ELSEVIER Thermochimica Acta 269/270 (1995) 61–72

thermochimica
acta

Detecting isokinetic relationships in non-isothermal systems by the isoconversional method[☆]

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Received 16 September 1994; accepted 25 February 1995

Abstract

The problem of detecting true isokinetic relationships (IKR) relates primarily to the problem of reliable evaluation of Arrhenius parameters. Two approaches (discriminating and non-discriminating) for evaluating Arrhenius parameters have been examined using modelled data to detect IKRs. The discriminating approach allows only for the detection of an IKR but not for unambiguously estimating the isokinetic temperature. The non-discriminating approach represented by the isoconversional method allows not only for detecting an IKR but also for determination of the isokinetic temperature. This may in turn be used to obtain information about the actual reaction pathway of the thermally induced process. The thermal decompositions of poly(ethyleneterephthalate) composites and of tetranuclear Cu(II) complexes with various ligands are used as experimental examples.

Keywords: Arrhenius parameters; Isoconversional method; Isokinetic relationships; Non-isothermal systems; Poly(ethyleneterephthalate); Tetranuclear Cu(II) complexes; Thermal decomposition

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[☆] Presented at the 6th European Symposium on Thermal Analysis and Calorimetry, Grado, Italy, 11–16 September 1994.

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SSDI 0040-6031(95)02354-2

1. Introduction

1.1. A true IKR and its use

An isokinetic relationship [1, 2] (IKR) refers to a common point of intersection of Arrhenius lines (i.e. $\ln k(T)$ versus (T^{-1}) for a series of reactions. An ordinate and an abscissa of the point of intersection define, respectively, the logarithm of the isokinetic rate constant, $\ln k_{\mathrm{iso}}$, and inverse isokinetic temperature, T_{iso}^{-1}. An IKR manifests itself as an interrelationship of Arrhenius parameters

$$\ln A_{\mathrm{i}} = a + bE_{\mathrm{i}} \tag{1}$$

where A_{i} is pre-exponential factor and E_{i} is activation energy; i refers to a particular reaction of the reaction series. The isokinetic temperature is determined through the b-parameter of Eq. (1) by use of Eq. (2)

$$T_{\mathrm{iso}} = (Rb)^{-1} \tag{2}$$

Accordingly a confidence interval for T_{iso} is estimated by the confidence interval for the b-parameter as Eq. (3)

$$|\delta T_{\mathrm{iso}}| = |\delta b|/(Rb^2) \tag{3}$$

It is important to realize 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, in both gas and condensed (homo- and heterogeneous) phases [1–3]. The existence of an IKR implies that only one reaction mechanism is followed by all members of the reaction series [4, 5], 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 [6–9].

The occurrence of an IKR has been explained theoretically [2, 3]. 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 following on from this is that, when an IKR occurs, the resonance vibrational frequency v_{iso} is related to the isokinetic temperature by Eq. (2)

$$v_{\mathrm{iso}} = k_{\mathrm{B}} \cdot T_{\mathrm{iso}}/h \tag{4}$$

(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 [2, 3]. 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 [1, 10] when an IKR for reactions in the solid state can be established. However, several specific problems arise when the widespread technique of thermal analysis measurements at non-isothermal conditions is used.

1.2. Problems of detecting IKRs by use of thermal analysis data

Thermal analysis methods (i.e. differential scanning calorimetry – DSC, differential thermal analysis – DTA, and thermogravimetry – TG) which measure an extensive property of a system are traditionally used [11, 12] to study the kinetics of thermal decomposition. Such measurements, as a rule, do not allow for the separation of contributions of single reactions into a change of a physical property being measured. This means that classical problems of solid-state kinetics [13, 14] related to a detailed study of primary processes such as nucleation, nuclei growth, and diffusion reach out of the scope of thermal analysis methods. However this does not mean that they may be ignored in kinetic processing of experimental data obtained by these methods. A method of kinetic processing of thermal analysis data should assume that a limiting step (and associated Arrhenius parameters) may change during the thermal decomposition of a solid. Nevertheless most popular methods [11, 12] yield one pair of Arrhenius parameters for the whole process of the thermal decomposition considering it a single-step reaction. The inconsistency of this assumption with reality emerges as an absence of a relationship between the calculated Arrhenius parameters and the actual activation parameters of the reactions comprising the process.

