SHORT COMMUNICATION

Radiolytic splitting of water molecules in the presence of some supramolecular compounds

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Abstract: This paper deals with the study of the hydrogen output during the catalyzed radiolysis of water in the presence of the supramolecular compounds $Fe_2NiO(TMAc)_6 \cdot 3HTMAc$, $FeCoO(TMAc)_6 \cdot 3HTMAc$, $[Cr_3O(C_6H_5COO)_6] \cdot ClO_4$, $Fe_3Ni_2O(OH)(TMAc)_7(Aacet)_3$, $Ni_2(H_2O)(TMAc)_4(HTMAc)_4$, $[Cr_3O(TMAc) \cdot 3H_2O](TMAc)$, and $Cr_8F_8(TMAc)_{16}$. A ^{60}Co γ-source of 5.1×10^{14} Bq activity at a rate dose of 8.038 kGy h^{-1} was used. The radiolysis products were determined by mass spectrometry. For a given irradiation time, it was found that quantity of hydrogen obtained by water radiolysis is 6 – 18 times greater in the presence of the supramolecular compounds as catalysts than in their absence from the irradiated system.

Keywords: hydrogen evolution, radiolysis, supramolecular catalysts, radioactive waste.

INTRODUCTION

There are many papers concerning the radiolytic production of hydrogen from water using various irradiation sources, such as: nuclear radiation emitted by radioactive nuclei or neutrons inside a nuclear reactor[1–6] under different experimental conditions.

Previous research[7,8] considered the hydrogen output during catalysed water radiolysis under the influence of γ-rays emitted by a ^{60}Co source of 5.1×10^{14} Bq activity at a rate dose of 8.038 kGy h^{-1}. After irradiation in hermetically closed vials, the radiolysis products: H_2, O, HO$^\bullet$, O_2, ..., as well as the N and N_2 species from the air composition in the aqueous samples, were established by mass spectrometry.

In this work these studies were extended in order to obtained higher quantities of hydrogen by catalysed water radiolysis when the irradiation would be done using more intense radiation sources ($10^{17} – 10^{19}$ Bq), corresponding to high level radioactive wastes supplied by spent nuclear fuel elements.

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EXPERIMENTAL

The supramolecular compounds used as catalysts: Fe$_2$NiO(TMAc)$_6$·3HTMAc, FeCoO(TMAc)$_6$·3HTMAc, Fe$_3$Ni$_2$O(OH)(TMAc)$_7$(Aacet)$_3$, Cr$_8$F$_8$(TMAc)$_{16}$, Ni$_2$(H$_2$O)(THAc)$_4$(HTMAc)$_4$, [Cr$_3$O(TMAc)·3H$_2$O](TMAc) and [Cr$_3$O(C$_6$H$_5$COO)$_6$] · ClO$_4$ (TMAc – trimethylacetic acid, Aacet – acetylacetone) were prepared and characterised in terms of structure and properties[9] at the Institute of Chemistry, Science Academy - Kishinew, Republic of Moldova. The compounds are not soluble in water and do not react with it.

The samples for irradiation were prepared in vials of 30 ml capacity by adding 10 ml of distilled water and 0.05 g of the given catalyst (as supramolecular compounds). After that, the vials were hermetically closed with rubber caps with parafihn on the outside. A sample without catalyst was prepared for comparison purposes. The sealing system of the vials was verified by immersing a hermetically closed vial containing 10 ml of a 0.1 M HCl solution and Zn powder into a glass cylinder filled with water. No gas emission after this reaction was observed in the cylinder during 10 days.

The samples containing water and catalyst were irradiated using a ^{60}C γ-source with a 5.1×10^{14} Bq activity and a rate dose of 8.038 kGy h^{-1} at 0.3 m and for different intervals of time: 24, 48, 72 and 120 h. The samples were arranged in a circle with the ^{60}Co source in the center. The whole irradiation device was immersed in a pool of water.

The separate determination of the radiolysis products: H$_2$, O, HO$^•$, O$_2$, as well as the nitrogen species N and N$_2$ from the air dissolved in the water was performed by mass spectrometry as suggested:

$$\text{Sample} \rightarrow \text{Mass spectrometer} \rightarrow \text{PC} \rightarrow \text{Mass spectrogram}$$

The chemical species formed in the irradiated samples were transferred into the mass spectrometer by a special hermetic connection in which the base of a syringe needle was fixed at the entrance of the mass spectrometer while its sharp part was pushed through the rubber septum of each vial.

