

## THE EFFECT OF ACETATES ON THE ACTIVITY OF COBALT BROMIDE CATALYSTS\*

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With a view to assess the effect of acetates of the groups *Ia* and *II* on the activity of cobalt bromide catalysts, oxidation of mesitylene and pseudo-cumene in a temperature range of 90 to 140°C has been investigated. At 100°C the acetate anions retarded the oxidation in the initial stage and increased selectivity of the oxidation of mesitylene to 3,5-dimethylbenzaldehyde, which intermediate was formed to a concentration of 42 mol%. The presence of acetates also affected distribution of isomers of aromatic dicarboxylic acids and the contents of aldehyde acids. The resultant effect of the simultaneous presence of acetate anions and nitrogen compounds on the activity of cobalt bromide catalysts depended on the nitrogen compound; with aminoacetic acid and hexamethylenediamine the oxidation rate and yields of aromatic acids were markedly increased. As conductance measurements indicated, the presence of acetates enhanced the formation of ionic forms of the complexes.

The catalytic effect of the transition metals on the oxidation of hydrocarbons and the decomposition of hydroperoxides have been widely studied from the viewpoints of both the reaction mechanism and the technological interest. Much less attention has been paid to systems containing, in addition to the transition metals, also metals of non-transitional valency, *viz.* those of the groups *Ia* and *II*. In the oxidation of alkanes to fatty acids the acetates initiate the reaction and simultaneously control the decomposition of hydroperoxides<sup>1-3</sup>. The transition metals not only influence the mechanisms of the individual elementary steps but also modify the structure of a homogeneous catalyst<sup>4-8</sup>.

In the oxidation of alkyl aromatic hydrocarbons catalysed by salts of cobalt, manganese and other metals, in the presence of bromine compounds and in the medium of acetic acids, the effect of metal acetates of the groups *Ia* and *II* is strongly dependent on the catalyst composition and the reaction conditions. This effect, at the initial stage of the oxidation, is studied in the present paper from a kinetic point of view. The formation of oxidation products, mainly aromatic acid, in the oxidation of mesitylene and pseudocumene is also dealt with.

\* Part IX of the series Oxidation of Polyalkylated Aromatic Hydrocarbons; Part VIII: This Journal 43, 728 (1978).

## EXPERIMENTAL

**Chemicals.** Pseudocumene and mesitylene (purity 99.5%) were purified by agitation with sulphuric acid; then they were washed, dried and distilled. 3,5-Dimethylbenzaldehyde was prepared by oxidation of mesitylene with manganese dioxide; prior to use it was distilled *in vacuo*<sup>9</sup>. The metal acetates, A. G., were dried under reduced pressure. Acetic acid was distilled in the presence of  $\text{CrO}_3$ . The other chemicals, of A.G. purity, were employed directly.

**Analysis.** The reaction mixtures were analysed by gas chromatography in an apparatus Hewlett-Packard 5750. The column, 2 mm in diameter and 1.8 m in length, was packed with Chromosorb W HMDS, 80–100 mesh, soaked with a methylvinylsilicone elastomer (10% UCCW 982). Hemimellitene, 3,4-dimethylbenzoic acid and 2-methylterephthalic acid were used as internal standards in analysis of the reaction mixture after the oxidation of mesitylene. The samples were esterified with diazomethane. Concentration of 3,5-dimethylbenzaldehyde was determined polarographically immediately on taking a sample, with an apparatus LP-60 (Laboratorní přístroje, Prague). Concentration of bromide ions was determined by potentiometric titration, a silver electrode being used.

**Conductance measurements.** Changes in conductance due to the formation and transformation of complexes in a solution of acetic acid were followed by a described method<sup>10</sup>. The mole fraction  $N(\text{Co})$  is defined as

$$N(\text{Co}) = n(\text{CoBr}_2) / [n(\text{CoBr}_2) + n(\text{NaOAc})].$$

The oxidation procedure is described in the previous papers.

