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SYNTHESIS, CHARACTERIZATION AND THERMOGRAVIMETRIC DECOMPOSITION OF 2-ETHYLPYRIDINIUM METATUNGSTATE MONOHYDRATE. KINETIC STUDY OF ITS THERMAL DEHYDRATION

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2-Ethylpyridinium dodecatungstate(VI) monohydrate was synthetized and characterized as α-$(C_5H_4NHC_2H_5)_5H[H_2W_{12}O_{40}]\cdot H_2O$ by chemical analysis and electronic, IR and ^{1}H NMR spectral studies.

The UV spectra showed the characteristic maximum absorption at 260 nm for the metatungstate anion. The two central protons in the anion were also characterized via IR and ^{1}H NMR spectroscopy.

The thermal behaviour of this compound was investigated by thermogravimetric and derivative thermogravimetric methods. The TG curves revealed four main steps of decomposition, viz. dehydration, partial organic base decomposition and pyrolysis of the organic base, leading to the formation of WO_3 in the final stage.

The intermediates obtained at the end of the various thermal decomposition steps were studied via the IR spectral data on the residues obtained by isothermal heating of the compound at different temperatures.

Kinetic parameters for the dehydration reaction were obtained through two methods of analysis.

At temperatures lower than 100°, the acidification of alkali metal tungstate solutions results in the formation of various polynuclear species. The results of a great number of studies to characterize the polytungstate species have been exhaustively reviewed by several authors [1–4].

The pH inflection observed at $H^+/WO_4^{2-} = 1.5$ in potentiometric titrations of aqueous alkali metal tungstates corresponds to the formation of pseudometatungstate (ψ). The latter anion is formed rapidly, but is metastable in solution and is slowly transformed first into "tungstate–X" and finally into true metatungstate, α-$[H_2W_{12}O_{40}]^{6-}$, the thermodynamically stable product. At 50° and 5 mM tungstate concentration, some 15 days are required for complete conversion to meta-

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tungstate; at 80° and pH 3, the half-lives of the $\psi \rightarrow X$ and $X \rightarrow$ metatungstate reactions are both about 70 min [5].

There is no doubt that the metatungstate anion has the structure α-Keggin [6, 7]; this has recently been confirmed by a structure analysis of $(Bu_3NH)_5H[H_2W_{12}O_{40}]$ [8, 9]. Strong evidence that the two protons are in the centre of the anion and therefore not susceptible to rapid exchange with solvent water was provided by a separate narrow ^1H NMR signal in solutions of sodium metatungstate [10].

The hydrogenometatungstate anion $H[H_2W_{12}O_{40}]^{5-}$ has neen synthetized as alkali metal, tributylammonium and tetraphenylphosphonium salts [11–13].

In the present work, a new dodecatungstate salt with an alkylpyridinium cation has been prepared. This has been found to contain one molecule of crystallization water. The dehydration reaction has been studied. Two different increasing temperature methods have been compared.

Experimental

Preparation of the compound

An aqueous solution of $Na_2WO_4 \cdot 2H_2O$ (0.2 mol dm^{-3}) was acidified with HCl to pH = 5.12. The stoichiometric amount of 2-ethylpyridinium chloride was added. The resulting solution was heated (80°) and stirred for 2 h until it was transparent. The compound was isolated only after allowing the solution to stand for several days. The crystals were colourless. They were filtered from the mother liquor, washed with water and acetone, and recrystallized from aqueous solution with the same characteristics.

The elemental analysis results were as follows: calcd. (found) C: 12.33% (12.30%): H: 1.61% (1.58%); N: 2.05% (2.03%); WO_3: 81.66% (81.56%).

Physical measurements

The electronic spectrum of the compound dissolved in CH_3CN (10^{-5} mol dm^{-3}) was recorded with a Shimazu–UV 260 spectrophotometer in the region 200–700 nm.

The IR spectrum was obtained on KBr pellets with a Perkin–Elmer 1430 instrument in the range 4000–200 cm^{-1}.

The ^1H NMR spectrum was recorded on a Varian instrument (300 MHz) in dimethylsulphoxide as solvent, with TMS as internal standard.

Thermogravimetric studies were carried out on a Perkin–Elmer TGS–7 system in a nitrogen atmosphere, at a heating rate of 2.5 deg/min^{-1}.

