دراسة مقارنة لحساب تنشيط طاقة التحلل الحرارى لمادة الكافيين باستخدام طرق مختلفة

ليلى كامل

تمت دراسه التحلل الحرارى لماده الكافيين فى جو نيتروجينى ابتداء من درجة حرارة الغرفة حتى ٥٠٠ درجة منوية ، وذلك من خلال ثلاثه معدلات حرارية مختلفة ٥ و ١٥ و ٢٠ درجة منوية فى الدقيقة الواحدة .

لوحظ اكتمال التحلل الحرارى لمادة الكافيين فى خطوتين رئيسيتين . تم حساب طاقات التنشيط (E_a) ، لهما عن طريق استخدام Isoconversional Methods باستخدام طرق [تانج ، وفلين- ول- أوزاوى (FWO) ، وكيسنجر- أكاهيرا- سانوز (KAS) ، و فريدمان (FR)] ، حيث أظهرت النتائج توافق الطرق المستخدمة .

تم أيضاً مقارنة نتائج تنشيط الطاقة (E_a) باستخدام طريقتى كيسنجر وأوجس- بينيت (AB) . أوضحت النتائج أن طاقات التنشيط (E_a) المحسوبة عن طريق استخدام طريقة كيسنجر وطريقة أوجس- بينيت (AB) قيمتهما أعلى من النتائج المحسوبة باستخدام Isoconversional Methods ، وأظهرت النتائج أن قيمة (E_a) للخطوة الأولى أكبر من الخطوة الثانية .

تفيد هذه الدراسة فى تحديد درجات الحرارة المناسبة لصناعة العقاقير الصيدلانية حتى لا يحدث تكسير حرارى للمركبات أثناء التصنيع .

19- Kissinger, H. E., op. cit.

20- Kumazawa, T.; Satoa, K.; Senob, H.; Ishifb, A. and Suzukib, O., Positive and negative ion mass spectrometry of ten xanthine derivatives and their rapid clean up with Sep-Pak C_{18} cartridges from biological samples, Foren. Sc. Inter., 68, 1994, p. 53.

21- Zhang, J.; Liu, Y. Y.; Sun, L. X.; Xu, F.; You, W. S.; and Sawada , Y., Thermal decomposition kinetics of the synthetic complex Pb(1,4-BDC)-(DMF)(H2O), Journal of Thermal Analysis and Calorimetry, 2008 , 91 (1), pp189–193.

22- Dong, J-X. et al., op. cit.

23- Zhang, J. et al., op. cit.

24- Rotar, A.; Moanta, A.; Sălăgeanu, I.; Budrugeac, P. and Segal, E., Thermal Decomposition Kinetics of Some Aromatic Azomonoethers Part I. Decomposition of 4-[(4chlorobenzyl) oxy] -4'-nitro-azobenzene, *Journal of Thermal Analysis and Calorimetry*, 87(2), 2007, pp. 395–400.

25- Chrissafis, K., Kinetics of Thermal Degradation of Polymers, Complementary Use of Isoconversional and Model-Fitting Methods, *Journal of Thermal Analysis and Calorimetry*, 95 (1), 2009, pp. 273–283.

26-Ibid.

11- Wesolowski, M. and Szynkaruk, P., Thermal Decomposition of Methylxanthines Interpretation of the Results by PCA, *Journal of Thermal Analysis and Calorimetry*, 93 (3) 2008, p. 739.

12- Dong, J-X.; Li, Q.; Tan , Z; Zhang, Z-H and Liu, Y., The standard Molar Enthalpy of Formation, Molar Heat Capacities and Thermal Stability of Anhydrous Caffeine, *Journal of Chemical Thermodynamics*, 39, (108), 2007, pp.108-114.

13- Brown, M.E.; Maciejewski, M.; Vyazovkin, S.; Nomen, R.; Sempere, J.; Burnham, A. Opfermann, J.; Strey, R.; Anderson, H.L.; Kemmler, A.; Keuleers, R.; Janssens, Desseyn, H.O.; Li, C.R.; Tang, T.B.; Roduit, B.; Malek, J. and Mitsuhashi, T., Computational Aspects of Kinetic Analysis: Part A, Aspects The ICTAC Kinetics Project-Data, *Methods and Results, Thermochim. Acta* , 355, 2000, p. 125.

14- Flynn, J. and Wall, L., A quick, Direct Method for the Determination of Activation Energy from Thermogravimetric Data, *Polym. Lett.*, 4(5), 1966, pp. 323–328.

And Also:
Ozawa T., A new Method of Analyzing Thermogravimetric Data, *Bull. Chem. Soc. Jpn.*, 38, 1965, pp. 1881–1888.

15- Doyle C.J., Synthesis and Evaluation of Thermally Stable Polymers. II. Polymer Evaluation, *Appl. Polym. Sci.*, 5, 1961, pp. 285–292.

16- Tang, W., Liu Y., Zhang C.H. and Wang C., New Approximate Formula for Arrhenius Temperature Integral, *Thermochim. Acta*, 408 (1–2), 2003, pp. 39–43.

17- Kissinger, H. E., Reaction kinetics in Differential Thermal Analysis, *Anal Chem.*, 29, 1957,pp. 1702-1706.

And Also:
Akahira , T. and Sunose , T. , Joint Convention of Four electrical Institutes, *Research Report Chiba Institute and Technol.*, 16, 1971, pp. 22–31.

Friedman, H. L., Kinetics of Thermal Degradation of Char-Forming Plastics from thermogravimetry. Application to a phenolic plastic, *J. Polym. Sci.*, part C, 6, 1964, pp. 183-195.

18- Augis, J. A. and Bennett, J. E., Calculation of the Avrami Parameters for Heterogeneous Solid State Reactions Using A modification of Kissinger Method, *J. Thermal Anal.*, 13 ,1978, p. 283.

