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Mechanism of the thermal decomposition of bisphenol C polycarbonate: nature of its fire resistance

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Abstract

Quantum chemical methods have been used to identify reaction pathways of the thermal decomposition of bisphenol C polycarbonate, one of the most fire-resistant polymers known to the scientific community. Despite substantial interest in its unusual high-temperature behavior, the mechanism of its thermal decomposition has been unknown. On the basis of computational results, a mechanism is proposed where the main feature is a shift of Cl atom from the β-styrene position to the adjacent aromatic ring, which leads to crosslinking and cyclization of the polymer. The proposed mechanism is consistent with experimental observations of char, HCl, and CO_2 as the main pyrolysis products.

Keywords: Polymer pyrolysis; Polymer flammability; B3LYP

1. Introduction

Synthetic procedures for preparation of bisphenol-C-based polymers have been known since early 1960s. Publications and patents on this subject have been recently reviewed by Rusanov [1]. In 1980, Factor and Orlando conducted an extensive study of physical, thermal, and mechanical properties of bisphenol C polycarbonate (BPC PC) [2]. The chemical structure of a repeat unit of this polymer is shown in Fig. 1. The authors found that in addition to attractive mechanical characteristics, this material possesses an exceptional fire resistance.

Recently, comprehensive experimental analyses of the thermal decomposition of BPC PC have been performed by Stewart [3] and Ramirez [4]. According these analyses, thermal degradation of the polymer starts at about 450 °C and leads to the formation of char (~50% by weight), gaseous HCl, and CO_2. The fact that the major products of the degradation process are essentially non-combustible provides a direct explanation of the exceptional fire resistance (polymer flammability is largely determined by the rate and heat of combustion of gas-phase pyrolysis products). However, the reaction mechanism responsible for the unusual high-temperature behavior of this polymer has not been understood. Detailed understanding of the mechanism is crucial to proposing structural variations that would have improved performance and processing characteristics.

In the present work, quantum chemical methods have been employed for the analysis of reaction pathways of the thermal decomposition of BPC PC. The computational results indicate that the decomposition process is most likely to be initiated by a shift of Cl atom from the β-styrene position to the adjacent aromatic ring, which leads to crosslinking and cyclization of the polymer.

2. Methodology

The B3LYP density-functional method [5,6] with the standard polarized split-valence 6-31G(d) basis set [7] was used in this study for the analysis of potential energy surfaces (PESs) of molecular structures containing up to 16 non-hydrogen atoms. The method was chosen to achieve the maximum accuracy within a reasonable computational time (see Refs. [8,9] for comparative analyses of performance of quantum chemical methods). The restricted version of the method was used for closed-shell species, while the unrestricted version was used for radicals.

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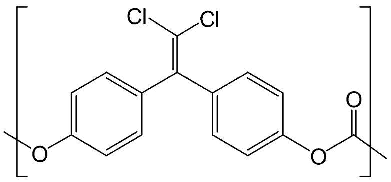

Fig. 1. Repeat unit of BPC PC.

PESs of the model compounds representing BPC PC were searched for stationary points. Vibrational frequency analysis of the optimized stationary structures was used to identify them as transition states (saddle points) or products (minima). An intrinsic reaction coordinate (IRC) reaction-path-following calculation [10] was performed for each transition state in order to establish the connected reactants and products. Computed energies of optimized molecular structures were tested for stability [11] and corrected for zero-point energy contributions. All calculations were carried out using the GAUSSIAN 98 package of programs [12].

3. Results and discussion

3.1. Bond dissociation energies

Results of calculations of the bond dissociation energies in BPC PC are shown in Fig. 2. The energies were obtained by calculating enthalpies (at 0 K) of the bond dissociation reactions for the hydrogen-atom-terminated molecular fragments *A* and *B* (see Fig. 2). These reactant molecules were represented by their lowest energy conformations. The geometries of the products were obtained by separating the reactant molecules into the radical fragments of interest and optimizing the structures of each of the radicals.

According to these calculations, the weakest bond in BPC PC is the single bond between oxygen atom and the carbonyl carbon (298 kJ/mol). The phenoxy-type radical formed as a result of this bond dissociation is strongly resonantly stabilized, which accounts for the low bond energy value. Ruptures of the O–C bonds during the thermal decomposition process would result in scissions of the polymer backbone, leading to generation of volatile chain fragments. According to the experimental results [3, 4], however, HCl and CO_2 are essentially the only gaseous products of the thermal degradation of BPC PC. Most of the elemental carbon is kept in the condensed phase in form of char. In order to explain these experimental observations, reaction channels must be identified that would successfully compete with the backbone scission reaction and lead to the formation of char.

