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Note

On the thermal decomposition of $(C_nH_{2n+1}NH_3)_2MnCl_4$ compounds with $n \leqslant 10$ in a dynamic temperature regime

M. J. TELLO*, E. H. BOCANEGRA AND M. A. ARRANDIAGA
Facultad de Ciencias, Universidad de Bilbao, Apd. 644 Bilbao (Spain)

H. AREND
Laboratory of Solid State Physics, Swiss Federal Institute of Technology, CH 8049 Zürich (Switzerland)

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$(C_nH_{2n+1}NH_3)_2MnCl_4$ compounds belong to a large family of related substances studied in the past mostly because of interesting magnetic ordering at low temperatures[1–4]. Their lattices consist of corner-sharing chlorine-octahedra layers with manganese ions in the central octahedra positions. The NH_3-groups lie on both sides of the layers in the cavities between octahedra, with the attached alkyl-groups oriented roughly perpendicular to the octahedra planes. A schematic representation of such a structural unit can be seen in ref. 5. Interlayer bonding is very weak and is due to Van der Waals forces acting between the end members of neighbouring carbon chains.

The recent discovery of structural phase transitions at higher temperatures in these "two-dimensional perovskites"[5–7] has expanded experimental research into a temperature range overlapping partly with thermal decomposition. This fact initiated the present study which aims at a better understanding of decomposition phenomena in compounds of the manganese group with $n \leqslant 10$. The following points were examined:

(1) The chemical reactions involved in decomposition;
(2) the nature of the rate-determining mechanism;
(3) the activation energy of the processes observed.

The treatment of the two latter points is based on a procedure of Šatava[8] permitting the analysis of thermogravimetric traces obtained in a dynamic temperature regime. Therefore, also all symbols used here are the same as those explained already in ref. 8.

EXPERIMENTAL

The preparation of all substances in aqueous media from $MnCl_2 \cdot 4H_2O$ and the corresponding alkyl-amine hydrochloride is based on refs. 4, 5 and 9.

A Perkin-Elmer thermobalance was used after calibration by means of magnetic

*Present address: Facultad de Ciencias, Dto. de Fisica, Universidad de Granada, Spain.

standards. Thermogravimetric runs were carried out in dry nitrogen with a flow-rate of 25 ml min^{-1} with batches of 2, 5, 4 and 6 mg of each substance and three different heating rates of 5, 10 and 20°C min^{-1}. Each run was repeated 2 to 3 times. Experimental reproducibility is good. All values of α (fraction of decomposed material) are mean values of the thermograms made. A typical spread of experimental values is pointed out graphically in Fig. 1.

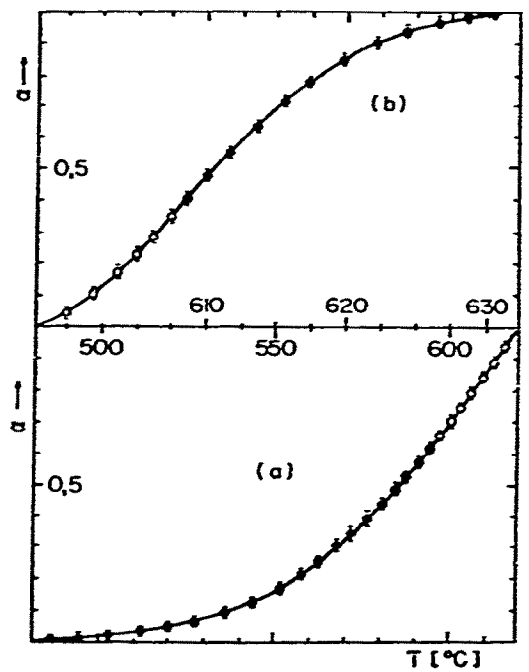

Fig. 1. Fraction of decomposed material (α) vs. temperature for the two steps of the $(C_3H_7NH_3)_2$-$MnCl_4$-compound. (a) First step; (b) second step.

RESULTS AND DISCUSSION

Fig. 1 shows a typical decomposition curve as observed in the $(C_3H_7NH_3)_2MnCl_4$ compound. Similar curves were observed for all other compounds examined. The weight loss of both steps reveals the following pattern:

$$\text{1st step: } (C_nH_{2n+1}NH_3)_2MnCl_4 \rightarrow C_nH_{2n+1}NH_3MnCl_3 + C_nH_{2n+1}NH_3Cl$$

$$\text{2nd step: } C_nH_{2n+1}NH_3MnCl_3 \rightarrow C_nH_{2n+1}NH_3Cl + MnCl_2$$

The original decomposition curves exhibit a small overlap of both steps. Both initial and final weight are well defined and can be used for the evaluation of α in both steps. The overlap concerns only small parts of the curve. All directly determined values are marked by black circles in Fig. 1, whereas white circles denote values obtained from a separation of both steps.

It must be mentioned that $C_nH_{2n+1}NH_3MnCl_3$ compounds are formed during

the first decomposition step. Similar unhydrated compounds with a 1:1 ratio of alkyl-amine hydrochloride and manganese dichloride were obtained up to now only for binary and higher amines[10,11]. A characterization of these compounds based on a synthesis by thermal decomposition of the bis-alkyl-amine maganese tetrachlorides will be attempted later.

