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INVESTIGATION OF THE DEHYDRATION KINETICS OF 2-ETHYLPYRIDINIUM METATUNGSTATE MONOHYDRATE USING A RISING TEMPERATURE TECHNIQUE

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ABSTRACT

The differences in the kinetic equations used and the values of the apparent activation energy and frequency factor for the thermogravimetric dehydration of 2-ethylpyridinium metatungstate monohydrate have been obtained.

Five different methods for the treatment of increasing temperature data have been attempted, taking into account 18 analytical forms of the $f(\alpha)$ or $F(\alpha)$ functions. One of these methods has been developed and checked for the first time in this work. The most probable mechanism is related to the $F(\alpha)$ expression, $[-\ln(1-\alpha)]$. The E and A values obtained were 127–160 kJ mol^{-1} and 10^{18}–4×10^{21} s^{-1} respectively.

INTRODUCTION

Thermogravimetric (TG) decomposition have been widely used for the determination of the water of crystallization and/or absorbed water and for the description of the decomposition process of poytungstates into WO_3 [1–4].

In our previous study of the synthesis, characterization and thermal behaviour of α-$(C_5H_4NH–C_2H_5)_5H[H_2W_{12}O_{40}]\cdot H_2O$ [5], the dehydration reaction was found to occur between 340 and 373 K. The kinetic analysis in ref. 5 was carried out using two methods of analysis on one TG curve: that proposed by Satava [6] and Sharp's method [7]. Two kinetic equations were then proposed but no definite conclusion could be drawn about which was the leading equation of the reaction.

Throughout this work, we have analysed the dehydration reaction in more detail using data from several TG and differential thermogravimetric (DTG) curves obtained at different heating rates and three new methods of analysis (considering the heating rate as a variable). The methods used for the non-isothermal thermogravimetric analysis were those proposed by Ozawa [8,9] and Urbanovici and Segal [10,11] and a modification of Sharp's (MS) method developed by us. This study has permitted us to choose the equation $F(\alpha) = -\ln(1-\alpha)$ as the most probable mechanism for the dehydration reaction, as we describe below.

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THE INTEGRAL METHODS

One run

In Satava's method, from the integral kinetic equation

$$F(\alpha) = \int_0^\alpha d\alpha/f(\alpha) = A/\beta \int_0^T e^{-E/RT} dT = (AE/\beta R)p(x) \tag{1}$$

where $x = E/RT$ and $p(x) = e^{-x}x^{-1} - \int_x^0 e^{-x}x^{-1}\, dx$, the final operative equation takes the form

$$\ln F(\alpha) - \ln p(x) = \ln(AE/\beta R) \tag{2}$$

$\ln p(x)$ is a linear function of $1/T$, to a first approximation, and therefore $\ln F(\alpha)$ must also be a linear function of $1/T$.

For the correct mechanism, $\ln F(\alpha)$ vs. $1/T$ should be a straight line, the slope of which ($\tan b$) can be used to evaluate E by the following equation

$$E = \frac{-449 + \tan b/2.303}{217} \text{ kcal mol}^{-1} \tag{3}$$

The intercept of the plot gives $\ln A$.

Several runs at different heating rates

Ozawa's method using Doyle's approximation for $\log p(x)$ [12,13]

$$\log p(x) = -2.315 - 0.4567x \tag{4}$$

proposes the following relationship

$$\log F(\alpha) + \log \beta = \log AE/R - 2.315 - 0.4567E/RT \tag{5}$$

The method entails the repetition of the TG data at various values of β and it uses temperature values for the same conversion at different heating rates. The activation energy can be evaluated from the slope of the straight line plot of $\log \beta$ vs. $1/T$ for each α value.

The next step is the determination of A and $F(\alpha)$. The theoretical curves of $1 - \alpha$ vs. $\log F(\alpha)$ are determined for the 18 $F(\alpha)$ functions tested in this work [5] and the experimental plots of $1 - \alpha$ against $\log[(E/R\beta)p(x)]$ are superimposed to fit one of the theoretical curves.

The Urbanovici and Segal method for the evaluation of non-isothermal kinetic parameters uses integration over small temperature intervals. Several heating rates must be used in order to determine whether or not the activation energy changes with the degree of conversion.

