STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, LIV, 3, 2009

ISOCONVERSIONAL LINEAR INTEGRAL KINETICS OF THE NON-ISOTHERMAL EVAPORATION OF 4-[(4-chlorobenzyl)oxy]-4'-trifluoromethyl-azobenzene

ANDREI ROTARU[a], **MIHAI GOŞA**[b,c], **EUGEN SEGAL**[d]

ABSTRACT. The activation energy of the linear non-isothermal evaporation of 4-[(4-chlorobenzyl)oxy]-4'-trifluoromethyl-azobenzene has been determined by various linear integral isoconversional methods. Activation energy may be evaluated using several isoconversional methods as the well-known Tang *et al.* method, Generalized KAS method, but also by means of two so-called "local linear integral" (Tang & Chen) and "average linear integral" (Ortega) isoconversional methods. A comparison study has been carried out in order to understand how the activation energy values are affected when using different approaches.

Keywords: *azomonoether dyes, non-isothermal kinetics, linear integral, local linear integral and average linear integral isoconversional methods.*

INTRODUCTION

Dyes from the category of azoic aromatics have been intensively studied since they are of large interest from the point of view of possible applications [1-4]. Thermal characterizations and stability studies are usually required before choosing them to be part of composite materials, moreover since they are used in thermal-controlled devices. Kinetic studies are required for predicting their behaviour in other conditions than in those that are accessible for normal runs [5-9].

This paper aims to present a isoconversional kinetic study of the linear non-isothermal evaporation of 4-[(4-chlorobenzyl)oxy]-4'-trifluoromethyl-azobenzene liquid crystal that has been previously investigated [7] only by KAS (Kissinger-Akahira-Sunose) [10,11] and FWO (Flynn-Wall-Ozawa) [12,13]

---

[a] *INFLPR – National Institute for Laser, Plasma and Radiation Physics, Laser Department, Bvd. Atomistilor, Nr. 409, PO Box MG-16, RO-077125 Magurele, Bucharest, Romania, andrei.rotaru@inflpr.ro*

[b] *University of Craiova, Faculty of Automatics, Computers and Electronics, Bvd. Decebal, Nr. 107, Craiova, Romania*

[c] *KineTAx, Str. Ştefan cel Mare, nr. 3, bl. L, sc. B, ap. 1, 200137 Craiova, Romania, mihai.gosa@kinetax.com*

[d] *University of Bucharest, Faculty of Chemistry, Bvd. Regina Elisabeta Nr. 4-12, Bucharest, Romania, esegal@gw-chimie.math.unibuc.ro*

isoconversional methods. Since for our early papers we have used regular calculations, we were able to report results only for a few methods and conversions. The new software package TKS-SP [14,15] for kinetic analysis allows the rapid evaluation of the activation energy by means of isoconversional methods (integral and differential), as well as by other more complex procedures.

With the increasing number of papers dealing with the approximation of the temperature integral, its evaluation improved [16-22] and led to the general opinion that other methods should be used instead of those consecrated ones [10-13]. The method of Tang *et al.* [16] and the generalized KAS [17, 18] methods have been used here, together with the new "local linear isoconversional" of Tang & Chen [19] and "average linear integral"of Ortega [20] methods as well.

RESULTS AND DISCUSSION

Thermal behaviour of 4-[(4-chlorobenzyl)oxy]-4'-trifluoromethyl-azobenzene was investigated in a previous paper [7], together with a couple of other liquid crystals from the same category of aromatic azomonoethers. Before evaporating in the temperature range of 190-310 ^{o}C (endothermic effect), at 155 ^{o}C the compound melts. The FTIR spectrum of the evolved gases perfectly matches to the FTIR spectrum of the solid compound. No influence of the gas atmosphere (air or inert flow) was found.

The complexity of a physical or chemical process can be expressed from the activation energy dependence on the conversion degree. Usually, "model-free" kinetic methods are the most popular. Such applications require the use of isoconversional methods for the evaluation of the activation energy.

