

In situ ATR-FT-IR study of the thermal decomposition of diethyl peroxydicarbonate in supercritical carbon dioxide

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Received 7 June 2006; received in revised form 10 November 2006; accepted 12 December 2006

Available online 17 December 2006

Abstract

The thermal decomposition of the organic free-radical initiator, diethyl peroxydicarbonate (DEPDC), was monitored by *in situ* ATR-FT-IR in heptane, and in the green solvent supercritical carbon dioxide (scCO₂) both with and without supercritical ethylene. It was observed that the characteristic peaks of DEPDC at 1802–1803 and 1194–1203 cm⁻¹ decreased significantly upon heating corresponding to the decomposition of DEPDC, while two new intense peaks simultaneously appeared at 1747 and 1262 cm⁻¹ in heptane, and similarly at 1756 and 1250 cm⁻¹ in scCO₂. The changes in the absorbance intensity of the characteristic peaks of the initiator during the decomposition were used for the measurement of the decomposition rate constant (*k_d*) of DEPDC. It was found that the thermal decomposition of DEPDC at low concentration in either heptane under atmospheric N₂ or scCO₂ under high pressure was via the first-order kinetics of unimolecular decomposition. The activation energy of the thermal decomposition of DEPDC was found to be 115 kJ/mol in heptane from 40 to 74 °C and 118 kJ/mol in scCO₂ from 40 to 60 °C. These new peaks revealed the formation of carboxyl groups contained in the decomposed products, indicating incomplete decarboxylation. During removal of CO₂ after the reaction in scCO₂, the instable intermediate monoethyl carbonate was decarboxylated and converted into the major end product, ethanol.

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Keywords: ATR-FT-IR; Initiator; Kinetics and mechanism

1. Introduction

Considerable effort has been devoted in recent years to find environmentally benign solvents and processes, particularly as a result of increased environmental regulations concerning the use of volatile organic compounds (VOCs) [1–6]. Supercritical carbon dioxide (scCO₂) has emerged as a viable “green” alternative to organic solvents for several applications, including polymer synthesis, modification, and nanotechnology [7,8]. In the supercritical state (*T_c* = 31.8 °C, *P_c* = 76 bar), carbon dioxide can have unique properties such as liquid-like density and gas-like diffusivity, and these properties are “tunable” by varying the pressure and/or temperature [9]. Previously, DeSimone and coworkers have shown that scCO₂ is a promising alternative medium for free radical, cationic, and step-growth

polymerizations [1,3,10]. Indeed, DuPont has recently commissioned a plant to manufacture Teflon™ in scCO₂ by the use of free-radical polymerization [11]. The reasons for the intense industrial interest are that CO₂ is inert to highly electrophilic radicals (i.e., no chain transfer to solvent), inexpensive, non-toxic, non-flammable, and environmentally benign [3].

In recent years, considerable attention has been attracted to investigate and study the mechanism of free-radical formation and the kinetics of the decomposition of organic peroxides [12–21], particularly due to their applications in organic synthesis [12,13], biological processes [14,15], polymerization [16,17], and as resin modifiers [18], additives for fuel [19], and explosives [20]. Free radical polymerization still dominates in the production of many commercial polymers such as polystyrene, polyethylene (low density), poly(ethylene-co-vinyl acetate), Teflon, and other fluorinated polymers. Due to the proven ability of scCO₂ in industrial continuous polymerizations, and a poor understanding of how CO₂

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influences reaction kinetics, a study of the chemistry of the thermal decomposition of the required organic peroxide initiators under supercritical conditions is important to understand and control the polymerizations under these conditions.

Dialkyl peroxydicarbonates ($R-O-CO_2$)₂ are used as free-radical initiators in many commercial processes such as the large-scale production of polymers and curing resins [12,18,21]. Compared with other classes of peroxides, the number of mechanistic studies on the decomposition of dialkyl peroxydicarbonates is relatively small, particularly in green solvents. According to the previous studies [16,22–26], a general decomposition mechanism of peroxydicarbonates or peroxyesters can be described as direct decomposition of the peroxides through breaking the weak O–O bond. The resulting alkoxy-carboxyl or carbonyloxy radical may either decarboxylate [24–28] or participate in a bimolecular reaction [22,23]. In addition, solvents may have some influence on the decomposition of peroxydicarbonates as the employed solvent is seldom inert due to the high activity of the formed free radicals. Thermal decomposition of initiators in supercritical CO₂ has been studied by Guan *et al.* [29], Bunyard [30], Charpentier *et al.* [4,5,31] and Kadla *et al.* [32]. It was reported that the rate constants of initiator decomposition in scCO₂ were different from that in other organic solvents due to its “zero-viscosity” [30] and low dielectric constant [29]. Charpentier *et al.* studied the thermal decomposition of diethyl peroxydicarbonate (DEPDC) in scCO₂ in a continuous stirred tank reactor (CSTR) [31], wherein reaction kinetics were simulated based on a one-bond radical fission mechanism. However, this study did not harness the power of *in situ* ATR-FT-IR.

