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Gas-phase reaction thermodynamics in preparation of pyrolytic carbon by propylene pyrolysis

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Abstract

Density functional theory and accurate model chemistry at G3(MP2) and G3//B3LYP levels of theory have been employed to explore the details of propylene pyrolysis gas-phase reaction thermodynamics. Geometries and vibrational frequencies for all of the interested possible species are calculated by B3PW91/6-31G(d). Standard thermodynamic data are derived by G3(MP2) and G3//B3LYP electronic energies combined with statistical thermodynamics. The data include heat capacities, entropies, enthalpies of formation and Gibbs free energies of formation at 298.15 K. Heat capacities and Gibbs free energies of formation at temperatures in 100–1500 K are calculated and fitted into analytical equations. The theoretical values are in excellent agreements with the available experimental values. Thus the theoretical predictions for all of the other species (stable intermediates in propylene pyrolysis) are believed reliable. Based on the thermochemical data, the equilibrium concentration distribution for all of the species in the temperature range of 100–1500 K (i.e. phase diagram) are calculated according to the chemical equilibrium principle. This work has supported the possibility of direct condensation of the high concentration carbon monomers and dimmers produced in the propylene pyrolysis dissociation reactions.
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1. Introduction

Carbon fiber reinforced silicon carbide composite (C/SiC) exhibits satisfactory mechanical properties and failure behaviors. This material has been used as important and advanced thermal protection material, brake material and the most promising candidate for high-temperature structural applications [1–5]. The pyrolytic carbon (PyC), as interfacial layer, plays significant roles for the composite in higher mechanical properties and excellent oxidation resistance properties [6]. Usually,

PyC layer is deposited on the carbon fibers prior to densification to provide a controlled and uniform interface with the silicon carbide matrix in decomposition process. The existence of the interfacial layer, which is loosely bonded to both of the matrix and fiber, may provide great thermal expansion mismatch between the fibers and the SiC matrix [3,7]. However, the details of reaction mechanisms for the formation of PyC remain unresolved [8] because of the complexity of the involved chemistry and its subtle entanglement processes either in the experiments or in the results interpretations [9]. Actually, only a few intermediate species have been observed [10,11].

Propylene (C_3H_6) is extensively used as a precursor for preparing PyC by chemical vapor deposition (CVD) or

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chemical vapor infiltration (CVI) technique due to its high deposition rate [12–14]. This system has been investigated experimentally [15–17] and theoretically by numerical simulations [18,19]. In the gas-phase reactions, experiments are able to observe the concentrations of the most stable species. Theoretical methods by utilizing ab initio bond-additivity correction and RRKM are proposed to investigate the gas-phase reaction thermo-chemistry and kinetics in the thermal CVD of hard coatings of silicon carbide and boron nitride [20]. For the system of propylene pyrolysis, however, a large number of hydrocarbons (including radicals and poly-atomic carbons) could be formed during the high temperature dissociation processes [21,22] and most of their thermal–chemical data are unknown. Propos-

als concerning PyC formation are also complex. The processes might directly be propylene dissociating into PyC [8,10,13] or firstly polymerizing into benzene and then into polycyclic aromatic hydrocarbons [23–28]. For the processes, important or dominant reactions are found to be elimination of molecular hydrogen [8,10,13,23] and dissociating into C_2H_2 or C_2H_4 [10]. For example, Becker and Hüttinger [13] observed the partial pressures of CH_4, C_2H_2 and C_2H_4 are much higher than that of C_6H_6 in the same system at the very beginning of the reactions.

