EFFECT OF ALKYLAMINES, ALKANOLAMINES, DIAMINES, AND AMINO ACIDS ON THE ACTIVITY OF COBALT BROMIDE CATALYSTS*

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Effect of alkylamines, alkanolamines, aliphatic diamines, and amino acids on the catalytic activity of cobaltous bromide in the oxidation of mesitylene was examined. At the reaction temperature of 140°C, the size and number of alkyl chains does not practically affect the properties of the corresponding amine types (except for amino acids) in contrast to the attached functional groups. At temperatures of about 100°C, the effect of amines depends on the number of 2-hydroxyethyl groups and increases in the order triethanolamine < diethanolamine < monoethanolamine. The catalyst activity and selectivity depends on the ratio of the amine to cobalt. In the case of triethanolamine, maximum yields of trimesic acids are obtained when this ratio is 1 : 1 to 2 : 1; higher concentrations of the amine result in a decreased selectivity of the reaction and deactivation of the catalyst. The effect of amino acids markedly depends on the type, size, and number of substituents.

The preceding paper of this series has demonstrated the highly positive effect of triethanolamine on the activity of cobalt bromide catalysts in oxidations of alkylated aromatic hydrocarbons to the corresponding benzenecarboxylic acids. Since the catalytic activity increased several times, it was possible to decrease the concentration of the bromide ions in the system without any effect on the yields of aromatic acids. The high activity of the catalyst is ascribed to the effect of ligands coordinated to cobalt. It has been shown that a suitable choice of transient metal ligands may affect both the activity and selectivity of oxidation catalysts.

In the present paper we wish to report the effect of various amines such as aliphatic amines, alkanolamines, diamines, and amino acids on the activity of cobalt bromide catalysts in oxidations of mesitylene in acetic acid.

EXPERIMENTAL

Materials. Mesitylene (99·3%) was washed with sulfuric acid, dried, and distilled. Triethylamine, n-hexylamine, methyldibutylamine, monoethanolamine, diethanolamine, monoiso-

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propanolamine, diisopropanolamine, and ethylene diamine were purified by distillation. Triethanolamine and triisopropanolamine were purified by crystallisation. Cobaltous acetate and cobaltous bromide were used in the form of the tetrahydrate and hexahydrate, resp. The [CoBr$_2$.(TEA)$_2$] complex of cobaltous bromide with triethanolamine was prepared according to ref.[1]. The remaining chemicals were of Analytical Grade purity and were used without any previous purification.

Oxidation. Oxidations at atmospheric pressure have been examined in an all-glass apparatus of the same type as reported in previous papers. Reactions at elevated temperatures and pressures were performed in a 50 ml stainless steel autoclave. Inner walls of the reactor were protected by glass to exclude the wall effect. The reactor was virogously shaken in an oil bath maintained at the required temperature. The shaking rate was adjusted in such a manner not to affect the rate of oxygen uptake. Prior to the reaction, the whole system was flushed with oxygen and then oxygen was introduced under pressure. After equalisation of the temperature (5 min), the vibrator was started and the oxidation begun. The apparatus ran at constant pressure and the oxygen volume taken up by the reaction was measured. About 10 ml of the solution was used per each experiment. When the oxidation was completed, the autoclave was cooled down, the pressure released, and the mixture of products set aside for 4 h to deposit crystals. The solid was collected with suction, washed with water, and dried. The material was weighed and an aliquot esterified

TABLE I

Effect of Aliphatic Amino Compounds on Oxidation of Mesitylene
140°C, 11 atm, [mesitylene] 1·23M, [CoBr$_2$.6 H$_2$O] 1·82 . 10^{-2}M, [Co]/[amino compound] 1 : 2.