References

1- Tiege, Z.; Ridderinkhof, K. R.; Snel J. and Kok, A, Caffeine Strengthens Action Monitoring: Evidence from the Error-Related Negativity, *Cognitive Brain Research*, 21, 2004, pp. 87– 93.

2- Ford, M., A., in, Ashurst, P. R. (Ed.), London, Production and Packaging of Non-Carbonated Fruit Juices and Fruit Beverages, *Blackie Academic and Professional*, 1995, pp. 310-330.

3- Varnam, A. H. and Sutherland, J. P., Beverages, Technology, Chemistry. and microbiology, London, Chapman, & Hall, 1994, p. 234 .

4- Wesołowski, M. and Szynkaruk, P., Thermal Decomposition of Purine Derivatives Used in Medicine, *J. Therm. Anal. Calorim.*, 65, 2001, p. 599.

5- Abd El-Wahed, M.G.; Refat, M.S and El-Megharbe, S.M., Metal Complexes of Antiuralethic Drug: Synthesis, Spectroscopic Characterization and Thermal Study on Allopurinol Complexes, *Journal of Molecular Structure*, 888 (1-3), 2008, pp. 416-429.

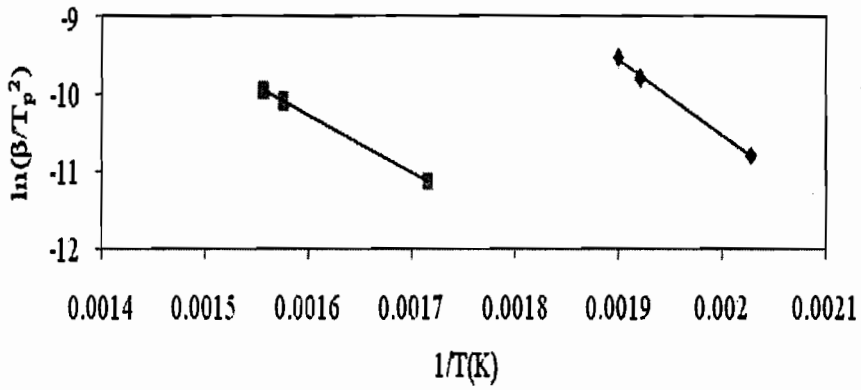
6- Sadeek,S. A., Synthesis, Thermogravimetric Analysis, Infrared, Electronic and Mass Spectra of Mn (II), Co (II) and Fe (III) Norfloxacin Complexes, *J. of Molecular Structure*, 753 (1-3), 2005, pp. 1-12.

7- Zayed M. A. and Abdallah, S. M., Synthesis and Structure Investigation of the Antibiotic Amoxicillin Complexes of d-block Elements, Spectrochimica Acta Part A, *Molecular and Biomolecular Spectroscopy*, 61 (9), 2005, pp. 2231-2238.

8- Abu-Eittah, R. H. and Kamel, L. T., Kinetics and Thermodynamic Parameters of the Thermal Decomposition of Imipramine Hydrochloride and Trimipramine maleate, *International Journal of Chemical Kinetics*, 35(4), 2003, pp. 166-179.

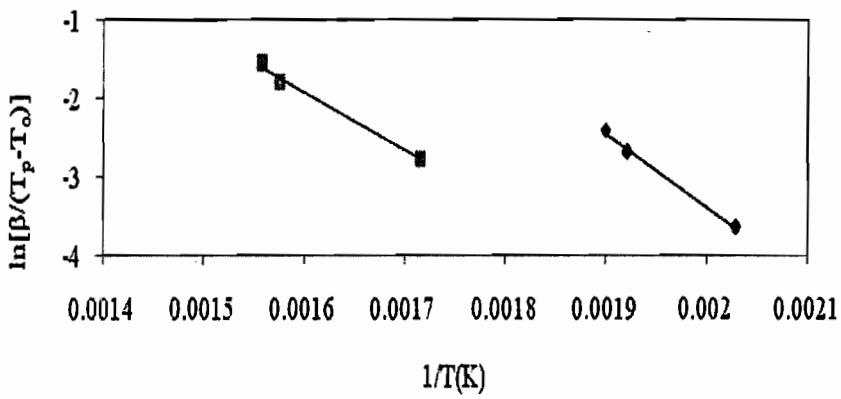
9- Rodante, F.; Vecchi, S. and Tomassetti, M., Kinetic Analysis of Thermal Decomposition for Penicillin Sodium Salts: Model-Fitting and Model-Free Methods, *Journal of Pharmaceutical and Biomedical Analysis*, 29 (6), 2002, pp. 1031-1043.

10- Dănilă, Gh.; Prifire, L. ; Bumbu, G.G. and Vasile, C., Thermal Characterization of Some New Xanthine Derivatives, *Thermochim. Acta*, 343(1,2), 2000, pp. 69 -79.



Fig(13) Kissinger Plots for CF (First and Second Step)

♦ First Step ■ Second Step



Fig(14) Augis and Bennett Plots for CF (First and Second Step)

♦ First Step ■ Second Step

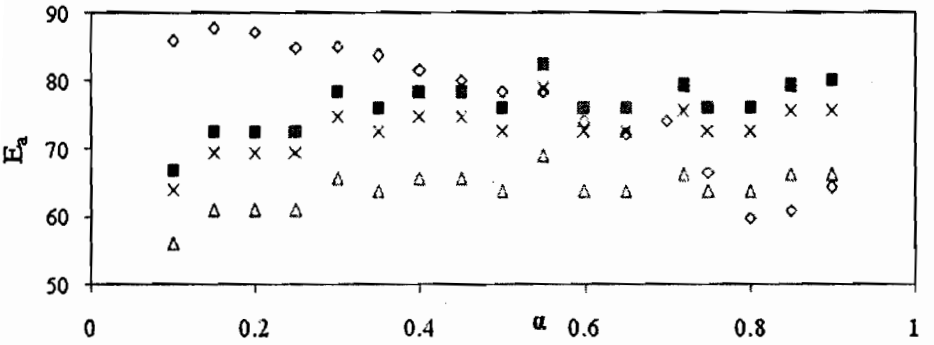


Fig (11) The Dependence of the Apparent Activation Energy (E_a) on the Degree of Conversion(α) for Nonisothermal Decomposition Process of CF (First Step)