It is clear that the formation and the properties of the PyC interlayer are closely related to the species generated in the gas phase. Therefore, a detail study of the gas-phase hydrocarbons is desirable [29,30] to ensure the correlation
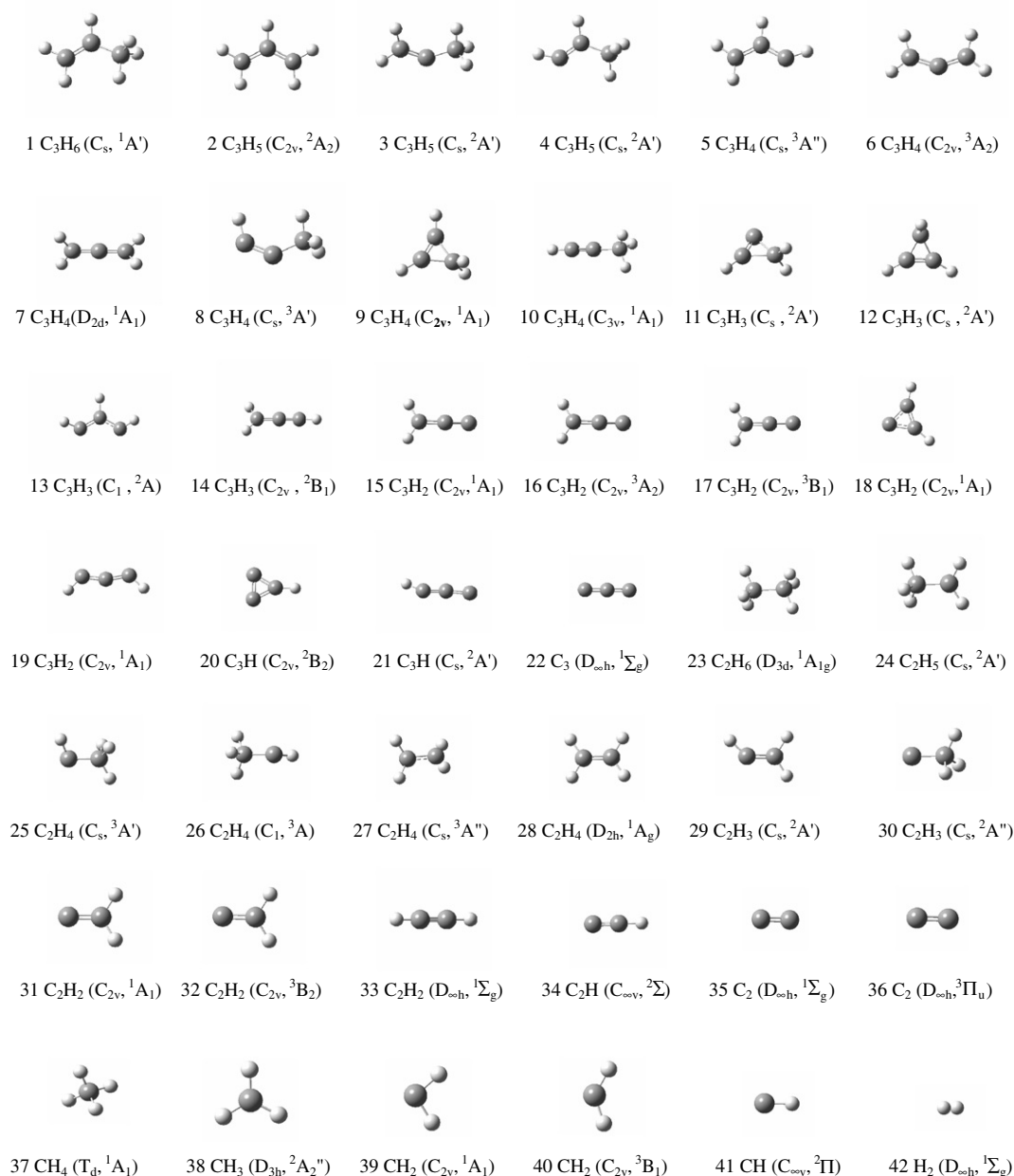

Fig. 1. Stable structure, symmetry and electronic state of propylene pyrolysis species obtained at B3PW91/6-31G* level of theory.