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Ab Initio and Experimental Study on Thermally Degradable Polycarbonates: The Effect of Substituents on the Reaction Rates

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Abstract: Thermal elimination reactions on polycarbonates are investigated from both theoretical and experimental points of view, to obtain insight into the microscopic aspects that influence the reaction mechanism and rates. In particular, attention is focused on the influence of the type of substituents in the polymer chain on the reaction rates. Ab initio density functional theory calculations are performed on a series of model compound systems for the polycarbonates under study, in particular carbonates differing by the groups attached at the α and β carbon atoms. Reactants, products, and transition states are optimized at the B3LYP/6-311g** level of theory. The structures of the activated complex give insight into the mechanistic details of this type of E_i elimination reactions. The C_α−O bond dissociates before the C_β−H bond, developing some carbocation character in the transition state on the C_α atom. The kinematics of the thermal decomposition reactions have been studied by means of transition state theory by construction of the microscopic partition functions. It turns out that the rates of the E_i elimination reactions are increased by the presence of those substituents on the C_α and C_β carbon atoms which are stabilizing the carbocation character in the transition state. In a second part, degradation temperatures have been experimentally measured for some polycarbonates through thermogravimetric analysis. It is investigated whether the relative rates of the model compound carbonate systems are representative of the behavior of the thermal degradation temperatures in polycarbonates. The study as presented here proves that ab initio calculations on small model systems, which are representative for the active area of the degradation process in polycarbonates, can provide insight into the principal ingredients that govern the reaction rates.

1. Introduction

Thermally or photochemically labile polycarbonates, which undergo drastic changes in properties when exposed to heat or radiation, have interesting potential applications. Examples have been reported by Fréchet.[1−3] These polycarbonates are submitted to a unique, thermally induced degradation process when heated to produce olefins and other low-molecular-weight components.[4] Each polymer is characterized by its specific degradation temperature, defined as the temperature that is typically required to achieve thermal decomposition in good yield. The thermal properties of several polycarbonates have been studied mainly from an experimental point of view by using various techniques such as differential scanning calorimetry (DSC), powder X-ray analyses at various temperatures, and thermogravimetric analyses (TGA).[5] The main purpose of this paper is to investigate from a microscopic point of view to what extent the thermal degradation route of polycarbonates can be influenced by tailoring the chemical structure of the polymer backbone. Therefore, it is essential to have a fundamental understanding of the reaction mechanism controlling the decomposition process. Thermolytic cleavage is known to proceed by a β-H elimination or syn-elimination, as generally depicted in Figure 1a. This process, known as internal elimination (E_i), is generally believed to be a single-step mechanism with a cyclic transition structure, as first proposed by Hurd and Blunck.[6] The detailed mechanism of these reactions and in particular the role and nature of substituents attached at the characteristic six-membered ring of the transition state are not completely understood. The

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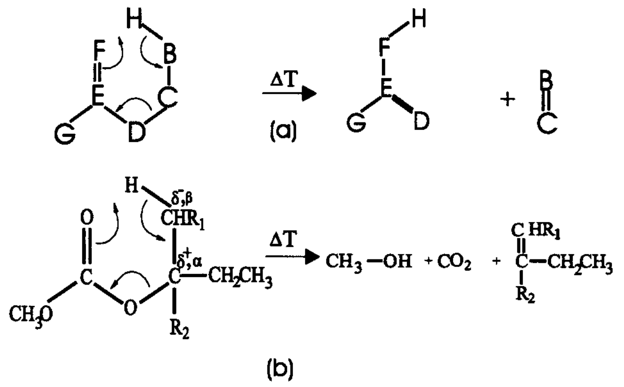

Figure 1. Schematic representation of β-elimination reactions.

thermal degradability, characterized by the degradation temperature, can be experimentally determined by TGA. The calculation of the kinetic parameters from the mass decay can be done, provided the degradation products are sufficiently volatile. In the latter case the degradation temperature is a measure of the reaction rates.

