# THERMOGRAVIMETRIC STUDY OF DMF LOSS FROM $(C_8H_{11}NH)_4W_{10}O_{32} \cdot 2DMF$

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The thermal behaviour of collidinium decatungstate with two *N,N*-dimethylformamide (DMF) crystallization molecules was studied by thermogravimetry. The kinetic parameters for the first stage of the thermal decomposition were established from isothermal and non-isothermal mass-change studies. The chemical reaction in this step is the loss of DMF:

$$(BH)_4W_{10}O_{32} \cdot 2DMF \, (s) \xrightarrow{\quad 135-170° \quad} (BH)_4W_{10}O_{32} \, (s) + 2\,DMF \, (g)$$
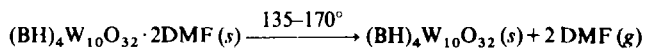
as confirmed by ¹H NMR.

The physical model of this reaction, nucleation-growth according to the Avrami–Erofeev law, with $n = 1/2$, was found by comparison of the isothermal and non-isothermal TG data.

Different decatungstate salts are known [1 3]. An attempt has been made to prepare a dimethylformamide solvate of collidinium (2,4,6-trimethylpyridinium) decatungstate. Solvates of $CaCl_2$ [4] and $U(SO_4)_2$ [5] have recently been prepared and studied.

The TG curves of hydrated polymetalates [6] generally show two steps. The first one, occurring at temperatures lower than about 120°, corresponds to the loss of crystallization water and/or adsorbed water, leading to the anhydrous compounds. The second step, always occurring at temperatures higher than 200° (temperatures varying depending on *M* and the counterion), corresponds to the decomposition of the compounds, involving the loss of organic material and protons. For the present collidinium salt, the total weight loss can be expressed in the concise form:

$$(BH)_4W_{10}O_{32}(s) \rightarrow 10\,WO_3\,(s) + 2\,(BH)_2O\,(g)$$
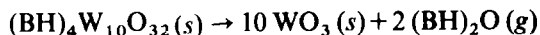
This solvate is thermally more stable than any of the known hydrates of polymetalates, indicating a strong interaction between DMF and the collidinium cation compared to those between water and some organic bases [7]. Isothermal

and non-isothermal study of the first decomposition step of the compound shows that the final weight loss is stoichiometric.

The influence of the experimental conditions, and the difference between the use of dynamic or isothermal regimes in solid-state kinetic studies employing thermogravimetric techniques, are of considerable interest [8]. Over many years, various methods have been evolved for the analysis of thermogravimetric data with the aim of evaluating kinetic parameters for solid decomposition reactions [8, 9].

It has been pointed out by several authors [10 12] from their theoretical analyses that the linearity of the $g(\alpha)$ vs. $1/T$ plot obtained from dynamic TG studies is a necessary but not sufficient criterion. They have reiterated the necessity of recording at least one isothermal measurement on the same reaction in the temperature interval of TG measurement, in order to assign the proper form of $g(\alpha)$. However, the results of isothermal and non-isothermal investigations can be compared only in special cases and then represent an additional criterion for the correctness of the kinetic model used. If there is disagreement between the isothermal and non-isothermal results, this fact too gives further information for the interpretation of the mechanism or the deduction of the overall rate equation (it must be checked especially under non-isothermal conditions).

In this paper, the DMF loss from the parent compound has been examined by a comparative study of the kinetic parameters obtained with dynamic and isothermal regimes.

Experimental

Materials

Collidinium decatungstate solvated with two DMF molecules was prepared for the first time in our laboratory. To a solution of $Na_2WO_4 \cdot 2H_2O$ (8.0 g) and 2,4,6-trimethylpyridinium chloride (1.7 g) in 100 ml of water, 60 ml of N,N-dimethylformamide was added, and the mixture was heated (80°) and stirred for 2 hours. By slow dropwise addition of 0.1 M aqueous HCl with intensive stirring, the solution was adjusted to pH 5.0. The compound was isolated only after allowing the solution to stand for several days. It was filtered off, washed with water and acetone and left to stand in vacuum over P_2O_5. Anal. Calcd: C, 15.28; H, 2.09; N, 2.80; W, 61.58. Found: C, 15.37; H, 2.10; N, 2.80; W, 61.60.

The salt was identified via its characteristic absorption maximum at 325 nm in CH_3CN ($\varepsilon = 1.43 \times 10^4$ dm^3 mol^{-1} cm^{-1}), which corresponds to the oxygen-to-tungsten charge-transfer band.

