

REACTION SCHEME IN THE NON-ISOTHERMAL DECOMPOSITION OF $(C_6H_5NH_3)_4Mo_8O_{26} \cdot 2H_2O$

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The thermogravimetric decomposition of anilinium octamolybdate has been studied under non-isothermal conditions to elucidate the chemical reactions taking place in the first step of decomposition of the anhydrous compound.

The decomposition products were analyzed by gas-liquid chromatography, gas chromatography-mass spectrometry (GC/MS), infrared spectroscopy and X-ray powder diffraction.

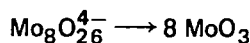
The main decomposition product of aniline turned out to be indole, which is different from the major product in the isothermal decomposition at the same temperature, i.e. N-ethyl-aniline.

A dehydrocyclization reaction is suggested as the rate-dependent process. This is probably due to the catalytic effect of the octamolybdate anion.

In the study of the isothermal decomposition of anilinium octamolybdate dihydrate [1], the complex degradation of aniline was found to occur between 468 and 493 K.

In the present work, we have analyzed in more detail the anilinium cation degradation process in the first decomposition step and the octamolybdate anion break-down under non-isothermal conditions.

The crystallization water is lost at 368–400 K, and the anhydrous octamolybdate anion undergoes thermal decomposition from 440 to 750 K:



This process has been studied by Kiss [2] on the ammonium salt, and it involves structural changes with Mo–O bond rupture near 550 K. Thus, extraction with ethyl acetate and quinoline has been carried out on samples from thermogravimetric decomposition under non-isothermal conditions, stopped at 573 K, in order to study the inorganic anion evolution in the first decomposition step by means of X-ray powder diffraction.

The organic products extracted into ethyl acetate and quinoline have been also analyzed, by GC/MS in the first case and IR spectroscopy in the second.

Experimental

Anilinium octamolybdate dihydrate was synthesized first in our laboratory [1]. Its X-ray, infrared, electron and magnetic nuclear resonance spectroscopy characterization, as well as solution studies, are described in [3].

Apparatus and measurements

The TG curves were obtained with a Perkin–Elmer TGS-1 apparatus. Experimental conditions and previous preparation of the samples were the same as described for the isothermal study [1].

The samples from non-isothermal decomposition during the first decomposition step of the anhydrous octamolybdate were characterized by stopping the decomposition at 423, 473, 503 and 568 K and analyzing by gas-chromatography the amount of aniline in the residual solid.

The amount of aniline in a sample was analyzed after dissolution in 10 cm^3 of 1 mol dm^{-3} sodium hydroxide. The reference solutions were previously prepared in the same way with 5 mg of anilinium octamolybdate dihydrate. The measurements were made on a Sigma 3B, Perkin–Elmer chromatograph with a flame ionization detector and Sigma 10 data station, with automatic integration. Gas-chromatographic conditions were:

Column: Carbowax HP-10% over Chromosorb B (a. w.) 80–100 mesh, 2 m long, 3.17 mm E. D., Injector and detector temperatures: 200° , oven temperature: 90° , carrier gas: nitrogen, $30\text{ cm}^3\text{ min}^{-1}$, sample size: $0.6\text{ }\mu\text{l}$.

Under these conditions the retention time for aniline was 1.62 min.

The residual solid from the thermal decomposition at 569 K was dissolved in ethyl acetate and quinoline, and characterized by means of X-ray powder diffraction. Data were obtained on an automated Phillips 1011 diffractometer internally calibrated with silicon, monochromated (PW 1152/20) using a $\text{CuK}\alpha$ radiation source (1.541 Å), up to $2\theta = 80^\circ$. The scan rate was 1° min^{-1} , and a constant scan width of 1° was adopted for all reflexions.

An infrared spectrum was made of the sample obtained at the same temperature after treatment with 1 mol dm^{-3} sodium hydroxide solution and ethyl acetate. This spectrum was recorded in a potassium bromide pellet at 20° , in the range $600\text{--}4000\text{ cm}^{-1}$, with a Perkin–Elmer 1430 spectrophotometer.

The organic solution in ethyl acetate was analysed by GC/MS, with a Hewlett–Packard 5992B instrument. Details of the conditions have been described [1].