Amino compound	Reaction time min	Yield, mol %		
		3,5-Dimethyl-benzoic acid	5-Methyliso-phthalic acid	Trimesic acid
—	210[a]	53·9	8·4	1·2
Ammonium acetate	230[a]	1·1	64·9	8·9
n-Hexylamine	265	—	7·8	77·1
Triethylamine	225	—	6·9	77·7
Methyldibutylamine	245	—	5·2	79·6
Tetramethylammonium	370[b]	—	5·9	81·3
Monoethanolamine	225	—	5·9	80·6
Diethanolamine	215	—	5·6	79·4
Triethanolamine	210	—	6·7	78·7
Monoisopropanolamine	210	—	5·1	78·5
Diisopropanolamine	200	—	4·9	79·6
Triisopropanolamine	210	—	5·6	78·8
[CoBr$_2$(TEA)$_2$]	170[c]	—	4·9	83·5
Ethylene diamine	130	—	6·2	77·9
Hexamethylene diamine	130	—	5·9	78·6

[a] The oxidation continued; [b] 1·82 . 10^{-2}M-(CH$_3$COO)$_2$Co . 4 H$_2$O was used as the catalyst; [c] This complex was used as the catalyst.

with diazomethane. The analysis was effected by gas chromatography with the use of internal standard as described previously[2].

Electronic spectra were recorded on a Specord apparatus (Carl Zeiss, Jena, German Democratic Republic).

RESULTS

The effect of aliphatic amino compounds on the activity of cobalt bromide catalysts was examined on the oxidation of mesitylene in acetic acid as solvent. The effect of various amino compounds on the reaction rate and formation of aromatic acids may be seen from Fig. 1 and results summarised in Table I. In the presence of the amino compounds tested, reaction rates and yields of polycarboxylic acids are considerably increased. It may be inferred from the data that the size and number of alkyl chains does not practically affect the catalytic activity of the corresponding amine types under the present reaction conditions. The activity is however markedly influenced by functional groups attached to these amino compounds. In the case of ammonia in acetic acid as solvent, the virtual active substance is ammonium acetate.
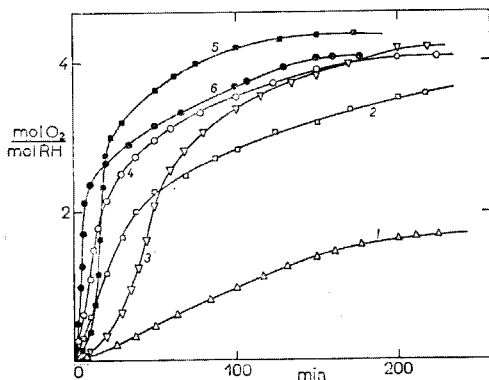

FIG. 1

Effect of Aliphatic Amino Compounds on Oxidation of 1·23M Solution of Mesitylene in Acetic Acid at 140°C and 11 atm under Catalysis of $1·82 . 10^{-2}$ M-$CoBr_2 . 6 H_2O$ (concentration of amino compounds, $3·65 . 10^{-2}$ M)

1 Without amines; *2* ammonium acetate; *3* alkylamines; *4* alkanolamines; *5* diamines; $[CoBr_2(TEA)_2]$ in concentration of $1·82 . 10^{-2}$ M was used as the catalyst.

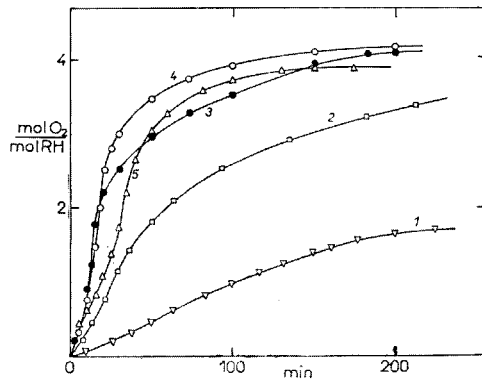FIG. 2

Dependence of the Oxidation Rate on the Concentration of Triethanolamine

140°C, 11 atm, [mesitylene] 1·23 mol/l, $[CoBr_2]$ $1·82 . 10^{-2}$ mol/l, [TEA] *1* 0; *2* $9·1 . 10^{-3}$ M; *3* $1·82 . 10^{-2}$ M; *4* $7·3 . 10^{-2}$ M; *5* $1·46 . 10^{-1}$ M.

