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DETERMINATION OF KINETIC PARAMETERS OF INORGANIC METALPORPHYRINS

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Abstract

The thermal properties of four heteropoly complexes α-$K_3H_3[SiW_{11}Ni(H_2O)O_{39}]\cdot 11.5H_2O$ (I), α-$K_3H_2[SiW_{11}Fe(H_2O)O_{39}]\cdot 9H_2O$ (II), α-$[(C_4H_9)_4N]_{3.5}H_{1.5}[SiW_{11}Fe(H_2O)O_{39}]\cdot 4.5H_2O$ (III) and α-$[(C_4H_9)_4N]_{3.5}H_{2.5}[SiW_{11}Cu(H_2O)O_{39}]\cdot 6H_2O$ (IV) were studied by means of TG, DTA and DSC. The activation energy and reaction order of the thermal decomposition reaction of these complexes have been calculated.

Keywords: activation energy, heteropoly tungstosilicate, reaction order, thermal analysis, thermal property

Introduction

The transition metal ion (M^{n+}) in the transition-metal-substituted heteropoly complexes of a porphyrin-like environment is said to have the structure similar to that of M^{n+} in metal porphyrin [1, 2]. In the olefin epoxidation reactions, these complexes have exhibited excellent catalytic activity and selectivity, especially a stronger ability of antioxidation and good thermal stability, because of having the oxidatively stable oxide (O^{2-}) and the d^0W^{VI} ions in the heteropolyanion framework. Furthermore, these complexes are more stable and have a longer catalytic life than metalporphyrin in the presence of olefin substrates. As a results, they are called inorganic metalporphyrin.

Recently the study about these complexes has attracted a lot of attention [1–3], but the reports on their thermal properties and kinetic parameters are rare. This paper gives the

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results of studies on the thermal properties of α-$K_3H_3[SiW_{11}Ni(H_2O)O_{39}]\cdot 11.5H_2O$, α-$K_3H_2[SiW_{11}Fe(H_2O)O_{39}]\cdot 9H_2O$, α-$[(C_4H_9)_4N]_{3.5}H_{1.5}[SiW_{11}Fe(H_2O)O_{39}]\cdot 4.5H_2O$ and α-$[(C_4H_9)_4N]_{3.5}H_{2.5}[SiW_{11}Cu(H_2O)O_{39}]\cdot 6H_2O$ by means of TG, DTA, DSC, temperature IR and X-ray diffraction. The activation energies and reaction orders of their thermal decomposition reactions were calculated from TG and DSC thermal analyses curves.

Experimental

Syntheses

Stereospecific synthesis was used in the preparation of the complexes. That is, pure lacunary heteropoly complexes (inorganic porphyrin) were first prepared and then used as ligands to react with transition metal ions. According to this procedure, the complexes were isolated with higher purity and yield, comparing with the degradation used in the reference [4].

Inorganic porphyrin ligand α-$K_8SiW_{11}O_{39}\cdot 13H_2O$ (abbreviated as α-SiW_{11}) was prepared with the procedure described in the reference [5].

α-$K_3H_3[SiW_{11}Ni(H_2O)O_{39}]\cdot 11.5H_2O$ (I) (abbreviated as α-$SiW_{11}NiK$). Into 30 ml aqueous solution of 6.4 g (2 mmol) α-SiW_{11} heated at 40°C, was added dropwise 4 ml 0.5 $mol\cdot l^{-1}$ (2 mmol) $NiSO_4$ solution with stirring. The solution was adjusted to *pH* 5.7 and maintained for 10 min, and then filtered. 2 g solid KCl was added into the filtrate. The resulting solution was stirred for ten minutes and kept at 5°C. Green crystals were collected and recrystallized from warm water.

α-$K_3H_2\{SiW_{11}Fe(H_2O)O_{39}\}\cdot 9H_2O$ (II) (abbreviated as α-$SiW_{11}FeK$). With the same procedure as that in preparation of (I), $Fe(NO_3)_3$ was used instead of $NiSO_4$. Yellow crystals were obtained at *pH* 5.06.

