

THE EFFECT OF AROMATIC N-OXIDES AND N-ACETYLATED COMPOUNDS ON THE ACTIVITY OF COBALT BROMIDE CATALYSTS*

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N-acetylated nitrogen compounds, amides and N-methylpyrrolidone did not activate cobalt-bromide catalysed oxidation of mesitylene at 140°C. In the presence of N-acetylacetyl derivatives and aromatic N-oxides under the same conditions the catalytic activity was markedly increased. The steric effect of the aromatic rings of N-oxides on the course of oxidation was very little. If the molecule of a nitrogen compound also contained a sulphur atom the catalyst was completely deactivated.

To enhance the activity of cobalt bromide catalysts in the oxidation of alkylaromates in acetic acid we previously studied¹⁻⁴ a number of diverse ligands with nitrogen donor atoms. For the sake of systemicity the reaction and concentration conditions were identical or very similar; thus we obtained a more complex information on their action and the main factors influencing this action. Except for some specific cases the results of these studies showed that the effect of nitrogen ligands on the activity of cobalt bromide catalysts was highly positive, unless very stable chelates were formed. Very efficacious ligands, among others, were, N,N-diethylaniline, some other tertiary amines and aliphatic diamines.

Further measurements, described in the present paper, were carried out to re-investigate the effects of N-acylated compounds and aromatic N-oxides on the activity of cobalt bromide catalysts.

EXPERIMENTAL

Reagents. Pyridine N-oxide (I), 2,6-lutidine N-oxide (II), quinoline N-oxide (III) and isoquinoline N-oxide (IV) were prepared by oxidation of the corresponding nitrogen compounds with hydrogen peroxide⁵⁻⁷. N-Acetylanthranilic acid and N,N'-tetraacetylenethylenediamine were prepared by acetylation⁸; N-acetylacetyl anthranilic acid and N,N'-diacetylacetyl ethylenediamine by reported procedures⁹. Complexes $\text{CoBr}_2(\text{PNO}_3)_3$, CoBr_2Py_2 and $\text{CoBr}_2(\text{QN})_2$ were obtained as previously described^{10,11}. The other chemicals were of A.G. purity and were used directly.

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Spectral measurements. Electron spectra of solid complexes were measured in a Specord apparatus (Zeiss, Jena, G.D.R.), using the "null method". IR spectra were measured in an apparatus Perkin-Elmer 225. The samples, ground in a nujol paste, were measured in KBr plates. Conductance was measured as previously described^{1,2}.

In the mole fraction

$$N_{\text{CoBr}_2} = n_{\text{CoBr}_2} / (n_{\text{CoBr}_2} + n_x)$$

n_x denotes mol of the corresponding nitrogen compound.

The oxidation procedure and analysis of the reaction mixture were described previously⁴.

RESULTS AND DISCUSSION

Most nitrogen compounds with a carbonyl group on the nitrogen atom have very similar effects on cobalt-bromide catalysed oxidation of alkylaromates. As can be seen from Figs 1 and 2, amides, N-methylpyrrolidone and N-acetyl derivatives at 140°C had practically no influence on the oxidation of mesitylene. Even nitrogen compounds

TABLE I

Yield of Trimesic Acid in Relation to Nitrogen Compound Used for Activation

Conditions: 140°C, 11 atm. Molar concentrations: mesitylene 1.23, $\text{CoBr}_2 \cdot 6 \text{H}_2\text{O}$ $1.82 \cdot 10^{-2}$, nitrogen compound $3.65 \cdot 10^{-2}$.