Procedure

The data on the dehydration reaction were analysed by applying 18 kinetic models [14], which included processes governed by nuclear growth, surface nucleation followed by the movement of the resulting interface, transport phenomena and order reaction.

Over many years, various methods have been evolved for the analysis of thermogravimetric data in order to evaluate the kinetic behaviour in solid decomposition reactions [15–19].

The fundamental classical equation of non-isothermal kinetics is

$$\mathrm{d}\alpha/\mathrm{d}T = A/\beta f(\alpha)e^{-E/RT} \tag{1}$$

In this rate equation, A = const, E = const and $f(\alpha)$ in principle has the same form throughout the whole reaction. Through variable separation and integration, Eq. (1) becomes

$$\int_0^\alpha \mathrm{d}\alpha/f(\alpha) = A/\beta \int_0^T e^{-E/RT}\,\mathrm{d}T \tag{2}$$

By introducing the usual notation:

$$F(\alpha) = A/\beta\, I(T) \tag{3}$$

These differential and integral kinetic equations can be used to evaluate E and A, and also to calculate $f(\alpha)$ from known values of α, T and $\mathrm{d}\alpha/\mathrm{d}T$.

To determine the non-isothermal kinetic parameters, Eq. (1) is easy to use from a mathematical standpoint. The treatment used in this paper was the modified Freeman and Carroll [20] procedure, MFC, proposed by Jerez [21].

$$\ln(\mathrm{d}\alpha/\mathrm{d}T) - \ln f(\alpha) = \ln(A/\beta) - E/RT \tag{4}$$

When the integral Eq. (2) is used, it has to be taken into account that the conversion integral $F(\alpha)$ and the temperature integral $I(T)$ can be solved only approximately (except in some usual cases for $f(\alpha)$ and some non-linear heating programmes for $I(T)$. Thus, rather simple approximations have to be introduced.

The Šatava method [22] has been used in this work to compare the E values from the two methods. Although the sensitivity of the Šatava method for the determination of mechanisms is not very high, it does yield very useful information [23].

Sample characterization

UV data: 262 (53750 $\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$) nm.

IR: $3420^{a,b}$(m, b) ν(OH); 965^{b}(sh) ν(OH); 950(s) $\nu(\mathrm{WO}_t)$; 880(s), 770(s, b), 390(m), 350(m) and 330(w), different stretching and bending W—O vibrational modes; and 410^b(m) ν(OH).

a: crystallization water,
b: internal hydrogen atoms in the anion
^{1}H NMR: δ(ppm): 6.73 s (2H, W—O—H).

Results and discussion

The TG and DTG curves are shown in Fig. 1. The dehydration process can be observed in the range 340–373 K. The weight loss corresponds to the loss of one water molecule, which is in agreement with the proposed formula.

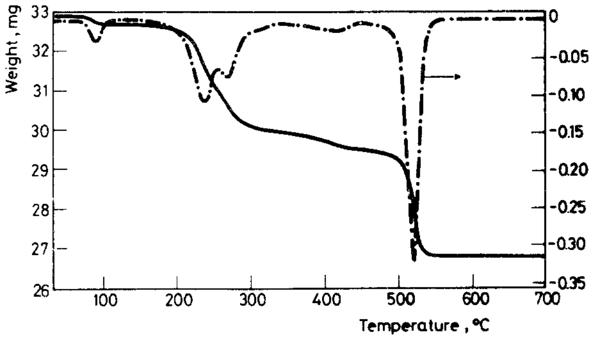

Fig. 1 TG and DTG of $[C_5H_4NH—C_2H_5]_5H[H_2W_{12}O_{40}]\cdot H_2O$

The anhydrous compound is stable up to 443 K, but then undergoes decomposition in four steps, which depend on the operating conditions [25]. The pyrolytic decomposition of the organic base occurs between 743 and 823 K, after which tungsten trioxide remains in the crucible.

Since no stable species are found as intermediates during this process, it was not possible to propose any hypothesis as concerns the decomposition pattern. However, one intermediate solid residue has been studied by means of IR spectroscopy.

The IR spectra of the anhydrous compound and the solid residues obtained in the isothermal runs at 623 and 823 K are given in Fig. 2.

