

Evaluation and Application of Isokinetic Relationships: The Thermal Decomposition of Solids under Nonisothermal Conditions

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Two approaches (discriminating (1) and isoconversional (2)) to the evaluation of Arrhenius parameters for the thermal decomposition of solids under nonisothermal conditions are investigated and applied to both modeled and experimental data: Approach (1) allows only for the detection of an isokinetic relationship (IKR) but not for unambiguously estimating its parameters and approach (2) makes it possible not only to detect an IKR but also to determine its parameters. These may in turn be used to obtain information about the actual reaction pathway of the thermally induced process. The thermal decomposition of tetranuclear Cu(II) complexes with various ligands is used as an experimental example.

INTRODUCTION

An isokinetic relationship (IKR) refers to a common point of intersection of Arrhenius lines (i.e., $\ln k$ versus T^{-1}) for a series of reactions and thus define an isokinetic rate constant k_{iso} at an isokinetic temperature (T_{iso}). Besides that, an IKR manifests itself as an interrelationship of the Arrhenius parameters of the reactions forming a series. It has been shown that a properly established IKR can be used as an efficient tool for understanding reaction mechanisms. This has been successfully applied to many reaction series, both in the gas and condensed (homo- and heterogeneous) phases.^{1,2} The existence of an IKR implies that only one reaction mechanism is followed by all members of the reaction series,^{3,4} i.e., all reactions have analogous reaction profiles. When reactions of an apparently similar series do not meet the IKR condition (or more than one IKR occurs), differing reaction mechanisms can be concluded.^{1,2}

The occurrence of an IKR has been explained theoretically.^{1,2} An important point for this is the existence of a resonant vibrational energy exchange between reactants and their molecular environment. The latter is in any case acting as a heat-bath providing the energy necessary for the reactants to overcome the potential barrier. One of the results from this is that, when an IKR occurs, the resonance vibrational frequency ν_{iso} is related to the isokinetic temperature by (1)

$$\nu_{\text{iso}} = k_{\text{B}} T_{\text{iso}} / h \quad (1)$$

(where k_{B} and h are Boltzmann's and Planck's constants, respectively). It has been shown for many isothermal reactions performed in solution or on catalyst surfaces that this frequency is to be found in the far IR spectra of the investigated reaction systems.^{1,2} In turn this means that a reliable evaluation of the isokinetic temperature helps to elucidate the reaction pathway, for example, the transformation of a specific reaction group.

This raises considerable interest when an IKR for reactions in the solid state^{5,6} can be established. However, several specific problems arise when the widespread technique of

thermal analysis measurements at nonisothermal conditions is used. The main problem with this is the ambiguity arising when computing the Arrhenius parameters of the nonisothermal decomposition of solids.

The aim of this work is the search for a method for the reliable computation of IKRs occurring when the nonisothermal decomposition of solids is studied. To achieve this aim we shall consider two different approaches (discriminating and isoconversional) to evaluating Arrhenius parameters from the point of view of detecting IKRs and computing their parameters. The problems associated with the above approaches will also be discussed.

ARTIFICIAL OR FALSE IKRS

In this section an artificial IKR being characteristic of nonisothermal kinetics will be discussed. Also the meaning of the isokinetic temperature found from an artificial IKR will be disclosed.

The general rate eq 2

$$dw/dt = k(T)f(w) \quad (2)$$

(where w is the extent of conversion, t is time, T is the temperature, $k(T)$ is the rate constant, and $f(w)$ is the reaction model) is usually used to describe the kinetics of the thermal decomposition of solids under both isothermal and nonisothermal conditions.^{7,8} For a nonisothermal condition, e.g., when the temperature varies in time with a constant heating rate, $q = dT/dt$, eq 2 takes the form of (3)

$$q dw/dT = k(T)f(w) \quad (3)$$

Both eqs 2 and 3 are based on the assumption that the temperature-dependent, $k(T)$, and conversion-dependent, $f(w)$, contributions to the rate of the process can be separated. The temperature dependence of the process rate is given by the Arrhenius eq 4

$$k(T) = A \exp(-E/RT) \quad (4)$$

(where E (the activation energy) and A (the pre-exponential factor) are the Arrhenius parameters). The change in the process rate with the extent of conversion is described by a set of alternate $f(w)$ models (Table 1). These models are