■FWO △KAS ×Tang ◇FR

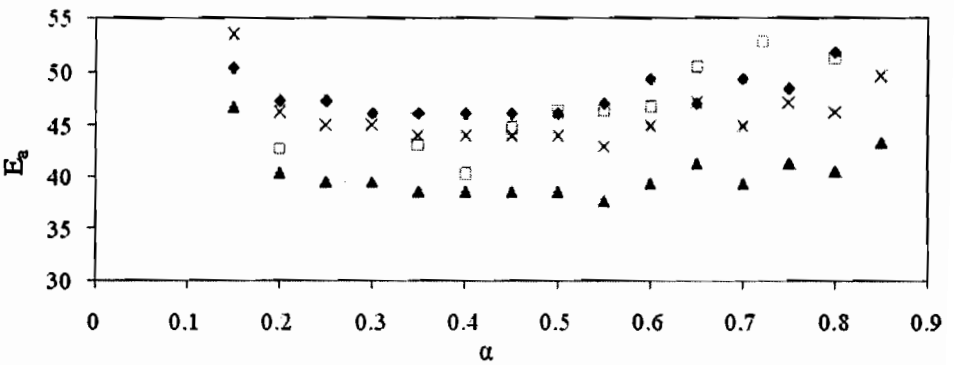


Fig (12) The Dependence of the Apperent Activation Energy (E_a) on the Dgree of Conversion(α) for Nonisothermal Decomposition Process of CF (Second Step)

◆FWO ▲KAS ×Tang □FR

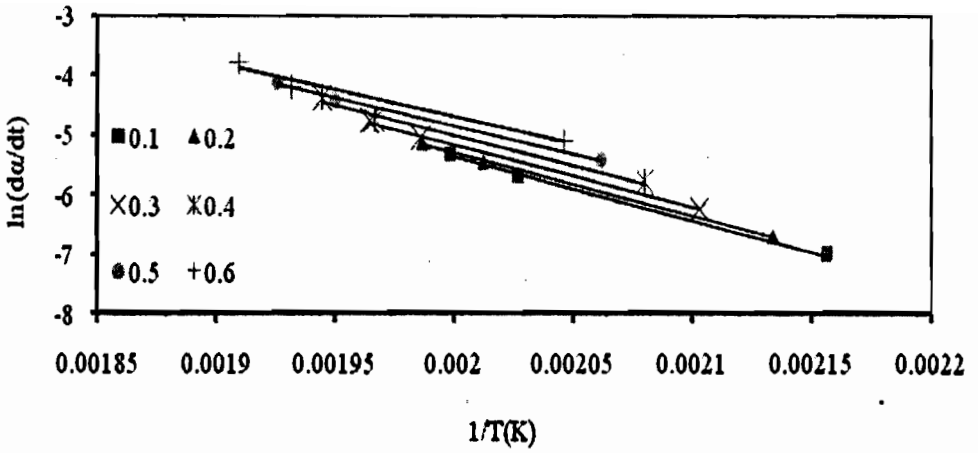
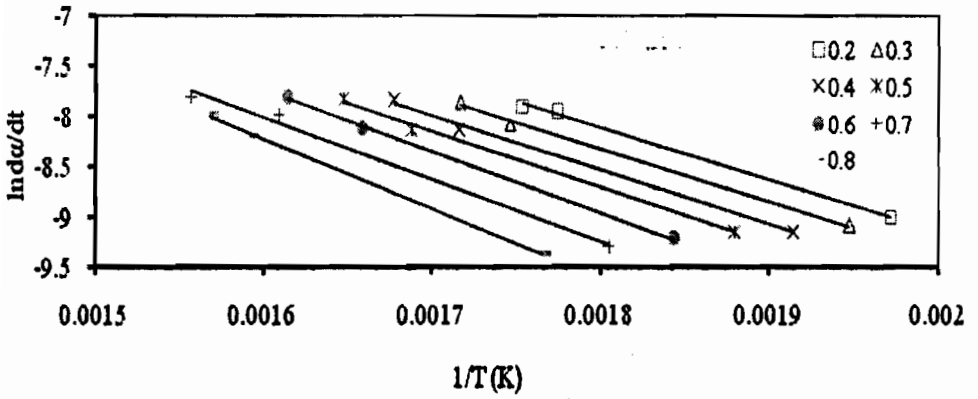


Fig (9) FR Plots of CF for Different Degrees of Conversation (α) (First Step)



Fig(10) FR Plots of CF for Different Degrees of Conversion (α) (Second Step)

