually the bromide ions convert to the less active forms of organic bromides,



or they recombine to give molecular bromine<sup>20</sup>,



In this manner, during the oxidation of mesitylene catalyzed by equimolar mixture of cobalt(II) acetate and sodium bromide, 11 molecules of hydrocarbon are oxidized by a bromide ion, but if the nitrogen-containing triethanolamine is present as many as 33 molecules are oxidized in the same conditions and the number depending only slightly on the initial bromide-to-cobalt concentration ratio<sup>1,21</sup>.

The nitrogen and some other compounds take part in several elementary reaction stages. They participate in the reactions with the bromide anions – for instance pyridine, reacts readily in acetic acid – with the formation of less dissociated ammonium bromide compounds<sup>2</sup>:

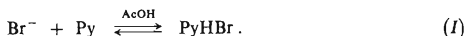


TABLE II

Effect of Halide Ligands on the Yield of Trimesic Acid  
For conditions see Fig. 4.

Catalyst	Reaction time min	Acid yield, mol. %	
		5-methylisophthalic acid	trimesic acid
Co(TEA) <sub>2</sub> Cl <sub>2</sub>	80 <sup>a</sup>	51.1	0.4
Co(TEA) <sub>2</sub> Br <sub>2</sub>	170	4.9	83.5
Co(TEA) <sub>2</sub> I <sub>2</sub>	160	0	0
Co(TEA) <sub>2</sub> OAc <sub>2</sub>	180 <sup>b</sup>	0	0

<sup>a</sup> The catalyst separated as brown slurry during the oxidation; <sup>b</sup> yield of 3,5-dimethylbenzoic acid 7.9 mol. %.

So the concentration of bromide anions or of HBr, which can bring about acid-catalyzed cleavage to phenolic substances, lowers. If the interaction of Co(III) with  $\text{Br}^-$ , according to reaction (E) or one giving rise to other complexes<sup>22-24</sup>, were the rate-controlling step, the catalytic activity should lower in the presence of nitrogen-containing substances, in accordance with reactions (E) and (I); the reverse was, however, observed experimentally. Moreover, in the presence of strongly coordinating ligands such as amines, the rate of Co(III) reduction is lower<sup>25</sup>.

We have found<sup>1-7</sup> that in the presence of nitrogen and some other ligands, the activity of cobalt catalysts rises considerably. The kinetic and spectral measurements pointed to some factors having a bearing on this phenomenon, and also indicated changes in the structure of the cobalt complexes. In acetic acid as the solvent, cobalt(II) bromo complexes of tetrahedral and octahedral configurations are formed, in dependence on the concentrations of the bromide ions and of the ligands<sup>2,5,26,27</sup>. In the presence of nitrogen ligands, tetrahedral  $\text{CoBr}_3\text{OAc}^{2-}$  and  $\text{CoBr}_4^{2-}$  species predominate. The  $\text{CoBr}_2\text{L}_2$  structures are conceivable as well, although in acetic acid they readily convert to the above-mentioned ionic forms<sup>2</sup>. Comparing the catalytic activity of, e.g.,  $\text{CoBr}_4[\text{PyH}]_2$ ,  $\text{CoBr}_2\text{Py}_2$ , and  $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$  for oxidation of alkylaromates in acetic acid or in solvents that are unable to coordinate into the complex and thus to alter the structure of the latter, we find the first complex to be most active and, the activity being independent of or only slightly dependent on the solvent used<sup>28</sup>. These results indicate that the catalytically highly active forms are the tetrahedral tetrabromocobalt(II) complexes; in solvents in which ligand exchange can occur, such as acetic acid, the  $\text{Co}[\text{Br}_3\text{OAc}]^{2-}$  complexes can be considered too. The creation of tetrahedral cobalt dibromide and monobromide complexes, such as  $\text{Co}[\text{Br}_2\text{OAc}_2]^{2-}$  and  $\text{Co}[\text{BrOAc}_3]^{2-}$ , and of the octahedral  $\text{CoBrOAc}$  complex is also conceivable, and so is their formation as intermediate products during the