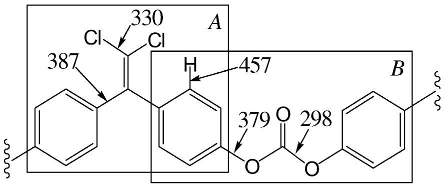

Fig. 2. Bond dissociation energies in BPC PC in kJ/mol. *A* and *B* designate molecular fragments that were used as model compounds for calculations of the bond energies.

Experimental analyses of the thermal degradation and flammability of bisphenol-based polymeric materials carried out by Stewart [3] and Factor and Orlando [2] indicate that diphenyldichloroethylene structural elements are primarily responsible for the char-forming ability and, consequently, high fire-resistance. A substitution of chlorine atoms in the diphenyldichloroethylene fragments of the polymer structures by methyl groups results in a substantial reduction in char yields (down to 2–20% by weight). Therefore, in the quantum chemical analyses described below, attention was focused on the reactions involving these fragments of the BPC PC structure (fragment *A* in Fig. 2). The general strategy of the present approach was to find the reaction channels that led to a crosslinking/cyclization of the polymer (formation of char) and that were, at the same time, energetically comparable with the backbone scission reaction.

3.2. Cl_2 elimination

Elimination of Cl_2 was suggested in Ref. [3] as one of the possible routes of the thermal decomposition of BPC PC. In the present work, the PES of this reaction was examined using 1,1-dichloroethylene as a model compound. The results are shown in Fig. 3 (top diagram). The elimination occurs via one of the two structurally distinct but energetically similar transition states (the energy difference is less than 1 kJ/mol). Both of the transition states lead to the same intermediate. This intermediate may undergo decomposition proceeding through vinylidene and Cl_2 (as confirmed by a relaxed scan of the shortest C–Cl bond distance). According to the B3LYP calculations, the intermediate and transition states are spin-contaminated singlets ($\langle s^2 \rangle \approx 0.5$), while the vinylidene is a closed-shell structure ($\langle s^2 \rangle = 0$).

The minimum energy required for the Cl_2 elimination is equal to the difference between the energy of the products and reactant (412 kJ/mol). In order to insure that the energy value is not affected by the small size of the model, it was recalculated using the diphenyldichloroethylene model compound (see the bottom diagram in Fig. 3). The ΔH^0 (0 K) of the elimination reaction obtained using the larger model is slightly lower (400 kJ/mol). Further analysis of the PES of the diphenylvinylidene revealed that only 7 kJ/mol is required for its isomerization to diphenylacetylene. Such a low value of the reaction barrier makes the presence of the minimum corresponding to the diphenylvinylidene intermediate questionable. Regardless of the details, the energy of the Cl_2 elimination is over 100 kJ/mol higher than the energy of the weakest BPC PC backbone bond. Thus, Cl_2

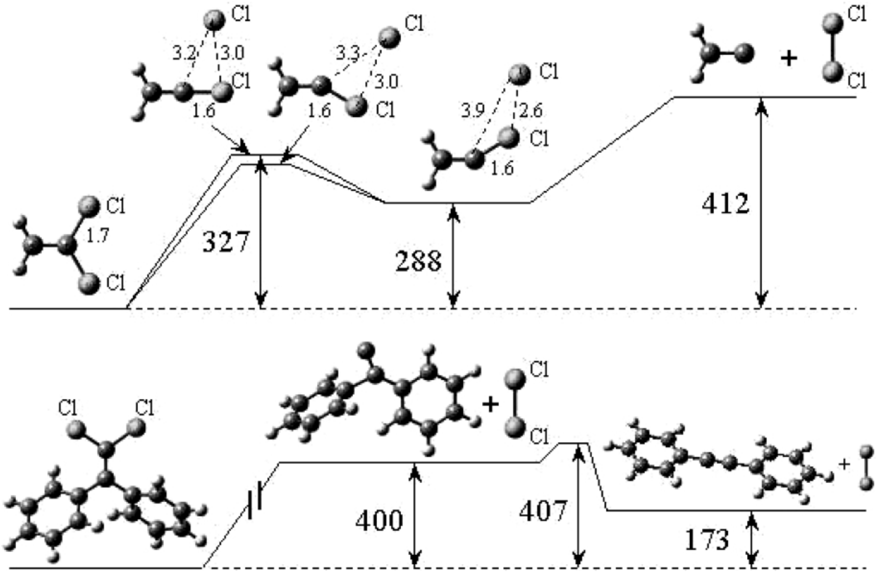

Fig. 3. Potential energy profiles of Cl_2 elimination from dichloroethylene (top) and diphenyldichloroethylene (bottom) model compounds. Energy values are in kJ/mol. Some key interatomic distances are given in Å.

elimination cannot compete with the backbone scission reaction and was ruled out.