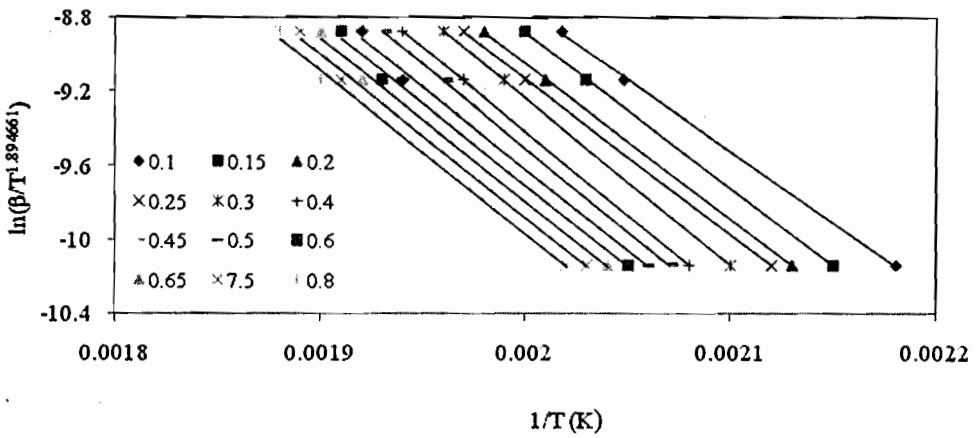
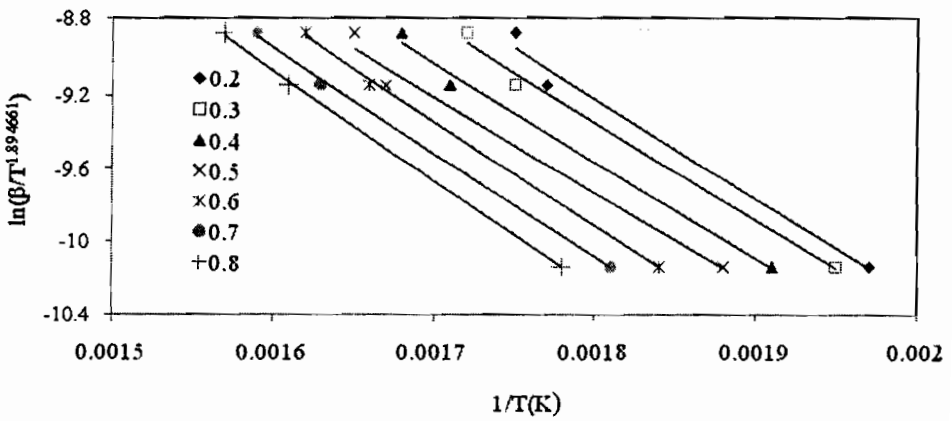
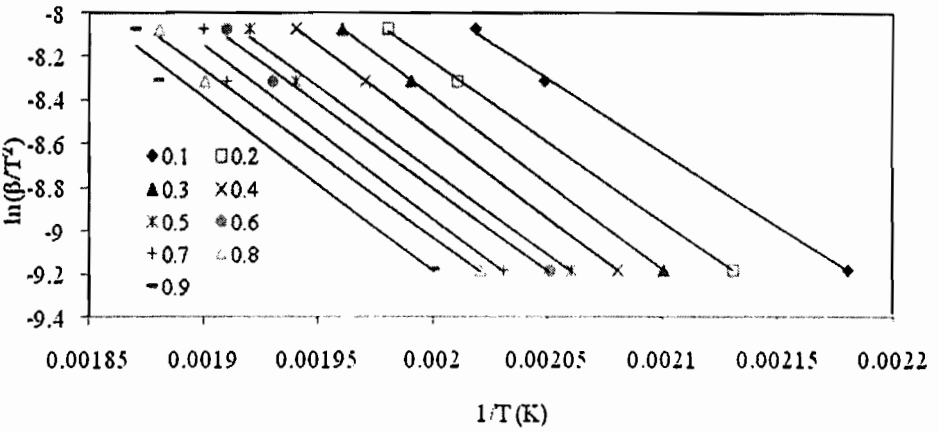


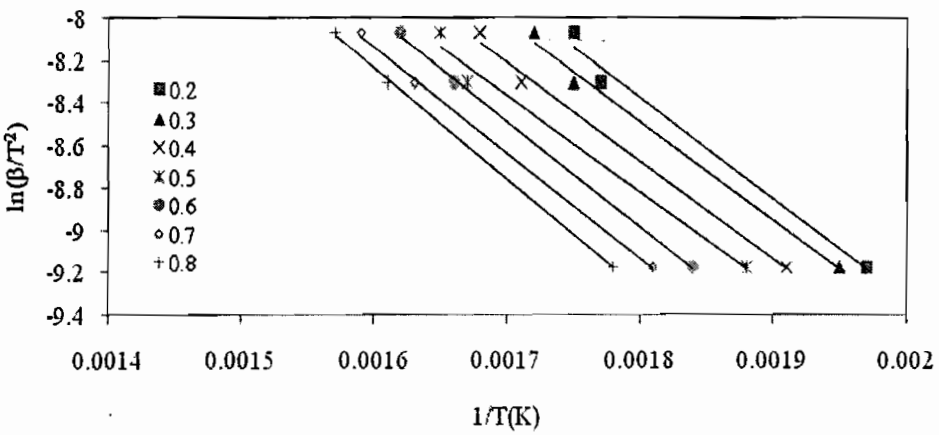
Fig (7) Tang Plots of CF for Different Degrees of Conversation (α) (First Step)



Fig(8) Tang Plots of CF for Different Degrees of Conversion (α) (Second Step)



Fig(5) KAS plots of CF for Different Degrees of Conversion (α) (First Step)



Fig(6) KAS Plots of CF for Different Degrees of Conversion (α) (Second Step)

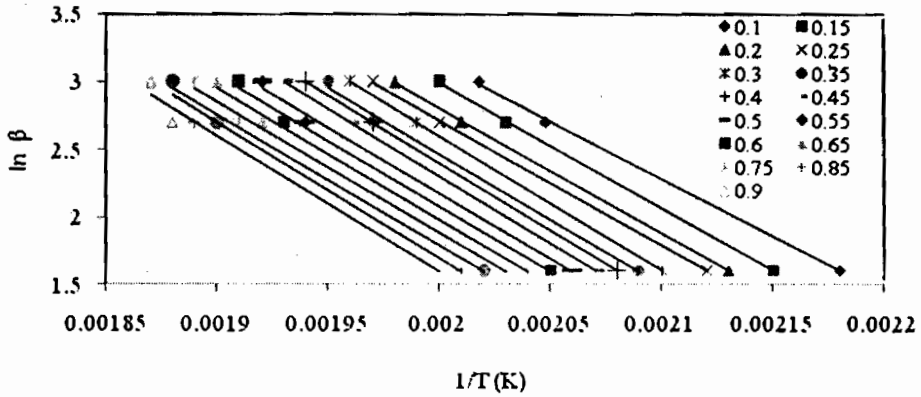
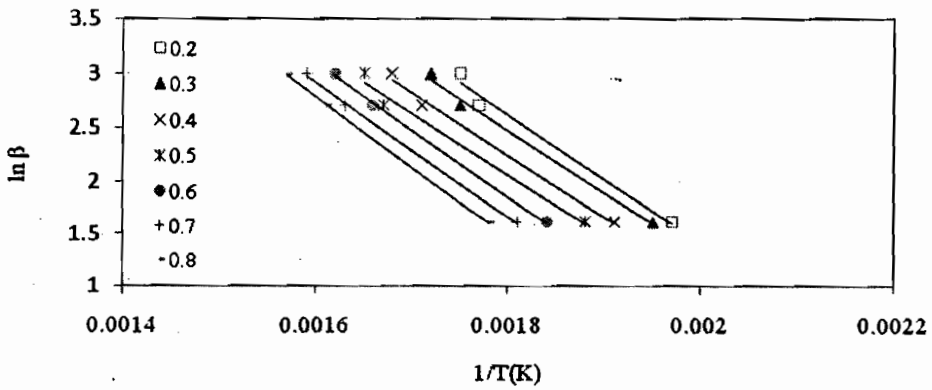


