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Formation and Dissociation of Uranium Antimonates

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Certain reactions occurring during the preparation of uranium antimonate catalysts have been investigated by observing the thermal behaviour of orthorhombic uranium (V, VI) oxide and uranium (VI) dioxide dinitrate hexahydrate. The thermal dissociation of the catalysts has also been examined. Although α-U_3O_8 is stable under oxygen, it dissociates progressively when heated under nitrogen forming $U_8O_{21+z'}$ which has a weak but characteristic absorption in the infrared at 645 cm^{-1}. When heated in oxygen, $UO_2(NO_3)_2 \cdot 6H_2O$ dissociates to UO_3 which, at higher temperatures, yields U_3O_8. In the formation of catalysts by solid-state reactions at about 1440 K under oxygen, α-U_3O_8 and Sb_2O_4 react incompletely to yield polyphasic material consisting of amorphous USb_3O_{10} together with $USbO_5$ and unreacted Sb_2O_4. Preparation of the catalysts in aqueous solution from $UO_2(NO_3)_2 \cdot 6H_2O$ and Sb_2O_3 achieves almost complete conversion to crystalline USb_3O_{10}. Although $USbO_5$ is an intermediate in both processes, UO_3, Sb_6O_{13+x} and Sb_6O_{13} are also formed in the latter synthesis. On heating to 1221 K in nitrogen, USb_3O_{10} dissociates via $USb_{1+x}O_{5+y}$ to $USbO_5$ which, in turn, forms U_8O_{21+z} and Sb_2O_3.

INTRODUCTION

Catalysts based on uranium antimonates are known to be active and selective in the oxidation and ammoxidation of alkenes (*1–4*). The existence of two uranium antimonates ($USbO_5$ and USb_3O_{10}) has been established (*5–7*). The former is the major component in preparations containing equimolar proportions of uranium and antimony, while the latter predominates as the proportion of antimony is increased. Although catalytic activity for the ammoxidation of propene to cyanoethene (acrylonitrile) has been observed with these catalysts over the composition range $1/99 <$ U/Sb $< 50/1$ (*2*), optimum efficiency appears to coincide with the maximum concentration of USb_3O_{10} (*2, 8*). It has also been observed, however, that the method of preparation can affect the composition of the catalysts and hence their performance (*8, 9*).

In the method of preparation of the antimonates reported by Grasselli and Callahan (*1*), the starting materials (Sb_2O_3 and $UO_2(NO_3)_2 \cdot 6H_2O$; U/Sb $= 1/\leq 3$) are combined initially in aqueous solution and subsequent decomposition of the product yields mainly USb_3O_{10}; UO_3, U_3O_8, Sb_2O_4, Sb_2O_5, and $USbO_5$ have been identified as intermediates in the reaction (*2, 10*). However, the part played by intermediates in the preparation has not been examined in detail. In this respect, the thermal stabilities of Sb_2O_3, Sb_2O_4, and Sb_2O_5 have already been reported (*11*) and in the present study, information on the thermal behav-

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iour of $UO_2(NO_3)_2 \cdot 6H_2O$, α-U_3O_8, and Sb_6O_{13} has been obtained. The formation and dissociation of $USbO_5$ and USb_3O_{10} are also discussed.

EXPERIMENTAL

Differential thermal analysis (DTA) was carried out using a Stanton–Redcroft Standata 6-25 instrument. Heat-treated α-alumina was used as reference material. Samples (ca. 60 mg) were heated under flowing atmospheres (oxygen or oxygen-free nitrogen, BOC) at a rate of 10 K min^{-1}.

Simultaneous thermogravimetry and derivative thermogravimetry were carried out using a Stanton–Redcroft TG-750 thermobalance. Samples (ca. 25 mg) were heated at 10 K min^{-1} to a maximum temperature of 1273 K in the presence of flowing or static gases.

X-Ray diffraction photographs were obtained with a Philips camera (Debye–Scherrer, radius 5.73 cm) using nickel-filtered Cu*Kα* radiation (Philips PW 1720), and finely ground samples held in glass capillary tubes (0.5-mm diam). Infrared (ir) spectra were recorded using a Perkin Elmer 577 spectrophotometer, samples having been incorporated into KBr disks (13 mm diam).

