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THERMAL DECOMPOSITION OF METAL COMPLEXES

III. URANYL NITRATE ADDUCTS WITH N-DONOR LIGANDS

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ABSTRACT

The thermal decomposition of some uranyl nitrate adducts with neutral N-donor ligands was investigated in order to correlate the "activation energy" ,E_a^*, of the first step, whose shape depends on the kind of the neutral ligand, with the antisymmetric stretching vibration ν_3 of the O–U–O group. The linear relationship $\bar{\nu}_3 = 883 + 0.596 E_a^*$ was found.

Some considerations about the identification of the symmetric stretching band ν_1 have been drawn.

INTRODUCTION

A relatively large number of uranyl nitrate adducts containing neutral ligands have been reported in the literature[1–7]. Some of these have also been investigated in relation to their thermal decomposition[4].

For the thermal decomposition of some simple and mixed complexes we observed that the "activation energy" E_a^* relative to the release of the ligand increased with the donor properties of the ligand itself[8].

Now we consider some uranyl nitrate adducts having neutral N-donor ligands, with the aim of estimating the E_a^* relative to the first step of their thermal decomposition and correlating this quantity with the IR data.

EXPERIMENTAL

Reactants

Reagent grade uranyl nitrate hexahydrate, neutral ligands and solvents were employed. When necessary, they were purified by conventional methods.

Preparation of adducts

As described in the literature, we have prepared: ethylenediamineuranyl dinitrate, $UO_2(NO_3)_2(en)$[1]; bis(pyridine)uranyl dinitrate, $UO_2(NO_3)_2(py)_2$[2]; and 1, 10-phenanthrolineuranyl dinitrate, $UO_2(NO_3)_2(o\text{-phen})$[5].

Bis(ammonia)uranyl dinitrate, $UO_2(NO_3)_2(NH_3)_2$, was prepared by passing a dry gaseous NH_3 stream into a concentrated solution of $UO_2(NO_3)_2 \cdot 6H_2O$ in anhydrous diethyl ether; the yellow precipitate was filtered off, washed repeatedly with ether and finally vacuum dried.

Bis(diethylamine)uranyl dinitrate, $UO_2(NO_3)_2(Et_2NH)_2$, was prepared by treating, at room temperature, a solution of uranyl nitrate hexahydrate in anhydrous diethyl ether with an excess of the liquid ligand. The pale-yellow precipitate which we obtained was filtered off, washed several times with the same solvent to eliminate the excess ligand, and finally vacuum dried.

Bis(methylamine)uranyl dinitrate, $UO_2(NO_3)_2(MeNH_2)_2$, and 1,3-diaminopropane uranyl dinitrate, $UO_2(NO_3)_2$(dap), were prepared in a similar way in a solution of acetone; methylamine was employed as a 37% aqueous solution.

The analytical results are reported in Table 1.

TABLE 1

ANALYTICAL RESULTS

Adduct	*Serial No.*	*N (%)*		*U (%)*	
		calc.	*found*	*calc.*	*found*
$UO_2(NO_3)_2$ (en)	1	12.34	12.20	52.41	53.10
$UO_2(NO_3)_2$ (dap)	2	11.97	11.75	50.84	51.52
$UO_2(NO_3)_2\ (MeNH_2)_2$	3	12.28	12.10	52.18	52.85
$UO_2(NO_3)_2\ (NH_3)_2$	4	13.09	12.82	55.60	56.05
$UO_2(NO_3)_2$ (py)$_2$	5	10.15	10.20	43.10	43.42
$UO_2(NO_3)_2\ (Et_2NH)_2$	6	10.37	10.25	44.05	44.42
$UO_2(NO_3)_2$ (*o*-phen)	7	9.76	9.82	41.45	41.98

IR spectra

They were obtained from samples in KBr pellets and in Nujol mulls with a Perkin-Elmer Model 257 spectrophotometer.

Thermal analyses

Simultaneous TG, DTG and DTA were carried out with a Mettler thermoanalyzer. The experimental conditions were: 10–25 mg of sample; heating rate, 0.5–4 °C min^{-1}; flow-rate of dry nitrogen, 10 l h^{-1}.