Another problem specific to these methods is ambiguously evaluating Arrhenius parameters even for a single-step process. This ambiguity goes from the discriminating nature [15] of these methods which allow only for Arrhenius parameters inextricably entwined with a reaction model. Arrhenius parameters are evaluated by discriminating among alternative reaction models which usually are equivalent descriptions of a process. This procedure results in a set of equivalent Arrhenius parameters which, however, crucially differ [15, 16] in their numerical values.

The above problems seem to be the main impediment to the reliable detection of IKRs by use of thermal analysis data. They also may be a reason that artificial IKRs (i.e. unrelated to a change in a physical property of the reacting system) are determined which can, however, disguise [17] the existence of a real one.

Therefore the calculation of Arrhenius parameters suitable for IKR analysis is first of all a problem of the validity of the method applied for kinetic processing of thermal analysis data. It has been shown [18–20] that reliable information about the mechanism and kinetics of complex processes can be obtained by isoconversional methods (also known as Flynn–Wall [21], Ozawa [22], Friedman [23] methods). Additionally, an attribute of these methods is that the effective activation energy specific for a given conversion can be found independently of a reaction model. This means that isoconversional methods are essentially non-discriminating.

By the isoconversional methods we can estimate the activation energy of the above mentioned primary processes, provided that in some interval of conversions this process dominantly contributes to a change in a physical property being measured by the applied thermal analysis method. The results of the isoconversional calculations are presented as a dependence of the activation energy on the extent of conversion. The shape of this dependence aids the interpretation of the mechanism of a process [24]. Not only the activation energy but also the pre-exponential factor can be estimated [25] for single reactions comprising the process. The resulting activation energy is governed by the activation energies of the single reactions as well as by their contributions to the overall process rate at a given extent of conversion. Obviously, if one of the reactions composing the process reveals a true IKR in a reaction series we have a chance to detect it at those conversions where the contribution of this reaction prevails.

It is the aim of this paper to demonstrate the feasibility of the isoconversional method as applied to detecting IKRs.

2. Methods to compute IKRs

In this section, methods representing the two above-mentioned approaches to compute Arrhenius parameters will be considered concerning their application to detect IKRs. The first is the method of Coats–Redfern [26]. It is a typical example for the discriminating approach. The basic equation of the method is Eq. (5)

$$\ln[g_j(w)/T^2] = \ln[(A_j R/qE_j)(1 - 2RT'/E_j)] - E_j/RT \tag{5}$$

where T' is the mean experimental temperature, R is the gas constant and q is the heating rate. A set of the reaction models, $g_j(w)$, is presented in Table 1. An IKR (Eq. (1)) will be computed for a reaction series assuming that all reactions forming it obey the same $g_j(w)$-model. Obviously, in the framework of the discriminating approach one can construct for a single reaction series as many IKRs as the number of the $g_j(w)$-models applied.

$$\ln A_{j,i} = a_j + b_j E_{j,i} \tag{6}$$

As an alternative to the Coats–Redfern method the isoconversional method representing the non-discriminating approach will be examined. It is well-known that

Table 1
Reaction models used to describe the thermal decomposition of solids

j	Reaction model	$g_j(w)$
1	Power law	$w^{1/4}$
2	Power law	$w^{1/3}$
3	Power law	$w^{1/2}$
4	Power law	$w^{3/2}$
5	One-dimensional diffusion	w^2
6	First-order (Mampel)	$-\ln(1-w)$
7	Avrami–Erofeev	$[-\ln(1-w)]^{1/4}$
8	Avrami–Erofeev	$[-\ln(1-w)]^{1/3}$
9	Avrami–Erofeev	$[-\ln(1-w)]^{1/2}$
10	Three-dimensional diffusion	$[1-(1-w)^{1/3}]^2$
11	Contracting sphere	$1-(1-w)^{1/3}$
12	Contracting cylinder	$1-(1-w)^{1/2}$