Fig (3) FWO Plots of CF For Different Degrees of Conversion (α) (First Step)



Fig(4) FWO Plots of CF For Different degrees of Conversion (α) (Second Step)

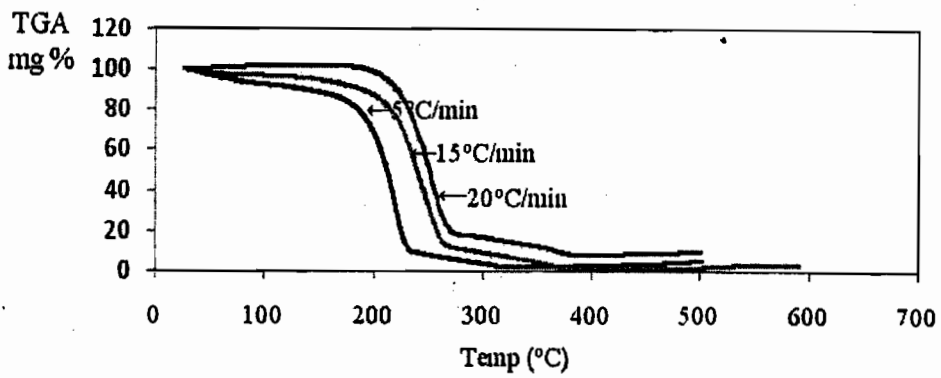


Fig (1) The TGA Curve of CF at Different Heating Rates

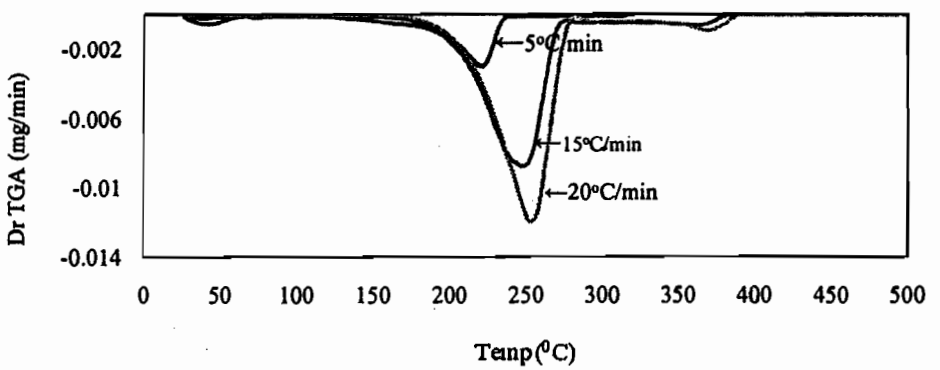


Fig (2) DTG Curves of CF at Different Heating Rates

Table (2)
The Apparent Activation Energies of Thermal Decomposition and Correlation Coefficient of CF Obtained by FR, FWO, KAS and Tang (Second Step)

Conversion	FR method		FWO method		KAS method		Tang method	
	E_a kJ/mol	R^2	E_a kJ/mol	R^2	E_a kJ/mol	R^2	E_a kJ/mol	R^2
0.2	43	0.999	47	0.987	39	0.985	45	0.986
0.3	44	0.997	46	0.994	39	0.992	43	0.993
0.4	45	0.997	46	0.994	39	0.992	43	0.993
0.5	46	0.994	45	0.986	38	0.984	44	0.985
0.6	50	0.995	49	0.999	41	0.999	47	0.993
0.7	51	0.993	49	0.999	41	0.999	47	0.994
0.8	57*		51*	0.999	40	0.999	49	0.995

*excluded

Table (3)
The Apparent Activation Energies of Thermal Decomposition and Correlation Coefficient of CF obtained by Kissinger Method and AB Method

Step	Kissinger method		Augis and Bennett's method	
	E_a kJ/mol	R^2	E_a kJ/mol	R^2
First	80	0.998	78	0.995
Second	60	0.999	61	0.996

Activation energy calculated using AB method was 78 kJ/mol for the first step and 61 kJ/mol for the second step. Where that using Kissinger method were 80 kJ/mol and 60 kJ/mol for the first and second step respectively.

The results obtained using Kissinger and AB methods showed higher activation energy values in both steps than the activation energy calculated from the isoconversional methods this may be attributed to the rely solely on the relative positions of T_p rather than considering the whole heat flow profile.