RESULTS AND DISCUSSION

The thermal decomposition of all the complexes under investigation occurs in steps. After the first step, UO_3 is formed in a stoichiometric amount. As indicated by the shape of the thermoanalytical curves (Fig. 1), the reaction rate depends on the kind of neutral ligand of the complex.

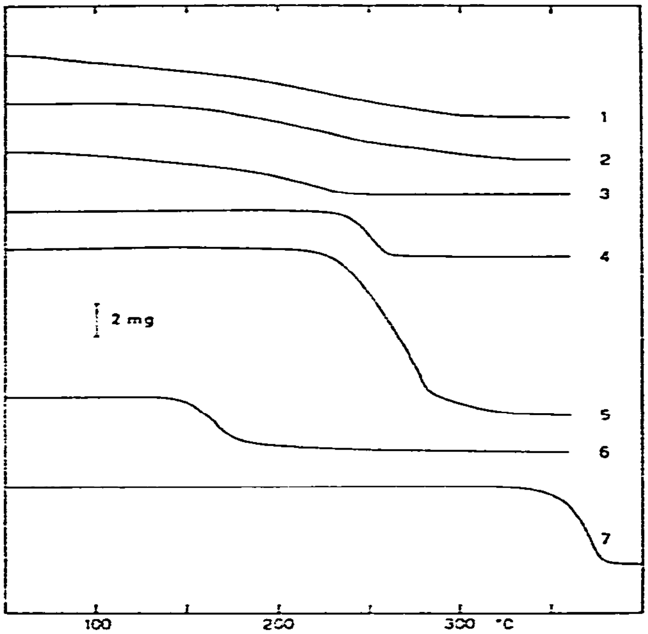

Fig. 1. TG curves of uranyl nitrate adducts. The serial numbers correspond to those used in Tables 1 and 2. Sample weight: (1) = 10.0 mg; (2) = 9.0 mg; (3) = 6.7 mg; (4) = 8.1 mg; (5) = 21.1 mg; (6) = 9.1 mg; (7) = 10.6 mg.

Sinitsyna and Sinitsyn[4] found that the initial temperature of thermal decomposition of uranyl nitrate and chloride complexes with neutral O-donor ligands increases in the same order as the donor properties of the ligand. However, the initial temperature of thermal decomposition is remarkably affected by the experimental conditions (principally by the heating rate) and the use of this quantity to evaluate a not well-defined "thermal stability" has been criticized[9].

It is our opinion that the "activation energy", i.e., the average excess of energy a reactant must have in order to react[10], should be, in the absence of perturbing effects, a parameter connected with the strength of the broken bond. In order to correlate the IR data of the investigated adducts and the "activation energy" of the first decomposition step, we have estimated this last parameter, with a known method from TG curves[11].

The uranyl ion assuming $D_{\infty h}$ symmetry has two, IR allowed, normal vibration modes: the non-degenerate asymmetric stretching ν_3 and the doubly-degenerate bending ν_2. The non-degenerate symmetric stretching mode ν_1 should be IR forbidden normally, but experimental data show that this frequency can be present in the IR spectra of complexes according to the hypothesis that the coordination of ligands in the equatorial plane leads to a change from $D_{\infty h}$ to groups of lower symmetry[12]. The equatorial coordination also induces changes in the frequencies which are characteristic of the O–U–O group owing to changes in the strength of the multiple apical bonds caused by the redistribution of the electron density throughout the entire molecule[3,4,7]. The change in the IR frequencies was also observed for uranyl nitrate complexes, including some adducts that we now consider[3,5,6], as well as for uranyl nitrate and chloride complexes with O-donor neutral ligands[4]. The strongest band observed in the range near 900 cm^{-1} in the spectra of uranyl complexes is assigned to the antisymmetric stretching frequency of the uranyl ion ν_3.

In Table 2 we report the E_a^* values we obtained together with the wave number of the antisymmetric stretching vibration $\bar{\nu}_3$ of the O–U–O group in Nujol mulls.

