

HOMOGENEOUS CATALYSTS FOR DIOXYGEN EVOLUTION FROM WATER. WATER OXIDATION BY TRISBIPYRIDYL RUTHENIUM(III) IN THE PRESENCE OF COBALT, IRON AND COPPER COMPLEXES

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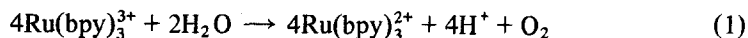
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Complexes of Co, Cu and Fe with bipyridyl, and cobalt complexes with ammonia, ethylenediamine and oxyacids are shown to be efficient catalysts for water oxidation by $\text{Ru}(\text{bpy})_3^{3+}$ in both alkaline and weakly acidic media. Partially hydrolyzed forms of these complexes are assumed to be active.

Показано, что эффективными катализаторами реакции окисления воды комплексом $\text{Ru}(\text{bpy})_3^{3+}$ как в щелочной, так и в слабокислой среде являются дипиридилные соединения Co, Cu и Fe, а также комплексы кобальта с аммиаком, этилендиамином и оксикислотами. Предполагается, что активными являются частично гидролизованные формы этих комплексов.

The development of systems for the photocatalytic conversion of solar energy via water decomposition into hydrogen and oxygen /1/ has revealed the efficiency of application of trisbipyridylruthenium(II) as a photocatalyst whose oxidized form can lead to dioxygen evolution from water. But the efficient four-electron oxidation of water to O_2 by one-electron oxidants, e.g., such as $\text{Ru}(\text{bpy})_3^{3+}$ (bpy is 2,2'-bipyridyl), via the reaction



is impossible without appropriate catalysts. Reaction (1) is susceptible to both heterogeneous (PtO_2 , RuO_2 , IrO_2) /2, 3/ and homogeneous (compounds of Co^{2+} , Fe^{3+} , Cu^{2+}) catalysis /4, 5/. We now describe the catalytic action of several homogeneous catalysts based on some complexes of the above ions.

The metal complexes with nitrogen-containing ligands (see Table 1) were prepared by known methods /6, 7/. All the reactants were analytical grade substances and were not further purified. Bidistilled water was used as the solvent.

Table 1
 Yields of O₂ in 9 x 10⁻⁴ M solutions of Ru(bpy)₃³⁺
 in the presence of catalysts at 20 °C

Catalyst (1 x 10 ⁻⁴ M)	pH _{init}	pH _{final}	O ₂ yield (%)
1. CoCl ₂	10	4-5	60
2. CoCl ₂	6	3	49
3. CoCl ₂ : C ₄ H ₆ O ₆ = 1 : 1	10	4-5	70
4. CoCl ₂ : C ₄ H ₆ O ₆ = 1 : 2	10	4-5	55
5. CoCl ₂ : C ₆ H ₈ O ₇ = 1 : 1	10	4-5	53
6. CoCl ₂ : C ₆ H ₈ O ₇ = 1 : 2	10	4-5	34
7. [Co(bpy) ₃] (ClO ₄) ₃	10	4-5	70
8. [Co(bpy) ₃] (ClO ₄) ₃	6	3	62
9. [Co(NH ₃) ₆]Cl ₃	10	4-5	10
10. [Co(NH ₃) ₅]Cl ₂ ·H ₂ O	10	4-5	39
11. [Co(NH ₃) ₅ ·H ₂ O]Cl ₃	10	4-5	42
12. cis-[Co(NH ₃) ₄ (H ₂ O) ₂]Cl ₃	10	4-5	65
13. cis-[Co(en) ₂ Cl ₂]Cl	10	4-5	68
14. cis-[Co(en) ₂ Cl ₂]Cl	6	3	48
15. trans-[Co(en) ₂ Cl ₂]Cl	10	4-5	62
16. CuCl ₂	10	4-5	43
17. [Cu(bpy) ₂]Cl ₂	10	4-5	43
18. [Cu(bpy) ₃]Cl ₂	10	4-5	32
19. 10 ⁻³ FeCl ₃	10	4-5	34
20. 4 x 10 ⁻⁴ M [Fe ₂ O phen ₄]Cl ₄	10	4-5	55

bpy - 2,2'-bipyridyl
 phen - 1,10-phenanthroline
 C₄H₆O₆ - tartaric acid
 C₆H₈O₇ - citric acid
 en - ethylenediamine

Experimental procedure is described elsewhere /4/. The yields of dioxygen (%) relative to its stoichiometric amount expected according to reaction (1) was used to characterize the efficiency of the catalysts (see Table 1). Part of the oxidant is uselessly consumed for a side reaction which is probably the oxidative destruction of bipyridyl. This side reaction is accompanied by the intense chemiluminescence of Ru(bpy)₃³⁺ and apparently proceeds without a catalyst. A catalyst at the concentration given in Table 1 and 9 x 10⁻⁴ M Ru(bpy)₃³⁺ were dissolved in 0.01M H₂SO₄. After evacuating the system for 15-20 min the pH of the solution was raised to pH = 6 or 10 by adding a solution of NaOH; the final pH of the solution after dioxygen evolution via reaction (1) was 3-4. The reaction time did not exceed 10 s.

