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REACTION OF URANIUM MONOCARBIDE POWDER IN OXIDIZING ATMOSPHERES

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ABSTRACT

Thermogravimetric records have been obtained of uranium monocarbide oxidized in oxygen and in carbon dioxide under similar conditions. It is shown that the reactions are very similar. Initially, free carbon is formed during oxidation as well as UO_3 in O_2 or UO_2 in CO_2. In a second reaction step non-stoichiometric carbonates are formed, depending on experimental conditions. The carbonates decompose to stoichiometric oxides in the next step.

Well crystallized α-UO_3 can be obtained by oxidation of uranium monocarbide in oxygen. The solid products containing UO_2 which slowly formed in carbon dioxide, are unstable in air.

Infrared and X-ray analysis have been used to compare related, solid structures. Activation energies have been determined of non-isothermal reactions, recorded below 750°C.

INTRODUCTION

Uranium monocarbide is a potentially useful fuel or fuel component for high-temperature reactors[1]. It is sensitive to oxygen and very sensitive to moisture. It must therefore be stored and handled in inert atmospheres. Ultra-pure argon in glove boxes is most frequently used for this purpose[2].

It was observed that our uranium monocarbide powder did not ignite in CO_2 by stimulation with strong electric sparks. Oxidation, shown by a glowing reaction zone, was only gradual after prolonged heating with a red-hot immersion heater. These preliminary experiments have shown that dried carbon dioxide shows promise for use in glove boxes for handling uranium monocarbide fuel on a large scale. This would reduce manufacturing and reprocessing cost considerably, although a less oxidizing atmosphere would still be necessary for sintering fuel pellets[2].

Uranium monocarbide was oxidized on a thermobalance in O_2 and CO_2 atmospheres under similar conditions to obtain more detailed thermoanalytical information.

EXPERIMENTAL

Thermogravimetric records were obtained from a Mettler thermobalance[3]. Kinetic experiments were carried out with a thermogravimetric (TG) crucible holder and a silica crucible of normal size for TG or combined TG–DTA in measurements, using heating rates of ½–2 °C/min in O_2 or 1½–6 °C/min in CO_2 and a 2 inch per hour chart feed in both cases.

The crucible was filled under argon with 0.05 g of fine uranium monocarbide powder (surface area 0.85 m^2/g by a BET method[4], and covered with analytically pure cyclohexane. In some cases a slurry with benzene was used instead. Each time, the slurry* was introduced on the thermobalance before the protective liquid could evaporate.

To change the atmosphere above the slurry, the weighing chamber was evacuated to 10 cm Hg pressure from the outlet side with an additional vacuum pump and each time subsequently filled to ambient pressure (*ca.* 66 cm Hg) with either O_2 or CO_2, the latter containing about 10 ppm CO.

Residual liquid was evaporated in a flowing gas stream (*ca.* 5 l/h) at about 30 °C in O_2 or 50 °C in CO_2. No weight increase of the dried samples was observed at these temperatures.

Silica gel and magnesium perchlorate were used to dry the gas stream. After obtaining constant weight, the sample was heated with a linear programme up to about 750 °C or to a lower temperature, to obtain more information about intermediate products. The sample was kept at these temperatures for at least 45 minutes.

Blind probes, without a sample, were run to make buoyancy corrections. O/U ratios were determined in the uranium oxide endproducts, according to a thermogravimetric reduction method described earlier[5] which uses hydrogen.

RESULTS AND DISCUSSION

General

Buoyancy corrected weight curves are shown in Fig. 1.

It was concluded from evidence given in the following sections that essentially the following chemical changes took place in the samples:

$$UC \xrightarrow{1} UO_3 + C \xrightarrow{2} UO_3 \cdot xCO_2 \xrightarrow{3} \alpha\text{-}UO_3 \xrightarrow{4} U_3O_8 \text{ in oxygen}$$

or

$$UC \xrightarrow{1} UO_2 + C \xrightarrow{2} UO_2 \cdot xCO_2 \xrightarrow{3} UO_2 \xrightarrow{4} UO_{2+y} \text{ in carbon dioxide}$$

Similar reactions also took place during oxidation of UC_2 instead of UC powder.

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*In similar experiments with more inert UC_2 instead of UC it was unnecessary to introduce the sample in a slurry.