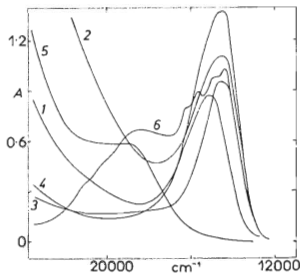


FIG. 5

Electronic Spectra of Oxidized Cobalt Complexes

$c_{\text{Co}} = 5.44 \cdot 10^{-2} \text{ mol l}^{-1}$ , cell thickness 0.1 cm. 1  $\text{CoBr}_2\text{TEA}_2$  in  $\text{Ac}_2\text{O}$ ; 2  $\text{CoBr}_2\text{TEA}_4$  in  $\text{Ac}_2\text{O}$ ; 3  $\text{CoBr}_2\text{TEA}_2$  in  $\text{AcOH}$ ; 4  $\text{CoBr}_2 \cdot \text{TEA}_2\text{Py}_2$  in  $\text{AcOH}$ ; 5  $\text{Co}(\text{OAc})_2\text{TEA}_2$  in  $\text{AcOH}$ , cell 0.5 cm; 6  $\text{CoBr}_2\text{TEA}_2$  partially oxidized in  $\text{AcOH}$ .

oxidation reaction<sup>15,29,30</sup>. In fact, however, the  $\text{CoBrOAc}$  complex in the presence of pyridine converts in acetic acid to  $\text{CoBr}_4^{2-}$  and  $\text{Co}[\text{Br}_3\text{OAc}]^{2-}$  complexes, whereby the catalytic activity of the system grows considerably<sup>2,5</sup>.

Many cobalt complexes with nitrogen ligands are known for their reactivity towards oxygen. The amine ligand controls to a large extent the rate of reaction of the complex with oxygen and also the reversibility of this process<sup>31-34</sup>. Triethanolamine-coordinated cobalt bromide and chloride complexes in acetic acid or anhydride solutions react with oxygen. As can be seen from Table III, the oxygen uptake is dependent upon the solvent and the Co : Br : TEA ratio. The very high amounts of oxygen absorbed per mol cobalt point to the oxidation of the triethanolamine ligand; the more triethanolamine is present in the system, the more oxygen is absorbed, whereas in the presence of bromides the reverse is true. The effect of solvent is substantial. In solid state or in nonpolar solvents (Table IV) the  $\text{CoBr}_2 \cdot \text{TEA}_2$  complex is inactive with respect to oxygen or in the oxidation reaction with hydrocarbons; it becomes active in acetic acid or anhydride, which is associated with the transformation of the complex chelate structure in these solvents<sup>13,35</sup>. In acetic acid, ionic tetrahedral structures, mainly  $\text{Co}[\text{Br}_3\text{OAc}]^{2-}$  and  $\text{CoBr}_4^{2-}$ , are formed among others. They probably do not react directly with molecular oxygen and hence do not activate it, for instance to the species  $[(\text{AcO})_2\text{CoBr}_3\text{O}_2]^{3-}$  or  $[(\text{AcO})_2\text{CoBr}_2\text{O}_2]^{2-}$ , which are sometimes considered to be the active complexes<sup>36</sup>. This is supported by the fact that the complex  $\text{CoBr}_2\text{Py}_2$ , although also converting in acetic acid *via* equilibrium reaction to the mentioned ionic species, does not absorb oxygen even at pressures 0.5 MPa and temperatures 70 to 130°C. Nonreactive with oxygen is also the  $\text{CoBr}_4(\text{PyH})_2$  complex. Moreover, these complexes are highly catalytically active for oxidation of alkylaromates also in nonpolar solvents<sup>28</sup>. This implies that the high absorption of oxygen in the case of triethanolamine complexes must be associated also with oxidation of the triethanolamine ligand. This was also confirmed by mass spectrometric measurements, which showed that the ligands are oxidized with the formation of aldehydic and carboxylic compounds. In acetic anhydride as the solvent, the hydroxyl groups of triethanolamine are esterified, and substances such as  $\text{N}-(\text{CH}_2-\text{CH}_2-\text{O}-\text{CO}-\text{CH}_3)_3$  are formed. The concentration of triethanolamine in the system has a bearing on the amount of oxygen absorbed, lengthening of the induction period, and of the reaction. In many cases the reaction with oxygen depends also on the intensity of stirring of the reaction mixture; if the stirring is not very vigorous, the overall oxygen uptake is the same, but a green, highly viscous substance forms on the walls of the reaction vessel. Occasionally, this substance separates also from homogeneous solutions on their cooling or several days' standing. This manifests itself in the electronic spectra by a decrease of the absorption peak at  $14300\text{ cm}^{-1}$ . An analysis revealed that the oxidation does not result in formation of molecular bromine or its organic forms — it remains bonded in the ionic form. In case that insoluble forms of cobalt complexes appear, the content