methods of Flynn–Wall and Ozawa compute activation energy from the slope of the straight line $\ln(q_n)$ versus $T_{w,n}^{-1}$ and require ensuing corrections [27]. It has been pointed out [28] that the dependence of $\ln(q_i/T_{w,n}^2)$ versus $T_{w,n}^{-1}$ rather than that used in the methods above, should be linear. Such a dependence is employed in the isoconversional method described in Ref. [29]. The basic equation for this method, Eq. (7), follows directly from the Coats–Redfern equation, Eq. (5)

$$\ln(q_n/T_{w,n}^2) = \ln[(A_w R/g(w)E_w)(1 - 2RT'/E_w)] - E_w/RT_{w,n} \qquad (7)$$

Here the subscript n refers to different heating rates whereas w denotes the values corresponding to a given conversion.

The main problem that constrains the isoconversional methods from computing a true IKR is ambiguously estimating the pre-exponential factor. A solution based on utilizing an artifical IKR has been suggested in Ref. [30]. It has been established that an actual value of $\ln A_w$ can be estimated via an artificial IKR (Eq. (8))

$$\ln A_j = c + dE_j \qquad (8)$$

where $\ln A_j$ and E_j may be computed, for instance, by the Coats–Redfern method when varying $g_j(w)$ for the set of w versus T data obtained under a single heating rate. After determination of c and d in Eq. (8) the E_w values found from Eq. (7) are substituted in Eq. (8) and $\ln A_w$ are estimated. When both Arrhenius parameters have been evaluated, the parameters of a true IKR become available from Eq. (9)

$$\ln A_{w,i} = a_w + b_w E_{w,i} \qquad (9)$$

The isoconversional method enables computation for a single series as many IKRs as the number of conversions used to evaluate Arrhenius parameters. It should be noted that if E_w depends on w (multi-step process), then both T_{iso} and $|\delta T_{iso}|$ estimated by Eqs. (2) and (3), respectively, will also depend on w.

3. Results and discussion

3.1. Model example

First of all, it is important to compare the efficiency of the above methods for a reaction series formed by single-step reactions. We modelled w versus T data for four

Table 2
Arrhenius parameters of the reactions whose Arrhenius lines have their common point of the intersection at $T_{iso} = 729$ K

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

first-order reactions with values of the Arrhenius parameter presented in Table 2. These values were taken so that the modelled reactions form a reaction series with a common point of intersection of the corresponding Arrhenius lines at $T_{\mathrm{iso}} = 729$ K. The data were modelled by use of Eq. (10)

$$w = 1 - \exp\left[(A/q)\int_0^T \exp(-E/RT)\,\mathrm{d}T\right] \tag{10}$$

using heating rates of 8, 12, 16 K min^{-1}. The integral over temperature is here replaced applying the Senum–Yang approximation [31].

Table 3 shows the Arrhenius parameters computed for this reaction series when varying the reaction model in Eq. (5). It provides a typical example of kinetic evaluation of non-isothermal data using the discriminating approach. Virtually all models furnish statistically acceptable descriptions of the first-order process (the corresponding correlation coefficients approach unity). At the same time, the extreme values of the activation energy determined for the same process differ by more than a factor of ten.

Table 3 also provides the T_{iso} values computed by use of Eq. (6) for each of 12 models varying the Arrhenius parameters of the model reactions (1–4 from Table 2) forming a series. The T_{iso} values estimated by means of the Arrhenius parameters, which were computed by the Coats–Redfern method vary within the interval of $654 \pm 1 - 746 \pm 7$ 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 T_{iso}. On the other hand, Fisher's test [32] for residual sums of squares (Table 3) gives no reason to prefer one of them to another.

