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THERMAL DECOMPOSITION OF AMMONIUM MONOCHLOROACETATE AND AMMONIUM MONOCHLOROACETATE SILICOMOLYBDATE

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The thermal behaviours of ammonium monochloroacetate and ammonium monochloroacetate silicomolybdate have been studied by thermogravimetry (TG), differential thermal analysis (DTA) and X-ray diffraction.

The DTA curves show that ammonium chloride and polyglycollide are obtained as intermediates in the course of the decomposition of ammonium monochloroacetate.

The same mechanism has been confirmed for the decomposition of ammonium monochloroacetate silicomolybdate.

Silicomolybdate complexes with basic molecules of the amine and oxine type have the property of quantitatively precipitating silica from its solutions; they have thus been employed for accurate gravimetric analysis of this substance, and consequently several aspects of these complexes have been widely studied. The first studies concerning their thermal decomposition were those carried out by Babko [1] on pyridine silicomolybdate.

Dupuis [2] studied the thermal behaviour of oxine silicomolybdate and antipyrine silicomolybdate.

The synthesis and determination of a silicomolybdate complex salt with the ligand ammonium monochloroacetate is described in this paper. This complex and its thermal decomposition are studied by means of thermogravimetry (TG), differential thermal analysis (DTA) and X-Ray diffraction techniques.

The interpretation of the experimental results was initially quite complicated, mainly because of the lack of bibliographic data on the thermal behaviour of ammonium monochloroacetate; the only available results were those concerning ammonium acetate obtained by Duval [3], which are not related to those obtained by ourselves. It was necessary then to study the thermal behaviour of NH_4ClCH_2COO, which is described below.

Experimental

Materials

The synthesis of ammonium monochloroacetate was carried out according to the method described by Bateman and Hoel [4], by passing dry NH_3 through a concentrated solution of monochloroacetic acid in dry alcohol. After successive recristallizations from this solvent and later drying in an inert atmosphere, the substance was analyzed for C, H, N and Cl, with the following results:

Experimental		Calculated for NH_4ClCH_2COO
%C	21.82	21.53
%N	12.32	12.56
%H	5.40	5.38
%Cl	31.98	31.81

To synthesize the complex compound, a concentrated solution of monochloroacetic acid was prepared, ammonium molybdate together with ammonium monochloroacetate were dissolved in it, and monomer silica was added to the resultant solution to obtain a 15-ppm concentration of SiO_2. In a strong acid medium and with a concentration of 7.06 g/l ammonium molybdate, a white crystalline powder was obtained after 10 days, which was dried at 100° and analyzed. The results were as follows:

Experimental		Calculated for $6NH_4ClCH_2COO.$ $12\ MoO_3\ SiO_2$
%C	5.89	5.86
%N	3.46	3.42
%H	1.73	1.47
%MoO_3	70.33	70.33

The Schöniger method for quantitative determination of chlorine in organic compounds was not applicable in this case because of interference by molybdenum. Nevertheless, the presence of chlorine was confirmed by means of X-ray fluorescence analysis and by the infrared spectrum of the compound as well.

The water content in the substance, as obtained from the TG curves, is 4.27% and the total formula can be written as follows:

$$6NH_4ClCH_2COO \cdot 12MoO_3 \cdot SiO_2 \cdot 6.3H_2O.$$

Apparatus

Differential thermal analysis and thermogravimetric data were obtained with the aid of Deltatherm models D-2000 and D-4000, respectively, manufactured by Technical Equipment Corporation. The experiments were carried out in a static air atmosphere at a heating rate of 10°/min for both DTA and TG. The sample weight was about 10 mg for TG and 100 mg for DTA, and thermocouples of chromel-alumel were employed.

The X-Ray diffraction analysis was carried out with a Philips diffractometer, model PW-1130-1050-1051; Ni-filtered CuKα radiation was used.

The elemental organic analyses were accomplished with a Perkin Elmer analyzer, model 240, at an oven temperature of 900°.

