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THERMAL DECOMPOSITION KINETICS OF SOME AROMATIC AZOMONOETHERS

Part III. Non-isothermal study of 4-[(4-chlorobenzyl)oxy]-4’-chloro-azobenzene in dynamic air atmosphere

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Thermal analysis of 4-[(4-chlorobenzyl)oxy]-4’-chloro-azobenzene dye, exhibiting liquid crystalline properties, was performed in dynamic air atmosphere. The compound behavior was investigated using TG, DTG, DTA and DSC techniques, under non-isothermal linear regime. The evolved gases were analyzed by FTIR spectroscopy. Kinetic parameters of the first decomposition step were obtained by means of multi-heating rates methods, such as isoconversioanl methods, IKP method and Perez-Maqueda *et al.* criterion.

Keywords: *IKP method, liquid-crystalline dyes, ‘model-free’ kinetics, Perez-Maqueda et al. criterion*

Introduction

Colorants containing ‘azo’ group in their molecules are of large interest from the point of view of possible applications (e.g. in non-linear optics). Thermal analysis and kinetic studies of thermal induced changes of new compounds designed for temperature controlled applications (like dyes exhibiting liquid-crystalline nature) is a real need and an advantageous pointer before trying to functionalize them [1, 2]. Part III on the thermal behavior of azomonoethers, aims to identify the physical and chemical transformations of 4-[(4-chlorobenzyl)oxy]-4’-chloro-azobenzene liquid crystal [3], related to non-isothermal increasing temperature regimes in dynamic air atmosphere and the evaluation of kinetic triplet $\{E, A, f(\alpha)\}$ of the first decomposition step. Previous studies on the thermal stability of azoic dyes [4, 5] and non-isothermal decomposition kinetics of such compounds [6–9] have been also reported.

For a single heterogeneous process under any non-isothermal regime, the reaction rate can be expressed by Eq. (1):

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = Af(\alpha)\mathrm{e}^{-\frac{\mathrm{E}}{\mathrm{RT}}} \qquad (1)$$

where α is the conversion degree, $(\mathrm{d}\alpha/\mathrm{d}t)$ is the reaction rate, A is the pre-exponential factor (frequency factor), E is the activation energy, $f(\alpha)$ is the differential conversion function and R is the universal gas constant. Recent papers have reported on the critical analysis of the single rate model-fitting methods [10–13], suggesting that using them would lead frequently to uncertain values of the activation parameters. Because of the impossibility of evaluating the entire kinetic triplet that describes a physical or chemical transformation, from more simple procedures like isoconversional methods, it was concluded the need of using more sophisticated kinetic methods (Invariant Kinetic Parameters method [14] and Perez-Maqueda *et al.* criterion [15]), combined with isothermal, non-isothermal non-linear (i.e. modulated temperature [16]) or sample controlled thermal experiments [17, 18].

Experimental

The aromatic azomonoethers were obtained by the condensation of some 4-(phenyl-azo)phenols with chloromethylated derivatives of chlorobenzene in alkaline medium (Williamson ether synthesis). Thermal analysis measurements (TG, DTG, DTA and DSC) of 4-[(4-chlorobenzyl)oxy]-4’-chloro-azobenzene (Fig. 1) were carried out in dynamic air atmosphere (150 mL min^{-1}), under non-isothermal linear regimes. A horizontal Diamond Differential/Thermogravimetric Analyzer from Perkin-Elmer Instruments was used during the experiments.

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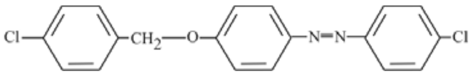

Fig. 1 4-[(4-chlorobenzyl)oxy]-4'-chloro-azobenzene molecule

Samples from 0.8 to 1.5 mg, contained in Al_2O_3 crucibles, were heated in the temperature range 20–800°C, with the heating rates of: 2, 6 and 8 K min^{-1}.