1) Regular linear integral methods (Tang et al. and Generalized KAS)

Here we made use of several isoconversional methods: The methods of Tang *et al.* [16] (very close to KAS method) and Generalized KAS [17,18]; are the isoconversional integral linear ones, based on the following integral form of the reaction rate:

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

where β is the heating rate, R is the universal gas constant, $g(\alpha)$ is the integral conversion function and $I(E_\alpha, T_\alpha)$ represents the temperature integral. Substitution of $I(E_\alpha,T_\alpha)$ in the equation (1) by various approximation mathematical expressions, provides various equations – therefore a multitude of isoconversional methods.

In the case of Tang *et al.* method [16], for $\alpha=const.$, the plot $ln(\beta/T^{1.894661})$ *vs.* $(1/T)$, obtained from the experimental thermogravimetric curves recorded for several constant-heating rates, should be a straight line whose slope could be used for the activation energy evaluation (E [kJ·mol^{-1}]= – slope·R/1001.45033). In the case of Generalized KAS method [17,18], for $\alpha=const.$, several plots of $ln(\beta/T^{n+m})$ *vs.* $(1/T)$, obtained from the experimental thermogravimetric curves recorded for several constant-heating rates, should gave straight lines whose slopes could be used for the activation energy evaluation (E [kJ·mol^{-1}]= – slope·R/1000). For KAS method, n=2, m=0.

Figure 1 shows the kinetic results of the non-isothermal evaporation of the investigated compound, obtained using Tang *et al.* and Generalized KAS (m=0.5, 1 and 2) methods, as values of the activation energy for various conversion degrees from 0.2 to 0.9 with a step of 0.01, using TKS software (SP 1.0 and SP2.0) [14,15].

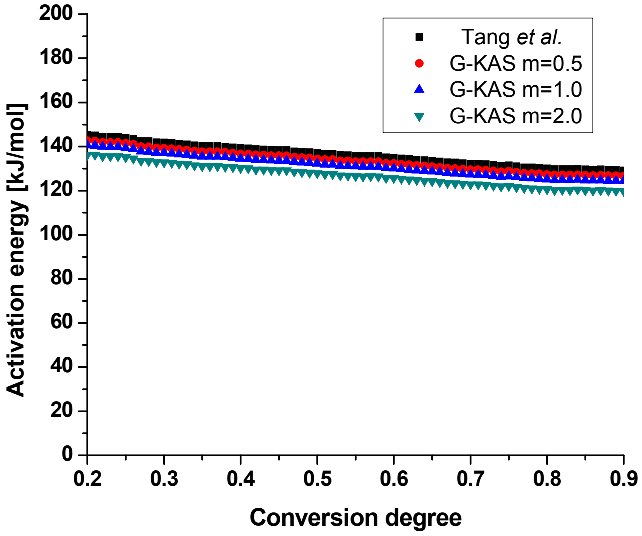

Figure 1. Isoconversional activation energy of the non-isothermal evaporation of 4-[(4-chlorobenzyl)oxy]-4'-trifluoromethyl-azobenzene (by Tang *et al.* and G-KAS methods)

All employed regular linear integral isoconversional methods exhibit a similar trend of the activation energy; for all of them, the activation energy decreases with about 10% in the conversion range of 0.2-0.9. Table 1 contains a statistic of the activation energy values:

Table 1. Statistics of the activation energy values by means of regular linear integral isoconversional methods

Method	Max. activation energy kJ/mol	Min. activation energy kJ/mol	Average activation energy kJ/mol
Tang *et al.*	145.2	129.3	136.2±4.8
G-KAS (m=0.5)	142.7	126.5	133.5±4.9
G-KAS (m=1.0)	140.6	124.3	131.3±4.9
G-KAS (m=2.0)	136.3	119.7	126.9±5.0

The differences between the results of the employed methods are due to the exponents (*n* and *m*) of the temperature that are used. With increasing the temperature exponent, the activation energy decreases, but the shape of the isoconversional evaluation remains the same. Although the absolute value is not determined, its trend is the same.