Table 3
Isokinetic temperatures estimated by the Arrhenius parameters computed for a series of reactions (Table 2) when varying the $g_j(w)$ model in Eq. (5). S^2 is a residual sum of squares for the regression line (Eq. (6))

j	E/(kJ mol^{-1}), ln(A/min^{-1})								T_{iso}/K	S^2
	$i =$ 1		2		3		4			
1	12.4	2.51	20.9	4.14	29.0	5.57	37.6	7.13	654 ± 1	0.0017[a]
2	18.4	4.58	30.2	6.86	41.2	8.79	52.9	10.86	681 ± 6	0.0058[a]
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[a]
7	16.5	4.16	26.4	5.96	36.3	7.71	46.4	9.49	733 ± 6	0.0004[a]
8	23.9	6.83	37.5	9.26	51.0	11.60	64.6	13.97	736 ± 6	0.0006[a]
9	38.7	12.08	59.7	15.75	80.3	19.25	101.0	22.77	741 ± 8	0.0015[a]
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] A residual sum of squares satisfies a condition of $S^2 \leq F \cdot S^2_{\mathrm{min}}$, where F is Fischer's criterion of a 95% confidence level, S^2_{min} is the minimum value of all S^2 values.

Using the isoconversional method the dependencies of E_w and $\ln A_w$ on w have been computed according to Eqs. (7) and (8). Then the obtained values were correlated by use of Eq. (9). The T_{iso} values were estimated at different conversions from b_w by use of Eq. (2). The result of the computations is presented in Fig. 1. 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 use of Eq. (3) passes through a minimum $|\delta T_{iso}| = 1$ K at $w = 0.25$. The T_{iso} value corresponding to this conversion is 727 K. It only slightly deviates from the exact value ($T_{iso} = 729$ K) used when modelling data. Taking the mean value of the interval of the change of T_{iso} as an estimate, and half of this interval as its confidence interval, one can also obtain $T_{iso} = 730 \pm 7$. This is the most pessimistic estimate obtained by the isoconversional method. Undoubtedly, even such an estimate is incomparably less ambiguous than that obtained within the framework of the discriminating approach (Table 3).

The model example suggests the use of the isoconversional (non-discriminating approach) method rather than the Coats–Redfern method (discriminating approach) to compute IKRs. Consider now the effectiveness of the isoconversional method in detecting IKRs by use of experimental data.

3.2. Experimental example I

As the first example we used data [33] on the thermal decomposition of three poly(ethyleneterephthalate) (PET) composites namely, i) pure PET, ii) PET with 2.4%

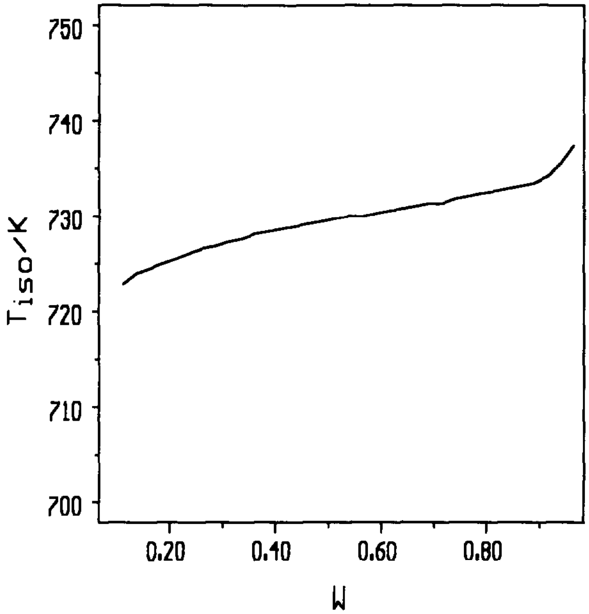


Fig. 1. Dependence of the isokinetic temperature on the extent of conversion, w, computed by the isoconversional method, Eq. (7), for the reaction series (Table 2).

