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THERMAL DECOMPOSITION OF METAL COMPLEXES. X. URANYL NITRATE—PHENYLUREA COMPLEXES

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ABSTRACT

The kinetics and mechanism of the thermal associative process (solid—solid interaction) and the reverse dissociative process

$UO_2(NO_3)_2\text{phenylurea}_n + m\ \text{phenylurea} \rightleftharpoons UO_2(NO_3)_2\text{phenylurea}_{n+m}$

(where $n = 2$—5; $m = 1$—4; $n + m = 3$—6) is discussed. The "activation energy" and the reaction order have been evaluated. It was found that the associative reaction is chemically controlled whereas the dissociative process is physical in nature; therefore no mutual agreement was found between the E_a^* values relative to the two associative and dissociative processes.

INTRODUCTION

In a previous paper we reported on the reactivity of the phenylurea ligand with uranylnitrate in the solid phase. Complexes having a stoichiometry of 2 : 1÷6 : 1 were studied by DSC and the enthalpy changes associated with these reactions were evaluated [1].

In all the papers in this series we have chosen the apparent activation energy, E_a^*, as an indirect measure of the bond strength, obviously within some well-defined conditions [2].

In this work we consider the kinetics and mechanism of the thermal association and decomposition of the UPh_n complexes (where $U = UO_2(NO_3)_2$; Ph = phenylurea; $n = 2$—6) in static air, dynamic air, and dynamic nitrogen atmospheres. The main purpose of this investigation is to determine whether the overall association or decomposition rates in the reactions under study are controlled by a chemical or a physical process [3—5]. Clearly the reaction order, n, reflects the mechanism of the various processes. Moreover, a comparison between the E_a^* values for the associative reaction

$UPh_n + mPh \rightleftharpoons UPh_{n+m}$

$(n = 2$—$5; m = 1$—$4; n + m = 3$—$6)$

and for the reverse dissociative process can provide a direct, unequivocal confirmation of deductions made using the above reaction order criterion.

EXPERIMENTAL

The complexes used in this study were prepared following the procedure reported previously [1].

Thermal decompositions

The simultaneous TG, DTG and DTA were performed with a Mettler thermoanalyzer in static air, dynamic air, and in dynamic nitrogen atmospheres (5 l h^{-1}). The sample weight amounted to about 5 mg and the heating rates were 0.5 and 2°C min^{-1}. A Mettler model T-TD3 crucible holder, 0.1 ml aluminium microcrucibles and Al_2O_3 as the thermally inactive reference material were used. The "activation energy", E^*_a, and the "apparent order" of reaction, n, were determined by the methods described in the literature [6,7].

DSC measurements

The associative reactions were performed using a Perkin-Elmer DSC model 1B as reported previously [1]. The E^*_a values were determined by Piloyan et al.'s method [7], and the apparent order of reaction, n, was evaluated by Kissinger's method [8].

RESULTS AND DISCUSSION

The associative reactions

The thermal behaviour of the solid—solid interactions (associative reactions) $UPh_n + mPh \rightarrow UPh_{n+m}$ has been described previously [1]. The endothermic effect observed at 100°C represents the sum of several contributions. In reactions involving UPh_n ($n \neq 2$) the thermal effect represents the enthalpies associated with the formation of the UPh_{n+m} complex and the melting process of the formed product. When the starting material is UPh_2 the thermal effect also includes the enthalpy associated with the $\alpha \rightarrow \beta$ transition.

Assuming that the $E^*_{a_t}$ value (Piloyan method from DSC peak at 100°C) is the apparent activation energy of the overall process, and remembering that the associative reactions are exothermic, it is reasonable to evaluate the activation energy of the association reaction, $E^*_{a_r}$, by

$$E^*_{a_r} = E^*_{a_m} - E^*_{a_t} + E^*_{a_{\alpha\rightarrow\beta}}$$

where m is the melting process, and $\alpha \rightarrow \beta$ is the $\alpha \rightarrow \beta$ transition. The E^*_a values are reported in Table 1.

The dissociative reactions

Thermal analysis in a dynamic nitrogen atmosphere.

