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Abstract

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STUDY OF HIGHER OXIDES AND PEROXIDES OF URANIUM BY THE ISOTOPIC METHOD

The complex uranium–oxygen system has been the subject of many studies (1,2) with contradictory results, owing to the formation of solid solutions of variable composition among different modifications of several oxides and to the slow establishment of equilibrium between the components of the solid phases and oxygen. Apparently, the existence of the stoichiometric oxides UO, UO_2, U_3O_8, and UO_3 may be regarded as proven. In addition to these, a peroxide of composition $UO_4 \cdot 2H_2O$ has long been known, and a second peroxide, U_2O_7 (3), has recently been discovered; its existence has been confirmed by the thermal decomposition of the first (4), as well as in the present work. Ideas about the structure of $UO_4 \cdot 2H_2O$ still remain contradictory. Most authors consider it to be a true hydrated peroxide (5) or peruranic acid (6), but Götte and Schröder (7) regard it as a product of the coordinative addition of variable amounts of H_2O_2 and H_2O to nonperoxidic UO_3. The experimental data on which these authors based such a structure proved to be erroneous (1), but Duval (8), having studied the thermal decomposition of this substance, again proposed for it the structure $UO_3 \cdot H_2O_2 \cdot H_2O$.

The U–O system has been studied in great detail in the high-temperature region with O : U ratios from 1 to 3 in solid phases. Far fewer data are available for the region below approximately 400°, where O : U ranges from 2.67 to 4. We studied this region using the isotopic label O^{18}, introduced into different positions of the initial $UO_4 \cdot 2H_2O$, which was subjected to slow thermal decomposition in vacuum at different temperatures up to 700°, with investigation of the composition of intermediate and final products.

$UO_4^{18} \cdot 2H_2O$, with O^{18} only in the peroxide oxygen, was obtained by precipitation from a solution of $UO_2(NO_3)_2$ in ordinary water with heavy $H_2O_2^{18}$ at room temperature (7) or with heating to 90° (9). $UO_4 \cdot xH_2O^{18}$ was obtained by exchange of freshly precipitated $UO_4 \cdot xH_2O$ with H_2O^{18}. After drying over $CaCl_2$ and heating in vacuum at 100° to constant weight, all samples corresponded to the composition $UO_4 \cdot 2H_2O$. The absence of oxygen exchange between UO_4 and the water of hydration was verified both during preparation of the compound and during its drying.

Preliminary experiments established, in agreement with (3,4), that upon gradual heating of $UO_4 \cdot 2H_2O$ to 195° an orange compound U_2O_7 is formed, which reacts vigorously with water or sulfuric acid solution, with liberation of oxygen and formation of UO_3 or, respectively, uranyl salt. When heated from 200 to 400°, U_2O_7 slowly decomposes with liberation of oxygen and formation of red UO_3. The content of U_2O_7 in the solid phase was determined from the volume of oxygen evolved upon treatment with water. On decomposition of $UO_4 \cdot 2H_2O$ to 195°, it increased as the oxygen pressure in the reaction vessel decreased and reached 50% at 15 mm Hg and below. This dependence is evidently due to the fact that, along with an increase in the oxygen pressure, the pressure of water vapor also increased, partially decomposing U_2O_7.

For isotopic analysis, oxygen from H_2O_2 was liberated with permanganate, peroxide oxygen from U_2O_7 by the action of water, and oxygen from U_3O_8 was converted into CO_2 by heating with $HgCl_2 + Hg(CN)_2$ (10). In the water, the oxygen was analyzed by the method described earlier (11).

Table 1 presents the results of several characteristic experiments on the stepwise thermal decomposition of $UO_4^{18} \cdot 2H_2O$. The oxygen evolved upon heating to 195° has the same isotopic composition as the initial $H_2O_2^{18}$.

Table 1

Thermal decomposition of $UO_4^{18} \cdot 2H_2O$, prepared from $H_2O_2^{18}$ with 1.00% O^{18} above natural abundance

Experiment no.	Heating time at given temperature, h	Temp., °C	U_2O_7 in solid phase, %	O^{18} content above natural abundance in oxygen, at. % — from hydrolysis	O^{18} content above natural abundance in oxygen, at. % — from thermal decomposition	O^{18} content above natural abundance in oxygen, at. % — in U_3O_8
1	24	195	24.5	1.00	1.01	
1	9	220			0.97	
1	16	250			0.93	
1	10	270	20.4	0.83	0.85	
1	17	300	20.2	0.37	0.39	
1	10.5	340			0.29	
1	1.5	370	6.0	0.28	0.28	
1	8	450	0		0.27	

