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THERMAL DECOMPOSITION KINETICS OF SOME AROMATIC AZOMONOEHTERS

Part II. Non-isothermal study of three liquid crystals in dynamic air atmosphere

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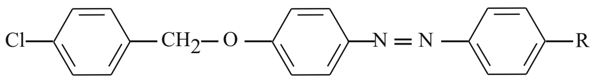
Thermal analysis of three azomonoether dyes, exhibiting liquid-crystalline properties, was performed in dynamic air atmosphere. Thermal stability studies and the evaluation of the kinetic parameters of each physical or chemical transformations are essential for a full characterization, before attempting accurate thin films' depositions of such materials used in non-linear optical applications. New synthesized dyes with general formula: where *R* is a nematogenic group: CN, CF_3 or a highly polarizable group: NO_2 were investigated using TG, DTG, DTA and DSC techniques, under non-isothermal regime. The evolved gases were analyzed by FTIR spectroscopy. The activation energies of the first decomposition step were evaluated for each compound, the obtained results revealing complex mechanisms.



Keywords: *dyes, isoconversional methods, liquid crystals, non-isothermal kinetics, thermal analysis*

Introduction

Part II of this series deals with azomonoether dyes of liquid crystalline nature [1] and aims the identification of physical and chemical transformations related to a non-isothermal increasing temperature regime in dynamic air atmosphere. Previous studies on the non-isothermal decomposition kinetics of such compounds, carried out in static air atmosphere, were also reported [2, 3]. Thermal analysis and kinetic studies of thermal induced changes of new compounds (designed for temperature controlled applications) is a real need and an advantageous pointer before trying to functionalize them [4].

Experimental data for the kinetic analysis of heterogeneous processes can be obtained under different temperature profiles; under non-isothermal conditions, for a single heterogeneous process, Eq. (1) describes the progress rate:

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

where α is the conversion degree, ($d\alpha/dt$) is the reaction rate, A is the frequency factor, E is the activation energy, $f(\alpha)$ is the differential conversion function and R is the universal gas constant. Taking into account the impossibility to separate its dependence on the temperature and on the conversion, almost every conversion function may describe the experimental data [5–7]. After a review of the single-heating rate methods for kinetic parameters' evaluation [8–12], it was concluded that they are providing only erroneous results and then decided the need to use multi-heating rate methods [13–18].

Methods based on at least three non-isothermal curves, recorded at different constant heating rates, will be used for the oxidative thermal and kinetic decomposition studies of 4-[(4-chlorobenzyl)oxy]-4'-cyno-azobenzene, 4-[(4-chlorobenzyl)oxy]-4'-trifluoromethyl-azobenzene and 4-[(4-chlorobenzyl)oxy]-4'-nitro-azobenzene.

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Experimental

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) were carried out in air dynamic atmosphere (150 mL min^{-1}), under non-isothermal conditions. A horizontal Diamond Differential/Thermogravimetric Analyzer from Perkin-Elmer Instruments was used during the experiments. 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, 4, 6, 8 and 10 K min^{-1}. For each compound, similar curves were obtained for every heating rate. The FTIR spectra of the evolved gases were recorded on a Bruker IFS66 spectrometer by transporting them from a Netzsch Thermobalance 209 via a thermostated pipe in the stream of air, in the same experimental condition.

Results and discussion

Liquid crystals with CN and NO_2 radicals have smectic A and nematic mesophases both at heating and cooling, while the one with CF_3 has only smectic mesophase [1].

The standard kinetic procedure, as described by Budrugeac [19], starts with the evaluation of the activation energy by means of isoconversional methods. The complexity of a single stage process can be expressed from the kinetic triplet dependence of the activation energy on the conversion degree. This can be done using the isoconversional methods, known as ‘model-free’ kinetic 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 – (E, A, $f(\alpha)$). If E changes with α, the process is complex and all activation parameters can be obtained only with the help of programs which can discriminate between occurring reactions [20, 21]. Our kinetic investigation is performed by means of two integral isoconversional methods: Flynn–Wall–Ozawa (FWO) [22, 23] and Kissinger–Akahira–Sunose (KAS) [24, 25].

