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NOTE

Kinetics and Mechanism of Thermal Decomposition of Uranyl Oxalate

CHARU ARORA CHUGH[1,2,*], ASMITA SHARMA[1], ADITI SHARMA[1], SHALU[1], Y.P. NAIK[3] and G.A. RAMA RAO[3]

[1]Department of Chemistry, Banasthali Vidyapeeth (Deemed University), Banasthali-304 022, India
[2]Department of Chemistry, Lovely Professional University, Jalandhar-144 402, India
[3]Product Development Division, Radiochemistry and Isotope Group, Bhabha Atomic Research Centre, Mumbai-400 085, India

*Corresponding author: E-mail: charuarora77@gmail.com

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Uranyl oxalate was prepared and its thermal decomposition in argon environment was studied using TGA, DTA, DSC and quadrupole mass analyzer. It was observed that uranyl oxalate decomposed into mixture of U_3O_8 and $UO_{2.13}$ with the evolution of carbon monoxide, oxygen and carbon dioxide in the temperature range of 573-673 K. But beyond this temperature U_3O_8 and $UO_{2.13}$ appeared as intermediate and the final product was found to be $UO_{2.12}$. This solid state decomposition was found to obey AE4 mechanism represented by the kinetic equation $k \times t = [-\ln (1 - \alpha)]^{3/4}$. The activation energy of the reaction was found to be 824.83 kJ/mol. The heat of reaction and the entropy of the reaction were found to be 832.2 kJ/mol and 902.0 J/K/mol, respectively.

Key Words: Kinetics, Mechanism, Thermal decomposition, Uranyl oxalate.

Uranium oxide is one of the most important compounds in the nuclear industry and is usually prepared by decomposing the oxalate. In the present study a kinetic model has been suggested for the decomposition of uranyl oxalate to a mixture of U_3O_8 and $UO_{2.13}$ in argon atmosphere.

Preparation of compound: Uranyl oxalate was precipitated by slowly adding 0.5 M solution of oxalic acid to a 1 M solution of uranyl nitrate tetrahydrate. The oxalate precipitate was filtered and dried in an oven under air flow at 45 ºC. The dried oxalate was ground and palletized. Uranyl oxalate was characterized on the basis of X-ray diffraction and Infrared spectroscopy.

A small portion of the pellet weighing *ca.* 20 mg was used for thermal analysis. TGA was obtained using Netzsch Model STA409PC/PGTGA/DTA unit. Argon gas flow rate of 30 mL/min and heating rate of 5 K/min were maintained while recording the thermogram as a function of time and temperature ranging from ambient to 1350 K. IR spectra were recorded on JASCO FT/IR-420 spectrophotometer. DIANO X-Ray diffractometer (copper K-α radiation 1.5431 Å with nickel filter) was used to record X-ray diffraction patterns.

Table-1 shows the XRD pattern obtained for uranyl oxalate which indicates some amount of crystallinity in uranyl oxalate.

The IR absorption peaks (Table-2) obtained are found in good agreement of the reported values[5] for uranyl oxalate.

TABLE-1
MAJOR X-RAY ABSORPTION PEAKS IN THE X-RAY POWDER DIFFRACTION PATTERNS OF URANYL OXALATE

2θ	20.42	22.84	31.45	42.41
d-value Å	4.34	3.89	2.84	2.13

Fig. 1 shows simultaneous TGA/DTA curve for the decomposition of uranyl oxalate. The TGA indicates that the dehydration occurs in three stages. The first broad endothermic peak in the temperature range 100-150 ºC corresponds to loss of adsorbed water. Subsequent two steps correspond to loss of water of crystallization in the temperature ranges of 160-200 and 180-200 ºC, respectively. Mass loss analysis indicated that there is 16.9 % water loss in these two steps corresponding to four molecules of water of crystallization. The decomposition of anhydrous uranyl oxalate starts at a temperature of 350 ºC, involving a mass loss of 19.37 %. The solid residue left after TGA/DTA run was characterized by XRD. For this purpose two different TGA/DTA runs were performed one unto a maximum temperature of 624 ºC and second upto 1300 ºC. Residues left after these runs were characterized by XRD. The XRD pattern obtained for the residues left after the TGA run of uranyl oxalate unto a temperature of 600 ºC. The XRD data (Table-3) suggest that the solid residue left after the TGA run was a mixture of $UO_{2.13}$ and U_3O_8 as the calculated δ values of the observed peaks which are in agreement with the published