Currently there is a lot of interest in new polymeric materials, of which the properties can be modified by heating or high-energy radiation.[7] More specifically, thermally degradable polymers are very promising for the design of dry imaging systems such as printing plates. Recently, there is a tendency to use infrared laser technology to write information digitally on a printing plate rather than the formerly used techniques based on UV light sources in combination with photomasks.[8] The new technique has many advantages, such as elimination of multistep processing including photomasks, the ability to work under daylight conditions, the absence of toxic solvents, etc. So far, only limited studies have been performed to obtain insight into the structural aspects that control the thermal degradation properties of the polymer. Such study is the main objective of the present paper. Due to increasing capabilities of computers and development of new numerical methods, it is now possible to predict polymer properties computationally, enabling the research chemist to exclude certain polymer structures prior to the costly process of synthesizing the polymer. In this respect, the quantitative structure−property relationship methods (QSPR), as proposed by Askadskii,[9] Bicerano,[10] and van Krevelen,[11] are very relevant. These methods allow us to predict in an easy way a whole range of physical properties of polymers based on the knowledge of the chemical structure. However, these methods do not provide microscopic insight in the mechanisms determining these properties. In particular, in order to understand the influence of the polymer structure on the thermal degradation temperature, one needs methods that are able to explain the reaction mechanism of the active site of the polymer from a microscopic point of view. In this respect, ab initio methods that account for the electronic structure on a correct quantum-mechanical level can describe the breaking and formation of chemical bonds in an accurate way. Only limited first-principles calculations are reported on the mechanism of thermal syn elimination. Theoretical studies of thermal elimination reactions of ethyl formate, ethyl xanthate, and ethyl phosphinate are reported by Erickson and Kahn,[12] those of amine oxide, sulfoxide, and phosphoxide by Jursic,[13] and those of phosphate by Zipse.[14] To the best of our knowledge, the effects of substituents on the rates of thermal elimination reactions in polycarbonates have not yet been studied by theoretical methods based on a correct description of the electronic structure. Ab initio methods are very accurate but are also computationally very expensive. Therefore, calculations have been performed on small model compounds for the polycarbonates under study.

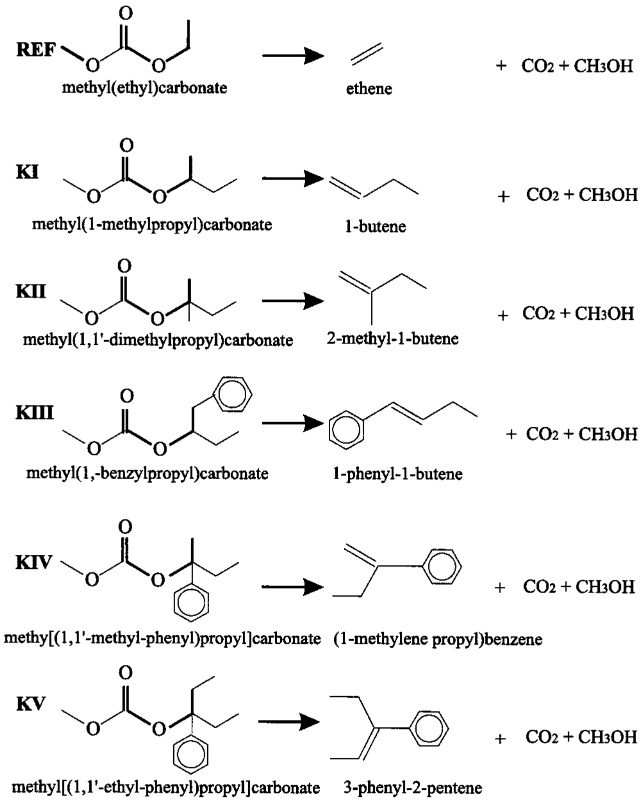

Figure 2. Schematic representation of β-elimination reactions for carbonates.

Carbonates are selected that differ by the groups R$_1$ and R$_2$ attached at the α and β carbon atoms, as defined in Figure 1b. A first product, methyl(ethyl)carbonate, having no substituents attached on the α and β carbon atoms, is chosen as the reference. The other model compounds (cf. Figure 2) have different R$_1$ and R$_2$ groups:

(i) R$_1$,R$_2$ = hydrogen for methyl(1-methylpropyl)carbonate (KI);

(ii) R$_1$ = hydrogen, R$_2$ = methyl for methyl(1,1′-dimethylpropyl)carbonate (KII);

(iii) R$_1$ = phenyl, R$_2$ = hydrogen for methyl(1-benzylpropyl)carbonate (KIII);

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(iv) R_1 = hydrogen, R_2 = phenyl for methyl[(1,1′-methylphenyl)propyl]carbonate (KIV); and

(v) R_1 = methyl, R_2 = phenyl for methyl[(1,1′-ethylphenyl)propyl]carbonate (KV).