Results and discussion

Thermogravimetry

The non-isothermal decomposition of anilinium octamolybdate dihydrate begins at 368 K, and the TG curve shows three steps [1]. The weight loss in the first decom-

position step of the anhydrous compound (473–511 K) was 4.9%, which can not easily be explained by using a simple reaction scheme taking into account water, ammonia or aniline losses. On the other hand, this quantity is minor compared to those in the isothermal decomposition at 468, 473, 483, 488 and 493 K, which were from 4.6 to 6.7%.

Analysis of aniline in the solid

In order to know the aniline contents of samples from the non-isothermal decomposition stopped at different temperatures during the first decomposition step of the anhydrous compound, the compounds were dissolved in sodium hydroxide solution and analyzed by gas-chromatography. The results are shown in Fig. 1.

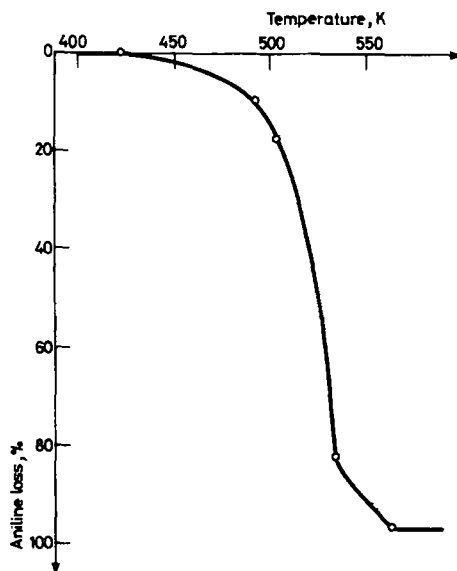


Fig. 1 Aniline loss during the first decomposition step

The first and fifth temperatures are on the plateau in the thermogravimetric curve, but the intermediate points are less good, because it is impossible to stop the decomposition reaction instantaneously. In any case, at the end of the first decomposition step aniline is not present. The same result was found previously in the isothermal decomposition experiments at these temperatures.

X-ray powder diffraction

The residual solid obtained from non-isothermal decomposition stopped at 568 K was treated with ethyl acetate and quinoline. X-ray diffraction patterns of the initial octamolybdate and the inorganic non-soluble solid were obtained and compared with

Table 1 Powder diffraction diagrams of: a) Anilinium octamolybdate dihydrate, b) Intermediate compound at 568 K, c) Final decomposition product (Molybdenum trioxide)

| a | | b | | c | |
|---------------|---------|---------------|---------|---------------|---------|
| $d, \text{Å}$ | I/I_0 | $d, \text{Å}$ | I/I_0 | $d, \text{Å}$ | I/I_0 |
| 12.11 | 36 | 12.62 | 99 | 6.93 | 34 |
| 11.94 | 31 | 11.47 | 100 | 3.81 | 82 |
| 11.32 | 100 | 9.11 | 48 | 3.47 | 61 |
| 9.20 | 14 | 9.02 | 59 | 3.26 | 100 |
| 8.97 | 7 | 8.22 | 36 | 3.01 | 13 |
| 8.54 | 8 | 8.11 | 41 | 2.705 | 19 |
| 8.07 | 10 | 7.88 | 43 | 2.655 | 35 |
| 7.96 | 8 | 6.25 | 48 | 2.530 | 12 |
| 7.31 | 7 | 5.77 | 18 | 2.326 | 12 |
| 6.91 | 7 | 5.47 | 21 | 2.310 | 31 |
| 6.41 | 6 | 4.90 | 13 | 2.272 | 18 |
| 6.36 | 7 | 4.51 | 25 | 2.131 | 9 |
| 6.27 | 17 | 4.33 | 15 | 1.982 | 4 |
| 5.86 | 24 | 4.23 | 20 | 1.961 | 17 |
| 5.71 | 32 | 3.94 | 21 | 1.850 | 21 |
| 4.52 | 44 | 3.81 | 14 | 1.823 | 11 |
| 4.25 | 7 | 3.56 | 28 | 1.733 | 17 |
| 4.12 | 8 | 3.44 | 31 | 1.664 | 13 |
| 3.70 | 11 | 3.40 | 26 | 1.632 | 13 |
| 3.40 | 12 | 3.36 | 34 | 1.598 | 15 |
| 3.35 | 8 | 3.29 | 23 | 1.569 | 16 |
| 3.29 | 7 | 3.24 | 30 | 1.477 | 10 |
| 3.22 | 12 | 3.20 | 18 | 1.443 | 12 |
| 3.12 | 23 | 3.14 | 17 | 1.435 | 12 |
| 3.005 | 7 | 2.891 | 16 | 1.386 | 5 |
| 2.489 | 11 | 2.777 | 15 | | |
| 2.434 | 8 | 2.744 | 12 | | |
| 2.396 | 16 | 2.576 | 14 | | |
| 2.333 | 10 | 2.476 | 15 | | |
| 2.307 | 9 | 2.434 | 11 | | |
| 2.061 | 7 | 2.342 | 9 | | |
| 1.951 | 13 | 2.290 | 9 | | |
| 1.934 | 8 | 2.260 | 8 | | |
| 1.669 | 98 | 2.338 | 8 | | |
| 1.667 | 98 | 2.209 | 8 | | |
| 1.520 | 7 | 2.137 | 10 | | |
| 1.453 | 9 | 2.083 | 11 | | |
| 1.288 | 8 | 2.030 | 9 | | |
| | | 1.971 | 8 | | |
| | | 1.943 | 8 | | |
| | | 1.679 | 8 | | |