The assignments for the isolated compound have been previously made according to the literature for the metatungstate anion [4, 8, 11–13]. As the bands in the 3600–3400 cm^{-1} region can be assigned to ν(OH) of water and the inner hydrogen in the anion, spectrum *a)* in Fig. 2 is practically the same as that of the hydrated compound. However, spectrum *b)* in Fig. 2 shows that most of the bands

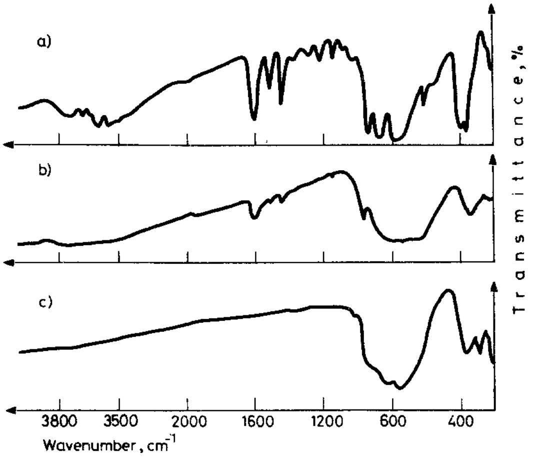

Fig. 2 Infrared spectra of samples obtained at: 388 K a); 623 K b); 823 K c)

have disappeared. It is not possible to make any assignment, but the bands in the 1600–1400 cm^{-1} range could relate to aromatic rings and N = N and N = C bonds. The broad band at 900–600 cm^{-1} is more similar to the characteristic band of WO_3 (spectrum *c)* in Fig. 2) than that of metatungstate. This could mean that before the abrupt weight loss in the TG curve (Fig. 1), the chemical reaction

$$[H/H_2W_{12}O_{40}]^{5-} \rightarrow 12\,WO_3 + 2\,H_2O$$

has taken place, and the last two steps correspond to the loss of residual organic material.

Kinetic analysis was performed on the data for the dehydration reaction. Table 1 gives the results obtained with the Šatava method. The plots ln $F(\alpha)$ *vs* $1/T$ showed poor linearity. Thus, the analysis makes it impossible to select a single mechanism on the basis of the r coefficients. However, it is obvious that the experimental results are best described by equations corresponding to nucleation and nuclear growth over the whole range of decomposition ($0.13 \leqslant \alpha \leqslant 0.95$) ($r = 0.989$). Application of this integral method to the determination of the decomposition kinetics and mechanism in many cases allows a description of the data from the TG curves by more than one equation.

Table 2 shows the results for the six equally probable models (from Table 1) obtained from the MFC method. As can be seen, this method allows a distinction on the basis of the r coefficients. The best least squares fit corresponds to the two last models. The comparison of the activation energy values calculated via the two different methods provides additional information. Nevertheless, the ambiguity

Table 1 Kinetic parameters obtained by Šatava's method

$F(\alpha)$	E, kJ mol^{-1}	A, s^{-1}	r
$[-\ln(1-\alpha)]^{1/4}$	32	$6\cdot 10^{1}$	0.989
$[-\ln(1-\alpha)]^{1/3}$	46	$8\cdot 10^{3}$	0.989
$[-\ln(1-\alpha)]^{1/2}$	73	$1\cdot 10^{8}$	0.989
$[-\ln(1-\alpha)]^{2/3}$	100	$1\cdot 10^{12}$	0.989
$[-\ln(1-\alpha)]$	154	$1\cdot 10^{20}$	0.989
$[-\ln(1-\alpha)]^{3/2}$	236	$2\cdot 10^{32}$	0.989
$1-(1-\alpha)^{1/2}$	128	$6\cdot 10^{15}$	0.954
$1-(1-\alpha)^{1/3}$	136	$7\cdot 10^{16}$	0.967
α^2	225	$1\cdot 10^{30}$	0.910
$(1-\alpha)\ln(1-\alpha)+\alpha$	247	$2\cdot 10^{33}$	0.936
$(1-2/3\alpha)-(1-\alpha)^{2/3}$	258	$1\cdot 10^{34}$	0.947
$[1-(1-\alpha)^{1/3}]^2$	280	$3\cdot 10^{37}$	0.967
α	108	$1\cdot 10^{13}$	0.910
$\alpha^{1/4}$	20	$8\cdot 10^{-1}$	0.910
$\alpha^{1/3}$	30	$3\cdot 10^{1}$	0.910
$\alpha^{1/2}$	49	$3\cdot 10^{4}$	0.910
$1-(1-\alpha)^2$	82	$2\cdot 10^{9}$	0.833
$1-(1-\alpha)^3$	66	$9\cdot 10^{6}$	0.771

