

CCA-357

546.791-3:546.791.03

Original Scientific Paper

Heats of Immersion of Uranium Oxides in *n*-Nitropropane III.*

D. Kolar and B. S. Brčić

Nuclear Institute »Jožef Stefan« Ljubljana, Slovenia, Yugoslavia

Received October 19, 1965

Heats of wetting of uranium oxides with different O/U ratios were measured in *n*-nitropropane and these heats were found to decrease with increasing oxygen content of the oxides. This behaviour was compared with the opposite tendency in water. It was concluded that a definite amount of UO_3 is relatively easily formed on the surface of UO_2 at lower temperatures.

INTRODUCTION

Recently reported results on the heats of wetting uranium oxides in water¹ showed an increase of immersion heats with increasing O/U ratio of uranium oxides. It was further observed that annealed samples gave generally lower values and that the increase of heat values of annealed samples when approaching U_3O_8 composition was much less marked². Two possible explanations for the above observation were proposed: (a) increasing strain in the surface layers of the oxides due to the difference in density and (b) the presence of small amounts of uranium trioxide on the surface of the oxidized samples. It was the aim of our further investigations to check the last assumption.

EXPERIMENTAL

The immersion heats of both uranium oxide samples »as prepared« (unannealed) and annealed, were measured calorimetrically in *n*-nitropropane at 25°C. The uranium oxide samples were carefully oxidized at low temperature to cover the whole range of O/U ratios from 2.00 to 2.67. The methods of preparation of the samples and the results of X-ray analysis were the same as described in reference².

The X-ray structures were in line with known data for uranium oxides³. The samples were examined for infrared spectra in the 2 to 15 μ region, where the characteristic spectra of UO_3 and U_3O_8 were expected⁴. Whereas the presence of U_3O_8 was easily detected in the samples with higher O/U ratio, the evidence for the presence of UO_3 was not conclusive.

The calorimeter and the methods of surface area and O/U ratio determinations were described in reference 1. The *n*-nitropropane was supplied by L. Light Co., Cornbrook, England. Since the stoichiometric UO_2 (i.e. the UO_2 powder which was not exposed to air after the preparation from ADU in a stream of hydrogen gas and had a composition of $\text{UO}_{2.00 \pm 0.01}$) was oxidized rapidly by the oxygen dissolved in organic liquid, the nitropropane had to be distilled in an argon atmosphere before the measurements were carried out. The tendency towards oxidation was much higher than in water and the argon atmosphere had to be maintained in the calorimeter during the measurements.

* Professor Vladimir Njegovan ad honorem.

RESULTS

The measured heat effects were expressed on the specific area basis and plotted *vs.* O/U ratio in Fig. 1. A single straight line obtained by the least squares method was drawn through the experimental points. However, the

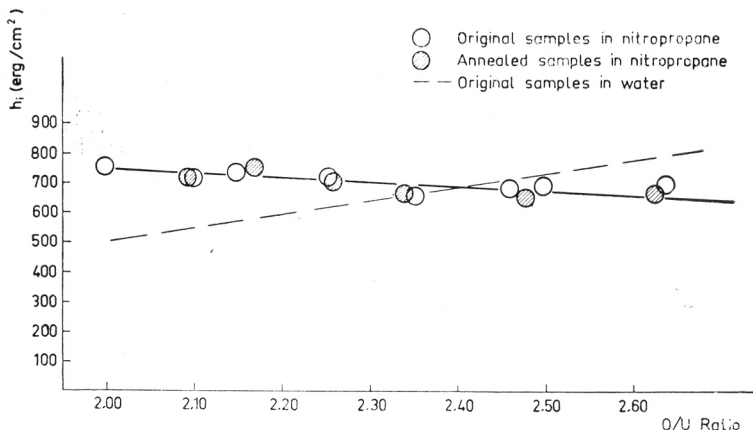


Fig. 1. — Heats of wetting of uranium oxides in *n*-nitropropane and water as a function of O/U ratio of uranium oxide

points might also be connected by two lines with a kink at $\text{UO}_{2.33}$. Our choice is based on the lowest standard deviation. The curve from previous investigations relating to heat effects in water was added for comparison. In addition, the heat values of UO_3 were determined in *n*-nitropropane and water. The measured values were 553 erg/cm^2 and 2470 erg/cm^2 , respectively. The value in water is felt to be still low since the effect was not merely wetting, but hydration. The thermal equilibration was slow, probably due to the formation of a surface shell of hydrate which impeded further reaction⁵.

DISCUSSION

As shown in Fig. 1, the heat of wetting effect of uranium dioxide in *n*-nitropropane is considerably higher than in water, which is a consequence of the higher dipole moment of the organic liquid (*n*-nitropropane 3.57 D, water 1.87 D).

It is further seen in Fig. 1 that the heat of wetting values in the organic liquid are slightly decreasing with increasing oxygen content of the uranium oxides. The effect is in accordance with De Boer's explanation of the influence of the density of substrate structure on the heat of wetting⁶ since the densities of uranium oxides are decreasing from 10.96 g/cm^3 for UO_2 to 8.3 g/cm^3 for U_3O_8 . The similarity of the heats of wetting of U_3O_8 and UO_3 is again in accordance with this explanation, as the densities are nearly equal. The same explanation was proposed in connection with the observed heat of wetting effects of SiO_2 ⁷.

