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A STUDY OF THE THERMAL DECOMPOSITION OF URANYL ACETATE USING INFRA-RED SPECTROSCOPIC TECHNIQUES

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ABSTRACT

In a previous study it was suggested that the thermal decomposition of uranyl acetate proceeds by primary fission into uranium dioxide and acetate radicals, followed by oxidation of the dioxide to U_3O_8 and pyrolytic fission of the acetate radicals into various secondary products. This study provides further evidence in support of this mechanism. It is shown that the relative intensities of the significant infra-red absorption bands do not change until decomposition is almost complete. If the process took place by the fission of other bonds, for instance the $C-CH_3$ bond which absorbs at $1390 cm^{-1}$ the absorption band due to this bond would diminish in intensity with respect to the uranyl ion band at $940 cm^{-1}$ and $850 cm^{-1}$. The results show this is not the case.

INTRODUCTION

In a study on the thermal decomposition of uranyl acetate by thermal analysis methods it was suggested that the initial stage in the decomposition could be fission of the UO_2-acetate bond (ref. 1). In air the UO_2 product is oxidized up to U_3O_8 whilst oxygen acting on the CH_3COO radical would produce various pyrolysis products (ref. 1). Other publications do not contradict these facts but there are some variations in the reported data (ref. 2,3). Dubrovin et al (ref. 4) however conclude that the first step is the breaking of the carbon oxygen bond of the carbonyl group.

EXPERIMENTAL

Materials - The uranyl acetate dihydrate supplied commercially was dehydrated to the anhydrous salt by heating in air at 120°C to a constant mass. Analysis (ref. 5) of the dihydrate and the anhydrous salt gave a uranium content which was 99.8% of the theoretical value.

Thermal Analysis - A Stanton Thermobalance (Model TR01) was used modified for use with controlled atmospheres. The mass of sample used was 0.1g and the heating rate was $5^{o}min^{-1}$; the gases were passed at a flow rate of $300 mls\ min^{-1}$ The nitrogen was dried and the last traces of oxygen removed DTA work was

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carried out on a Netzsch DTA unit. The sample consisted of 0.8g of a 10% mixture of the salt and calcined alumina. The heating rate was $5^{o}min^{-1}$. All other equipment was standard.

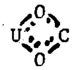
RESULTS AND DISCUSSION

The uranyl acetate dihydrate lost its water in a single stage, the anhydrous salt decomposes around $300^{o}C$ and the end decomposition product in air is U_3O_8. The decomposition product in nitrogen contains carbon making it unsuitable for catalytic processes. The product is βUO_2 (a non-stoichiometric oxide, $UO_{2.15}$). No carbide formation could be detected.

The DTA of the salt in air showed an endothermic peak at $120^{o}C$ corresponding to the dehydration stage on the TG data. The decomposition at $320^{o}C$ gave an exothermic peak on the DTA unit preceeded by a small endotherm at $295^{o}C$. In nitrogen the dehydration at $125^{o}C$ gave an endothermic peak with an endothermic decomposition stage at $330^{o}C$. The small endotherm in air at $295^{o}C$ and the endotherm in the DTA in nitrogen have been identified with the reaction,

$UO_2(CH_3COO)_2 \rightarrow UO_2$ + Volatile Products

In the previous study (ref. 1) the kinetics of the decomposition stage were reported together with surface area, X-ray diffraction and electron microscope data. In this report the gaseous products are studied together with infra-red spectroscopy data. A time of flight mass spectrometer (ref. 6) was used to monitor mass numbers corresponding to CO, CO_2 and CH_3COOH. In this experiment the anhydrous material was decomposed in a vacuum (10^{-6}mm) at a temperature of $200^{o}C$. There were high initial concentrations of mass numbers corresponding to acetic acid but these diminished quite markedly as decomposition progressed (Figure 1). Carbon monoxide and carbon dioxide were the main volatile products throughout most of the decomposition.

