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The kinetic analysis of non-isothermal carisoprodol reaction in nitrogen atmosphere using the invariant kinetic parameters method

Laila Tosson Kamel

Narcotic Department, National Center for Social and Criminal Research, Zamalek, Giza, 11561, Egypt

**Corresponding author at: Narcotic Department, National Center for Social and Criminal Research, Zamalek, Giza, 11561, Egypt. Tel.: +2.02.33461440. Fax: +2.02.33036069. E-mail address: lailatosson.1160@hotmail.com (L.T. Kamel).*

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ABSTRACT

The non-isothermal kinetic parameters corresponding to the thermal decomposition of carisoprodol under nitrogen atmosphere was investigated at four different heating rates 5, 10, 15 and 20 °C/min. The activation energy was determined using three linear isoconversional methods, Friedman, Flynn-Wall-Ozawa and Kissinger-Akahira-Sunose. Results showed good agreement with each other. Invariant kinetic parameters (IKP) method was applied in the conversion range of $0.2 \le \alpha \le 0.8$ for the determination of the kinetic triplet. E_{inv}= 95.81 kJ/mol, A_{inv} = 2.275×10^7 1/min and the decomposition mechanism corresponds to nucleation and growth, following the Avrami-Erofeev model, A1.5, as the kinetic model. The Perez-Maqueda *et al.* criterion associated with the independence of activation parameters on the heating rate (by means of Coats-Redfern and Flynn-Wall equation) confirmed the model.

1. Introduction

Carisoprodol (Soma), *N*-isopropoyl-2-methyl-2-propyl-1,3-propanediol dicarbamate, a nervous system depressant with a well-known mechanism of pharmacologic action, is categorized as muscle relaxant (Figure 1). It is used for the treatment of acute, painful musculoskeletal conditions secondary to muscle injury or spasm or chronic diseases such as multiple sclerosis. Carisoprodol is a synthetic carbamate, once absorbed, is rapidly metabolized to meprobamate, a central nervous system (CNS) depressant with sedative hypnotic properties and is indicated for the treatment of anxiety [1]. A number of reports indicated that carisprodol is abused upon in combination with tramadol (Ultam) to obtain psychotropic effect [2]. Also carisoprodol causes severe driving impairment when the combined plasma concentrations of carisoprodol and meprobamate are 10 µg/mL or greater [3].

Thermal analytical techniques are well-established techniques for investigating the stability and decomposition of organic pharmacologically active compounds used in medicine to characterize their physical and chemical properties. Thermal analytical techniques may provide new information about the temperature and energy associated with events, such as melting, oxidation and reduction reactions, glass transition, boiling, sublimation, decomposition, crystallization, or gel to liquid. They can also provide important information regarding storage and stability of pharmaceuticals [4].

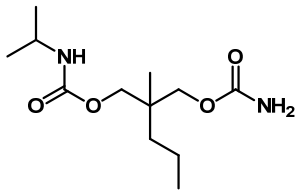

Figure 1. Structural formula of carisoprodol.

TG, DTG, and DTA, were used by many authors to study the thermal decomposition of hundreds pharmacologically active compounds, e.g. glycine [5], Folnak [6], imipramine, trimipramine [7] and anti-tuberculosis drugs [8]. The invariant kinetic parameters (IKP) method was applied to study thermal decomposition of few pharmacologically active compounds, e.g. *N*,*N*'-*bis*(3,5-di-*t*-butylsalicylidene)-1,3-ethylene-diamine metal complexes [9] and *N*-(salicylidene)-*L*-leucine [10].

The invariant kinetic parameters method was rarely applied to study the thermal decomposition of active pharmacological organic compounds to calculate the kinetic triplet corresponding to the process.

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So, the main objective of this paper is to show the usefulness of the IKP method for determining both the activation kinetic parameters as well as the kinetic model in comparison with conventional kinetic methods.

2. Experimental

2.1. Materials

Carisoprodol was supplied by Minapharm Pharmaceuticals in a pure grade.

