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Use of Some Complexes of Ru in Radiolytical Decomposition of Water

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Abstract: The radiolysis of water in the presence of complexes of Ru with pyridine and DMSO acting as catalysts of the hydrogen production is reported. A radionuclide of ^{60}Co with an activity of about $5x10^4$ Ci was employed as an irradiation γ source. A considerable increase of the amount of hydrogen resulting from the radiolysis of water in the presence of the above mentioned complex combinations was noticed in comparison with the reference sample, irradiated under the same experimental conditions, but without any catalyst. The products have been identified by means of a method based on mass spectrometry.

Keywords: Ruthenium complexes; Water radiolysis; Hydrogen.

Introduction

Due to the importance of hydrogen as a non-polluting energy source, several studies have been devoted to its production with respect to the profitable economic conditions in electrolysis, thermolysis, pyrolysis, etc., either in the presence or absence of certain substances, acting as catalysts in

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the decomposition of water or other chemical compounds. Some well known thermodynamic cycles describing the decomposition have also been considered. [1-5]

The possibility of using radiation emitted by the unstable fission products, which are contained in the spent nuclear fuel elements (10^7-10^9 Ci), for low-cost hydrogen production by catalyzed water radiolysis has been mentioned. As catalysts, usually oxides resistant to the action of nuclear radiations and with very low chemical reactivity on water splitting (under normal conditions), have been used: BeO, SiO_2, TiO_2 and ZrO_2.[6] Here, we report the use of complexes of ruthenium as a method for obtaining hydrogen from catalyzed water radiolysis.

Experimental

A ^{60}Co irradiation source with an activity of $5x10^4$ Ci and a dose of $8.6x10^4 Gyh^{-1}$ was used. Complexes of Ru have been employed as catalysts. The reaction system, made of 50 mg catalyst and 10 mL water, was irradiated. The dose collected by each system was of $1.6x10^3$ Gy.

The water radiolysis products, as well as those of the initial air, have been determined by mass spectrometry.

Results and discussions

It is generally known that radiolysis of water leads to different chemical species, such as: H_2, O_2, H_2O_2, $HO^{\cdot}$, O, $HO_2^{\cdot}$, etc., via a number of reactions outlined below.

$$H_2O \rightarrow H_2O^{*} \rightarrow H^{\cdot} + HO^{\cdot} \quad (1)$$

$$H_2O \rightarrow H_2O^{+} + e^{-} \quad (2)$$

$$H_2O^{+} + e^{-} \rightarrow H_2O \quad (3)$$

$$H_2O^+ + H_2O^- \rightarrow 2H_2O^* \rightarrow 2H^\cdot + 2HO^\cdot \quad (4)$$

$$H^\cdot + H^\cdot \rightarrow H_2 \quad (5)$$

$$HO^\cdot + HO^\cdot \rightarrow HO_2^* + H^* \quad (6)$$

$$H^\cdot + O \rightarrow HO^\cdot \quad (7)$$

$$HO_2^\cdot + HO_2^\cdot \rightarrow H_2O_2 + O_2 \quad (8)$$

In the presence of catalyst (1)-(7) the radiolysis can be represented as follows:

$$X \xrightarrow{\gamma} X^* \text{ (activated state)} \quad (9)$$

$$X^* + H_2O \rightarrow [H_2O^\cdot X]^* \text{ (activated complex)} \quad (10)$$

$$[H_2O^\cdot X]^* \rightarrow H^\cdot + HO^\cdot + X + h\nu \quad (11)$$

These species (H, HO, HO_2, O_2, H_2O_2) were found in the mass spectra.

Results of the analyses are collected in Table 1.

Table 1. Radiolysis products in the presence of some complex Ru combinations.

Catalyst	Radiolysis product	Intensity (arbitrary units)
$[Ru(DMSO)_4Cl_2]$	H_2	199210
	O_2	459650
	OH	290670
$[Ru(Py)_4Cl_2]$	H_2	177120
	O_2	442800
	OH	287350
Uncatalyzed sample	H_2	39 120
	O_2	298 010
	OH	95 480

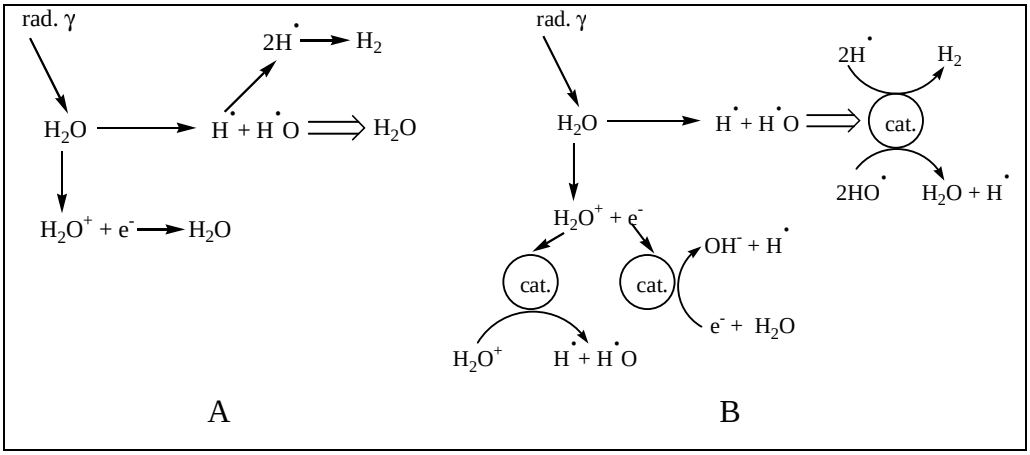
Complex combinations of Ru have been examined as catalysts of the radiolysis of water.[7, 8]

Under the radiation conditions, the catalyst molecules are activated, and the energetically activated state forms unstable intermediates of the $[H_2OX]^*$ type which include coordinated water. This intermediate assists radiolysis and hydrogen release hydrogen-an indirect action of nuclear radiation on the considered systems.

When a water molecule approaches the catalyst's surface, a distribution of delocalized electron density leads to an intimate contact between the orbital of the water molecule and the catalyst's localized d-orbital. The density of localized electrons is redistributed. The transition state is sufficiently long lived to permit relaxation of the delocalized electrons into a new density distribution, the interaction of the reactant's weakened links with neighboring superficial complexes or with other molecules, the complete dissociation of the weakened links so that to permit their separate migration, their reaction with other species, or their recombination.

It was observed that, in the case of Ru complexes used as catalysts of water's radiolytic decomposition, the intensity of the peak corresponding to H_2 is higher for complex combinations as uncatalyzed water radyolisis.

Based on the experimental data of the present study, a possible mechanism for explaining the reaction of hydrogen release through the irradiation of some water-catalyst aqueous suspensions might be as shown in Scheme 1.



Scheme 1.

A-uncatalyzed water radiolysis;

B-catalyzed water radiolysis.

Conclusions

Some complexes of Ru with pyridine and DMSO acting as catalysts in water radiolysis have been tested. It was observed that, in the presence of complexes of Ru, the intensity of the peak corresponding to H_2 in the mass spectrum is much higher, compared to that found for water in uncatalyzed radiolysis.

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