The application of borate buffers instead of the alkali changed the O₂ yield insignificantly for cobalt complexes as catalysts and considerably decreased the activity of iron compounds. Phosphate and acetate buffers significantly inhibited the O₂ yields in all cases.

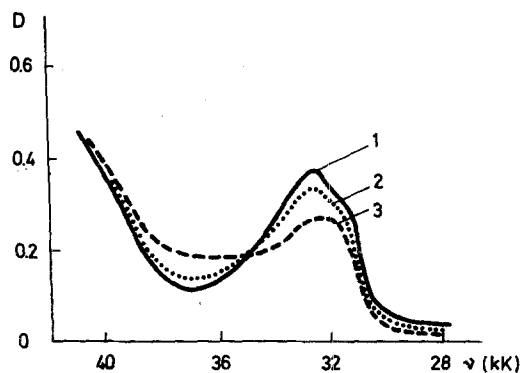


Fig. 1. Spectra of $\text{Co}(\text{bpy})_3^{3+}$ solutions in various conditions: 1) solution with $\text{pH} = 1$, immediately after preparation; 2) same after 30 min; 3) fresh and aged solutions with $\text{pH} = 10$, $\text{Co}(\text{bpy})_3^{3+} = 2 \times 10^{-4} \text{M}$; $l = 0.05 \text{ cm}$

RESULTS AND DISCUSSION

O_2 yields in the presence of Co, Fe and Cu complexes are listed in Table 1. For comparison, the data for the chlorides of these metals are presented as well. It can be seen that the efficiency of the complexes is not lower and in several cases is even higher than that of the chlorides (or aqua ions) of the respective metals. We assume that in all the cases the partially hydrolyzed, i.e. coordinatively unsaturated forms of the above complexes are catalytically active. In agreement with this, cobalt complexes with oxyacids are highly active at a ratio of 1:1, while in an excess of the oxyacids, when more highly coordinated compounds are expected to be formed, the yields of O_2 significantly decrease.

In a set of cobalt complexes with ammonia the O_2 yield is the lowest for the coordinatively saturated $\text{Co}(\text{NH}_3)_6^{3+}$ and the highest for $\text{cis-Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{3+}$.

$\text{Co}(\text{bpy})_3^{3+}$ is also quite effective, but in the experimental conditions the partial hydrolysis of this tris-complex is likely to occur, as can be judged by the significant changes in its absorption spectra (Fig. 1). It is interesting to note that *cis*- and *trans*- $\text{Coen}_2\text{Cl}_2^+$ are almost equally efficient. This can be attributed to the fact that in aqueous solutions these complexes are rather rapidly aquated (hydrolyzed) and isomerized, the equilibrium in the mixture of hydrolyzed compounds being shifted to the *cis*-forms [8].

The mechanism of the catalytic action of the compounds studied in water oxidation is not yet clear, but it can be assumed that active should be the forms with two adjacent oxygen atoms, i.e. either monomeric *cis*-diaqua or dihydroxo complexes or various hydroxo or oxo bridged dimers.

The formation of dimeric structures is characteristic for a large number of iron /9/ and cobalt /10/ complexes. It was shown /11/ that dimeric di- μ -oxo- and di- μ -hydroxocomplexes of copper with phenanthroline are catalysts for some oxidation reactions. Our results indicate that $\text{Fe}_2\text{O}(\text{phen})_4^{4+}$ which presumably is in equilibrium with its di- μ -hydroxo-form in solution, is notably more efficient than ferric chloride.

The observed efficient catalysis of reaction (1) permits to conclude that at least in weakly acidic solutions the most probable route of the catalytic reaction is a mechanism without the formation of free H_2O_2 /1, 4/. Actually, for the two-electron oxidation of water to free H_2O_2 at $\text{pH} < 5$ an oxidant is required with a potential exceeding, 1.4 V, which is higher than that of the pair $\text{Ru}(\text{bpy})_3^{3+}/\text{Ru}(\text{bpy})_3^{2+}$ (1.26 V). From these data it follows that the equilibrium concentration of H_2O_2 in our conditions cannot be higher than 10^{-6} – 10^{-7} M. It can readily be shown that the observed rate of O_2 evolution ($W > 10^{-4} \text{ M s}^{-1}$) cannot be provided by the added amount of the catalyst even if the rate is controlled by the most rapid diffusion-controlled bimolecular processes.

An interesting fact is that almost all the complexes found to be active in reaction (1) are also catalytically active in H_2O_2 decomposition for which the participation of dimeric forms of the catalyst seems to have been demonstrated in several cases /12/.

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