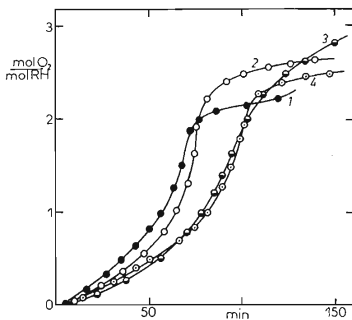


FIG. 1

Effects of Sodium and Ammonium Acetates on the Oxidation of Mesitylene

Temperature  $90^\circ\text{C}$ ;  $[\text{mesitylene}] = 0.545\text{M}$ ;  $[\text{Co}] = 4.04 \cdot 10^{-2}\text{M}$ ;  $[\text{NH}_4\text{Br}] = 4.0 \cdot 10^{-2}\text{M}$ ;  $[\text{NH}_4\text{OAc}]$ : 1 0, 2  $4.04 \cdot 10^{-2}\text{M}$ , 3  $1.62 \cdot 10^{-1}\text{M}$ , 4  $4.04 \cdot 10^{-2}\text{M-NaOAc}$ .

## RESULTS AND DISCUSSION

The oxidation rate of mesitylene at 90°C and atmospheric pressure in the initial stage was retarded by the presence of sodium or ammonium acetate (Fig. 1). These acetates, depending on their concentration, affect the oxidation rate and the course of the kinetic curves expressing the consumption of oxygen<sup>11</sup>, but at the time of transient retardation of the oxidation (130 min) they cause a deeper oxidation of mesitylene (Table I). To get some insight into the mechanism of their action we studied oxidation

TABLE I

Effects of Sodium and Ammonium Acetates on Yields of Aromatic Acids after 130 or 210<sup>a</sup> min Oxidation of Mesitylene

For conditions see Figs 1 and 3<sup>a</sup>. 3,5-DMB 3,5-dimethylbenzoic acid; 5-MIP 5-methylisophthalic acid; TMA trimesic acid; 3-FMT 3-formylmetatoluic acid.

| [OAc <sup>-</sup> ]<br>M · 10 <sup>2</sup> | Yields of aromatic acids, mol% |       |     |       |
|--|--------------------------------|-------|-----|-------|
|  | 3,5-DMB                        | 5-MIP | TMA | 3-FMT |
| O  | 45.2                           | 35.6  | 0   | 11.4  |
| 4.04 NaOAc                                 | 37.7                           | 40.1  | 4.0 | 5.7   |
| 4.04 NH <sub>4</sub> OAc                   | 19.3                           | 51.8  | 3.1 | 8.5   |
| O <sup>a</sup>                             | 53.9                           | 8.4   | 1.2 | —     |
| 3.65 NaOAc <sup>a</sup>                    | 1.9                            | 67.9  | 6.8 | —     |
| 3.65 NH <sub>4</sub> OAc <sup>a</sup>      | 1.5                            | 66.7  | 8.2 | —     |

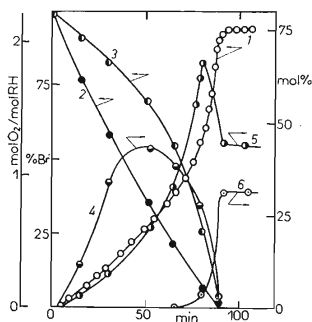


FIG. 2

Concentrations of Reaction Components in Relation to Time

Temperature 90°C; [mesitylene] = 0.545M; [Co] = 4.04 · 10<sup>-2</sup>M; [NaBr] = 4.04 · 10<sup>-2</sup>M; [NaOAc] = 8.08 · 10<sup>-2</sup>M; 1 reacted mol O<sub>2</sub>/mol RH; 2 % of unreacted mesitylene; 3 % of Br<sup>-</sup>; 4 3,5-dimethylbenzaldehyde; 5 3,5-dimethylbenzoic acid; 6 5-methylisophthalic acid.

