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THERMOANALYTICAL METHODS IN DETECTING SOLID STATE PHOTOLYSIS REACTIONS OF $[Co(NH_3)_5H_2O]X_3$*

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ABSTRACT

The solid state photolysis of $[Co(NH_3)_5H_2O]X_3$ compounds has been studied by reflectance spectroscopy and thermogravimetric analysis. The reflectance spectra have been transformed, in order to obtain a f(r) trend related to the absorbance exhibited by the compound, with the advantage of a more "significant" spectrum. The TG analysis of the compounds at different photolysis times shows that during the irradiation two different kinds of reactions take place: anation and/or photooxidoreduction. The extent of the two reactions is analysed and discussed.

INTRODUCTION

The coordination compounds of type $[Co(NH_3)_5H_2O]X_3$ where $X = Cl^-, Br^-, I^-$ in function of the temperature give a reaction as

$$[Co(NH_3)_5H_2O]X_3 \rightleftharpoons [Co(NH_3)_5X]X_2 + H_2O$$

Many authors studied the thermal behaviour of these compounds[1-5] showing reactions of the above-mentioned type.

The photolysis of this type of compounds was carried out in solution[6,7] giving reactions as

$$H_2O + [(Co(NH_3)_5X]X_2 \xrightarrow{h\nu} [Co(NH_3)_5H_2O]X_3$$

and at the same time photooxidoreduction reactions with formation of Co^{II} compounds and free halogens.

We studied the solid state photolysis of these complexes to make a correlation between the thermochemical stability and sensitivity to light exposure in order to clarify reaction mechanism when no bulk solvent is present.

The reflectance spectroscopy and the thermogravimetric analysis is used to study these systems.

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EXPERIMENTAL

Apparatus

The TG curves are obtained by use of a DuPont 951 thermobalance with dynamic air furnace atmosphere. The sample sizes are 10–12 mg; a furnace heating rate of 10°C min^{-1} is employed.

The reflectance studies are carried out with a Beckman Model DBG spectroreflectometer. Magnesium oxide is used as a reflectance standard.

Photolysis apparatus: samples of the complexes are irradiated with ultraviolet radiations using a 100 W mercury lamp with about 85% abundance of 2537 Å line.

The samples are irradiated using as a sample holder a 5 × 5 cm aluminum block with an indentation of 2 cm diameter and 1 mm deep. The sample is covered with a quartz plate and then photolyzed in nitrogen atmosphere. During the irradiation the block is opportunely cooled.

With this system only the surface of the sample is photolyzed. To obtain a quantity of photolyzed compound sufficient to thermochemical analysis, the sample is placed in a quartz tube, 2 cm in diameter by 15 cm in length, which is slowly rotated by an electric motor. N_2 atmosphere is used.

Chemicals

All the chemicals employed are Merck for analysis.

Preparation of compounds

The intermediate is prepared by the method of Briggs[8] modified by Lamb and Mysels[9]. The final compounds are prepared by the general method of the *Inorganic Synthesis*[10].

Analysis of compounds

Water content of complexes is determined by mass-loss on the thermobalance. Metal content is determined using an EDTA titration and thermoanalytical method.

Methodology

In order to give an interpretation of the reactions taking place when compounds $[Co(NH_3)_5H_2O]X_3$ are photolyzed reflectance spectra and TG analysis have been carried out at different times of light exposure.

Because both anations and photooxidoreductions may occur

$$[Co(NH_3)_5H_2O]X_3 \rightarrow [Co(NH_3)_5X]X_2 + H_2O$$

$$[Co(NH_3)_5X]X_2 \rightarrow Co^{II} + \text{other products}$$

a way to evaluate the extent of both reactions (almost over a qualitative point of view) is needed.

This can be accomplished by evaluating at several times the water loss and the metal content by TG. The metal content (expressed as oxide Co_3O_4) referred to the amount of anhydrous compound (weight recorded after the water loss at about

100 °C) is related to the extent of the photooxidoreduction reaction because of the loss of volatile products as X_2 and/or nitrogen containing species[11] (NH_3, N_2O, N_2). On the other hand the water loss referred to the oxide weight is an indication of the extent of the anation reactions owing to the fact that free water is removed during the drying process, prior to TG analysis, and consequently only the coordinated water is lost in TG.