Experiment	Nitrogen compound	Reaction time min	Yields of aromatic acids mol%	
			5-methylisophthalic	trimesic
1	—	210 ^a	8.4	1.2
2	urea	210 ^a	54.9	7.9
3	N,N'-diphenylurea	315	7.2	70.9
4	N,N'-tetraacetylenediamine	210 ^a	53.6	2.7
5	N,N'-diacetylacetonylethylene diamine	220	4.1	73.6
6	N-acetylanthranilic acid	250 ^a	54.3	2.2
7	N-acetylacetonylanthranilic acid	270	5.1	75.3
8	ethylene diamine	130	6.2	77.9
9	anthranilic acid	310	4.3	77.8
10	pyridine N-oxide	200	4.7	74.0
11	2,6-lutidine N-oxide	280	6.3	71.9
12	quinoline N-oxide	200	3.9	74.2
13	isoquinoline N-oxide	200	4.1	75.8
14	$\text{Co-Br}_2 (\text{C}_5\text{H}_5\text{NO})_3$	285 ^b	4.4	76.1

^a Oxidation still continued, ^b concentration of the complex $1.48 \cdot 10^{-2}$ mol/l.

with high activation effects (*e.g.* ethylene diamine) lost them upon acetylation. Activation was also observed with urea, its N,N' -diphenyl derivative was active even more. The effects of N -acetylacetyl derivatives of amines on the catalytic activity of cobalt dibromide were the same as those of the non-substituted amines.

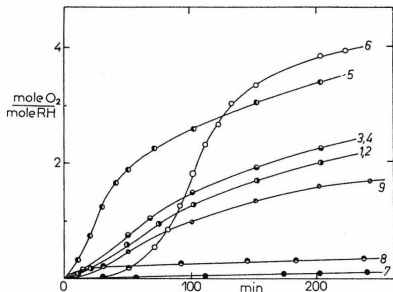


FIG. 1

Effect of N -Substituted Compounds and Thiocyanates on Oxidation of Mesitylene in Acetic Acid (1.23 mol/l)

Conditions: 140°C , 11 atm, $[\text{CoBr}_2 \cdot 6\text{H}_2\text{O}] = 1.82 \cdot 10^{-2}$ mol/l, concentration of nitrogen compounds $3.65 \cdot 10^{-2}$ mol/l. 1 Acetamide, 2 acetanilide, 3 dimethylformamide, 4 N -methylpyrrolidone, 5 urea, 6 N,N' -diphenylurea, 7 thiourea, 8 KSCN, 9 CoBr_2 alone.

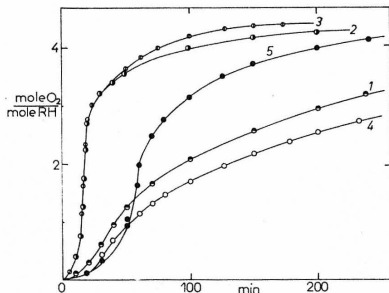


FIG. 2

Effect of N -Acetyl and N -Acetylacetyl Derivatives of Ethylene Diamine and Anthranilic Acid on Oxidation of Mesitylene

Conditions as in Fig. 1. 1 N,N' -Tetraacetylene diamine, 2 N,N' -diacetylacetyl ethylene diamine, 3 ethylene diamine, 4 N -acetyl anthranilic acid, 5 N -acetylacetyl anthranilic acid.

The inactivity of amides and N-acetylated amines can be explained by inability of these compounds to coordinate with cobalt in acetic acid¹². With urea and its derivatives the steric and the electron-withdrawing effects of the carbonyl group bound to two neighbouring amino groups are weaker; this manifests itself in the

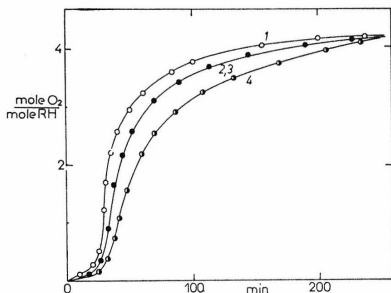


FIG. 3

Effect of Pyridine N-Oxide Derivatives on Oxidation of Mesitylene

Conditions as in Fig. 1. 1 Pyridine N-oxide, 2 quinoline N-oxide, 3 isoquinoline N-oxide, 4 2,6-lutidine N-oxide.

