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THERMAL DECOMPOSITION KINETICS OF SOME AROMATIC AZOMONOETHERS

Part I. Decomposition of 4-[(4-chlorobenzyl)oxy]-4'-nitro-azobenzene

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The non-isothermal kinetic parameters corresponding to the decomposition of 4-[(4-chlorobenzyl)oxy]-4'-nitro-azobenzene were evaluated. The kinetic analysis was performed by means of different multi-heating rates methods: isoconversional ('model-free') (Flynn–Wall–Ozawa), Kissinger–Akahira–Sunose (KAS) and invariant kinetic parameters (IKP) methods associated with the criterion of the independence of activation parameters on the heating rate. The values of the obtained non-isothermal kinetic parameters are in satisfactory agreement.

Keywords: *invariant kinetic parameters method, model-free method, multi-heating rates methods*

Introduction

The critical analysis of single heating rate methods applied to evaluate the non-isothermal kinetic parameters showed that many such procedures lead to relatively uncertain values of the activation energy and pre-exponential factor [1]. Taking into account the impossibility to separate the dependence of the reaction rate on the temperature and on the conversion, almost any conversion function $f(\alpha)$ fits the experimental data with the price of important deviations of the values of the Arrhenius parameters with respect to the true ones [1–6]. Under such conditions it was concluded on the necessity to use many heating rate thermal analysis curves in order to evaluate the non-isothermal kinetic parameters [7–9]. Methods based on thermoanalytical curves recorded at several heating rates are going to be used for the non-isothermal kinetic investigation of the thermal decomposition of 4-[(4-chlorobenzyl)oxy]-4'-nitro-azobenzene.

It is well known that this type of aromatic azomonoethers exhibit dying properties and liquid crystalline nature generating interest as new materials for non-linear optics applications.

Experimental

The aromatic azomonoethers can be obtained by the condensation in alkaline medium of some 4-(phenylazo)phenols with chloromethylated derivatives of chlorobenzene, also known as the Williamson ether synthesis. The investigated compound has smectic A and nematic mesophases both at heating and cooling. The complete synthesis of 4-[(4-chlorobenzyl)oxy]-4'-nitro-azobenzene as well as its liquid crystalline properties have been described elsewhere [10].

The thermogravimetric and DTA curves of the powders obtained through synthesis were recorded on a MOM Hungary Q-1500 D type Paulik–Paulik–Erdey derivatograph, in the temperature range 20–500°C, using ceramic crucibles, at the heating rates of 3.5, 6.2 and 9.6 K min^{-1}, in static air atmosphere. Sample masses ranging from 43.90 to 49.58 mg were used.

Methods for kinetic parameters evaluation

The noticeable weakness of the 'single curve' methods (determination of the kinetic parameters from a single run recorded with one heating rate only) [11–19] has lead to the introduction of 'multi-curve' methods over past few years [20–24]. The use of a method for the kinetic triplet evaluation should be proceeded by the application of an isoconversional method through which the dependence of the activation energy on the conversion degree should be established. If activation energy (E) is independent on conversion degree (α), the kinetic triplet could be evaluated by the discrimination of $f(\alpha)$ from a pre-established set of kinetic mod-

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els [4, 25–29] or by using the IKP method [7] associated with Perez-Maqueda *et al*. criterion [27] (the independence of the activation parameters on the heating rate). If E values changes in time with α, the investigated process is a complex one.

Isoconversional methods

The integral isoconversional (‘model-free’) methods are based on the following integral form of the reaction rate:

$$g(\alpha) \equiv \int_0^{\alpha} \frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^{T_\alpha} \mathrm{e}^{-\frac{E}{RT}} \mathrm{d}T \equiv \frac{A}{\beta} I(E_\alpha, T_\alpha) \qquad (1)$$

where β is the heating rate, A is the pre-exponential factor, $f(\alpha)$ is the differential conversion function, $g(\alpha)$ is the integral conversion function and $I(E_\alpha, T_\alpha)$ represents the temperature integral.

Flynn–Wall–Ozawa method (FWO) [30, 31]

The isoconversional integral method suggested independently by Flynn and Wall [30] and Ozawa [31] uses Doyle’s approximation [32] of the temperature integral. This method is based on the equation:

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

Thus, for α=const., the plot $\ln\beta$ *vs*. $(1/T)$, obtained from curves recorded at several heating rates, should be a straight line whose slope allows to evaluate the activation energy.