Table (1)
The Apparent Activation Energies of Thermal Decomposition and Correlation Coefficient of CF Obtained by FR, FWO, KAS and Tang (First Step)

Conversion	FR method		FWO method		KAS method		Tang method	
	E_a kJ/mol	R^2	E_a kJ/mol	R^2	E_a kJ/mol	R^2	E_a kJ/mol	R^2
0.2	87	0.991	73	0.997	61*	0.998	69*	0.999
0.3	85	0.994	78	1.00	66	0.995	74	1.00
0.4	81	0.992	78	0.996	66	0.994	75	0.995
0.5	78	0.991	76	0.996	64	0.994	73	0.995
0.6	73	0.997	76	0.996	64	0.981	73	0.996
0.7	74	0.971	79	0.990	67	1.00	76	0.995
0.8	69*		76	0.985	64	0.997	73	0.995

*excluded

$\ln[\beta/(T_p-T_0)]$ *vs.* $1/T_p$, were plotted as shown in Fig (14), where the E_a was 78 kJ/mol for the first step and 61 kJ/mol for the second step.

The calculated values of activation energy, E_a, using AB and Kissinger's methods and the correlation coefficients are listed in Table(3).

It can be observed that the calculated apparent activation energy for Kissinger and AB methods which correspond to the peak temperature of the DTG curve are very similar.

The results obtained from Kissinger and AB methods show higher activation energy values in both steps than the activation energy calculated from the isoconversional methods. The reason could be because Kissinger and AB methods rely solely on the relative positions of T_p rather than considering the whole heat flow profile[26].

Conclusion

The thermal decomposition of CF in nitrogen atmosphere occurs in two steps. The apparent activation energies, E_a, for the two steps were calculated by four different isoconventional methods, one differential (FR), three linear intergal (KAS, FWO and Tang). A comparison has been made between E_a calculated from the isoconversional methods and the E_a values calculated using the Kissinger and AB methods.

Calculated E_a mean values were 77 kJ/mol for the first step and 47 kJ/mol for the second step using FWO method, while E_a was 74 kJ/mol for the first step and 45 kJ/mol for the second step using Tang method. Using KAS method the E_a was 65 kJ/mol and 37 kJ/mol for the first and second step respectively. As shown the activation energy calculated by KAS is lower than that calculated from FWO and Tang methods. E_a calculated using FR method was 77 kJ/mol for the first step and 46 kJ/mol for the second step.

using Tang, KAS, FWO and FR methods are listed in Tables (1, 2) for the first and second step respectively.

Fig. (11) shows that the curves of E_a versus α have the same shapes , corresponding to Tang, KAS, and FWO methods. Same behavior have been observed in the second step, Fig.(12), where the curves of E_a versus α have the same shapes of the corresponding to Tang, KAS, and FWO methods also. This means that the thermal decomposition of CF in N_2 atmosphere presented a same behavior for Tang, KAS and FWO method. The average values of E_a for Tang, KAS and FWO methods obtained in the range $0.2 \leq \alpha \leq 0.8$ are lower than the average values of E_a obtained for FR (for both steps). That may be due to the well known that FR method is very sensitive to experimental noise[24] and tends to be numerically unstable because of employing instantaneous rate value. Some of the differences observed between the values of E_a obtained using linear integral methods (Tang, KAS and FWO) can be assigned to the different approximations of the temperature integral which ground them[25].

The calculation of the activation energy using more than one isoconversional method can give an area of values for every particular value of α, where the true values of E can be found. As observed the larger activation energy of the first step of decomposition may be due to the additional destroy of crystal lattice.

Using Kissinger equation (8) the plots line $ln\left(\frac{\beta}{T_p^2}\right)$ versus $1/T_p$. for each step of thermal decomposition of CF were plotted as shown in Fig (13). The activation energy of decomposition was 80 kJ/mol for the first step and 60 kJ/mol for the second step.

Augis - Bennett's equation (9) was also used to calculate , activation energy E_a can be obtained from the slope of the straight line

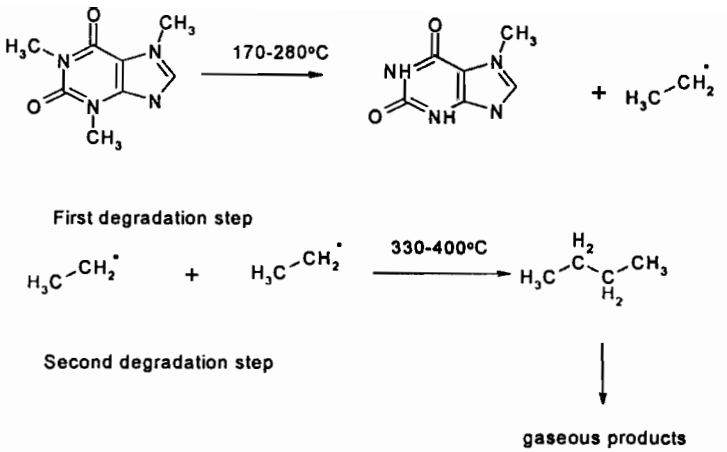
slope of such a line given by -0.456E/RT. Figs (3,4) illustrates the plots of lnβ versus 1/T at varying conversion for the first and second step respectively. The apparent activation energies calculated from the slopes were tabulated in Tables (1 and 2) and the mean values are 77 kJ/mol for the first step and 47 kJ/mol for the second step.

Another isoconversion method used in this paper was KAS where the activation energy can be calculated from the slopes of the straight lines obtained from the plots of $\ln(\beta/T^2)$ against 1/T as shown in Figs (5,6) for the two steps and the mean apparent activation energies were 65 kJ/mol for the first step and 37 kJ/mol for the second step.

Using Tang equation (5) the plots of $\ln(\beta/T^{1.894661})$ versus 1/T for each step of thermal decomposition of CF were plotted as shown in Figs (7,8). The calculated decomposition activation energies were 74 kJ/mol for the first step and 45 kJ/mol for the second step.

Friedman method is also used to determine the apparent activation energy from the slope of the plot of $ln(d\alpha/dt)$ versus 1/T gives a straight line with a slope of $-E_a/R$. as shown in Figs (9,10) for the two steps. The mean apparent activation energies were 77 kJ/mol for the first step and 46 kJ/mol for the second step.