These carbonates are expected to undergo thermolysis with formation of an olefin and monomethylcarbonate. The latter rapidly decomposes at the elevated temperatures encountered during degradation into volatile carbon dioxide and methanol. For some carbonates, syn elimination can occur at different sites of the molecule, leading to a mixture of olefins. In this work, we consider only pathways for thermal elimination with the β hydrogen atom belonging to the side chain. Initially, a conformational analysis is performed for all reactants, products, and transition states. The geometries and electronic properties of the optimized E_i transition structures reveal important information about the reaction mechanism. Insight is obtained into the synchronicity of the breaking of the two bonds. The reaction rates are evaluated within transition state theory (TST),[15−18] which has proven its success in many studies for the quantitative prediction of kinetic parameters.[19−22] The reaction rates in TST are completely determined by microscopic quantities such as the energy difference between the activated complex and reactants at zero temperature and the molecular partition functions, which can all be determined from the ab initio calculations. This enables us to predict an Arrhenius plot for each of the studied carbonates and to deduce activation energies and pre-exponential factors. The influence of substituents on the reaction rates for thermal decomposition is studied from a theoretical point of view by comparing the barrier heights for the different model compound systems. One of the main objectives of this paper is to focus on the various ingredients that may alter the reaction rates. In a next step it is investigated to what extent the calculated rates behave like the experimental degradation temperatures for the polymers. A series of polycarbonates differing by the groups attached at the α and β carbon atom are synthesized by a polycondensation reaction. The degradation temperature is determined by thermogravimetric analysis (TGA). Other experimental techniques such as DSC are less suited since the degradation process of the polycarbonate can be complicated by further decomposition of already formed degradation products. TGA is a valuable tool to detect the degradation temperature of the polycarbonate. During degradation carbon dioxide is formed, which leads to detectable weight loss.

2. Computational Details

All ab initio calculations are carried out with the Gaussian 98 software package.[23] Initial optimizations of the reactants, transition states, and products are performed using the semiempirical PM3 method.[24] For all compounds several stationary points are localized. Within each class of compounds—determined by the choice of R_1 and R_2 as schematically shown in Figure 2—the conformation with a minimal distance between the β hydrogen atom and the nearby oxygen atom is selected for further, more extensive density functional theory (DFT)[25] calculations. For the DFT calculations, Becke's three-parameter B3LYP functional is used.[26] The molecular orbitals are expanded in a triple-ζ 6-311G basis augmented with single first d and p polarization functions.[27] B3LYP functionals are known to give a reliable and quantitatively good description of geometries, frequencies, and reaction barriers.[28] Energy minima have been determined by full geometry optimizations with the Berny algorithm.[29] The transition structures are determined according to the following procedure: First, all variables but the reaction coordinate are optimized while the reaction coordinate is varied stepwise. The maximum of this linear transit serves as the starting structure in a transition-state optimization using the transit-guided quasi-Newton (STQN) method or the Berny algorithm with the specific option to optimize to a transition state (TS).[29] Vibrational frequencies of all optimized structures are calculated at the same level of theory. It is well known that the B3LYP harmonic vibrational frequencies are systematically larger than the observed experimental frequencies. The overestimation, however, is found to be relatively uniform, and as a result generic frequencies are often applied. A scaling factor of 0.9614 is applied to the frequencies in the evaluation of the partition functions,[30] while the zero-point vibrational energies are scaled by 0.9806.[30]

The reaction rates are determined by means of transition state theory (TST). In TST, the rate equation for the reaction $A \rightarrow B + C$ is given by[16,17]

$$k(T) = \frac{k_B T}{h}\frac{q_{\ddagger}}{q_A}\,e^{-\Delta E_0/k_B T} \qquad (1)$$

where k_B represents Boltzman's constant, T is the temperature, h is Planck's constant, ΔE_0 (for further reference called the critical energy) represents the molecular energy difference at the absolute zero between the activated complex and the reactant (with inclusion of the zero-point vibrational energies), and $q_{\ddagger}$ and q_A are the molecular partition functions of the transition state and reactant, respectively. The molecular properties, such as the geometries (moments of inertia) and fundamental frequencies, required for the evaluation of the partition functions and the critical energy ΔE_0 are obtained from the ab initio molecular calculations. At this stage it is possible to obtain reliable prediction

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for the empirical kinetic parameters, namely the activation energy E_a and the pre-exponential factor A defining the Arrhenius rate law:

$$k(T) = A\, e^{-E_a/(RT)} \tag{2}$$

with R the universal gas constant. The two kinetic parameters are computed by a least-squares fit from a set of rate coefficients at different temperatures determined through eq 1.