Kissinger–Akahira–Sunose method (KAS) [33]

The isoconversional integral method is based on the Coats–Redfern [34] approximation of the temperature integral. It was shown that:

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

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

The invariant kinetic parameters method (IKP) [7]

This method, suggested by Lesnikovich and Levchik [7], is based on the observation that the experimental curve $\alpha(T)$ could be relatively correct described by several conversion functions and that for a single $\alpha(T)$ curve, recorded at a certain heating rate, the values of the activation parameters obtained for different analytical expressions of the conversion function (Table 1 lists the expressions of $f(\alpha)$ and $g(\alpha)$ for the most common kinetic models operating in heterogeneous reactions) are correlated through the compensation effect relation:

$$\ln A = a + bE \qquad (4)$$

where a and b are constant parameters (compensation effect parameters).

In order to apply this method for a given heterogeneous reaction, $\alpha=\alpha(T)$ curves for several heating rates (β_ν, ν=1, 2, 3,…) should be recorded. A set of

Table 1 Analytical forms of differential and integral conversion functions for known solid-state reaction mechanisms

Mechanism	Symbol	$f(\alpha)$	$g(\alpha)$
Reaction order	Fn*	$(1-\alpha)^{n}$	$-\ln(1-\alpha)$, for $n=1$ $\frac{1-(1-\alpha)^{(-n+1)}}{-n+1}$, for $n\neq1$
Nucleation and nuclei growth (Avrami–Erofeev equation)	An	$n(1-\alpha)[-\ln(1-\alpha)]^{(1-1/n)}$	$[-\ln(1-\alpha)]^{1/n}$
Uni-dimensional diffusion (parabolic law)	D1	$\frac{1}{2\alpha}$	α^2
Two-dimensional diffusion	D2	$\frac{1}{-\ln(1-\alpha)}$	$(1-\alpha)\ln(1-\alpha)+\alpha$
Three-dimensional diffusion in a sphere (Jander equation)	D3	$\frac{3(1-\alpha)^{2/3}}{2[1-(1-\alpha)^{1/3}]}$	$[1-(1-\alpha)^{1/3}]^2$
Three-dimensional diffusion (Ginstling–Brouhnstein equation)	D4	$\frac{3}{2[(1-\alpha)^{-1/3}-1]}$	$\left(1-\frac{2\alpha}{3}\right)-(1-\alpha)^{2/3}$
Prout–Tompkins equation	B1	$\alpha(1-\alpha)$	$\ln\left(\frac{\alpha}{1-\alpha}\right)$
Power law	Pn	$n(\alpha)^{(n-1)/n}$	$\alpha^{1/n}$
Exponential law	E1	α	$\ln\alpha$

n=1/2 corresponds to the two-dimensional shift of the interface (R2) and n=2/3 – to the three-dimensional shift of the interface (R3) conversion functions, (f_j,j=1, 2, 3…), is also considered. For each heating rate, β_v, using an integral or differential method, the pairs (A_{vj},E_{vj}) characteristic for the conversion functions are determined. In this work, the values of the activation parameters corresponding to a kinetic model are evaluated using the integral method suggested by Coats and Redfern [34], which is based on the following relation:

$$\ln\frac{g(\alpha)}{T^2}=\ln\frac{AR}{\beta E}-\frac{E}{RT} \qquad (5)$$

Thus, the plot $\ln[g(\alpha)/T^2]$ *vs*. $1/T$ should be a straight line whose parameters allow evaluating the activation parameters.

Using the relation of the apparent compensation effect, for each heating rate, the compensation parameters (a_v,b_v) are determined. The straight lines $\ln A_v$ *vs*. E_v for several heating rates should intersect in a point which corresponds to the true values of A and E. These were called by Lesnikovich and Levchik [7], the invariant activation parameters (A_{inv},E_{inv}). Certain variations of the experimental conditions actually determine a region of intersection in the space $\ln A$, E. For this reason, the evaluation of the invariant activation parameters is performed using the relation:

$$\ln A_{inv}=a_v+b_vE_{inv} \qquad (6)$$

which leads to the supercorrelation relation:

$$a_v=\ln A_{inv}-b_vE_{inv} \qquad (7)$$

Thus, a plot of a_v *vs*. b_v is actually a straight line whose parameters allow evaluation of the invariant activation parameters.

Using the values of A_{inv} and E_{inv} and the integral rate equation (for example Coats–Redfern equation), the numerical evaluation of $g_{inv}(\alpha)$ can be performed. It was pointed out that the values of the invariant conversion function are proportional to their true values [22, 35]. Therefore, IKP method must be associated with the criterion suggested by Perez-Maqueda *et al*. [27] (see below).