For two curves obtained at β_1 and β_2 the expression for the activation energy is

$$E = R\frac{T_{1ik}T_{2ik}}{T_{2ik} - T_{1ik}} \ln \frac{\Delta t_1}{\Delta t_2} \tag{6}$$

where Δt_1 and Δt_2 are the time differences corresponding to the interval $\alpha \in [\alpha_i, \alpha_k]$ and $T_{1ik} = (T_{1i} + T_{1k})/2$. The resulting activation energy corresponds to the degree of conversion given by

$$\alpha = \frac{\alpha_i + \alpha_k}{2} \tag{7}$$

This method is based on the assumption that $F(\alpha)$ does not change for various heating rates and degrees of conversion in the interval $\alpha \in (\alpha_i, \alpha_k)$.

THE DIFFERENTIAL METHODS

One run

Sharp's treatment is very similar to that proposed by Dollimore and coworkers [14,15]. It starts with the rate equation

$$\alpha' = \frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{A\ \mathrm{e}^{-E/RT}}{\beta} f(\alpha) \tag{8}$$

The plot of $\ln \alpha' - \ln f(\alpha)$ against $1/T$ must give a straight line, for the correct $f(\alpha)$, the slope of which $(-E/R)$ gives the activation energy.

Several runs at different heating rates

In this work a new method is proposed which analyses data from several runs at different heating rates.

Starting from the same expression

$$\ln \alpha' - \ln f(\alpha) = \ln A/\beta - E/RT \tag{9}$$

the influence of the temperature and the conversion on the kinetic parameters can be evaluated. Therefore the plots of $\ln \alpha' - \ln f(\alpha)$ vs. $\ln \beta$ using α and α' values for each temperature in the different runs must be straight parallel lines of slope 1 for the correct function $f(\alpha)$. The intercepts of the lines are equal to $\ln A - E/RT$.

The A and E values can be obtained from the least-square fit of the intercept values against $1/T$. Although the use of the intercept as the dependent variable is statistically less precise, the value obtained can be used to indicate the influence of temperature on the values of the activation energy.

The activation energy can be obtained from the plots of $\ln \alpha' - \ln f(\alpha) + \ln \beta$ vs. $1/T$ by using temperature values for the same conversion at the different heating rates.

This technique has been applied to $n = 1$ and $3/2$ functions in order to check the method and its adequacy for distinguishing between the two mathematical equations.

EXPERIMENTAL

2-Ethylpyridinium metatungstate monohydrate was prepared for the first time in our laboratory. To an aqueous solution of Na_2WO_4 (0.2 mol dm^{-3}, pH 5.12), the stoichiometric amount of 2-ethylpyridinium chloride was added, and the mixture was heated (80 °C) and stirred for 2 h. The compound was isolated only after allowing the solution to stand for several days. The salt was identified as $(BH)_5H[H_2W_{12}O_{40}]$ [5]. The experimental techniques, calibration and working conditions have been described in a previous work [5].

RESULTS AND DISCUSSION

The thermogravimetric dehydration reaction

$$(C_5H_4NH\text{-}C_2H_5)_5H[H_2W_{12}O_{40}] \cdot H_2O(s)$$
$$\rightarrow (C_5H_4NH\text{-}C_2H_5)_5H[H_2W_{12}O_{40}](s) + H_2O(g)$$

has been carried out at seven different heating rates: 0.5, 0.7, 1.0, 1.2, 1.5, 1.7 and 2.0 °C min^{-1}. Figure 1 shows the curves obtained at 1.2 °C min^{-1}. The α vs. T plots (see Fig. 2) are sigmoidal for the seven heating rates, with initial induction and acceleration regions followed by a decay period.

Kinetic analysis of the seven curves was first performed using the Satava integral method. The results obtained appear in Table 1 for the six equally probable $[-\ln(1-\alpha)]^n$ functions which present the best least-squares fit in all cases.