α-$[(C_4H_9)_4N]_{3.5}H_{1.5}[SiW_{11}Fe(H_2O)O_{39}]\cdot 4.5H_2O$ (III) (abbreviated as α-$SiW_{11}FeTBA$) Into 30 ml solution of 6.4 g (2 mmol) α-SiW_{11}, 4 ml 0.5 $mol\cdot l^{-1}$ $Fe(NO_3)_3$ (2 mmol) was added dropwise on a 40°C bath, $pH=5.06$. 10 min later, TBABr saturated solution was added. The resulting yellow precipitates were filtered and washed with water, dryed in air. The crude product was recrystallized in CH_3CN.

α-$[(C_4H_9)_4N]_{3.5}H_{2.5}[SiW_{11}Cu(H_2O)O_{39}]\cdot 6H_2O$ (IV) (abbreviated as α-$SiW_{11}CuTBA$). Following the synthetic preparation of III, $CuSO_4$ was used instead of $Fe(NO_3)_3$. Blue precipitates were separated at *pH* 5.28 and recrystallized from CH_3CN.

The above complexes were characterized with IR. UV-Vis spectrography and polarography. α-SiW11NiK. IR(KBr):998, 956, 903, 790, 709, 525 cm^{-1}; electronic spectra: 210, 251, 411, 698 nm; polarographic $E_{1/2}$ (*pH* 4.7, 1 $mol\cdot l^{-1}$ HAc-NaAc buffer, droping mercury and calomel electrodes): −0.752,

–0.948 V; crystallographic data: orthogonal system with space group P nn2, a=14.203 (8), b=14.214 (6), c=12.460 (3) Å, V=2515.4 $Å^3$, Z=2, Dc=4.03 g·cm^{-1}, α-SiW_{11} FeK IR: 909, 793, 717, 668, 532 cm^{-1}; ULV-Vis: 211.0, 257 nm; $E_{1/2}$: –0.216, –0.772, –0.912V. α-SiW_{11}Cu-TBA IR; 960, 911, 801, 743 cm^{-1} UV-Vis: 199.0, 254, 841 nm; $E_{1/2}$: –0.184, –0.606, –0.758 V. These spectra are all of the characteristic Keggin structure, showing that these anions have the Keggin structure. The measurements of TG, DTA and DSC curves were carried out at scanning rate 10 deg·min^{-1} and 20 deg·min^{-1} and under the flow of N_2 20 ml/min in Pt crucible.

Instruments and analytical procedure

DU-8D spectrophotometer (Backman), Alpha Centaurt FT-IR spectrograph, BAS 100A electrochemical analyzer, PE 3030 atomic absorption spectrophotometer, TGA-7, DTA-1700, DSC-7 and GW 386 computer (Perkin-Elmer).

The content of potassium was determined with atomic absorption spectrophotometry, and contents of other elements, with ICP emission spectroscopy. Thermal analyses gave the contents of TBA group and H_2O. As seen in Table 1, elemental analysis results are consistent with the calculated values.

Results and discussion

Thermal property of the complexes

The TG, DTA and DSC data listed in Table 2 and curves drawed in Figs 1–3 of the complexes indicate that two potassium salts were very stable. They lose water molecules in two stages before 300°C. The weight of α-SiW_{11}NiK decreased 4.97% in the first stage of 26–94.6°C, or released 8.5 crystalline water molecules per mole heteropoly complex. In the second stage between 94.6–291.8°C, 3.02% weight loss consisted of two steps: fast dehydration of 3 crystalline water molecules and slow dehydration of 2.5 structural water molecules, which included the coordination water molecules ligating to unshared oxygen atom in the octahedron of substituted transition metal ion and the water molecules formed by the protons as counterions during the thermal decomposition. In its DTA curve there was an overlapped endothermic peak caused by the two-stage dehydrations with its peak temperature at 124.6°C. SiW_{11}FeK loses 5.28% of its mass 9 crystalline water molecules when heated till 150°C, and in the range of 152.6–243°C loses 1.2% of its mass corresponding to two structural water molecules. An overlapped endothermal peak in the range of 30–290°C with peak temperature 111.5 °C in the SiW_{11} FeK DTA curve was caused by the thermal effect of the two-stage dehydration. The endothermic

