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THERMOGRAVIMETRIC STUDY OF $(C_6H_5NH_3)_4Mo_8O_{26} \cdot 2\,H_2O$. ISOTHERMAL DECOMPOSITION OF ANILINE

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The thermal decomposition of anilinium octamolybdate dihydrate has been studied by thermogravimetry.

The compound was synthetized and characterized for the first time in our laboratories.

The residual solid from isothermal thermogravimetric decomposition was analysed by chromatography and mass spectrometry analysis.

The aniline degradation products *N*-ethylaniline and *N,N*-diethylaniline were detected. These are probably formed through catalytic action of the octamolybdate ion.

Although the thermal decomposition of ammonium and nitrogen organic derivatives of polymetalates has been studied extensively in order to describe the thermal behaviour of these kinds of compounds [1–14] as well as to apply them as specific materials for industrial purposes [15], the degradation reactions of the organic bases in these salts have scarcely been reported.

It is known that the salts display two decomposition steps. The first involved dehydration, and the second polymetalate decomposition.

The literature results agree, especially as concerns the composition of the intermediate in the second step, which are given as $nMO_3 \cdot xB$ (where *B* is the initial organic base).

In the present experiment we have found that the dehydrated compound starts to become black at about 453 K, and there is scarcely any aniline in the residual solid sample at 563 K.

Accordingly, the thermal degradation of aniline in the octamolybdate has been studied by means of isothermal thermogravimetry and analysis of the decomposition products at 573 K. Gas-liquid chromatography and gas chromatography – mass spectrometry (GC/MS) have been used for this. The elucidation of cleavage products, however, is more uncertain than when a direct thermal balance – mass spectrometer system is used. The intermediates may react with the solvent or change in other ways before analysis.

Experimental

Reagents, syntheses and analyses of the compound

Anilinium octamolybdate dihydrate was prepared from an aqueous solution of aniline and molybdenum trioxide at about pH 2–3. The solution was heated for 4 hours and the precipitate was recrystallized from an ethanol-water solution as monocrystals. The purity of the starting materials was 99.9% (purchased from Merck). X-ray and infrared characterizations were made. The experimental process and characterization data are described in ref. [16].

The carbon, hydrogen and nitrogen contents of the compound were determined by micro combustion analyses. The metal content of the compound was obtained as molybdenum trioxide by thermogravimetric analysis. These results are as follows:

	C	H	N	MoO_3
Found data, %	18.20	2.24	3.62	27.70
Calculated data, %	18.06	2.27	3.51	27.85

Apparatus and measurements

The product was pulverized in a mortar with a pestle and sieved to a narrow fraction of 150–200 mesh in order to carry out all the experiments under the same conditions. The TG curves were recorded on a Perkin–Elmer TGS-1 apparatus with a dry nitrogen flux of 25 $cm^2\ min^{-1}$. About 5 mg of sample was weighed into an aluminium crucible and measured by use of a reference material. Non-isothermal TG curves were run at a heating rate of 5 degree. min^{-1}, and isothermal ones at 360 degree. min^{-1} during some seconds, in order to avoid the artificial induction and acceleratory periods.

In this paper, we also report the qualitative and quantitative analyses of the aniline decomposition products. The analytical method consists of one solvent extraction (ethyl acetate), gas-liquid chromatography and gas chromatography – mass spectrometry (GC/MS).

The GC/MS data were obtained on a 5992B Hewlett–Packard instrument. Gas chromatography was performed on a fused silica capillary column containing 5% phenylmethylsilicone (25 m, 0.2 mm i.d., 0.33 μm) Hewlett–Packard. The gas chromatograph was equipped for split/splitless injections (30 sg). The carrier gas helium at a column head pressure of 21 p. s. i. The initial column temperature was held at 70° for 4 minutes and then raised at 15 degree. min^{-1} and maintained at 250° until all components had eluted. The total GC run time was 30 min.

The quantitative gas chromatography analyses were performed on a 5790A Hewlett–Packard instrument. Details of the gas chromatography conditions are as follows:

- Column: Fused silica, 25 m length, 0.31 mm i.d., 0.71 μm film, cross-linked 5% phenylmethylsilicone, H. P.
- Detector type: FID.
- Injection type: capillary splitless.
- Capillary details: column pressure 21 p. s. i., valve program number 2, valve time 0.5 min.
- Column temperature: from 40 to 250° at 5 degree. min^{-1}. Hold at 40° for 0.75 min.

Results and discussion

TG data

The studied compound presents a three-step decomposition pattern in the non-isothermal run (Fig. 1).

The hydration water is removed during the first decomposition process [17]. The final residual weight is equal to that expected for molybdenum trioxide, which was confirmed by means of X-ray diffraction.

The second step has been studied in this paper, attempts being made to find the chemical reactions that take place during it. The stable intermediate plateau at 511–573 K allowed GC/MS analysis of the solid residue obtained from isothermal runs at 568 K.