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Table 1. Set of Alternate Reaction Models Usually Applied to Describe the Thermal Decomposition of Solids^a

N	reaction model	$f(w)$	$g(w)$
1	power law	$4w^{3/4}$	$w^{1/4}$
2	power law	$3w^{2/3}$	$w^{1/3}$
3	power law	$2w^{1/2}$	$w^{1/2}$
4	power law	$2/3w^{-1/2}$	$w^{3/2}$
5	one-dimensional diffusion	$1/2w^{-1}$	w^2
6	first-order (Mampel)	$1 - w$	$-\ln(1 - w)$
7	Avrami-Erofeev	$4(1 - w)[- \ln(1 - w)]^{3/4}$	$[- \ln(1 - w)]^{1/4}$
8	Avrami-Erofeev	$3(1 - w)[- \ln(1 - w)]^{2/3}$	$[- \ln(1 - w)]^{1/3}$
9	Avrami-Erofeev	$2(1 - w)[- \ln(1 - w)]^{1/2}$	$[- \ln(1 - w)]^{1/2}$
10	three-dimensional diffusion	$3/2(1 - w)^{2/3}(1 - (1 - w)^{1/3})^{-1}$	$[1 - (1 - w)^{1/3}]^2$
11	contracting sphere	$3(1 - w)^{2/3}$	$1 - (1 - w)^{1/3}$
12	contracting cylinder	$2(1 - w)^{1/2}$	$1 - (1 - w)^{1/2}$

^a $f(w)$ and $g(w)$ are differential and integral forms of a model, respectively.

Table 2. Arrhenius Parameters Used for Modeling Data

N	$E(\text{kJ mol}^{-1})$	$A(\text{min}^{-1})$
1	83.6	10^{12}
2	125.4	10^{15}
3	167.2	10^{18}
4	209.0	10^{21}

based on various theoretical ideas⁸ concerning the mechanism of the thermal decomposition.

To determine the Arrhenius parameters one should separate the contributions of $k(T)$ and $f(w)$ to the rate of a process. Normally this is done by the selection (discrimination) of a reaction model which best fits the experimental kinetic curves, i.e., dw/dt (or w) versus t . In isothermal kinetics the separation of the conversion and temperature components is realized by the regime of performing the experiment ($k(T) = \text{const}$ at $T = \text{const}$). The kinetic curve obtained under these conditions contains only information about the conversion component of the process rate, $f(w)$. This fact provides potential legitimacy of the use of the discriminating approach for isothermal kinetics.

In nonisothermal kinetics the temperature varies during the experiment and contributes continuously to the reaction rate. Thus the kinetic curve under nonisothermal conditions contains information about the temperature and conversion components in unseparated form. Consequently, there is no

real basis for the use of the discriminating approach in nonisothermal kinetics. However, most of the commonly accepted computation methods^{7,8} are based on it. Such a discrepancy reveals itself as an ambiguity of kinetic description which means that the rate of a process can be satisfactorily described with practically any model $f_j(w)$ and fitting $k_j(t)$ which compensates the error of the reaction model choice.

$$q \, dw/dT = k_j(T)f_j(w) \quad (5)$$

A quantitative relation between the errors of choosing $f(w)$ and the accordingly computed activation energy can be found in ref 9.