The FTIR spectrum of the evolved gases was recorded on a Perkin-Elmer Instruments SPECTRUM 100 by transporting them from the thermobalance through a thermostated pipe in the stream of air.

Results and discussion

Thermal analysis

Figure 2 shows the thermoanalytical curves (TG, DTG, DTA and DSC) of 4-[(4-chlorobenzyl)oxy]-4'-chloro-azobenzene, recorded for 6 K min^{-1}; similar curves were obtained for all other heating rates.

Before melting, as can be seen from these curves, an endothermic phase transition occurs. After melting at 168°C, a weak endothermic decomposition undergoes in the temperature range 200–350°C. The endothermic effect of the first decomposition step is small because of its oxidative–exothermic nature, which however compensates the real endothermic fracture of bonds. The experimental mass loss (Δm_{exp}=90%) of the first step, correlated with the FTIR spectra of the evolved gases, reveal the destruction of the molecule into Cl–Ar–CH_3 ($\nu_{(C–Cl)}$ 700 cm^{-1}, aliphatic $\nu_{(C–H)}$ 2400 cm^{-1}), N_2 and CO_2 – Fig. 3. The remaining 10% are due to the formation of various carbon-based residues. The second decomposition step (450–580°C) corresponds to the combustion of these rests.

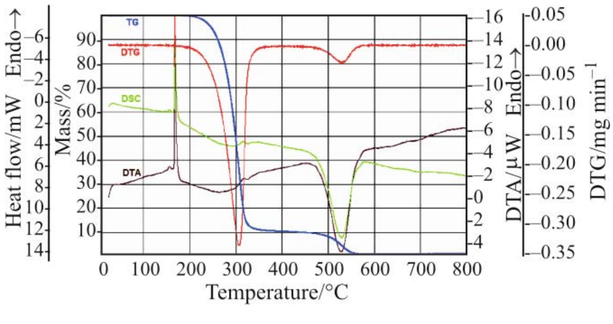

Fig. 2 Thermoanalytical curves of 4-[(4-chlorobenzyl)oxy]-4'-chloro-azobenzene for 6 K min^{-1} in dynamic air atmosphere

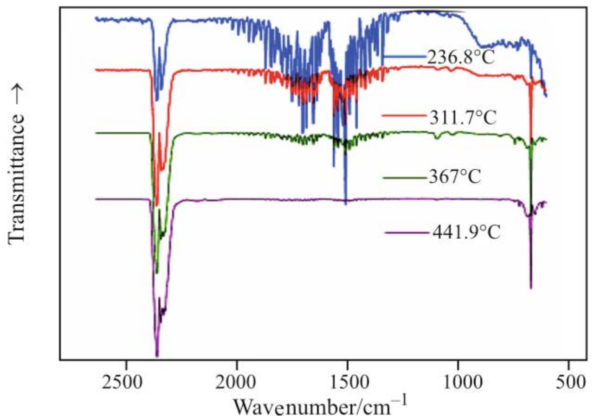

Fig. 3 FTIR spectra of the evolved gases during the oxidative decomposition of 4-[(4-chlorobenzyl)oxy]-4'-chloro-azobenzene for β=6 K min^{-1}

DSC parameters for the thermal analysis of 4-[(4-chlorobenzyl)oxy]-4'-chloro-azobenzene at 6 K min^{-1} in dynamic air atmosphere are presented in Table 1.