For all the sets of α values, the linear isoconversional plots of FR, KAS, FWO and Tang methods result in a correlation coefficient (r^2) higher than 0.9950. The straight lines fitting the data are nearly parallel, which is an indication that the activation energies at different degrees of conversion are almost similar. The dependence of the apparent activation energy (E_a) on the degree of conversion (α) ($E_a - \alpha$ curve) for the nonisothermal decomposition process of CF obtained by isoconversional methods for the first and second step are presented in Figs (11,12) respectively. The calculated apparent activation energies



The DTG curves for CF for the three rates are shown in Fig. (2) .The main weight loss about 88% for the three rates occurs in one step in the temperature range 155-230, 170-280 and 200-270°C for the rates 5, 15 and 20°C /min respectively with a temperature peak 220.11 °C, 247.59°C and 253.54°C respectively. A second step with a smaller weight loss 12% in the temperature range 230.23-315.45, 271.72-360.75 and 272.15-379.25°C with peak temperature 307.97, 361.64 and 369.05°C for the rates 5, 15 and 20°C /min respectively.

Several techniques using different approaches have been developed for solving the integral equation (2). The nonisothermal decomposition process of CF was analyzed by Friedman (FR), Kissinger-Akahira-Sunose (KAS), Flynn-Wall-Ozawa (FWO) and Tang isoconversional methods. All mentioned methods are based on multiple heating rates experiments, where no kinetic model is needed before activation energy is calculated.

FWO method is an integral method independent of the degradation mechanism. Equation (4) has been used and the apparent activation energy of CF can therefore be obtained for the two steps from a plot of lnβ against 1/T for a fixed degree of conversion since the

two C-N bonds attaching $-CH_3$ groups to the quinonoide nucleus and the breakdown of a C-H bond from ethane molecule formed. The largest weight loss in the first decomposition step includes the loss of 7-methyl xanthine.

In the second step of decomposition, ethylene molecule, as a result of increasing temperature is fragmented and the fragments (gaseous products) leave the crucible without any residue.

The TG, DTG curves results of CF agree with similar results obtained when investigating the thermal stability of anhydrous CF[22]. In that study, DSC curve has shown a phase transition of CF, from the crystal form α to the crystal form β at a peak temperature 147°C. The mass-loss curve (TG) shows that most of the decompositions occur in the temperature range 181-291°C in a single step and no residue was found in the crucible after the experiment was completed.

In the light of these results, a possible decomposition route of CF is proposed based on the results of mass spectra of xanthines[23] and are represented. The two well-defined stages were selected for the study of the kinetics of decomposition of CF.

The activation energy E can be obtained from the slope of the straight line $ln\left(\frac{\beta}{T_p^2}\right)$ versus $1/T_p$. This method provides the value of A apart from the value of activation energy E. Here one gets a single value of E using Eq. (8).

Augis-Bennett's method[20]

According to the method suggested by Augis and Bennett,

$$ln\left(\frac{\beta}{T_p - T_0}\right) = -\frac{E}{RT_p} + \ln A \qquad (9)$$

where T_p and T_0 are the peak temperature and the onset temperature of the DTG peak respectively. The activation energy E can be obtained from the slope of the straight line $\ln[\beta/(T_p - T_0)]$ versus $1/T_p$.

Results and Discussion

Thermal analysis of CF was studied starting from room temperature up to 500°C in nitrogen atmosphere. The TG and DTG curves of the decomposition process of CF obtained at different heating rates (5, 15 and 20°C /min) are shown in Figs 1 and 2 respectively. TG curves are shifted to higher temperatures at higher heating rates, although the shapes of curves are quite similar. The first decomposition step in rates 5, 15, 20°C /min occurs in the 155-230, 170-280 and 200-270°C temperature range respectively with a weight loss of about 88% for the three rates. This weight loss occurs at a peak temperature of 220.11 °C, 247.59°C and 253.54 °C for the rates 5, 15 and 20°C /min respectively whereas the melting point of CF is 236°C. This means that the CF decomposes before melting. A weight loss of 88% corresponds to the loss of 7-methyl xanthine nucleus and agrees with the appearance of a peak at m/z=165 in the mass spectrum of CF[21]. The loss of 7-methyl xanthine nucleus necessities the breakdown of

The dependence of $\ln(\beta/T^2)$ on 1/T, calculated for the same α values at the different heating rates (β) can be used to calculate the activation energy.

Friedman method[18]

The derivative techniques are based on the comparison of the rates of mass loss α for a given fractional mass loss determined using different linear heating rates (β). This method utilizes the following logarithmic differential equation:

$$ln\left(\frac{d\alpha}{dt}\right) = ln[Af(\alpha)] - \frac{E_a}{RT} \qquad (7)$$

Where $d\alpha/dt$ is the rate of conversion and $f(\alpha)$ differential expression of kinetic function. A plot of $ln(d\alpha/dt)$ versus 1/T gives a straight line with a slope of $-E_a/R$.

Kissinger method[19]

This well-known method assumes that the reaction rate reaches its maximum at the temperature (T_p) at the DTG peak. This assumption also implies a constant degree of conversion (α) at T_p. In many cases, the degree of conversion (α) at T_p varies with the heating rate and hence raises doubt about grouping this method into isoconversional category.

The Kissinger equation is

$$ln\left(\frac{\beta}{T_p^2}\right) = -\frac{E}{RT_p} \ln\left(\frac{AR}{E}\right) \qquad (8)$$

Flynn-Wall-Ozawa method[14]

This method is derived from the integral method. The technique assumes that the A , $f(\alpha)$ and E are independent of T while A and E are independent of α then Eq. 2 may be integrated to give the following in logarithmic form:

$$\log g(\alpha) = log(AE/R) - log\beta + \log p(E/RT) \qquad (3)$$

Using Doyle's approximation[15] for the integral which allows for E/RT > 20, Eq 3 now can be simplified as

$$log\beta = log(AE/R) - logg(\alpha) - 2.315 - 0.456 / RT \qquad (4)$$

Tang method[16]

Tang method is an approximation formula for resolution of Eq. 2 where following equation can be obtained

$$ln\left(\frac{\beta}{T^{1.894661}}\right) = \ln\left(\frac{AE}{Rg(\alpha)}\right) + 3.635041 - 1.894661 \ln E - \frac{1.001450E}{RT} \qquad (5)$$

The plots of $\ln\left(\frac{\beta}{T^{1.894661}}\right)$ versus 1/T give a group of straight lines. The activation energy can be obtained from the slope -4.001450 E/R of the regression line.