of mesitylene catalysed by an equimolar mixture of cobalt acetate and sodium bromide (Fig. 2). It appeared that in the absence of the acetates the consumption rates of the hydrocarbon and bromide anions were considerably different<sup>11</sup>. In the absence of sodium acetate the consumption of mesitylene and the consumption of bromide anions obeyed the kinetics of first-order reactions, the consumption of the bromide anions being faster. Oxidation of 50% of the original amount of mesitylene corresponded to a consumption of 65% of bromide anions, whereas in the presence of sodium acetate the consumption of bromide anions was only 20% (Fig. 2). A marked difference was also observed in selectivity of the consecutive reactions; although 3,5-dimethylbenzaldehyde is a readily oxidizable intermediate it accumulated in the reaction mixture up to a concentration of 42 mol%. At higher temperatures and pressures in the presence of acetates at the beginning stage of the reaction (Fig. 3) the retardation was not observed, but the oxidation was markedly accelerated; this manifested itself also in composition of the oxidation products (Table I). Toward the end of the oxidation of mesitylene the effects of sodium and ammonium acetates were negative. The contents of 5-methylisophthalic acid were practically equal in the final oxidation products (Table II). This shows that the decrease in yield of trimesic acid in the presence of the acetates was not caused by incomplete oxidation of the aromatic diacid to the tricarboxylic acid, but that it was due to a lower selectivity of the reaction (formation of by-products).

In the oxidation of pseudocumene the effect of the acetates at 100°C was strongly retarding, especially with the catalyst having a higher ratio of bromine to cobalt. As can be seen from Table III, at higher temperatures and pressures and in a solvent

TABLE II

Yield of Trimesic Acid in Relation to Concentration of Acetates in Oxidation of Mesitylene at 100°C and 0.1 MPa; [mesitylene] = 0.545M, [Co] =  $4.04 \cdot 10^{-2}$ M, [NH<sub>4</sub>Br] =  $4.04 \cdot 10^{-2}$ M, reaction time 17 h.

| Acetate             | OAc <sup>-</sup><br>M · 10 <sup>2</sup> | Yields of aromatic acids<br>mol% |      |
|---------------------|---|----------------------------------|------|
|                     |   | 5-MIP                            | TMA  |
| —                   | 0                                       | 5.2                              | 79.1 |
| NH <sub>4</sub> OAc | 20.2                                    | 6.1                              | 75.2 |
| NH <sub>4</sub> OAc | 28.3                                    | 5.9                              | 72.0 |
| —                   | 0 <sup>a</sup>                          | 5.8                              | 78.4 |
| NH <sub>4</sub> OAc | 4.04 <sup>a</sup>                       | 6.2                              | 77.1 |
| NaOAc               | 4.04 <sup>a</sup>                       | 7.6                              | 74.1 |
| NaOAc               | 8.08 <sup>a</sup>                       | 7.4                              | 67.6 |

<sup>a</sup> Catalyst  $4.04 \cdot 10^{-2}$ M-CoBr<sub>2</sub>·6 H<sub>2</sub>O.

TABLE III

Effect of Sodium Acetate on Yields of Aromatic Acids in the Oxidation of Pseudocumene