An implication of the $f_j(w) - k_j(T)$ compensation is a linear correlation (6)

$$\ln A_j = a + bE_j \quad (6)$$

(where subscript j refers to one of the possible models $f_j(w)$ assumed to describe the process). Equation 6 is often referred to as a "compensation effect", and is in fact an artificial IKR. The parameters of (6) are $a = \ln k_{\text{iso}}$ (an artificial isokinetic rate constant) and $b = (RT_{\text{iso}})^{-1}$ (R is the gas constant and T_{iso} an artificial isokinetic temperature). In terms of the Arrhenius lines this effect implies the existence of a common point of intersection with coordinates $(T_{\text{iso}}^{-1}, \ln k_{\text{iso}})$. Some mathematical transformations make it possible to find a rational explanation for this effect. From (5) and (6) the expression (7)

$$\ln k_{\text{iso}} = \ln \{ [f_j(w)]^{-1} q \, dw/dT \} \quad (7)$$

can be deduced. This equation allows T_{iso} to be explained as a temperature at which the right hand side of (7) is independent of the particular form of $f_j(w)$. Since both q and dw/dT do not depend on the form of the reaction model we can define T_{iso} as a temperature corresponding to the extent of conversion for which $\ln[f_j(w)]$ does not depend on j . Taking into account that (6) is a correlation we cannot expect strict independence. Thus the condition of minima

Table 3. Isokinetic Temperatures Estimated by Arrhenius Parameters Computed for a Series of Four First-Order Reactions (Arrhenius Parameters Are Given in Table 2) with $T_{\text{iso}} = 729 \text{ K}$ ^a

N	$j =$								T_{iso} (K)	S^2
	1		2		3		4			
	E (kJ mol ⁻¹)	$\ln A$ (min ⁻¹)	E (kJ mol ⁻¹)	$\ln A$ (min ⁻¹)	E (kJ mol ⁻¹)	$\ln A$ (min ⁻¹)	E (kJ mol ⁻¹)	$\ln A$ (min ⁻¹)		
1	12.4	2.51	20.1	4.14	29.0	5.57	37.6	7.13	654 ± 1	0.0017 ^b
2	18.4	4.58	30.2	6.86	41.2	8.79	52.9	10.86	681 ± 6	0.0058 ^b
3	30.4	8.77	48.7	12.21	65.7	15.11	83.5	18.19	677 ± 2	0.0123
4	102.7	32.91	159.8	43.18	212.4	51.79	267.0	60.92	700 ± 6	0.0929
5	138.8	44.74	215.4	58.42	285.8	69.88	358.7	82.02	702 ± 3	0.1558
6	83.1	27.42	126.2	34.75	168.3	41.70	210.4	48.68	721 ± 7	0.0057 ^b
7	16.5	4.16	26.4	5.96	36.3	7.71	46.4	9.49	733 ± 6	0.0004 ^b
8	23.9	6.83	37.5	9.26	51.0	11.60	64.6	13.97	736 ± 6	0.0006 ^b
9	38.7	12.08	59.7	15.75	80.3	19.25	101.0	22.77	741 ± 8	0.0015 ^b
10	157.6	49.78	240.9	64.19	319.7	77.00	399.7	90.20	734 ± 4	0.0816
11	76.0	23.55	117.0	30.77	156.0	37.20	195.7	43.84	738 ± 5	0.0236
12	73.1	22.84	113.2	29.98	151.0	36.21	189.6	42.69	746 ± 7	0.0306

^a S^2 is a residual sum of squares for the regression line $\ln A_j = a + bE_j$. ^b A residual sum of squares satisfies a condition of $S^2 \leq F \cdot S_{\text{min}}^2$, where F is Fischer's criterion of a 95% confidence level, S_{min}^2 is a minimal value of all S^2 values.

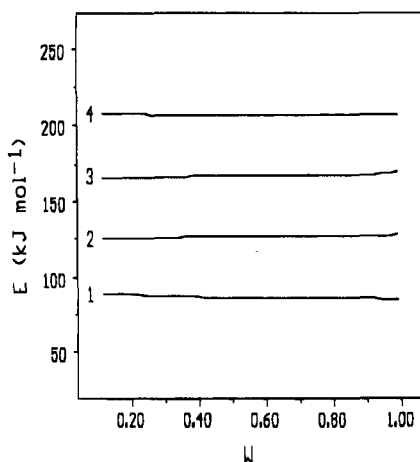


Figure 1. Dependencies of the activation energy upon conversion computed by the isoconversional method (eq 16) for four first-order reactions models. The Arrhenius parameters used to model these reactions are given in Table 3 under the corresponding numbers.