All the UPh_n complexes under investigation show an endothermic effect

TABLE 1

Apparent activation energy, E_a^*(kcal mole^{-1}), and apparent order, n, of the associative reactions (solid—solid interactions)

Reaction	n	$E_{a_t}^*$	$E_{a_m}^*$	$E_{a_{\alpha\rightarrow\beta}}^*$	$E_{a_r}^*$
UPh_2 + Ph	0.7	127	176	80	129
UPh_2 + 2 Ph	0.7	213	200	80	67
UPh_2 + 3 Ph	0.7	226	199	80	53
UPh_2 + 4 Ph	0.7	240	177	80	17
UPh_3 + Ph	0.7	130	200		70
UPh_3 + 2 Ph	0.7	132	199		67
UPh_3 + 3 Ph	0.7	160	177		17
UPh_4 + Ph	0.7	150	199		49
UPh_4 + 2 Ph	0.7	140	177		37
UPh_5 + Ph	0.7	150	177		27

$E_{a_t}^*$ = activation energy of the overall process.
$E_{a_m}^*$ = activation energy of the melting process.
$E_{a_{\alpha\rightarrow\beta}}^*$ = activation energy of the $\alpha \rightarrow \beta$ transition of the UPh_2 reactant.
$E_{a_r}^*$ = activation energy of the associative reaction.

at 100°C in the DTA curve. This is due to the melting process, in accordance with our earlier studies [1].

At $\phi = 2°C\ min^{-1}$ and $\phi = 0.5°C\ min^{-1}$, the complexes decompose in several steps, as indicated by the thermoanalytical TG, DTA and DTG curves

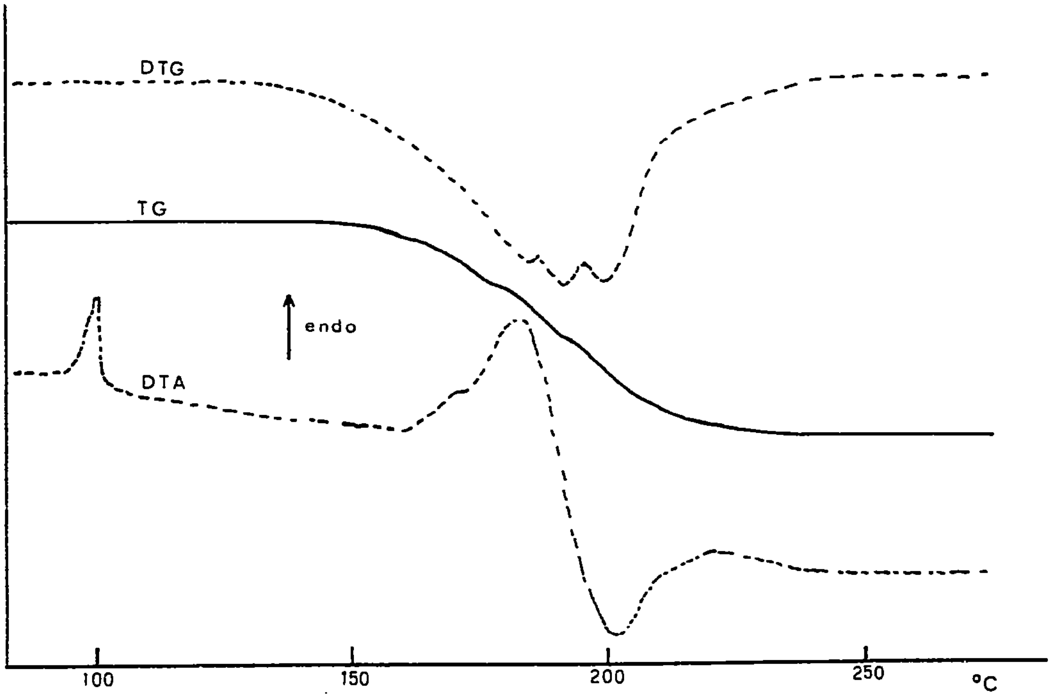

Fig. 1. The thermal behaviour of the UPh_4 complex in a dynamic nitrogen atmosphere at $\phi = 2°C\ min^{-1}$.