3.3. HCl elimination

The PES of hydrochloride elimination from BPC PC was studied using the β,β-dichlorostyrene model compound. The results are shown in Fig. 4. The reaction occurs via a single 377-kJ/mol barrier and leads to internal cyclization. The transition state is a highly spin-contaminated structure ($\langle s^2 \rangle = 1.0$), which may indicate that it is a biradical (two unpaired electrons) in a singlet state. While the products of this reaction are consistent with experimental observations (the internal cyclization can be interpreted as a first step in the formation of char), the reaction barrier is almost 80 kJ/mol higher than the energy of the weakest backbone bond in BPC PC. Therefore, the probability that this HCl elimination channel plays an important role in the thermal decomposition of the polymer is also low.

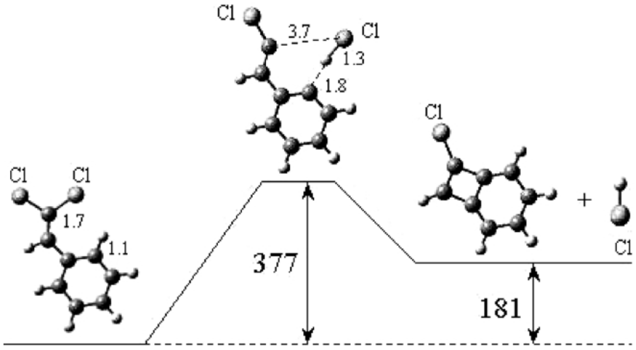

Fig. 4. Potential energy profile of HCl elimination from dichlorostyrene model compound. Energy values are in kJ/mol. Some key interatomic distances are given in Å.

3.4. C–Cl bond dissociation

The second weakest bond in BPC PC is the one between vinylic carbon and chlorine atom (see Fig. 2). In spite of the fact that this bond is about 30 kJ/mol stronger than the weakest backbone bond, the energy difference is not sufficiently large to exclude homolytic C–Cl bond dissociation from the processes potentially important in the thermal decomposition of the polymer. Assuming that the C–Cl bond dissociation reactions were to occur, Cl atoms formed in the process are likely to be involved in H-atom abstractions from the phenyl rings of BPC PC. These abstraction reactions would lead to the formation of HCl and phenyl radical sites that could recombine, forming strong crosslinks between the polymer chains. Diphenylchlorovinyl radical sites, the second product of the C–Cl bond dissociation, could also participate in the crosslinking or undergo a phenyl-ring shift with a subsequent elimination of the Cl atom. The potential energy profile of the model shift-elimination reaction is shown in Fig. 5. According to the B3LYP calculations, the phenyl-ring shift occurs via a series of two transition states separated by an intermediate. However, the differences between energies of the intermediate and transition states are too small to be considered as a conclusive evidence of the existence of the intermediate minimum. Cl-atom elimination following the ring shift is a barrierless reaction (as confirmed by a relaxed scan of the C–Cl bond distance). The energy required for the overall shift-elimination process is determined by the height of the first phenyl-ring-shift barrier (137 kJ/mol). The final product of the model reaction is phenylacetylene, which corresponds to the formation of diphenylacetylene structural elements in the decomposing polymer.

It is apparent that the reaction mechanism described above may lead to the formation of char. Some experimental