Table 1 Elemental analytic data of the complexes (%)*

Complex	Content			
	K/TBA	M*	W	H_2O
α-$K_3H_3[SiW_{11}Ni(H_2O)O_{39}]\cdot 11.5H_2O$	3.39(3.80)	1.92(1.91)	65.20(65.70)	7.98(8.19)
α-$K_3H_2[SiW_{11}Fe(H_2O)O_{39}]\cdot 9H_2O$	3.80(3.86)	1.86(1.85)	67.56(66.76)	6.48(6.53)
α-$(TBA)_{3.5}H_{1.5}[SiW_{11}Fe(H_2O)O_{39}]\cdot 4.5H_2O$	23.14(23.03)	1.53(1.52)	54.80(55.00)	3.28(3.59)
α-$(TBA)_{3.5}H_{2.5}[SiW_{11}Cu(H_2O)O_{39}]\cdot 6H_2O$	22.81(22.82)	1.79(1.72)	54.80(54.46)	3.91(3.99)

*M stands for Ni^{2+}, Fe^{3+}, Cu^{2+}; calculation values in parentheses

Table 2 Thermal property of inorganic metalporphyrin

Compound		$SiW_{11}Ni$-K(I)	$SiW_{11}Fe$-K(II)	$SiW_{11}Fe$-TBA(III)	$SiW_{11}Cu$-TBA(IV)
	temperature/°C	26–94.61	25.9–152.6	122.6–243.3	30.95–178.55
	weight loss/%	4.97	5.28	2.28	3.11
I	component	$8.5H_2O$	$9H_2O$	$4.5H_2O$	$6H_2O$
	temperature of endothermal peak/°C	124.6	111.5		
	temperature/°C	94.61–291.8	152.6–243.6	243.3–361.96	182.36–336.6
	weight loss/%	3.02	1.2	17.13	11.72
II	component	$5.5H_2O$	$2H_2O$	$41.6CO_2$ $93.6H_2O$	$28.8CO_2$ $64.8H_2O$
	amount of heat/ $kJ\cdot mol^{-1}$			79.84	
	temperature/°C			361.96–478.5	336.6–457.56
	weight loss/%			6.00	11.16
III	component			$14.4CO_2$ $32.4H_2O$	$27.2CO_2$ $61.2H_2O$
	amount of heat/ $kJ\cdot mol^{-1}$			635.08	10925.87
	temperature/°C			478.5–500	457.56–500
	weight loss/%			1.04	1.17
IV	component			$1.75H_2O$	$2.25H_2O$
	temperature/°C			500–660	500–660
	weight loss/%			5.9	6.88
	component			$1.75N_2$	$1.75N_2$
	temperature of endothermal peak/°C	731.4, 785.5	785.1		

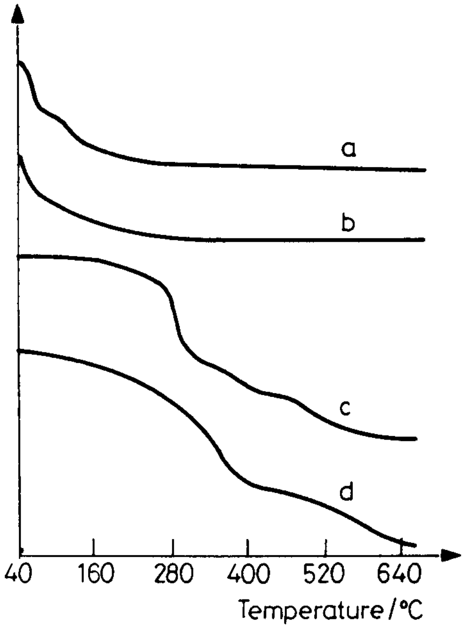

Fig. 1 TG curve of the compounds. a) $SiW_{11}NiK$; b) $SiW_{11}FeK$; c) $SiW_{11}FeTBA$