Results and discussion

a) Ammonium monochloroacetate

The DTA and TG curves for NH_4ClCH_2COO are shown in Fig. 1(a, b).

In the interval 100–150° in the DTA curve, a sharp endothermic effect can be observed, followed by a somewhat wider exothermic one. The former is ascribed to a decomposition process in which NH_4Cl is evolved, and the latter to the immediate crystallization of NH_4Cl and the subsequent formation of a polymer of the polyglycollide type $(-CH_2COO-)_n$, similar to that described for the silver and sodium salts of monochloroacetic acid by Johnson et al. [5].

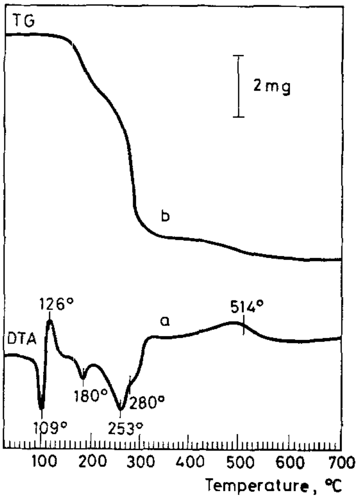

Fig. 1. DTA and TG curves of NH_4ClCH_2COO

After heating to 150°, the compound was shown basically to consist of a material of plastic appearance. X-Ray diffraction analysis also showed the presence of NH_4Cl.

Apart from these two thermal effects, a small endothermic one can be observed at 180°, corresponding to the structural change of NH_4Cl from a NaCl lattice type to a CsCl one, as shown by X-Ray diffraction analysis of the substance above this temperature.

The two subsequent endothermic effects are due to the decomposition of the polymer and the volatilization of NH_4Cl, giving a mixture of polyglycollide with ammonium chloride. Different fractions of this mixture have been isolated according to their solubilities in water and in dry alcohol. Figure 2 (a, b and c) shows DTA curves for the different fractions:

Fraction a: polymer insoluble in water and in dry alcohol
Fraction b: polymer soluble in water and in dry alcohol
Fraction c: NH_4Cl soluble in water and insoluble in dry alcohol

The thermal behaviours of fractions a) and b) differ, even though the contrary would be expected. These differences could be explained by the different degrees of polymerization of the polyglycollides; while fraction a) (insoluble in water and in dry alcohol) remains stable up to 310°, fraction b), less polymerized (soluble in water and in dry alcohol), remains stable only below 200°. We conclude that the polymerization degree depends on the time for which the substance is maintained at 150° and also on the heating rate to reach this temperature.

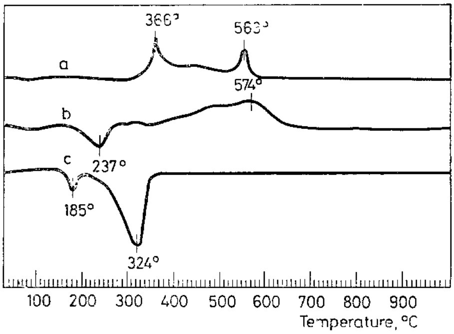

Fig. 2. DTA curves for the fractions obtained by heating NH_4ClCH_2COO up to 150°
Fraction a). Polymer insoluble in water and in dry alcohol
Fraction b). Polymer soluble in water and in dry alcohol
Fraction c). NH_4Cl soluble in water and insoluble in dry alcohol

Consequently, in the DTA curve for ammonium monochloroacetate it is possible to assign the endothermic effect at 253° to the decomposition of the polyglycollide with a low degree of polymerization, and the endothermic effect at 280° to the volatilization of NH_4Cl. The latter value does not agree either with that in Fig. 2 (fraction c) or with that reported by Tsin-Shen and Tronev [6], who give a temperature of 346° for the endothermic effect to volatilization. The difference between this value and our result can be attributed to the fact that, in this special case, the small crystal size of the NH_4Cl considerably decreases the volatilization temperature.