With the use of mono-, di-, and triethanolamines at 100°C and atmospheric pressure, the oxidation rate of mesitylene was dependent upon the number of 2-hydroxyethyl groups and increased in the order triethanolamine < diethanolamine < < monoethanolamine. In the presence of triethanolamine, the reaction rate was several times faster than in its absence; it was however not possible to increase this acceleration by the addition of the otherwise more active monoethanolamine.

As shown by the present experiments, the activity of the resulting catalyst also depends on the ratio of the amine to cobalt (Fig. 2). The oxidation rates increase several times with the increasing concentration of the amine. Evaluation of the catalyst activity on the basis of reaction rate values only might lead to incorrect conclusions due to non-selective reactions in the presence of higher amine concentrations. In the oxidation of mesitylene in acetic acid, that catalyst proved as the most selective which is formed with the use of the triethanolamine–cobalt molar ratio of 1 : 1 to 2 : 1. As it may be seen from Fig. 3, such a ratio results in maximum yields of trimesic acid. With the use of higher ratios, the reaction rates increase at expense of the trimesic acid formation. With the triethanolamine–cobalt molar ratios of 0 : 1, 1 : 1, and 8 : 1, the yields of trimesic acid are 1·2 mol% (*i.e.* in the absence of trimethanolamine), 77·9 mol %, and only 18·9 mol %. In the last mentioned case, the reaction comes spontaneously to a standstill in spite of the fact that the
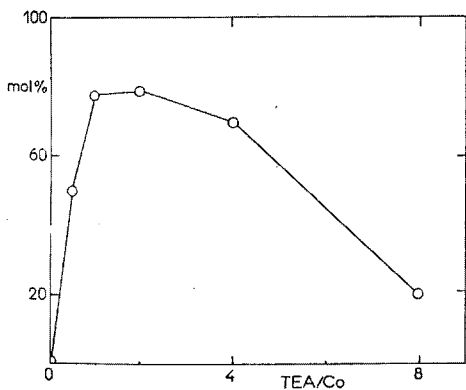

FIG. 3

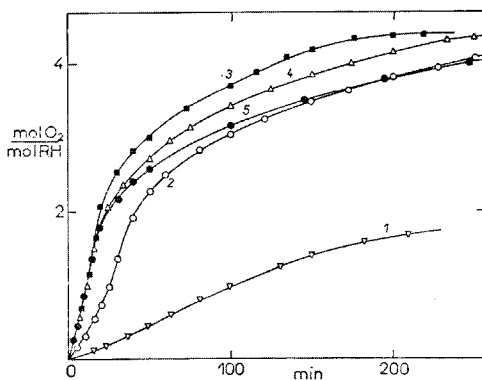Dependence of the Yield of Trimesic Acid on the TEA : Co Ratio

FIG. 4

Effect of α-Amino Acids on Oxidation of 1·23M Solution of Mesitylene in Acetic Acid at 140°C and 11 atm under Catalysis of $1·82 . 10^{-2}$M-CoBr$_2$. 6 H$_2$O ([Co]/[α-amino acid] 1 : 2)

1 Without amino acid; *2* aminoacetic acid; *3* α-alanine; *4* α-aminobutyric acid; *5* isoleucine.

system contains 48·5 mol % of 5-methylisophthalic acid susceptible to a further oxidation. Noteworthy, an almost equal amount of oxygen is consumed in reactions performed in the presence of the last two ratios mentioned. High concentrations of the amine obviously bring about a decreased reaction selectivity as well as a lowered catalyst selectivity resulting in a spontaneous suppression of the conversion to trimesic acid.