of bromide anions in this moiety is higher. As is seen from Fig. 5, if the  $\text{CoBr}_2\text{TEA}_2$  complex in acetic acid is oxidized, the ionic  $\text{Co}[\text{Br}_3\text{OAc}]^{2-}$  complex, with the spectral maxima at 16180, 15750, and 14360  $\text{cm}^{-1}$ , converts to complexes possessing an absorption band at 14300  $\text{cm}^{-1}$ . Their molar absorptivities depend, in addition to the solvent, also on the concentration of triethanolamine or pyridine; in the case of pyridine complexes, the absorption maximum in addition shifts to 15000  $\text{cm}^{-1}$  (Table III).

The catalytic activity of the oxidized complexes were tested during oxidation of pseudocumene. The oxidised complex was isolated from the solution by distilling the solvent off at reduced pressure, cobalt and bromine were determined in the residue, and an aliquot of the latter was used as the catalyst in the oxidation reaction. As Table IV demonstrates, the oxidized  $\text{CoBr}_2\text{TEA}_2$  complex is catalytically equally active as the initial complex, whereas in the case of  $\text{CoBr}_2\text{TEA}_2\text{Py}_4$  the activity of the oxidized complex is lower. Moreover, oxidized  $\text{CoBr}_2\text{TEA}_2$  becomes catalytically active also in *o*-dichlorobenzene, a solvent in which the nonoxidized  $\text{CoBr}_2\text{TEA}_2$  complex does not exhibit activity.

TABLE III

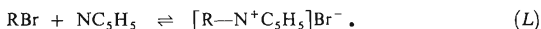
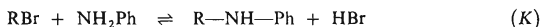
Absorption of Oxygen by Cobalt Complexes in Acetic Acid  
 $c_{\text{Co}} = 5.44 \cdot 10^{-2} \text{ mol l}^{-1}$ , temperature 100°C, pressure 0.5 MPa.

Reaction system <sup>a</sup>	mol O <sub>2</sub> /mol Co	$\epsilon_{14300}^{b, -}$ 1 mol <sup>-1</sup> cm <sup>-1</sup>
$\text{CoBr}_2\text{TEA}_2$	3	183
$\text{CoBr}_2\text{TEA}_4$	4	—
$\text{CoBr}_2\text{TEA}_6$	8—9	—
$\text{CoBr}_4\text{TEA}_4$	1.5—2 <sup>c</sup>	—
$\text{CoBr}_2\text{TEA}_2\text{Py}_4$	3	164 <sup>d</sup>
$\text{CoBr}_2\text{TEA}_2 + \text{CoBr}_2\text{Py}_2$ (1 : 10)	0.3	—
$\text{CoBr}_2\text{Py}_2 + \text{Co}(\text{AcAc})_3$	0.05 <sup>e</sup>	—
$\text{CoBr}_2\text{TEA}_2$	3 <sup>f</sup>	—
$\text{CoCl}_2\text{TEA}_2$	3 <sup>f</sup>	—
Triethanolammonium bromide	0	—
$\text{Co}(\text{OAc})_2\text{TEA}_2$	5—6	—
$\text{Co}(\text{OAc})_2\text{TEA}_4$	9	—
$\text{CoBr}_2\text{TEA}_2$	1 <sup>g</sup>	266
$\text{CoBr}_2\text{TEA}_4$	4 <sup>g</sup>	204