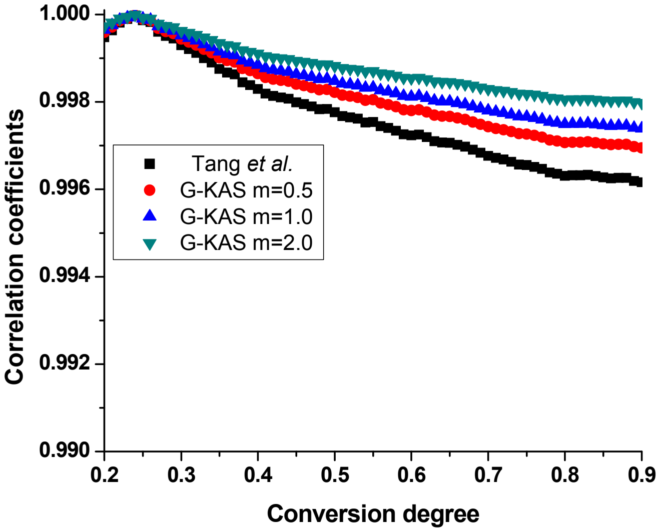

Figure 2. Correlation coefficients for the isoconversional activation energy of the non-isothermal evaporation of 4-[(4-chlorobenzyl)oxy]-4'-trifluoromethyl-azobenzene (by Tang *et al.* and G-KAS methods)

During the evaporation process, the activation energy may be however considered to remain practically constant; the accuracy in determining the activation energy is very high – correlation coefficients over 0.99650 (Figure 2). Since this compound is a liquid crystal, it may be used in specific devices; knowing the dependence of the activation energy behaviour with the consumption of the evaporation, it may help manufacturers when designing their products and establish the limits the devices may be used. It can be easily noticed that with increasing value of the temperature's exponent *m*, the activation energy is evaluated with higher accuracy.

2) Local linear (Tang & Chen) and Average linear (Ortega) integral isoconversional methods

In 2005 Tang & Chen [19] have proposed an integral isoconversional procedure that they have called "local linear" method. This method is basically the linear version of Vyazovkin's "advanced integral isoconversional" method [21], called by Tang & Chen: "modified integral non-linear isoconversional procedure".

Equation 2 was derived by the authors and used for Δα→0; however it was concluded that integration over very small segments provides activation energy values close to those obtained using Friedmann [23] method.

$$ln\frac{\beta[1/(1+\alpha)]}{T_{\alpha+\Delta\alpha}-T_{\alpha-\Delta\alpha}}=ln\,A_{\alpha}-ln[g(\alpha+\Delta\alpha)-g(\alpha-\Delta\alpha)]-\frac{E}{RT_{\alpha}} \qquad (2)$$

For very small intervals of conversion, this method is no more an integral one, but rather a differential isoconversional method. Here we made use of Δα=0.2, which is quite a high value, therefore the method being no more a differential one (Figure 3).

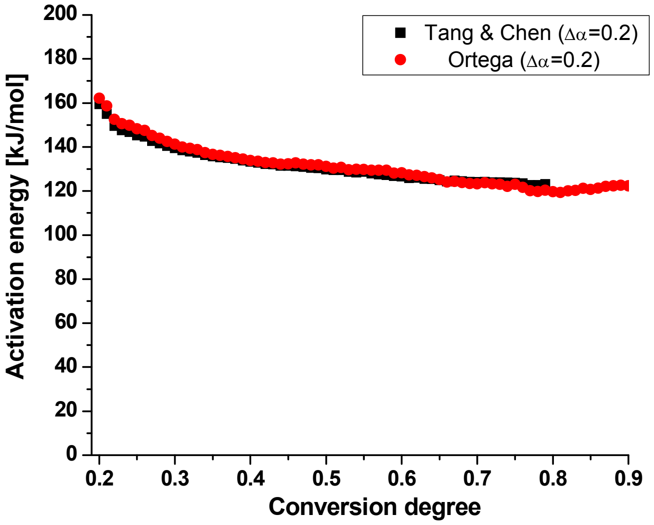

Figure 3. Isoconversional activation energy of the non-isothermal evaporation of 4-[(4-chlorobenzyl)oxy]-4'-trifluoromethyl-azobenzene (by Tang&Chen and Ortega methods)