2.2. Instrumentation

Thermal analysis measurements (TG, DTG, and DTA) were obtained using Shimadzu TGA-50 thermobalance. The measurements were performed with dynamic nitrogen furnace atmosphere at a flow rate of 20 mL/min. Samples of masses 4.311, 3.310, 3.284 and 3.979 mg contained in an alumina crucible were heated starting from room temperature up to 400 °C with heating rates 5, 10, 15 and 20 °C/min, respectively.

2.3. The methods used to evaluate the kinetic parameters

All kinetic analyses of non-isothermal data are based on the rate equation (1)

$$\frac{d\alpha}{dt} \cong \beta\frac{d\alpha}{dT} = A\exp\left(-\frac{E}{RT}\right)f(\alpha) \quad (1)$$

where α is the degree of conversion, f (α) is the differential conversion function, β is the linear heating rate (°C/min), A is the pre-exponential factor (1/min), T is the absolute temperature (K), R is the gas constant (J/mol.K), E is the activation energy (kJ/mol) and t is the time (min).

2.4. Isoconversional methods

Budrugeac [11] proposed that the kinetic triplet (E, A and $f(\alpha)$) evaluation kinetic analysis must begin with the evaluation of the activation energy dependence on the conversion degree.

The effect of different temperature regimes upon the thermal behavior of the investigated compounds can provide kinetic parameters indicating change in the reaction pathway and thus a more complex process. When E does not depend on α, only a single reaction is involved, a unique kinetic triplet being expected to describe it. If E changes with α the process is complex.

The isoconversional methods are considered the most reliable methods for calculating E and E vs. α dependence of thermally activated reactions [12,13], without the knowledge or assumption of kinetic model (model-free).

Pre-exponential factor and conversion function cannot be determined using isoconversional methods. If the isoconversional activation energy, E_{iso}, remains constant, no variation of the pre-exponential factor should be encountered. Thus, the invariant activation parameters (E_{inv} and A_{inv}) may be obtained by relating the apparent activation parameters to the compensation effect formalism [14].

The isoconversional methods, are based on multiple heating rates experiments, they are the most utilized methods that enable determination of activation energy, E, directly from experimental α-T data. α is the degree of conversion, $\alpha = \frac{m_o - m_t}{m_o - m_f}$, m_t represents the mass of the sample at arbitrary time t (or temperature T), whereas m_o and m_f are the mass of the sample at the beginning and at the end of the process, respectively. Isoconversional methods are classified to linear (when the activation energy is evaluated from the slope of a straight line) and non-linear (when the activation energy is evaluated from a specific minimum condition). In our work we used linear isoconversional methods, Friedman [15] (FR), Flynn-Wall-Ozawa [16,17] (FWO), and Kissinger-Akahira-Sunose [18,19] (KAS) methods.

FR method, a linear differential method based on Equation 2.

$$\ln\frac{d\alpha}{dt} \equiv \ln\beta\frac{d\alpha}{dT} = \ln A f(\alpha) \frac{E}{RT} \quad (2)$$

FWO method, a linear integral method based on Equation 3.

$$\ln\beta = \ln\frac{AE}{Rg(\alpha)} - 5.331 - 1.052\frac{E}{RT} \quad (3)$$

KAS method, a linear integral method based on Equation 4.

$$\ln\frac{\beta}{T^2} = \ln\frac{AR}{Eg(\alpha)} - \frac{E}{RT} \quad (4)$$

where α is the conversion degree, A is the pre-exponential factor, E is the activation energy, g(α) is the integral conversion function and R is the universal gas constant.

For α = constant, the plot of ln (dα/dt) *vs.* 1/T , or ln β *vs.* 1/T, or ln (β/T^2) *vs.* 1/T from the experimental thermogravimetric curves recorded for several constant-heating rates, should be a straight line, the activation energy E_{iso} being evaluated from these slopes, by means of FR, FWO, and KAS method, respectively.