that of the final product of decomposition at 743 K, molybdenum trioxide. These diagrams are detailed in Table 1. The d spacings of all observed lines are listed in sequence, together with their relative intensities. We can observe that the product obtained at 568 K is rather crystalline and is different from the initial and final compounds. These results agree with the results of Chojnacka [4] for potassium paradecatungstate hexahydrate.

Analysis of organic compounds in quinoline

The black residual solid after dissolution of the samples from the decomposition stopped at 568 K in sodium hydroxide and ethyl acetate, is a mixture of organic compounds of high molecular weight. Elemental analysis by microcombustion gave:

C: 77.08%, H: 6.99%, N: 15.94%

The nitrogen content is similar to that in aniline, which would mean that the thermal degradation does not occur by loss of ammonia molecules.

The infrared spectrum of the sample (Fig. 2) was taken to obtain supplementary information. It is not possible to make any assignment, but the strong band at about 1600 cm^{-1} could mean an aromatic ring and $\text{N}=\text{N}$ and $\text{N}=\text{C}$ bondings [5, 6].

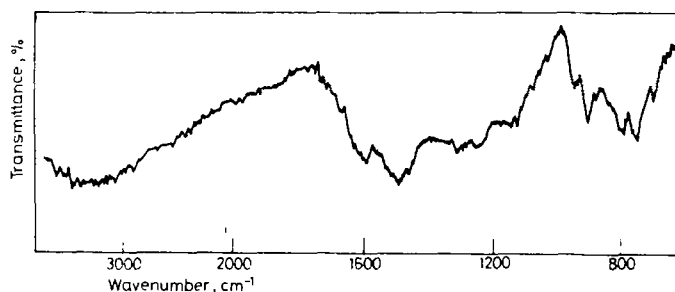


Fig. 2 Infrared spectrum of the organic mixture soluble in quinoline

GC/MS analysis of the organic compounds in ethyl acetate

The obtained chromatogram is shown in Fig. 3.

The mass spectrum of peak number 1 (Fig. 4) suggests indole [7], with a retention time of 11.8 min. Peak number 2, with a retention time of 16.6 min, has the empirical formula $\text{C}_{15}\text{H}_{16}\text{N}_2$, corresponding to benzylazo-(2-phenyl)-ethane.

The major component in the sample, indole, is probably formed from N-ethyl-aniline. This was the major product in the isothermal decomposition at the same temperature [1].