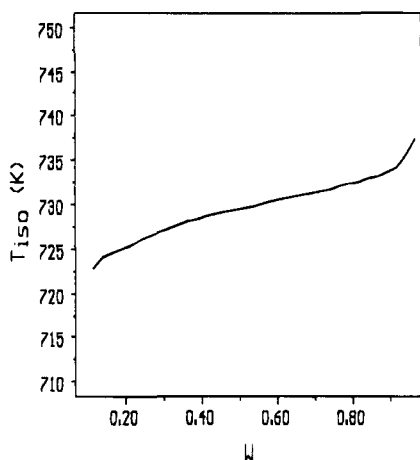


Figure 2. Dependence of the isokinetic temperature on the extent of conversion computed by the conversion dependencies of the activation energy presented in Figure 1.

(8) instead of equality to zero

$$\min_{w \in [0,1]} \sum_i \sum_j (\ln[f_i(w)] - \ln[f_j(w)])^2 \quad (8)$$

should be applied to find the considered amount of conversion. This value depends on the set of the reaction models used. Specifically for the set of $f(w)$ models presented in Table 1 it results as 0.515. It follows that the temperature corresponding to this conversion, $T_{0.515}$, is an estimate for T_{iso} .

To examine this, model data dw/dT versus T were generated. The data for a given heating rate (q) were modeled by the integral form of (3) namely (9)

$$g(w) = (A/q) \int_0^T \exp(-E/RT) dT \quad (9)$$

where $g(w) = \int_0^w [f(w)]^{-1} dw$ is the integral form of a respective reaction model given in Table 1. The integral over temperature is here replaced applying the Senum–Yang approximation.¹⁰ A dependence of the conversion on temperature obtained after an inverse transformation of $g(w)$

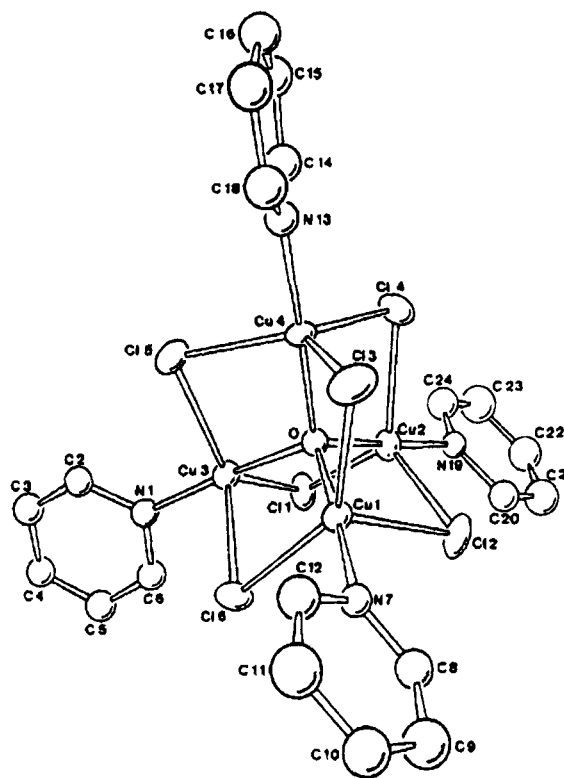


Figure 3. General structure of $\text{Cu}_4\text{OCl}_6\text{L}_4$ complexes (L = piperidine).