| [Co]<br>M · 10 <sup>2</sup> | Temperature<br>°C | Pressure<br>MPa | Ratio<br>NaOAc/<br>/Co | Reaction<br>time<br>min | Yield, mol%           |                        |                     |
|-----------------------------|-------------------|-----------------|------------------------|-------------------------|-----------------------|------------------------|---------------------|
|                             |                   |                 |                        |                         | 2-MT + 4-MIP<br>4-MOP | methylphthalic<br>acid | trimellitic<br>acid |
| 4·04 <sup>a</sup>           | 100               | 0·1             | 0                      | 156                     | 6·1                   | 13·2                   | 55·5                |
|                             |                   |                 | 1                      | 200                     | 2·0                   | 36·6                   | 26·3                |
|                             |                   |                 | 4                      | 240                     | 3·3                   | 52·9                   | 13·6                |
| 4·04 <sup>b</sup>           | 100               | 0·1             | 0                      | 235                     | 3·8                   | 29·6                   | 38·3                |
|                             |                   |                 | 1                      | 235                     | 1·4                   | 26·4                   | 33·1                |
|                             |                   |                 | 4                      | 400                     | 3·1                   | 40·6                   | 23·5                |
| 3·65 <sup>c</sup>           | 120               | 0·7             | 0                      | 310                     | 16·7                  | 46·8                   | 12·4                |
|                             |                   |                 | 0                      | 145                     | 8·5                   | 21·8                   | 43·3                |
|                             | 140               | 1·1             | 1                      | 135                     | 8·1                   | 15·1                   | 45·1                |
|                             |                   |                 | 2                      | 175                     | 3·4                   | 13·1                   | 47·2                |
| 1·82 <sup>d</sup>           | 140               | 1·1             | 0                      | 300                     | 6·8                   | 40·2                   | 19·5                |
|                             |                   |                 | 2                      | 250                     | 3·5                   | 43·6                   | 18·6                |

<sup>a</sup> Catalysed by  $\text{CoBr}_2 \cdot 6 \text{H}_2\text{O}$ ; [pseudocumene] = 0·545M. <sup>b</sup> Catalysed by an equimolar mixture of  $\text{CoBr}_2 \cdot 6 \text{H}_2\text{O}$  and  $\text{Co}(\text{OAc})_2 \cdot 4 \text{H}_2\text{O}$ ; [pseudocumene] = 0·545M. <sup>c</sup> Catalysed by an equimolar mixture of  $\text{CoBr}_2 \cdot 6 \text{H}_2\text{O}$  and  $\text{Co}(\text{OAc})_2 \cdot 4 \text{H}_2\text{O}$ ; [pseudocumene] = 1·23M. <sup>d</sup> Acetic acid containing 8% of water. <sup>e</sup> 2-MT = 2-methylterephthalic acid, 4-MIP = 4-methylisophthalic acid, 4-MOP = 4-methylorthophthalic acid.

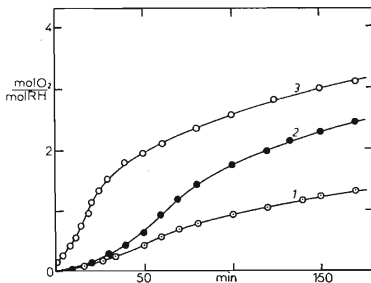


FIG. 3

Effects of Sodium and Ammonium Acetates on the Oxidation of Mesitylene

Temperature 140°C; 1·1 MPa; [mesitylene] = 1·23M;  $[\text{CoBr}_2 \cdot 6 \text{H}_2\text{O}] = 1·82 \cdot 10^{-2}\text{M}$ ; 1 without acetate; 2  $3·65 \cdot 10^{-2}\text{M-NaOAc}$ ; 3  $3·65 \cdot 10^{-2}\text{M-NH}_4\text{OAc}$ .

containing 8% of water the acetate no longer had a negative effect. Small increase in yield of trimellitic acid was due to longer reaction times. In these conditions sodium acetate also influenced the proportion of the individual isomers of aromatic dicarboxylic acids. In its presence the content of 4-methylphthalic acid was increased. The effects of ammonium, lithium and potassium acetates on oxidation of pseudocumene were similar to that of sodium acetate, whereas, as can be seen from Table IV, acetates of metals of the second group of the periodic table strongly retarded the oxidation, which ceased on the second step, *i.e.* on the oxidation of pseudocumene to aromatic dicarboxylic acids. The formation of the individual isomers of methylphthalic acid was also substantially affected by the acetates, particularly by lithium and ammonium acetates, which gave maximum quantities of 4-methylphthalic acid.