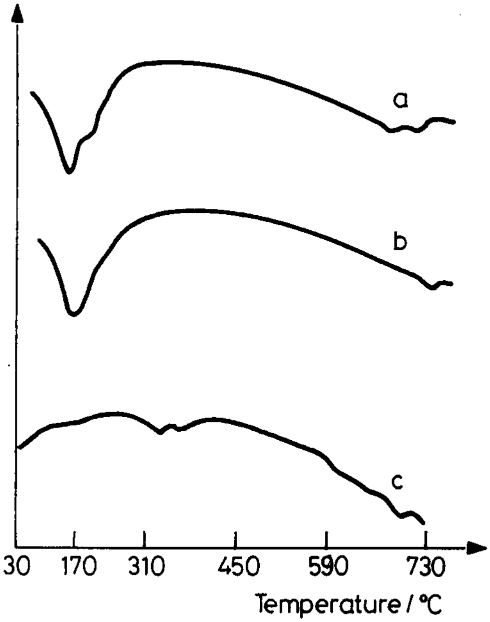

Fig. 2 DTA curve of the compounds. a) $SiW_{11}NiK$; b) $SiW_{11}FeK$; c) $SiW_{11}FeTBA$

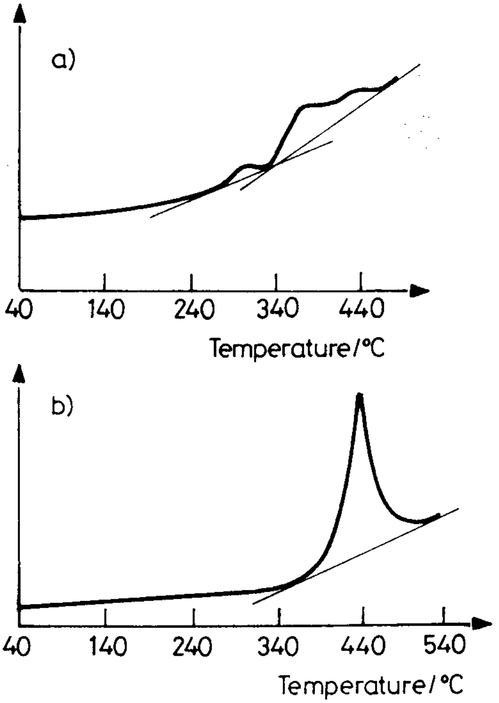

Fig. 3 DSC curve of the compounds. a) $SiW_{11}FeTBA$; b) $SiW_{11}CuTBA$

peaks in 700–800°C on the DTA curves of two potassium salts might be a result due to crystalline phase transformation.

The tetrabutylammonium salts of inorganic metalporphyrin exhibited more complicate thermal properties. For example, α-$SiW_{11}FeTBA$ underwent four-step weight losses. From its TG curve, the first step occurs in the range of 122.6–243.3°C with 2.28% mass loss, corresponding to 4.5 crystalline water molecules. The weight loss from 243 to 478.5°C includes two-stage redox reactions [6]:

$$2Bu_4N^+ + O_2 \rightarrow H_2O + 2Bu_3N + 2C_4H_8$$

In the first stage from 243 to 362°C, 2.6TBA ions have reacted with 17.13% mass loss, that is, one mole of heteropoly complex released 2.6 moles Bu_3N, 2.6 moles C_4H_8 and 1.3 moles H_2O; 6.0% mass loss of the second stage from 362.0 to 478.5°C corresponds to the loss of 0.9 moles Bu_3N, 0.9 moles C_4H_8 and 0.45 moles H_2O accompanying with the transformation of TBA salt to NH_4^+ salt and heteropoly acid (Fig. 4b) (which were of isomorphism with $(NH_4)_3PMo_{12}O_{40}\cdot 4H_2O$ and $H_3PW_{12}O_{40}\cdot 21H_2O$). Finally the complex slowly loses 1.04% weight, $1.75H_2O$. Between 500–660°C the ammonium salt decomposes, releasing 1.75 moles N_2 molecules with 5.9% mass reduction.