Table 2 Kinetic parameters obtained by MFC method

$f(\alpha)$	E, kJ mol^{-1}	A, s^{-1}	r
$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	13	$2\cdot 10^{1}$	0.289
$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	28	$3\cdot 10^{2}$	0.662
$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	57	$6\cdot 10^{6}$	0.896
$3/2(1-\alpha)[-\ln(1-\alpha)]^{1/3}$	87	$1\cdot 10^{11}$	0.951
$(1-\alpha)$	146	$3\cdot 10^{19}$	0.992
$2/3(1-\alpha)[-\ln(1-\alpha)^{-1/2}$	235	$9\cdot 10^{31}$	0.990

cannot be overcome between the mechanisms $F(\alpha) = [-\ln(1-\alpha)]^{3/2}$ and $F(\alpha) = [-\ln(1-\alpha)]$.

Thus, the apparent activation energy of the thermal dehydration process for the first mechanism is 236 kJ mol^{-1} with the Šatava method and 235 kJ mol^{-1} with the MFC method, whereas the two methods lead to activation energies of 154 and 146 kJ mol^{-1}, respectively, for the second mechanism.

Conclusion

A new compound has been synthetized. The results obtained with the different characterization techniques are in agreement with those reported in the literature for other metatungstates of different cations.

The dehydration of this compound has been studied by means of non-isothermal kinetic analysis.

Two different methods have been used to explain the dehydration reaction in terms of some common mechanism.

The E and A values obtained from the two methods are fairly close for both mechanisms. Thus, it is necessary to continue this study by using other methods.

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Zusammenfassung — 2-Äthylpyridindodekawolframat(VI) monohydrat wurde hergestellt und durch chemische Analyse, Elektronenspektrum, IR und ^{1}HNMR Spektraluntersuchungen als α-$(C_5H_4NHC_2H_5)_5H[H_2W_{12}O_{40}]\cdot H_2O$ charakterisiert. Das UV Spektrum zeigte bei 260 nm ein für das Metawolframat Anion charakteristisches Absorptionsmaximum. Die zwei Zentralprotonen des Anions wurden auch durch IR und ^{1}HNMR Spektroskopie charakterisiert. Das thermische Verhalten dieser Verbindung wurde mittels TG und DTG untersucht. Die TG-Kurven zeigten vier Hauptzersetzungsschritte u. z. Dehydratisierung, partielle Zersetzung der organischen Base, Pyrolyse der organischen Base und Bildung von WO_3 als letzte Stufe. Die nach verschiedenen thermischen Zersetzungsschritten erhaltenen Zwischenprodukte wurden durch die Spektraldaten der Rückstände der isothermisch auf verschiedene Temperaturen erhitzten Verbindung untersucht. Die kinetischen Parameter der Dehydratisierung wurden nach zwei Analysenmethoden bestimmt.

Резюме — Моногидрат 2-этилпиридинийдодекавольфрамата(VI) — α-$(C_5H_4NHC_2H_5)_5H[H_2W_{12}O_{40}]$ — был охарактеризован химическим анализом, электронными спектрами поглощения, ИК- и ПМР спектрами. УФ спектры показали наличие максимума поглощения при 250 нм, характерного для метавольфрамат-иона. Наличие в анионе двух основных протонов было также подтверждено ИК- и ЯМР спектроскопией. Термическое поведение этого соединения было исследовано методами ТГ и ДТГ. Кривые ТГ показали четыре основные стадии разложения: дегидратация, частичное разложение органического основания и пиролиз органического основания, приводящего к образованию трехокиси вольфрама на конечной стадии разложения. Промежуточные продукты, образующиеся в конце каждой стадии разложения были изучены ИК спектроскопией остатков, получаемых при изотермическом нагреве соединений при соответствующих температурах. Анализ данных, проведенный двумя методами, позволил определить кинетические параметры реакции дегидратации.