Experiment no.	Heating time at given temperature, h	Temp., °C	U_2O_7 in solid phase, %	O^{18} content above natural abundance in oxygen, at. % – from hydrolysis	O^{18} content above natural abundance in oxygen, at. % – from thermal decomposition	O^{18} content above natural abundance in oxygen, at. % – in U_3O_8
1	2	700–800			0.27	0.27
2	24	195	34.8	1.00	1.00	
2	5	220			0.98	
2	13	270			0.87	
2	16	320	19.4	0.29	0.28	
2	46	340			0.29	
2	2	500			0.29	0.29
3	24	195	50.5	1.00	1.00	
3	20	250			0.98	
3	15	320	27.3	0.29	0.30	
3	10	400			0.31	
3	2	500			0.30	0.30

The same composition is possessed by the peroxide oxygen from U_2O_7, liberated upon treatment of the solid phase with acidified water; the O^{18} content in this oxygen is much higher than its average content in the solid phase. Thus, both in UO_4 and in U_2O_7 the oxygen atoms are not equivalent to one another. In them, the peroxide oxygen retains a structurally isolated position and is the first to split off during thermal decomposition.

When uranium peroxide is heated to 195°, 1.9 moles of water are evolved from it per 1 mole of UO_4 (Table 2). This water contains only from 13 to 24% O^{18} from the initial H_2O_2. If heavy uranium peroxide had the structure of the perhydrate $UO_3 \cdot H_2O_2 \cdot H_2O$, the water from its thermal decomposition would have about 50% peroxide O^{18} in the absence of exchange with the solid phase, or, in any case, no less than in the latter if such exchange occurred. Meanwhile, the O^{18} content in the oxygen from thermal decomposition is always greater than in the water. In agreement with this, thermal decomposition of light uranium peroxide prepared in H_2O^{18} always gives water with a higher O^{18} content than in the solid phase (experiments 4 and 5 of Table 2).

The fraction of peroxide oxygen passing into the water evolved up to 195° is the greater, the less U_2O_7 remains undecomposed to the lower oxides. This is seen from Table 2, both for experiments with heavy peroxide oxygen and for experiments with the reverse label. From these data it follows that the incorporation of small amounts of peroxide oxygen into the water is caused by isotopic exchange with the decomposition products of U_2O_7, namely with UO_3. Indications of such exchange were available

earlier ([12]), and we confirmed it by direct experiments. A mixture of 0.012 mol of UO_3^{18} with 0.48% O^{18}* and 0.005 mol of $UO_4 \cdot 2H_2O$ of normal isotopic composition, when heated to 195°, gave water with 0.21% O^{18}, and on further heating above 400° (decomposition of the exchange UO_3)—oxygen with 0.30% O^{18}. In another experiment with a different composition of the mixture, the water and oxygen contained, respectively, 0.39 and 0.45% O^{18}. Table 2 gives the O^{18} contents in water, calculated on the assumption of complete oxygen exchange between it and UO_3, contained in the solid phase.

Table 2

Dependence of the isotopic composition of the water evolved on heating $UO_4 \cdot 2H_2O$ to 195° on the content of U_2O_7 in the solid phase

Experiment No.	$H_2O : U$	U_2O_7 in solid phase, U %	O^{18} content above natural, at. % in H_2O, found	O^{18} content above natural, at. % in H_2O, calc.*	O^{18} content above natural, at. % in UO_3	Experiment No.	$H_2O : U$	U_2O_7 in solid phase, U %	O^{18} content above natural, at. % in H_2O, found	O^{18} content above natural, at. % in H_2O, calc.*	O^{18} content above natural, at. % in UO_3
A. $UO_4^{18} \cdot 2H_2O$ from $H_2O_2^{18}$ with 1.00% O^{18}	A. $UO_4^{18} \cdot 2H_2O$ from $H_2O_2^{18}$ with 1.00% O^{18}	A. $UO_4^{18} \cdot 2H_2O$ from $H_2O_2^{18}$ with 1.00% O^{18}	A. $UO_4^{18} \cdot 2H_2O$ from $H_2O_2^{18}$ with 1.00% O^{18}	A. $UO_4^{18} \cdot 2H_2O$ from $H_2O_2^{18}$ with 1.00% O^{18}	A. $UO_4^{18} \cdot 2H_2O$ from $H_2O_2^{18}$ with 1.00% O^{18}	B. $UO_4 \cdot 2H_2O^{18}$ from H_2O^{18} with 0.71% O^{18}	B. $UO_4 \cdot 2H_2O^{18}$ from H_2O^{18} with 0.71% O^{18}	B. $UO_4 \cdot 2H_2O^{18}$ from H_2O^{18} with 0.71% O^{18}	B. $UO_4 \cdot 2H_2O^{18}$ from H_2O^{18} with 0.71% O^{18}	B. $UO_4 \cdot 2H_2O^{18}$ from H_2O^{18} with 0.71% O^{18}	B. $UO_4 \cdot 2H_2O^{18}$ from H_2O^{18} with 0.71% O^{18}
1	1.92	24.5	0.22	0.18	0.27	4	1.90	26.0	0.32	0.34	0.18
2	1.85	34.8	0.18	0.17	0.29	5	1.95	49.7	0.40	0.41	0.15
3	1.91	50.5	0.13	0.14	0.30						