Kinetic analysis

The influence of different temperature regimes upon the thermal behavior of the investigated compounds can provide kinetic parameters indicating change in the reaction pathway. The complexity of a stage can be expressed from the activation energy dependence on the conversion degree. This can be done using the isoconversional methods for the evaluation of the activation energy. If E does not depend on α, the investigated process is a simple one and should be described by a unique kinetic triplet. If E changes with α, the process is complex [19]. Vyazovkin and Lesnikovich [20] established an algorithm for identifying the type of complex processes. When E increases with conversion degree, the process involves parallel reactions. When E decreases and the shape of its evolution is concave, then the process has revers-

Table 1 DSC parameters for 4-[(4-chlorobenzyl)oxy]-4'-chloro-azobenzene decomposition at β=6 K min^{-1}

Change	Thermal effect endo/exo	Temp. of the max. decomposition rate, T_{max}/°C	Transferred heat ΔH/kJ kg^{-1}
Phase transition	endothermic	157.7	3.1
Melting	endothermic	168.0	107.0
Oxidative decomposition	endothermic	321.5	17.4
Combustion	exothermic	535.8	–901.7

ible stages. For decreasing convex shape, the process changes the limiting stage. In order to discriminate between the occurring reactions, automatic programs were developed, assuming that the overall reaction is the sum of individual reaction steps [21–23].

Isoconversional methods

The isoconversional procedures (‘model-free’ kinetics) can be classified as linear (the activation energy is evaluated from the slope of a straight line) and non-linear (the activation energy is evaluated from a specific minimum condition). The isoconversional integral linear methods are based on the following integral from of the reaction rate:

$$g(\alpha)=\int_0^\alpha \frac{d\alpha}{f(\alpha)}=\frac{A}{\beta}\int_0^\alpha e^{-\frac{E}{RT}}dT=\frac{A}{\beta}I(E_\alpha,T_\alpha) \qquad (2)$$

where β is the heating rate, $g(\alpha)$ is the integral conversion function and $I(E_\alpha,T_\alpha)$ represents the temperature integral. In our paper we make use of Kissinger–Akahira–Sunose (KAS method) – integral linear method [24, 25] and Flynn–Wall–Ozawa (FWO method) – integral linear method [26, 27].

Substitution of $I(E_\alpha,T_\alpha)$ in Eq. (2) with Coats–Redfern approximation [28]:

$$I(E_\alpha,T_\alpha)=\frac{RT_\alpha^2}{E_\alpha}e^{-\frac{E_\alpha}{RT_\alpha}}$$

gives Eq. (3) – used by KAS method:

$$\ln\frac{\beta}{T^2}=\ln\frac{AR}{Eg(\alpha)}-\frac{E}{RT} \qquad (3)$$

Similar substitution with Doyle approximation [29]:

$$I(E_\alpha,T_\alpha)=\frac{E_\alpha}{R}e^{\left(-5.331-1.052\frac{E_\alpha}{RT_\alpha}\right)}$$

gives Eq. (4) – used by FWO method:

$$\ln\beta=\ln\frac{AE}{Rg(\alpha)}-5.331-1.052\frac{E}{RT} \qquad (4)$$

Thus, for α=const., the plot $\ln(\beta/T^2)$ *vs.* $1/T$ or $\ln\beta$ *vs.* $1/T$, obtained from the experimental thermogravimetric curves recorded for several constant-heating rates, should be a straight line whose slope could be used for the activation energy evaluation.

Figure 4 shows the results obtained using KAS and FWO methods, as values of the activation energy at various conversion degrees from 0.2 to 0.8 with a step of 0.01.

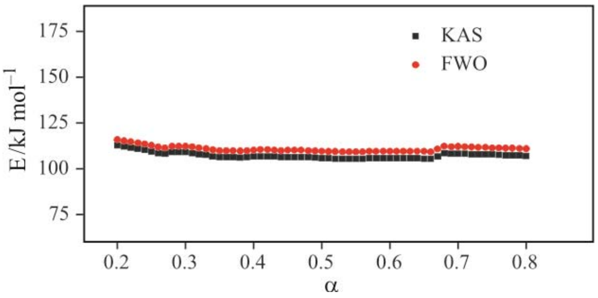

Fig. 4 Isoconversional activation energy of the non-isothermal decomposition of 4-[(4-chlorobenzyl)oxy]-4’-chloroazobenzene in dynamic air atmosphere