Flynn–Wall–Ozawa (FWO method) – integral linear method

This isoconversional integral linear method, suggested independently by Flynn and Wall [22] and by Ozawa [23] uses Doyle’s approximation [26] of the temperature integral. This method is based on the equation:

$$\ln\beta = \ln\frac{AE}{Rg(\alpha)} - 5.331 - 1.052\frac{E}{RT} \tag{2}$$

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

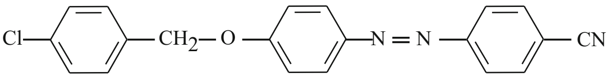
Kissinger–Akahira–Sunose (KAS method) – integral linear method

This isoconversional integral linear method is based on the Coats–Redfern’s approximation [27] of the temperature integral. It was shown that:

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

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

*Thermal analysis of 4-[(4-chlorobenzyl)oxy]-4’-cyano-azobenzene **(1)***



(compound **1**)

Figure 1 shows the thermoanalytical curves (TG, DTG, DTA and DSC) of 4-[(4-chlorobenzyl)oxy]-4’-cyano-azobenzene recorded at 10 K min^{-1}. After melting at 158°C, as can be seen

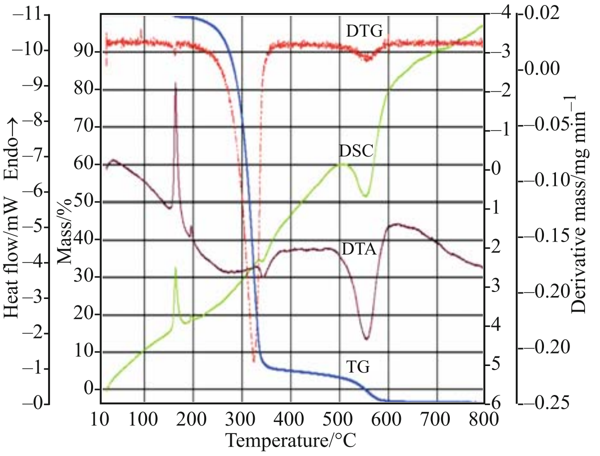


Fig. 1 Thermoanalytical curves for the non-isothermal decomposition of 4-[(4-chlorobenzyl)oxy]-4’-cyano-azobenzene at 10 K min^{-1}

Table 1 DSC thermal parameters of 4-[(4-chlorobenzyl)oxy]-4’-cyano-azobenzene for β=10 K min^{-1}

Change	Max. temp. T_{max}/°C	T. range T_i–T_f/°C	Transferred heat ΔH/kJ kg^{-1}
Melting	158	154–180	100
Phase transition	194	191–200	4
Decomp.	320	305–341	10
Pyrolysis	555	500–592	–632

from these curves, it undergoes a weak endothermic phase transition, followed by an exothermic oxidative decomposition in the temperature range 200–400°C.

The experimental mass loss (Δm_{exp}=95%) of the first step, correlated with the FTIR spectra of the evolved gases (Fig. 2), reveal the entire destruction of the molecule. First, Cl–Ar–CH_3 (Cl–C bond at 700 cm^{-1} and CH_3 bond at 2400 cm^{-1}) is formed, followed by the destabilization of N=N. The remaining 5% correspond to the formation of carbon-based residues from benzene groups, that are burned after 450°C.

In Table 1 are shown the thermal decomposition parameters of compound **1**, obtained under non-isothermal conditions in dynamic air atmosphere.

Figure 3 represents the activation energy of the oxidative decomposition, as a function of conversion degree evaluated by means of FWO and KAS methods. The small differences between the values by using the two methods are due to the different approximations of the temperature integral they are based on. Between 0.2 and 0.9 the activation energy decreases continuously, from 135 to 114 kJ mol^{-1} (FWO method) and from 132 to 111 kJ mol^{-1} (KAS method).