Uranium (VI) dinitrate dioxide hexahydrate (AnalaR) was obtained from BDH Ltd. Antimony (III) oxide (Puratronic), supplied by Lancaster Synthesis Ltd., was shown by X-ray diffraction and ir spectroscopy to consist of a mixture of the cubic and orthorhombic modifications of Sb_2O_3. Uranium (V, VI) oxide, supplied by Lancaster Synthesis Ltd., was confirmed as orthorhombic α-U_3O_8.

USb_3O_{10} was prepared according to the method of Grasselli and Callahan (*1*), and $USbO_5$ was prepared by the thermal dissociation of USb_3O_{10} at 1363 K (*1, 2*). No impurities in these compounds were detected by X-ray diffraction or ir spectroscopy. Formulations containing various proportions of USb_3O_{10} were prepared using a method similar to that of Fujino *et al.* (*12*) for the preparation of magnesium uranates, in which mixtures of Sb_2O_4 and $UO_2(NO_3)_2 \cdot 6H_2O$, or α-U_3O_8, were heated slowly in air to 1173 K, maintained at this temperature for 24 h and then at 1073 K for a further 48 h.

RESULTS AND DISCUSSION

Thermal Behaviour of Single Components

(i) *α-U_3O_8.* Differential thermal analysis was performed on α-U_3O_8 in atmospheres of either oxygen or nitrogen. Several repeatable changes in baseline were observed. Below 773 K, two extremely small reversible endotherms were detected having peak temperatures of 488 ± 5 and 568 ± 2 K. The former coincided with the reversible transition from the orthorhombic to the hexagonal form of U_3O_8 reported to occur at 486 ± 1 K (*13*). The occurrence of a peak at ca. 1173 K reported by other workers (*14, 15*) was not observed.

Thermogravimetry showed that when heated above 523 K in nitrogen, U_3O_8 gradually lost mass, to the extent of 0.22 ± 0.05% at 1273 K. Assuming a stoichiometric sample at room temperature, this loss would have corresponded to a change in composition from $UO_{2.667}$ to $UO_{2.626}$. X-Ray diffraction showed that, after cooling in nitrogen, the structure of orthorhombic U_3O_8 was retained. IR spectroscopy, however, revealed an additional weak adsorption at 645 cm^{-1} compared to the spectrum of unheated U_3O_8. For samples heated in oxygen or air, no loss in mass was observed between 523 and 1273 K. IR spectroscopy and X-ray diffraction revealed no changes in the structure even after prolonged (7 h) heating at 1173 K. These results are at variance with reports (*14, 16*) which suggest that, on heating in air, U_3O_8 loses oxygen above 773 K.

(ii) *$UO_2(NO_3)_2 \cdot 6H_2O$.* Thermogravimetric analysis revealed that, on heating crystalline $UO_2(NO_3)_2 \cdot 6H_2O$ in nitrogen or oxygen, the compound lost mass almost immediately. Between 303 and 573 K, the magnitude of the decrease agreed very closely with that expected for the loss of six

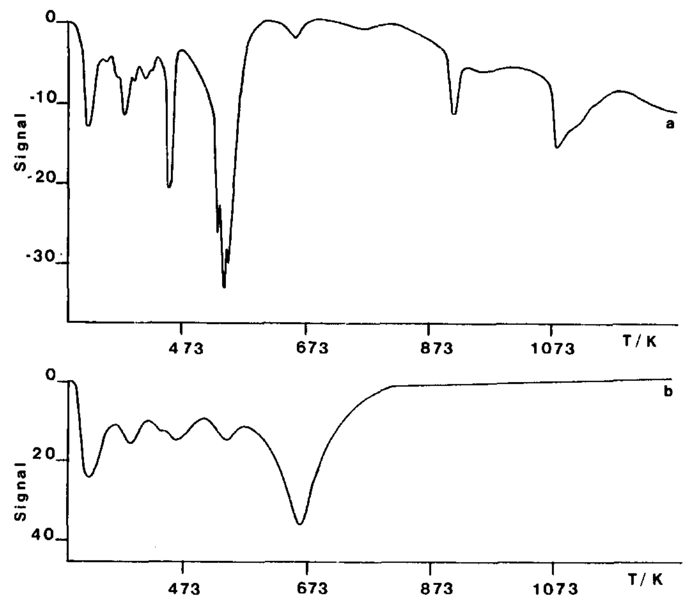

FIG. 1. Thermal analysis of $UO_2(NO_3)_2 \cdot 6H_2O$ in oxygen; (a) differential thermal analysis, (b) derivative thermogravimetry.