2.5. The invariant kinetic parameters method

The invariant kinetic parameters (IKP) method [14,20] is based on the observation that the same experimental curve α = α(T) can be described relatively correctly by several functions of conversion and for a single α = α(T) curve. The values of activation parameters obtained for various analytical forms of g(α) are correlated through an apparent compensation affect, where α^* and β^* are constant parameters (compensation effect parameters).

$$\ln A = \alpha^* + \beta^* E \quad (5)$$

To apply this method for a given heterogeneous reaction, α = α(T) curves for several heating rates(β_υ, υ = 1, 2, 3, …) should be recorded . A set of conversion functions, g_j where j = 1, 2, 3, …. are also considered. The differential and integral functions of conversion used in this work are listed in Table 1. For each heating rate β_υ, using and integral or differential method the pairs of ($A_{\upsilon j}$ and $E_{\upsilon j}$), characteristic for each conversion function , are determined. In this work, the Coats and Redfern [21] (CR) method was used to integrate Equation 1. It leads to the following relation:

$$\ln\left[\frac{g_j(\alpha_{\upsilon i})}{T_{\upsilon i}^2}\right] = \ln\left(\frac{A_{\upsilon j} R}{\beta_\upsilon E_{\upsilon j}}\right) = \frac{E_{\upsilon j}}{RT_{\upsilon i}} \quad (6)$$

where i is a data point, j is the number of the conversion function. A plot $\ln\left[\frac{g_j(\alpha_{\upsilon i})}{T_{\upsilon i}^2}\right]$ *vs.* $\frac{1}{T_{\upsilon i}}$ for a given analytical form of g(α) should be a straight line whose slope and intercept allow the evaluation of activationenergy and pre-exponential factor, respectively.

Nineteen activation energies ($E_{\upsilon i}$) and pre-exponential factors ($A_{\upsilon i}$) are calculated using the CR method.

Using the relation of the apparent compensation effect, for each heating rate the compensation parameters (α_υ^* and β_υ^*) are determined. The straight lines ln A_υ *vs.* E_υ for several heating rates should intersect at a point that corresponds to the true values of A and E. These are called by Lesnikovich and Levchik [14,20] as the invariant activation parameters (A_{inv} and E_{inv}). Certain variations of the experimental conditions actually determine a region of intersection in the ln A, E space.

Table 1. Algebric expression for the most frequently used mechanisms of solid state process.

No		Symbol	Differential form $f(\alpha)$	Integral form $g(\alpha)$
Sigmoidal curves (Nucleation and nuclei growth, Avrami-Erofeev equation)				
1	N and G (n=1)	A1	(1-α)	[-ln(1-α)]
2	N and G (n=1.5)	A1.5	$(3/2)(1-\alpha)[-ln(1-\alpha)]^{1/3}$	$[-\ln(1-\alpha)]^{2/3}$
3	N and G (n=2)	A2	$2(1-\alpha)[-ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
4	N and G (n=3)	A3	$3(1-\alpha)[-ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
5	N and G (n=4)	A4	$4(1-\alpha)[-ln(1-\alpha)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$
Deceleration curves				
6	Diffusion, 1D	D1	$1/(2\alpha)$	α^2
7	Diffusion, 2D	D2	$1/-(ln(1-\alpha))$	$(1-\alpha)ln(1-\alpha)+\alpha$
8	Diffusion, 3D	D3	$1.5[(1-\alpha)^{-1/3}-1]$	$(1-2\alpha/3)-(1-\alpha)^{2/3}$
9	Diffusion, 3D	D4	$[1.5(1-\alpha)^{2/3}][1-(1-\alpha)^{1/3}]^{-1}$	$[1-(1-\alpha)^{1/3}]^2$
10	Diffusion, 3D	D5	$(3/2)(1+\alpha)^{2/3}[(1+\alpha)^{1/3}-1]^{-1}$	$[(1+\alpha)^{1/3}-1]^2$
11	Diffusion, 3D	D6	$(3/2)(1+\alpha)^{4/3}[1/(1+\alpha)^{1/3}-1]^{-1}$	$[1/(1+\alpha)^{1/3}-1]^2$
12	Contracted geometry shape (Cylindrical symmetry)	R2	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$
13	Contracted geometry shape (Sphere symmetry)	R3	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$
Acceleration curves				
14	Power law (n=2)	P2	$2\alpha^{1/2}$	$\alpha^{1/2}$
15	Power law (n=3)	P3	$1.5\alpha^{2/3}$	$\alpha^{1/3}$
16	Power law (n=4)	P4	$4\alpha^{3/4}$	$\alpha^{1/4}$
17	Power law (n=2/3)	P3/2	$2/3\alpha^{-1/2}$	$\alpha^{3/2}$
18	Mample power law (n=3/2)	P2/3	$3/2\alpha^{1/3}$	$\alpha^{2/3}$
19	Mample power law (n=4/3)	P3/4	$4/3\alpha^{-1/3}$	$\alpha^{3/4}$