The IKP method makes possible the determination of the complete kinetic triplet without discriminating the kinetic model from a pre-established set of conversion functions.

In the last few years, IKP method was used [9, 19, 36–41] to evaluate the kinetic triplet from non-isothermal data.

Perez-Maqueda et al. criterion

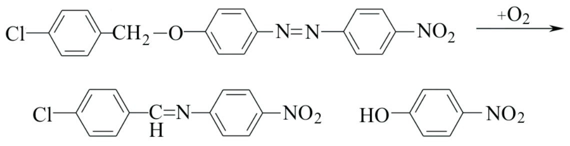
According to the criterion suggested by Perez-Maqueda *et al*. [27], the correct kinetic model corresponds to the independence of the activation parameters on the heating rate. So, if the Coats–Redfern equation written in the form:

$$\ln\frac{\beta g(\alpha)}{T^2}=\ln\frac{AR}{E}-\frac{E}{RT} \qquad (8)$$

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

Results and discussion

Figure 1 shows the TG, DTG and DTA curves of the investigated compound recorded at 3.5 K min^{-1}; similar curves were obtained for all heating rates. After melting at 188°C, as can be seen from these curves it undergoes oxidative decomposition in the temperature range 250–340°C, leading to a solid residue and a gaseous product (*para*-nitrophenol). Mass spectra of the investigated compound indicates the cleavage between $H_2C–O$ [42]. Usually this cleavage is followed by the destabilisation of the double bound N=N. The experimental loss of mass (Δm_{exp}=29.95%) corresponds to the theoretical one (Δm_{theor}=29.15%), leading to para-nitrophenol. The proposed mechanism is correlated to the elementary analysis of the solid residue, where chlorine was found:



The obtained TG, DTG and DTA curves indicate a single reaction thus suitable for getting information concerning decomposition kinetics.

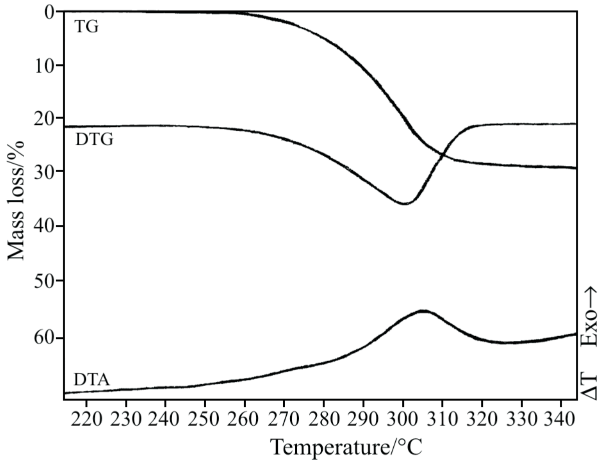


Fig. 1 TG, DTG and DTA curves of 4-[(4-chlorobenzyl)oxy]-4'-nitro-azobenzene for β=3.5 K min^{-1}

The use of Flynn–Wall–Ozawa [30, 31] and Kissinger–Akahira–Sunose [32] methods

Table 2 shows the results of using the isoconversional Flynn–Wall–Ozawa (FWO) and Kissinger–Akahira–Sunose (KAS) methods as values of the activation energy at various conversions.

The differences between the values of the activation energy obtained by using the two methods are due to the different approximations of the temperature integral, which ground them. Beginning with $\alpha=0.8$ the differences exceed 10% which is the admitted error for the activation energy. The mean values of the activation energy calculated for $0.1<\alpha<0.7$ are:

$$\bar{E}_{FWO}=76.8\pm1.6\ \text{kJ mol}^{-1}\quad \bar{E}_{KAS}=71.3\pm1.6\ \text{kJ mol}^{-1}$$

Table 2 Activation parameters obtained by means of FWO and KAS methods

α	FWO		KAS	
	E/kJ mol^{-1}	$-r$	E/kJ mol^{-1}	$-r$
0.1	75.7±4.7	0.99809	70.5±4.9	0.99763
0.2	76.1±5.7	0.99722	70.7±5.9	0.99653
0.3	75.7±5.4	0.99743	70.2±5.6	0.99678
0.4	76.2±7.2	0.99552	70.7±7.5	0.99435
0.5	76.2±6.0	0.99691	70.6±6.2	0.99611
0.6	77.2±7.2	0.99567	71.6±7.5	0.99455
0.7	80.2±7.9	0.99519	74.7±8.2	0.99398
0.8	83.2±9.5	0.99348	77.8±10.0	0.99187
0.9	81.0±14.2	0.98501	75.4±14.9	0.98112

The use of the invariant kinetic parameters (IKP) method [7]

Table 3 lists the values of the activation parameters evaluated by Coats–Redfern method and obtained for different kinetic models and heating rates.