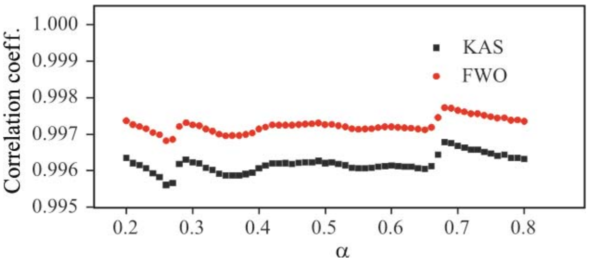

Fig. 5 Correlation coefficients of the activation energies obtained by means of KAS and FWO methods

During the first decomposition step, the activation energy remains practically constant, describing a single reaction. As can be seen from Fig. 5, the accuracy in determining the activation energy was very high – over 0.99550.

The mean values of the activation energy for 0.2<α<0.8 are:

$$\bar{E}_{\mathrm{KAS}}=107.2\pm1.7\ \mathrm{kJ\ mol^{-1}}$$
$$\bar{E}_{\mathrm{FWO}}=110.7\pm1.5\ \mathrm{kJ\ mol^{-1}}$$

The results obtained by KAS and FWO methods are comparable. The differences between the values of the activation energy obtained using these two isoconversional integral methods may be attributed to the different approximations of the temperature integral.

Invariant kinetic parameters (IKP) method

Based on Criado and Morales early observation [30], that almost any $\alpha=\alpha(T)$ or $(d\alpha/dt)=(d\alpha/dt)(T)$ experimental curve may be correctly described by several conversion functions, the use of an integral or differential model-fitting method leading to different values of the activation parameters. Although being obtained with high accuracy, the values change with different heating rates and among conversion functions. In the present study, the chosen model-fitting method was Coats–Redfern [28]. The apparent activation parameters, obtained for each heating rate of

Table 2 Apparent activation parameters by Coats–Redfern equation for each applied heating rate

Kinetic model	β=2 K min^{-1}			β=6 K min^{-1}			β=8 K min^{-1}		
	E/kJ mol^{-1}	ln$A$/s^{-1}	r	E/kJ mol^{-1}	ln$A$/s^{-1}	r	E/kJ mol^{-1}	ln$A$/s^{-1}	r
F0.3	97.0±0.3	13.97±0.9	0.99975	94.2±0	13.55±0.8	0.99998	91.1±0	12.81±0.8	0.99997
F0.5	104.7±0	15.8±1.9	0.99999	101.7±0	15.27±3.2	0.99989	98.4±0.3	14.46±3.7	0.99966
A0.1	1342.3±8	286±6.1	0.99897	1309.8±10	268±7.2	0.99820	1271.0±11	256±6.4	0.99755
D1	181.8±1.2	32.31±5.2	0.99867	177.2±0.8	30.78±4.8	0.99935	171.7±0.6	29.28±4.4	0.99965
D2	204.5±0.5	36.93±4.3	0.99979	199.3±0.1	35.08±2.8	0.99998	193.1±0.2	33.37±3.2	0.99935
D3	232.0±0.4	41.82±4.1	0.99988	226.0±0.8	39.59±4.8	0.99954	219.1±1.1	37.60±5.2	0.99916
D4	213.6±0.2	37.55±3.4	0.99996	208.1±0.2	35.57±3.3	0.99997	201.7±0.5	33.76±4.2	0.99982

the best-fitting kinetic models are presented in Table 2.

Lesnikovich and Levchik suggested that correlating these values by the apparent compensation effect: ln$A$=a_β+$b_\beta E$, one obtains the compensation effect parameters, a_β and b_β, which strongly depend on the heating rate (β) as well as on the considered set of conversion functions [14]. The straight lines lnA_β *vs.* E_β for several constant heating rates should intersect in a point (isoparametric point [31]) which corresponds to the true values of the activation energy and pre-exponential factor. They were named invariant kinetic parameters ($E_{\rm inv}$, $A_{\rm inv}$).