Furthermore, exothermic peaks could be observed at 570°, corresponding to those obtained for fraction b) in Fig. 2; these must be attributed to the combustion of the organic matter graphitized by pyrolysis processes.

The analysis of the TG curve for NH_4ClCH_2COO is fairly simple: no loss of weight can be observed up to 150°; above this temperature, a first loss of weight of irregular slope is observed, and this is followed by another with a steeper slope, corresponding respectively to the process of volatilization of the NH_4Cl formed and to the decomposition of the polymer.

On the TG curve, a gradual loss of weight can be observed above 300°, with a deep step around 600°, probably originating from the combustion of the calcined matter.

b) $SiO_2(MO_3)_{12} \cdot 6ClCH_2COONH_4 \cdot 6.3H_2O$

DTA and TG curves for ammonium monochloroacetate silicomolybdate are shown in Fig. 3 (a and b).

The DTA curve presents first an endothermic effect at 190°; this is coincident with a loss of weight of 4.7% in the TG curve, corresponding to the dehydration of the complex.

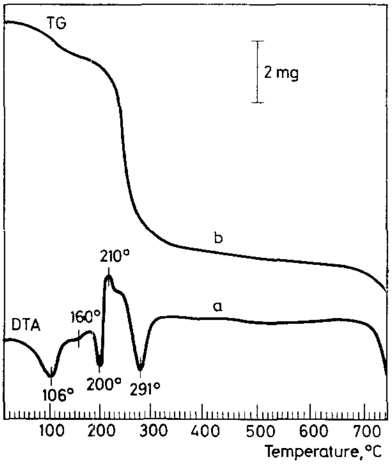

Fig. 3. DTA and TG curves of ammonium monochloroacetate silicomolybdate

Another small endothermic effect can be observed at 160°, without loss of weight, and must be due to a process of structural reorganization.

Two effects, endo- and exothermic, follow between 200° and 210°; because of the resemblance with the thermal decomposition curve of ammonium monochloroacetate, these must be ascribed to the breakdown of the complex and the simultaneous decomposition of the ligand molecule, this happening later because the molecule is protected by a coordinate bond. Just after the double endo-exothermic effect, the TG curve shows a pronounced and continuous loss of weight, corresponding to the last endothermic effect in the DTA curve; this can be attributed to the volatilization which, in this case, is simultaneous for $(-CH_2-COO)_n$ and NH_4Cl.

Finally, at 730°, the TG and DTA curves show the sublimation of MoO_3 in a temperature interval agreeing with published data.

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Résumé — On a étudié par TG, ATD et diffraction des rayons X le comportement thermique du monochloracétate d'ammonium et du monochloracétate silicomolybdate d'ammonium.

Les courbes ATD indiquent qu'il se forme intermédiairement du polyglycolate et du chlorure d'ammonium pendant la décomposition du monochloracétate d'ammonium.

On a confirmé le même mécanisme pour la décomposition du monochloracétate silicomolybdate d'ammonium.

Zusammenfassung — Das thermische Verhalten von Ammoniummonochloracetat und Ammonium-monochloracetat-silicomolybdat wurde unter Anwendung der Methoden der Thermogravimetrie (TG), Differentialthermoanalyse (DTA) und Röntgendiffraktion untersucht.

Den DTA-Kurven entsprechend werden im Verlauf der Zersetzung von Ammoniummonochloracetat Ammoniumchlorid und -polyglycollid als Zwischenprodukte erhalten.

Derselbe Mechanismus wurde für die Zersetzung von Ammonium-monochloracetat-silicomolybdat gefunden.

Резюме — Изучено термическое поведение монохлорацетата аммония и кремний-молибдата монохлорацетата аммония методами термогравиметрии (ТГ), дифференциального термического анализа (ДТА) и диффракции рентгеновских лучей. В соответствии с кривыми ДТА, при распаде монохлорацетата аммония образуются промежуточные продукты — хлорид аммония и полигрихлорид. Такой же механизм подтверждается при распаде кремний-молибдата монохлорацетата аммония.