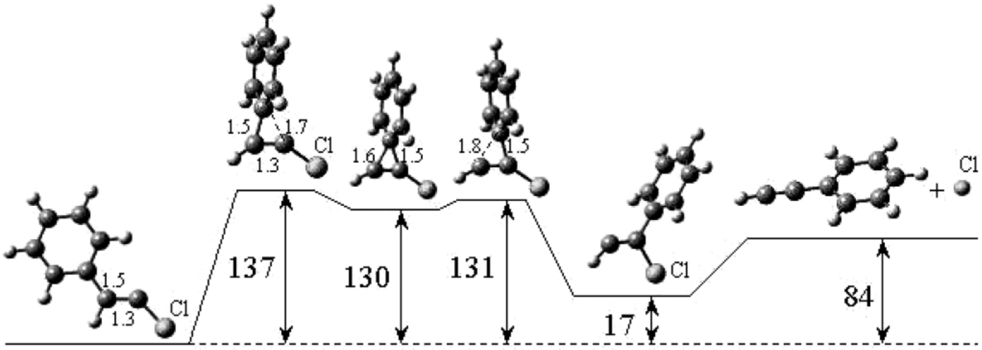

Fig. 5. Potential energy profile of phenyl-ring shift followed by Cl-atom elimination. Energy values are in kJ/mol. Some key interatomic distances are given in Å.

evidence of the presence of diphenylacetylene structural elements in the chains of a partially decomposed BPC PC was reported in Ref. [4]. However, in spite of the fact that the products are in agreement with experimental observations, this is insufficient evidence to contend that a C–Cl-dissociation-initiated process is the major route of the thermal decomposition of BPC PC. PES analysis described in Section 3.5 indicates that there exists a yet more energetically favorable reaction pathway that leads to the experimentally observed products.

3.5. Cl-atom shift

According to the B3LYP calculations, the β,β-dichlorostyrene model compound may undergo Cl-atom-shift reactions. The potential energy profile of these reactions is shown in Fig. 6. The first shift leads to the formation of a complex, where Cl atom is attached to the phenyl ring in an *ortho* position with respect to the substituent. Two other local minima on the PES correspond to the Cl atom in the *para* and other *ortho* position. The minima are interconnected by transition states in such a way that the Cl atom can move around the phenyl ring structure. Geometrical parameters of the Cl–phenyl complexes (corresponding to the minima) suggest that the attachment of the chlorine atom to the phenyl ring does not result in any substantial perturbation of the ring aromaticity. All stationary structures on the PES (with the exception of the reactant) are highly spin contaminated ($\langle s^2 \rangle \approx 1.0$). Analysis of the B3LYP atomic spin densities and CASSCF(4,8) calculations [13–15] performed with the 6-31G(d) basis set on the B3LYP-optimized structures indicate that the Cl–phenyl complexes are singlet state biradicals.

The energy required for the initial Cl-atom shift (from vinylic carbon to phenyl ring) is 300 kJ/mol, which is approximately equal to the energy of the weakest backbone bond in BPC PC. Also, energy barriers separating the Cl–phenyl complexes are negligibly small. Thus, once the initial shift reaction occurs, the Cl atom can move freely around the ring structure.

Further analysis revealed that the ability to form Cl–phenyl complexes is not specific to the dichlorostyrene model compound. Chlorine atoms can form bonds with one or two benzene molecules. B3LYP structures of the Cl–benzene complexes are shown in Fig. 7. The bonding energy is essentially the same for all the complexes, including those derived from the dichlorostyrene. 40–45 kJ/mol is required to break the Cl–phenyl bond or the two bonds that are present in the case of complexes with two aromatic rings.

These findings lead to the conclusion that when the Cl–phenyl complex is formed in an environment with a high density of phenyl rings, the chlorine atom has a sufficient mobility to move away from the formation reaction zone by transferring within and between the aromatic structures.

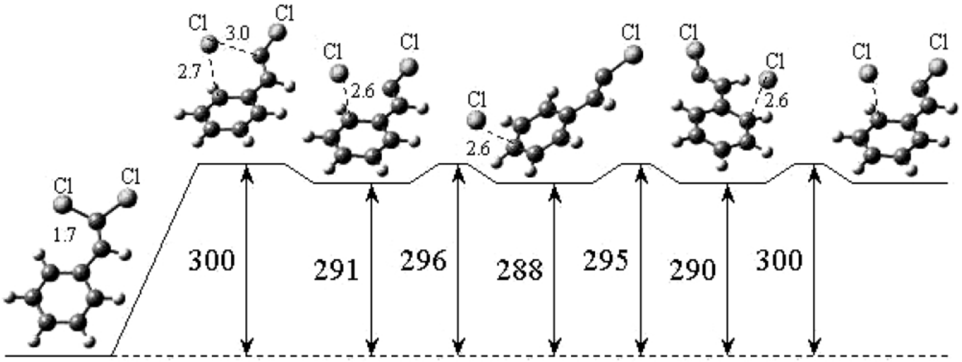

Fig. 6. Potential energy profile of Cl-atom shifts in dichlorostyrene model compound. Energy values are in kJ/mol. Some key interatomic distances are given in Å.