The apparent kinetic parameters of the thermal decomposition in air flow of 4-[(4-chlorobenzyl)oxy]-4'-chloro-azobenzene are represented in ln$A$ *vs.* E space (Fig. 6).

Certain variations of the experimental conditions, as well as the straight lines (corresponding to different heating rates) junction at low values, determine a region of intersection rather than a unique point in the ln$A$ *vs.* E plot. For these reasons, the evaluation of the invariant kinetic parameters is performed using the supercorrelation equation:

$$a_\beta = \ln A_{\rm inv} - b_\beta E_{\rm inv} \qquad (5)$$

The plot of a_β *vs.* b_β, obtained for several constant heating rates, is a straight line whose parameters allow the determination of ln$A_{\rm inv}$ and $E_{\rm inv}$. The detailed image of the plot (Fig. 6 – undersized figure in up-left corner) shows the incompatibility of D4 model among all other conversion functions, although its apparent parameters were obtained with high correlation coefficients.

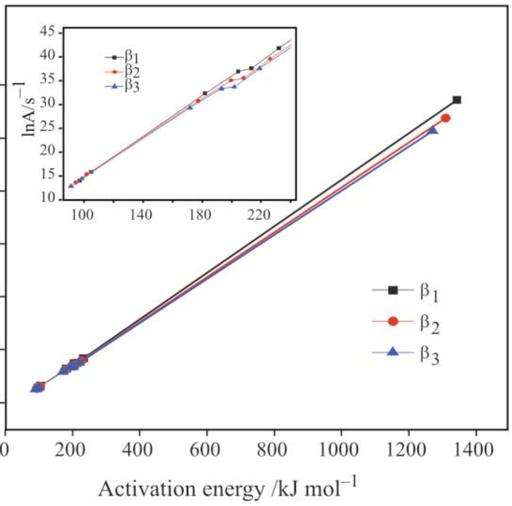

Fig. 6 ln$A$ *vs.* E space of all best-fitting kinetic models

It is easily to notice from Fig. 6 that Fn functions (for n=0.3–0.6) are the most adequate, because the intersection is around 100±20 kJ mol^{-1}. As it was previously shown [32, 33], in such cases (liquid state decomposition), the contribution of diffusion functions is less probable, they even providing increased errors. This fact can not be entirely avoided since from the existing possibilities, some of them are necessary to be used.

For several groups of apparent activation parameters listed in Table 2, obtained by different kinetic models (all kinetic models: AKM={F0.3; F0.5; A0.1; D1; D2; D3; D4}), we tried to establish the best combination (r→1), a better resolution in determining the invariant kinetic parameters and the closest value to the mean isoconversional activation energies [33–35].

For AKM-{D3;D4}, the plot of lnA_β *vs.* E_β has the highest correlation coefficient (r=1) and is a true straight line – Fig. 7.

Depending on the chosen group of kinetic models, the compensation effect parameters are obtained with different accuracies, their values and derived invariant activation parameters varying substantially. A short look on Table 3 makes compulsory the exclusion of some mechanisms: D4 and/or D3. Even if some apparent activation parameters may look as 'fantastic' – the case of A0.1, the efficiency of IKP method is strongly revealed by AKM-{D3;D4}, AKM or AKM-{D4} groups.