TABLE-2
PROMINENT EMISSION ABSORPTION BENDS IN THE IR SPECTRA OF URANYL OXALATE

Assignments	ν(O-H)	ν_{sy}(O-C-O)	ν_{as}(O-C-O)	ν_{sys}(C=O)	ν(O=U=O)	Oop ρCOO
Peak position (cm^{-1})	3595.63, 3459.67	1690.30, 1676.66	1355.71, 1313.19	926.63	802.24	485.01

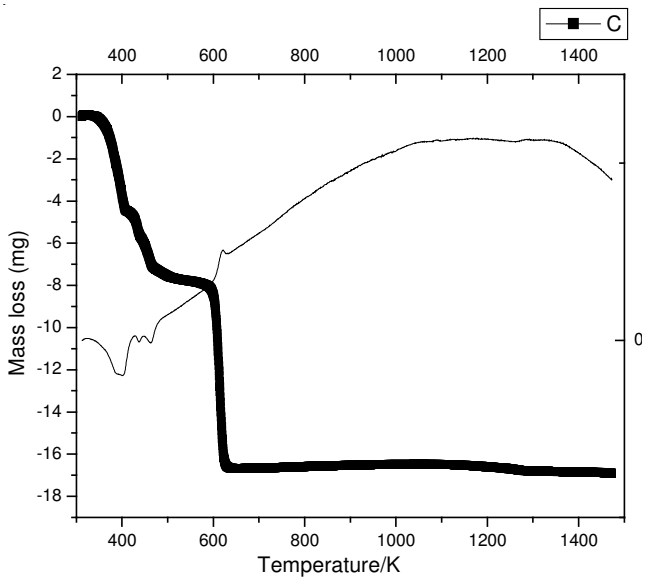

Fig. 1. TGA/DTA curves for the decomposition of uranyl oxalate in argon at the heating rate of 5 ºC/min

TABLE-3
OBSERVED "d" VALUES OF X-RAY ABSORPTION INTENSITIES FOR THE URANYL OXALATE DECOMPOSITION PRODUCTS WHEN HEATED IN ARGON AT THE RATE OF 5º C/min UP TO A TEMPERATURE OF 600 ºC DURING TGA/DTA RUN

U_3O_8		$UO_{2.13}$.	
d-value	Relative intensity	d-value	Relative intensity
4.168	44	3.154	100
3.430	56	2.726	56
2.631	45	1.922	63
–	–	1.639	56
–	–	1.572	41

data for U_3O_8 and $U_{2.13}$ with JCPDF file No. 47-1493 and 74-2432, respectively. In a separate experiment the evolved gas analysis by using quadruple mass analyzer indicated the presence of gas mixture of O_2, CO and CO_2. These observations together with those of XRD suggests that the decomposition of uranyl oxalate first takes place to a mixture of $UO_{2.13}$ and U_3O_8 with the evolution of O_2, CO and CO_2 gases during the decomposition step at temperature of 624 ºC. The mass loss data obtained beyond 600 ºC was attributed to the reduction of $UO_{2.13}$ and U_3O_8 to $UO_{2.12}$ or U_4O_9 by carbon monoxide. The characteristic peak at 3.144 is in agreement with JC-PDF file No. 75-0944 for U_4O_9 and 71-0258 for $UO_{2.12}$. The effluent gas during this weight loss stage was found to be essentially CO_2.

Decomposition mechanism of uranyl oxalate: Tel *et al.*[1] have studied the TGA of uranyl oxalate. The mass loss data was used to predict the mechanism of the solid state decomposition of uranyl oxalate. Various model equations have been proposed for the decomposition reactions both in iso and non-isothermal heating modes[2-4]. The reaction mechanism followed may be represented by the eqn. 1 below;

$$k \times t = [-\ln (1 - \alpha)]^{3/4} \quad (1)$$

This solid state decomposition was found to obey AE4 (Avrami Erofeev) mechanism. The variation of integral function with time for thermal decomposition of uranyl oxalate in argon at heating rate of 5 K/min has been plotted (not shown). The activation energy for the decomposition was found to be 824.83 kJ/mol.

The variation of rate constant of the reaction with temperature may be represented by the eqn. 2.

$$\ln k = [-100.10/T + 108.58]/1000 \quad (2)$$

The variation of rate constant for solid state decomposition of uranyl oxalate as a function of temperature has been plotted. The value of heat of reaction and entropy of the reaction are found to be -832.2 kJ/mol and 920.0 J/K/mol, respectively.

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