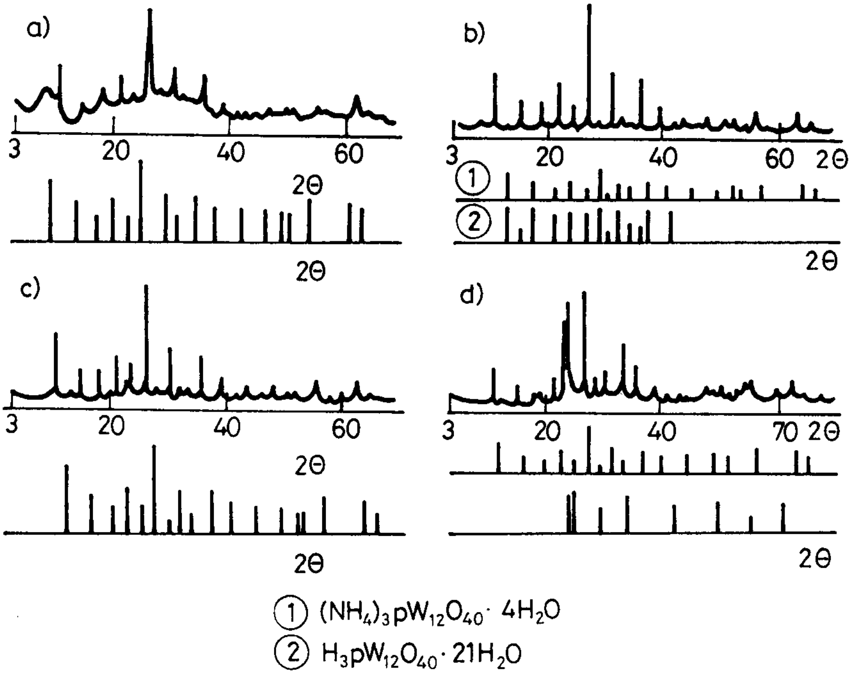

Fig. 4 X-ray diffraction spectra of thermal decomposition products at different temperatures. a) $SiW_{11}CuTBA$ (330°C); b) $SiW_{11}FeTBA$ (360°C); c) $SiW_{11}FeTBA$ (500°C); d) $SiW_{11}CuTBA$ (500°C)

The solubility tests (Tables 3 and 4) and the temperature infrared spectra (Figs 5 and 6) of the thermal decomposition products in air show that α-$SiW_{11}FeTBA$, being yellow, dissolved in CH_3CN and having a high intensity of C–H flexural vibration bands in 1380 and 1480 cm^{-1}, existed in the from of TBA salt below 250°C; the product at 360–479°C did not dissolve either in CH_3CN or in H_2O and the C–H flexural vibration band nearly dissappeared, implying that the TBA salt transformed into NH_4^+ salt. The temperature infrared spectra (Fig. 5, c) consist of the characteristic bands of Keggin anionic framework but the intensity of the bands decreased. The X-ray diffraction spectra of the product heated at 500°C (Fig. 4, c) was very similar to that of $(NH_4)_3PW_{12}O_{40}\cdot 4H_2O$ and the product was considered to be in the form of NH_4^+ salt. $SiW_{11}CuTBA$ underwent a similar procedure as $SiW_{11}FeTBA$, except that α-$SiW_{11}CuTBA$ decomposed partially into WO_3 (Fig. 4, d) at 500°C, showing that its thermal stability was lower than that of α-SiW_{11}Fe-TBA. From Fig. 5, d and Fig. 6, d, it can be seen that anionic framework of the two salts were completely destroyed and transformed into the corresponding oxides.

