Journal of Thermal Analysis, Vol. 35 (1989) 1213–1221

SOLID STATE REACTIVITY OF ORGANIC COMPOUNDS WITH INORGANIC COMPOUNDS. IV SYNTHESIS AND THERMAL DECOMPOSITION OF URANIUM OXINATE IN THE SOLID STATE

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8-hydroxyquinoline (oxine) and uranyl acetate react in the solid state in 1 : 3 stoichiometry to give $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$. This reaction is diffusion controlled with an activation energy of 44.4 kJ mol^{-1}. The reaction occurs by the surface migration of 8-hydroxyquinoline, which penetrates the product lattice to react with uranyl acetate. The isothermal decomposition of the solution phase product $UO_2Q_2 \cdot HQ$ ($Q = C_9H_6NO$) obeys the Prout–Tompkins equation with an energy of activation of 53.3 kJ mol^{-1}.

8-hydroxyquinoline has found extensive use in the gravimetric determination of different metals [1]. Its bactericidal nature makes the study of its complexes with different metals very important [2]. Actinide complexes of 8-hydroxyquinoline have been a source of interest for the past many years [3]. Various types of complexes of 8-hydroxyquinoline with uranyl ion have been reported and by far the most stable one has been found to be $UO_2Q_2 \cdot HQ$.

Studies of the reactions in the solid state are intended to provide information regarding the kinetic and mechanistic aspects of the reactions. The reactions of thiourea and *n*-phenylthiourea with uranyl acetate have been reported [4, 5] in which an addition product first formed between the reactants decomposes subsequently. In this paper we report the solid state reaction between uranyl acetate and 8-hydroxyquinoline. The product has been characterized by spectral and thermal methods. The kinetics of formation has been studied by measuring the thickness of the coloured boundary formed at the reactant/product interface.

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Experimental

Anhydrous uranyl acetate was obtained by drying the hydrated form at 383 K for six hours [6]. The composition of the anhydrous sample was checked by analysing for uranium gravimetrically [7]. Percentage found: 44.2 (calculated value for $UO_2C_4H_6O_4$, 44.1). The purity of 8-hydroxyquinoline was checked from the melting point obtained from DSC (348 K) which agrees with the literature value, 349–350 K. These compounds were sieved using GEOSYN sieves and particles of size (44 ± 2 μm) were collected. The solution phase reaction product was prepared by the method given in the literature [7].

The reflectance spectra were recorded on a VSU–2P type spectrophotometer in the region 250–850 nm using magnesium oxide as the reference material. The infrared spectra were recorded on a SP3–300 Pye Unicam instrument in potassium bromide in the range 200–4000 cm^{-1}. TG, DTA and DTG curves were recorded on a Stanton–Redcroft (STA–780) model at a heating rate of 5 deg min^{-1} in nitrogen atmosphere using a 10–15 mg sample for each run. Thin layer chromatography was done in benzene methanol (3 : 1) mixture as the eluent.

As the colour of the product formed is distinctly different from that of the reactants, the kinetics was studied by measuring the thickness of the coloured boundary as a function of time at 318, 323, 328 and 333 K by the capillary technique first used by Rastogi et al. [8]. Glass capillaries of inner diameter of 0.3 cm and a scanning microscope with least count of 0.002 cm were used for these studies. Uranyl acetate and 8-hydroxyquinoline (each of particle size 44 ± 2 μm) were used for the kinetic studies. Each experiment was repeated twice to check the reliability of the data.

The isothermal decomposition studies were carried out in a manually operated thermobalance. The same amount of the powder sample was put each time in a crucible connected to the pan of a balance, in a thermostat set at a constant temperature within ±0.5 deg. Isothermal measurements were made by allowing the reaction to proceed and recording the loss in weight after intervals of time till weight constancy was achieved.