molecules of water of crystallisation. Derivative thermogravimetry (Fig. 1b) and DTA (Fig. 1a) showed that dehydration occurred in four stages, the loss of three molecules of water taking place at 363 ± 10 K and the loss of each of the remaining molecules occurring thereafter. The onset and peak temperatures of the four distinct endothermic peaks corresponding to dehydration were sensitive to conditions (initial mass of sample, particle size, etc). Additional peaks below 573 K shown by differential thermal analysis were typical of the boiling of saturated aqueous solutions. Nitrogen dioxide was evolved at temperatures between 573 and 773 K, and the residual mass at 823 K was 58.8% of the original, in excess of that expected for the formation of UO_3. The corresponding DTA curve contained a well-defined endothermic peak (extrapolated onset temperature T_E, 638 ± 5 K; peak temperature T_M, 658 ± 5 K) and a smaller broad endotherm (T_M, 773 ± 5 K). The final stages of decomposition, above 823 K, were found to be affected by the oxygen content of the atmosphere. For a sample heated in flowing oxygen, the DTA trace (Fig. 1a) showed an endothermic peak at 913 K (T_E, 905 ± 2 K) and changes in baseline at 958, 1073 and 1163 K. The product was confirmed as α-U_3O_8 by X-ray diffraction and ir spectroscopy. In nitrogen, an endotherm appeared at 858 K (T_E, 836 ± 2 K).

Identification of the intermediates formed during the thermal decomposition of $UO_2(NO_3)_2 \cdot 6H_2O$ was carried out by ir spectroscopy (Fig. 2). The spectrum below 1200 cm^{-1} of the unheated compound (Fig. 2a) exhibited absorptions at 1025 ± 5, 940 ± 5, 801, 747, and 738 cm^{-1}, and a broad complex at 600–300 cm^{-1}. The strongest band at 940 cm^{-1} was typical of the U–O stretching mode of the uranyl (UO_2^{2+}) group (*17*). After heating in nitrogen to 613 K, the absorption bands (Fig. 2b) at 1025, 940, 801, 747, and 738 cm^{-1} were weaker, but the intensity of the broad complex, 600–300 cm^{-1}, was increased. It appeared to include vibrational modes at 420 and 530 cm^{-1}, probably U–O stretches (*18*). An additional band at 845 ± 5 cm^{-1} was observed which is typical of derivatives of UO_3 (*19*). The ir spectrum of a sample heated to 728 K (Fig. 2c) re-

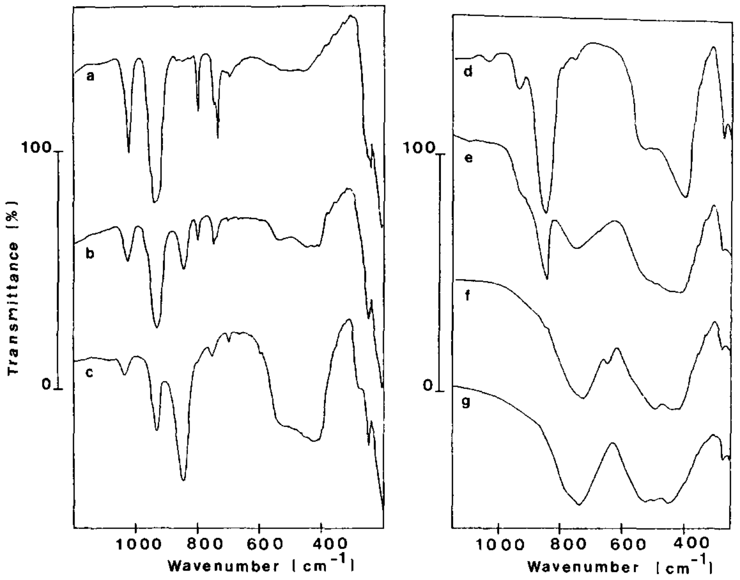

FIG. 2. Infrared spectra of $UO_2(NO_3)_2 \cdot 6H_2O$ and its products of decomposition in nitrogen; (a) $UO_2(NO_3)_2 \cdot 6H_2O$; after heating to (b) 613 K, (c) 728 K, (d) 903 K, (e) 1033 K, (f) 1273 K, (g) after reheating in air to 1273 K.

vealed that the bands at 1025, 801, 747, and 738 cm^{-1} had virtually disappeared. The shoulder at 275 cm^{-1} suggested the formation of U–O–U–O chains which are present in UO_3 (*18*). The product was identified as a mixture of UO_3 and $UO_2(NO_3)_2$ (alternatively $UO_3N_2O_5$ (*20*)).