<sup>a</sup> Mixture of the  $\text{CoBr}_2\text{TEA}_2$  complex or  $\text{Co}(\text{OAc})_2 \cdot 4 \text{H}_2\text{O}$  with the corresponding amount of TEA or Py; <sup>b</sup> molar absorptivity after the oxidation; <sup>c</sup> mixture of  $\text{Co}(\text{OAc})_2 \cdot 4 \text{H}_2\text{O}$  with TEA.HBr; <sup>d</sup>  $\epsilon$  at 15000  $\text{cm}^{-1}$ ; <sup>e</sup> concentration of  $\text{Co}(\text{AcAc})_3$   $1 \cdot 10^{-2} \text{ mol l}^{-1}$ ; <sup>f</sup> at 75°C and 0.1 MPa; <sup>g</sup> in acetic anhydride.



The experimental data showed that in the presence of nitrogen and some other compounds, not only the catalytic activity but also the selectivity of the reaction increases, particularly amount of aldehydes. Usually, when the maximum quantity of aldehydes is formed in the system, so the concentration of bromine is minimal<sup>20,21</sup>. However, if cobalt complexes with nitrogen ligands (or in the presence of acetate anions) are used as catalysts, aldehydes form in amounts as high as 46 mol%, but the concentration of the bromide anions lowering within this period by 20% only (with respect to their initial content)<sup>1,7</sup>. Hence, in the presence of nitrogen compounds, either reaction (G) is affected or the organic bromide species thus formed are converted *via* reactions (J)–(L) back to bromide ions, whereavly the activity of the catalysts restores<sup>37,38</sup>.



The dehalogenation of benzyl bromide was studied experimentally at 70 and 92°C using acetic acid as the solvent. The effect of cobalt(II) acetate and pyridine, respectively, or mixture of the former with the latter or with sodium acetate on the rate of these reactions was investigated. In the above conditions, which approach those

TABLE IV

Oxidation of Pseudocumene in Acetic Acid Catalyzed by Cobalt Complexes

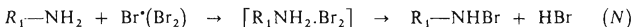
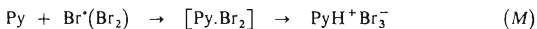
 $c_{\text{pseudocumene}} = 1.2 \cdot 10^{-2} \text{ mol l}^{-1}, c_{\text{Co}} = 1.8 \cdot 10^{-2} \text{ mol l}^{-1}, t = 140^\circ\text{C}, p = 0.96 \text{ MPa.}$ 

Catalyst	Reaction time min	Yield of aromatic acids, mol.%		
		monocarboxylic acids	dicarboxylic acids	trimellitic acid
CoBr <sub>2</sub> TEA <sub>2</sub> Py <sub>4</sub>	150 <sup>a</sup>	—	16.2	60.1
CoBr <sub>2</sub> TEA <sub>2</sub>	180 <sup>b</sup>	1.9	54.0	29.4
CoBr <sub>2</sub> TEA <sub>2</sub>	180 <sup>c</sup>	0.9	51.4	30.1
CoBr <sub>2</sub> TEA <sub>2</sub> Py <sub>4</sub>	210 <sup>c</sup>	—	3.9	83.9
CoBr <sub>2</sub> TEA <sub>2</sub>	180 <sup>c,d</sup>	oxidation did not set in within 3 h		
CoBr <sub>2</sub> TEA <sub>2</sub>	120 <sup>b,d</sup>	0.9 mol O <sub>2</sub> absorbed per mol pseudocumene		

<sup>a</sup> Complex oxidized in AcOH; <sup>b</sup> complex oxidized in Ac<sub>2</sub>O; <sup>c</sup> nonoxidized complex; <sup>d</sup> *o*-dichlorobenzene served as the solvent instead of acetic acid.