A vacuum of approximately 10^{-7} torr was applied to the mass spectrometer before each measurement, in order to avoid any risk of contamination of the subsequent sample by chemical species remaining from the previous sample. Mass spectrograms were recorded by a computer in the coordinates Peak intensity = f(Mass number).

The mass spectrometer was calibrated in order to determine the hydrogen quantities in grams, on the basis of the following chemical reaction also performed in a hermetically closed vial:

$$Al + NaOH_{(c)} + 3\ H_2O \rightarrow Na[Al(OH)_4] + 3/2\ H_2$$
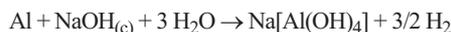
In this way, 3.34×10^{-2} g hydrogen results from 0.3 g Al powder, which correspond to a peak intensity (in arbitrary units) of 7984830 in the mass spectrogram, for the species with the mass number 2.

The radiochemical yield for the formation of H$_2$ from the radiolysis of water was established using the following relation:

$$G(\text{H}) = \frac{\text{moles of H}_2 \times 6.023 \times 10^{23}}{\text{absorbed dose (J} \cdot \text{h}^{-1}) \times \text{irradiation time(h)} \times 6.24 \times 10^{16}} = \frac{\text{H}_2 \text{ molecules}}{100 \text{ eV}}$$

RESULTS AND DISCUSSIONS

The radiolysis processes can be presented as[10]:

$$H_2O \xrightarrow{\gamma} H_2O^+ + e^-$$
$$H_2O + e^- \rightarrow H_2O^-$$
$$H_2O^+ + H_2O^- \rightarrow 2\ H_2O^• \rightarrow 2\ H^• + 2\ HO^•$$
$$H_2O \xrightarrow{\gamma} H_2O^• \rightarrow H^• + HO^•$$
$$H^• + H^• \rightarrow H_2$$
$$HO^• + HO^• \rightarrow H_2O + O$$

$$HO^{\bullet} + HO^{\bullet} \rightarrow HO_2^{\bullet} + H^{\bullet}$$
$$H^{\bullet} + O \rightarrow HO^{\bullet}$$
$$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2$$
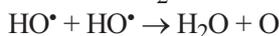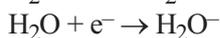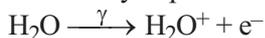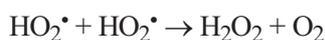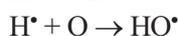
The most probable catalytic mechanism could be based on the formation of interactions between the dipolar water molecules and the cations at the surface of the solid catalyst.[11] Under γ-ray irradiation, the linkage H–OH of water molecules adsorbed on the catalyst surface is broken easier than that of non-adsorbed water molecules.

The obtained results are summarized in Tables I and II.

In order to prove that the supramolecular compounds played a catalytic role in the radiolytic splitting of water, their X-ray diffraction pattern were recorded before and after the γ-irradiation. No differences were observed in the X-ray spectrograms which leads to the conclusion that these supramolecular compounds did not change their structure, and hence acted as catalysts in the radiolysis of water.

From the data presented in Tables I and II, the following conclusions can be made:

TABLE I. The principal chemical species established by mass spectrometry

No	Catalyst	Irradiation time/h	Peak intensity (a.u.) for:						$G(H_2)$	mg H_2
			H_2	O	$HO^{\bullet}$	O_2	N_2	N		
1	$Fe_2NiO(TMAc)_6 \cdot 3HTMAc$	24	174710	2935	4576	16305	6305	710	1.75	0.73
2	$Fe_2NiO(TMAc)_6 \cdot 3HTMAc$	48	229520	3750	6135	20590	7860	755	1.15	0.95
3	$Fe_2NiO(TMAc)_6 \cdot 3HTMAc$	72	254180	3580	6760	24385	8860	760	1.29	1.16
4	$Fe_2NiO(TMAc)_6 \cdot 3HTMAc$	120	1132600	16850	341156	157240	19160	3640	2.24	4.74
5	$Fe_2CoO(TMAc)_6 \cdot 3HTMAc$	24	137800	3805	6335	22280	8460	730	1.38	0.57
6	$Fe_2CoO(TMAc)_6 \cdot 3HTMAc$	48	243470	3835	6570	24380	8835	835	1.22	1.02
7	$Fe_2CoO(TMAc)_6 \cdot 3HTMAc$	72	382420	4750	8595	40270	13250	1085	1.28	1.51
8	$Fe_2CoO(TMAc)_6 \cdot 3HTMAc$	120	829640	11330	23385	125960	18460	2315	1.70	3.46
9	$Cr_8F_8(TMAc)_{16}$	24	181530	3000	4530	15260	6610	620	1.82	0.75
10	$Cr_8F_8(TMAc)_{16}$	48	209720	3555	5425	18495	7590	760	1.05	0.87
11	$Cr_8F_8(TMAc)_{16}$	72	423140	5465	10175	50045	15300	1195	1.42	1.76
12	$Cr_8F_8(TMAc)_{16}$	120	953130	14035	28180	146830	17935	2925	1.92	3.98
13	$[Cr_3O(C_6H_5COO)_6] \cdot ClO_4$	24	122870	1985	1380	4830	7635	990	1.23	0.51
14	$[Cr_3O(C_6H_5COO)_6] \cdot ClO_4$	48	247600	4065	6565	24300	8570	815	1.24	1.03
15	$[Cr_3O(C_6H_5COO)_6] \cdot ClO_4$	72	438170	5185	10330	51125	8110	1260	1.47	1.83
16	$[Cr_3O(C_6H_5COO)_6] \cdot ClO_4$	120	849550	6710	13960	86720	18065	2240	1.72	3.55
17	$Fe_3Ni_2O(OH)(TMAc)_7(Aacet)_3$	24	212070	3530	5740	18670	7235	660	2.13	0.88
18	$Ni_2(H_2O)(TMAc)_4(HTMAc)_4$	24	193145	3180	4800	15335	6460	850	1.94	0.80
19	$[Cr_3O(TMAc) \cdot 3H_2O]TMAc$	24	194745	3085	4990	16330	6915	765	1.96	0.84,
20	Uncatalysed water	24	33400	745	1095	5375	3320	540	0.35	0.14

TABLE II. Interdependence between the determined and theoretical amounts of oxygen resulting in the experiments

No.	Catalyst	Irradiation time/h	Amount of oxygen (arbitrary units)			
			Total amount of O_2 m_1	From air composition m_2	Found from radiolysis only/m_3	Theoretical accounted m_4
1	$Fe_2NiO(TMAc)_6 \cdot 3HTMAc$	24	21590	2125	19465	87355
2	$Fe_2NiO(TMAc)_6 \cdot 3HTMAc$	48	27480	2670	24810	114760
3	$Fe_2NiO(TMAc)_6 \cdot 3HTMAc$	72	31925	2861	29064	127090
4	$Fe_2NiO(TMAc)_6 \cdot 3HTMAc$	120	194995	5244	189751	566300
5	$Fe_2CoO(TMAc)_6 \cdot 3HTMAc$	24	29345	2320	27025	68900
6	$Fe_2CoO(TMAc)_6 \cdot 3HTMAc$	48	31785	2914	28871	121735
7	$Fe_2CoO(TMAc)_6 \cdot 3HTMAc$	72	49950	4140	45810	191210
8	$Fe_2CoO(TMAc)_6 \cdot 3HTMAc$	120	151660	4478	147182	414820
9	$Cr_8F_8(TMAc)_{16}$	24	20315	2210	18105	90765
10	$Cr_8F_8(TMAc)_{16}$	48	24680	2565	22117	104860
11	$Cr_8F_8(TMAc)_{16}$	72	61415	4775	56640	211570
12	$Cr_8F_8(TMAc)_{16}$	120	177935	14253	163682	476565
13	$[Cr_3O(C_6H_5COO)_6] \cdot ClO_4$	24	8200	2212	5988	11435
14	$[Cr_3O(C_6H_5COO)_6] \cdot ClO_4$	48	24680	2563	22117	104860
15	$[Cr_3O(C_6H_5COO)_6] \cdot ClO_4$	72	61415	4775	56640	211570
16	$[Cr_3O(C_6H_5COO)_6] \cdot ClO_4$	120	102920	4870	98050	424775
17	$Fe_3Ni_2O(OH)(TMAc)_7(Aacet)_3$	24	25070	2475	22595	106035
18	$Ni_2(H_2O)(TMAc)_4(HTMAc)_4$	24	20985	2217	18768	96572
19	$[Cr_3O(TMAc) \cdot 3H_2O]TMAc$	24	22085	2300	19785	97372
20	Uncatalysed water	24	7010	934	16700	15766