Heating $UO_2(NO_3)_2 \cdot 6H_2O$ to 903 K yielded UO_3 (Fig. 2d). The absorption at 275 cm^{-1} was more pronounced. The presence of the band at 940 cm^{-1} suggested that possibly some hydration of the sample had occurred during handling, since it is reported (*17*) that UO_2^{2+} does not occur in UO_3. (Two hydrates of UO_3, $UO_3 \cdot 0.8H_2O$, and $UO_2(OH)_2$, absorb at 930 and 945 cm^{-1}, respectively (*19*).) After heating to 1033 K, the decomposition product had an inhomogeneous appearance with distinct black areas present at the surface of the dark-red mass. The absorption bands at 850 and 420 cm^{-1} were present (Fig. 2e) but reduced in intensity and the absorption at 740 ± 5 cm^{-1} was typical of α-U_3O_8. The band at 940 cm^{-1} persisted as a weak shoulder. It was concluded that the product consisted of U_3O_8 on the surface of (red) UO_3. A further sample was heated to 1273 K, and the ir spectrum of the cooled product (Fig. 2f) was almost identical to that of α-U_3O_8 similarly treated (see above). Thus, the weak absorption at 645 cm^{-1} indicated the oxide of composition $UO_{2.626}$. However, the shoulder at 850 cm^{-1} suggested that a small amount of UO_3 remained unconverted. Finally, reheating this sample to 1273 K in air gave a product whose ir spectrum (Fig. 2g) was identical to that of α-U_3O_8.

(iii) Sb_6O_{13}. In accordance with the standard procedure for the preparation of uranium antimonates (*1*), Sb_2O_3 was oxidised by heating under reflux with nitric acid, after which the product was dried and heated to 723 K in air for 16 h. The X-ray powder diffraction pattern of the yellow-coloured cooled product showed only the more prominent lines due to α-Sb_2O_4 (*21a*), with very low intensities.

Differential thermal analysis of the product showed a sharp exotherm (T_E, 977 ± 3 K; T_M, 988 ± 2 K, unaffected by the atmosphere) and a broad endotherm (T_E in nitrogen, 1026 K; in air, 1029 K; in oxygen, 1042 K). Above 1273 K, a further broad endotherm was observed, typical of the decomposition of α-Sb_2O_4.

X-Ray diffraction of the product, cooled after heating to 1000 K, showed relatively intense lines attributable to Sb_6O_{13} (*21b*) together with weaker lines due to α-Sb_2O_4, while a sample after prolonged heating at 1200 K gave the clearly defined pattern of α-Sb_2O_4 (white).

Thermogravimetric analysis of the product under oxygen showed a slow loss of mass between 723 and 1023 K followed by a more appreciable decrease between 1023 and 1223 K. The total reduction in mass, although not reproducible, always exceeded the value expected for the formation of Sb_2O_4 from Sb_6O_{13}.

These observations are consistent with the formation of a product consisting mainly of amorphous Sb_6O_{13+x}, but containing a small proportion of α-Sb_2O_4. Oxygen is lost as this mixture is heated above 723 K, but some nonstoichiometric oxide is still present when the amorphous form becomes crystalline at 997 K. The temperature at which Sb_6O_{13} decomposes to α-Sb_2O_4 depends on the ambient pressure of oxygen, However, it has been shown that, under the conditions used in the standard preparation of uranium antimonates, the dissociation of Sb_6O_{13} to α-Sb_2O_4 is complete.

Preparation of Uranium Antimonates from Solid Components

(i) *$USbO_5$*. α-Sb_2O_4 is the most stable oxide of antimony (*11*) under conditions leading to the formation of antimonates. Mixtures of this oxide with either α-U_3O_8 or $UO_2(NO_3)_2 \cdot 6H_2O$ (U/Sb = 1/1) were prepared and heat-treated in different ways. First, the mixtures U_3O_8 + Sb_2O_4 and $UO_2(NO_3)_2 \cdot 6H_2O$ + Sb_2O_4 were heated under flowing oxygen at a rate of 10 K min^{-1} to 1440 K, the temperature associated with the decomposition of Sb_2O_4 to volatile Sb_2O_3 (*11*). Secondly, mixtures of Sb_2O_4 with either U_3O_8 or $UO_2(NO_3) \cdot 6H_2O$ were heated under similar conditions, but were maintained at ca. 1420 K for 2 h before being allowed to cool slowly. In heating mixtures of Sb_2O_4 and $UO_2(NO_3)_2 \cdot 6H_2O$, it was noted that records from DTA showed very similar features to those for the decomposition of pure $UO_2(NO_3)_2 \cdot 6H_2O$, up to ca. 1173 K.

