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The reaction kinetics of cyclopentadiene dimerization using differential scanning calorimetry: Experiments and modelling

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ABSTRACT

The reaction kinetics of cyclopentadiene (CPD) dimerization is studied using differential scanning calorimetry (DSC). Both dynamic and isothermal reactions are investigated. The experimental data were fit to a second order autocatalyzed reaction, taking into account the effect of elevated pressure on concentration which results from heating the easily volatilized reactant mixture in a sealed DSC pan. The rate constants and associated activation energies are obtained from the kinetic model, as well as from a model-free method. The results from the modeling with and without pressure effects are compared with one another and literature data.

1. Introduction

Cyclopentadiene (CPD) and dicyclopentadiene (DCPD) are two important products obtained from oil cracking [1], which are interconvertable through a Diels–Alder reaction. The dimer (endo-DCPD) can be formed easily at room temperature although full conversion takes several days [1]. The reaction product has been claimed to be solely endo-DCPD [2]. Given its importance, several groups of researchers have studied dimerization of cyclopentadiene to form DCPD [3–17]. The reaction is generally regarded as a second order [2–17] reaction or a second order autocatalyzed reaction [4,5]. In some works, this reaction is also treated as an equilibrium reaction [4,6–8]. The activation energy reported in the literature for dimerization ranges from 67 to 77 kJ/mol [4,5,7–16], whereas that for dicyclopentadiene cracking is reported to range from 112 to 151 kJ/mol [4,7,12,13]. The rate constant of dimerization at different temperatures is also reported [2–4,6–15,17], and the values range from 0.19×10^{-3} to 0.42×10^{-3} L mol^{-1} s^{-1} at 100 °C.

The dimerization reaction has been studied by dilatometry [9], pressure changes [5,10–13], chemical analysis using chromatography [3,7,8,14–16], and calorimetry [4,9], as well as by theoretical modeling [6,17], for the pure reactant system [3–5,9,10,14,16] and for systems containing solvent [7–15,17]. Only one calorimetric study has been performed for the neat system over a broad temperature range [4]. In that work, Flammersheim and Opfermann [4] performed dynamic DSC scans at different heating rates to temperatures as high as 165 °C and fit their data with an equilibrium kinetic model. Their model described the experimental data well and the activation energies for both forward and reverse reactions were in agreement with other data from the literature [4–16]. However, Flammersheim and Opfermann [4] failed to discuss the type of DSC pans used, any weight loss, and the effect of pressure changes due to reactant volatilization in their study.

In this work, the reaction kinetics of the cyclopentadiene Diels–Alder reaction is studied using differential scanning calorimetry in both dynamic and isothermal modes. The reaction kinetics model is extended to include the pressure change during the reaction which is important for the sealed DSC reaction system and has never been examined to the best of our knowledge. The results are compared with that from the standard constant pressure model, as well as with isoconversion methods and literature results.

2. Reaction model

Cyclopentadiene dimerization can be described using a second order autocatalyzed reaction model [3,4]:

$$-\frac{dC_{\mathrm{CPD}}}{dt} = kC_{\mathrm{CPD}}{}^{2}(C_{\mathrm{DCPD}} + b) \qquad (1)$$

where k is the rate constant, C_{CPD} and C_{DCPD} are the instantaneous monomer and dimer concentrations, respectively, and b is a constant related to possible impurities which initially accelerate

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the reaction. Eq. (1) assumes that the reaction is not reversible; this assumption is supported by our data and some prior work in the literature [2,3,5,9–17] and will be addressed in more detail in the discussion. The rate constant k has an Arrhenius dependence on temperature T:

$$k = k_o e^{-\frac{E_a}{R}\left(\frac{1}{T}-\frac{1}{T_o}\right)} \tag{2}$$

where k_o is the rate constant at reference temperature T_o (=373 K), E_a is the activation energy, and R is the gas constant. The molar concentration of monomer C_{CPD} and dimer C_{DCPD} can be written in terms of conversion x and the molar volume V:

$$C_{CPD} = \frac{n_{CPD}}{V_{total}} = \frac{n_{CPD}}{n_{total}V} = \frac{1-x}{(1-0.5x)V} \tag{3}$$

$$C_{DCPD} = \frac{n_{DCPD}}{V_{total}} = \frac{n_{DCPD}}{n_{total}V} = \frac{0.5x}{(1-0.5x)V} \tag{4}$$

where n_{CPD} and n_{DCPD} are the instantaneous moles of monomer and dimer, respectively, n_{total} is the total moles of reactant mixture and V_{total} is the volume in the reaction system. The molar volume V is influenced by conversion x, temperature T, and pressure P for our system (i.e., in the sealed DSC pan):

$$dV = \left(\frac{\partial V}{\partial x}\right)_{T,P} dx + \left(\frac{\partial V}{\partial T}\right)_{x,P} dT + \left(\frac{\partial V}{\partial P}\right)_{x,T} dP \tag{5}$$

and the molar volume can be written as follows:

$$V = V_o + \int \Delta V^* dx + \int \alpha dT - \int \gamma dP$$

where V_o is the initial molar volume of cyclopentadiene and ΔV^* is the difference between the initial molar volume of cyclopentadiene and the final molar volume of dicyclopentadiene. The parameters α and γ are the derivatives of volume with respect to the temperature and the pressure, respectively, which are assumed to be constant and equal to the values for pure liquid cyclopentadiene. This latter assumption is reasonable and introduces errors in molar volume of less than 3% for our temperature range from −20 to 220 °C and pressure range from 0.3 to 19.4 bar. The α and γ values of pure liquid dicyclopentaidene were estimated using Bhirud's method [18].