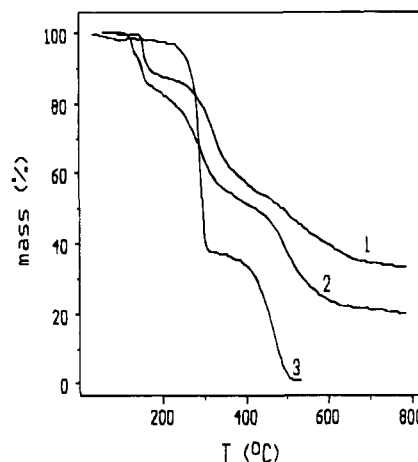


Figure 4. TG curves for the thermal decomposition of the tetranuclear complexes $\text{Cu}_4\text{OCl}_6\text{L}_4$ with different ligands (1, piperidine; 2, morpholine; 3, triphenylphosphine oxide). Heating rate is 5 K/min.

was then substituted in (10)

$$dw/dT = (A/q) \exp(-E/RT) f(w) \quad (10)$$

Two reaction models (N 1 and 12 from Table 1) were used to model data at the heating rate 8, 12, and 16 K/min. The values of Arrhenius parameters used for modeling are presented in Table 2.

Arrhenius parameters were computed by (11)

$$\ln[dw/dT q f_j(w)^{-1}] = \ln A_j - E_j/RT \quad (11)$$

varying $f_j(w)$ models (Table 1). The isokinetic temperature was found from (6) as $T_{iso} = (Rb)^{-1}$. A confidence interval for it was estimated through the confidence interval for the b parameter as in (12)

$$|\delta T_{iso}| = |\delta b|/(Rb^2) \quad (12)$$

Comparing the values of T_{iso} with $T_{0.515}$ for model data an excellent correlation ($R = 0.999\,97$) between these values has been found

$$T_{\text{iso}} = 1.00T_{0.515} + 0.79$$

Because a confidence interval for T_{iso} amounted to $3 \div 6$ K a displacement of 0.79 K is not crucial and an equality $T_{\text{iso}} \approx T_{0.515}$ can be concluded. Therefore T_{iso} found from the artificial IKR being considered has a meaning of a temperature corresponding to the extent of conversion at which the difference between $\ln[f_i(w)]$ is minimal.

REAL OR TRUE IKRS

In this section, the possibility of detecting a true IKR and of computing its parameters for the case of thermal decomposition of solids under nonisothermal conditions will be analyzed. For this purpose we use model data, because these are the only data for which the existence of a true IKR as well as its parameters are known exactly. The w versus T data were modeled by (9) for four first-order reactions (N 6 from Table 1) using Arrhenius parameter values presented in Table 2. The Arrhenius parameter values were taken so that the corresponding Arrhenius lines have their common point of intersection at $T_{\text{iso}} = 729$ K.

For such a reaction series we attempt to detect a true IKR and to estimate its T_{iso} value using the discriminating approach. Arrhenius parameters will be evaluated by the Coats–Redfern equation¹¹ (13)

$$\ln [g(w)/T^2] = \ln[(AR/qE)(1 - 2RT'/E)] - E/RT \quad (13)$$

(where T' is the mean experimental temperature). Equation 13 is a convenient integral approximation of (11).

Table 3 shows Arrhenius parameters computed for this reaction series when varying the reaction models in (13). The T_{iso} values were then computed by the Arrhenius parameters found for different reactions but for the same model. It is seen from Table 3 that the T_{iso} values estimated by means of the Arrhenius parameters, which were computed by the discriminating approach vary within the interval of $654 \pm 1 \div 741 \pm 8$ K. From this a very unusual situation arises. On the one hand we cannot reject the possibility of detecting a true IKR in this way, since any of the models used clearly suggests the existence of an IKR with a reasonable confidence interval for the T_{iso} . On the other hand, the Fisher's test¹² for residual sums of squares (Table 3) gives no reason to prefer one of them to another.

