

Mechanism of Thermal Decomposition of Bisphenol C Polycarbonate: Nature of Its Fire Resistance

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Introduction

Bisphenol C polycarbonate (BPC PC) is one of the most fire-resistant polymers known to the scientific community. Mechanical characteristics of this material make it suitable for transportation applications requiring toughness and durability.¹ According to experimental analysis,^{1,2} thermal degradation of BPC PC starts at 450°C (T_{onset}) and leads to the formation of char (~50 % by weight) and non-flammable gaseous products, CO₂ and HCl. These experimental observations provide a straightforward explanation of the exceptional fire resistance. However, the chemical mechanism responsible for the high-temperature behavior of this polymer is not understood.

In this work, quantum chemical methods have been employed for analysis of reaction pathways of the thermal degradation of BPC PC. On the basis of the computational results, a mechanistic explanation of the high-temperature transformation of this material is proposed.

Method

Potential energy surfaces (PES) of model compounds representing BPC PC were studied using B3LYP density-functional method³ with a 6-31G(d) Gaussian basis set.⁴ The method was selected to provide maximum accuracy within reasonable computational time. The PES's were searched for stationary points. Vibrational frequency analysis of the optimized stationary points was used to identify them as products (or intermediates, minima) or transition states (saddle points). Intrinsic reaction coordinate calculations (IRC)⁵ were performed for each transition state structure in order to determine the connected reactants and products. Computed energetics (with zero-point energies taken in to account) was used to compare identified reaction pathways.

Results

First, dissociation energies of single bonds in BPC PC were calculated. Results of these

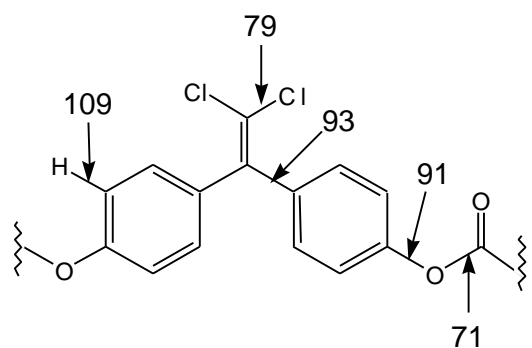


Figure 1. BPC PC bond energies in kcal/mol.

calculations are presented in Figure 1. The weakest bond was identified to be the bond between oxygen atom and carbon in carbonyl group (71 kcal/mol). Rupture of this bond would result in scission of polymer chain and, as a consequence, generation of volatile chain fragments. However, according to experimental results,^{1,2} CO₂ and HCl are the only gaseous products of thermal degradation of BPC PC (most of the elemental carbon is kept in the condensed phase and is eventually transformed into char.). Thus,

in order to explain these experimental observations, we need to identify reaction channels that would lead to crosslinking/cyclization of the polymer while being energetically comparable with the weakest bond dissociation reaction.

A number of potential reaction pathways of thermal decomposition of BPC PC were analyzed. Reaction channels for elimination Cl_2 and HCl from bisphenol C were identified and ruled out. The energy barriers of these reactions were found to be ~ 20 kcal/mol higher than the energy of the weakest bond. The reaction pathway of elimination of Cl-atom followed by phenyl-ring shift

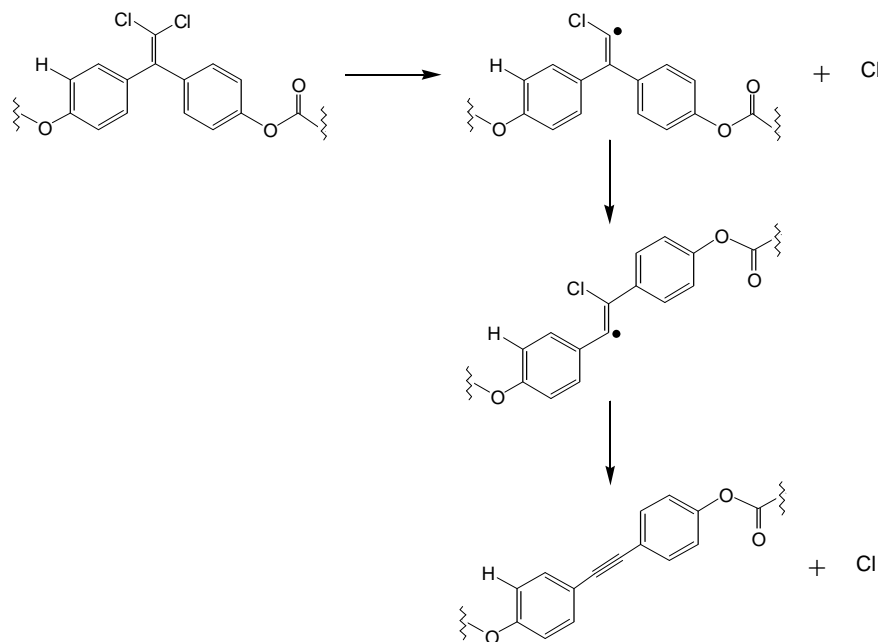


Figure 2. Cl-atom elimination - phenyl shift reaction.

phenyl ring intermediate. The potential energy profile of this reaction is shown in Figure 3. According to the B3LYP results, the height of the reaction energy barrier is about the same as the energy of the weakest bond in BPC PC. Analysis of the PES of the Cl-phenyl intermediate indicates that the chlorine atom bound to an aromatic carbon can move freely along the ring structure,

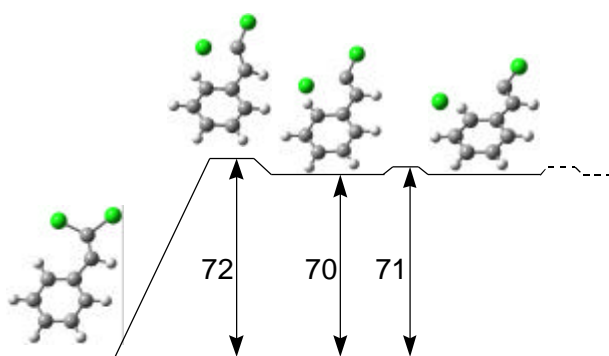


Figure 3. Cl-atom shift (energies are in kcal/mol)

and elimination of the other Cl-atom is shown in Figure 2. Although this reaction can not be completely ruled out on the basis of energetics (the most energetically demanding step is dissociation of the C-Cl bond, 79 kcal/mol), it does not provide a direct explanation for formation of char in the thermal degradation process.

Study of the PES of a dichlorophenylethylene model compound revealed a reaction leading to formation of a Cl-atom-

phenyl ring intermediate. Further studies of Cl-phenyl type compounds showed that Cl-atom has an ability to form weakly-bound complexes with one as well as two phenyl rings ("sandwich" type structures). It was also established that these Cl-phenyl complexes can undergo elimination of HCl . The height of the energy barrier of the elimination reaction was found to be between 15 and 25 kcal/mol (depending on the particular structure of Cl-phenyl reactant).

On the basis of the results of the quantum chemical analyses, a mechanism of thermal degradation of BPC PC is proposed. According to this mechanism, the degradation occurs via formation of Cl-phenyl complexes, which provide weak crosslinks between the polymer chains at initial stages of the process. These complexes subsequently decompose via elimination of HCl . The radical sites formed as a result of these reactions recombine, forming strong covalent bonds between

bisphenol fragments of the polymer chains. The process of crosslinking, which eventually leads to the formation of char, competes with the process of backbone cleavage, which leads to the formation of CO₂. The proposed mechanism provides a plausible explanation of the numerous experimental observations.^{1,2}

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