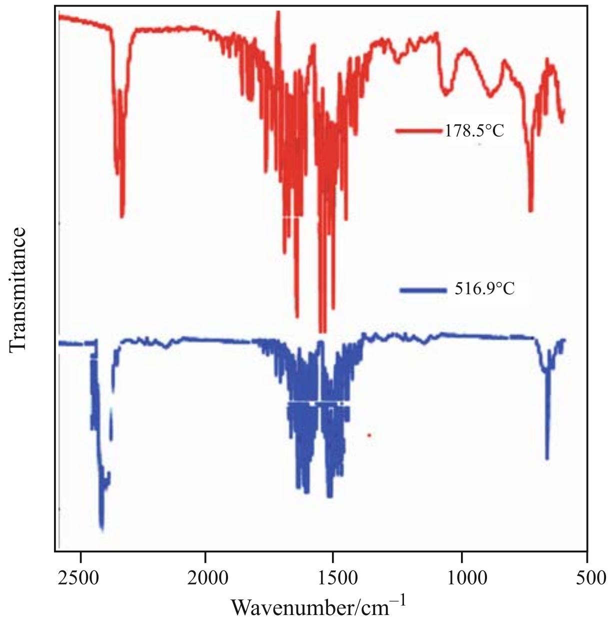


Fig. 2 FTIR spectra of the evolved gases during the oxidative decomposition of 4-[(4-chlorobenzyl)oxy]-4’-cyano-azobenzene **(1)** for β=10 K min^{-1}

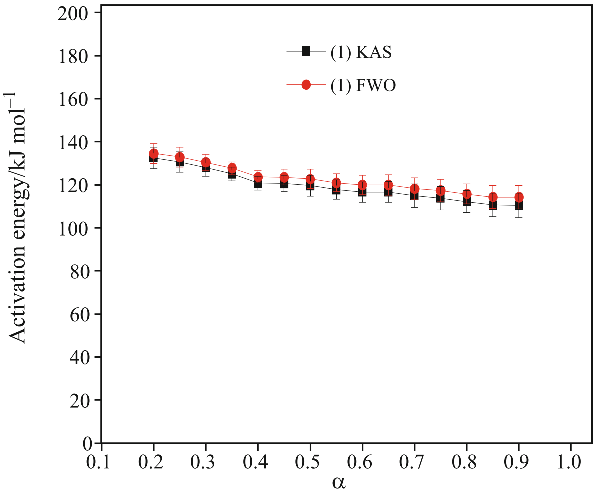
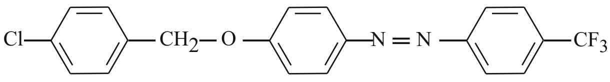


Fig. 3 Activation energy of the non-isothermal oxidative decomposition of 4-[(4-chlorobenzyl)oxy]-4’-cyano-azobenzene **(1)** in dynamic air atmosphere

Thermal analysis of 4-[(4-chlorobenzyl)oxy]-4’-trifluoro-methyl-azobenzene ***(2)***



(compound **2**)

Figure 4 shows the thermoanalytical curves (TG, DTG, DTA and DSC) of 4-[(4-chlorobenzyl)oxy]-4’-triflouromethyl-azobenzene recorded at 10 K min^{-1} in dynamic air atmosphere. After melting at 155°C, as can be seen from these curves, it undergoes an endo-

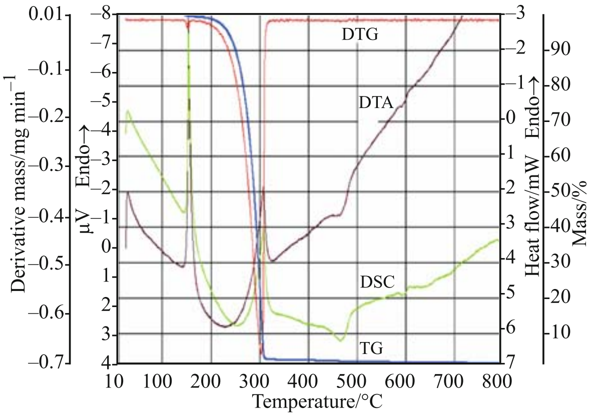


Fig. 4 Thermoanalytical curves for the non-isothermal decomposition of 4-[(4-chlorobenzyl)oxy]-4’-trifluoromethyl-azobenzene **(2)** at 10 K min^{-1}