Hence, the goal of the present work was to study the decomposition of a previously studied initiator DEPDC in high-pressure scCO₂ and ethylene using high pressure *in situ* ATR-FT-IR, and to compare the kinetic decomposition results with previous non-FT-IR techniques. Offline NMR was used as a complementary tool for studying the decomposition mechanism. Understanding the initiator decomposition by ATR-FT-IR in scCO₂ is the first step for analyzing more complex spectroscopic data during polymerizations to provide an understanding of the formation of inorganic/organic hybrids for our work in the one-pot synthesis of polymer nanocomposites.

2. Experimental

2.1. Materials

Ethylene (99.99% Polymer Grade) was purchased from Matheson Gas Products Canada, and further passed through columns filled with 5 Å molecular sieves and reduced 20% copper oxide/Al₂O₃ to remove moisture and oxygen, respectively. Instrument grade CO₂ (from BOC Gases, 99.99%, with dip-tube) was purified by passing through columns filled with 5 Å molecular sieves and reduced 20% copper oxide/Al₂O₃ to remove moisture and oxygen, respectively. Ultra high-purity N₂ (from BOC, 99.99%) was further purified by passing through columns filled with 5 Å molecular sieves and reduced 20% copper oxide/Al₂O₃ to remove moisture

and oxygen, respectively. The initiator diethyl peroxydicarbonate (DEPDC) was homemade as described below. Heptane (Aldrich, HPLC grade) was distilled under vacuum. NaOH, 30% H₂O₂, ethyl chloroformate, 0.1 N sodium thiosulfate solution, sodium bicarbonate, sodium sulfate, glacial acetic acid, potassium iodide, and diethyl carbonate were purchased from Aldrich and used as received.

2.2. Preparation of DEPDC initiator

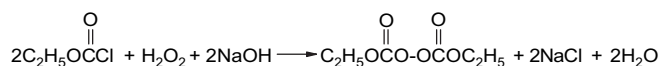
Distilled water (100 ml) was charged in a glass reactor (250 ml) equipped with a magnetic agitator and a thermometer. The reactor was cooled to ≤ 5 °C in an ice/water bath. Ethyl chloroformate (12 ml) and 30% H₂O₂ (6.64 g) were added to the reactor under powerful stirring. Then NaOH solution (24 ml, 5 N) was introduced to the reactor dropwise. The reaction was carried out under gentle stirring for 10 min with the reaction temperature controlled below 10 °C. Heptane was utilized to extract the formed DEPDC from the mixture and the solution was dried over sodium sulfate. The dried solution was filtered and separated from the solvent by means of a rotary evaporator under vacuum at less than 2 °C. The yield of DEPDC was measured using a standard iodimetric titration analysis technique (ASTM E298-91) to exceed 90%. *Owing to the instability of DEPDC, highly concentrated DEPDC must be stored at very low temperature (–20 °C). Scheme 1 provides the overall reaction.

2.3. Reactor and *in situ* ATR-FT-IR measurements

In situ Fourier transform infrared (FT-IR) monitoring of solution concentration in the stirred 100 ml high-pressure autoclave (Parr 4842) was performed using a high-pressure immersion probe (Sentinel-Mettler Toledo AutoChem). The DiComp ATR probe consists of a diamond wafer, a gold seal, a ZnSe support/focusing element, housed in alloy C-276. The probe was attached to an FT-IR spectrometer (Mettler Toledo AutoChem ReactIR 4000) via a mirrored optical conduit, connected to a computer, supported by ReactIR 2.21 software (MTAC). This system uses a 24-hour HgCdTe (MCT) photoconductive detector. The light source is a glow bar from which the interferometer analyzes the spectral region from 650 to 4000 cm^{–1}. The beamsplitter inside the RIR4000 is ZnSe. Spectra were recorded at a resolution of 2 cm^{–1} and the absorption spectra were the results of 64 scans. *In situ* ATR-FT-IR was applied to monitor the thermal decomposition of DEPDC and the product formation.

2.4. Gas chromatography–mass spectrometry

Gas chromatography–mass spectrometry (GC–MS) (Varian, Saturn 2100D/GC–MS) was applied to analyze the



Scheme 1. The overall reaction of synthesis of DEPDC.

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