The effect of acetates was also studied in the use of cobalt bromide catalysts activated with nitrogen compounds. Strong chelating agents, such as *o*-phenanthroline, 2,2'-dipyridyl and bis-salicylideneethylenediamine, invariably decreased the activity of cobalt bromide catalysts and the presence of acetates produced no more changes (Fig. 4). In the presence of picolinic acid, which just slightly affected oxidation of mesitylene under the conditions studied (Figs 3 and 4), the addition of sodium acetate increased the reaction rate and yield of aromatic acids by practically the same value as in absence of picolinic acid (Fig. 5), so that compound was indifferent. With hexamethylenediamine and aminoacetic acid the activating effect of sodium acetate was considerable. High concentrations of the acetate, above the molar ratio  $\text{OAc}^-/\text{Co} > 4$ , reduced the oxidation rate and moderately decreased the yield of trimesic acid (Fig. 5).

TABLE IV

Effect of Acetates on the Oxidation of Pseudocumene Temperature 140°C; 1.1 MPa; [pseudocumene] = 1.23M;  $[\text{CoBr}_2] = [\text{Co}(\text{OAc})_2] = 1.82 \cdot 10^{-2}\text{M}$ ;  $[\text{Co}] : [\text{OAc}^-] = 1 : 2$

| Acetate              | Reaction time min | Yield, % mol                       |                     |                  |
|----------------------|-------------------|------------------------------------|---------------------|------------------|
|                      |                   | 2-MT + 4-MIP<br>4-MOP <sup>a</sup> | methylphthalic acid | trimellitic acid |
| —                    | 145               | 8.5                                | 21.8                | 43.3             |
| NH <sub>4</sub> OAc  | 160               | 3.0                                | 19.1                | 45.7             |
| LiOAc                | 125               | 1.5                                | 24.3                | 43.7             |
| KOAc                 | 180               | 3.6                                | 13.9                | 46.8             |
| Mg(OAc) <sub>2</sub> | 225               | 6.0                                | 38.4                | 15.6             |
| Zn(OAc) <sub>2</sub> | 230               | 8.0                                | 51.8                | 6.4              |
| Ba(OAc) <sub>2</sub> | 150               | 6.2                                | 53.3                | 8.4              |

<sup>a</sup> See Table III.

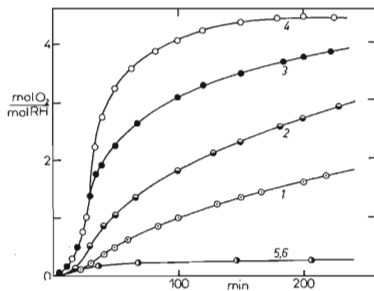


FIG. 4

Combined Effect of Sodium Acetate and a Nitrogen Compound in the Oxidation of Mesitylene  
 Temperature  $140^{\circ}\text{C}$ ;  $1.1\text{ MPa}$ ; [mesitylene] =  $1.23\text{M}$ ;  $[\text{CoBr}_2 \cdot 6\text{H}_2\text{O}] = 1.82 \cdot 10^{-2}\text{M}$ ; [nitrogen compound] =  $3.65 \cdot 10^{-2}\text{M}$ ; 1 picolinic acid; 2 picolinic acid +  $7.3 \cdot 10^{-2}\text{M-NaOAc}$ ; 3 hexamethylenediamine; 4 hexamethylenediamine +  $7.3 \cdot 10^{-2}\text{M-NaOAc}$ ; 5 *o*-phenanthroline; 6 *o*-phenanthroline +  $7.3 \cdot 10^{-2}\text{M-NaOAc}$ .