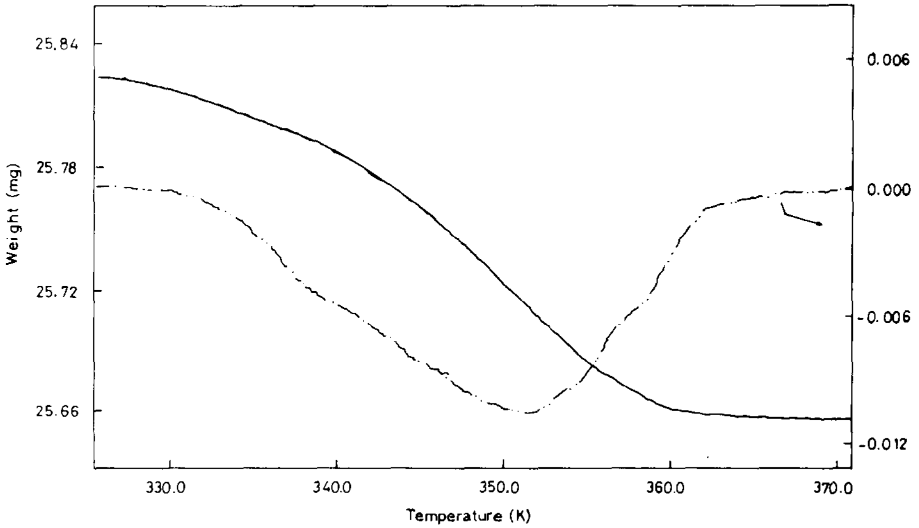

Fig. 1. TG and DTG curves of the dehydration reaction at 1.2 °C min^{-1}.

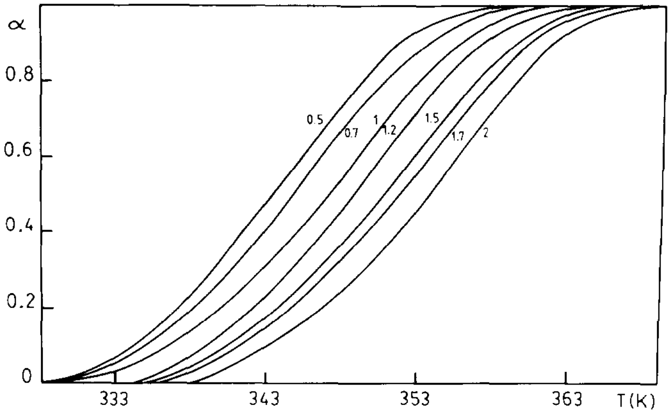

Fig. 2. $\alpha - T$ plots for the different heating rates.

Then the Sharp (S) method was used to analyse the data for the seven heating rates. The results are shown in Table 2. It should be noted that the ambiguity between the two functions related to $n = 1$ and $3/2$ cannot be overcome by using more than one heating rate.

TABLE 1

Satava method. Kinetic parameters E (kJ mol^{-1}), A (s^{-1}) and r for $F(\alpha) = [-\ln(1-\alpha)]^n$

n		Heating rate β (°C min^{-1})						
		0.5	0.7	1.0	1.2	1.5	1.7	2.0
3/2	E	243	255	249	293	240	251	242
	A	9×10^{33}	10^{35}	8×10^{34}	2×10^{41}	2×10^{33}	8×10^{34}	3×10^{33}
	r	0.990	0.989	0.980	0.942	0.981	0.979	0.991
1	E	159	161	163	165	157	164	159
	A	10^{21}	2×10^{21}	7×10^{21}	10^{22}	6×10^{20}	9×10^{21}	10^{21}
	r	0.990	0.989	0.980	0.942	0.981	0.979	0.991
2/3	E	103	104	106	126	102	107	103
	A	3×10^{12}	5×10^{12}	10^{13}	10^{16}	3×10^{12}	2×10^{13}	4×10^{12}
	r	0.990	0.989	0.980	0.942	0.981	0.979	0.991
1/2	E	75	78	77	92	74	78	75
	A	10^{8}	7×10^{8}	5×10^{8}	9×10^{10}	2×10^{8}	8×10^{8}	2×10^{8}
	r	0.990	0.989	0.980	0.942	0.981	0.979	0.991
1/3	E	48	50	49	58	47	49	47
	A	6×10^{3}	5×10^{4}	2×10^{4}	6×10^{5}	10^{4}	3×10^{4}	10^{4}
	r	0.990	0.989	0.980	0.942	0.981	0.979	0.991
1/4	E	33	35	34	42	33	35	33
	A	30	10^{2}	80	10^{3}	70	10^{2}	90
	r	0.990	0.989	0.980	0.942	0.981	0.979	0.991

