INFLUENCE OF NITROGEN LIGANDS ON SYNERGIC EFFECT OF METAL CATALYSTS IN OXIDATION OF ALKYLAROMATIC COMPOUNDS*

Milan HRONEC, Štefan HOLOTÍK and Ján ILAVSKÝ
Department of Organic Technology,
Slovak Institute of Technology, 880 37 Bratislava

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Synergic effect of metal mixtures Co–Mn, Co–Ce and Co–U in oxidation of 1,2,4- and 1,3,5-trimethylbenzenes dissolved in acetic acid has been studied in dependence of the presence of nitrogen ligands 2,2′,2″-nitrilotrisethanol, 1,6-hexanediamine and pyridine. The complex $CoBr_2Py_2$ and its equimolar mixture with the complex $MnBr_2Py_2$ are highly active in oxidation of alkylaromatic derivatives containing other alkyl than methyl. Their activity has been tested experimentally in oxidations of ethylbenzene, 1,3- and 1,2-dimethylbenzenes, 1-ethyl-4-methylbenzene, (1-methylethyl)benzene, propylbenzene, 1-methyl-4-(1-methylethyl)benzene, dodecylbenzene, 1,3-diethylbenzene and 4-octyl-1,1′-biphenyl.

Activity and selectivity of homogeneous metal catalysts in oxidation reactions of alkylaromatic hydrocarbons can be increased in a number of ways. In many cases this is done by the presence of halogenide ions, coordination with nitrogen compounds[1], or by combined influence of several metals[2–5]. The highest synergic effect is observed with salts of manganese, cerium, zirconium nickel *etc.* Character of influence of the mixed catalysts depends often on the hydrocarbon structure and the metals ratio[6–10]. Reasons of this behaviour are not quite clear. They are ascribed *e.g.* to formation of complexes type Co^{2+}–O–O–Mn^{2+} which are more active in the reaction with hydrocarbon[11] or to increase in chain propagation[9,12,13] by reactions (*1*) and (*2*).

$$\mathrm{Mn(II)Br} + \mathrm{RO_2\cdot} \rightarrow \mathrm{Mn(III)Br} + \mathrm{RO_2^-} \qquad (1)$$

$$\mathrm{Mn(III)Br} \rightarrow \mathrm{Mn(II)} + \mathrm{Br\cdot} \qquad (2)$$

The mixed metal catalysts affect not only the oxidation rate but also distribution of the reaction products and selectivity of the process. These effects are very important from technological viewpoint, as many industrial processes use catalysts containing mixtures of several metals. This communication deals with study of synergic effects of nitrogen compounds which can act as ligands.

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EXPERIMENTAL

Reagents: (1-Methylethyl)benzene, ethylbenzene, propylbenzene, 1,3- and 1,2-dimethylbenzenes, 1,2,4- and 1,3,5-trimethylbenzenes, 1-methyl-4-(1-methylethyl)benzene, 1-ethyl-4-methylbenzene and 1,3-diethylbenzene were of 99% purity and were purified by distillation. Dodecylbenzene contained about 5% admixtures of alkyl-1,2,3,4-tetrahydronaphthalenes and alkyl-2,3-dihydro-1-indenes and was purified by adsorption chromatography on silica gel. 4-Octyl-1,1′-biphenyl (97%) was prepared by alkylation of 1,1′-biphenyl and purified by crystallization. The complexes $CoBr_2Py_2$, $CoBr_2(TEA)_2$, $MnBr_2Py_2$ were prepared by the procedure described previously[1]. The other reagents were analytical grade purity and were used without purification. The oxidation procedure was the same as in the previous communications[1].

Analyses: The oxidation products were analyzed by gas chromatography using a Packard 417 apparatus. Identification of the oxidation side products was carried out by combined gas chromatography and mass spectrometry using a Varian MAT-111 apparatus.

RESULTS AND DISCUSSION

Catalytic properties of mixtures of metal salts and complexes were studied in oxidations of various alkylaromatic hydrocarbons dissolved in acetic acid. In oxidations

TABLE I

Influence of Manganese and Cerium on Cobalt Bromide-Catalyzed Oxidation of 1,3,5- and 1,2,4-Trimethylbenzenes

Reaction conditions: $[RH] = 1\cdot23$ mol dm^{-3}; 1·1 MPa; [metal] : [NaBr] = 4 : 1 (mol); $[N(CH_2CH_2OH)_3] = 3\cdot65$ mol dm^{-3}.