Reflectance spectra may be transformed in order to obtain a trend f(*r*) related to the absorbance exhibited by the compounds[12]. Unfortunately, transformation depends on the scattering factor which is difficult to evaluate in an absolute way. Therefore, we use the ratio between two maxima in the f(*r*) curve to estimate in a qualitative way the change in composition of the compounds. These ratios are compared with those obtained when anated compounds $[Co(NH_3)_5X]X_2$, separately prepared, are photolyzed.

The latter correlation may give information about the appearance of a totally anated compound when $[Co(NH_3)_5H_2O]X_3$ are photolyzed.

It has to be pointed out that the transformation used is very sensitive to numerical errors, especially for low reflectance values; thus the advantage of a more "significant" spectrum is payed by a loss in sensitivity.

RESULTS

$[Co(NH_3)_5H_2O]Cl_3$

The f(*r*) spectrum shows two maxima at 360 and 480 nm (Fig. 1a). When increasing the time of photolysis the relative abundance of the two maxima reverts while the maximum at 480 nm shifts to higher wave-lengths (Fig. 1b, c). If compared with the f(*r*) spectrum of $[Co(NH_3)_5Cl]Cl_2$ unphotolyzed (Fig. 1d) a similar trend is approached, while the f(*r*) spectrum of the latter compound after 24 h of photolysis slightly varies, except for the appearance of a little band near 640 nm (Fig. 1d). That band can be attributed to the formation of an amount of Co^{II} when photolysis of the anhydrous compound is performed for a long time.

This behaviour can be explained if together with a predominant anation reaction there is a contribution of the photooxidoreduction. This agrees with traces of free chlorine detected in the reaction tube after photolysis.

The predominant anation reaction is confirmed in a quantitative way if the amount of oxide and water loss (calculated as above described) are examined over a range of 24 h (Table 1). The first values ranges from 32.4 to 34.6 with a relative variation of 6.8% while the second ranges from 23.0 to 8.1 with a variation of 65%.

The little variation in the amount of oxide, from 32.2 to 32.8, corresponding to 1.9%, detected in the photolysis of $[Co(NH_3)_5Cl]Cl_2$ accounts for some slight photooxidoreduction even if the anation reaction does not occur.

$[Co(NH_3)_5H_2O]Br_3$

The f(*r*) spectrum shows two maxima at 350 and 490 nm (Fig. 2a). Their

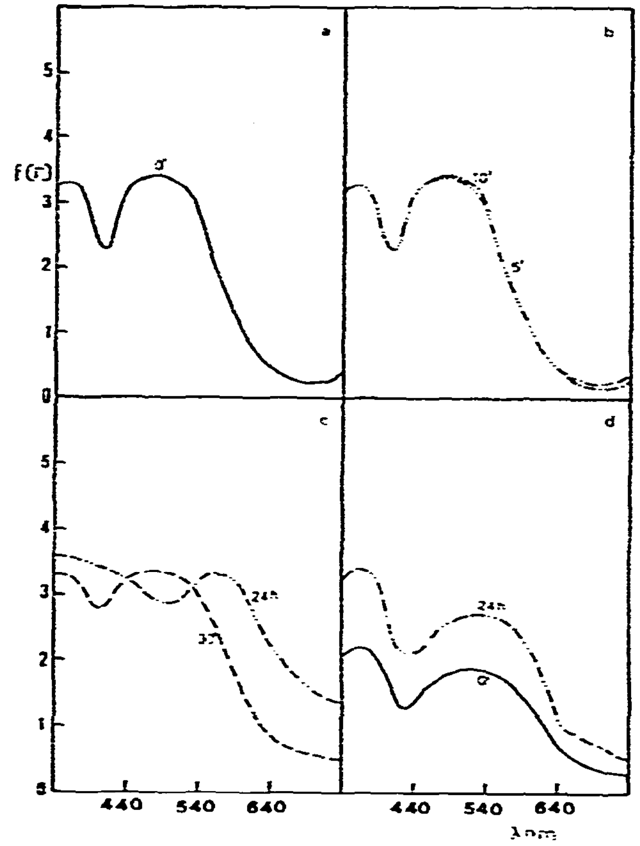

Fig. 1. f(r) spectra at different photolysis times of: a, b, c = $[Co(NH_3)_5H_2O]Cl_3$; d = $[Co(NH_3)_5Cl]Cl_2$.