Kissenger-Akahira-Sunose method[17]

This method (KAS) is integral isoconversional methods as FWO

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

Experimental

Materials

CF was supplied by Sigma (St. Louis, MO). It is used without any further purification.

Physical Measurements

The thermogravimetric (TG) curves were obtained using Shimadzu TGA-*50 thermobalance. The measurements were performed with dynamic nitrogen furnace atmosphere at a flow rate of 20 mL* min^{-1} *starting at room temperature up to* 500^0C. *The heating rates used were 5, 15 and* $20^oC\ min^{-1}$ *and the samples were of masses 1.233, 1.955, 1.689 mg respectively which were contained in an alumina* crucible.

Kinetic methods

The rate of solid-state non-isothermal decomposition reactions is expressed as

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

Rearranging Eq. 1 and integrating both sides of the equation leads to the following expression

$$g(\alpha) = \left(\frac{A}{\beta}\right) \int_{T_0}^{T} exp\left(\frac{-E}{RT}\right) dT = \left(\frac{AE}{\beta R}\right) p(u) \qquad (2)$$

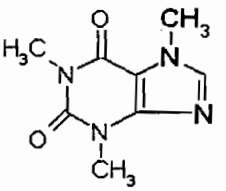
Where $p(u) = \int_{\infty}^{u} -\left(\frac{e^{-u}}{u^2}\right) du$ and u = E/RT

amoxicillin complexes of d-block elements[7] , imipramine hydrochloride and trimipramine maleate[8] penicillin sodium salts[9], other ones were also done.

Study of the thermal behaviors of some new xanthine derivatives by TG and DSC were used to determine the thermal stability, the purity of the compounds and crystallinity[10]. Thermal decomposition of CF and other methylxanthines was studied by DTA, TG and DTG methods to determine the influence of heating rate and sample size on thermal destruction of the selected methylxanthines[11]. Anhydrous CF thermal behavior was investigated by TG, DTG, DSC where a (solid-solid) and a (solid-liquid) phase transitions of the compound were found at T= (413.39 and 509.00) k respectively. Molar enthalpies of these transitions were determined[12].

The aim of this study is to investigate the thermal behavior and to determine the apparent activation energies of thermal degradation of CF in N_2 atmosphere by isoconversional methods through which the activation energy depends on the conversion degree. Isoconversional methods provide a comprehensive description of the decomposition process of a heterogeneous solid-state reaction. Based on the results of the International Confederation for Thermal Analysis and Calorimetry (ICTAC) kinetics project[13] , the multi-heating rate methods together with isoconversional methods are the most reliable techniques for the analysis of thermal data. In this study, isoconversional methods of Friedman (FR), Tang, Flynn-Wall-Ozawa (FWO) and Kissenger-Alkahira-Sunose (KAS) were used to evaluate the activation energy (E_a) values at different stages of fraction decomposed (α) during the thermal decomposition of CF. The results are compared to the E_a values calculated using Kissinger method and Augis - Bennett's methods.

Caffeine (CF) (1,3,7-trimethylxanthine) is the most widely consumed psychoactive substance in the world. While it is present in a number of dietary sources such as tea, chocolate and soft drinks, the largest intake of caffeine has always been through coffee[1].



Caffeine

Caffeine can be used in soft drinks as a flavoring ingredient and recently also in so-called ``sports drinks" to increase the basal metabolic rate[2]. They are occasionally components of some over-the-counter pharmaceutical preparations. As a central nervous system stimulant, caffeine can also stimulate the cardiac muscle[3].

Thermal decomposition helps in studying the drug behavior at various temperatures, which is important for the prediction of storage conditions for drug formulations. It also gives important information on temperatures, at which the drug substance can be subjected to technological processes without loss of its specific physico-chemical and pharmacological properties[4]. Decomposition reactions are carried out in order to obtain the solid products, which are characterized by proper phase composition and activity for further technological applications.

In literature, there are many examples treated with the application of thermal methods of analysis, especially DSC, DTA, TG and DTG, in the studies of thermal stability and decomposition of organic and inorganic compounds used in medicine. Studies on allopurinol[5], Mn(II), Co(II) and Fe(III) norfloxacin complexes[6] ,

COMPARATIVE STUDY FOR ACTIVATION ENERGY OF THERMAL DEGRADATION OF CAFFEINE USING DIFFERENT METHODS

Laila T. Kamel*

The thermal decomposition of caffeine was studied by thermogravimetry in nitrogen atmosphere from room temperature up to 500°C at three different heating rates 5, 15 and 20°C min^{-1}. Two main steps were observed for the thermal decomposition. The activation energies, E_a of decomposition were calculated by means of isoconversional methods using Tang, Flynn–Wall–Ozawa (FWO), Kissenger–Akahira–Sunose (KAS) and Friedman (FR). Results show that the methods used were in good agreement with each other. Activation energy results were compared by using Kissinger's and Augis-Bennett (AB) methods. The activation energy values obtained using Kissinger and AB methods showed higher values in both steps than that calculated using isoconversional methods. Results showed that the activation energies of the first step are greater than the second step.

Introduction

In recent years the food, nutrition, and pharmaceutical industries have devoted increasing attention to methylxanthine derivatives because of their various physiological effects.

* Expert, Narcotic Research Department, National Center for Social and Criminological Research.

The National Review of Criminal Sciences, Volume 53, Number 2, July 2010.