Hydrocarbon	Temperature °C	Reaction time min	Catalyst concentration mol dm^{-3}			Yield of aromatic acid mol%	
			Co . 10^2	Mn . 10^3	Ce . 10^3	dicarboxylic	tricarboxylic
1,3,5-Trimethylbenzene	140	120	3·65	—	—	5·7	82·8
		85	3·29	3·65	—	11·9	70·2
		60	3·29	—	3·65	5·9	83·3
1,2,4-Trimethylbenzene	150	70	3·65	—	—	17·1	60·4
		45	3·29	3·65	—	7·6	67·6
		50	3·29	—	3·65	0·9	90·1
	140	60	3·29	—	3·65	4·1	83·9
	125	170	3·29	—	3·65	17·2	70·3
	150	90[a]	3·29	—	3·65	12·1	71·9
		120[b,c]	1·15	—	1·82	17·8	53·2

[a] NaBr concentration = 2·2 . 10^{-3} mol dm^{-3}, [b] NaBr concentration = 4·5 . 10^{-3} mol dm^{-3} and $[N(CH_2CH_2OH)_3] = 1\cdot82 \,.\, 10^{-2}$ mol dm^{-3}, [c] the oxidation continued.

catalyzed by cobaltbromide catalysts the highest synergistic effect was observed with mixtures of Co–Mn salts or Co–Ce salts. From Table I it can be seen that synergic effect of these metals depends on the reacting hydrocarbon. Whereas the presence of manganese or cerium salts in oxidations of 1,2,4-trimethylbenzene increases both the oxidation rate and yields of 1,2,4-benzenetricarboxylic acid, in oxidations of 1,3,5-trimethylbenzene this effect is not so unambiguous. It must, however, be noted that activity of pure cobalt catalyst is higher due to the presence of nitrogen compound in the reaction system (2,2′,2″-nitrilotrisethanol)[15].

TABLE II

Influence of Nitrogen Compounds on Synergism of Metals in Oxidation of 1,2,4-Trimethylbenzene

Reaction conditions: [RH] = $1 \cdot 23$ mol dm^{-3}; $1 \cdot 1$ MPa; [$Co(OAc)_2 . 4 H_2O$] = $3 \cdot 29 \,.\, 10^{-2}$ mol dm^{-3}; [NaBr] = $9 \cdot 1 \,.\, 10^{-3}$ mol dm^{-3}; [$Mn(OAc)_2 . 4 H_2O$] = [$Ce_2(CO_3)_3 . 5 H_2O$] = = [$UO_2(OAc)_2 . 4 H_2O$] = $3 \cdot 65 \,.\, 10^{-3}$ mol dm^{-3}; TEA = 2,2′,2′-nitrilotrisethanol; HMDA = = 1,6-hexanediamine; Py = pyridine.

Catalyst	Nitrogen compound	Temperature °C	Reaction time min	Yield of aromatic acids, mol%		
				dicarboxylic	tricarboxylic	dicarboxybenzyl acetate
Co–Ce	—	125[a]	150	16·1	71·8	0·7
	TEA		170	17·2	70·3	0·1
	Py		300	18·1	72·2	3·7
	HMDA		240	18·9	68·3	0·1
Co–Mn	—	150[b]	20[c]	22·2	53·7	1·0
	TEA		45	7·6	67·6	0·2
	Py		50	1·7	85·3	1·6
Co–U	—		100	42·6	45·5	1·9
	TEA		80	28·1	57·7	2·4
	Py		90	1·1	84·1	6·7
Co	—	150	80[d]	25·7	46·2	0·9
$CoBr_2Py_2$		150[e]	75	0·1	86·3	6·8
$CoBr_2Py_2 : MnBr_2Py_2 = 1 : 1$			65	0·7	85·5	9·6
$CoBr_2Py_2 : MnBr_2Py_2 = 9 : 1$		125[e]	210	0·7	84·1	8·7

[a] Concentration of the amines = $3 \cdot 65 \,.\, 10^{-2}$ mol dm^{-3}; [b] concentration of the amines = $7 \cdot 3 \,.\, 10^{-2}$ mol dm^{-3}; [c] reaction temperature 170°C; concentrations [$Co(OAc)_2 . 4 H_2O$] = $3 \cdot 65 \,.\, 10^{-2}$ mol dm^{-3} and [NaBr] = $1 \cdot 82 \,.\, 10^{-2}$ mol dm^{-3}; [e] concentration of the complex catalyst $1 \cdot 82 \,.\, 10^{-2}$ mol dm^{-3}.