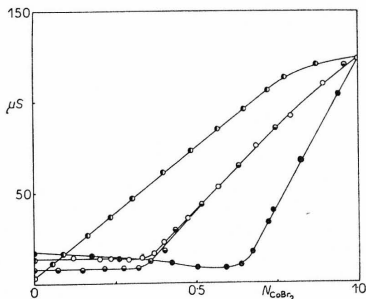


FIG. 4

Conductance Change (μS) vs Mole Fraction of N_{CoBr_2} in Reaction of Cobalt Dibromide (0.1 mol/l) with: \ominus Pyridine N-oxide, 2,6-Lutidine N-oxide, \circ Quinoline N-oxide, \square Isoquinoline N-oxide, \bullet N,N'-diacetylacetonylethylene Diamine, \blacklozenge N-Acetylacetonylanthrnic Acid at 20 °C

complex formation and in the activating effects. If the carbonyl group is farther, as in N-acetylacetylaminines, the properties of the nitrogen donor atom are not much affected. As can be seen from Fig. 4, N,N'-diacetylacetylamine in acetic acid at 20°C reacted with cobalt dibromide in the same way as ethylene diamine¹², forming a complex with it in a molar ratio of 1 : 2. N-Acetylacetyl anthranilic acid, owing to its internal hydrogen bonds as in anthranilic acid itself, did not react with cobalt dibromide under the conditions of the conductance measurements. In the reaction conditions, however, the complex gets formed, whereby the catalytic activity increases.

Attention was also paid to the effect of aromatic N-oxides. These "oxo-ligands" are coordinated to metallic ions through oxygen¹³⁻¹⁶. Fig. 3 shows that pyridine N-oxide (*I*) and some of its derivatives are efficient activators of cobalt-bromide catalysts. This effect is weaker than that of pyridine itself, but stronger than that of pyridine derivatives, whose activating effect is given mainly by the steric factors of the ligands⁴. Thus the considerable decrease in activity in the series pyridine < < isoquinoline < 2,6-lutidine < quinoline becomes negligible in the case of their N-oxides. This confirms that the aromatic rings of N-oxides *I-IV* are no steric hindrance in the formation of metal complexes¹⁶⁻¹⁷.

Spectral studies of the reaction of N-oxide *I* with cobalt dibromide in acetic acid at low concentrations of *I* indicate formation of complexes $[\text{CoBr}_4]$. $\text{Co}(\text{C}_5\text{H}_5\text{NO})_6$. Their electron spectra are very similar to those of the $[\text{CoBr}_4^{2-}]$ complexes, formed by reaction of amines with cobalt dibromide in acetic acid¹². These complexes are structurally similar to complexes $\text{CoBr}_2(\text{C}_5\text{H}_5\text{NO})_3$ in solid state^{16,18}. Conductance measurements (Fig. 4) show that in acetic acid at concentration ratios of *I* : $\text{CoBr}_2 = 2 : 1$ the conductance of the solution was lowest and an insoluble complex was formed. Its electron spectrum in nujol exhibits two intense absorption bands at 16950 cm^{-1} and 20400 cm^{-1} , which are absent in the spectrum of the complex $\text{CoBr}_2(\text{C}_5\text{H}_5\text{NO})_3$. Presence of CoBr_4^{2-} species was not demonstrated. IR spectra revealed N—O stretching vibrations at 1196 cm^{-1} , N—O bend at 831 cm^{-1} , ring deformation at 1600 cm^{-1} and revealed presence of acetate ligands^{6,7,19}. Complexes of low conductance are also formed in alcoholic solutions at low concentrations of *I*. They are assumed to give rise to polynuclear complexes (in various stoichiometric ratios), which are well known with N-oxides¹⁶.

By studying a great number of nitrogen compounds it has been found that activation of cobalt bromide catalysts, at constant concentrations and experimental conditions, depends mainly on geometry of the nitrogen compound. Blocking the nitrogen atom which forms a bond with the central metal atom reduces the activation effect⁴. The basicity and the activation effect of amines do not seem to be related²⁰. Besides strong chelating agents with N,N or N,O donors, compounds containing an atom with a higher affinity to cobalt than that of nitrogen are also unsuitable for the activa-

tion. Thus potassium thiocyanate or thiourea coordinates into a complex through the sulphur atom and completely inactivates the catalyst (Fig. 1).

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