Results and discussion

The solid–solid reaction of uranyl acetate with 8-hydroxyquinoline occurs in the stoichiometric ratio of 1 : 3 according to the equation

$$\underset{(s)}{UO_2(CH_3COO)_2} + 3\,\underset{(s)}{C_9H_7NO} \rightarrow \underset{(s)}{UO_2(C_9H_6NO)_2\cdot C_9H_6NOH} + 2\,\underset{(g)}{CH_3COOH}$$

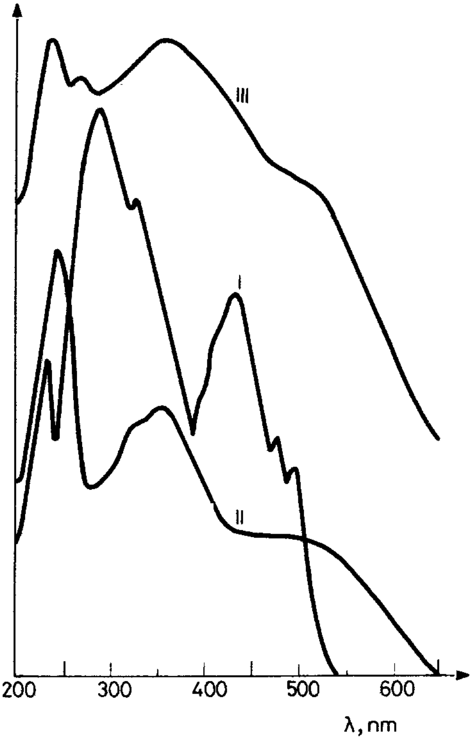

Fig. 1 Reflectance spectra of I. $UO_2(CH_3COO)_2$; II. $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$ solution product; III. $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$ from solid state reaction between $UO_2(CH_3COO)_2$ and C_9H_7NO

The nature of the product has been ascertained from various spectral and analytical measurements. Acetic acid has been identified as the gaseous product from its characteristic smell and the fruity odour smell test. The solid phase product and solution phase product were analysed for C, H, N and the results of the elemental analysis support the stoichiometry as $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$.

Analysis: For solid phase product: C, 46.07; H, 2.72; N, 5.97
For solution phase product: C, 46.07; H, 2.71; N, 5.94

Reflectance spectra of U(VI) complexes show absorptions in the ultraviolet and visible regions due to electron transfer process. Electron transfer can arise from the ligand to U(VI) or from within the ion i.e. from the oxygens of the uranyl group to the central uranium atom. The second transition involves much less energy resulting in the characteristic yellow colour of U(VI) compounds. In case of uranyl acetate this band is observed at 440 nm with weak shoulders at 485 nm and 505 nm. The spectra of freshly mixed reactants are similar to that of uranyl acetate and contain an additional band in the charge transfer region assignable to 8-hydroxyquinoline. In the solid phase product a band at 365 nm and a broad shoulder in the visible region at 500 nm are observed. The spectrum of the solution phase product is similar to that of the solid phase product. The reflectance spectra of the decomposition product UO_2Q_2 obtained after heating the $UO_2Q_2 \cdot HQ$ at 513 K has bands at 372 nm and 520 nm in the visible region.

The principal absorption peaks observed in the spectrum of U(VI) chelate with oxine are as follows:

2050, 1945, 1608, 1592, 1572, 1470, 1428, 1377, 1174, 1109, 1090, 1067, 1052, 890, 818, 798, 780, 769, 625, 505, 465, 357.

After the solid state reaction of 8-hydroxyquinoline with uranyl acetate the band due to ν_{OH} absorption (in case of 8-hydroxyquinoline appearing at 3400 cm^{-1}) disappears. It was also observed that the chelate obtained by solid state reaction does not show any oxine bands which indicates that the extra oxine molecule is an integral part of the complex. If the extra oxine of the uranium oxinate were bound to the chelate only by crystal lattice forces the vibrational frequencies of free oxine should be observed.