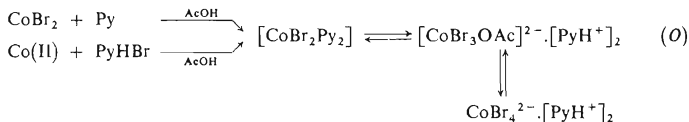
of the oxidation reaction, no significant differences in the effect of the compounds on the dehalogenation of benzyl bromide was found. The rate of bromide recovery is low: after 2 h reaction, only 20–30% of the bromide anions is recovered.

Nitrogen compounds therefore will not exert an essential effect on the reactions (J)–(L), but they probably will prevent formation of organic bromides owing to competitive reactions leading to organic bromo complexes<sup>39</sup>,

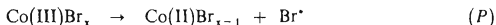


which readily form catalytically active complexes with cobalt. The bromine radical or molecular bromine thus formed during the cobalt bromide-catalyzed oxidation of alkylaromatic hydrocarbons can convert back to the ionic form, for instance, by reactions (M) and (N); therefore, in the presence of amines the concentration of bromide ions decreases slowly during the oxidation<sup>1</sup>. From this point of view, it should be convenient to maintain a high amine concentration in the system; on the other hand, however, this brings about shift of equilibria and conversion of the active tetrahedral complexes to octahedral ones or to other structures, whereby the system becomes less active and selective or the oxidation is even inhibited. Thus the oxidation must proceed at optimum concentration of nitrogen compound, which is highly dependent upon the cobalt-to-bromine molar ratio<sup>3,5</sup>. The observed differences in the activation effects of the various types of nitrogen, sulphur, phosphorus, arsenic, and antimony compounds result from their influence on the formation of catalytically active complexes and on their reactivity with bromine atoms, through reaction analogous to reactions (M)–(O). All of these types of ligands possess unpaired electrons, and during the reaction they remain to a greater or lesser extent bonded to the metal<sup>40</sup>. In addition to the dominating effect of the donor atom on the reactivity, steric effect play a part too; in this respect even small changes produce high differences in the activity of the complexes, *e.g.*, in pyridine<sup>5</sup> or phosphine ligands (Fig. 2, Table I). Probably the stability of the complexes is thus affected the cobalt–bromine bond being weakened<sup>41</sup>. Complexes in which intramolecular oxidation–reduction process readily occurs, such as unstable copper(II) iodide or cobalt(II) iodide complexes, can be stabilized by nitrogen ligands, *e.g.*, by bipyridyl  $\gamma$ -picoline, or pyridine<sup>42</sup>; still, these compounds do not exhibit catalytic activity in oxidation reaction (Fig. 4).

Study of the effect of nitrogen- and some other compounds on the oxidation of alkylaromates catalyzed by cobalt and bromine ions revealed that these compounds affect mainly the formation of the highly active tetrahedral ionic complexes,



which participate in the catalytic cycle by processes analogous to reactions (A)–(D). Since the activity of cobalt complexes is substantially affected by their coordination by nitrogen ligands at temperatures up to 180°C, the hydrocarbon attack is likely to proceed *via* the bromide ligands bonded in complex with cobalt rather than *via* free bromide radicals. The latter can be formed under some conditions through electron transfer oxidation of bromide ions,



but in the presence of nitrogen compounds their reaction with the hydrocarbon ((F) and (G)) is limited because of the competitive reactions (M) and (N), which lead to the active forms of the catalyst (reaction (O)). In this manner the conversion of bromide ions to the inactive organic bromide forms is slowed down.

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