Identical experimental conditions were used in investigations on the effect of amino acids with respect to the activity of the cobalt bromide catalyst. Simple derivatives were applied, mainly α-amino acids substituted by alkyl, carboxyalkyl, and aminoalkyl residues (Figs 4 and 5). The effect of these derivatives on the oxidation rate and yield of aromatic acids (Table II) is considerably more dependent upon the type and size of substituents than in the above mentioned cases. Aminoacetic acid brings about a considerable increase of the oxidation rate but the amount of the reacted oxygen is at expense of the selectivity. In spite of the fact that the oxygen uptake is almost the same as with other derivatives of α-amino acids, only half a yield of 1,3,5-benzenetricarboxylic acid is obtained. Longer or branched alkyl chains of the amino acid result in longer reaction periods of time and decreased yields of the aromatic acid, probably because of the lowered stability of the appropriate amino acids towards oxidation. When the aminoacetic acid is substituted with carboxyalkyl or aminoalkyl groups, the reaction rates decrease under particular concentrations. When compared with aminoacetic acid, the reaction selectivity and the yields of trimesic acid increase. As shown on comparison of the aspartic acid and α-aminoadipic acid effects, lengthening of the alkyl chain in the carboxyalkyl group results in a decrease of the negative influence of the carboxylic groups leading to increased rates and yields. A particularly detrimental effect of carboxyalkyl groups may be observed when they are attached to an amino group, *e.g.*, in nitrilotriacetic acid. In those cases, the catalyst is deactivated owing to the formation of chelates. A similar
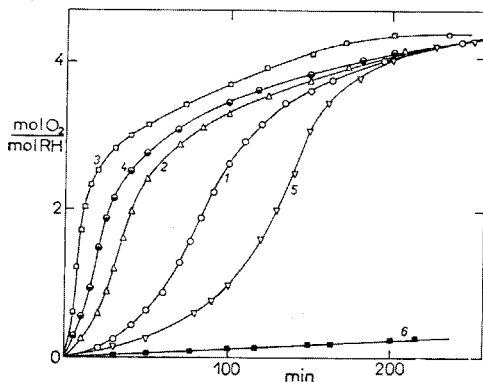

FIG. 5

Effect of Substituted Amino Acids on Oxidation of Mesitylene (for conditions see Fig. 2)
   1 Aspartic acid; *2* α-aminoadipic acid; *3* β-alanine; *4* β-phenylalanine; *5* L-lysine; *6* nitrilotriacetic acid.

effect is also exhibited by some amino acids substituted by aminoalkyl groups. Such compounds with several donor atoms are able to comprise the metal catalyst into a chelate as confirmed by a considerable decrease of the reaction rate and selectivity with increasing concentration of L-lysine with respect to cobalt. Thus, as it may be inferred from Table II, an increase of the L-lysine concentration from $9 \cdot 1 \cdot 10^{-3}$M to $3 \cdot 65 \cdot 10^{-2}$M corresponding to the molar ratio L-lysine–cobalt of $0 \cdot 5 : 1 \cdot 0$ and $2 : 1$, resp., results in a decreased reaction rate, longer reaction time, and lower yield of trimesic acid. On the other hand, when the cobalt bromide catalyst is activated with hexamethylene diamine under otherwise the same experimental conditions, the oxidation rates increase and the yield of trimesic acid becomes higher ($78 \cdot 6$ mol %). L-Lysine differs from hexamethylene diamine particularly in the presence of a carboxylic group; when compared with amino acids substituted by carboxyalkyl groups, the effect on the activity and selectivity of the $CoBr_2$ catalyst is of a different character.

DISCUSSION

As it has been confirmed by experiments, some nitrogenous compounds react with cobaltous bromide with the formation of complexes, the catalytic activity of which is several times higher than of cobaltous bromide alone. It appears of interest to examine the structure and composition of the catalytically active forms of the
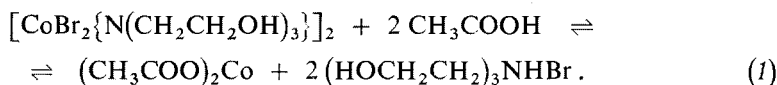
TABLE II

Effect of Amino Acids on the Yield of Aromatic Acids (for conditions see Table I)