The metal oxinate UO_2Q_2 obtained by the thermal decomposition of $UO_2Q_2 \cdot HQ$ exhibits approximately the same absorption bands as $UO_2Q_2 \cdot HQ$

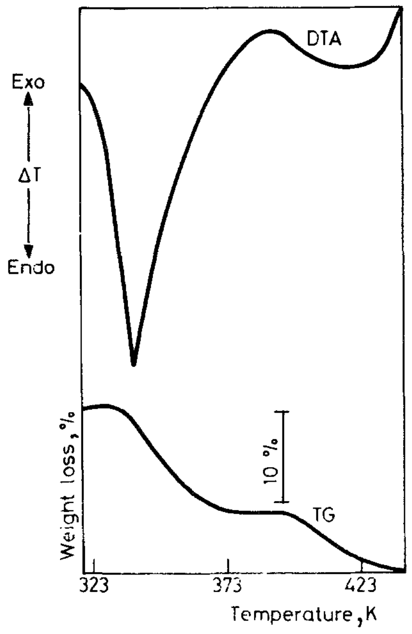

Fig. 2 TG and DTA curves of a fresh mixture of $UO_2(CH_3COO)_2$ and 8-hydroxyquinoline (1 : 2)

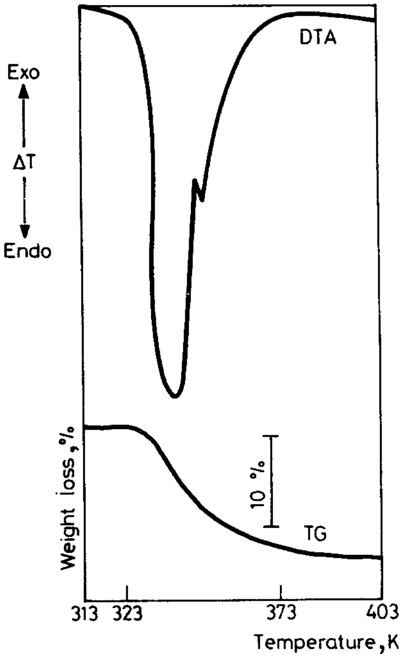

Fig. 3 TG and DTA curves of a fresh mixture of $UO_2(CH_3COO)_2$ and 8-hydroxyquinoline (1 : 3)

but they are slightly shifted due to chelation. The peak appearing at 890 cm^{-1} due to UO_2^{2+} in case of uranium oxinate ($UO_2Q_2 \cdot HQ$) is also shifted to 920 cm^{-1} in case of the green complex UO_2Q_2.

TLC studies of the solid state reaction product show that the pure product is formed as the chromatogram is a single spot and also that no residual reactants are present in the final product. The R_f values for the solid and solution phase product are identical.

The TG–DTA curves of uranyl acetate and 8-hydroxyquinoline were primarily obtained in order to compare their thermal behaviour with those of the stoichiometric mixtures. $UO_2(CH_3COO)_2 \cdot 2H_2O$ shows sharp endothermic dehydration in the temperature range 363–403 K and decomposition at ~523 K. 8-hydroxyquinoline shows a sharp melting endotherm at 348 K. The DTA curve of anhydrous uranyl acetate which has been reported in the literature [9] shows five distinct allotropic species of anhydrous uranyl acetate but no energy effect or mass loss is observed below 423 K.

Since both 1 : 2 and 1 : 3 products are reported in the literature, in order to ascertain the stoichiometry of the reaction, the thermal curves of uranyl acetate and 8-hydroxyquinoline (fresh mixture) in both ratios were recorded. In 1 : 2 mixture the DTA curve shows two endothermic effects at 321–346 K (T_{max} = 336 K) and

400–435 K (T_{max} = 415 K). The TG shows a two step weight loss from 323–356 K of 11.5% and a further loss of 5.5% in the temperature range 400–425 K. The total calculated loss for the two molecules of acetic acid should be 17.7%. These results show that the reaction occurs in the temperature range 323–356 K in which all of the 8-hydroxyquinoline reacts to give 1 : 3 complex and eliminates 2/3 of the acetic acid present, the remaining acetate then decomposes at 400 K and the total weight loss in both steps corresponds to the complete removal of two acetic acid molecules. To ascertain the nature of the product in 1 : 2 mixture it was kept in a thermostat at 360 K for 24 h and analysed by spectral methods. It was found that the product consisted of $UO_2Q_2 \cdot HQ$ and unreacted uranyl acetate.