One notes that, even if the correlation coefficients have close values to 1, the differences among the activation parameters corresponding to these models are very large. Thus, using a single α *vs*. T curve recorded at a certain heating rate C–R method and a statistical criterion one cannot find the true kinetic model.

Table 4 lists the values of the compensation parameters corresponding to the data from Table 3. Like in a previous work [22], the calculations were performed for two sets of conversion functions, namely: all considered kinetic models; the functions Fn and An.

As a_v and b_v are correlated by supercorrelation relation (Eq. (7)), one obtains the values of the invariant activation parameters listed in Table 5.

One can see that for both sets of the conversion functions, E_{inv} has appropriate values that are practically equal with E values obtained using isoconversional

Table 3 Values of the activation parameters for the considered conversion functions and the applied heating rates

Conversion function	β=3.5 K min^{-1}			β=6.2 K min^{-1}			β=9.6 K min^{-1}		
	E/kJ mol^{-1}	ln$A$ A/s^{-1}	$-r$	E/kJ mol^{-1}	ln$A$ A/s^{-1}	$-r$	E/kJ mol^{-1}	ln$A$ A/s^{-1}	$-r$
F1	198.0±1.7	36.79	0.99982	197.6±3.5	35.65	0.99920	207.8±5.7	37.31	0.99811
F1.3	211.8±3.7	39.95	0.99925	211.3±5.9	38.69	0.99805	222.1±8.3	40.40	0.99651
R2	176.6±2.5	31.90	0.99949	176.4±1.3	30.97	0.99986	185.7±2.5	32.53	0.99954
R3	183.5±1.7	33.48	0.99979	183.2±1.5	32.48	0.99983	192.8±3.3	34.07	0.99925
A0.5	405.1±3.4	81.67	0.99983	404.6±7.1	78.91	0.99923	425.3±11.5	81.78	0.99819
A1.5	128.9±1.1	21.64	0.99982	128.5±2.3	21.04	0.99917	135.3±3.8	22.30	0.99803
A2	94.4±0.8	13.97	0.99981	94.0±1.8	13.64	0.99913	99.0±2.8	14.69	0.99794
A2.5	73.7±0.7	9.30	0.99980	73.3±1.4	9.14	0.99909	77.3±2.3	10.07	0.99785
A3	59.9±0.5	6.15	0.99980	59.5±1.2	6.09	0.99905	62.8±1.9	6.94	0.99774
D1	324.1±10.2	63.33	0.99755	324.3±7.0	61.34	0.99885	341.4±5.8	63.84	0.99928
D2	348.4±7.0	68.13	0.99898	348.3±3.9	65.90	0.99969	366.5±4.3	68.53	0.99966
D3	376.2±3.3	72.93	0.99980	376.0±3.1	70.46	0.99983	395.3±6.7	73.19	0.99928
D4	357.6±5.7	68.72	0.99936	357.7±3.0	66.46	0.99983	376.1±4.6	69.07	0.99962

Table 4 Compensation effect parameters

β/K min^{-1}	All the conversion functions			All the conversion functions – {D1, D2, D3, D4}		
	a_v, A/s^{-1}	b_v/mol kJ^{-1}	$-r$	a_v, A/s^{-1}	b_v/mol kJ^{-1}	$-r$
3.54	–5.991±0.493	0.2130±0.0019	0.99955	–6.681±0.137	0.2186±0.0007	0.99996
6.215	–5.506±0.492	0.2052±0.0019	0.99951	–6.192±0.135	0.2110±0.0007	0.99996
9.615	–5.059±0.492	0.2009±0.0018	0.99954	–5.749±0.137	0.2063±0.0006	0.99996

Table 5 Invariant kinetic parameters

	All the conversion functions	All the conversion functions – {D1, D2, D3, D4}
E_{inv}/kJ mol^{-1}	75.7±10.9	74.2±9.1
lnA_{inv}, A/s^{-1}	10.11±2.25	9.53±1.92
$-r$	0.98977	0.99263