(Fig. 1), according to the following scheme

for UPh_2:

UPh_2 (s) → $UPh_{1.7}$ (s) + 0.3 Ph (g) (endothermic)
$UPh_{1.7}$ (s) → $UPh_{1.4}$ (s) + 0.3 Ph (g) (endothermic)
$UPh_{1.4}$ (s) → $UPh_{0.23}$ (s) + 1.17 Ph (g) (endothermic)
$UPh_{0.23}$ (s) → UO_3(s) + gaseous products (exothermic)

for UPh_3:

UPh_3 (s) → $UPh_{0.64}$ (s) + 2.36 Ph (g) (endothermic)
$UPh_{0.64}$ (s) → UO_3 (s) + gaseous products (exothermic)

for UPh_4:

UPh_4 (s) → $UPh_{1.6}$ (s) + 2.3 Ph (g) (endothermic)
$UPh_{1.6}$ (s) → $UPh_{0.15}$ (s) + 1.45 Ph (g) (endothermic)
$UPh_{0.15}$ (s) → UO_3 (s) + gaseous products (exothermic)

for UPh_5:

UPh_5 (s) → $UPh_{0.5}$ (s) + 4.5 Ph (g) (endothermic)
$UPh_{0.5}$ (s) → UO_3(s) + gaseous products (exothermic)

for UPh_6:

UPh_6 (s) → $UPh_{3.2}$ (s) + 2.8 Ph (g) (endothermic)
$UPh_{3.2}$ (s) → $UPh_{0.6}$ (s) + 2.6 Ph (g) (endothermic)
$UPh_{0.6}$ (s) → UO_3 (s) + gaseous products (exothermic)

The observed exothermic effect is due to the simultaneous release of phenylurea and the thermal decomposition of the nitro groups. The starting temperature of the first step of decomposition for each complex is reported in Table 2. At temperatures above 500°C UO_3 gives U_3O_8. The "activation energy", E_a^*, was calculated for the first step of the thermal decomposition at $\phi = 2°C\ min^{-1}$ and the relative values are reported in Table 2.

Thermal analysis in air.

The thermal behaviour of the products in both static and dynamic air atmospheres is quite similar to that previously reported in a dynamic nitrogen atmosphere. Nevertheless, the slope of the TG curve and the starting temperature of decomposition is different for the same complex, depending upon the experimental conditions; this influences the E_a^* values (Table 2).

The exothermic effect (shown by the DTA curve) due to the simultaneous release of the phenylurea and the decomposition of the nitro groups, increases in air with respect to that observed in a dynamic nitrogen atmosphere.

As shown in Table 1, the 2/3 order was found for all the associative processes, thus indicating that the crystal structure of the reactants allows the nucleation of the new species [9—11]. Therefore the solid—solid interaction can be considered to be a chemically-controlled process. The $E_{a_r}^*$ values

TABLE 2

Apparent order, n, apparent activation energy E_a^*(kcal mole^{-1}) and starting temperature of decomposition, T_i(°C), of the dissociative reaction at $\phi = 2°C\ min^{-1}$

Complex	In dynamic nitrogen			In static air		In dynamic air	
	n	T_i	E_a^*	T_i	E_a^*	T_i	E_a^*
UPh_2	0.98	178	57	172	76	170	66
UPh_3	0.90	140	20	134	19	146	19
UPh_4	0.95	145	23	134	21	140	20
UPh_5	1.2	144	20	130	17	130	19
UPh_6	1.3	155	16	128	17	134	16

associated with the process involving UPh_2 clearly indicate that the compound reacts in the β form; this fact was previously only supposed [1]. If the α form was considered as the reactant species, negative $E_{a_r}^*$ values were found!

The trend of the $E_{a_r}^*$ values obtained for $UPh_n + mPh$ systems confirms, as found previously, that the greater the number of identical ligand molecules, the higher the facility of phenylurea to coordinate with uranyl ion. Furthermore, the particularly higher value of $E_{a_r}^*$ for the reaction $UPh_2 + Ph$ can be rationalized when considering that the monomeric structure of UPh_2 changes to a polymeric packing upon formation of UPh_3 [12]. In analogy, the low $E_{a_r}^*$ values observed for the formation of UPh_6 (Table 1) can be related with the monomeric structure of this product.

Turning to the dissociative reactions, no linear correlation between T_i and E_a^* values was found (Table 2). This behaviour confirms the impossibility of using the starting temperature of decomposition reaction as a parameter indicative of the metal—ligand bond strength in a series of complexes.

The apparent order of reactions (Table 2) is at variance to that found for the associative processes, thus indicating that, in the dissociation reactions, the rate-controlling step is not the U—Ph bond rupture. The same conclusion can be drawn by comparing the obtained $E_{a_r}^*$ values (Table 1) with the E_a^* of the dissociation reaction (Table 2), no mutual agreement being found.

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