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On the Influence of Gaseous Ammonia on Uranyl Formate

B. CLAUDEL, J. P. PUAUX, D. REHOREK,* AND H. SAUTEREAU

Laboratoire de Cinétique et Génie Chimiques, 404, INSA, 20, avenue Albert Einstein, F-69621 Villeurbanne Cedex, France

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The interaction of gaseous ammonia on anhydrous uranyl formate has been studied. Depending on the temperature, three different compounds can be obtained: $UO_2(HCOO)_2 \cdot 2NH_3(A)$, $UO_3 \cdot 2HCONH_2 \cdot H_2O(B)$, $UO_3 \cdot HCONH_2 \cdot H_2O(C)$. *A* is unstable at room temperature, and transforms into *B*, which leads to *C* by thermal evolution. *B* and *C* are each characterized by infrared spectra, microanalysis, and X-ray diffraction patterns.

1. Introduction

In an earlier study (*1*), we assumed that the photosensitivity of uranyl formate could be enhanced by interaction of the solid with ammonia. However, this interaction seems to be rather complicated. In that study, we have shown that the action of gaseous ammonia at 180°C on anhydrous uranyl formate leads to the formation of the compound $UO_3 \cdot HCONH_2 \cdot 0.5H_2O$ (labeled *S* in (*1*)). The initial step of the formation of this compound required more investigation. This is why we tried to isolate the uranyl formate diammoniate (*2*) (UFDA) and to describe thoroughly the intermediates formed during the preparation of *S*.

2. Experimental

A. Preparations

Uranyl formate monohydrate is prepared as already described (*3*) and dehydrated at 150°C in a vacuum of 10^{-2} Torr for 2 hr. At this stage, different experiments have been carried out:

—by mixing anhydrous formate with liquid ammonia, a compound labeled *A* has been obtained.

—by passing gaseous NH_3 through the solid anhydrous uranyl formate as indicated by Wiel (*2*), but cooling the sample at −20°C, we obtained a compound labeled *B*.

—using the same preparation as Wiel—without cooling—led to the compound labeled *C*.

B. Experimental Techniques

The infrared spectra were carried out in KBr pellets with a Perkin–Elmer 257 spectrophotometer. Thermogravimetric analysis (TGA) was obtained with a Setaram B 60 thermobalance. Photoluminescence experiments were carried out with a homemade setup (*4*). We give in Table I the infrared spectra of the three compounds *A*, *B*, and *C*. The compound *A* is unstable at room temperature. It leads, after some min-

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* Present address: Sektion Chemie der K.M.U. Liebigstrasse 18, 7010 Leipzig, GDR.

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TABLE I

INFRARED SPECTRA OF $UO_2(HCOO)_2 \cdot 2NH_3$(*A*); $UO_3 \cdot 2HCONH_2 \cdot H_2O$(*B*); $UO_3 \cdot HCONH_2 \cdot H_2O$(*C*)

A			*B*			*C*		
I^a	(cm^{-1})	ascription	I^a	(cm^{-1})	ascription	I^a	(cm^{-1})	ascription
m	3440	ν_{as}(NH)	m	3380	ν_{as}(NH)	m	3440	ν_{as}(NH)
s	3160	ν_s(NH)	s	3180	ν_s(NH)	s	3180	ν_s(NH)
w_{sd}	3030							
w_{sd}	2860	ν(CH)	w_{sd}	2880	ν(CH)	w_{sd}	2880	ν(CH)
			w_{sd}	2780				
			w	2510				
				2540				
w	2335	$\nu(OH)_{ass}$	w	2340	$\nu(OH)_{ass}$	w	2320	$\nu(OH)_{ass}$
			m_{sh}	1690	ν(CO)	m_{sh}	1690	ν(CO)
s_{sd}	1635	$\delta(NH_2)$				m_{sd}	1630	$\delta(NH_2)$
							1610	
m	1595	ν_{as}(COO)	s	1575	$\nu(NH_2) + \nu(CN)$ (*9*, *10*)			
s_{sd}	1540	$\delta_{as}(NH_2)$		1545		s	1545	$\nu(NH_2) + \nu(CN)$
s	1400	ρ(COO)						
			s	1385	$\nu(CO) + \nu(CN)$ (*9*, *10*)			
			m_{sd}	1365				
				1355				
m_{sd}	1310	ν_s(CO)				w_{sd}	1310	ν_s(CO)
			w	1100			1275	
			w_{sd}	1090	π(CH)	w	1090	π(CH)
			w	1050	π(CH)	w	1050	π(CH)
m	915	$\nu_{as}(UO_2^{2+})$						
m	840	$\nu_s(UO_2^{2+})$	m	850	ν(UO)	m	880	ν(UO)
			w_{sd}	820		m	840	
			w_{sh}	790		w_{sh}	755	
				780				
w	770	δ(OCO)		765				
w	755			755				
				740				
			w	690	$\rho(H_2O) + \rho_r(NH_2)$ (*10*)			