It was found experimentally that synergic effect of metal mixtures is affected substantially by ligands coordinated with the metals. This effect can be seen in Table II (the metal mixtures Co–Mn, Co–Ce and Co–U). For comparison we used identical experimental conditions in spite of the fact that they did not represent the optimum for the individual metal mixtures. Magnitude of the synergic effect was affected by nitrogen ligands increasing substantially activity of the cobaltbromide catalysts[15,16]. 1,2,4-Trimethylbenzene was used as the oxidized substrate, because with this hydrocarbon influence of mixed metal catalysts is the most distinct. From results in Table II it follows that mixtures of Co–Ce catalysts are retarded by the presence of nitrogen compounds under the given conditions, but prolongation of the reaction times does not substantially increase yield of 1,2,4-benzenetricarboxylic acid. Different effect of the mentioned amines can be observed in case of synergism of Co–Mn and Co–U catalysts. Although the oxidation rates are affected but slightly, their activity is substantially increased by action of the nitrogen ligands. In absence of the nitrogen ligands the metal mixtures Co–U do not exhibit synergism, whereas with the mixtures Co–Mn or Co–Ce synergism is already significant. Coordination of the Co–U catalyst with *e.g.* 2,2′,2″-nitrilotrisethanol and especially pyridine results in a higher activity increase than it would correspond to pure cobalt catalyst, *i.e.* the new catalytic system exhibits synergism.

As the highest activation effect was observed in the presence of pyridine, several experiments were carried out with the complex catalyst $CoBr_2Py_2$ or its mixture with $MnBr_2Py_2$. Very high activity of the complexes enables *e.g.* oxidation of 1,2,4-trimethylbenzene at low temperatures, yields of 1,2,4-benzenetricarboxylic acid being (with the complex $CoBr_2Py_2$) equal to those obtained with the most active Co–Ce mixed catalysts at higher temperatures and higher catalyst concentrations.

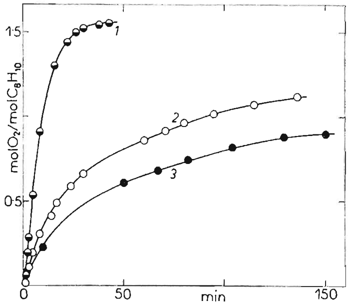

FIG. 1

Oxidation of Ethylbenzene in Acetic Acid at 140°C at 1·0 MPa [ethylbenzene] = 4·14 mol dm^{-3}; [catalyst] = $9·0 . 10^{-3}$ mol dm^{-3} *3* $CoBr_2,6\,H_2O$; *1* $CoBr_2Py_2$; *2* $CoBr_2Py_2$ + + $MnBr_2Py_2$ 1 : 1 (mol).

The highly positive influence of cobaltbromide complexes or synergistic mixtures of metals coordinated with nitrogen ligands is significant also in oxidations of alkylaromatics with alkyls other than methyl ($R \neq CH_3$). This effect is clear in oxidation of ethylbenzene (Fig. 1) or 1-ethyl-4-methylbenzene (Fig. 2), increasing the oxidation rate as well as selectivity and yields of the aromatic acids (Table III). Extension of the alkyl chain and especially its branching lowers selectivity of formation of the aromatic acids and causes untimely deactivation of catalysts (Fig. 3, Table III).

The high selectivity of oxidation of alkylaromatic hydrocarbons catalyzed by cobalt complexes with pyridine ligands is due to active tetrahedral bromocomplexes[17]. The oxidation mechanism involves attack of the hydrocarbon by the bromide ligands which are activated by the presence of pyridine ligand. It means that oxidation of alkylaromatic hydrocarbon begins with the attack by the active bromocomplexes (reaction (*3*)) and not by free bromine atoms.

$$L_XCo(III)Br_Y + RH \rightarrow L_XCo(II)Br_Y + R\cdot \qquad (3)$$

Composition of the oxidation products of 1-ethyl-4-methylbenzene and 1-methyl-4-(1-methylethyl)benzene indicates preferential oxidation of ethyl and isopropyl groups, respectively. Such reactivities were found in reactions going *via* radical mechanisms[18,19]. On the contrary, oxidation of these hydrocarbons with Co(III) acetate in acetic acid in absence of bromides goes by the electron-transfer mechanism involving reversible formation of radical-cation (reactions (*4*) and (*5*)).