Instruments

Thermogravimetric studies were carried out on a Perkin–Elmer model TGS–1 system in a nitrogen atmosphere. Non-isothermal measurements were made at a rate of 5 deg min^{-1}. The amount of the sample was 5–7 mg. The isothermal mass-loss curves were recorded at 5 different temperatures in the range 407–423 K. In each experiment the recording was continued until a well-defined plateau was obtained. Computational work was done with an IBM 5110 computer.

^{1}H NMR spectra of the compound and the solid residue obtained from isothermal runs at 423 K were obtained in dimethylsulfoxide solvent, with tetramethylsilane as internal standard, with a Perkin–Elmer model R–12B spectrometer.

Procedure

The kinetic parameters were determined on the basis of the general relation:

$$d\alpha/dt = K(T)f(\alpha)$$

where $K(T) = K_0 \exp(-E_a/RT)$ (Arrhenius law); $K_0 =$ frequency factor; $E_a =$ activation energy; and $\alpha =$ mole fraction. Mathematically, this expression can be converted to

$$\int_0^1 d\alpha/f(\alpha) = \int_{T_0}^T K(T) \, dt$$

with

$$\int_0^1 d\alpha/f(\alpha) = g(\alpha).$$

The main difficulty in solid kinetics is to find the appropriate expression of $g(\alpha)$ or $f(\alpha)$. In this work, we have used all the principal expression of $g(\alpha)$ indicated in the literature [13, 14], as were used in a previous work [7], following the four physical models of solid-state chemistry. In the non-isothermal measurements, the approximation of Satava et al. [15] was employed.

Results and discussion

It is relevant to mention that the solid is not associated with lattice water at all, and the only moieties undergoing decomposition are the organic materials (DMF and the collidinium cation). The stable solid obtained by thermal decomposition at 900 K is WO_3. This decomposition is irreversible and no melting of the solid is observed.

The compound showed four distinct weight losses during heating up to 900 K, as can be seen in Fig. 1. The first weight loss of 4.46% occurs in the temperature range 407–444 K and corresponds to the calculated weight loss of 4.90% for the removal of two DMF molecules from the parent compound. Elemental analysis of the samples after this first decomposition step showed that the mass loss involved only
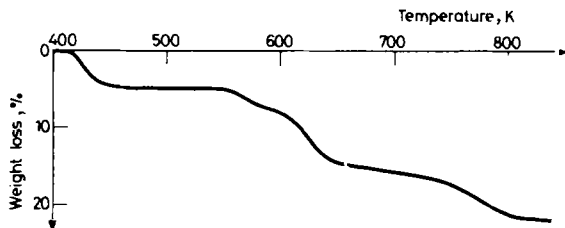

Fig. 1 Non-isothermal TG of $(BH)_4W_{10}O_{32} \cdot 2DMF$

DMF. The ${}^1H$ NMR spectra of the initial compound and the solid residue obtained in an isothermal run at 423 K are given in Fig. 2. These spectra were recorded in order to study the resonance lines appearing due to DMF. The chemical shifts of these absorption appear at 7.92 (H—C=O), 2.90 and 2.74 ppm (—CH$_3$). The integrated intensity of these absorption lines in spectrum (a), that of the initial compound, showed that they were due to 2, 6 and 6 hydrogen atoms, respectively,
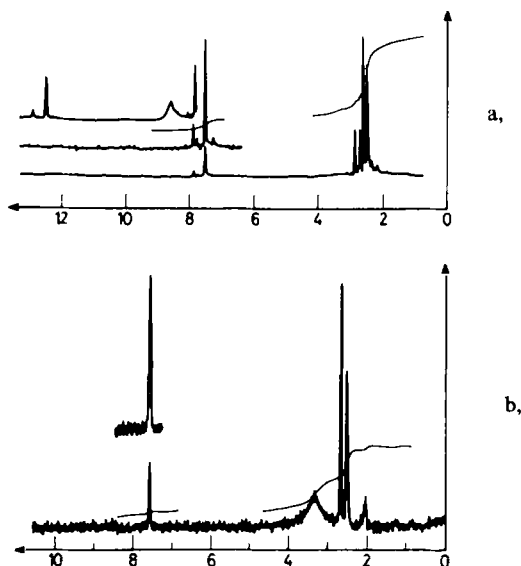

Fig. 2 ^{1}HNMR of the compound (a) and of the solid residue obtained at 423 K (b)

per unit formula. In the spectrum of the compound obtained at 423 K (b), these lines did not appear, as can be seen in Fig. 2. The chemical shifts and the integrated intensities due to the collidinium cation are the same in both samples.