Applying Šatava's analysis to both decomposition steps we were looking for a relation yielding a straight line plot for a $\log g(\alpha)$ versus $1/T$ relation. From Fig. 2 we can see that the straight line criterion is fulfilled for the first step for all compounds

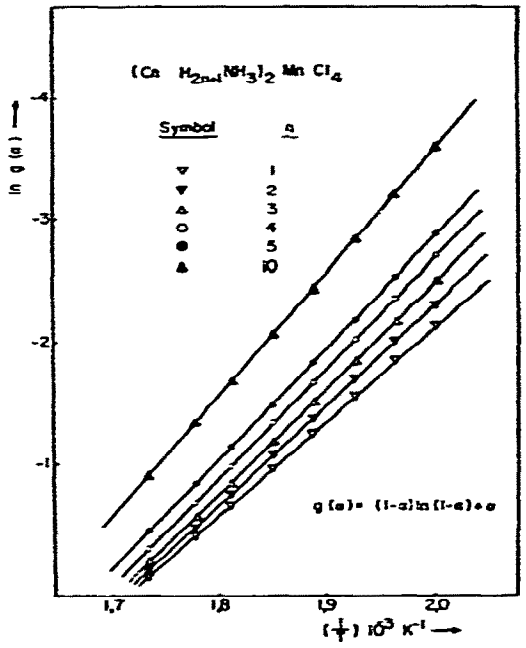

Fig. 2. Validity of the two-dimensional diffusion-controlled mechanism function $\ln[(1-\alpha)\ln(1-\alpha)+\alpha]$ vs. $1/T$ for the first decomposition step of all compounds examined.

for an equation with two-dimensional nucleation as rate-determining process. The reaction product formed shows a defined orientation with respect to the undecomposed matrix[12] and is probably the result of a topotactic reaction. The structure of the product is unknown at present, but contains probably from analogy with related compounds[13] parallel columns of face sharing Cu–Cl octahedra in directions parallel to the original octahedral planes. Whether the rate-limiting two-dimensional diffusion would be connected with surface diffusion on the undecomposed original layer structure compound or with the evaporation of the alkyl-amine hydrochloride through the partly decomposed matrix cannot be decided at present.

Fig. 3 shows that the second decomposition step is controlled by a random nucleation mechanism in all substances examined.

Finally we have estimated the activation energy of both decomposition steps. The temperature interval of each step permits a simplified treatment based on eqn (8)

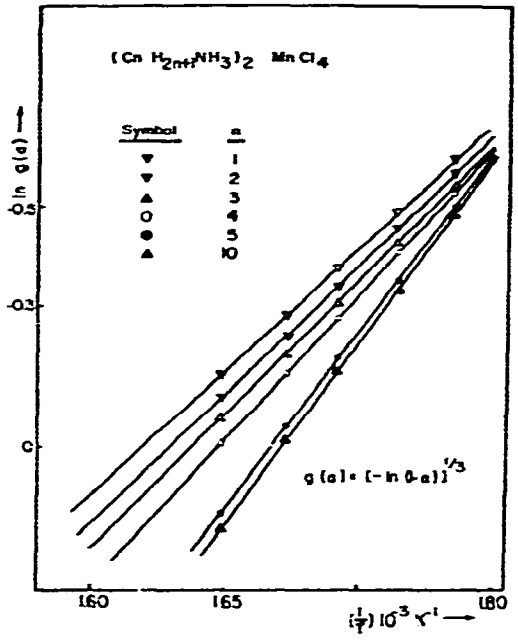

Fig. 3. Validity of the random nucleation mechanism function $\ln[-\ln(1-\alpha)]^{1/3}$ vs. $1/T$ for the second decomposition step of all compounds examined.

TABLE 1

ACTIVATION ENERGIES OF BOTH DECOMPOSITION STEPS OF THE OBSERVED $(C_nH_{2n+1}NH_3)_2MnCl_4$-COMPOUNDS

Sample	*Activation energies (kcal mol^{-1})*	
Values of "n"	*1st step*	*2nd step*
1	13.19	5.98
2	14.23	7.04
3	15.13	7.76
4	15.81	8.83
5	16.28	9.63
10	19.59	11.90

in ref. 8. The set of values obtained for the activation energies of both steps of all compounds is listed in Table 1.

A continuation of the decomposition study of this type of layer-structure compounds by means of isothermal techniques and microscopic observations is intended.

CONCLUSION

The thermal decomposition of $(C_nH_{2n+1}NH_3)_2MnCl_4$ with $n \leqslant 10$ occurs in two steps:

1st step: $(C_nH_{2n+1}NH_3)_2MnCl_4 \rightarrow C_nH_{2n+1}NH_3MnCl_3 + C_nH_{2n+1}NH_3Cl$
2nd step: $C_nH_{2n+1}NH_3MnCl_3 \rightarrow C_nH_{2n+1}NH_3Cl + MnCl_2$

Thermogravimetry in a dynamic temperature regime shows the first step to be rate-controlled by two-dimensional diffusion and the second step by random nucleation. Activation energies of both processes increase with increasing carbon chain length and amount from 13.19 to 19.59 kcal mol^{-1} for the first step and from 5.98 to 11.90 kcal mol^{-1} for the second step.

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