CUMENE HYDROPEROXIDE DECOMPOSITION REACTION CATALYZED BY RUTHENIUM(III) β-DIKETONATES

A. M. Trzeciak, R. Grobelny and J. J. Ziółkowski

Institute of Chemistry, University of Wroclaw, 50-383 Wroclaw, Poland

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Catalytic decomposition of cumene hydroperoxide (ROOH) in the presence of Ru(III) β-diketonates has been investigated. Activation of ROOH via outer sphere [ROOH] — [Ru] interaction has been proposed.

Исследован каталитический распад гидроперекиси кумола в присутствии β-дикетонатов Ru(III). Найдено что активация ROOH происходит вследствие внешнесферного взаимодействия [ROOH] c [Ru(III)].

INTRODUCTION

Cumene hydroperoxide decomposition catalyzed by transition metal complexes is usually described by the Haber—Weiss mechanism /1/, following the scheme:

\[
\text{ROOH} + M^{n} \rightarrow \text{RO}^\cdot + M^{(n+1)} + \text{OH}^-
\]

\[
\text{ROOH} + M^{(n+1)} \rightarrow \text{RO}_2^\cdot + M^{n} + \text{H}^+
\]

which has been proved experimentally for a series of [ROOH] and Co(II) complexes /2—4/. Activity of such a catalyst was expected to be dependent upon the redox potential of the metal ion. That relation was evidenced for complexes of Cr(II) and Co(II) /5/ as well as for complexes of [Co₂ (III)Co (II)O], [Mn₃ (III)O], [Fe₃ (III)O]
and \([Cr_3^{(III)}O]\) of the type \([M_3O(O_2CR_6)(L)_3]^n\) /6/. However, the Haber–Weiss mechanism cannot be regarded as universal /7, 9/. In this paper we have tried to ascerten whether the catalytic activity of the metal ion in Ru(III) \(\beta\)-diketonates is determined by its redox potential \((Ru^{(III)^+} + e = Ru^{(II)^+})\).

RESULTS AND DISCUSSION

The redox potential of isostructural Ru(III) \(\beta\)-diketonates varies in dependence on the kind of ligand /10, 11/. For the most powerful oxidants, i.e. Ru(TTA)\(_3\) (TTA = C\(_4\)SH\(_3\)(CO)CH\(_2\)(CO)CF\(_3\)) and Ru(BTA)\(_3\) (BTA = C\(_6\)H\(_5\)(CO)CH\(_2\)(CO)CF\(_3\)) the reaction:

\[
Ru(III) + ROOH \rightarrow Ru(II) + RO' + H^+
\]

was expected to be the fastest. Kinetic results contradicted that supposition. Moreover, the increase of oxidizing ability was simultaneous with the decay of the catalytic activity of Ru(III) compounds in ROOH decomposition (Fig. 1).

Fig. 1. ROOH concentration decrease in the decomposition reaction catalyzed by Ru(III) complexes: o Ru(TTA)\(_3\); • Ru(BTA)\(_3\); o Ru(FTA)\(_3\) Ru = 3.4 \times 10^{-3} M, + Ru(BAC)\(_3\); x Ru(ACA)\(_3\) Ru = 1.2 \times 10^{-2} M A Ru(ACA)\(_3\) Ru = 3.9 \times 10^{-3} M solvent: CH\(_3\)OH; T = 328 K