relative abundances vary with increasing photolysis time until disappearance of the maximum at 490 nm which transforms to an inflection point after 24 h (Fig. 2c). If compared with the f(*r*) spectrum of $[Co(NH_3)_5Br]Br_2$ (Fig. 2d) it can be seen that, after 24 h of photolysis both spectra approach the same trend which resembles neither the spectrum of the unphotolyzed $[Co(NH_3)_5H_2O]Br_3$ nor that of the unphotolyzed $[Co(NH_3)_5H_2O]\,Br_3$.

This behaviour accounts for an anation reaction and a subsequent photooxido-reduction. Free bromine found in the atmosphere of the reaction even after 1 h supports this interpretation.

After 24 h of photolysis the amount of oxide and water loss (Table 1) range from 21.0 to 24.4 and from 20.0 to 13.3, respectively, showing relative variations of 16% and 34%.

The amount of oxide in $[Co(NH_3)_5Br]Br_2$ ranges from 21.1 and 25.0 during the same time of photolysis, with a variation of 18%. The value, similar to that obtained when starting with the hydrated compound, agrees with the f(*r*) spectral data.

TABLE 1

MEASUREMENTS AT SEVERAL TIMES OF PHOTOLYSIS

M = $Co(NH_3)_5$; a = oxide Co_3O_4 (weight percent with respect to anhydrous compound) by TG; b = water (weight percent with respect to oxide Co_3O_4) by TG; c = f(r) ratios at some significant wavelengths X_1/X_2 (reported as fractions) by reflectance spectroscopy.

Compound	*Time of photolysis, t*																
	Theor.		*0*			*5 min*			*10 min*			*30 min*			*24 h*		
	a	*b*	*a*	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*
$[M\ H_2O]\ Cl_3$	32.06	22.40	32.4	23.0	540/360 1.03	33.9	19.4	540/360 1.03	34.1	19.5	540/360 1.03	34.4	18.9	540/360 1.04	34.6	8.1	540/360 0.89
$[M\ Cl]\ Cl_2$	32.06	—	32.2	—	540/360 0.84										32.8	—	540/360 0.80
$[M\ H_2O]\ Br_3$	20.92	22.40	21.0	20.0	490/350 0.69	21.7	17.5	490/350 0.68	21.9	17.5	490/350 0.63	22.2	15.8	490/350 0.67	24.4	13.3	490/350 0.64
$[M\ Br]\ Br_2$	20.92	—	21.1	—	490/350 0.61										25.0	—	490/350 0.61
$[M\ H_2O]\ I_3$	15.30	22.40	15.4	23.0	490/380 0.78	17.4	22.0	490/380 0.79	17.1	21.1	490/380 0.78	20.0	14.7	490/380 0.85	21.8	12.5	490/380 0.83
$[M\ I]\ I_2$	15.30	—	15.4	—	490/380 0.75										22.6	—	490/380 0.78