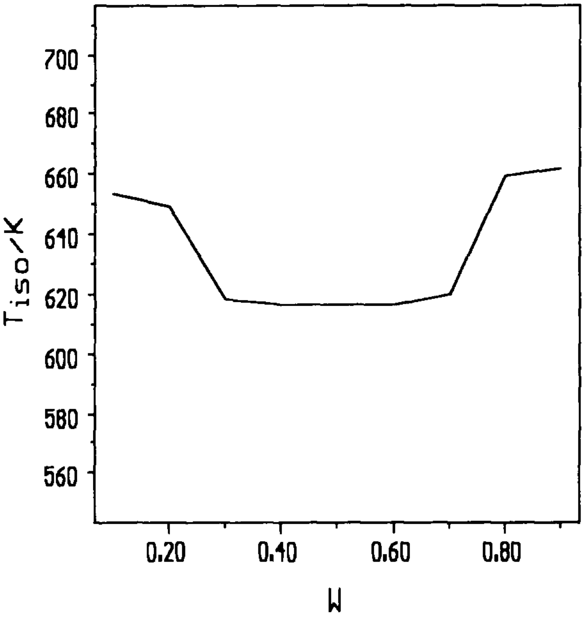
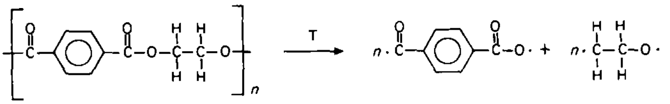


Fig. 2. Dependence of the isokinetic temperature on the extent of conversion, w, computed by the isoconversional method, Eq. (7), for the thermal decomposition of poly(ethyleneterephthalate) composites [33].

of polyethylene carrier, iii) PET with 8% of aluminium. Fig. 2 displays the dependence of T_{iso} on the extent of conversion. Within the interval of 0.3–0.7 conversions T_{iso} is almost constant. The minimum of the confidence interval value of 10 K is found at $w = 0.5$ which corresponds to $T_{iso} = 618$ K. Inserting the latter value into Eq. (4) gives a vibrational frequency of $v_{iso} = 430$ cm^{-1} which is in excellent agreement with the experimentally observed far IR absorption band at 450–430 cm^{-1} [34]. This absorption is assigned to a O–CH_2–CH_2 deformational vibration in PET. From this we can suppose that the rate-limiting step of PET thermal decomposition is breakage of C–O linkages in the polymer chain.



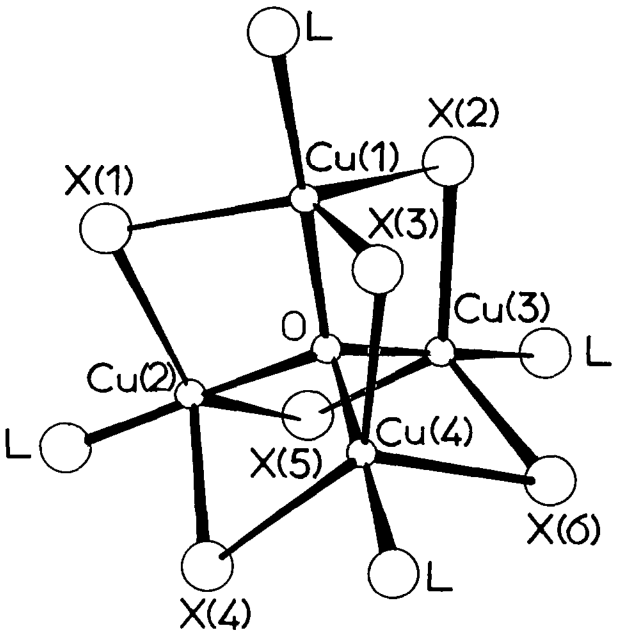


Fig. 3. General structure of $Cu_4OCl_6L_4$ complexes (X = Cl).

This assumption complies with mass spectrometric analysis of the gaseous products of PET thermal decomposition [35] in the yield of which 80 mole per cent of the CH_2CHO constituent was found. The above example shows that the isokinetic relationship found is in fact a real one.

3.3. Experimental example II

As the second example, the thermolyses of tetranuclear Cu(II) complexes [36] with the general composition $Cu_4OCl_6L_4$ are considered; complexes with piperidine (I), morpholine (II) and triphenylphosphine oxide (III) as a ligand (L) were studied. The general structure of these complexes is depicted in Fig. 3. It can be expected that thermolyses of these complexes with different ligands may form a reaction series and reveal true IKRs.

