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Note

A THERMOGRAVIMETRIC STUDY OF THE $(C_nH_{2n+1}NH_3)_2MCl_2Br_2$ COMPOUNDS WITH $10 < n < 18$ AND M = Cd, Cu AND Zn

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In the last few years the compounds with general formula $(C_nH_{2n+1}NH_3)_2MCl_4$ have been the subject of an extensive study due to the large variety of structural and magnetic phase transitions they present (see refs. 1—4 and refs. cited therein). Recently, increasing interest has arisen in determining the influence of partial Cl—Br substitution [5—7]. This interest has led to some attempts aimed at the understanding of decomposition phenomena in monohalogenoid compounds [8,9].

The purpose of this paper is to present a study of the thermal stability and decomposition phenomena in the $(C_nH_{2n+1}NH_3)_2MCl_2Br_2$ compounds with $n \geqslant 10$ and M = Cd, Cu, Zn. Analysis of the experimental results in order to obtain the thermal decomposition kinetic mechanism is based on Satava's procedure [10], including the kinetic equations usually employed by Johnson and Gallagher [11].

However, for those cases in which the least minimum fit is not relevant to the elucidation of a most probable mechanism, we have also made use of a procedure recently proposed by Abou-Shaaban and Simonelli [12]. In this case the kinetic mechanism is derived from a comparison of the kinetic values obtained from both procedures.

EXPERIMENTAL

The preparation of all compounds, as well as the chemical and spectroscopic characterization, have been described previously [5—7]. The apparatus, calibration, experimental conditions and accuracy of measurements were described in refs. 9 and 14. Complementary observations were made by means of a hot-stage microscopy and melting point apparatus.

RESULTS AND DISCUSSION

The experimental results for cadmium compounds reveal three decomposition steps. The first step begins at $T_i = 170°C$ and shows no appreciable dependence on the chain length. However, the initial temperature for the

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other two steps increases with n. From the thermogravimetric experimental results it is not possible to develop a decomposition pattern with stoichiometric intermediate chemical compounds for the first two steps. In the third step loss of $CdBr_2$ occurs. This was confirmed by a study of the thermogravimetric curves of cadmium bromide, alkylamine hydrochloride and our cadmium compound for each value of n, Also, by means of optical observations, we found that at about 270°C both powder and crystal samples reach a liquid state.

For the copper compounds the experimental results reveal two decomposition steps. In this case the initial and final temperatures for each step do not seem to be a function of n. Experiments were carried out in an atmosphere of air in order to make a comparison with previous results for tetrachloride compounds [8]. For the first step a transformation of $CuBr_2$ into CuBr was found, which was confirmed by comparison with the $CuBr_2$ thermogram.

Zinc compounds show three decomposition steps, but they present important differences with respect to cadmium compounds. In this case the initial decomposition temperature for zinc bromide is lower than the initial temperature of the third step for the zinc compound. Therefore, the melting temperature (154°C) is lower than the initial temperature for the first decomposition step, so in zinc compounds decomposition commences from a quasi-liquid phase.

The most relevant thermogravimetric data are shown in Table 1 for all the compounds studied. Also, as an example, the original weight loss curves for the $n = 15$ zinc compound, zinc bromide and 15-alkylamine hydrochloride are shown in Fig. 1.

In order to determine the most probable kinetic mechanism, Satava's method was applied; the best fit of thermogravimetric data for the first decomposition step of all compounds studied was given by an Erofeev-type equation

$$[-\ln(1-\alpha)]^{1/n} = KT$$

with $n = 1$, 3/2, 2, and 3. Using the Abou-Shaaban method, which requires a numerical differentiation of the thermogravimetric curves, the most probable mechanism was found to be that with $n = 1$. These results show the existence of a random nucleation (unimolecular decay law [13]) as the rate-determining process for the first decomposition step, therefore differing from those found for manganese monochloride compounds [9] for which a two-dimensional nucleation occurs.

In the case of Zn compounds the results obtained can be understood if we take into account that the first decomposition step occurs when the crystal has changed to a quasi-liquid phase. For cadmium and copper compounds, structural aspects such as position of the Br ions in the octahedron, layer or non-layer structure, etc., have not yet been established, and therefore it is not possible to make a correlation between the kinetic mechanisms and the compounds' structure as in the case of manganese compounds [9].

Finally, we have estimated the kinetic parameters for the first decomposition step. The set of values for the activation energies and frequency factors

TABLE 1

Kinetic parameters for the first decomposition step and initial temperatures for the other two

Parameter	Com pounds	10	11	12	13	14	15	18
T_i^I (K)		163	170	170	170	170	170	160
E_a^I (kJ mole^{-1})		96.86	96.49	95.73	94.63	86.02	82.47	78.11
A^I (s^{-1})	A	1.6×10^8	2.5×10^8	9.7×10^7	3.9×10^7	1.1×10^7	6×10^6	1.1×10^6
T_i^{II}		298	283	307	321	330	322	337
T_i^{III}		440	440	450	450	460	492	490
T_i^I		140	140	130	140	130	140	140
E_a^I (kJ mole^{-1})		84.14	84.39	77.02	77.23	73.09	66.18	54.0
A^I (s^{-1})	B	1.8×10^7	3×10^7	1.3×10^7	5×10^6	5×10^6	3×10^5	1.2×10^4
T_i^{II}		310	300	280	310	290	310	340
T_i^I		170	170	180	170	170	180	160
E_a^I (kJ mole^{-1})		85.65	81.88	88.45	80.71	83.55	81.88	81.89
A^I (s^{-1})	C	9.2×10^6	3.4×10^6	1.1×10^6	1.5×10^6	4.6×10^6	1.42×10^6	2.5×10^6
T_i^{II}		328	330	340	350	350	350	340
T_i^{III}		490	490	490	490	490	490	415

A = $(C_nH_{2n+1}NH_3)_2CdCl_2Br_2$; B = $(C_nH_{2n+1}NH_3)_2CuCl_2Br_2$; C = $(C_nH_{2n+1}NH_3)_2ZnCl_2Br_2$.

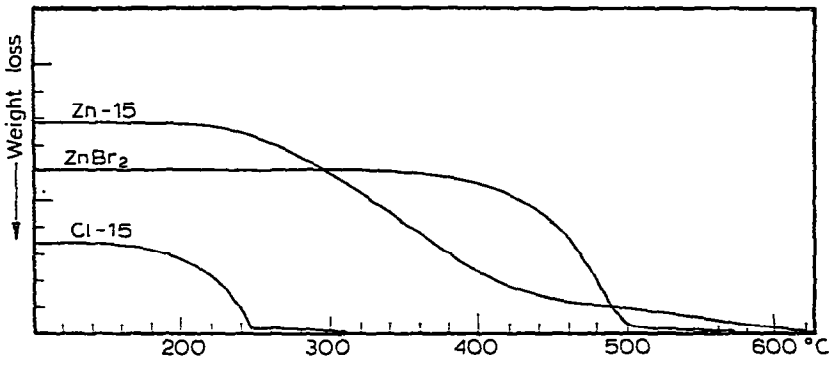

Fig. 1. Thermogravimetric curves of $(C_{15}H_{31}NH_3)_2ZnCl_2Br_2$ (Zn-15), zinc bromide, and 15-alkylamine hydrochloride (Cl-15).

are listed in Table 1. It is seen that for the cadmium and copper compounds the activation energies decrease when the organic chain length increases, whereas for Zn compounds the activation energy is practically constant, in agreement with their structural configuration when the decomposition begins.

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