$$R—CH_3 + Co(III) \rightleftharpoons R—CH_3^{+}\cdot + Co(II) \qquad (4)$$

$$R—CH_3^{+}\cdot \rightleftharpoons R—CH_2\cdot + H^+ \qquad (5)$$

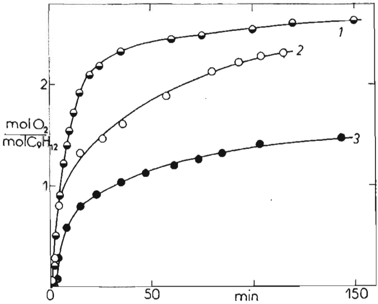

FIG. 2

Oxidation of 1-Ethyl-4-methylbenzene in Acetic Acid at 140°C and 1·0 MPa [1-Ethyl-4-methylbenzene] = 2·5 mol dm^{-3}; [catalyst] = 1·82 . 10^{-2} mol dm^{-3}; *3* $CoBr_2 . 6 H_2O$; *2* $CoBr_2Py_2$; *1* $CoBr_2Py_2 + MnBr_2 . Py_2$ 1 : 1 (mol).

TABLE III

Dependence of Yields of Aromatic Acids on Catalysts Composition in Oxidation of Alkylaromatic Hydrocarbons
Reaction conditions: 140°C, 1·0 MPa.

Hydrocarbon	Catalyst	[RH] mol dm^{-3}	Reaction time min	Yield of the aromatic acid, mol%			
				benzoic	2-,3-,4-methyl- benzoic	1,2-,1,3-,1,4- benzene dicarboxylic	byproducts
Ethylbenzene[a]	$CoBr_2.6\,H_2O$	4·14	140	43·3	—	—	5·1[h]
	$CoBr_2Py_2$	4·14	170	64·7	—	—	4·0[h]
	$CoBr_2Py_2$	4·14	45	81·8	—	—	0·7[h]
Propylbenzene[a]	+	3·56	50	74·9	—	—	12·2[d]
Dodecylbenzene[a]	$MnBr_2Py_2$	1·74	80	15·8	—	—	—[i]
(1-Methylethyl)benzene[a]	1 : 1	3·20	50	0	—	—	53·2[e]
1-Ethyl-4-methylbenzene[b]	$CoBr_2.6\,H_2O$	2·50	145	—	42·7	26·9	5·1[j] + 0·8[c]
	$CoBr_2Py_2$	2·50	150	—	5·2	48·3	12·9[j] + 0·8[c]
	$CoBr_2Py_2$	2·50	55	—	18·2	68·3	6·7[j] + 0·7[c]
1-Methyl-4-(1-methyethyl)benzene[b]	+	2·16	60	7·8[f]	50·2	1·4	3·1[c]
1,3-Diethylbenzene[b]	$MnBr_2Py_2$	2·16	85	1·9[k]	—	49·8	10·2[l]
1,3-Dimethylbenzene[b]	1 : 1	2·73	55	—	0·2	89·6	—
1,2-Dimethylbenzene[b]		2·73	115	—	33·8	56·4	—
4-Octyl-1,1′-biphenyl[a]		0·79	30	56·8[g]	—	—	—[i]

[a] [catalyst] = 9·0 . 10^{-3} mol dm^{-3}; [b] [catalyst] = 1·82 . 10^{-2} mol dm^{-3}; [c] 1-(4-methylphenyl)ethanone; [d] 1-phenyl-1-propanone; [e] 1-phenylethanone; [f] 4-(1-methylethyl)benzoic acid; [g] 4-phenylbenzoic acid; [h] 1-phenylethyl acetate; [i] aliphatic carboxylic acids + aryl ketones; [j] 1-(4-methylphenyl)ethyl acetate; [k] 3-ethylbenzoic acid; [l] 3-(1-acetyloxyethyl)benzoic acid.

Methyl groups take preference over other groups at aromatic nucleus, so that the main oxidation products are 4-ethylbenzoic and 4-(1-methylethyl)benzoic acids, respectively[20]. Mechanism of synergistic effect of metal mixtures (as it was found in oxidations of various alkylaromatic hydrocarbons) is ascribed either to influence of chain propagation of the reaction[9,12,13] or, to a great extent, to possible formation of polynuclear complexes[11,21]. This conclusion is supported by the results given in Table II wherefrom it is seen that coordination with nitrogen ligands can affect catalytic activity of these mixed complexes, which is probably due to change in their redox properties.