For this reason, the evaluation of the invariant kinetic parameters is performed using the super correlation equation:

$$\ln A_{\text{inv}} = \alpha_v^* + \beta_v^* E_{\text{inv}} \quad (7)$$

which leads to the super correlation relation:

$$\alpha_v^* = \ln A_{\text{inv}} - \beta_v^* E_{\text{inv}} \quad (8)$$

Thus, a plot α_v^* *vs.* β_v^* is actually a straight line whoseparameters allow evaluation of the invariant activationparameters. Although the IKP method aims to determine the invariant parameters independently of the kinetic model, comparing them to those obtained using other methods (the CR method, isoconventional methods, ... etc.) also allows us to decide which kinetic model best describes the process. The IKP method can be used only if *E* is independent of α [22].

2.6. Perez-Maqueda et al. criterion

The IKP method must be associated with the criterion suggested by Perez-Maqueda *et al.* [23], which suggests that the appropriate 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 should provide both the same constant activation energy as well as the pre-exponential factor.

Coats-Redfern equation written in the form:

$$\ln \frac{\beta\, g(\alpha)}{T^2} = \ln \frac{AR}{E} - \frac{E}{RT} \quad (9)$$

and Flynn-Wall equation written in the form:

$$\ln(\beta\, g(\alpha)) + 5.331 = \ln \frac{AE}{R} - 1.052 \frac{E}{RT} \quad (10)$$

A plot of $\ln(\beta\, g(\alpha)/T^2)$ *vs.* 1/T or $\ln(\beta\, g(\alpha)) + 5.331$ *vs.* 1/T corresponding to all the heating rates must lie on the same straight line.

3. Results and discussion

Thermal decomposition of carisoprodol was studied starting from room temperature up to 400 °C in nitrogen atmosphere. Figure 2 shows the TG and DTG curves. TG curves are shifted to higher temperatures as the heating rates increases from 5 to 20 °C/min, the shapes of curves are quite similar. TG curves show no mass loss up to 145 °C. As the temperature increases, the TG curves of carisoprodol exhibit a total mass loss from 145 to 250-280 °C. The temperature corresponding to the maximum reaction rate, T, for the thermal decomposition of carisoprodol was determined from the DTG curves as being 237.55, 242.22, 249.35, and 268.21 °C for heating rates corresponding to 5, 10, 15 and 20 °C/min, respectively.

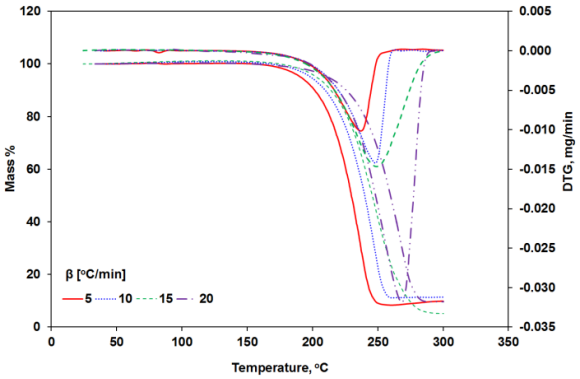


Figure 2. TG-DTG curves for the thermal decomposition of carisoprodol in nitrogen atmosphere at different heating rates (5, 10, 15, and 20 °C/min).