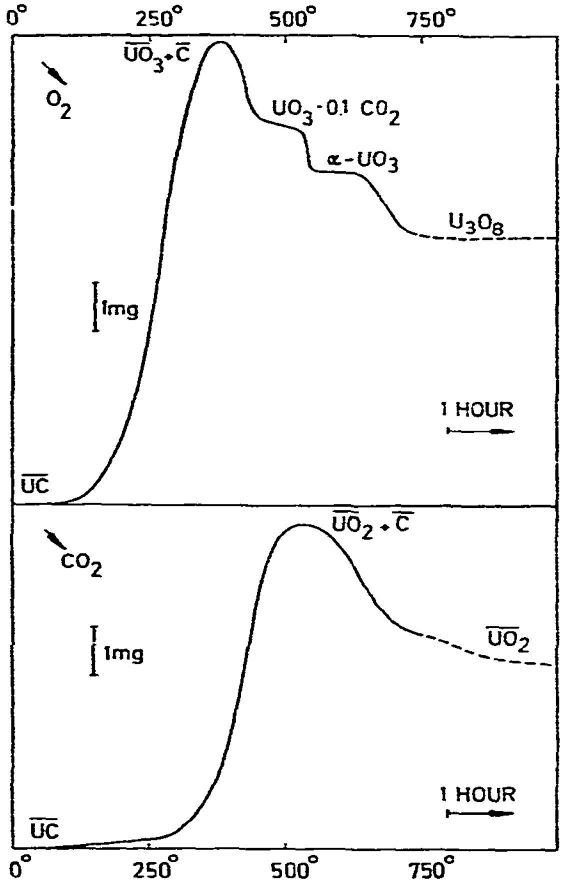

Fig. 1. Oxidation of uranium monocarbide in buoyancy corrected thermogravimetric records in oxygen and carbon dioxide atmospheres using 0.05 mg samples. Specific surface area, 0.85 m^2/g (BET); Heating rate, 2 °C/min; (——), Non-isothermal, up to 750 °C; (– – –), Isothermal, from 750 °C.

Arrhenius plots of non-isothermal rate changes at fixed levels of completion ($\alpha = \frac{1}{4}$, $\frac{1}{2}$ or $\frac{3}{4}$) versus reciprocal temperature are shown in Fig. 2. Regression lines and activation energies, shown in Table 1, were calculated from these plots, using

TABLE 1

ACTIVATION ENERGIES

Reaction	α	*In O_2*		*In CO_2*	
		E_a *(kcal/mole)*	*°C*	E_a *(kcal/mole)*	*°C*
1	$\frac{1}{2}$	42.0 ± 1.9	235–254	25.4 ± 1.2	416–452
2	$\frac{1}{4}$*[a]	34.4 ± 2.5	380–409	30.6 ± 0.2	637–703
3	$\frac{3}{4}$*[a]	110.5 ± 9.0	522–535	—	—
4	$\frac{1}{2}$	93 ± 24	677–683	—	—

[a] Level of completion in the combined reaction steps 2 + 3, resulting in loss of carbon only.