As it was expected, the best results for invariant kinetic parameters determination were obtained by AKM-{D4}, AKM and AKM-{D3;D4}, in this order. For these three groups, the invariant activation energy

Table 3 Compensation effect parameters for several combinations of kinetic models

β/K min^{-1}	AKM			AKM–{A0.1}		
	a_β, A/s^{-1}	b_β/mol J^{-1}	r	a_β, A/s^{-1}	b_β/mol J^{-1}	r
2	-7.94358 ± 0.43	$2.1885\cdot10^{-4}\pm8.2\cdot10^{-7}$	0.99997	-5.7919 ± 0.79	$2.062\cdot10^{-4}\pm4.38\cdot10^{-6}$	0.99910
6	-6.95155 ± 0.43	$2.1035\cdot10^{-4}\pm8.4\cdot10^{-7}$	0.99996	-4.8082 ± 0.79	$1.974\cdot10^{-4}\pm4.5\cdot10^{-7}$	0.99895
8	-6.72304 ± 0.43	$2.0697\cdot10^{-4}\pm8.7\cdot10^{-7}$	0.99996	-4.5819 ± 0.79	$1.936\cdot10^{-4}\pm4.7\cdot10^{-7}$	0.99883
	AKM–{D4}			AKM–{A0.1;D4}		
2	-7.6777 ± 0.38	$2.1869\cdot10^{-4}\pm6.7\cdot10^{-7}$	0.99998	-6.0427 ± 0.64	$2.0857\cdot10^{-4}\pm3.72\cdot10^{-6}$	0.99952
6	-6.6839 ± 0.38	$2.10192\cdot10^{-4}\pm6.8\cdot10^{-7}$	0.99998	-5.0612 ± 0.64	$1.9987\cdot10^{-4}\pm3.81\cdot10^{-6}$	0.99945
8	-6.45738 ± 0.38	$2.06799\cdot10^{-4}\pm7.1\cdot10^{-7}$	0.99998	-4.8300 ± 0.65	$1.9611\cdot10^{-4}\pm4.05\cdot10^{-6}$	0.99936
	AKM–{D3;D4}			AKM–{A0.1;D3;D4}		
2	-7.3674 ± 0.16	$2.1853\cdot10^{-4}\pm2.75\cdot10^{-7}$	1	-6.6501 ± 0.24	$2.1359\cdot10^{-4}\pm1.60\cdot10^{-6}$	0.99940
6	-6.3744 ± 0.17	$2.1002\cdot10^{-4}\pm2.81\cdot10^{-7}$	1	-5.6651 ± 0.25	$2.0500\cdot10^{-4}\pm1.65\cdot10^{-6}$	0.99993
8	-6.1421 ± 0.16	$2.0662\cdot10^{-4}\pm2.81\cdot10^{-7}$	1	-5.4536 ± 0.24	$2.0159\cdot10^{-4}\pm1.65\cdot10^{-6}$	0.99993

Table 4 IKP for several combinations of kinetic models

Kinetic models	E_{inv}/kJ mol^{-1}	lnA_{inv}/s^{-1}	r
AKM	105.4±10.8	15.154±2.3	0.99473
AKM – {A0.1}	98.9±12.0	14.633±2.4	0.99263
AKM – {D4}	105.3±11.1	15.383±2.3	0.99448
AKM – {A0.1;D4}	100.0±11.8	14.854±2.4	0.99305
AKM – {D3;D4}	105.5±10.7	15.723±2.2	0.99485
AKM – {A0.1;D3;D4}	102.6±11.6	15.294±2.4	0.99358

is slightly above 105 kJ mol^{-1}, close to 107.2 kJ mol^{-1} obtained by KAS method and 110.7 kJ mol^{-1} by FWO method. For AKM-{D3;D4}, the invariant kinetic parameters are E_{inv}=105.5 kJ mol^{-1} and lnA_{inv}=15.723 (A=6.5·10^6 s^{-1}), obtained with r=0.99485.