* In the calculation it was assumed that, on heating to 195°, $UO_4 \cdot 2H_2O$ decomposes according to the scheme
$2(UO_4 \cdot 2H_2O) = xU_2O_7 + (2-2x)UO_3 + (1-x/2)O_2 + 4H_2O$,

and that the water formed exchanges only with UO_3. Instead of x, the numbers from the second column of Table 2 were substituted. The experimentally found O^{18} contents in UO_3 are the mean between the contents of it in $(2-2x)UO_3$, which has exchanged with water, and xUO_3, obtained in the thermal decomposition of xU_2O_7 after removal of all the water.

Their satisfactory agreement with the observed values serves as further confirmation of the rapid oxygen exchange between UO_3 and water, leading to transfer into the latter of peroxide oxygen that had partly entered UO_3 during the thermal decomposition of uranium peroxides: the vapor of light water from $UO_4^{18} \cdot 2H_2O$ decomposes the $U_2O_7^{18}$ formed during thermal decomposition and rapidly exchanges oxygen with the UO_3^{18} obtained thereby.

The data presented definitively confirm that uranium tetroxide is a true peroxide of the structure $UO_4 \cdot 2H_2O$. In accordance with this structure, it does not exchange oxygen with an H_2O_2 solution. Such exchange should have been expected for bound H_2O_2 in the structure of the perhydrate $UO_3 \cdot H_2O_2^{18} \cdot H_2O$. We did not find it even after 500 h of residence of heavy-oxygen uranium peroxide in a solution of light H_2O_2.

From Table 1 it is seen that between 195° and approximately 400° decomposition of U_2O_7 occurs. Up to 270° it is small, and the change in the O^{18} content in the evolved oxygen, as also in the oxygen from hydrolytic decomposition of U_2O_7, is likewise small. Near 300° the isotopic composition of the oxygen changes sharply, although, as is seen from experiment 1, the U_2O_7 content remains almost the same. At this temperature, evidently, a phase transformation of the solid solution occurs, after which the oxygen atoms acquire the ability to migrate readily in the lattice, so that the isotopic label is distributed among all oxygen atoms in U_2O_7 and UO_3. As a result, the O^{18} content in peroxide oxygen from U_2O_7 above 300° is the same as its average content in the final decomposition product U_3O_8, obtained on heating above 700°. At all temperatures the isotopic composition of the peroxide oxygen from hydrolysis of U_2O_7 coincides with the composition of the oxygen from its thermal decomposition, and in U_2O_7 the peroxide oxygen retains a structurally distinct position despite its exchange with the other oxygen atoms. Easy migration of oxygen atoms was previously detected by other me–

* Everywhere the numbers refer to the excess content of O^{18} above natural.

by the same methods also in the region of higher temperatures, with the composition of the solid phase between U_3O_8 and UO_2 [2].

At 400–420° the decomposition of U_2O_7 is completed and the evolution of oxygen ceases even under prolonged heating. In this case the color of the solid phase changes from orange to red; it does not give off oxygen upon interaction with water, and its composition approaches UO_3. At 450–500° the evolution of oxygen begins again and continues on heating to 700–800°. In this interval the color of the solid phase becomes dark green and its composition approaches U_3O_8. Between 350 and 700° the isotopic composition of the evolved oxygen does not change and remains the same as in the final U_3O_8. This confirms the equivalence of the oxygen atoms in UO_3 and U_3O_8, which is also consistent with X-ray structural data [1].

Thus, in contrast to UO_3 and U_3O_8, which have the structure of oxides, $UO_4 \cdot 2H_2O$ and U_2O_7 are true peroxide compounds with structurally distinct atoms of peroxide oxygen.

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Note: Figure translations are in progress. See original paper for figures.