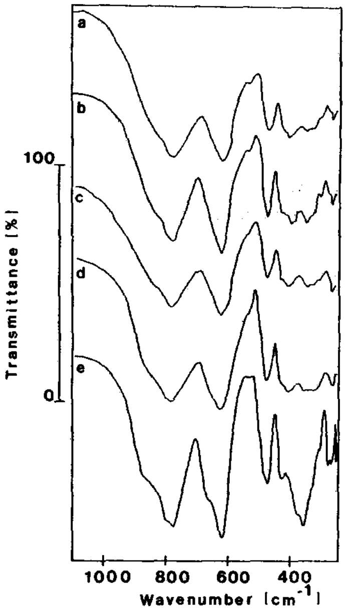

FIG. 3. Infrared spectra of uranium–antimony oxides U/Sb = 1/1: (a) U_3O_8 + Sb_2O_4 heated in oxygen to 1440 K, (b) $UO_2(NO_3)_2 \cdot 6H_2O$ + Sb_2O_4 heated in oxygen to 1440 K, (c) U_3O_8 + Sb_2O_4 heated in oxygen at 1420 K, (d) $UO_2(NO_3)_2 \cdot 6H_2O$ + Sb_2O_4 heated in oxygen at 1420 K, (e) $USbO_5$, prepared by the dissociation of USb_3O_{10} in air at 1363 K.

The ir spectra of the products of these mixtures (Fig. 3) were very similar but exhibited a slight difference from the spectrum of $USbO_5$ prepared by the dissociation of USb_3O_{10} in air at 1363 K (*1*). Thus, in all cases, the mixtures exhibited two broad complex bands of almost equal absorbance between 300 and 450 cm^{-1} similar to those observed with α-Sb_2O_4 (*11*), whereas $USbO_5$ absorbed strongly at 355 cm^{-1} and displayed weaker bands at 380 and 425 cm^{-1}.

(ii) *USb_3O_{10}*. Mixtures of Sb_2O_4 with either U_3O_8 or $UO_2(NO_3)_2 \cdot 6H_2O$ were prepared having atomic compositions U/Sb = 1/2, 1/3, and 1/4, and subjected to prolonged heating in air at temperatures not exceeding

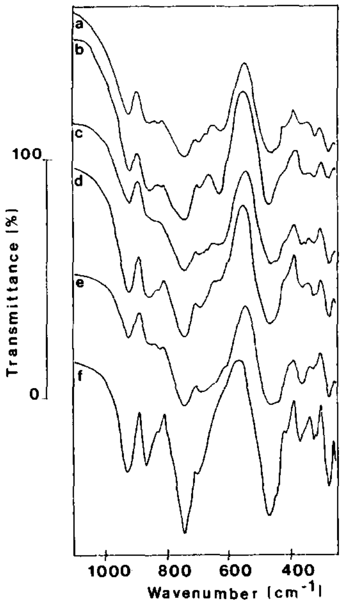

FIG. 4. Infrared spectra of uranium–antimony oxides, U < Sb, heated in air at 1173 K: (a) $U_3O_8 + Sb_2O_4$ (U/Sb = 1/2), (b) $UO_2(NO_3)_2 \cdot 6H_2O + Sb_2O_4$ (U/Sb = 1/2), (c) $U_3O_8 + Sb_2O_4$ (U/Sb = 1/3), (d) $UO_2(NO_3)_2 \cdot 6H_2O + Sb_2O_4$ (U/Sb = 1/3), (e) $U_3O_8 + Sb_2O_4$ (U/Sb = 1/4), (f) $UO_2(NO_3)_2 \cdot 6H_2O + Sb_2O_4$ (U/Sb = 1/4).