Amino acid	Reaction time min	Yield, mol %	
		5-Methyliso-phthalic acid	Trimesic acid
Aminoacetic acid	250^a	$21 \cdot 9^b$	$39 \cdot 5$
α-Alanine	205	$4 \cdot 3$	$8 \cdot 14$
α-Aminobutyric acid	260	$5 \cdot 2$	$79 \cdot 3$
Isoleucine	300	$5 \cdot 9$	$73 \cdot 5$
Aspartic acid	270	$4 \cdot 8$	$74 \cdot 4$
α-Aminoadipic acid	300	$5 \cdot 6$	$78 \cdot 3$
L-Lysine	285	$4 \cdot 1$	$63 \cdot 9^c$
Nitrilotriacetic acid	200^a	—^{d}	—
β-Alanine	230	$4 \cdot 5$	$78 \cdot 5$
β-Phenylalanine	270	$4 \cdot 2$	$75 \cdot 2$

^{a} The oxidation continued; ^{b} 0·3 mol % of 3,5-dimethylbenzoic acid; ^{c} at the L-lysine concentration of $9 \cdot 1 \cdot 10^{-3}$M and reaction time of 230 min, the yield of trimesic acid was 79·9 mol %; ^{d} 0·6 mol % of 3,5-dimethylbenzoic acid.

resulting complexes and to propose the mechanism of action of these nitrogenous compounds. As it may be seen from Fig. 1, the $[CoBr_2(TEA)_2]$ complex exhibits a high catalytic activity. In the solid state, this complex possesses an intramolecular structure with a cobalt-nitrogen coordination bond[1,3]. Owing to the bond geometry, the triethanolamine molecule exists in a specific shape, the cobalt ions lying approximately in the plane of three oxygen atoms. In the case of diethanolamine or monoethanolamine, binuclear or polynuclear complexes are formed with cobaltous bromide[4−6].

In a polar medium, the coordination sphere is to a lesser or greater extent affected by solvent molecules, an equilibrium being formed. The structure of cobaltous bromide complexes with amines in solutions therefore differs from that one in the solid state. Thus, *e.g.*, when the $[CoBr_2(TEA)_2]$ complex is added into acetic acid, the solution turns pink and deposits a white insoluble precipitate. As indicated by analysis, the precipitate is triethanolammonium bromide which is formed by the following reaction:

$$[CoBr_2\{N(CH_2CH_2OH)_3\}]_2 + 2\,CH_3COOH \ \rightleftharpoons$$
$$\rightleftharpoons \ (CH_3COO)_2Co + 2\,(HOCH_2CH_2)_3NHBr. \qquad (1)$$
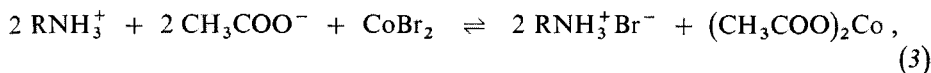
As confirmed by spectra in the visible region, cobaltous acetate remains in solution and the equilibrium of this reaction is shifted to the right at lower temperatures. Provided that reaction (1) takes place to a sufficient extent at the reaction temperature of the oxidation, cobaltous acetate and triethanolammonium bromide should assert themselves as catalytically active components. It is well known that cobaltous acetate is a poorly active catalyst of oxidations of alkylated aromatic hydrocarbons. The ammonium compounds as catalysts of oxidations, do not almost accelerate the oxidation[−7,9]. Some other compounds must therefore operate in the function of a catalytically active complex. Such compounds might be formed by interaction of the two components under the reaction conditions. As it may be seen from Table I, a complex of a considerably high activity is formed by reaction of tetramethylammonium bromide with cobaltous acetate in acetic acid.