Perez-Maqueda *et al.* criterion

In order to obtain the appropriate kinetic model, one can discriminate between the set of best-fitting conversion functions by applying the Perez-Maqueda *et al.* criterion [15]. Even if model-fitting methods and IKP method select a group of presumable conversion functions, they cannot precisely establish the right and unique model from a type of kinetic models (i.e. in our case, all possibilities of Fn type models, with n=0.3-0.6). According to Perez-Maqueda *et al.* criterion, the correct kinetic model corresponds to the independence of the activation parameters on the heating rate. By applying any differential or integral model-fitting method, for every constant heating rate, the true kinetic model shall provide both the same constant activation energy as well as the pre-exponential factor. If the Coats–Redfern equation written in the form:

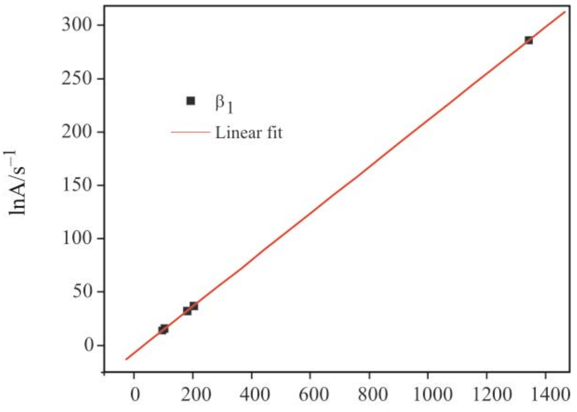

Fig. 7 ln$A$ *vs.* E straight line for AKM–{D3;D4} combination and β=2 K min^{-1}

$$\ln\frac{\beta g(\alpha)}{T^2}=\ln\frac{AR}{E}-\frac{E}{RT} \qquad (6)$$

is used, for the correct conversion function, all the points {ln[$\beta g(\alpha)/T^2$] *vs.* 1/T} corresponding to all applied heating rates lie on the same straight line.

For F0.5 kinetic model, the best overlapping of the {ln[$\beta g(\alpha)/T^2$] *vs.* 1/T} points corresponding to the different heating rates was obtained and the following activation parameters:

$$E=106.7\pm0.7 \text{ kJ mol}^{-1}$$
$$\ln A=16.30\pm4.6\ (A/\text{s}^{-1})$$
$$A=1.1\cdot10^7\pm9.5\cdot10^1 \text{ s}^{-1}$$

F0.5 conversion function is also known as R2, and corresponds to phase boundary controlled reactions (contracting area, i.e. bidimensional shape). Although R2 model belongs to the empirical expression of the conversion function suggested by Šesták and Berggren [36], it is one of the few kinetic models that have true physical meaning. R2 was found to be one of the most frequent kinetic model describing thermal induced decompositions of liquid systems [37, 38]. The thermal analysis in air flow of 4-[(4-chlorobenzyl)oxy]-4'-chloro-azobenzene and characteristic kinetic parameters lead to the conclusion that the carbon-based residues are melts that do not influence at all the first decomposition step.

Conclusions

Thermal analysis of 4-[(4-chlorobenzyl)oxy]-4'-chloro-azobenzene dye, exhibiting liquid crystalline properties, was performed in dynamic air atmosphere. After an endothermic phase transition at 157.7°C and melting at 168°C, a weak endothermic decomposition undergoes in the temperature range 200–350°C. This is followed by the combustion of carbon-based residues between 450 and 580°C. Kinetic parameters of the first decomposition step were evaluated by means of multi-heating rates methods, such as isoconversional (KAS and FWO) methods, IKP method and Perez-Maqueda *et al.* criterion. It is not possible to establish the kinetic triplet by comparing the results of only kinetic models obtained by model-fitting methods with those obtained by isoconversional methods, since F0.3, F0.5, D2, D3 or D4 are providing very accurate apparent activation parameters. The gather of different kinetic models lead finally to invariant kinetic parameters in the region of low reaction order models, and close to the isoconversional activation energies (~107±3 kJ mol^{-1}). The use of Perez-Maqueda *et al.* criterion confirmed the 10^7 order of pre-exponential factor (similar to the invariant pre-exponential factor) and pointed to F05(R2) as the unique and right kinetic model.

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