1173 K. IR spectra of the products (Fig. 4) showed bands attributable to USb_3O_{10} (*2*) at 920, 860, 740, 690, and 275 cm^{-1}, and to $USbO_5$ (*2*) at 630 cm^{-1}. From the results it was apparent that USb_3O_{10} can be formed more effectively by starting with Sb_2O_4 + $UO_2(NO_3)_2 \cdot 6H_2O$ than with $Sb_2O_4 + U_3O_8$. Thus with mixtures of atomic ratio U/Sb = 1/3, the bands due to USb_3O_{10} were less well-defined in the case of $Sb_2O_4 + U_3O_8$ (Fig. 4c) than with $Sb_2O_4 + UO_2(NO_3)_2 \cdot 6H_2O$ (Fig. 4d). Furthermore, the larger shoulders at 630 and 440 cm^{-1} (Fig. 4c) indicated unreacted $USbO_5$ and Sb_2O_4. Particularly good evidence is found in a comparison between Figs. 4e and 4f. The former contained broad, poorly defined bands caused by the association of bands due to USb_3O_{10} with those due to unreacted $USbO_5$ and excess Sb_2O_4. In contrast, the spectrum of the product of heating Sb_2O_4 + $UO_2(NO_3)_2 \cdot 6H_2O$ (Fig. 4f) is almost identical to the published (*1*) spectrum of USb_3O_{10}.

Thermal Stability of Uranium Antimonates

DTA showed that the dissociation of USb_3O_{10} occurred in three endothermic stages, a result in agreement with Grasselli and Suresh (*2*). In nitrogen, the onset temperature of the first endotherm was 1221 ± 5 K although this was found to increase with increasing oxygen concentration, reaching 1448 K in pure oxygen at atmospheric pressure. The corresponding temperatures for the second stage were 1328 K in nitrogen and 1453 K in oxygen. The ir spectrum of USb_3O_{10} heated in nitrogen in 1333 K (Fig. 5a), exhibited bands between 800 and 250 cm^{-1} which could be attributed to $USbO_5$. An additional band at 885 cm^{-1}, approximately midway between two bands observed in this region for USb_3O_{10} was due to a phase previously referred to as "anomalous $USbO_5$" (*2*). Thermogravimetry

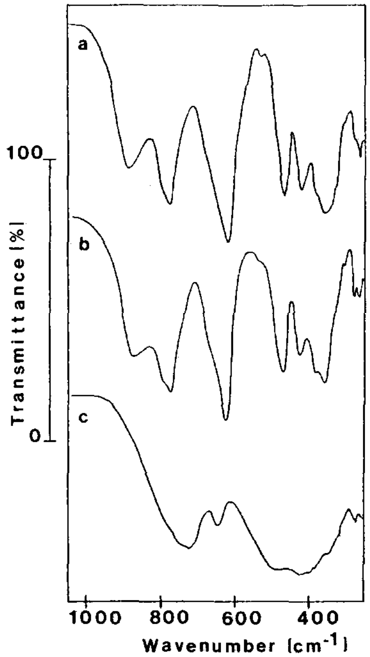

FIG. 5. Infrared spectra of the products of dissociation of USb_3O_{10} in nitrogen, after heating to (a) 1333 K, (b) 1423 K, (c) 1523 K.

showed that, on heating USb_3O_{10} in nitrogen at 1273 K, a slow, continuous loss of mass occurred. After approx 8 h, the mass stabilised at 77.2% of its starting value. The product was again found to consist mainly of "anomalous $USbO_5$." Since the dissociation of USb_3O_{10} to $USbO_5$ and gaseous Sb_2O_3 would be expected to result in a decrease in mass of 42.4%, the observed decrease of 22.8% cannot be due solely to an excess of oxygen in the product. Considering the possibility that some Sb_2O_4 is formed during the decomposition of USb_3O_{10}, it is recalled that Sb_2O_4 decomposes in nitrogen at 1335 K and in oxygen (at atmospheric pressure) at 1440 K (*11*). Hence, Sb_2O_4 could be formed in the first two stages of the decomposition of USb_3O_{10} under nitrogen. However, Sb_2O_4 was not detected in the products of these stages by either X-ray diffraction or ir spectroscopy. Therefore it appears that "anomalous $USbO_5$" contains an excess of both antimony and oxygen and that the first stage in the dissociation of USb_3O_{10} occurs as

$$USb_3O_{10}(s) \rightarrow USb_{1+x}O_{5+y}(s) + ((2 - x)/2)Sb_2O_3(g) + (a/2)O_2(g)$$

where $a = 2 - y + (3x/2)$. In view of the uncertainty regarding the stoichiometry of the anomalous phase, it was not possible to make a precise determination of the change in enthalpy of the above reaction from the variation of onset temperature with oxygen pressure. However, the observed change in mass lies between the expected values for the processes

$$USb_3O_{10}(s) \rightarrow USb_2O_{7.5}(s) + \tfrac{1}{2}Sb_2O_3(g) + \tfrac{1}{2}O_2(g) \quad (1)$$

