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ORIGINAL ARTICLE

Kinetics and vaporization of anil in nitrogen atmosphere – Non-isothermal condition

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Abstract The thermal vaporization kinetics of Schiff's base was studied by thermogravimetry (TG) and differential thermal analysis (DTA) techniques using non-isothermal conditions. The kinetic parameters were calculated under model-free (Friedman's, Kissinger–Akahira–Sunose (KAS) and Flynn–Wall–Ozawa (FWO) methods) and model-fitting (Coats–Redfern, CR) methods. The results of the Friedman's isoconversional analysis of the TG data suggest that the investigated vaporization process follows a single-step reaction. Based on the obtained results, the mass loss is caused mainly by vaporizations and not by decomposition. The most probable kinetic model for vaporization of the compound is P2 (power law).

1. Introduction

Schiff bases are nitrogen donor ligands (–CH=N̈–) that form complexes by donating an electron pair to a metal atom in the formation of coordination compounds. Schiff bases have found wide applications in the field of coordination chemistry (Sallam, 2006), biological processes (Snatos et al., 2005), several enzymes (Clarkson and Basolo, 1973), microcalorimetry (Li-Xia et al., 2006), cytotoxic (Tarafder et al., 2002), insulin mimetic agents (McNeill et al., 1992), anticonvulsant (Panchagnula et al., 2004), antiproliterative (Vicini et al., 2003), antifungal activities (Pignatello et al., 1974), transport of oxygen in mammalian and other respiratory systems (Singh et al., 2010). Few Schiff's bases are prepared, characterized and determined the kinetic parameters of chitosan with salicylaldehyde (Guinesi and Cavalheiro, 2006), *trans* 1,2-cyclohexadiamine with salicylaldehyde (Aranha et al., 2007) and 4-aminoantipyridine with 2-aminophenol (Mohamed et al., 2009). Literature data show that no work has been reported on thermal decomposition of anil at different heating rates (10, 15 and 20 K min^{-1}) under non-isothermal condition in nitrogen atmosphere.

2. Experimental

2.1. Preparation of anil

Anil was prepared by refluxing equimolar quantities of benzaldehyde and aniline in alcohol for about 1–2 h. The resulting solution was cooled and poured into cold water. The precipitated anil was filtered off, washed with cold ethanol and dried. It was recrystallized from alcohol. The purity of anil was

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checked by melting point and FT-IR spectrum (m.p. 53 °C, lit. 54 °C), microanalysis; Found %C: 86.10, %H: 6.02, %N: 7.68; Calculated %C: 86.18, %H: 6.07, %N: 7.73.

2.2. Measurements

Elemental analysis was performed on a Carlo Analyzer at Central Drug Research Institute (CDRI), Lucknow, India. FT-IR spectrum was recorded in a KBr-pellet on an Avatar-330 spectrometer (with resolution 2 cm^{-1}). The simultaneous TGA and DTA curves were obtained with the thermal analysis system model Perkin Elmer TAC 7/DX Thermal Analysis Controller TAC-7. The TG and DTA analyses of anil were carried out under static nitrogen atmosphere (100 mL min^{-1}), in an alumina crucible with sample mass around 10 mg with heating rates of 10, 15 and 20 K min^{-1} from 308 to 973 K. The kinetic parameters E_a and $\ln A$ were calculated using Microsoft® Excel 2007® Software. The sample temperature, which is controlled by a thermocouple, did not exhibit any systematic deviation from the preset linear temperature program.

3. Theoretical background

3.1. Model fitting method

The integral method (Horowitz and Metzger, 1963) of Coats and Redfern (1964) has been most successfully used for studying the kinetics of dehydration and vaporization of different solid substances (Wendlandt, 1974). The kinetic parameters can be derived from modified Coats and Redfern Eq. (1),

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\left(\frac{AR}{\beta E_a}\right)\left(1-\frac{2RT}{E_a}\right) - \frac{E_a}{RT} \quad (1)$$

where $g(\alpha)$ is an integral form of the conversion function, the expression of which depends on the kinetic model of the occurring reaction. If the correct $g(\alpha)$ function is used, a plot of $\ln[g(\alpha)/T^2]$ against $1/T$ should give a straight line from which the values of the activation energy, E_a and the pre-exponential factor, A can be calculated.