The marked influence of pyridine on activity of cobalt as well as on mixed metal catalysts is accompanied by formation of acetylated products (Tables II and III). In comparison with current cobaltbromide catalysts (where their formation is explained by acetolysis of intermediary aralkyl bromides, Eq. (*6*)), amounts of the mentioned benzyl acetates are substantially higher in the presence of pyridine.

$$\mathrm{R{-}CH_2Br} + \mathrm{AcO^-} \rightleftharpoons \mathrm{R{-}CH_2OAc} + \mathrm{Br^-} \qquad (6)$$

As the presence of nitrogen ligands does not significantly affect[17] the reaction (*6*), and, in addition to it, formation of acetates is increased only with complexes and synergistic mixtures of metals coordinated with pyridine ligands, these products must be formed by another reactions. Little likely is their formation by the reaction (*7*)

$$\mathrm{RCH_2}\cdot + \mathrm{Co(III)} \rightarrow \mathrm{RCH_2^+} + \mathrm{Co(II)} \xrightarrow{\mathrm{AcOH}} \mathrm{RCH_2OAc}\,, \qquad (7)$$

because under the oxidation conditions reaction of benzyl radical with oxygen is preferred[22,23].

$$\mathrm{RCH_2}\cdot + \mathrm{O_2} \rightarrow \mathrm{RCH_2O_2}\cdot \rightarrow \text{products} \qquad (8)$$

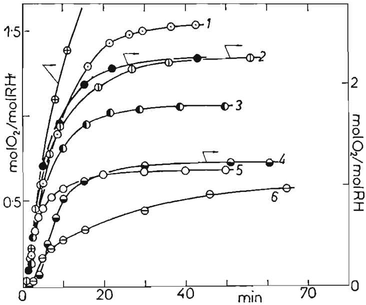

FIG. 3

Oxidation of Ethylbenzene *1*, Propylbenzene *3*, (1-Methylethyl)benzene *5*, Dodecylbenzene *6*, 1,3-Dimethylbenzene ⊕, 1-Ethyl-4-methylbenzene *2*, 1-Methyl-4-(1-methylethyl)benzene *4*, 1,3-Diethylbenzene ● in Acetic Acid (for reaction conditions see Table III)

Mechanism of formation of benzylacetate products was not studied in detail, it can, however, be presumed that cobalt complexes with pyridine ligands support formation of alcohols as intermediates which are, under the reaction conditions (acetic acid as solvent), transformed into acetate esters.

REFERENCES

1. Hronec M., Veselý V.: This Journal *43*, 728 (1978).
2. Chester A. W., Scott E. J. Y., Landis P. S.: J. Catal. *46*, 308 (1977).
3. Standard Oil (Ind): U.S. 3 931 304.
4. Dynamit Nobel A. G.: Ger. Offen. 2 163 031.
5. Kagami K.: Bull. Chem. Soc. Jap. *41*, 1552 (1968).
6. Alexandrov V. N., Khomin V. V., Gitis S. S., Golubev G. S.: Neftekhimiya *12*, 737 (1972).
7. Kamiya Y.: Tetrahedron *22*, 2029 (1966).
8. Manokov M. N., Tazin V. L., Krukhinin V. A.: Neftekhimiya *12*, 556 (1973).
9. Reich L., Stivala S. S.: *Autooxidation of Hydrocarbons and Polyolefins.* Dekker, New York 1969.
10. Kamiya Y., Nakajima T., Sakoda K.: Bull. Chem. Soc. Jap. *39*, 2211 (1966).
11. Alexandrov V. N., Gitis S. S.: Kinet. Katal. *15*, 505 (1974).
12. Kamiya Y.: Advan. Chem. Ser. *76*, 193 (1968).
13. Sheldon R. A., Kochi J. K.: Advan. Catal. *25*, 272 (1976).
14. Gill N. S., Nyholm R. S.: J. Inorg. Nucl. Chem. *18*, 88 (1961).
15. Hronec M., Veselý V.: This Journal *40*, 2165 (1975); *41*, 350 (1976).
16. Hronec M., Veselý V.: This Journal *42*, 3392 (1977).
17. Hronec M.: This Journal, in press.
18. Kamiya Y.: J. Catal. *33*, 480 (1974).
19. Holtz H. D.: J. Org. Chem. *37*, 2069 (1972).
20. Onopchenko A., Schulz J. G. D., Seekircher R.: J. Org. Chem. *37*, 1414, 2564, 2950 (1972).
21. Kawai R., Kamiya Y.: Nippon Kagaku Kaishi *1974*, 933.
22. Heiba E. I., Dessau R. M., Koehl W. J.: J. Amer. Chem. Soc. *91*, 6830 (1969).
23. Gilmore J. R., Mellor J. M.: Chem. Commun. *1970*, 507.

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