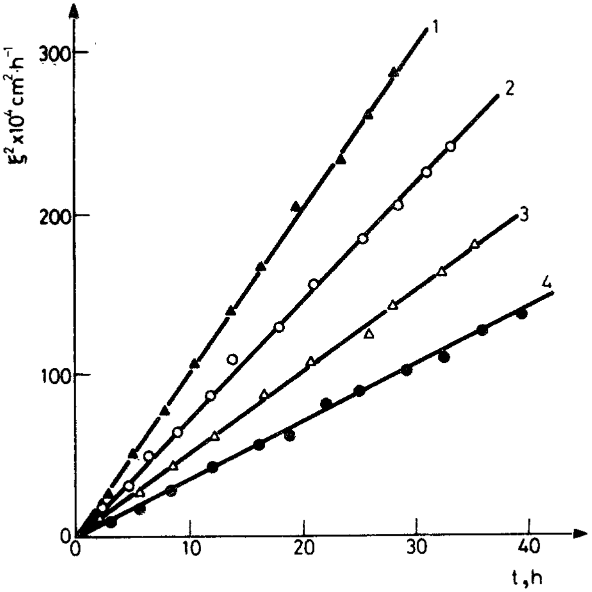

Fig. 4 Kinetic data for the reaction between C_9H_7NO and $UO_2(CH_3COO)_2$ by capillary technique. 1: 338 K, 2: 333 K, 3: 328 K, 4: 323 K

The DTA curve of 1 : 3 mixture shows only one endothermic effect at 324–341 K (T_{max} = 334 K) and a weak shoulder at 341–365 K. The TG curve shows a single step weight loss from 323 to 346 K with loss of 14.5% (calculated 14.6). In this step the complete reaction of uranyl acetate with 8-hydroxyquinoline occurs as evidenced by the complete weight loss and also by the characterization of the final product which was found to be only $UO_2Q_2 \cdot HQ$. No melting was detected when 1 : 2 and 1 : 3 mixtures were examined on a hot stage. At about 323 K, the colour of the mixture changed from yellow to red with the evolution of a gaseous product which indicates that it is a true solid–solid reaction. In 1 : 4 stoichiometric mixture two endothermic effects are observed. The first effect corresponds to the solid state reaction only accompanied by a weight loss of 12.1% (calculated 12.3%) at 323–338 K. The second endotherm with which no mass change is observed is due to the melting of the excess 8-hydroxyquinoline. This sequence of events is also substantiated by hot stage microscopic observations, in which first a colour change from yellow to red is seen in the solid state which is followed by the melting of the mixture.

The capillary experiments enable the movement of reaction boundary and thickness of the product layer to be measured. The kinetic data for the reaction of uranyl acetate with 8-hydroxyquinoline, obtained by capillary technique at a temperature of 323 to 338 K is best fitted to the equation

$$\xi^2 = kt + c$$

where ξ is the thickness of the coloured product layer at time t, and k and c are constants. The ξ^2 *vs.* t relationship is linear and the value of the energy of activation calculated from the Arrhenius plot is 44.4 kJ mol^{-1}. The parabolic nature shows that the reaction is diffusion controlled and the penetration of either uranyl acetate or 8-hydroxyquinoline through the product is rate determining. The diffusing species was found to be 8-hydroxyquinoline by a separate experiment in which the position of the boundary was marked on the glass capillary and the direction of movement of the coloured product boundary with time was noted. The diffusion can occur either in the bulk or through vapour phase or by surface migration and through grain boundaries. The bulk diffusion of 8-hydroxyquinoline into the uranyl acetate lattice is not possible through defect mechanism because this would require molecular movement and very high energy of activation. To study the contribution from vapour phase diffusion, the kinetics was studied in a capillary in which 8-hydroxyquinoline was separated by an air gap. The boundary of the product was formed in the direction of uranyl acetate but the thickness of the boundary did not grow significantly with growing air gap. This shows that the initial reaction occurs by vapour phase diffusion and its contribution decreases as the thickness of the phase boundary at the reactant-product interphase increases. This is also supported by the high value of heat of sublimation for 8-hydroxyquinoline (108.8 kJ mol^{-1}). The reaction can then proceed by surface migration and grain boundary diffusion of 8-hydroxyquinoline through pores and cracks which develop during the reaction.