The total pressure of the reaction also changes with the reaction time due to the closed system (constant total volume of the DSC pan). The initial pressure is the saturation pressure for cyclopentadiene P^{sat}_{CPD}, whereas the final pressure is the saturation pressure for dimer P^{sat}_{DCPD}. The total pressure in the system is assumed to follow the bubble point, and it can be described as follows:

$$P = P^{sat}_{DCPD} + \Delta P^* \left(\frac{n_{CPD}}{n_{total}}\right) = P^{sat}_{DCPD} + \Delta P^* \left(\frac{1-x}{1-0.5x}\right) \tag{7}$$

where ΔP^* is the difference between the saturation pressures of monomer and dimer, which are obtained from the Soave–Redlich–Kwong (SRK) equation of state [19] by equating the liquid and vapor fugacities, with SRK parameters calculated from the critical temperature T_c, critical pressure P_c, critical volume V_c, and acentric factor w. The relationship between the derivatives of concentration and conversion with respect to time can be obtained by taking the derivative of Eq. (3) and substituting total pressure P and molar volume V from Eqs. (6) and (7):

$$-\frac{dC_{CPD}}{dt} = \frac{-(1-x)}{V(1-0.5x)^2}\left[\frac{0.5}{(1-x)} + \frac{(1-0.5x)\Delta V^*}{V} + \frac{0.5\gamma\Delta P^*}{V(1-0.5x)}\right]\frac{dx}{dt} - \frac{\alpha(1-x)}{(1-0.5x)V^2}\beta \tag{8}$$

where β is the heating rate of the dynamic reaction.

3. Methodology

3.1. Materials

Cyclopentadiene (M_n = 66.1 g/mol) was prepared from dicyclopentadiene (M_n = 132.2 g/mol) (95% stabilized, Acros Organics) by destructive distillation. The experimental procedure of obtaining cyclopentadiene followed the work from Magnusson [20] and Eastwood and co-workers [21]: the dicyclopentadiene was heated to approximately 170 °C, fractional distillation was performed using a three-segment Snyder column, and then the monomer with a boiling point around 39–43 °C was condensed in a receiver maintained at −78 °C; a Liebig condenser is used for the water-cooled system and nitrogen gas was purged at a constant flow rate to the whole system to prevent any side reactions. After the distillation, the sample was quickly placed in a freezer maintained at −80 °C where it was stored for no more than two weeks prior to use.

Solid phase micro-extraction gas chromatography-mass spectrometry (SPME/GC–MS) was employed to check the purity of the monomer immediately after distillation and also after at most two weeks storage. The results show that the sample is pure cyclopentadiene (99.75%) with a trace amount of dicyclopentadiene (0.25%) present. SPME/GC–MS and nuclear magnetic resonance (NMR) experiment were also used after reaction to check the purity of the product; the reacted sample was removed from the DSC pan immediately after reaction and put on dry ice until the SPME/GC–MS and NMR experiment, which was performed within 20 min. Reacted DSC samples show no presence of reactant or exo-DCPD, indicating the resulting product is fully converted to endo-DCPD dimer.

3.2. DSC measurements

A Mettler Toledo DSC 823 with a freon cooling system maintained at −80 °C was employed with nitrogen gas purge. Stainless steel medium pressure capsules (PerkinElmer, 1240 μL) with *o*-rings were used as in-situ reaction vessels to prevent loss of sample due to volatilization during the DSC measurements. DSC samples were prepared under nitrogen atmosphere. The samples were quickly weighed at room temperature then immediately put into the DSC furnace at −20 °C. Sample weights range from 40 to 60 mg; weight measurements before and after DSC scans agreed within 3%. No significant moisture was introduced on loading samples based on the absence of a water melting peak.

For dynamic DSC experiments, samples were stabilized at −20 °C for 3 min and then a dynamic temperature scan was performed to 220 °C at one of six different heating rates: 0.3, 0.8, 1.6, 3.2, 6.4, and 30 K/min. For isothermal experiments, samples were first heated at 30 K/min from −20 °C to a given isothermal temperature to avoid overpressurization of the DSC pans. Isothermal reaction temperatures ranged from 60 to 135 °C. Two or three different runs were carried out for each heating rate and for each isothermal temperature for purposes of reproducibility.

The temperature and heat flow for DSC temperature scans were calibrated and checked using indium at 10 K/min. The isothermal temperature calibration was performed using indium at 0.1 K/min. The temperature corrections for dynamic runs at rates other than 10 K/min were based on the linear relationship between the heating rate and the melting temperature of indium.

3.3. Modeling methodology

Reaction conversion as a function of time is calculated from the model using numerical integration of Eqs. (1)–(8). The physical