Alkylamines, alkanolamines, aliphatic diamines, and some amino acids as relatively strong bases undergo reaction (2) in acetic acid as solvent. Reaction (2) is strongly shifted to the right.

$$R—NH_2 + CH_3COOH \ \rightleftharpoons \ R—NH_3^+.^-OOCCH_3 \ \rightleftharpoons$$
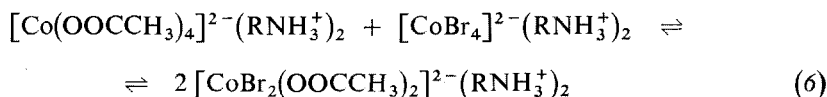$$\rightleftharpoons \ R—NH_3^+ + CH_3COO^- \qquad (2)$$
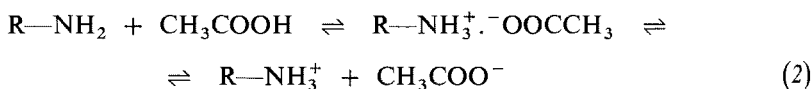
After the addition of the above amino compounds into the solvent, equilibrated amounts of the corresponding ammonium salts are therefore formed. When cobaltous

acetate is also present in the solution, reaction (2) is accompanied by subsequent reactions (3) and (4) and the like:

$$2 \, RNH_3^+ + 2 \, CH_3COO^- + CoBr_2 \; \rightleftharpoons \; 2 \, RNH_3^+Br^- + (CH_3COO)_2Co \, ,$$

$$(3)$$

$$2 \, RNH_3^+Br^- + CoBr_2 \; \rightleftharpoons \; [CoBr_4]^{2-}(RNH_3^+)_2 \, ,$$ (4)

The existence of reactions (3) and (4) was established by conductivity measurements and spectra in the visible region. At room temperature, only the alkylamines and aliphatic diamines react in this way, but not the alkanolamines and some amino acids[2]. In the last mentioned cases, only the corresponding ammonium bromide compounds are formed while the reaction (4) does not almost occur. At temperatures similar to those applied in oxidations, reaction (4) also takes place even with alkanolamines and amino acids. Spectra of the solution exhibit bands of tetrahedric $[CoBr_4]^{2-}$ complexes[10]. Since equilibrium reactions are involved, the formation of complexes some of which are catalytically active, also depends upon the ratio of the appropriate amino compound to cobaltous bromide. As it may be inferred from Fig. 3, the activity of the catalytic system decreases in the presence of excess amine. In accordance with reaction (2), such conditions result in an increased concentration of acetate anions which are capable of affecting the course of the oxidation[11] and reactions leading to the formation of the catalytically active complex. The increased concentration of acetate ions favours the formation of tetrahedric anionoid complexes[12,13] and/or complexes with a heterogeneous coordination sphere.

$$2 \, RNH_3^+ + 2 \, CH_3COO^- + (CH_3COO)Co \; \rightleftharpoons \; [Co(OOCCH_3)_4]^{2-}(RNH_3^+)_2$$

$$(5)$$

$$[Co(OOCCH_3)_4]^{2-}(RNH_3^+)_2 + [CoBr_4]^{2-}(RNH_3^+)_2 \; \rightleftharpoons$$

$$\rightleftharpoons \; 2 \, [CoBr_2(OOCCH_3)_2]^{2-}(RNH_3^+)_2$$ (6)

Despite the involvement of acetic acid (capable of coordination), a complex might also be formed under the experimental conditions from the nitrogeneous compound present in the system and cobaltous bromide, namely, by mediation of the nitrogen atom in neutral form. Complexes of this type are indicated by NMR spectra of cobalt complexes with ethylene diamine in deuterated acetic acid as solvent at mild temperatures[14]. As it follows from Fig. 1, such a type might be indicated by a moderately increased catalytical activity of the $[CoBr_2(TEA)_2]$ complex in comparison to a catalyst prepared from the corresponding amounts of cobaltous bromide and triethanolamine.