The above shows that the main problem of detecting a true IKR in the case of solids undergoing thermal decomposition under nonisothermal conditions is associated with the ambiguity of computing Arrhenius parameters. This ambiguity may be overcome by measuring several kinetic curves taken at different heating rates. Such data allows for a correct separation of the contributions of the temperature and conversion components to the actual process rate. Writing (3) for different heating rates q_i and considering it at a constant conversion leads to (14)

$$q_i(dw/dT)_{w,i} = k(T_{w,i})f(w) \quad (14)$$

(where the subscript w refers to the value related to a constant conversion and i to a given heating rate). If the mechanism of the process does not depend on the heating rate, then the

$f(w)$ value at $w = \text{const}$ also does not depend on it. This means that (for a given conversion) a change in the temperature derivative of conversion $(dw/dT)_{w,i}$ with the temperature $T_{w,i}$, due to the application of different heating rates q_i , is determined only by the rate constant. Such an approach (later referred to as "isoconversional") makes it possible to compute the activation energy unambiguously, i.e., independently of the $f(w)$ model. Linearizing (14) and differentiation yields eq 15 for the activation energy E_w at a given conversion.

$$d \ln[q_i(dw/dT)_{w,i}]/d(T_{w,i})^{-1} = -E_w/R \quad (15)$$

Integral approximations of (15) form the basis of isoconversional methods of Flynn–Wall¹³ and Ozawa.¹⁴ These methods compute E_w from the slope of the straight line $\ln(q_i)$ versus $T_{w,i}^{-1}$ and require ensuing corrections.¹⁵ It has been pointed out¹⁶ that the dependence of $\ln(q_i/T_{w,i}^2)$ versus $T_{w,i}^{-1}$, rather than that used in the methods above, should be linear. Such a dependence is employed in the isoconversional method described in ref 17. The basic eq 16 for this method follows directly from the Coats–Redfern equation (13)

$$\ln(q_i/T_{w,i}^2) = \ln[(AR/g(w)E_w)(1 - 2RT'/E_w)] - E_w/RT_{w,i} \quad (16)$$

Here the E_w value is estimated from the slope of $\ln[q_i/T_{w,i}^2]$ versus $T_{w,i}^{-1}$ without the necessity of any corrections.

Beside unambiguously estimating the activation energy, the isoconversional methods give a unique possibility of obtaining information about the mechanism and kinetics of complex (multistep) processes, which include a clear majority of solid-phase thermal decompositions. This information is extracted¹⁸ from the dependence of the activation energy upon the conversion, i.e., E_w on w . A number of practical examples of analyzing complex processes by such a method can be found elsewhere.^{19–21}

The main problem that constrains the isoconversional methods from computing a true IKE is ambiguously estimating the pre-exponential factor. A solution based on utilizing an artificial IKR has been suggested in ref 22. It has been established that an actual value of $\ln A_w$ can be estimated when substituting E_j in (6) with E_w . After computing both Arrhenius parameters by the isoconversional method, the parameters of a true IKR become available from (17)

$$\ln A_{w,i} = a_w + b_w E_{w,i} \quad (17)$$

(where i refers to a given reaction of the reaction series). It should be noted that if E_w depends on w , then the T_{iso} estimated via the b_w value will also depend on w .

Figure 1 shows the conversion dependence of activation energies computed by (16) for a series of first-order reaction models. The Arrhenius parameter values are given in Table 3. Using these dependencies as well as the parameters for the artificial IKRs the dependencies of $\ln A_w$ on w were calculated. The T_{iso} values were then estimated at different conversions from (17). The result of these computations is presented in Figure 2. A dependence of T_{iso} on w seems to result from the slight variation of E_w with w for the particular reactions. The confidence interval for T_{iso} estimated by (12) passes through a minimum $|\delta T_{\text{iso}}| = 1$ K at $w = 0.25$. The T_{iso} value corresponding to this conversion is 727 K. It is

Table 4. Isokinetic Temperatures Estimated by the Arrhenius Parameters Computed for the Thermal Decomposition of $\text{Cu}_4\text{OCl}_6\text{L}_4$ with Diverse Ligands (1, Piperidine; 2, Morpholine; 3, Triphenylphosphine Oxide) When Varying the Reaction Models (Table 1) in Eq 13