TABLE 2

Activation energy (kJ mol^{-1}), frequency factor (s^{-1}) and correlation coefficient for the equations $f(\alpha)=\{d[-\ln(1-\alpha)^n]/d\alpha\}^{-1}$ (Sharp method)

n		Heating rate β (°C min^{-1})						
		0.5	0.7	1.0	1.2	1.5	1.7	2.0
3/2	E	242	248	220	237	209	227	235
	A	9×10^{35}	10^{38}	2×10^{32}	4×10^{34}	2×10^{30}	6×10^{32}	6×10^{33}
	r	0.976	0.980	0.994	0.991	0.996	0.994	0.985
1	E	159	142	136	140	126	137	144
	A	2×10^{23}	4×10^{21}	3×10^{19}	10^{20}	7×10^{17}	3×10^{19}	3×10^{20}
	r	0.975	0.987	0.992	0.990	0.998	0.991	0.987
2/3	E	103	73	80	75	71	78	84
	A	6×10^{14}	3×10^{10}	10^{11}	2×10^{10}	4×10^{9}	3×10^{10}	3×10^{11}
	r	0.890	0.923	0.936	0.920	0.956	0.923	0.870
1/2	E	76	37	52	43	44	48	54
	A	3×10^{10}	8×10^{4}	5×10^{6}	2×10^{5}	2×10^{5}	10^{6}	9×10^{6}
	r	0.810	0.656	0.820	0.680	0.850	0.770	0.696
1/3	E	49	3	24	11	16	18	24
	A	10^{6}	5×10^{-3}	2×10^{2}	3	10	30	2×10^{2}
	r	0.620	0.198	0.420	0.009	0.360	0.270	0.270
1/4	E	35	-15	10	-5	3	3	10
	A	8×10^{4}	3×10^{-4}	10	8×10^{-3}	10^{-1}	10^{-1}	10^{-1}
	r	0.450	0.136	0.100	0.164	0.010	0.001	0.005

The results in Tables 1 and 2 for these two mathematical functions show that the activation energy does not depend on the heating rate in the range 0.5–2.0 °C min^{-1}.

The Ozawa method permits us to obtain the activation energy without having in mind any $F(\alpha)$ or $f(\alpha)$ functions. The plots log β vs. $1/T$ show

TABLE 3

Ozawa method. Activation energies (kJ mol^{-1})

α	E	r	Slope
0.2	127	0.987	-6992
0.3	128	0.991	-7052
0.4	130	0.992	-7147
0.5	128	0.993	-7063
0.6	129	0.989	-7075
0.7	129	0.996	-7078
0.8	129	0.998	-7114
0.9	129	0.997	-7100

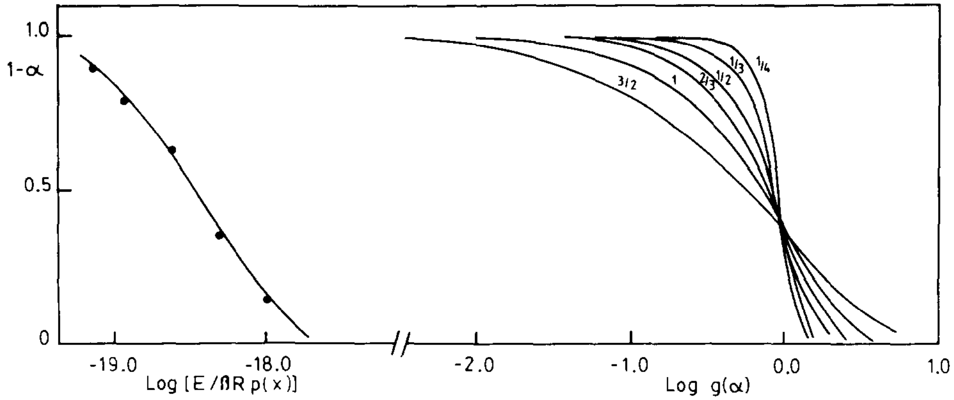

Fig. 3. The theoretical thermogravimetric curves for the kinetic equation, $F(\alpha) = [-\ln(1-\alpha)]^n$ (right) and the experimental curve (left).

good linearity for the chosen values. The results are presented in Table 3. As can be seen these values agree with those obtained for $F(\alpha) = -\ln(1-\alpha)$ from the two rising temperature methods used before.

Using 129 kJ mol^{-1} as the E value, the $1-\alpha$ vs. $\log[E/\beta R\, p(x)]$ curves were plotted and superimposed to fit one of the theoretical curves $1-\alpha$ vs. $\log F(\alpha)$ in Fig. 3. The best fit is for $n = 1$ and the A value obtained from the length of the lateral shift is 1.74×10^{19} s^{-1}.

The method proposed by Urbanovici and Segal was utilized by considering data from curves obtained at 0.5 and 2.0°C min^{-1}. The results are shown in Table 4. As can be seen the E values are very close to those obtained using Ozawa's method.