Figure 3 shows the DTA curves of carisoprodol at different heating rates (5, 10, 15 and 20 °C/min). DTA curves exhibit two endothermic peaks. The first peak, at 93 °C, which is attributed to the melting point of carisoprodol, at higher temperatures, a second broad endothermic peak is shown which is related to the total mass loss decomposition of carisoprodol.

It is clear from Figures 2 and 3 that carisoprodol decomposes in a single step with a total mass loss.

The one step decomposition of carisoprodol, a straight chain compound containing amide function, is due to the breakdown of the secondary amide bond which is weaker than the primary amide bond which has lone electron pairs of the carbonyl oxygen and the adjacent nitrogen which stabilize the primary amide group [24].

Table 2. Activation energies and correlation coefficient of carisoprodol obtained by FWO, KAS and FR.

Conversion	FWO method		KAS method		FR method	
	Activation energy	Correlation coefficient	Activation energy	Correlation coefficient	Activation energy	Correlation coefficient
	E_{iso} (kJ/mol)	r^2	E_{iso} (kJ/mol)	r^2	E_{iso} (kJ/mol)	r^2
0.2	94.866	0.999	95.399	0.993	93.519	0.983
0.3	94.919	0.995	94.331	0.973	93.219	0.993
0.4	97.825	0.993	97.797	0.982	93.067	0.997
0.5	98.557	0.998	97.979	0.973	94.147	0.966
0.6	97.683	0.998	95.787	0.976	92.130	0.961
0.7	97.572	0.996	95.832	0.969	92.023	0.909
0.8	95.623	0.999	95.250	0.989	91.918	0.994
Mean	96.864		96.053		92.432	

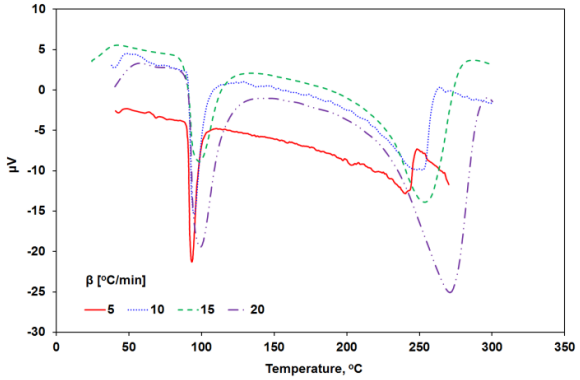


Figure 3. DTA curves for the thermal decomposition of carisoprodol in nitrogen atmosphere at different heating rates (5, 10, 15, and 20 °C/min).

The kinetics of non-isothermal decomposition process of carisoprodol was analyzed by isoconversional methods (FR, KAS, and FWO). These methods are based on multiple heating rates experiments, and no kinetic model is needed before activation energy is calculated.

Figure 4 shows the isoconversional activation energy, E_{iso} changes with α, is evident that the values of activation energies obtained by the FR method are little lower than the values of activation energies obtained by the FWO and KAS methods. Regardless of the calculation procedure used, the activation energy remains practically constant in the $0.20 \leq \alpha \leq 0.80$ conversion range. This α range was selected because, although theoretical curves are free of error, experimental curves have experimental error mainly for low and high values of α, and therefore kinetic studies are very often limited to such a range [23].The average values of E_{iso} is 96.86±1.92 kJ/mol for KAS, 96.05±2.10 kJ/mol for FWO, and 92.43±2.30 kJ/mol for FR methods. Activation energies calculated from the slopes were tabulated in Table 2.