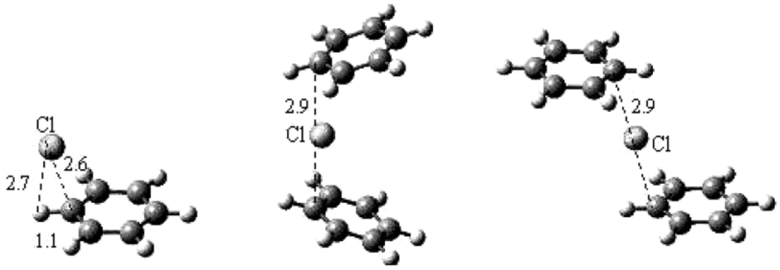

Fig. 7. Cl–benzene complexes. Some key interatomic distances are given in Å.

Thus, the initial Cl-atom shift in BPC PC should be similar to the C–Cl bond dissociation reaction, with the exception that the energy required for the former process is lower due to the stabilization provided by Cl–phenyl interactions. The fact that chlorine atom can bind together phenyl rings also indicates that it may act as a crosslinking agent at the early stages of the BPC PC decomposition. This hypothesis is consistent with the experimental results reported by Ramirez [4], who observed that after BPC PC is heated to 200 °C it becomes insoluble.

Furthermore, quantum chemical analysis of decomposition pathways of the Cl–phenyl complexes showed that they may easily undergo HCl elimination reactions. Examples of the HCl elimination pathways are shown in Fig. 8. The top potential energy diagram describes hydrochloride elimination from the *ortho* Cl–phenyl complex derived from the β,β-dichlorostyrene. The elimination is accompanied by internal cyclization of the molecule. The middle diagram shows HCl elimination from the *para* Cl–phenyl complex, also derived from the dichlorostyrene. In that case, the Cl–phenyl complex undergoes a rearrangement reaction prior to the elimination. The rearrangement leads to the formation of a dicyclic (non-aromatic) closed-shell intermediate with the Cl atom bonded to the six-member ring in a *meta* position with respect to the original position of the ring substituent. The bottom diagram shows potential energy profile of HCl elimination from a Cl–benzene complex. This elimination reaction has no classical barrier (as confirmed by a relaxed scan of the C–H bond distance). The B3LYP calculations indicate that only 64–100 kJ/mol is required for the elimination of hydrochloride from the Cl–phenyl model compounds.

On the basis of the analyses described above, the following mechanism for thermal decomposition of bisphenol C polycarbonate is proposed. Decomposition is initiated by formation of Cl–phenyl complexes, which provide weak crosslinks between the polymer chains at the early stages of

