

NEW CATALYSTS FOR BELOUSOV-ZHABOTINSKII REACTION

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Received September 27th, 1979

It was found that cobalt, nickel, and copper as central ions in complexes with various amines can act as catalysts of the Belousov-Zhabotinskii reaction. Also sole 8-hydroxyquinoline is a catalyst.

The classical Belousov-Zhabotinskii (B-Z) oscillating reaction is catalysed with Ce^{4+} ions¹. Other catalysts were found later: *o*-phenantroline and dipyriddy complexes of Fe^{2+} (ref.²), dipyriddy complexes of Ru^{3+} (ref.³) and Mn^{3+} (ref.^{4,5}). Since the mechanism of the B-Z reaction is, in spite of numerous investigations, by far not elucidated⁶, it appears desirable to look for other catalysts and to obtain thus more informations.

The reactions were followed by recording continually, automatically and simultaneously the electric potential difference of a platinum, a Br-selective, and a silver bromide electrodes against mercurous sulphate electrode in a reaction mixture of the initial composition: 25 ml 0.4M- H_2SO_4 , 1 ml 1M malonic acid, complex, and 10 ml 0.4M- $KBrO_3$ at 25°C. The components were mixed in the order indicated. The analytical concentration of the complexes in the reaction mixture and the obtained results are given in Table I, from which it is apparent that five new catalysts from the group of Co^{2+} complexes were found.

Since with the use of Co^{2+} , Cu^{2+} , and Ni^{2+} complexes with oxine the colour changes during the oscillations were the same and since other ligands catalytically active with central Co^{2+} ions were inactive with central Ni^{2+} or Cu^{2+} ions, we conclude that the catalytic effect is due to the oxine molecules. Indeed, the addition of oxine in a resulting concentration of $6.85 \cdot 10^{-4} - 1.3 \cdot 10^{-2}$ mol/dm³ in the reaction mixture causes an oscillating course of the B-Z reaction. This is the first case where the B-Z reaction is catalysed by an organic compound without a central cation through its own redox system (reduced form is yellow and oxidised form is red).

Complexes of aniline with Co^{2+} , Cu^{2+} , and Ni^{2+} ions show an interesting behaviour. The oscillations are provoked only in a very narrow concentration range of the complexes and in the temperature range from 31 to 35°C. The colour changes during

TABLE I

Catalytic Activity (C.a.) of Co(II), Ni(II), and Cu(II) Complexes

The complexes were prepared by mixing the corresponding sulphates with a 20% excess of ligands in 0.4M-H₂SO₄ in a resulting concentration of 0.025 mol/dm³ in most cases. Pyridine, *o*-phenylenediamine, ethylenediamine, α -nitroso- β -naphthol, dimethylglyoxime, and acetylacetonone gave negative results.

Ligand	Co(II)	C.a.	Conc. range . 10 ³ mol/dm ³	Ni(II)	C.a.	Conc. range . 10 ³ mol/dm ³	Cu(II)	C.a.	Conc. range . 10 ³ mol/dm ³
<i>o</i> -Phenanthroline	CoL ₃	+	3.85 — 71.5	NiL ₃	0	0.98 — 1.35	CuL ₂	0	1.9 — 8.9
2,2-Dipyridyl	CoL ₃	+	2.6 — 8.14						
<i>p</i> -Phenylenediamine	CoL ₆	+	17.9	NiL ₆	0	6.1 — 18	CuL ₄	0	6.1 — 18
8-Hydroxyquinoline	CoL ₃	+	0.685—13	NiL ₃	+	0.435— 2.8	CuL ₂	+	0.685—15.3
Aniline	CoL ₆	+	0.17 — 0.56	NiL ₆	+	0.34— 0.5	CuL ₄	+	0.46 — 0.53

the oscillations were in the presence of any of these complexes the same (oxidised form is red, reduced form is violet). In contrast to oxine, however, aniline in the concentration range $1.7 \cdot 10^{-7}$ – $5.8 \cdot 10^{-4}$ mol/dm³ does not cause oscillations. Even oscillations that could correspond to a reaction of bromate with aniline⁷ were not observed in the mentioned concentration range. Hence, complexes of Cu²⁺ and Ni²⁺ ions with aniline must also be considered as new catalysts of the B–Z reaction.

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Translated by K. Micks.