The kinetics of isothermal decomposition for $UO_2Q_2 \cdot HQ$ was studied at 503, 513, 523 and 533 K. Figure 5 shows a plot of fractional decomposition α *vs.* time for the decomposition of $UO_2Q_2 \cdot HQ$. The complex $UO_2Q_2 \cdot HQ$ decomposes at 513 K to give the green coloured complex UO_2Q_2 with a weight loss of 20.60% (calculated loss 20.62%). The data obtained were tested for various models; linear, diffusion controlled, phase boundary or nucleation-growth controlled, to see whether a single kinetic model operates in this reaction. The results for all nucleation and growth models had a correlation coefficient of 0.990 or so. The highest correlation coefficient (0.998) corresponds to the Prout–Tompkins equation ($\log \alpha/1-\alpha = kt$). Therefore the results were analysed using this model. The value of E_a as determined by the Arrhenius plot is 53.3 kJ mol^{-1} with a frequency factor of 3×10^{12}s^{-1}. The decomposition is accompanied by sublimation of 8-hydroxyquinoline which is bulky. Because of the large difference in the sizes of the product and reactant, the reactant/product interface will be in stress and will generate cracks in the structure and hence branching of nuclei occurs.

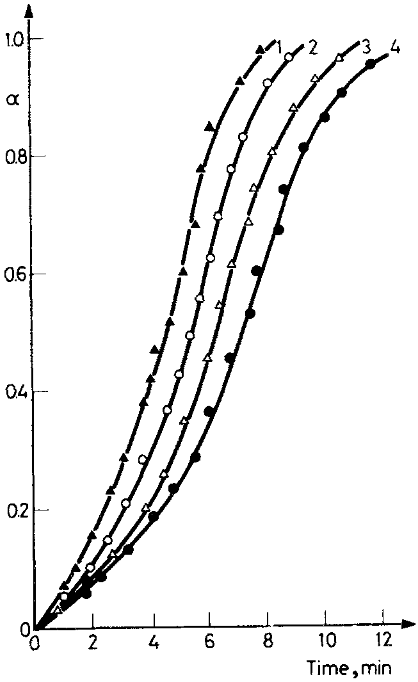

Fig. 5 α *vs.* time plots for isothermal decomposition of $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$. 1: 533 K, 2: 523 K, 3: 513 K, 4: 5i3 K

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Zusammenfassung — Die Festkörperreaktion von 8-Hydroxychinolin und Uranylazetat im Verhältnis 1 : 3 liefert $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$. Die Reaktion ist diffusionsbestimmt und besitzt eine Aktivierungsenergie von 44.4 kJ · mol^{-1}. Die Reaktion verläuft durch die Oberflächenmigration von 8-Hydroxychinolin, welches zur Reaktion mit Uranylazetat in das Gitter des Produktes eindringt. Die thermische Zersetzung der Mischphase $UO_2Q_2 \cdot HQ$ mit $Q = C_9H_6NO$ unterliegt der Prout–Tompkins-Gleichung mit einer Aktivierungsenergie von 53,3 kJ · mol^{-1}.

Резюме — 8-оксихинолин и уранилацетат реагируют в твердом состоянии в стехиометрическом соотношении 1 : 3, образуя соединение $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$. Реакция определяется диффузионным механизмом с энергией активации 44,4 кдж · моль$^{-1}$. Реакция протекает путем поверхностной маграции 8-оксихинолина, который проникает в решетку уранилацетата и реагирует с ним. Изотермическое разложение жидкой фазы $UO_2Q_2 \cdot HQ$ ($Q = C_9H_6NO$) подчиняется уравнению Праута–Томпкинса с энергией активации 53,3 кдж · моль$^{-1}$.