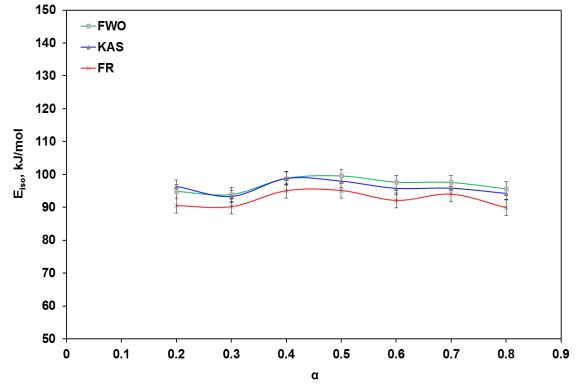


Figure 4. Dependence of the activation energy (E_{iso}) on the degree of conversion (α) determined using the FR, KAS, and FWO methods for the thermal decomposition of carisoprodol.

It is clear that the average value of E_{iso} obtained by the FR method is lower than corresponding average values of E_{iso} obtained using the FWO and KAS methods. These differences could be due to the approximation of the temperature integral that was used in the derivations of the relations that ground the FWO and KAS methods and because of this fact the FWO and KAS methods involve a systematic error in E that does not appear in the FR method [25]. Thus, the activation energies obtained as a function of the conversion from the FR method are more reliable than those obtained from the FWO and KAS methods.

It is clear from Figure 4 that E_{iso} does not depend on α, therefore the investigated process is simple (overall single-stage) and can be described by unique kinetic triplet and the IKP method can be used for evaluation of the true kinetic triplet of the investigated process.

In order to obtain the invariant (true) activation parameters (E_{inv} and ln A_{inv}), CR method (Equation 6) was used to calculate the apparent activation energies and apparent pre-exponential factors corresponding to each heating rate (5, 10, 15 and 20 °C/min). Results are presented in Table 3. Values of ln A and E from g(α) show correlation coefficient $r^2 > 0.950$ at all heating rates.

From Table 3 it is clear that the only Avrami-Erofeev model, A1.5, give values of linear correlation coefficient r^2 higher than 0.990 at all considered heating rates. Comparing the activation energy calculated by isoconversional methods with that in the table, it is clear that at rate 5 °C/min the calculated E = 96.64 kJ/mol whereas that E_{iso} = 96.72 and 96.05 kJ/mol for KAS and FWO methods, respectively. While at rate 10 °C/min the E value equal 94.86 kJ/mol which is in good agreement to the activation energy values obtained by the isoconversional methods. The value of E calculated for rates 15, and 20 °C/min equal 91.94 and 90.74 kJ/mol which is in good agreement to the activation energy values obtained by FR method. The obtained values of activation energies for A2, A3 and A4 models are considerably lower than the value of activation energy obtained by the chosen isoconversional methods. Therefore, the Avrami-Erofeev kinetic model, A1.5, had best agreement with the values obtained by KAS, FWO and FR methods.

A plot of ln A *vs.* E is shown in Figure 5, it is clear that the straight lines corresponding to each heating rate intersect in a region not in a point (isoparametric point) due to certain variations of experimental conditions. This point (isoparametric point) corresponds to the true values of the activation energy and pre-exponential factor. For this reason the evaluation of IKP is performed using super correlation (Equation 5).The values of compensation parameters (α^* and β^*) were calculated from the intercepts and the slopes of the straight lines for each heating rate. Results are shown in Table 4.

The plot of α^* and β^* shown in Figure 6 for the studied heating rates shows a straight line with r^2 = 0.992 which allows the determination of the invariant activation parameters, E_{inv} = 95.81 kJ/mol and A_{inv} = 2.275×10^7 1/min. Thus, the value of activation energy (E_{inv}) practically equals the value of that obtained by means of isoconversional methods for $0.2 \leq \alpha \geq 0.8$.

Table 3. The kinetics parameters for the thermal decomposition ofcarisoprodol in nitrogen atmosphere obtained for each kinetic function .