TABLE 2

E^* AND $\bar{\nu}_3$ (IN NUJOL MULLS) VALUES OF URANYL NITRATE ADDUCTS

Adduct	*Serial No.*	*E^* (kcal mol^{-1})*	*$\bar{\nu}_3$ (cm^{-1})*	$\bar{\nu}_3$ (refs.)
$UO_2(NO_3)_2$ (en)	1	4	885	888 (3)
$UO_2(NO_3)_2$ (dap)	2	16	895	
$UO_2(NO_3)_2$ $(MeNH_2)_2$	3	42	905	
$UO_2(NO_3)_2$ $(NH_3)_2$	4	60	918	895 (3)
$UO_2(NO_3)_2$ $(py)_2$	5	73	928	926 (3); 921, 911 (5); 930 (6)
$UO_2(NO_3)_2$ $(Et_2NH)_2$	6	85	936	
$UO_2(NO_3)_2$ (*o*-phen)	7	101	942	945 (3); 942 (5); 940 (6)

The wave number value obtained in KBr pellets differs considerably from that in Nujol mulls, owing to, uncontrolled in extent, anation reaction occurring during the preparation of the pellets.

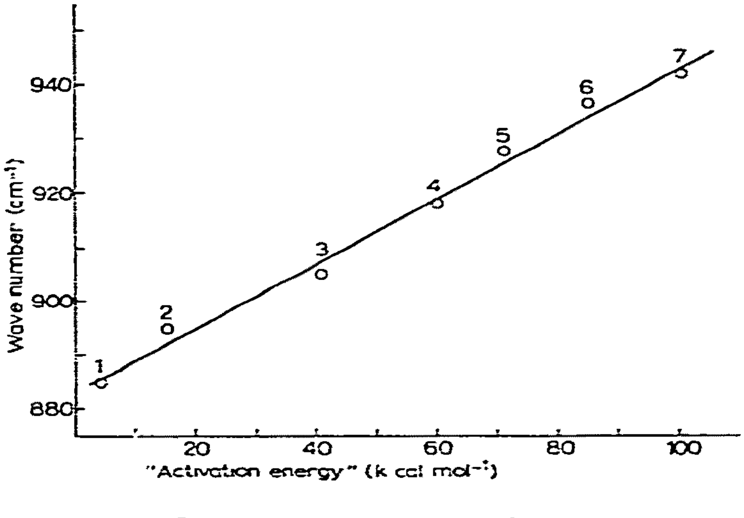

Fig. 2. Plot of $\bar{\nu}_3$ (cm^{-1}) vs. E_a^* (kcal mol^{-1}) of uranyl nitrate adducts. The serial numbers correspond to those used in Tables 1 and 2.

The plot of $\bar{\nu}_3$ versus E_a^* is reported in Fig. 2. The straight line representing the best fit of all the points was obtained by a least squares treatment and obeys the equation:

$$\bar{\nu}_3 = 883 + 0.596 E_a^*$$

The correlation coefficient was 0.995; the greatest deviation of the experimental $\bar{\nu}_3$ value from the calculated one was 2–3 cm^{-1}.

Difficulties were encountered in identifying the symmetric stretching frequency ν_1 of the O–U–O group. In order to predict the position of ν_1, this frequency was correlated with the antisymmetric frequency ν_3, and the linear equation $\bar{\nu}_1 = 21 + 0.89\,\bar{\nu}_3$ was obtained for some uranyl complexes[3]. The magnitude of the ν_1 frequency was also calculated from the $\nu_1 + \nu_3$ combination band frequency and, the ν_3 frequency[5].

In fact the combination band $\nu_1 + \nu_3$ cannot always be identified with certainty. The equation suggested by McGlynn et al.[3] disagrees with their data grafically reported and tabulated; at least the slope of the straight line is much too approximate (according to the plot it should be nearly 0.895). Furthermore, for some complexes, more than one band (or a shoulder) can satisfy the equation; for some others a very doubtful shoulder is observed. Therefore, we cannot consider the possible correlation between the symmetric stretching frequency and the "activation energy".

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