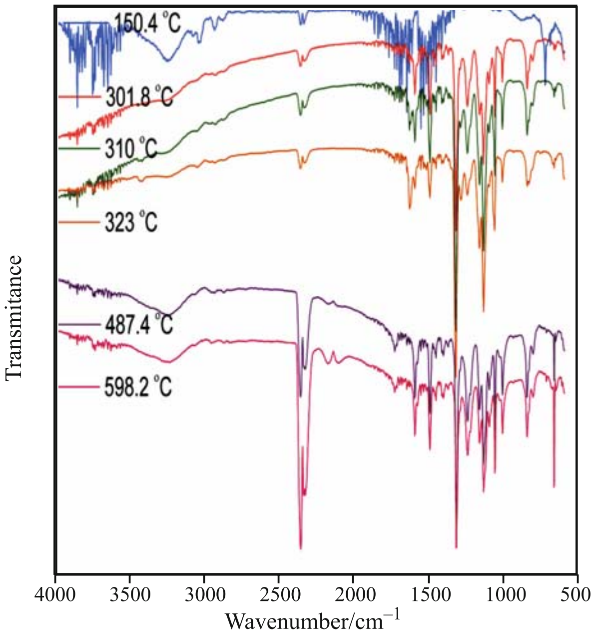


Fig. 5 FTIR spectra of the evolved gases during the evaporation of 4-[(4-chlorobenzyl)oxy]-4'-trifluoromethyl-azobenzene **(2)** for β=10 K min^{-1}

thermic mass loss in the temperature range 200–310°C.

The experimental mass loss (Δm_{exp}=99%), correlated with the FTIR spectra of the evolved gases (Fig. 5), reveal the evaporation of the compound. The FTIR spectrum of the evolved gases is identical with the spectrum of the solid compound **2**. Also, during the recordings, on the external pipe of the thermal analyzer there were found red crystals, similar to the color and appearance of the initial investigated compound. The remaining 1% may correspond to the formation of carbon-based residues from the impurities incorporated during synthesis, which are burned after 470°C.

In Table 2 are presented the thermal parameters of compound **2**, obtained under non-isothermal conditions in dynamic air atmosphere.

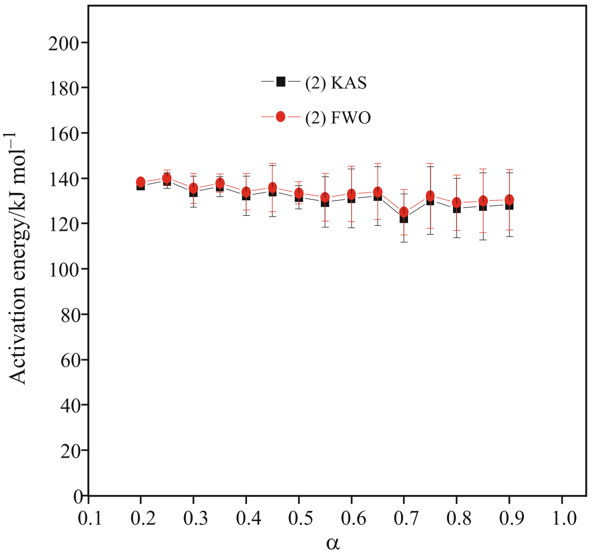


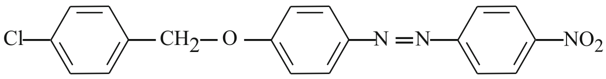
Fig. 6 Activation energy of the non-isothermal evaporation of 4-[(4-chlorobenzyl)oxy]-4'-trifluoromethyl-azobenzene **(2)** in dynamic air atmosphere

Figure 6 represents the activation energy of the evaporation, as a function of conversion degree evaluated by means of FWO and KAS methods. There are no significant differences between the obtained values using the two isoconversional methods, but the errors are higher than in the previous case. Because the process is only a physical one, where no chemical reaction is involved, it is obviously that the activation energy does not change with respect to the evaporation degree of the compound. Between 0.2 and 0.9 the main value of the activation energy is: 133 (FWO method) and 132.5 kJ mol^{-1} (KAS method).