[a] s, strong; m, medium; w, weak; sd, shoulder; sh, sharp; ass: associated.

utes to the compound *B*. Owing to the instability of *A*, we were able to perform microanalysis and X-ray powder diffraction patterns of *B* and *C* only. The latter are given in Table III. Microanalyses are given in Table II.

C. Discussion

C.1. Let us first draw attention to compound *C*. X-ray diffraction pattern agrees with that already obtained by Wiel (*2*), but our microanalysis and spectroscopic results depart from the formula, $UO_2(HCOO)_2 \cdot 2\ NH_3$, that he proposed for his compound. It is therefore likely that it corresponds in fact to another formula.

Two arguments support this deduction:

—The luminescence (Fig. 1) and the reflectance spectra at room temperature do not exhibit the characteristic vibronic structure of uranyl salts.

—The infrared spectrum does not exhibit

TABLE II

COMPOSITION (wt%)

	U	C	H	N
Experimental for *B*	59.8	6.10	2.09	7.04
Calculated for $UO_2(HCOO)_2 \cdot 2\ NH_3(A)$ or $UO_3 \cdot 2\ HCONH_2 \cdot H_2O(B)$	60.4	6.09	2.04	7.11
Experimental for *C*	67.5	3.59	1.45	4.07
Calculated for $UO_3 \cdot HCONH_2 \cdot H_2O(C)$	68.4	3.45	1.44	4.02

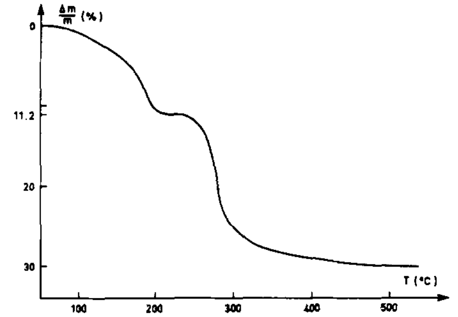

FIG. 1. Thermogravimetric analysis of $UO_3 \cdot 2\ HCONH_2 \cdot H_2O$ (*B*) in air.

TABLE III

X-RAY DIFFRACTION DIAGRAM OF $UO_3 \cdot 2\ HCONH_2 \cdot H_2O(B)$ AND $UO_3 \cdot NCONH_2 \cdot H_2O(C)$[a]

B		C	
I^b	d_{obs} (Å)	I^b	d_{obs} (Å)
w	10.62	w	9.06
w	7.73		
s	7.34		
vw	6.95		
vw	6.60	s	6.65
vw	6.30		
vw	6.06		
w	4.05		
vvw	3.92	m	3.84
vw	3.70		
vw	3.67		
vvw	3.57	w	3.57
vvw	3.47		
w	3.33		
w	3.23	vs	3.11
w	3.06		
w	2.70	vw	2.61
vw	2.53		
vw	2.46		
vw	2.11	vw	2.12
		vvw	2.06
vw	2.03	vw	2.02

[a] CuKα radiation = 1.5418 Å; Debye–Scherrer camera of 360 mm circumference; intensities visually estimated and corrected for absorption.

[b] v, very; s, strong; m, medium; w, weak.

the broad ν_{as}(COO) band of the formate ion, but shows peaks at 1690, 1090, and 1050 cm^{-1} which are characteristic of formamide (*1*). The observed U–O vibrations are not as well resolved as in UO_2^{2+} compounds, but appear more like UO_3 in the compound *S* already described (*1*). ν_{as} and ν_s of UO_2^{2+} are lacking.

This leads us to propose for *C* the formula $UO_3 \cdot HCONH_2 \cdot H_2O$ which has the same empirical formula as $UO_2(OH)(HCOO) \cdot NH_3$ proposed by Wiel (*2*) for one of his compounds.

The compound *B*, prepared at a lower temperature, exhibits an infrared spectrum (Table I) and a luminescent spectrum at room temperature similar to *C*, but a different microanalysis (Table II) and a different and well-resolved X-ray diffraction pattern, and we propose for it the formula: $UO_3 \cdot 2\ HCONH_2 \cdot H_2O$.