It is established that the uranyl ion has three vibrational frequencies, a symetric stretching frequency at $850cm^{-1}$ to $880cm^{-1}$, an antisymetric stretching frequency at $930cm^{-1}$ to $960cm^{-1}$ and a bending frequency at $199cm^{-1}$ to $210cm^{-1}$ (ref. 7) Caldow et al (ref. 8) assigned the band that appeared at a frequency of $680cm^{-1}$ to the (UO_2)-O bond and suggested that the band at $640cm^{-1}$ was due to the vibration of the  group. The relative intensities of the absorption bands that appear in the spectrum of uranyl acetate during its decomposition in air at $300^{o}C$ were obtained at various values of fraction decomposed from zero to one (see Figure 2). The data shows that the relative intensities for most of the bands remained sensibly constant over almost the full extent of the decomposition.

The evidence is consistent with the idea that the initial stages in the decomposition of uranyl acetate are fission of the bonds between the uranyl

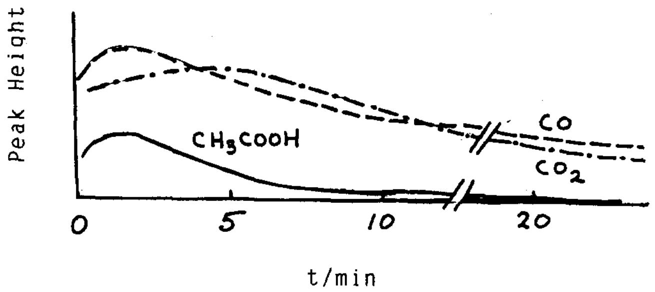


Figure I. Mass Spectrometer Data on the Decomposition of Uranyl Acetate at 220°C

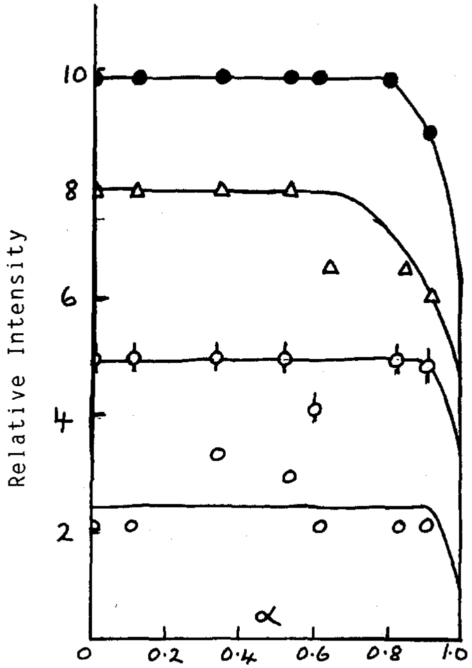


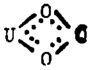
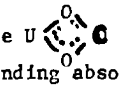
Figure 2. Changes in the Relative Intensities Observed for Several Infra-red Absorption Bands in the Spectrum of Uranyl Acetate During Decomposition.

● Band at 954cm^{-1}
△ Band at 678cm^{-1}
ϕ Band at 1390cm^{-1}
○ Band at 608cm^{-1}

group and the acetate radical. The large exotherm in air is due in part to the reaction

$3UO_2 + O_2 \rightarrow U_3O_8$

and the small endotherm which preceeds it is probably due to the fission of the (UO_2)-O bond which produced initially acetate radicals. Primary fission of this bond is thus supported by the mas spectroscopic and infra red spectroscopic data. It is considered that if the process took place by fission of any other bonds, for instance the C-CH_3 bond at 1390cm^{-1} the absorption band due to this bond would diminish in intensity with respect to the uranyl ion bands at 940cm^{-1} and 850cm^{-1}. This is not the case.

The spectroscopic data also gave information on the nature of the bonding in the uranyl acetate molecule. Jones and Mclaren (ref.9) consider that the band at 640cm^{-1} originally assigned by Caldow et al (ref.8) to vibration of the  group is more probably due to a CO bending on the grounds that a similar band can be seen in the spectrum of sodium acetate. The band at 608cm^{-1} could be due to the  group. If the (UO_2)-O bond were completely covalent the CO bending absorption molecule is a hybrid between various formulae. The band originally assigned to symetrical stretching of the uranyl ion at 850cm^{-1} gradually broadens throughout the decomposition until at $\alpha = 1$ it covers the range 950cm^{-1} to 800cm^{-1} and probably includes several unresolved bands due to some vibration of the U_3O_8 molecule. It is thought also that the bands that appeared at 660cm^{-1} towards the end of the decomposition had a similar origin.

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