N	j =						T _{iso} (K)	S ²
	1		2		3			
	E (kJ mol ⁻¹)	ln A (min ⁻¹)	E (kJ mol ⁻¹)	ln A (min ⁻¹)	E (kJ mol ⁻¹)	ln A (min ⁻¹)		
1	9.7	0.13	7.5	1.08	0.6	-7.20	133 ± 47	4.5365 ^a
2	15.2	1.33	12.3	0.77	1.6	-5.90	217 ± 29	0.5790 ^a
3	26.3	4.40	22.0	3.43	6.0	-3.85	286 ± 26	0.3629 ^a
4	92.6	22.39	80.1	19.72	32.7	2.42	352 ± 26	1.3428 ^a
5	125.8	31.16	109.2	27.66	46.1	4.84	355 ± 27	2.3519 ^a
6	74.6	18.49	70.9	18.09	25.6	2.04	350 ± 16	0.3812 ^a
7	13.5	1.10	12.5	1.02	0.9	-6.34	197 ± 12	0.1406 ^a
8	20.3	3.01	18.9	2.85	3.7	-4.43	262 ± 13	0.1184 ^a
9	33.9	6.96	31.9	6.73	9.2	-0.57	387 ± 16	0.0779 ^a
10	144.1	34.86	133.1	33.06	53.1	4.96	358 ± 20	1.8415 ^a
11	68.6	15.42	63.0	14.47	22.9	0.05	349 ± 19	0.4881 ^a
12	66.0	14.97	59.6	13.77	21.8	0.10	349 ± 21	0.5184 ^a

^a A residual sum of squares satisfies a condition of $S^2 \leq F \cdot S^2_{\text{min}}$, where F is Fischer's criterion of a 95% confidence level, S^2_{min} is a minimal value of all S^2 values.

clear that such an estimate only slightly deviates from the exact value ($T_{\text{iso}} = 729$ K) used when modeling data. Taking a mean of the interval of the change of T_{iso} as an estimate and a half of this interval as its confidence interval, one can also obtain $T_{\text{iso}} = 730 \pm 7$. This is the most pessimistic estimate for the isokinetic temperature, which can be obtained by an isoconversional method. Undoubtedly, even this estimate is incomparably less ambiguous than that obtained within the framework of the discriminating approach (Table 3).

EXPERIMENTAL EXAMPLE

As an example, the thermolyses of tetranuclear Cu complexes with the general composition $\text{Cu}_4\text{OCl}_6\text{L}_4$ are considered: Complexes with piperidine (I), morpholine (II) and triphenylphosphine oxide (III) as a ligand (L) were studied. The structure of these complexes is depicted in Figure 3. It can be expected that thermolyses of these complexes with different ligands may form a reaction series and reveal true IKRs.

The complexes $\text{Cu}_4\text{OCl}_6(\text{MeOH})_4$ were prepared by stirring of anhydrous CuCl_2 and CuO in dried methanol at 60 °C in the required molar ratios for 4 h. The complexes $\text{Cu}_4\text{OCl}_6\text{L}_4$ were prepared by the replacement of methanol by adding the respective ligands L (molar ratio of the initial complex to ligand 1:1) and refluxing the mixtures for 6 h under nitrogen atmosphere. Far-IR spectra of all complexes have been recorded with a Nicolet 20F Far-IV Vacuum Spectrometer (FT-IR). Due to possible ligand exchange in KBr wafers, polyethylene was applied as a matrix. Detailed information on the IR and electronic spectra of the complexes is available from ref 23. The thermogravimetric (TG) curves were recorded on a DuPont 9900 thermoanalyzer at the heating rates (q) of 5, 10, 20, and 30 K min $^{-1}$. Flowing nitrogen was used as purge gas. Samples with weight of 11–14 mg were heated in open platinum pans. Figure 4 shows a general shape of TG curves.

The TG curves were transformed into their conversion versus temperature form. Then the computations of IKRs were performed via the two above-mentioned approaches.