Table 2 DSC thermal parameters of 4-[(4-chlorobenzyl)oxy]-4'-trifluoromethyl-azobenzene **(2)** for β=10 K min^{-1}

Change	Max. temp. T_{max}/°C	T. range T_i–T_f/°C	Transferred heat ΔH/kJ kg^{-1}
Melting	155	144–165	76
Evapor.	300	260–323	105
Pyrolysis	460	431–488	–43

Thermal analysis of 4-[(4-chlorobenzyl)oxy]-4'-nitro-azobenzene (3)



(compound **3**)

Figure 7 shows the thermoanalytical curves (TG, DTG, DTA and DSC) of 4-[(4-chlorobenzyl)oxy]-4'-nitro-azobenzene recorded at 10 K min^{-1} in dynamic air atmosphere. After melting at 188°C, as can be seen from these curves, it undergoes an endothermic phase transition at 241°C, followed by an exothermic mass loss in the temperature range 240–390°C.

The experimental mass loss (Δm_{exp}=75%) of the first step, correlated with the FTIR spectra of the evolved gases (Fig. 8), indicates the formation of benzene-based macromolecular residues. The pyrolysis of the residue starts after 390°C.

In Table 3 there are presented the thermal parameters of compound **3**, obtained under non-isothermal conditions in dynamic air atmosphere.

In order to evaluate the activation energy, the conversion degree of the investigated reaction is required. The estimation of the conversion degree as

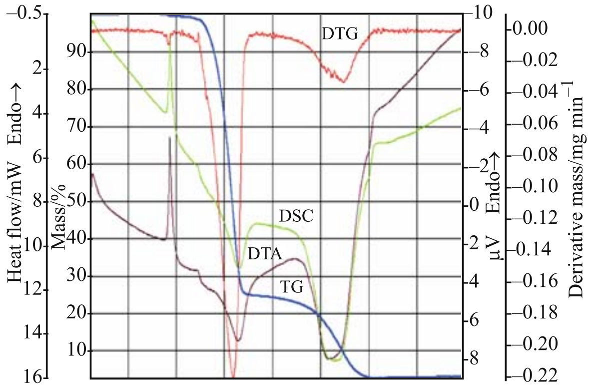


Fig. 7 Thermoanalytical curves for the non-isothermal decomposition of 4-[(4-chlorobenzyl)oxy]-4'-nitro-azobenzene **(3)** at 10 K min^{-1}

Table 3 DSC thermal parameters of 4-[(4-chlorobenzyl)oxy]-4'-nitro-azobenzene for β=10 K min^{-1}

Change	Max. temp. T_{max}/°C	T. range T_i–T_f/°C	Transferred heat ΔH/kJ kg^{-1}
Melting	188	179–194	79
Phase transition	241	235–245	2
Decomp.	335	287–357	–326
Pyrolysis	516	437–608	–3096

function of temperature depends on the TG value considered to be the end of the reaction. For the TG curves corresponding to the decomposition of compound **3**, the end of first reaction step (oxidative decomposition) is overlapped by the beginning of the second reaction step (burning). Thus, the end of the first decomposition stage cannot be accurately determined. In order to avoid this error source, it is preferable to consider the mass loss (%), corresponding to the entire destruction of compound **3**, instead the conversion degree of each reaction. The integral isoconversional methods (FWO and KAS) do not use the conversion degree or any form of conversion function to evaluate the activation energy.

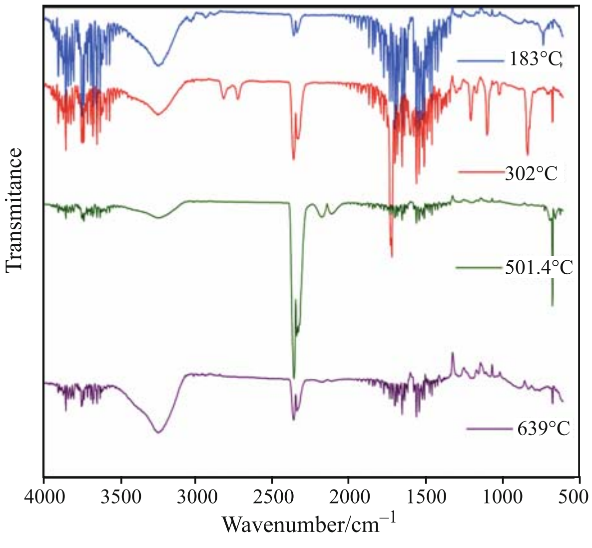


Fig. 8 FTIR spectra of the evolved gases during the oxidative decomposition of 4-[(4-chlorobenzyl)oxy]-4'-nitro-azobenzene **(3)** for β=10 K min^{-1}