Symbol	Rate 5 °C/min			Rate 10°C/min			Rate 15 °C/min			Rate 20 °C/min		
	E (kJ/mol)	ln *A*	r^2	E (kJ/mol)	ln *A*	r^2	E (kJ/mol)	ln *A*	r^2	E (kJ/mol)	ln *A*	r^2
A1	140.95	32.38	0.992	126.23	27.72	0.994	122.41	25.75	0.982	118.81	22.23	0.983
A1.5	96.63	18.57	0.993	94.86	10.79	0.995	91.94	13.68	0.990	90.74	12.21	0.993
A2	72.47	12.58	0.992	63.11	10.55	0.992	56.20	6.08	0.987	50.80	8.63	0.985
A3	58.31	6.47	0.992	42.07	5.32	0.995	35.40	4.58	0.972	30.87	4.19	0.990
A4	36.23	3.33	0.992	30.15	2.17	0.994	28.05	2.20	0.972	25.31	1.05	0.989
D1	237.74	50.57	0.985	200.60	41.20	0.959	130.15	32.75	0.972	125.15	29.50	0.954
D2	264.76	55.25	0.990	210.62	43.26	0.961	190.57	38.03	0.972	180.03	38.82	0.975
D3	85.22	10.62	0.979	66.86	10.05	0.958	60.43	8.90	0.972	58.38	9.22	0.965
D4	88.22	15.98	0.972	70.86	10.05	0.954	65.43	9.63	0.972	38.38	9.91	0.959
D5	230.18	47.98	0.985	195.01	35.89	0.974	194.23	32.44	0.972	180.99	30.50	0.985
D6	300.95	69.47	0.984	285.92	62.26	0.975	270.32	52.94	0.987	315.14	58.47	0.976
R2	45.51	4.27	0.985	33.43	2.04	0.962	50.21	2.47	0.982	30.19	2.00	0.987
R3	45.51	4.27	0.985	55.15	6.38	0.984	40.32	7.11	0.982	50.05	6.94	0.975
P2	64.86	9.37	0.983	35.43	2.76	0.987	30.21	2.43	0.972	29.36	2.00	0.979
P3	45.57	4.27	0.985	33.43	2.76	0.985	30.21	2.73	0.972	22.02	2.15	0.987
P4	35.437	1.64	0.982	22.56	2.150	0.986	22.66	0.56	0.972	119.15	25.43	0.988
P3/2	184.59	38.62	0.985	142.24	27.86	0.988	135.97	26.61	0.972	66.38	8.96	0.987
P2/3	81.11	14.35	0.985	66.86	10.79	0.985	60.43	9.63	0.972	74.68	10.71	0.974
P3/4	91.29	17.81	0.985	75.22	12.74	0.985	67.98	11.36	0.972	63.45	11.29	0.985

Table 4. Values of compensation effect parameters at different heating rates for the thermal decomposition of carisoprodol in nitrogen atmosphere.

B (°C/min)	α* (1/min)	β* (mol/kJ)	r^2
5	-6.214	0.242	0.991
10	-5.118	0.229	0.986
15	-3.695	0.213	0.961
20	-2.208	0.201	0.962

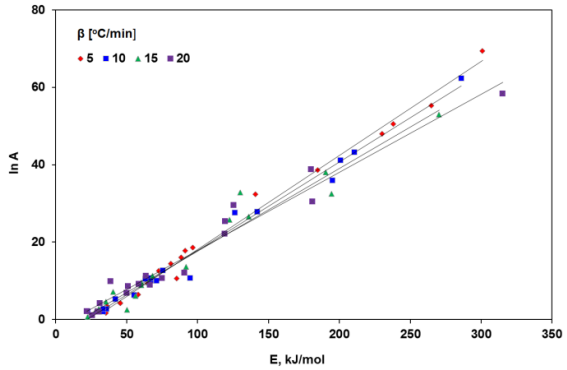


Figure 5. Compensation effect observed between apparent activation energy and pre-exponential factor for the thermal decomposition of carisoprodol at different heating rates.