(calculated change in mass = −21.2%),

$$USb_3O_{10}(s) \rightarrow USb_2O_{6.5}(s) + \tfrac{1}{2}Sb_2O_3(g) + O_2(g) \quad (2)$$

(calculated change in mass = −23.3%). Support for process (1), however, comes from the fact that the onset temperature of the second stage was found to vary with oxygen pressure. Assuming that no significant amount of Sb_2O_4 is formed in the first stage, this variation is consistent with

$$USb_2O_{7.5}(s) \rightarrow USbO_5(s) + \tfrac{1}{2}Sb_2O_3(g) + \tfrac{1}{2}O_2(g) \quad (3)$$

and not with

$$USb_2O_{6.5}(s) \rightarrow USbO_5(s) + \tfrac{1}{2}Sb_2O_3(g). \quad (4)$$

Thus, plotting $\ln(p_{O_2})^{1/2}$ against reciprocal onset temperature, yielded a value of ΔH = 190 ± 15 kJ mol^{-1}.

The ir spectrum (Fig. 5b) of USb_3O_{10} which had been heated in nitrogen to 1423 K, i.e., above the temperature observed for the second endotherm, still showed the band at 885 cm^{-1} associated with "anomalous $USbO_5$." Therefore, in order to achieve effective conversion of USb_3O_{10} to $USbO_5$, either a very slow rate of heating or prolonged heating at 1363 K under static air (*1*) is required.

Finally, by using a homogeneous sample of $USbO_5$, it was possible to determine accurately the onset of the final stage of decomposition. DTA showed a large endotherm which occurred at 1340 K in nitrogen and 1525 K in oxygen. It has been proposed (*10*) that dissociation of $USbO_5$ occurs according to the equation

$$3USbO_5 \rightarrow U_3O_8 + \tfrac{3}{2}Sb_2O_3 + \tfrac{5}{4}O_2.$$

Thus, the variation of $\ln(p_{O_2})^{5/12}$ against reciprocal onset temperature was plotted and a value of 225 ± 10 kJ mol^{-1} obtained for the enthalpy change. The ir spectrum of the final product of dissociation (Fig. 5c) was characteristic of oxygen-deficient U_3O_8 (i.e., $UO_{2.626}$).

CONCLUSIONS

On heating α-U_3O_8 in nitrogen, gradual depletion of oxygen occurs from 523 to 1273 K with the formation of $UO_{2.626}$. This is consistent with the transition from orthorhombic U_3O_{8-x} to U_8O_{21+z} (*22*) (also referred to as U_5O_{13+z} (*23*)) which has been suggested on the basis of various studies

(*16, 22, 23*). The phase is associated with an ir absorption band at 645 cm^{-1}. In oxidising atmospheres, α-U_3O_8 is stable at temperatures up to 1273 K, for short periods, and up to ca. 1173 K for prolonged heating.

During the decomposition of $UO_2(NO_3)_2 \cdot 6H_2O$, the six molecules of water of crystallisation are liberated between 303 and 573 K. Decomposition of the nitrate groups occurs as a two-stage process between 573 and 773 K to yield UO_3. As has been reported (*19*), the dissociation of UO_3 proceeds via UO_{3-x}, detected at 1023 K. It was found, however, that UO_{3-x} is not a single phase but a mixture of the oxides UO_3 and U_3O_8. In inert atmospheres, further dissociation yields U_8O_{21+z} but some UO_3 may remain. On heating in static air at 1273 K, U_8O_{21+z} is oxidised to α-U_3O_8. Thus the decomposition of $UO_2(NO_3)_2 \cdot 6H_2O$ in oxygen yields α-U_3O_8.