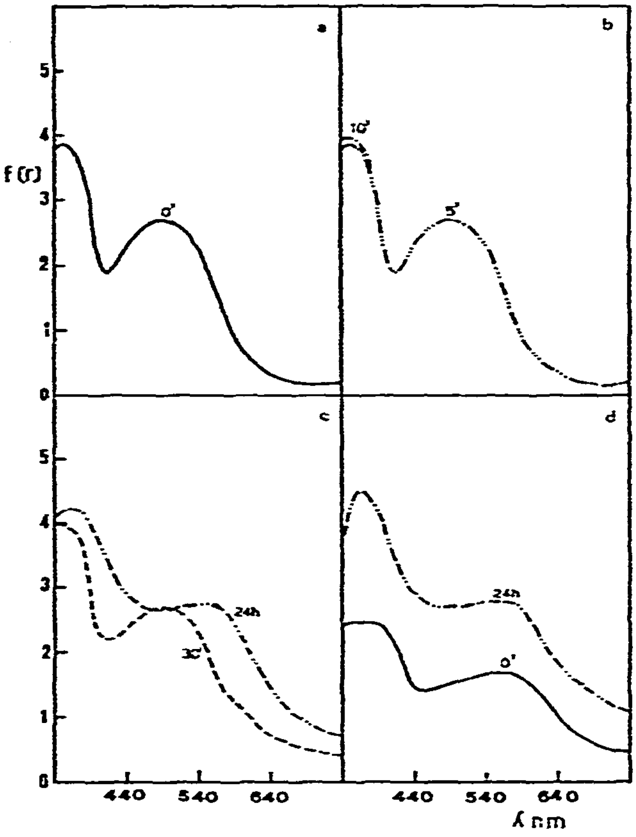

Fig. 2. f(r) spectra at different photolysis times of: a, b, c = $[Co(NH_3)_5H_2O]Br_3$; d = $[Co(NH_3)_5Br]Br_2$.

$[Co(NH_3)_5H_2O]I_2$

The f(*r*) spectrum shows one maximum at 380 nm and an inflection point near 490 nm (Fig. 3a). When increasing the photolysis time the abundance of the maximum relative to the inflection point decreases (Fig. 3b, c). A similar behaviour is observed for $[Co(NH_3)_5I]I_2$ (Fig. 3d).

After 30 min of photolysis both spectra approach the same trend. Unfortunately the absence of a second maximum gives poorly "significant" spectra. Therefore, it is difficult to establish when the two spectra become equal. However, the presence of free iodine detected in the reaction quartz tube after short times (10 min) accounts for a higher contribution of the photooxidoreduction reactions, with respect to the anation one, which becomes important more rapidly than in the case of the aquo-bromide compound.

In this case the oxide amount and water loss after 24 h of photolysis (Table 1) ranges from 15.4 to 21.8 and from 23.0 to 12.5 showing relative variations of 42% and 46%, respectively.

The amount of oxide for $[Co(NH_3)_5I]I_2$ after the same time of photolysis ranges from 15.4 to 22.6 with a variation of 47%.

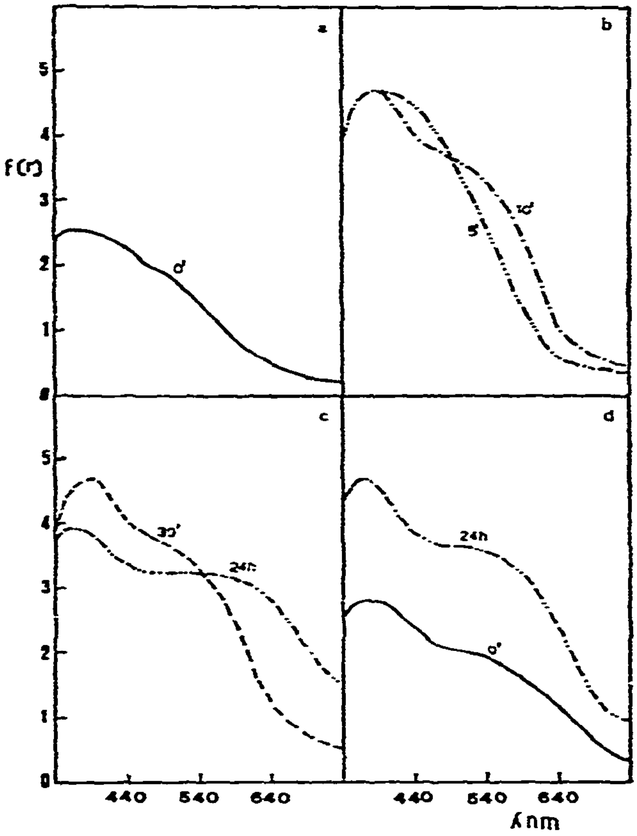

Fig. 3. f(r) spectra at different photolysis times of: a, b, c = $[Co(NH_3)_5H_2O]I_3$; d = $[Co(NH_3)_5I]I_2$.