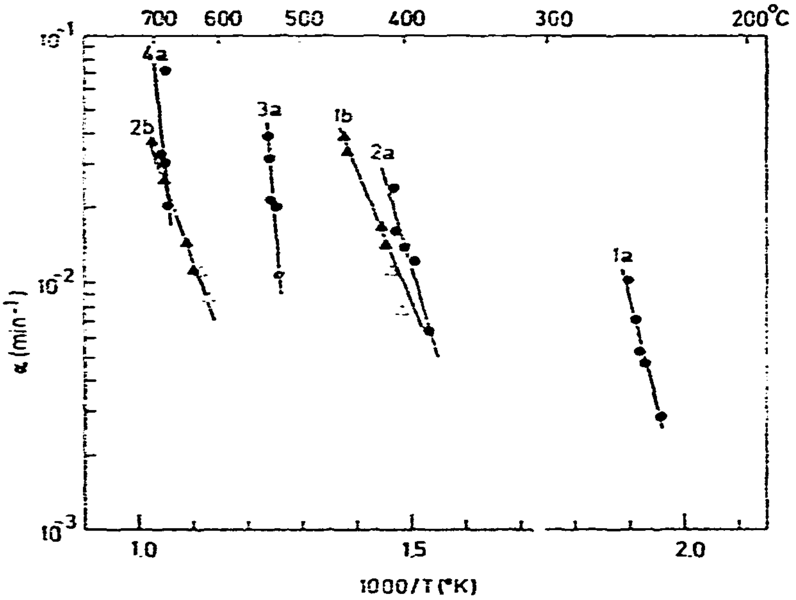

Fig. 2. Reaction rates versus reciprocal temperature at fixed levels of completion (see Table 1). 1, 2, 3 or 4 stands in the order of the following reaction steps: a stands for oxygen atmosphere, b stands for carbon dioxide atmosphere; therefore 1a indicates the first reaction step in oxygen. Heating rates: ● ½–2 °C/min in cyclohexane slurry, ▲1½–6 °C/min in cyclohexane slurry, and △ 1–1½ °C/min in benzene slurry.

data from cyclohexane slurries only. Some data from benzene slurries are included in Fig. 2 and show slight deviations from the calculated[6] regression lines.

Overlap in the reaction steps occurred, especially in CO_2. Furthermore, slight temperature differences between the sample and the thermocouple on the outside of the crucible were likely. It was assumed that these and other complications, discussed in the following sections, had no significant influence on the rate of weight change as a function of temperature in the above mentioned degrees of completion. However, the non-isothermic, thermogravimetric records were definitely unsuitable for reaction mechanism tests. Therefore no further kinetic evaluation was carried out.

First reaction step

In oxygen $UC \rightarrow UO_3 + C$

In carbon dioxide $UC \rightarrow UO_2 + C$

The O/U ratios in the products were first calculated from the initial UC sample weights. From the weight of U_3O_8 obtained as an endproduct in oxygen, it was also possible to calculate the O/U ratio, but with CO_2 as oxidant the end products were unstable in air and this approach could not be used. It was possible, however, to make the calculation by assuming that the thermogravimetric minimum, corresponding to the completion of the third reaction step, indicated the tempory formation of pure UO_2.

The results are summarized in Table 2 and are seen to correspond closely with the values to be expected from the equations suggested for the first oxidation steps, especially as no allowances were made for possible surface oxidation of the original UC, for possible hyperstoichiometry in the intermediate UO_2 and for slight overlapping of the first and second oxidation stages.

TABLE 2

CALCULATED OXYGEN/URANIUM RATIOS IN SOLID, INTERMEDIATE PRODUCTS FROM STAGE 1

Reaction in O_2			*Reaction in CO_2*		
Heating rate[a]	*O/U ratio*		*Heating rate*[a]	*O/U ratio*	
	Method A[b]	*Method B*[c]		*Method A*[b]	*Method C*[d]
½	2.87	3.07	1½	2.00	2.08
1	2.83	3.08	2	2.00	2.10
1	2.82	3.00	4	1.95	2.06
1½	2.84	3.01	6	1.92	2.06
2	2.75	3.02			

[a] In units of °C/min. [b] A calculated from original weight of UC. [c] B calculated from final weight of $U_3O_{8\pm x}$. [d] C calculated from intermediate weight of UO_2.

As was expected, the higher rates of heating gave slightly lower values in the determined O/U ratios, corresponding to the maximum weight levels (Fig. 1).

The activation energy of 42.0+1.9 kcal/mole for oxidizing UC powder with oxygen leading to UO_3+C, is much higher than the 21–28.7 kcal/mole, found by other authors[7–9] for sintered UC, leading to U_3O_8 and CO_2. In view of the different stoichiometric results this is not surprising.

Uranium monocarbide powder starts to react with CO_2 below 300°C (Fig. 1) to form UO_2+C. Moreau and Philipot[10] have found the same stoichiometric results for sintered UC in CO_2 above 500°C. They have shown that the reaction kinetics for sintered material depend on the temperature range. They have found activation energies between 16.6 and 42.5 kcal/mole. An intermediate value is shown in Table 1.

Second reaction step

In oxygen $UO_3+C \rightarrow UO_3 \cdot xCO_2$

In carbon dioxide $UO_2+C \rightarrow UO_2 \cdot xCO_2$

Tentative values of the activation energy in these complicated, heterogenic reactions are given in Table 1. The carbonate products were amorphous or at least of poor crystallinity. The carbonate product formed in CO_2, could not be isolated from elemental carbon without decomposition.