Another problem in elucidation attempts of the activation mechanism of the nitro-

gen-containing substances is connected with the formation of chelate structures. A great number of the present test substances with two or more donor atoms, such as trialkanolamines, diamines, and amino acids is capable of forming chelates. It has been however concluded from examinations of the particular amine types with respect to their effect on activation of cobaltous bromide catalysts at the temperature of 140°C that in acetic acid as solvent no chelates (or to a small extent only) are formed except for the case of diamines and some very strong chelate agents such as nitrilotriacetic acid. Nitrogen-containing compounds of this type form the complex with cobaltous bromide by mediation of the nitrogen atom while the other donor, the oxygen atom, contributes to the formation of the chelate to a negligible extent only despite its ability to participate to a certain extent on the bond formation with the cobaltous ion. This behaviour is due to the considerably different affinity of the mentioned donors to the formation of a bond with the cobaltous ion. The extent of this effect depends on reaction conditions. As it may be seen from Fig. 1, there is no difference at the temperature of 140°C in effects of the mono-, di-, and triethanolamines. When the reaction temperature was lowered to 100°C, the effect of the particular ethanolamines was different. A lowest activation effect was observed in the case of triethanolamine which is able to form chelate structures.

Formation of chelate structures cannot be excluded even in the case of aliphatic diamines. As shown by experiments with various concentrations of L-lysine, there is in this special case even at the temperature of 140°C a high probability of the chelate formation. Also the strong chelate-forming agents such as nitrilotriacetic acid or ethylene diamine tetraacetic acid are able to form chelates in the present case and thus deactivate the catalyst. In the case of other amino acids, the chelate formation hardly represents the dominant reaction since only small differences have been observed in activation effects of the α-amino and β-amino acids; notwithstanding, there is a marked difference in the stability of the corresponding chelates of α-aminoadipic acid or aspartic acid and L-lysine due to a different basicity. Any formation of a chelate in the reaction medium containing the amino acid and cobaltous bromide would be accompanied by liberation of the bromide ligand by a substitution reaction. The catalytic effect of the bromide alone in oxidations is known to be small[15]. As shown in an earlier paper of this series, the complex activated by nitrogen-containing compounds must contain the catalytically active cobalt–bromine bond. To keep this bond intact, the amino acid must be bound to cobaltous bromide through the nitrogen atom; the carboxyalkyl residue affects both the donor and sterical properties of the resulting complex.

In conclusion, the examined amines (except for some amino acids) affect the catalytic activity of cobaltous bromide in the oxidation of mesitylene in acetic acid at the temperature of 140°C in the following order: aliphatic diamines > alkanolamines > > amino acids, alkylamines > ammonium acetate.

REFERENCES

1. Sen B., Dotson R. L.: J. Inorg. Nucl. Chem. *32*, 2707 (1970).
2. Hronec M., Přikryl R., Veselý V.: Chem. Zvesti *29*, 443, (1975).
3. Follner H.: Monatsh. Chem. *102*, 245 (1971).
4. Evreev V. N., Golub V. A.: Zh. Neorg. Khim. *18*, 739 (1973).
5. Gerasenkova A. N., Udovenko V. V.: Zh. Neorg. Khim. *17*, 444 (1972).
6. Udovenko V. V., Tanchik V. M.: Ukr. Khim. Zh. *38*, 141 (1972).
7. Bredereck H., Wagner A.: Angew. Chem. *70*, 503 (1958).
8. Ohkubo K., Yamabe T.: Bull. Jap. Petrol. Inst. *12*, 130 (1970).
9. Ohkubo K., Yamabe T., Fukui K.: Bull. Chem. Soc. Jap. *42*, 2220 (1969).
10. Cotton F. A., Goodgame D. M. L., Goodgame M.: J. Amer. Chem. Soc. *83*, 4690 (1961).
11. Scott E. J. Y.: J. Phys. Chem. *74*, 1174 (1970).
12. Proll P. J., Sutcliffe L. M.: J. Phys. Chem. *65*, 1993 (1961).
13. Lande S. S., Kochi J. K.: J. Amer. Chem. Soc. *90*, 5196 (1968).
14. Chester W. A.: J. Inorg. Nucl. Chem. *33*, 3471 (1971).
15. Kamiya Y., Nakajima T., Sakota K.: Bull. Chem. Soc. Jap. *39*, 2211 (1966).

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