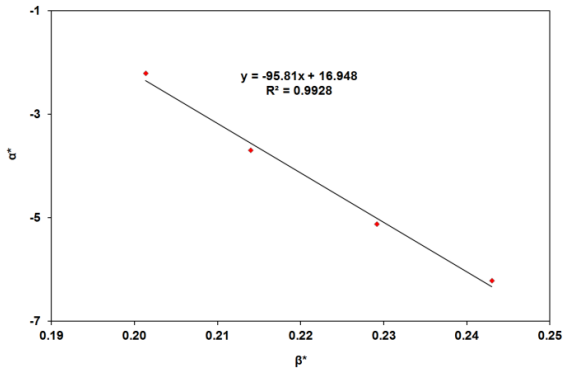
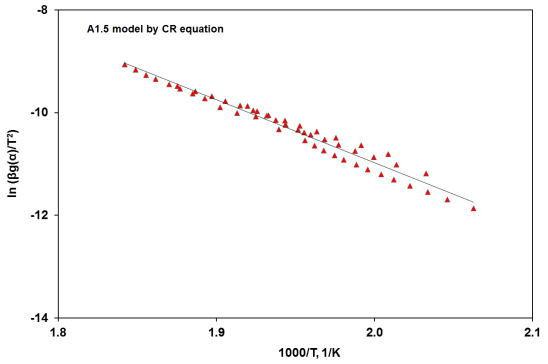
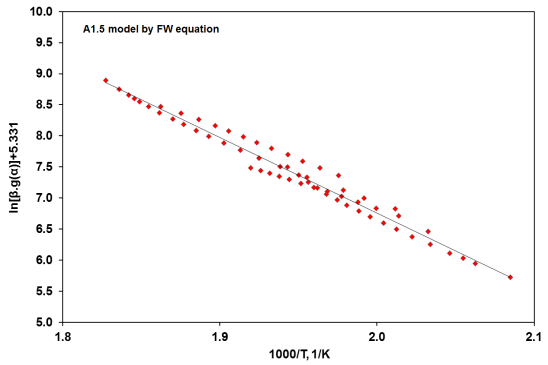


Figure 6. Verifying the supercorrelation relation.

In order to confirm the appropriate kinetic model, Perez-Maqueda *et al.* [23] criterion was applied for the Avrami-Erofeev kinetic model, A1.5. The best overlapping of the $\ln\frac{\beta\, g(\alpha)}{T^2}$ *vs.* 1/T for CR plot, (Equation 9) and $\ln(\beta\, g(\alpha)) + 5.331$ *vs.* 1/T, for FW plot, (Equation 9) points, corresponding to the different heating rates was obtained, as shown in Figure 7a and b, all the points lie on the same straight line. Where the values of activation parameters, E = 98.856 kJ/mol and A = 6.147×10^7 1/min for CR plot, and E = 97.234 kJ/mol and A = 9.897×10^7 1/min for FW plot. The results at hand confirm that the best fitting kinetic model is Avrami-Erofeev model, A1.5, which are in good agreement with those obtained by IKP method.



(a)



(b)

Figure 7. Perez-Maqueda *et al.* straight lines for different heating rates, (a) CR equation, (b) FW equation.

4. Conclusions

The kinetic analysis of the thermal decomposition of carisoprodol in nitrogen atmosphere from room temperature up to 400 °C was presented. Non-isothermal thermogravimetric measurements at four different heating rates, (5, 10, 15 and 20 °C/min) proceeded by a one-step process. Kinetic parameters were evaluated using multi-heating rates, isoconversional methods, FR, FWO, and KAS, as well as the IKP method and Perez-Maqueda *et al.* criterion. The application of isoconversional methods and the IKP method led to the values of the activation energy, which are all in a very good agreement. It was pointed out that the investigated process is well described by the decomposition mechanism corresponds to nucleation and growth following the Avrami-Erofeev model, A1.5, as the kinetic model. The Perez-Maqueda *et al*. criterion fits the Avrami-Erofeev model, A1.5, and confirmed the 10^7 order of pre-exponential factor. The IKP method together with the isoconversional methods, the Perez-Maqueda *et al.* criterion of the independence of the kinetic parameters on the heating rate represented a very reliable combined kinetic analysis for the investigated thermal decomposition process of carisoprodol.

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