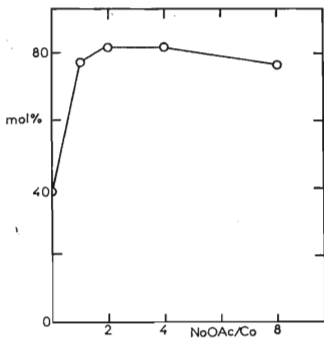


FIG. 5

Effect of Concentration of Sodium Acetate on the Oxidation of  $1.23\text{M}$  Mesitylene Catalysed by  $1.82 \cdot 10^{-2}\text{M-CoBr}_2$  in Acetic Acid at  $140^{\circ}\text{C}$  and  $0.9\text{ MPa}$

Reaction time 230 min, concentration of aminoacetic acid  $3.65 \cdot 10^{-2}\text{M}$ .

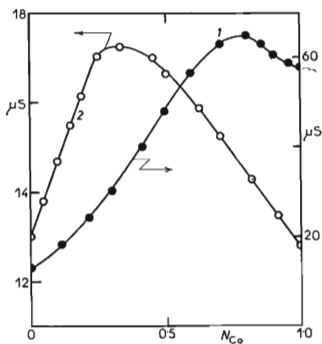
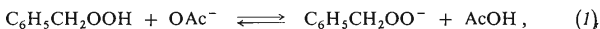


FIG. 6

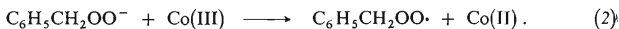
Effect of Sodium Acetate on Conductance of  $4.37 \cdot 10^{-2}\text{M-CoBr}_2$  in (1) Acetic Acid and (2) a Mixture of  $\text{CoBr}_2$  and Aminoacetic Acid (1 : 2 mol) in Acetic Acid at  $20^{\circ}\text{C}$

The influencing of the reactions catalysed by transition metals by alkali-metal acetates is associated with structural changes of homogeneous metallic catalysts. As can be deduced from the increased conductance and maxima in Fig. 6, sodium acetate in a solution of acetic acid enhanced the formation of ionic forms of the complexes. In the solution containing cobalt dibromide and aminoacetic acid in a molar ratio of 1 : 2 the maximum conductance was measured at a molar ratio of  $\text{Co} : \text{NaOAc} = 1 : 2$ . Fig. 5 shows that also the yield of trimesic acid was highest at this ratio.

Studying the kinetics of decomposition of benzylhydroperoxide by Co(III) acetate, Scott found<sup>4</sup> that sodium acetate inhibited the decomposition from its very start, whereas with cobalt acetate did not affect the reduction rate of benzylhydroperoxide until 3/4 of the hydroperoxide had reacted. The presence of sodium acetate also increased conversion of Co(III) to Co(II) (refs<sup>4,5</sup>). This fact was ascribed to an effect of acetate ions on the reaction



the arising peroxy anions undergoing the consecutive reaction



The promoting effect of sodium acetate on the initial oxidation rate and reduction of Co(III) was interpreted by Kamiya and Kashimo<sup>5</sup> as due to the formation of active cobalt species with a coordination number higher than 3 by coordination of the acetate anions with the cobaltic cations. The anionic Co(III) complexes<sup>6</sup> are formed by the

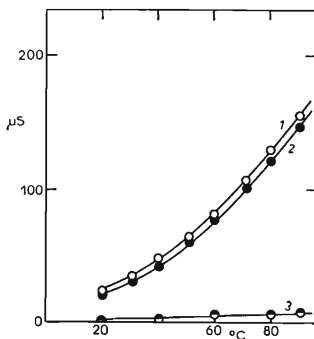
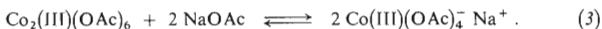


FIG. 7  
Conductance of  $4.37 \cdot 10^{-2} \text{M}$  Sodium Acetate (1) and Ammonium Acetate (2) in Acetic Acid in Relation to Temperature.

Curve 3 corresponds to acetic acid itself.