Both products were non-stoichiometric with calculated CO_2/U ratios of 0.11–0.12 in O_2 or about 0.1 in CO_2.

An infrared absorption spectrum of the orange-red coloured, hygroscopic product in oxygen is shown in Fig. 3. The $UO_3 \cdot xCO_2$ spectrum shows similarity with the absorption of U_3O_8[5,11] in the 250–800 cm region. Further oxide absorption is observed at 840 cm^{-1} and at 900 cm^{-1}. At least one of these two peaks can be ascribed partly to a carbonate group. Other carbonate absorption peaks are observed at 1370 and 1515 cm^{-1}. The absorption at 1610 cm^{-1} can be ascribed to chemisorbed water.

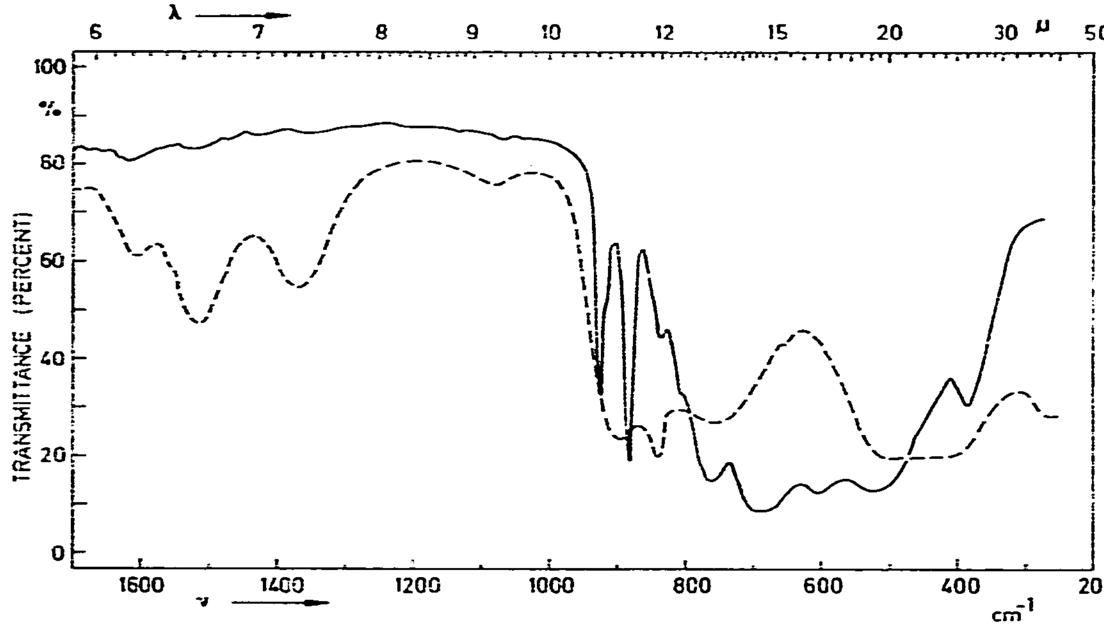

Fig. 3. Infrared absorption spectra of UO_3 in KBr pellets on Perkin–Elmer model 521. (– – –) $UO_3 \cdot xCO_2$ (UC heated to constant weight in O_2 at 400 °C), and (——) α-UO_3 (UC heated to constant weight in O_2 at 600 °C).

An amorphous product with a similar spectrum has been obtained in two reaction steps by slow decomposition of uranyl oxalate with a heating rate of $\frac{1}{2}$ °C/min from 280 to 400 °C in hydrogen and subsequent oxidation to constant weight in oxygen at 420 °C. A trace of carbon is retained in this product, but its spectrum shows much less intensity in the two characteristic carbonate absorption bands above 1200 cm^{-1}, mentioned above. Another similar product with a CO_2/UO_3 ratio of 0.29 was obtained by Dell *et al.*[12] by oxidation of uranium monocarbide up to 330 °C only.

Third reaction step

In oxygen $UO_3 \cdot xCO_2 \rightarrow \alpha\text{-}UO_3$

In carbon dioxide $UO_2 \cdot xCO_2 \rightarrow UO_2$

Calculated O/U ratios of the products in O_2 are shown in Table 3. These values are slightly higher than those of the initial products (see Table 2). The apparent differences may be due to retained traces of carbon dioxide during crystallization and not to an increase in oxygen content only.