A possible reaction mechanism is dehydrocyclization, probably involving vinyl intermediates:

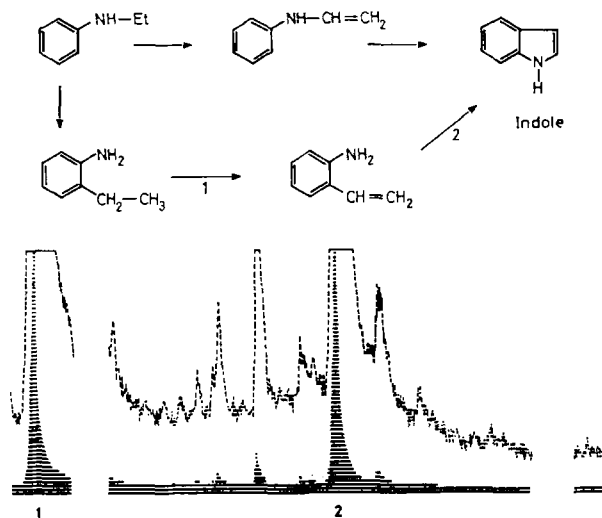


Fig. 3 GC/MS chromatogram

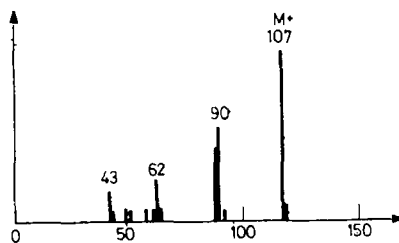


Fig. 4 Mass spectrum of indole

In any case, the main route seems to be the isomerization of N-ethylaniline, followed by dehydrocyclization (steps 1 and 3) to yield indole.

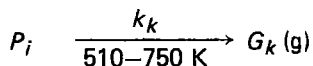
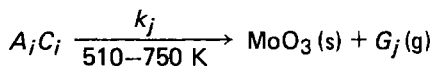
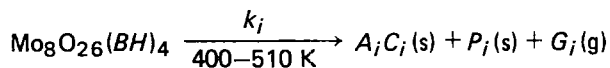
The formation of indole from N-alkylanilines with catalysts such as MoO_3 is a method used in the gas phase at high temperatures [8, 9].

Conclusions

In this paper we have studied the degradation of anilinium octamolybdate dihydrate under non-isothermal conditions.

The TG curve shows that there is no weight loss between 511 and 573 K. The amount of aniline in the residual solid decreases along this plateau until it practically disappears at 560 K, giving a high number of different organic compounds.

The reaction scheme can be written as:



where *BH* is the anilinium cation; *P_i* are different organic products, which have been analyzed after dissolution in ethyl acetate and quinoline; and *G_i*, *G_j* and *G_k* are gaseous products.

One of the most important conclusions of this work is the different product distributions (*P_i*) under isothermal and non-isothermal conditions.

N-Ethylaniline is the major product under isothermal conditions [1] whereas indole is the major product under non-isothermal conditions. A reaction mechanism for this transformation is suggested.

References

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Zusammenfassung — Die thermische Zersetzung von Anilinoctamolybdat wurde unter nicht-isothermen Bedingungen thermogravimetrisch untersucht, um die im ersten Zersetzungsschritt der wasserfreien Verbindung verlaufenden chemischen Reaktionen aufzuklären. Die Zersetzungsprodukte wurden mittels Gas-Flüssigkeits-Chromatographie, Gaschromatographie-Massenspektrometrie (GC/MS), Infrarotspektroskopie und Röntgendiffraktometrie analysiert. Als Hauptprodukt der Zersetzung von Anilin wurde Indol gefunden, während bei isothermer Zersetzung bei gleicher Temperatur vorwiegend N-Äthylanilin entsteht. Es wird angenommen, daß beim nicht-isothermen Prozeß eine wahrscheinlich durch das Octamolybdat katalysierte Dehydrocyclisierungsreaktion verläuft.

Резюме — В неизотермических условиях проведено термогравиметрическое разложение октамолибдата анилина с целью выяснения химических реакций, протекающих на первой стадии разложения безводного соединения. Анализ продуктов разложения проведен методом газо-жидкостной хроматографии, методом газовой хроматография-масс-спектрометрия, ИК спектроскопией и порошковой рентгенографией. Основным продуктом разложения анилина являлся индол, тогда как при изотермическом разложении *N*-этиланилин. Для процесса образования индола предложена реакция дегидроциклизации, которая возможно, вызвана каталитическим действием октамолибдат-аниона.