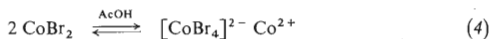


reaction



Under the given reaction conditions they are modified by alkali metal acetates, which produce anionic Co(III) acetates in a dimeric or monomeric form. The difference in catalytic activity between the dimeric and the monomeric forms of the complexes in the oxidation reactions, which may be due to the presence of acetate ions, was investigated from the kinetic point of view<sup>5,8,12</sup>.

Experiments have shown that in the presence of acetate anions in acetic acid as medium the forms of cobalt bromide complexes were altered too. These changes depended not only on concentration of acetate anions but also on the nature of the corresponding cations<sup>13</sup> (Table IV), which seem to form an outer coordination sphere. Although sodium and ammonium acetates were about equally dissociated, sodium acetate more strongly retarded the oxidation of mesitylene in the initial stage than ammonium acetate (Fig. 1). The function of a cation also shows itself in equilibrionic changes of the complexes<sup>14-16</sup>, even with complexes activated by certain nitrogen compounds, such as hexamethylenediamine and aminoacetic acid. The shift of equilibrium toward tetrahedral ionic complexes  $\text{CoBr}_3^-$  and  $\text{CoBr}_4^{2-}$



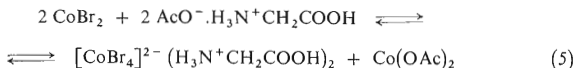
occurs in acetic acid as solvent in the presence of many a nitrogen compound<sup>10</sup>, and also in the presence of acetates, which results in either case in an increased catalytic activity of cobalt bromide complexes (Fig. 3). If the shift in equilibrium is only small,

TABLE V  
Effect of Sodium Acetate on the Oxidation of Mesitylene  
For conditions see Fig. 4.

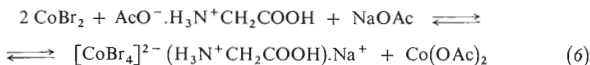
| Activator            | NaOAc<br>M. 10 <sup>2</sup> | Reaction<br>time<br>min | Yield, % mol <sup>b</sup> |       |      |
|----------------------|-----------------------------|-------------------------|---------------------------|-------|------|
|                      |                             |                         | 3,5-DMB                   | 5-MIP | TMA  |
| Picolinic acid       | 0                           | 265                     | 50.6                      | 10.8  | 2.1  |
|                      | 7.3                         | 250 <sup>a</sup>        | 7.1                       | 52.7  | 3.9  |
| Hexamethylenediamine | 0                           | 190 <sup>a</sup>        | 0.1                       | 31.3  | 36.8 |
|                      | 7.3                         | 190                     | 0                         | 4.9   | 82.2 |

<sup>a</sup> The oxidation still continued. <sup>b</sup> See Table I.

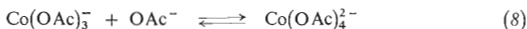
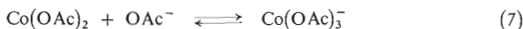
*e.g.* with aminoacetic acid,



or with hexamethylene in a low concentration, the cobalt bromide complex is activated only partially (Fig. 4 and Table V). Further shift in equilibrium, and thus a further increase in activity, can be effected by an addition of alkali metal acetates. The higher conductance (Fig. 5) and the electron spectra of such solutions suggest the reaction



because equilibrations between sodium and cobalt acetates in acetic acid, which produce ionic forms of complexes (7) and (8),



occur under conductance measurements conditions to a slight extent only<sup>17</sup>.

In the presence of strong chelating agents, such as *o*-phenanthroline, 2,2'-dipyridyl and others, the reaction with cobalt bromide does not produce any ionic structures, but the bromide ligands are displaced by the linkage of cobalt in the chelate. The result is a catalyst of weak activity, which is not influenced even by the presence of acetates (Fig. 4).

Apart from their effect on activity and selectivity of cobalt bromide catalysts, the acetates influenced the contents of aldehyde acids (Table I), as well as purity and colour of the final oxidation products, *i.e.* aromatic acids<sup>18,19</sup>.

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