Table 3 Physical properties of heated α-$SiW_{11}FeTBA$

Temperature/°C	25	343	360	470	500	600
Color	bright yellow	soil yellow	black	brown yellow	brown red	soil yellow
Solubility	CH_3CN	CH_3CN	–	–	–	–

Table 4 Physical properties of heated α-$SiW_{11}CuTBA$

Temperature/°C	25	170	330	450	500	660
Color	blue	green	black	soil yellow	yellow green	bright yellow
Solubility	CH_3CN	CH_3CN	–	–	–	–

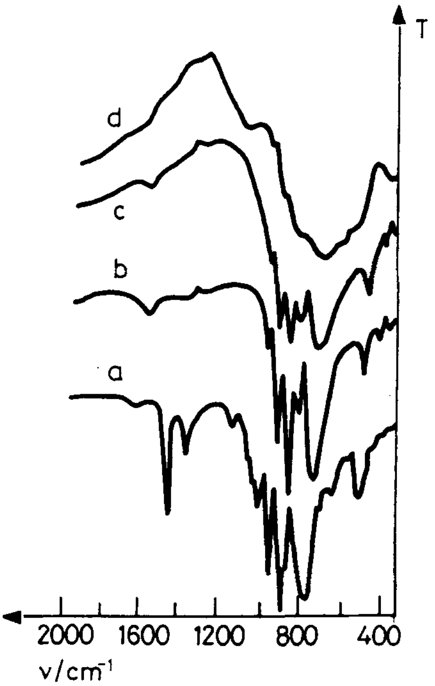

Fig. 5 Temperature IR spectra of α-SiW_{11}FeTBA. a) 240°C; b) 360°C c) 470°C; d) 650°C

Two endothermal peaks in DSC curves of TBA salts appeared in the decomposition of tetrabutylammonium ions. From the curve of α-SiW_{11}FeTBA, peak temperatures (T) and endothermal amount (Q) were obtained: T_1=310.09°C, Q_1=79.84 kJ/mol at 263.59–331.45°C, T_2=374.42°C, Q_2=635.08 kJ/mol at 331.45–458.74°C. For α-SiW_{11} CuTBA, the peak temperature of a continuous mass loss occurred at T=427.72°C, Q=10925.87 kJ/mol at 341.22–495.11°C.

Reaction order and activation energy

Among many thermal analysis methods, TG and DSC were chosen to calculate the activation energy (E) and reaction order (n) of the main thermal decomposition reaction of the inorganic metalporphyrin. The calculation formulas are as follow:

1. Freeman-Carroll integral method [7]

$$\Delta\log(\mathrm{d}W / \mathrm{d}t) \,/\, \Delta\log W_\gamma = [-E \,/\, (2.303\mathrm{R})]\cdot\Delta(1 \,/\, T) \,/\, \Delta\log W_\gamma + n \qquad (1)$$

From the plot of $(\Delta\log(\mathrm{d}W/\mathrm{d}t)/\Delta\log W$ *vs.* $\Delta(1/T)/\Delta\log W$ a straight line is obtained. The slope and the intercept of the line are $-E/(2.303R)$ and n respectively.

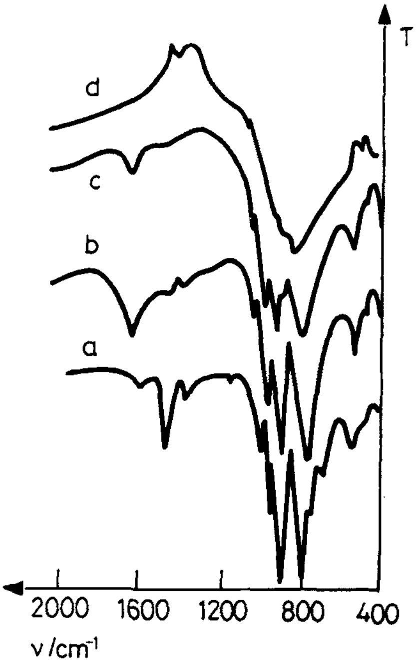

Fig. 6 Temperature IR spectra of α-$SiW_{11}CuTBA$. a) 170°C; b) 330°C; c) 450°C; d) 660°C

2. Coats and Redfern differential method [7]

When $n = 1$,

$$\log[-\ln(1-\alpha)/T^2] = [\log AR/\Phi E](1-2RT/E) - [E/2.303]\cdot 1/T \quad (2)$$

From the plot of $\log[-\ln(1-\alpha)/T^2]$ *vs.* $1/T$ a straight line is obtained. Its slope is $-E/(2.303R)$.