After oxidation with nitric acid and heating at 723 K, Sb_2O_3 yields a mixture of, mainly, amorphous Sb_6O_{13+x} together with orthorhombic α-Sb_2O_4. At 988 K, cubic Sb_6O_{13} is formed from the nonstoichiometric phase. (As has been pointed out by Stewart *et al.* (*24*), Sb_6O_{13} has often been mistakenly identified as Sb_2O_5. Such instances include studies of the intermediates involved in the formation of uranium antimonates (*2, 10*).) At temperatures above 1026 K, Sb_6O_{13} loses oxygen. At ca. 1223 K, the sample becomes α-Sb_2O_4. Thus, by maintaining the temperature at 1200 K during the standard preparation of USb_3O_{10}, the complete dissociation of Sb_6O_{13} is assured.

From the present results and those of a previous study (*11*), it is apparent that, the preparation of uranium antimonates from Sb_2O_3 and $UO_2(NO_3)_2 \cdot 6H_2O$ mainly involves the reaction of α-Sb_2O_4 and α-U_3O_8:

$$2U_3O_8 + 3Sb_2O_4 + O_2 \rightarrow 6USbO_5.$$

In the presence of excess Sb_2O_4, $USbO_5$ is an intermediate in the formation of USb_3O_{10}:

$$USbO_5 + Sb_2O_4 + \tfrac{1}{2}O_2 \rightarrow USb_3O_{10}.$$

The reported reactions (*2*)

$$2UO_3 + Sb_2O_4 \rightarrow 2USbO_5$$

and

$$USbO_5 + Sb_2O_5 \rightarrow USb_3O_{10}$$

are unlikely to be significant unless mixtures are heated rapidly. This is because UO_3 begins to dissociate at below 900 K in air and the major proportion of Sb_2O_4 is not formed until ca. 1200 K. Further, Sb_2O_5 cannot be produced by the oxidation of either Sb_2O_3 or Sb_2O_4 under air at atmospheric pressure (*25, 26*).

Heating a mixture of $UO_2(NO_3)_2 \cdot 6H_2O$, Sb_2O_3 and nitric acid under reflux yields a mixture of products which, on further heat treatment, forms crystalline USb_3O_{10}. This cannot be formed readily by reaction in the solid phase. Further, the product of the re-

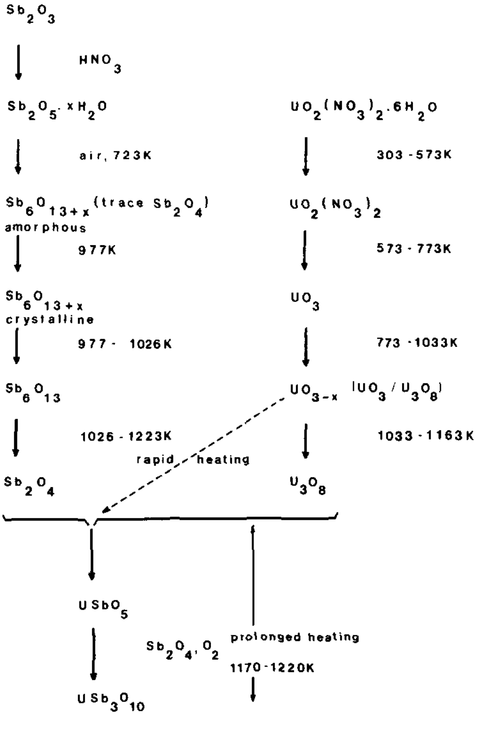

FIG. 6. Stages in the formation of crystalline USb_3O_{10}.

action of $UO_2(NO_3)_2 \cdot 6H_2O$ and Sb_2O_4 (U/Sb = 1/4) may be of considerable interest since it consisted of amorphous USb_3O_{10} together with excess crystalline Sb_2O_4. The presence of uncombined Sb_2O_4 has been detected in other antimony-based catalysts (*27, 28*) and has been shown to be extremely important in selective allylic oxidation (*27*).

The above results are summarised in Fig. 6.

Finally, the dissociation of USb_3O_{10} occurs in three consecutive stages, the onset of each being markedly dependent on the oxygen content of the ambient atmosphere. Thus, between 1221 and 1448 K, USb_3O_{10} loses gaseous Sb_2O_3 and oxygen in an endothermic process to produce the phase $USb_{1+x}O_{5+y}$. Thereafter, the endothermic transformation to $USbO_5$ is immediate. Between 1340 and 1525 K, $USbO_5$ decomposes yielding gaseous Sb_2O_3, U_8O_{21+z}, and oxygen.

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