DISCUSSION

A correct evaluation of the extent of both anation and photooxidoreduction reactions cannot be done directly from the experimentally accessible data, i.e., water loss relative to metal oxide and metal oxide amount relative to anhydrous compound. Especially when considering that the different halogen loss affects in a different way the oxide amount relative to the anhydrous compound. However, it is possible to calculate the water lost at each photolysis time as well as the weigth loss of anhydrous compound with respect to $[MX]X_2$. Results are shown in Table 2 expressed as moles of water and atoms of halogen per cobalt atom in the residual. Obviously, it is not correct to describe the loss of the anhydrous compound only as due to halogen release because other products as NH_3, NO_2, N_2 may result from the photooxidoreduction.

In spite of this consideration this seems the only way to compare the results obtained if taking into account that the halogen weight, is generally greater than that of the other products. Values of halogen lost per cobalt atom greater than unity,

TABLE 2

CALCULATED VALUES AT SEVERAL TIMES OF PHOTOLYSIS

$M = Co(NH_3)_5$; a = water molecules lost per cobalt atom during photolysis; b = global loss of the anhydrous compound during photolysis, expressed as atoms of halogenide per cobalt atom.

Compound	*Time of photolysis*									
	0		*5 min*		*10 min*		*30 min*		*24 h*	
	a	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*
$[M\ H_2O]\ Cl_3$	−0.02	0.08	0.13	0.38	0.13	0.42	0.16	0.48	0.64	0.52
$[M\ Cl]\ Cl_2$		0.03								0.16
$[M\ H_2O]\ Br_3$	0.11	0.02	0.22	0.15	0.22	0.19	0.29	0.24	0.41	0.59
$[M\ Br]\ Br_2$		0.04								0.71
$[M\ H_2O]\ I_3$	−0.02	0.02	0.02	0.48	0.06	0.42	0.34	0.94	0.44	1.18
$[M\ I]\ I_2$		0.02								1.30

obtained for the iodide compounds, may be justified by the participation of other products, while negative water losses are due to traces of humidity.

The trend in function of the time is monotonic except for the $[MH_2O]I_3$ compound: this is probably due to a lack in the homogeneity of the sample which shows the faster rate in the series with respect to photooxidoreduction. From Table 2 it can be seen that the extent of the anation reaction, estimated from the values after 24 h of irradiation, is greater than that of the photooxidoreduction only for aquo-complexes with chloride anions, while the initial rate (up to 30 min of irradiation) is not higher than that of the other complexes. If compared with data obtained for the $[MCl]Cl_2$ compound an important observation can be done: when the anation reaction takes place the photooxidoreduction is strongly favoured while it does not occur in solution[6]. This behaviour may be explained considering that water in the coordination sphere of cobalt(III) can labilize the complex with respect to a reduction reaction[13]. Moreover, when the reaction occurs in solid state the role of the excitation induced by the anation reaction, requiring a reticle reassessment, becomes more and more important.

On the contrary, this behaviour is not exhibited by the two other complexes with bromide and iodide. It is not in contrast when considering a possible set of reactions

$$[MH_2O]X_3 \xrightarrow{h\nu} [M^*H_2O]X_3 \qquad (1)$$

$$[M^*H_2O]X_3 \longrightarrow [MX]X_2 + H_2O \qquad (2)$$

$$[M^*H_2O]X_3 \longrightarrow \text{reduction products} \qquad (3)$$

$$[MX]X_2 \xrightarrow{h\nu} \text{reduction products} \qquad (4)$$

where step 4, which is subsequent to step 2, practically does not occur when X is chloride, as evidenced in Table 2 accordingly with solutions, because of the lower reducing power exhibited by chloride with respect to the other halogenides.

The extent of the anation reactions for the aquocomplexes agrees with the temperatures of the dehydration reactions in the unphotolized complexes, i.e., with respect to the halogenide

$$Cl < Br \simeq I$$

which implies that the chloride complex retains water less than the others.

The decomposition temperatures of unphotolized anhydrous compounds show the sequence: $Cl > Br > I$, which accounts for a greater stability in the same order as shown in Table 2 with respect to the photooxidoreduction. This fact supports the hypothesis that irradiation as well as temperature increase induce the same type of reactions.

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