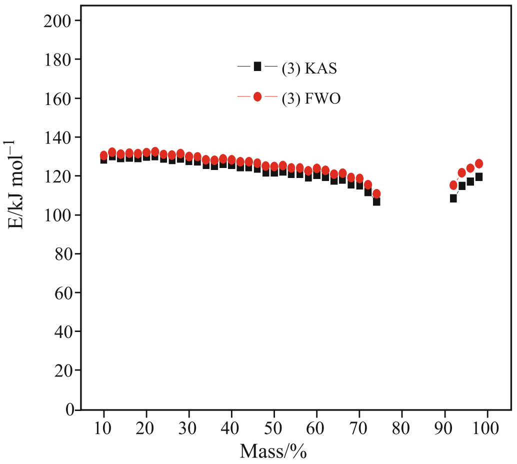


Fig. 9 Activation energy of the non-isothermal decomposition of 4-[(4-chlorobenzyl)oxy]-4'-nitro-azobenzene **(3)** in dynamic air atmosphere

Figure 9 represents the activation energy of the decomposition, as a function of total mass loss (%), evaluated by means of FWO and KAS methods. For the oxidative decomposition, between 10 and 74% mass loss, the activation energy decreases – FWO method: from 132 to 111 kJ mol^{-1}; KAS method: from 129 to 107 kJ mol^{-1}. When overlapping with the second step, the correlation coefficients start to decrease – Fig. 10. After the separation of the steps, the activation energy of the pyrolysis process is increasing.

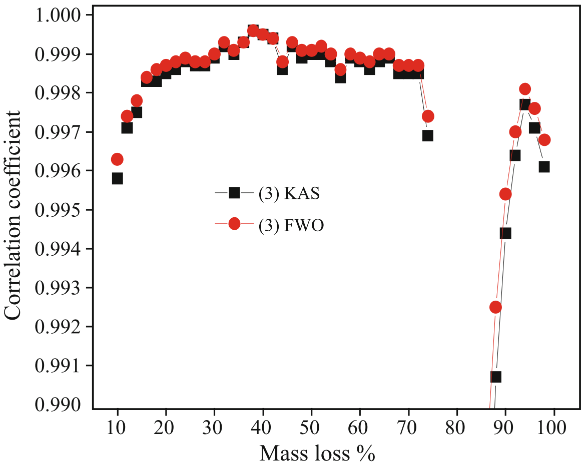


Fig. 10 Correlation coefficients of the activation energy of the non-isothermal decomposition of 4-[(4-chlorobenzyl)oxy]-4'-nitro-azobenzene **(3)** in dynamic air atmosphere

These unreliable results (from 74 to 94%) are also due to the formation of different benzene-based molecules, which undergo different decomposition pathways with respect to different heating rates.

The decomposition kinetics of the same compound, performed in static air atmosphere provides very different results; the gaseous reaction product of the first step was found to be para-nitrophenol (29.15%). The average activation energy, according to our previous paper [2], obtained by FWO method is 76.8 kJ mol^{-1} and by KAS is 71.3 kJ mol^{-1}. This is due to the different pathways, when the reaction conditions are changed (partial pressure of gaseous products).

Conclusions

Part II of the thermal decomposition study, deals with the non-isothermal kinetics of three liquid crystals from the series of new aromatic azomonoethers. The evolved gases were analyzed by FTIR spectroscopy, indicating oxidative decomposition for two of them and evaporation for the third. The activation energies of the first decomposition step were evaluated for each compound by means of isoconversional methods, as function of conversion degree or mass loss percentage. The activation energy of the evaporation process practically remains constant because of no change in composition. For chemical decompositions, during the evolution of the process, the activation energy decreases due to non-formation of intermediate products that necessitate a supplementary energy for their rising. The elimination of other types of gases ($R=NO_2$), requires higher activation energies than those needed in static air atmosphere, when only para-nitrophenol was formed.

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