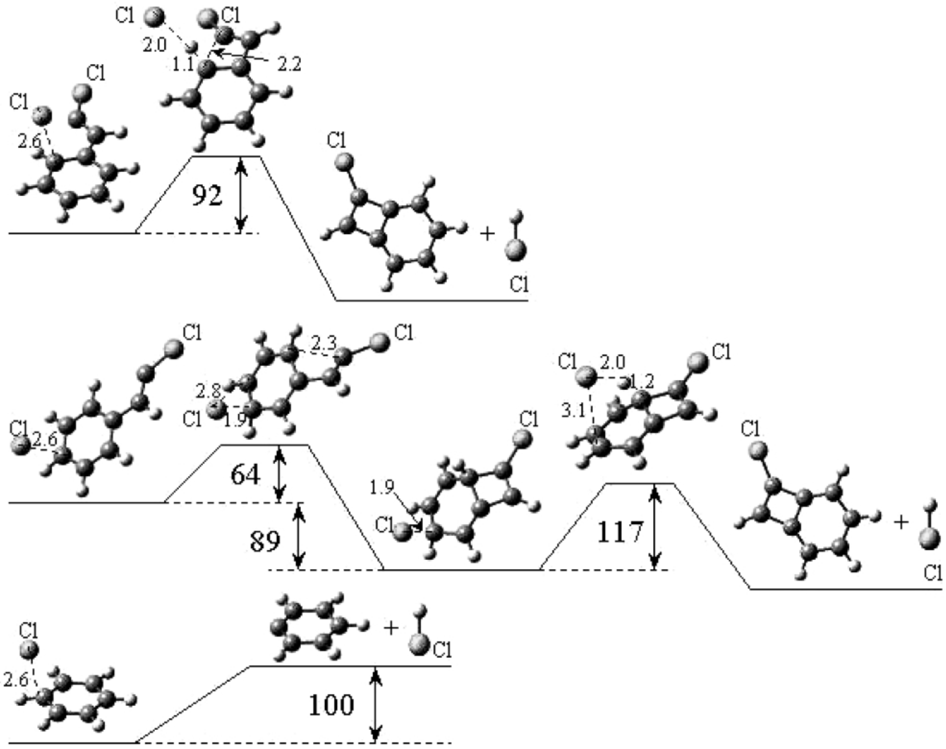

Fig. 8. Potential energy profiles of HCl elimination from Cl–phenyl complexes. Energy values are in kJ/mol. Some key interatomic distances are given in Å.

the process. These complexes subsequently decompose by elimination of HCl. The elimination reactions lead to the formation of phenyl radical sites on the polymer chains or internal cyclization of the polymer. The radical sites recombine, forming strong covalent bonds between the chains. The processes of crosslinking and cyclization, which eventually lead to the formation of char, compete with the process of cleavage of the O–C(O) backbone bonds. Phenoxycarbonyl-type radicals formed as a result of the backbone scissions will most likely decompose further by elimination of CO_2. The energy barrier for the CO_2 elimination is expected to be very low (if any) because, in this reaction, rupture of the phenyl–oxygen bond is accompanied by the formation of the oxygen–carbon π bond, which is about 80 kJ/mol stronger (the energy of the π bond was estimated from the model compound thermochemistry calculated earlier [16]).

The proposed mechanism suggests that chlorine atoms incorporated into the diphenyldichloroethylene structural units of the BPC PC play a key role in the process of the formation of char. At the same time, some experimental evidence [2,3] indicates that the same high char yields and the same high fire-resistance may be achieved with half of the halogen content by blending bisphenol-C-based polymers with similar aromatic macromolecular compounds that do not contain halogens. This observation can also be explained in the framework of the proposed mechanism. The same reactions that lead to crosslinking of the pure BPC PC may operate in the blends of a bisphenol-C-based polymer with non-halogen macromolecular structures, as long as these structures have a sufficient density of phenyl rings incorporated into their backbones.

4. Concluding remarks

Four possible reaction pathways of the thermal decomposition of bisphenol C polycarbonate have been investigated using the B3LYP/6-31G(d) quantum chemical method. The most probable reaction mechanism (described in Section 3.5) has been identified using the calculated energetics and experimental observations reported in Refs. [2–4]. According to this mechanism, interactions between chlorine atoms and phenyl rings and unique structural features of diphenyldichloroethylene fragments of the polymer are responsible for an exceptional fire resistance of this material.

It should be noted that the B3LYP/6-31G(d)-calculated energies are subject to uncertainties. Curtiss and co-authors [17] evaluated accuracy of the B3LYP method combined with a similar basis set, 6-31+G(d) [7], using 297 experimental enthalpies of formation, ionization potentials, electron affinities, and proton affinities of organic and inorganic compounds (G2/97 test set). They found that an average absolute deviation of the method from experiment is 27 kJ/mol. Wiener and Politzer [18] tested the accuracy of the method in computing bond energies using experimental data on dissociation of 26 small molecules containing H, C, N, O, Si, S, F, and Cl atoms. Average absolute errors of 18 and 12 kJ/mol were reported for the 6-31+G(d) and 6-31G(d,p) basis sets [7], respectively. A root mean square error of 22 kJ/mol was reported by Vreven and Morokuma [19] for the B3LYP/6-31G energies of C–H and single C–C bonds in a series of C1–C15 hydrocarbons. Substantial spin contaminations observed for some of the molecular structures calculated in this study may have caused larger errors in the energetics. However, it is known that, in general, density-functional methods are relatively insensitive to spin contaminations [20], even in case of transition states [21].

Uncertainties in the calculated energies associated with the limited accuracy of the quantum chemical method and, possibly, with a relatively small size of the model compounds used to describe chemical behavior of a polymer prevent us from making more definitive conclusions on the roles of the considered reaction pathways. However, even if we had a perfect description of the PESs at our disposal, the absence of a consistent reaction rate theory applicable to macromolecules would make a complete quantitative kinetic analysis impossible. An effort should be made to develop such theory, in order to qualitatively improve our understanding of the mechanisms of the thermal decomposition of polymers.

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