The second weight loss, which commenced at 523 K, can be attributed to the partial desorption of collidine, while the third and fourth can be correlated with the condensation of the polyanion and the decomposition of carbonized collidine.

The first decomposition step, DMF loss, was studied under isothermal and non-isothermal conditions. The kinetic analyses of the dynamic data were made with the Satava integral methods [15]. Table 1 shows the E, k_0 and r values found, together with the kinetic model.

Table 1 Activation energy and frequency factor values obtained by Satava's methods

$g(\alpha)$		E_a, kJ mol^{-1}	$k_0 = 10^x s^{-1}$, x	r
$(-\ln(1-\alpha))^{1/4}$	1.1	50	3	0.994
$(-\ln(1-\alpha))^{1/3}$	1.2	69	6	0.994
$(-\ln(1-\alpha))^{1/2}$	1.3	70	10	0.994
$(-\ln(1-\alpha))^{2/3}$	1.4	147	15	0.994
$(-\ln(1-\alpha))$	1.5	225	25	0.994
$(-\ln(1-\alpha))^{3/2}$	1.6	342	39	0.994
$1-(1-\alpha)^{1/2}$	2.1	188	20	0.942
$1-(1-\alpha)^{1/3}$	2.2	199	21	0.954
α^2	3.1	327	37	0.906
$(1-\alpha)\ln(1-\alpha)+$	3.2	360	41	0.928
$(1-2/3\alpha)-(1-\alpha)^{2/3}$	3.3	375	42	0.937
$(1-(1-\alpha)^{1/3})^2$	3.4	406	46	0.954
$\alpha^{1/4}$	4.1	33	1	0.906
$\alpha^{1/3}$	4.2	47	3	0.906
$\alpha^{1/2}$	4.3	76	6	0.906
$1-(1-\alpha)^2$	5.1	123	12	0.839
$1-(1-\alpha)^3$	5.2	100	9	0.786

The best fit of the experimental values was obtained with the nucleation-growth-controlled mechanism KEKAM equations (Kolmogorov–Erofeev–Kazeev–Avrami–Mampel) [14]. The use of the Satava methods, however, requires a choice from among the six equally probable KEKAM models.

The kinetic analyses of DMF desorption, carried out on the isothermal weight-loss curves, were made on data obtained in the temperature range 405–425 K. The α vs. time plots are given in Fig. 3. These are sigmoidal in nature, with initial induction and acceleratory regions, followed by a decay period at all temperatures. The values of the kinetic parameters and the corresponding correlation coefficients for the
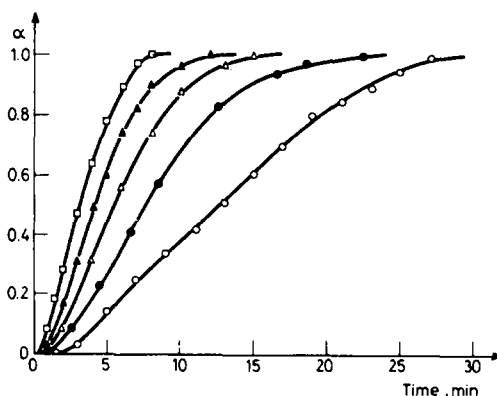
Fig. 3 Isothermal decomposition between 407–423 K. ○ 407 K, ● 411 K, △ 415 K, ▲ 419 K, □ 423 K

KEKAM equations are given in Table 2. The plot of $\ln\left(-\ln(1-\alpha)\right)$ *vs. nt* gives a straight line whose slope is the exponent n. The least squares fit for this equation is also shown in Table 2. The obtained n value is 2 and the best fit for the KEKAM equations also corresponds to $(-\ln(1-\alpha))^{1/2} = kt$. The exponent seems to be constant with temperature.

The correlation coefficient for the least squares fit for the Arrhenius law to obtain the pre-exponential factor $(k_0 = 1.07 \cdot 10^{11}\ s^{-1})$ and the activation energy $(55.42\ kJ\ mol^{-1})$ is 0.999.

Conclusions

The crystallization molecules of DMF are removed during the first process of $(C_8H_{11}NH)_4W_{10}O_{32} \cdot 2DMF$. The stable intermediate plateau at 444–523 K allowed a ^1H NMR spectrum of the solid residue for characterization.