1. For each of the compounds $Fe_2NiO(TMAc)_6 \cdot 3HTMAc$, $FeCoO(TMAc)_6 \cdot 3HTMAc$, $Cr_8F_8(TMAc)_{16}$, $[Cr_3O(C_6H_5COO)_6] \cdot ClO_4$ having a catalytic function in the radiolysis of water, the quantity of formed hydrogen increases when irradiation time increases (*i.e.*, with increasing adsorbed dose);

2. For the same irradiation time (24 h), the obtained amount of hydrogen depends on the catalyst, in the order: $Fe_2NiO(TMAc)_6 \cdot 3HTMAc < Cr_8F_8(TMAc)_{16} < [Cr_3O(C_6H_5COO)_6] \cdot ClO_4 < Ni_2(H_2O)(TMAc)_4(HTMAc)_4 < [Cr_3O(TMAc) \cdot 3H_2O]TMAc < Fe_2CoO(TMAc)_6 . 3HTMAc < Fe_3Ni_2O(OH)(TMAc)_7(Aacet)_3$;

3. The quantity of hydrogen produced in the presence of the catalysts is 6 – 18 times greater than the amount resulting from uncatalysed radiolysis of water;

4. The presence of $HO^\bullet$ radicals as species less stable than H_2, O or O_2 can be explained in various ways. Perhaps the probability of their remaining as $HO^\bullet$ specie after ceasation of the γ-irradiation is smaller than that corresponding to their appearance by decomposition of H_2O_2 molecules (in vapour phase) under the action of the electron beams which produce the ionization of the chemical atoms and molecules inside of the mass spectrometer. The formation enthalpy of H_2O_2 is smaller than that of H_2O[12] and this leads to the conclusion that the decomposition of H_2O_2 molecules into two $HO^\bullet$ radicals is energically easier than the splitting of H_2O in the vapour phase in the hermetically closed vial – after irradiation.

On the other hand, the subsequent formation of $HO^\bullet$ specie from the other radiolysis products is also less likely. In any case, the formation of $HO^\bullet$ from the species resulting from the water radiolysis process is certain.

Moreover, it was observed that, in every case, the quantity of oxygen calculated by summing the values of the peak intensities from the mass spectrograms:

$$m_1 = [O]+[O_2]$$

is greater than that which would result from the presence of air in the hermetically closed vial, (m_2), which was indirectly established from the peak intensities of nitrogen.

$$m_2 = 0.23 \, ([N]+[N_2])$$

The difference $m_3 = m_1 - m_2$ would represent the amount of oxygen resulting from the radiolysis and should be identical with the quantity (m_4) which could be obtained from water decomposition:

$$[H_2O]_v \rightarrow [H]_v + 1/2 \, [O_2]_v$$

as a half of the hydrogen quantity determined in the mass spectrograms.

However, if was experimentally observed that $m_3 \ll m_4$, due to the fact that a part of the oxygen can be dissolved in the water or adsorbed on the catalyst, *etc*.

ИЗВОД

РАДИОЛИТИЧКО РАЗЛАГАЊЕ МОЛЕКУЛА ВОДЕ У ПРИСУСТВУ НЕКИХ СУПРАМОЛЕКУЛСКИХ ЈЕДИЊЕЊА

ALEXANDRU CECAL[1], ANDREI PARASCHIVESCU[1], KARIN POPA[1], DAN COLISNIC[1], GRIGORE TIMCO[2] and LIDIA SINGEREAN[2]

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Рад разматра производњу водоника током радиолизе воде у присуству супрамоле-кулских једињења $Fe_2NiO(TMAc)_6 \cdot 3HTMAc$, $Fe_2CoO(TMAc)_6 \cdot 3HTMAc$, $[Cr_3O(C_6H_5COO)_6] \cdot ClO_4$, $Fe_3Ni_2O(OH)(TMAc)_7(Aacet)_3$, $Ni_2(H_2O)(TMAc)_4(HTMAc)_4$, $[Cr_3O(TMAc) \cdot 3H_2O](TMAc)$, и $Cr_8F_8(TMAc)_{16}$. За озрачивање је коришћен ^{60}Co γ-извор активности од $5,1 \times 10^{14}$ Bq и брзином дозе од 8,038 kGy h^{-1}. Производи радиолизе одређивани су масеном спектроме-тријом. Уочено је да је количина добијеног водоника радиолизом воде током одре-ђеног времена озрачивања 6 до 18 пута већа у присуству супрамоекулских једињења као катализатора него без њих.

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