As regards the compound *A*, its infrared spectrum:

—does not exhibit the vibrations of $HCONH_2$ (especially at 1690, 1090, and 1050 cm^{-1})

—exhibits $\nu_{as}(UO_2^{2+})$ at 915 cm^{-1}.

This compound is unstable and leads to the compound *B* at room temperature. Let us remark that *A* and *B* have the same composition. Although we were not able to perform the microanalysis of *A*, owing to its instability, its infrared spectrum agrees with the formula $UO_2(HCOO)_2 \cdot 2\,NH_3$. In other words, *A* and *B* could be isomers.

C.2. We noticed a strong exothermic effect upon admission of ammonia on anhydrous uranyl formate. This can explain the fact that Wiel prepared in fact $UO_3 \cdot HCONH_2 \cdot H_2O$ instead of $UO_2(HCOO)_2 \cdot 2NH_3$, as is claimed in Ref. (*2*). As a matter of fact, the X-ray pattern given in (*2*) is that which we observe for *C*.

The DTA under ammonia published in our previous paper (*1*) shows that temperature excursions are difficult to avoid in the preparations. In the DTA experiment, *C* corresponds to the shoulder at 100°C, whereas $UO_3 \cdot HCONH_2 \cdot 0.5\ H_2O$ is obtained at 180°C. The loss of formamide with formation of *C* when *B* is heated in dry air is shown by the TGA curve (Fig. 1). Although we have not carried out the analysis of the gases, the weight loss (11.2%) corresponds well to the evolution of 1 mole of formamide according to the reaction:

$$UO_3 \cdot 2\ HCONH_2 \cdot H_2O \rightarrow UO_3 \cdot HCONH_2 \cdot H_2O + HCONH_2.$$

At temperatures above 350°C, the compound *C* decomposes to UO_3 (weight loss of 30%)

C.3. Photoluminescence of B and C at liquid nitrogen temperature. As we have already reported, the photoluminescence spectra of *B* and *C* at room temperature do not exhibit the characteristic vibronic structure of the uranyl salts. The spectra obtained at liquid nitrogen temperature are shown Fig. 2, and exhibit a broad band for *B* and a vibronic structure for *C* with bands peaking at 5115, 5340, 5580, 5840, and 6130 Å which are equidistant by about 830 cm^{-1}. These emission spectra depend strongly upon the site symmetry of uranium, the luminescent center being $U^{6+}(O^{2-})_n$ (*7*). Our observations show that the oxygen environment of U atoms is quite different in the compounds *B* and *C*. In *B* this environment seems octahedral (*8*), whereas for *C* the luminescence is more akin to that observed in U-activated oxides such as $SrZnP_2O_7$–U (*7*) or $SrLaMoWo_6$–U (*8*).

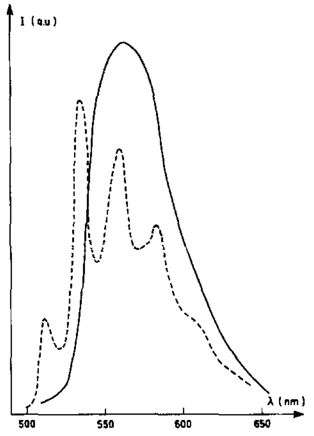

FIG. 2. Corrected photoluminescence spectra of $UO_3 \cdot 2HCONH_2 \cdot H_2O$ (*B*) (solid line) and $UO_3 \cdot HCONH_2 \cdot H_2O$ (*C*) (dotted line) at 77 K (intensity scales are not comparable).

D. Conclusion

Two new compositions in the ternary diagram UO_3–$HCONH_2$–H_2O have been characterized: the compounds $UO_3 \cdot 2\ HCONH_2 \cdot H_2O$(*B*) and $UO_3 \cdot HCONH_2 \cdot H_2O$(*C*).

The compound *B* is the result of the thermal isomerization of $UO_2(HCOO)_2 \cdot 2NH_3$(*A*), which is a rather unusual reaction in the solid state, occurring at a surprisingly low temperature. When heated in dry air, at 200°C *B* leads to *C*.

The compound *C* can also be obtained at 100°C by reaction of gaseous ammonia on anhydrous uranyl formate. The ternary diagram UO_3–$HCONH_2$–H_2O also includes the already described compound $UO_3 \cdot HCONH_2 \cdot 0.5H_2O$ (*1*).

The characterization of $UO_2(HCOO)_2 \cdot 2\ NH_3$ and of eventual intermediates between this compound and *B* requires further investigation.

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