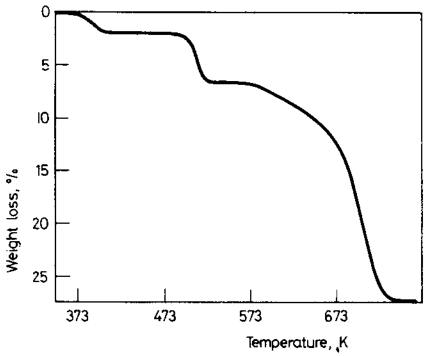

Fig. 1 Non-isothermal decomposition of $(C_6H_5NH_3)_4Mo_8O_{26} \cdot 2\ H_2O$

Gas chromatographic and mass spectrometric data

The residual solid obtained from isothermal decomposition at 568 K was treated with 0.1 mol dm^{-3} sodium hydroxide solution. The non-soluble organic material was partially extracted into ethyl acetate. This solution was analyzed by GC/MS. The

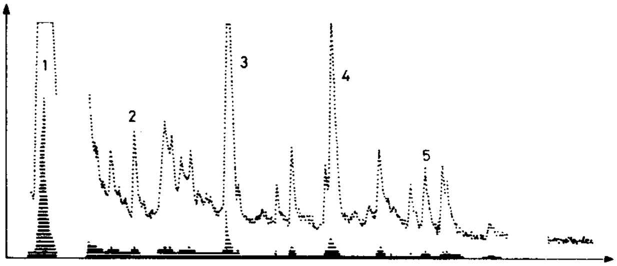

Fig. 2 GC/MS chromatogram

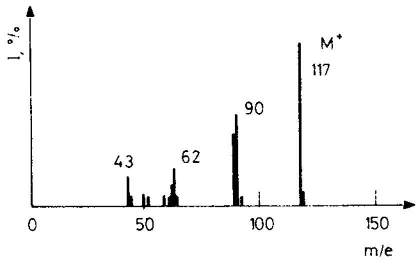

Fig. 3 Mass spectrum of *N*-ethylaniline

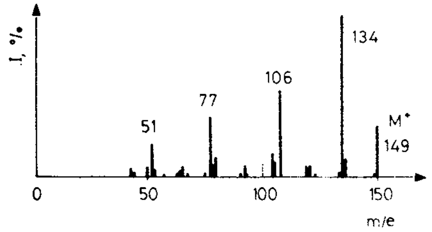

Fig. 4 Mass spectrum of *N,N*-diethylaniline

record obtained is shown in Fig. 2. Peak number 1 suggests *N*-ethylaniline (9.5 min, mass spectrum, Fig. 3), and number 2 suggests *N,N*-diethylaniline (10.8 min, mass spectrum, Fig. 4).

Peaks number 3, 4 and 5 in Fig. 2, with retention times 12.8, 14.4 and 16.5 min, were obtained in traces. They could correspond to the empirical formulas $C_{11}H_{10}N_2$, $C_{11}H_7N$ and $C_{15}H_{16}N_2$, respectivley.

On the other hand, the quantitative analyses were carried out via the internal pattern; 60% *N*-ethylaniline, 9% *N,N*-diethylaniline and 8.7% of the total organic material was extracted by ethyl acetate.

Conclusion

In the non-isothermal thermogravimetric plots we observed a plateau between the initial step and the final decomposition run. This usually involves a stable intermediate compound. We point out that in these kinds of compounds the plateau appears because some chemical reactions occur without loss in weight.

The anilinium cation undergoes degradation during the initial step of decomposition of anilinium octamolybdate.

Finally, we have found a great number of different organic compounds, such as *N*-ethylaniline and others that we describe in the present paper.

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Zusammenfassung — Die thermische Zersetzung von Aniliniumoctamolybdate-Dihydrat wurde thermogravimetrisch untersucht. Die Substanz wurde zuerst in unserem Laboratorium synthetisiert und charakterisiert. Der feste Rückstand der isothermen Zersetzung wurde gaschromatographisch und massenspektrometrisch analysiert. Als Anilinabbauprodukte wurden *N*-Äthylanilin und *N*,*N*-Diäthylanilin nachgewiesen. Diese werden wahrscheinlich durch die katalytische Wirkung des Octamolybdat-Ions gebildet.

Резюме — С помощью термогравиметрии изучено термическое разложение дигидрата октамолибдата анилиния. Соединение впервые было синтезировано и охарактеризовано в лаборатории авторов. Твердый остаток, полученный в результате изотермического термогравиметрического разложения, был проанализирован хроматографическим и масс-спектрометрическим методом. В качестве продуктов распада анализа были обнаружены *N*-этил- и *N*,*N*-диэтиланилины. Возможно, что эти продукты образуются вследствии каталитического действия октамолибдат-иона.