Finally, the modified Sharp's (MS) technique was applied to $n = 1$ and 3/2 functions in order to check the method and its adequacy for distinguishing between the two mathematical equations. Figure 4 shows the $\ln \alpha' - \ln f(\alpha)$ vs. $\ln \beta$ plots for different temperatures for the function $F(\alpha)$ with $n = 1$. The frequency factors in all cases were 0.99 and the slopes of the straight lines were between 0.935 and 1.056.

TABLE 4

Urbanovici method. Activation energies (kJ mol^{-1})

α	E
0.25	130
0.35	134
0.45	126
0.55	130
0.65	133
0.75	135
0.85	132

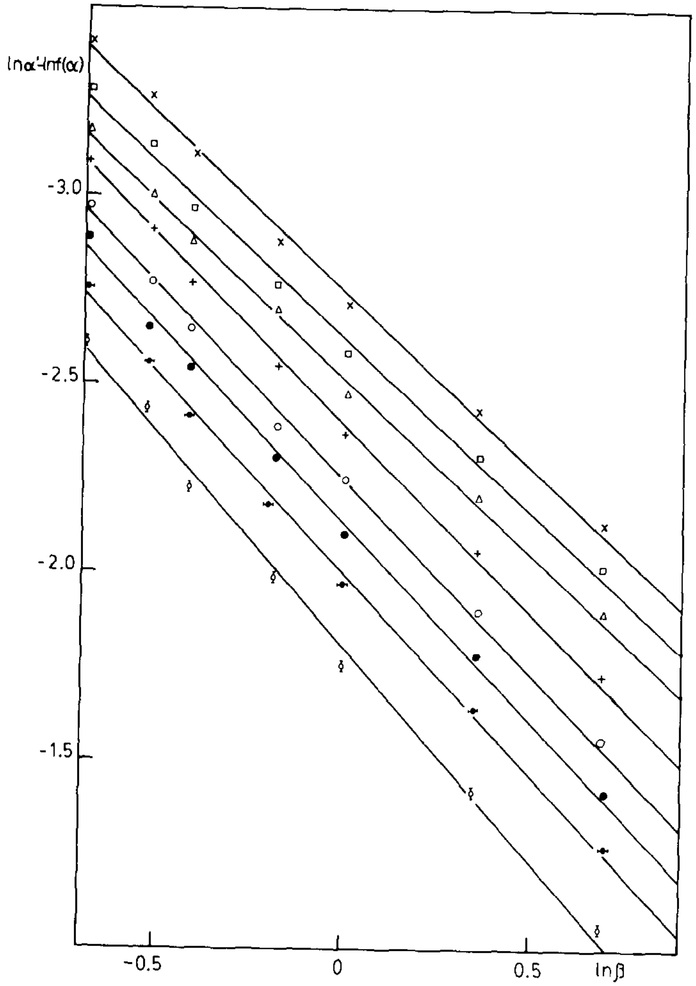

Fig. 4. ln α' − ln $f(\alpha)$ vs. ln β for the function $f(\alpha) = \{d[-\ln(1-\alpha)]/d\alpha\}^{-1}$: × = 343.5 K; □ = 344.5 K; △ = 345.5 K; + = 346.5 K; ○ = 347.5 K; ● = 348.5 K; ⊢●⊣ = 349.5; ⧲ = 350.5 K.

For $f(\alpha) = \{d[-\ln(1-\alpha)]^{3/2}/d\alpha\}^{-1}$ the correlation coefficients were between 0.954 and 0.978 and the slopes were between 1.386 and 1.630.

The E values obtained from the least-square fits of the intercept values (Fig. 4) vs. $1/T$ and of the ln α' − ln $f(\alpha)$ + ln β vs. $1/T$ were 127 kJ mol^{-1} ($r = 0.991$) and 129 kJ mol^{-1} ($r = 0.990$) respectively.

TABLE 5

Activation energy from the different methods

	Satava	Sharp	Ozawa	Urbanovici	MS
E (kJ mol^{-1})	160	140	129	132	127–129

Table 5 shows the E values obtained from the different methods for the expression $F(\alpha) = -\ln(1-\alpha)$.

CONCLUSIONS

The Satava and Sharp methods are not selective enough to determine the most probable mathematical expression for the α functions, even when applied to several TG and DTG curves obtained at different heating rates. On the other hand, these two methods show that the E values and the α functions seem to be independent of the β values.

The Ozawa method and the modification made to the Sharp method permitted us to choose the most probable mathematical obedience and the values obtained for the activation energy were very similar.

The Urbanovici and Segal method shows that the activation energy is independent of the α values. The E values were very similar to those of the above methods, but somewhat different to those obtained using only one TG or DTG curve.

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