The same judgement was used when applying Ortega [20] method (recently published in 2008). Ortega method, or Average linear (Ortega) integral isoconversional method uses equation 3. This method takes into account the history of the process as well.

$$ln\frac{\beta}{T_{\alpha} - T_{\alpha-\Delta\alpha}} = ln\, A_{\alpha} - ln[\, g(\alpha + \Delta\alpha\,) - g(\alpha - \Delta\alpha\,)] - \frac{E}{RT_{\alpha}} \qquad (3)$$

From Figure 3 it can be seen that these two methods provide similar results.

Even if the correlation coefficients (Figure 4) are higher for Tang & Chen method, Ortega method permits the evaluation until a higher conversion degree.

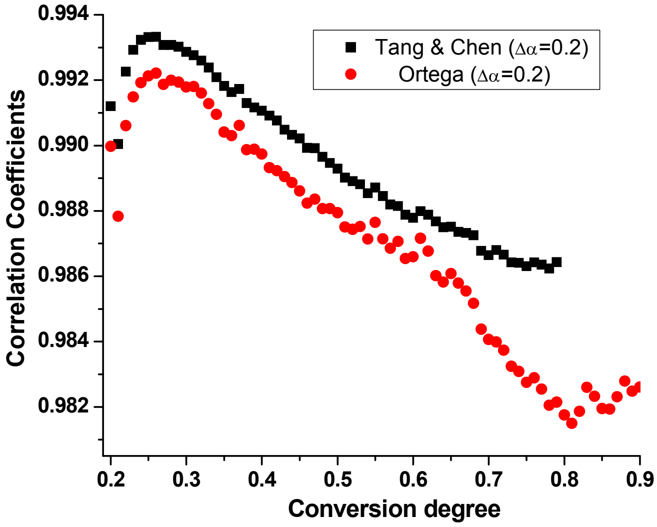

Figure 4. Correlation coefficients for the isoconversional activation energy of the non-isothermal evaporation of 4-[(4-chlorobenzyl)oxy]-4'-trifluoromethyl-azobenzene (by Tang&Chen and Ortega methods)

These two methods that strongly depend on the history and future of the process, provide in this case however similar results to the results of regular isoconversional ones. In the conversion degree range of 0.25-0.75, for Tang & Chen method the activation energy decreases from 145 to 123 kJ·mol^{-1}, while in the conversion degree range of 0.25-0.75, for Ortega method the activation energy decreases from 148 to 120 kJ·mol^{-1}.

CONCLUSIONS

The non-isothermal evaporation of 4-[(4-chlorobenzyl)oxy]-4'-trifluoromethyl-azobenzene has been investigated by several isoconversional methods; regular integral methods provided different, but symmetric trends of the isoconversional activation energy, that are strongly dependent on the temperature exponents (*n* and *m*). New methods like Tang & Chen and Ortega methods have been derived by using two other concepts and have to be still used until they will be completely understood. An imposed range of conversion confidence $\Delta\alpha=0.2$ should overcome the problem of differential approach; however, these methods induce a higher inaccuracy in the evaluation of activation energy. It is not clear how this $\Delta\alpha$ interval should be chosen, but it is obvious that the same value of it provides the same activation energy values for both methods.