The complexes $Cu_4OCl_6(MeOH)_4$ were prepared by stirring anhydrous $CuCl_2$ and CuO in dried methanol at 60°C in the required molar ratios for 4 h. The complexes $Cu_4OCl_6L_4$ 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. Far-IR spectra of all complexes have been recorded with a Nicolet 20 F Far-IR 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. [35]. The thermogravimetric (TG) curves were recorded on a DuPont 9900 thermoanalyzer at the

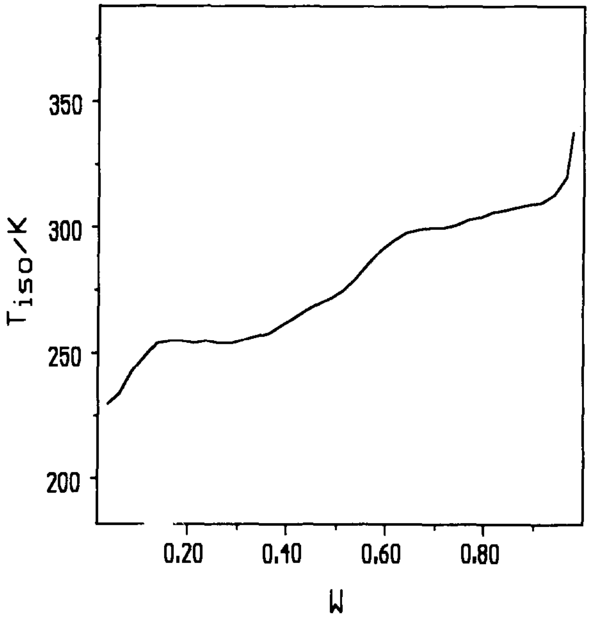


Fig. 4. Dependence of the isokinetic temperature on the extent of conversion, *w*, computed by the isoconversional method, Eq. (7), for the thermal decomposition of the tetranuclear complexes $Cu_4OCl_6L_4$ with diverse ligands (L = piperidine, morpholine, triphenylphosphine oxide).

heating rates (q) of 5, 10, 20, 30 K min^{-1}. Flowing nitrogen was used as purge gas. Samples with weight of 11–14 mg were heated in open platinum pans.

The TG curves were transformed into their conversion versus temperature form. 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 the corresponding equations, Eqs. (2) and (3).

Fig. 4 displays the dependencies of T_{iso} upon the extent of conversion. Within the interval of 0.15–0.30 conversions, T_{iso} is almost constant. The confidence interval goes through a minimum of 15 K at $w = 0.2$ which relates to $T_{\mathrm{iso}} = 255$ K. The substitution of the latter value into Eq. (4) gives a vibrational frequency of $v_{\mathrm{iso}} = 177 \pm 10$ cm^{-1}. This value accords well with the experimentally observed far-IR absorption bands assigned [36] to stretching vibration in the trigonal $CuCl_3$ chromophore in piperidine, morpholine and triphenylphosphine oxide. This suggests consideration of the $CuCl_3$ group as a possible centre of the reaction, which thus appears to be the rate-limiting step of the thermal decomposition of the complexes at its beginning.

By data from [37, 38] at the very beginning of the process (up to 4% of mass loss) the structure moiety Cu_4O does not break and only small changes are observed for Cu–Cl, Cu–O and ligand vibrations. Further decomposition (up to 50% of mass loss) is accompanied by the disappearance of the IR vibrations of Cu_4O, Cu–Cl and Cu–O moieties in the complexes. X-ray powder patterns obtained for the residue at this stage of decomposition reveal the presence of significant amounts of amorphous phases and a phase identified as CuCl [37, 38] which is the only crystalline phase formed while decomposing.

These experimental results confirm the assumption made above regarding the $CuCl_3$ group acting as a possible reaction. At least two facts are counted in favour of this: (i) the observed change in Cu–Cl vibration at the very early stage of the decomposition, and (ii) the formation of CuCl as a decomposition product in the late stages.

4. Conclusions

After considering two approaches to the computation of Arrhenius parameters of thermal decomposition under non-isothermal conditions it can be concluded that 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 non-discriminating approach represented by the isoconversional approach gives reliable values for Arrhenius parameters which can be efficiently 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 [39].

Acknowledgement

Thanks are due to the "Fonds zur Förderung der wissenschaftlichen Forshung in Österreich" for financial support under the projects M170 and 8795.

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