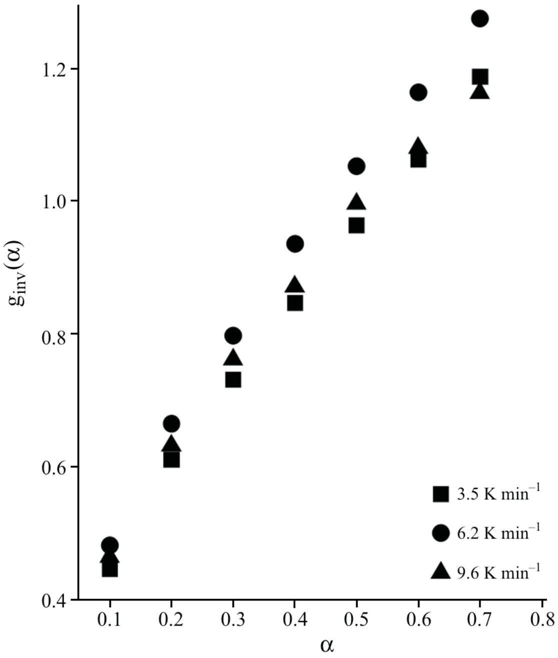


Fig. 2 Dependence of $g_{inv}(\alpha)$ on α

methods. Nevertheless, a noticeable difference between A_{inv} for the two considered sets should be observed.

Using the values of E_{inv} and A_{inv} and the Coats–Redfern equation (Eq. (5)), the numerical values of $g_{inv}(\alpha)$ were calculated. The obtained results (Fig. 2) show a weak dependence of $g_{inv}(\alpha)$ on the heating rate, which is due to the inherent errors in the activation parameters determination.

Use of Maqueda–Criado–Gotor–Malek [27] method

From Table 3 one can see that the activation energy values corresponding to the conversion function A2.5 are practically independent on the heating rate and close to those determined by isoconversional methods.

Figure 3 shows the straight lines {ln[$\beta g(\alpha)/T^2$], $1/T$} for the conversion functions A2.5 and F1.3. In order to check this observation, we applied the Perez-Maqueda *et al.* criterion. The inspection of this figure shows that: (1) for each kinetic model the slopes of these straight lines do not depend on the heating rate; (2) unlike for F1.3 kinetic model, the intercept of these lines corresponding to A2.5 kinetic model is independent on β. Consequently, the Perez-Maqueda *et al.* criterion is fulfilled for A2.5 kinetic model. From the parameters of this straight line, one obtains:

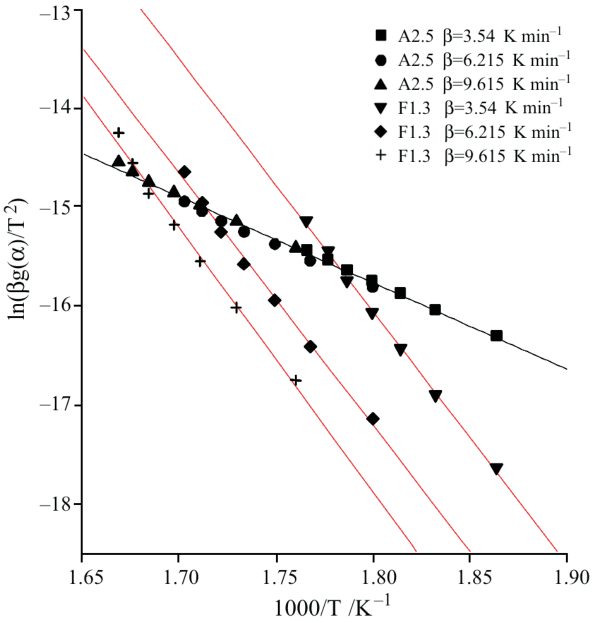


Fig. 3 The Perez-Maqueda *et al.* straight lines

$$E=72.5\pm1.4\ \text{kJ mol}^{-1} \quad \ln A,\ \text{A/s}^{-1}=8.995\pm0.290$$

These values are in agreement with those obtained by IKP method.

Although the conversion function corresponds to a nucleation model, the description of our experimental data by this function does not necessary mean that the reaction presents the mechanism for witch the conversion function was originally derived. In fact, A2.5 model belongs to the empirical expression of the conversion function suggested by Šesták and Berggren [43].

Conclusions

A non-isothermal kinetic investigation of the decomposition of 4-[(4-chlorobenzyl)oxy]-4’-nitroazobenzene was carried out.

The use of methods based on multiple-heating rates led to values of the kinetic parameters in satisfactory agreement whit each other.

These values could be used for the prediction of the reaction system change in time, in other conditions than those in which the experiments were performed.

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