EXPERIMENTAL SECTION

Aromatic azomonoethers were obtained by the condensation of some(phenyl-azo)phenols with chloromethylated derivatives of chlorobenzene in alkaline medium (Williamson ether synthesis) [24]. Thermal stability (TG, DTG and DSC) measurements of 4-[(4-chlorobenzyl)oxy]-4'-trifluoromethyl-azobenzene were carried out in air flow (150 $mL\cdot min^{-1}$) in a horizontal Diamond Differential/Thermogravimetric Analyzer from Perkin-Elmer Instruments [7]. Samples from 0.8 to 1 mg, contained in Al_2O_3 crucibles, were heated from room temperature to 800 ^oC, with the heating rates of: 2, 4, 6 and 8 $K\cdot min^{-1}$.

REFERENCES

1. A. Rotaru, C. Constantinescu, P. Rotaru, A. Moanta, M. Dumitru, M. Socaciu, M. Dinescu, E. Segal, *J. Therm. Anal. Cal.*, **2008**, *92*, 279.
2. T.-Y. Chao, H.-L. Chang, W.-C. Su, J.-Y. Wu, R.-J. Jeng, *Dyes Pigments*, **2008**, *77*, 515.
3. H. Dincalp, F. Toker, J. Durucasu, N. Avcibasi, S. Icli, *Dyes Pigments*, **2007**, *75*, 11.
4. M. Gűr, H. Kocaokutgen, M. Taş, *Dyes Pigments*, **2007**, *72*, 101.
5. A. Rotaru, A. Moanță, I. Sălăgeanu, P. Budrugeac, E. Segal, *J. Therm. Anal. Cal.*, **2007**, *87*, 395.
6. A. Rotaru, B. Jurca, A. Moanta, I. Salageanu, E. Segal, *Rev. Roum. Chim.*, **2006**, *51*, 373.
7. A. Rotaru, A. Kropidłowska, A. Moanță, P. Rotaru, E. Segal, *J. Therm. Anal. Cal.*, **2008**, *92*, 233.

8. A. Rotaru, A. Moanta, P. Rotaru, E. Segal, *J. Therm. Anal. Cal.*, **2009**, *95*, 161.
9. A. Rotaru, G. Bratulescu, P. Rotaru, *Thermochim. Acta*, **2009**, *489*, 63.
10. H. E. Kissinger, *Anal. Chem.*, **1957**, *29*, 1702.
11. T. Akahira, T. Sunose, *Res. Report Chiba Inst. Technol.*, **1971**, *16*, 22.
12. J. H. Flynn, L. A. Wall, *J. Res. Natl. Bur. Stand., A. Phys. Chem.*, **1966**, *70*, 487.
13. T. Ozawa, *Bull. Chem. Soc. Jpn.*, **1965**, *38*, 1881.
14. A. Rotaru, M. Gosa, P. Rotaru, *J. Therm. Anal. Cal.*, **2008**, *94*, 367.
15. A. Rotaru, M. Gosa, *J. Therm. Anal. Cal.*, **2009**, *96*, x.
16. W. Tang, Y. Liu, H. Zhang, C. Wang, *Thermochim. Acta*, **2003**, *408*, 39.
17. H. X. Chen, N. A. Liu, *J. Therm. Anal. Cal.*, **2007**, *90*, 449.
18. H. X. Chen, N. A. Liu, *J. Therm. Anal. Cal.*, **2008**, *92*, 573.
19. W. Tang, D. Chen, *Thermochim. Acta*, **2005**, *433*, 72.
20. A. Ortega, *Thermochim. Acta*, **2008**, *474*, 81.
21. S. Vyazovkin, *J. Comput. Chem.*, **2001**, *22*, 178.
22. P. Budrugeac, *J. Therm. Anal. Cal.*, **2002**, *68*, 131.
23. H. L. Friedmann, *J. Polym. Sci. C*, **1963**, *6*, 183.
24. S. Radu, C. Sarpe-Tudoran, A. Jianu, G. Rau, *Rev. Roumaine. Chim.*, **1998**, *43*, 735