The results of computations by the discriminating approach are presented in Table 4. In comparison to computations performed on the model data (Table 3) we can observe a wider interval of T_{iso} variation for the same set of the reaction

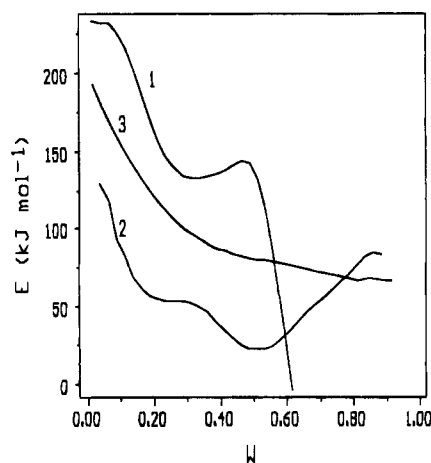


Figure 5. Dependencies of the activation energy upon conversion computed by the isoconversional method (eq 16) for the thermal decomposition of the tetranuclear complexes $\text{Cu}_4\text{OCl}_6\text{L}_4$ with diverse ligands (1, piperidine; 2, morpholine; 3, triphenylphosphine oxide).

models. It seems that in this case true IKRs may also be detected for most of the reaction models used. However, the ambiguity in computing the isokinetic temperature manifests itself here much more profoundly. The T_{iso} value varies from 133 \pm 47 to 387 \pm 16 K depending on the model used for computation.

The conversion dependencies of the activation energy computed by the isoconversional method (16) are depicted in Figure 5. Despite the differences in these dependencies, similar kinetic behavior can be concluded for all these complexes within the interval of conversion of 0–0.3. This interval can be considered as a possible region where an IKR may be found for the thermal decomposition of these complexes. After computing the conversion dependencies of the pre-exponential factor, as given above, the isokinetic temperature and a confidence interval for it were estimated from corresponding eqs 17 and 12.

Figure 6 displays the dependencies of T_{iso} and its confidence interval upon the extent of conversion. It is seen that within the interval of 0.15–0.30 conversions T_{iso} is almost constant and that the confidence interval goes through a minimum. The minimum of the confidence interval value of 15 K is found at $T_{\text{iso}} = 255$ K. It is satisfactory to note that this value according to (1) corresponds to a vibrational frequency of $\nu_{\text{iso}} = 177 \pm 10$ cm $^{-1}$. The latter value accords

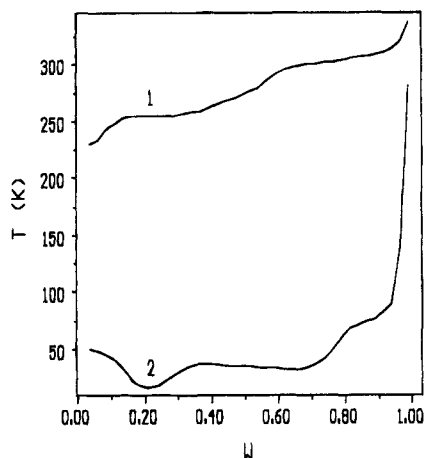


Figure 6. Dependence of the isokinetic temperature (1) and its confidence interval (2) on the extent of conversion computed by the conversion dependencies of the activation energy presented in Figure 5.

well with the experimentally observed far-IR absorption bands found at 185–250, 180–255, and 210–260 cm^{-1} assigned²³ to stretching vibration in the trigonal CuCl_3 chromophore in the piperidine, morpholine, and triphenylphosphine oxide, respectively. This suggests considering the CuCl_3 group as a possible center of the reaction, which thus appears to be the rate-limiting step of the thermal decomposition of the complexes at its beginning.

CONCLUSIONS

After considering two approaches to the computation of Arrhenius parameters of thermal decomposition under nonisothermal conditions the following can be concluded: The discriminating approach, which requires the assumption of a specific reaction model to compute Arrhenius parameters, leads to ambiguous values. These values may be used to detect an IKR but not for determining its parameters. The isoconversional approach gives meaningful values for the activation energy, and this value, together with the pre-exponential factor estimated via an artificial IKR, can be used to detect an IKR as well as to evaluate its parameters. The results of this analysis can in turn be used to obtain information about the actual reaction pathway.

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