3.2. Model free methods

Friedman's method (Friedman, 1963) is a differential method and was one of the first isoconversional methods. The non-isothermal rate law Eq. (2)

$$\beta\frac{d\alpha}{dT} = Ae^{\frac{-E_a}{RT}}f(\alpha) \quad (2)$$

gives

$$\ln\left[\beta\frac{d\alpha}{dT}\right] = \ln[A_\alpha f(\alpha)] - \frac{E_{a,\alpha}}{RT_\alpha} \quad (3)$$

A plot of $\ln(\beta\, d\alpha/dT)$ versus $1/T$ at each α gives E_a from the slope of the plot.

In the present study to evaluate the values of the activation energies of thermal vaporization of solid materials, Flynn–Wall–Ozawa equation (Flynn and Wall, 1966; Ozawa, 1965) (Eq. (4))

$$\ln\beta = \ln\frac{0.0048AE_a}{g(\alpha)R} - 1.0516\frac{E_a}{RT} \quad (4)$$

and Kissinger–Akahira–Sunose (KAS) equation (Kissinger, 1957; Akahira and Sunose, 1971) (Eq. (5)) were used.

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\frac{AE_a}{g(\alpha)R} - \frac{E_a}{RT} \quad (5)$$

The plots of $\ln(\beta\, d\alpha/dT)$ versus $1/T$ (Eq. (3)), $\ln\beta$ versus $1/T$ (Eq. (4)) and $\ln(\beta/T^2)$ versus $1/T$ (Eq. (5)) have been shown to give the values of apparent activation energies for the vaporization of anil at different α values. According to these equations, the reaction mechanism and shape of $g(\alpha)$ function do not affect the values of the activation energies of the vaporization stage.

3.3. Thermodynamic parameters

The kinetic parameters, energy of activation and pre-exponential factors are obtained from Kissinger single point (Kissinger, 1957) kinetic method using the Eq. (6).

$$\ln(\beta/T_m^2) = -E_a/RT_m + \ln(AR/E_a) \quad (6)$$

where T_m is temperature that corresponds to the maximum of $d\alpha/dT$. This 'model-free' kinetic method can be applied with a reasonable approximation without being limited to n-order kinetics (Malek, 1989), providing a single E_a value for each reaction step.

Based on the values of activation energy and pre-exponential factors for the vaporization stage, the values of $\Delta S^{\neq}$, $\Delta H^{\neq}$ and $\Delta G^{\neq}$ for the formation of activated complex from the reactants were calculated (Cordes, 1968).

4. Results and discussion

4.1. TG and DTA curves of vaporization of anil

The TG and DTA curves of vaporization of anil obtained at three heating rates (10, 15 and 20 K min^{-1}) are shown in Fig. 1. The weight loss observed in TG curves on heating the anil from room temperature to 350 °C is associated with the peak of curves. The weight loss is due to complete vaporization of the anil and curves are asymmetric figures and move to high temperature with increase in heating rates (Fig. 1).

4.2. Model-free analysis

The non-isothermal vaporization kinetics of anil was first analyzed by model-free methods viz., Friedman, Kissinger–Akahira–Sunose and Flynn–Wall–Ozawa. The data show that the variation of apparent activation energy E_a, as a function of extent of conversion α, for vaporization of anil. E_a value increases slightly in the conversion range of $0.20 \leqslant \alpha \leqslant 0.90$. It was pointed out (Vyazovkin and Linert, 1995) that when E_a changes with α, the Friedman and KAS isoconversional methods lead to close value of E_a. The applied isoconversional method does not suggest a direct way for evaluating either the pre-exponential factor (A) or the analytical form of the reaction model ($f(\alpha)$), for the investigated vaporization process of anil. In addition, the obtained data reveal that the dependence of the apparent activation energy (E_a) on the extent of conversion (α) helps not only to disclose the complexity of vaporization process, but also to identify its sublimation or evaporation