TABLE 3

CALCULATED OXYGEN/URANIUM RATIOS IN α-UO_3 INTERMEDIATE PRODUCTS FROM STAGE 3

Heating rate (°C/min)	*O/U ratio*	
	Method A[a]	*Method B*[b]
½	2.88	3.07
1	2.87	3.09
1	2.89	3.05
1½	2.92	3.05
2	2.84	3.02

[a] A calculated from original weight of UC. [b] B calculated from final weight of $U_3O_{8\pm x}$.

An infrared absorption spectrum of brown α-UO_3, prepared by oxidation of uranium monocarbide, is also shown in Fig. 3. The oxide absorption bands in the 300–1000 cm^{-1} region show a finer structure than α-UO_3, prepared from uranyl peroxide, containing traces of nitrate[11,13]. The absorption peak[5] at 600 cm^{-1} is clearly resolved. Additional peaks are observed at 800 cm^{-1} (w.sh.), 835 cm^{-1} (m), 850 cm^{-1} (vw. sh.) and 915 cm^{-1} (w.sh.). No explanation for their appearance is given, because the exact stoichiometry and crystal structure of pure α-UO_3 is still unknown[14]. Hardly any absorption due to traces of retained carbonate or chemisorbed moisture in the 1300–1700 cm^{-1} region is observed in contrast to the absorption spectrum of the amorphous phase (Fig. 3).

Table 4 presents the *d*-values of the same crystalline product. These X-ray values differ only slightly from diffraction data of $UO_{2.9}$, prepared by Hoekstra and

TABLE 4

DIFFRACTION DATA ON α-UO_3, PREPARED FROM UC

d-value Å	*X-ray intensity I/I_0*	*d-value Å*	*X-ray intensity I/I_0*
4.157	100	1.774	45
3.462	90	1.731	<10
3.403	95	1.703	<10
2.660	80	1.576	<10
2.632	85	1.436	<10
2.078	20	1.423	<10
1.988	15	1.386	<10
1.955	<10	1.317	<10
1.794	35	1.284	<10
1.782	<10		

Siegel[15] from U_3O_8 by high-pressure oxidation. Two *d*-values have been found near 1.78 Å in our product instead of only one. On the other hand two weak diffraction lines, formerly observed at 1.60 Å and 1.33 Å, could not be confirmed. The similarity of the two diffraction patterns shows that the crystal structures of these products are essentially the same.

Strong overlapping was evident between the second and third reaction steps in CO_2 on each thermogravimetric record (Fig. 1). The third and fourth reaction steps in CO_2 took place at approximately the same temperature (750 °C), and it was thus not possible to determine their activation energies.

Broad minima on each record between these last steps indicated that no significant overlapping between these reactions had taken place. The weight difference of each minimum, compared with the initial sample weight, corresponded to the addition of 1.9 oxygen atoms and the loss of one carbon atom per uranium atom. It is likely that our starting material had picked up about 0.1 O/U atom by surface oxidation[2]. This explanation is confirmed by the results on the right-hand side of Table 2. The minima obtained at 750 °C, therefore indicate the temporary formation of stoichiometric, pure UO_2.

Fourth reaction step

In oxygen $\alpha\text{-}UO_3 \rightarrow U_3O_8$

In carbon dioxide $UO_2 \rightarrow UO_{2+y}$

α-UO_3 prepared by oxidation of UC in O_2, on further heating decomposed directly to U_3O_8. Constant weight levels were obtained with U/O ratios in the 2.65–2.68 range at 750 °C. The activation energy of this reaction could not be determined accurately because this would necessitate changing the experimental conditions chosen mainly to suit the initial reaction step. However, the high value of the activation energy at 50% completion (Table 1) agrees well with the values found by Karkhanavala and Phadnis[16] for the decomposition of $UO_{2.89}$ intermediates with a similar crystal structure.

Less than 0.01 O/U atom per hour was added at 750 °C during oxidation in the fourth reaction step in CO_2. Endproducts with O/U ratios in the 2.10–2.13 range picked up further oxygen in contact with air at room temperature. Infrared spectra of these oxides with O/U ratios increased to the 2.24–2.31 range, showed significant absorption at 740 cm^{-1} similar to U_3O_8 and amorphous $UO_3 \cdot xCO_2$ (Fig. 3).

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