When $n \neq 1$,

$$\log\{1-(1-\alpha)^{1-n}/[(1-n)T^2]\} = [\log AR/\Phi E][1-2RT/E] - -[E/(2.303R)]\cdot 1/T \quad (3)$$

From the plot of $\log\{1-(1-\alpha)^{1-n}\}/(1-n)T^2]$ *vs.* $1/T$ a straight line is obtained. It's slope is $-E/(2.303R)$

3. Kissinger method [8]

This method is called 'maximum rate method'. The DSC peak temperatures of the same reaction are recorded with two different heating rates.

Table 5 Reaction order and activation energy ($kJ \cdot mol^{-1}$) of thermal decomposition of the inorganic metalporphyrin

Compound		$SiW_{11}Ni$-K (I)	$SiW_{11}Fe$-K (II)	SiW11Fe-TBA (III)	SiW11Ca-TBA (IV)
Range of temperature	/°C	30–90	30–150	250–360	190–330
Integration	*n*	1	0.8	1	0.9
	E	43.56	12.28	136.06	57.78
Differentiation	*n*	1	0.8	1.27	1.02
	E	35.58	13.63	98.90	51.33
Range of temperature	/°C	100–300	160–300	370–470	350–450
Integration	*n*	1	0.7	0.9	0.8
	E	40.55	48.66	133.68	83.56
Differentiation	*n*	1.16		1	0.6
	E	34.81		110.05	54.72
Range of temperature	/°C			263.6–331.5	
Kissinger method	*n*			1.19	
	E			122.14	
Maycook method	*n*				
	E			108.64	
Range of temperature	/°C			331.45–458.7	341–495
Kissinger method	*n*				0.9
	E			112.99	104.79
Maycook method	*n*				
	E			114.48	81.01

The following relationship exists between activation energy and the heating rate:

$$E / R = [\ln\Phi_1 / T^2_{m_1}) - \ln(\Phi_2 - T^2_{m_2}) \quad (4)$$

4. Maycook method [8]

The peak heights d_1 and d_2 correspond to temperatures T_1 and T_2, respectively.

$$- E = 4.575\log(d_1 / d_2) / (1 / T_1 - 1 / T_2) \quad (5)$$

The calculation results obtained by least-square linear regression are listed in Table 5, based on TG curves with differential and integral method.

Comparison between integration data and differentiation data in Table 5 indicates that the integration is a more precise and reliable method than differentiation, which gave dispersing and less accurate data caused of drawing technique. The simpler calculation method by DSC gave basically consistent results with those of integration and differentiation methods of TG.

Small activation energies of the dehydration reaction of potassium salts indicate a rather fast dehydration of crystal water. For α-SiW_{11}Fe-K, the dehydration may be completed in a twinkle. In the other hand, the activation energy of α-SiW_{11}CuTBA is smaller than that of α-SiW_{11}FeTBA, showing that the redox reaction velocity of the former is many times faster than that of the latter. In fact, α-SiW_{11}Cu-TBA decomposed partially into WO_3 at 500°C, which is an evidence that α-SiW_{11}Cu-TBA has a small E value for thermal decomposition.

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Zusammenfassung — Mittels TG, DTA und DSC wurden die thermischen Eigenschaften der vier heteropolaren Komplexe α-$K_3H_3[SiW_{11}Ni(H_2O)O_{39}]\cdot 11.5H_2O$ (I), α-$K_3H_2[SiW_{11}Fe(H_2O)O_{39}]\cdot 9H_2O$ (II), α-$[(C_4H_9)_4N]_{3.5}H_{1,5}[SiW_{11}Fe(H_2O)O_{39}]\cdot 4.5H_2O$ (III) und α-$[(C_4H_9)_4N]_{3.5}H_{2,5}[SiW_{11}Cu(H_2O)O_{39}]\cdot 6H_2O$ (IV) untersucht. Die Aktivierungsenergie und Reaktionsordnung der thermischen Zersetzungsreaktion dieser Komplexe wurde berechnet.