The reaction falls in the category $A(s) \rightarrow B(s) + C(g)$, which is explained in terms of the well-known mechanism involving a nucleation and growth-controlled reaction. The α *vs.* time plots are sigmoidal in nature. The data could be fitted into a single rate law over the entire range of the reaction. The values of the correlation coefficients for the KEKAM equation with $n = 2$ for isothermal and non-isothermal data are near unity.

The K_0 values found with this equation are consistent on comparison of the isothermal and non-isothermal measurements. However, the E_a values are different for the two regimes.

Table 2 Least squares fit for KEKAM equations ($[-\ln(1-\alpha)]^{1/n} = kt$) of the isothermal data

T(K)	1/n = 1/4			1/n = 1/3		
	k	r	0.0	k	r	0.0
407	0.0367	0.973	0.4	0.0479	0.980	0.3
411	0.0500	0.980	0.5	0.0660	0.990	0.3
415	0.0691	0.974	0.5	0.0909	0.986	0.4
419	0.0976	0.949	0.4	0.1254	0.971	0.3
423	0.1274	0.988	0.5	0.1666	0.994	0.3

T(K)	1/n = 1/2			1/n = 2/3		
	k	r	0.0	k	r	0.0
407	0.0702	0.973	0.0	0.0941	0.943	0.3
411	0.0987	0.999	0.1	0.1337	0.995	0.2
415	0.1346	0.997	0.1	0.1801	0.995	0.1
419	0.1789	0.995	0.1	0.2330	0.997	0.2
423	0.2442	0.994	0.1	0.3241	0.981	0.2

T(K)	1/n = 1			1/n = 3/2		
	k	r	0.0	k	r	0.0
407	0.1521	0.849	0.9	0.2894	0.697	2.3
411	0.2171	0.964	0.8	0.4039	0.890	2.0
415	0.2845	0.963	0.7	0.5049	0.877	1.8
419	0.3563	0.965	0.6	0.6190	0.880	1.5
423	0.5072	0.929	0.7	0.8991	0.824	1.7

$$\ln[-\ln(1-\alpha)] = \ln k' + n\ln t$$

T(K)	n	r	ln k'
407	2.02	0.982	5.43
411	1.84	0.999	4.09
415	1.85	0.996	3.53
419	1.99	0.990	3.28
423	1.80	0.997	2.40

The agreement between the results of the isothermal and non-isothermal methods was considered reasonable. In the rising temperature methods the sensitivity of selecting the correct rate equation is not good enough and in this case Satava's integral method does not discriminate at all between the different KEKAM equations.

The absolute validity of E_a may be questioned, but the selection of a common method of analysis allows a comparison to be made which can be relied upon.

8

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Zusammenfassung — Das thermische Verhalten von Collidinium-dekawolframat mit zwei N,N-Dimethylformamid-Molekülen (DMF) wurde thermogravimetrisch untersucht. Die kinetischen Parameter des ersten Schrittes der thermischen Zersetzung wurden aus isothermen und nicht-isothermen Massenveränderungen ermittelt. Die in diesem Schritt verlaufende Reaktion ist der Verlust von DMF

gemäß $(BH)_4W_{11}O_{32} \cdot 2DMF\ (s) \xrightarrow{135-170°C} (BH)_4W_{11}O_{32}\ (s) + 2\ DMF\ (g)$ wie durch ^{1}H-NMR

bestätigt wurde. Das physikalische Modell dieser Reaktion, nämlich ein Keimwachstum entsprechend dem Avrami–Erofeev-Gesetz mit $n = 1/2$, wurde durch Vergleich der isothermen und nicht-isothermen TG-Daten gefunden.

Резюме — Методом ТГ изучено термическое поведение аддукта соли коллидиния с двумя молекулами диметилформамида (ДМФ). На основе изотермических и неизотермических измерений изменения веса определены кинетические параметры первой стадии разложения этого аддукта. Спектрами ПМР было подтверждено, что на первой стадии разложения происходит потеря двух молекул диметилформамида по следующей схеме:

$$(BH)_4W_{10}O_{32} \cdot 2ДМФ\ (тв.) \xrightarrow{135-170°} (BH)_4W_{10}O_{32}\ (тв.) + 2ДМФ\ (газ.)$$
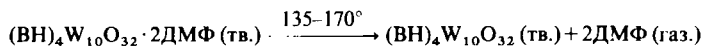
При сопоставлении данных изотермической и неизотермической ТГ было найдено, что физическая модель этой реакции состоит в образовании центров кристаллизации и их роста и подчиняется закону Аврами-Ерофеева с $n = 1/2$.