The bond type of the substrate structure is another factor which could influence the wetting results. On the basis of available information it has been concluded that the lattice forces in uranium dioxide are largely ionic in

character, whereas the higher oxides of uranium, U_3O_8 and UO_3 , show a much greater tendency towards covalent bonding⁸. Since the heat effects due to ion-dipole interaction are generally found to be higher than the effects based on residual Van der Waals forces, this may constitute another cause of the lower heat values obtained when wetting the oxides with higher oxygen content.

Accepting the above offered explanation for the decreasing tendency of the heat of wetting as a general one, the question arises why the effects in water show the opposite character. The increasing immersional heats with increasing oxygen content must be ascribed to some specific interaction of uranium oxides with water. Since neither UO_2 nor U_3O_8 react with water under normal conditions we ascribe the effect to UO_3 . The presence of some UO_3 on the surface of the uranium oxide samples with higher oxygen content would not influence significantly the wetting heats in nitropropane since the values of U_3O_8 and UO_3 are comparable (648 and 553 erg/cm² resp.). The opposite is true for the experiments with water as wetting agent. The effect of hydration (2470 erg/cm² for UO_3) is several times larger than the effect of normal wetting, and even so small amounts of UO_3 in the outermost surface layer that they are undetectable by X-ray or infrared technique can greatly influence the results. The fact that essentially the same results were obtained with annealed and with unannealed samples in nitropropane while widely different results were obtained with these two samples in water, are also evidence in favour of the invoked role of UO_3 .

It is generally agreed that the oxidation of UO_2 proceeds until the composition U_3O_8 is reached. UO_3 is not obtained easily from the lower oxides and the successful preparation requires increased oxygen pressure⁴.

Up to some 700°C the formation of UO_3 is thermodynamically preferable and the general observation that the oxidation of UO_2 leads only to the formation of U_3O_8 was explained by kinetic reasons⁹. Lebau, as quoted by Katz¹⁰ concluded in his early work that U_3O_8 prepared below red heat might contain some UO_3 . Boule and coworkers¹¹ prepared crystalline UO_2 which can be oxidized directly to UO_3 at low temperature. On one of the active oxide samples with a specific area of 30 m²/g and an equilibrium composition approaching $UO_{2.5}$ Hoekstra found an infrared spectrum characteristic of amorphous UO_3 ³. Belbeoch and coworkers¹² and Jakeš and Sedlakova¹³ also observed that UO_3 is formed at low temperature by oxidation of UO_2 having a large surface area. The self-consistency in our interpretation of the presented experimental evidence here and earlier¹ may be taken as strongly suggestive of UO_3 formation in the outermost layers of UO_2 at low temperature. Indeed, it would be the first evidence of UO_3 formation on a surface of medium active UO_2 , since the increase of heat effects was observed even on powders with specific surfaces of 2 m²/g. This would imply that UO_3 can form relatively easily on the surface of oxidized UO_2 particles.

Acknowledgment. The authors are indebted to Mr. J. Kristan and coworkers for the construction of the calorimeter and to Mr. A. Urbanc for performing the X-ray investigations. The technical assistance of Miss L. Drinovec and Mr. J. Snoj is also acknowledged.

REFERENCES

1. D. Kolar, *Croat. Chem. Acta* **35** (1963) 123.
2. D. Kolar, *Croat. Chem. Acta* **35** (1963) 289.
3. H. R. Hoekstra, A. Santoro, and S. Siegel, *J. Inorg. Nucl. Chem.* **18** (1961) 166.
4. H. R. Hoekstra and S. Siegel, *ibid.* p. 164.
5. R. M. Dell and V. J. Wheeler, *Trans. Farad. Soc.* **59** (1963) 485.
6. J. H. De Boer, *Advances in Catalysis* **8** (1956) Academic Press 1956, p. 34.
7. W. H. Wade, N. Hackerman, *J. Phys. Chem.* **66** (1962) 1823.
8. J. Belle, *Uranium Dioxide*, U. S. AEC, Washington 1961, p. 230.
9. L. E. J. Roberts, *Quart. Rev.* **4** (1961) 443.
10. J. Katz and E. Rabinowitch, *The Chemistry of Uranium*, Mc Graw-Hill, New York 1951, p. 282
11. A. Bouille, R. Jary, and M. Dominé Bergés, *Comptes-Rendus* **230** (1950) 300.
12. B. Belbeoch, C. Piekarski, and P. Perio, *J. Nucl. Mat.* **3** (1961) 60.
13. D. Jakeš and L. Sedláková, *New Nuclear Materials Including Non Metallic Fuels*, Vol. 1, IAEA, Vienna 1963, 155.

IZVLEČEK

Omakalne toplote uranovih oksidov v n-nitropropanu (III)

D. Kolar in B. S. Brčić

Omakalne toplote uranovih oksidov z različno vsebnostjo kisika so bile izerjene v *n*-nitropropanu. Vrednosti padajo z naraščajočo vsebnostjo kisika. Na podlagi primerjave z nasprotno tendenco pri omakanju v vodi zaključujemo, da na površini uranovega dioksida pri oksidaciji pri nizki temperaturi nastane določena množina uranovega trioksida.

NUKLEARNI INŠTITUT JOŽEF STEFAN
LJUBLJANA

Sprejeto 19. oktobra 1964.