3. Results and Discussion

For all compounds under study, several local minima exist on the potential energy surface. Most of them are the result of internal rotations of some principal subgroups of the molecule. As the molecular structure becomes larger, more internal rotational degrees of freedom are present, and more stationary points appear. The question arises which conformer in each class of compounds should be selected that serves as the reference conformer in the evaluation of the partition functions required for the final derivation of the kinetic parameters (eq 1). An obvious choice is the conformer corresponding to the most stable structure. However, as most energy conformers are mutually related by one or more internal rotations, an exact treatment of these rotational degrees of freedom[22,31] shows that the rotational partition functions are not affected by the specific choice of the reference conformer. In view of the final intent of this work to present a qualitative description of the reaction mechanism, and taking into account the computational cost of handling the internal rotations exactly following the lines given in refs 22 and 31, the harmonic oscillator approach is used for all internal rotations. For convenience, the conformer corresponding to a minimal distance between the β hydrogen atom and the nearby oxygen atom is selected as reference in each class of compounds. The fully optimized reference structures at the B3LYP/6-311g** level are shown in Figure 3. In the discussion we point out only the most striking features of the selected conformers. The optimized geometries in Cartesian coordinates, absolute binding energies, and zero-point vibrational energies for all studied species are presented in the Supporting Information.

3.1. Reactants. *Methyl(ethyl)carbonate (REF)* has two stable conformers which are related to each other by applying an internal rotation of the ethyl group about the C_2-O_3 bond. The selected structure, REF, has a gauche orientation of the side chain about the C_2-O_3 bond ($C_4O_3C_2C_1 = -84°$). The distance between the β hydrogen atom and the nearby oxygen atom amounts to 2.43 Å in this structure. In the second carbonate, *methyl(1-methylpropyl)carbonate (KI)*, the conformers are principally related by two internal rotations, one about the C_2-O_3 bond and another about the C_2-C_7 bond. The corresponding torsional angles $C_4O_3C_2C_1$ and $O_3C_2C_7C_8$ reach respectively 84°and 62°. The distance O_5-H_6 amounts to 2.76 Å. *Methyl-(1,1′-dimethylpropyl)carbonate (KII)* has two methyl groups attached at the α carbon atom. They are oriented symmetrically toward the plane formed by the carbonate group. For *methyl (1-benzylpropyl)carbonate (KIII)*, several (more than nine) stationary points have been localized at the PM3 level. Of these we selected the energetically most stable structure with a minimal distance between the β hydrogen atom and the oxygen atom O_5. This distance amounts to 2.69 Å in the conformation KIII. The phenyl group is oriented almost orthogonal to the rest of the molecule ($C_2C_1C_7C_8 = 74°$). The orientation of the ethyl chain about the C_2-C_9 bond is gauche ($O_3C_2C_9C_{10} = 63°$). In *methyl[(1,1′-methylphenyl)propyl]carbonate (KIV)*, the ethyl group and the methyl group attached at the α carbon atom are oriented symmetrically toward a plane formed by the carbonate group and the phenyl substituent. The distance between the β hydrogen atom of the side chain and the oxygen atom O_5 amounts to 2.40 Å. The last compound, *methyl[(1,1′-ethylphenyl)propyl]carbonate (KV)*, has two ethyl groups and a phenyl group attached at the α carbon atom. The distance between the β hydrogen atom and the oxygen amounts to 2.43 Å.

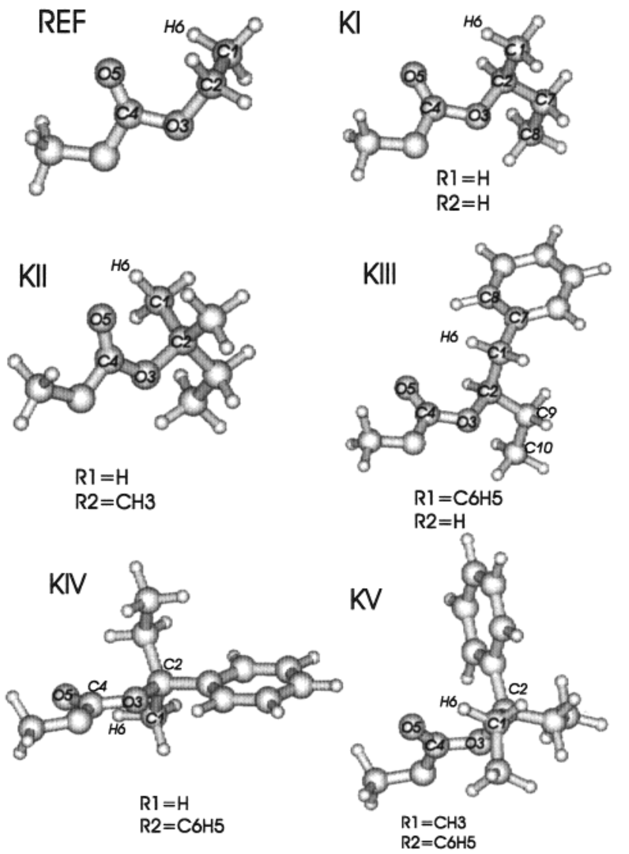

Figure 3. Conformations of the reactants. C_2 and C_1 are respectively the C_α and C_β carbon atoms.

3.2. Transition States. The optimized transition structures for thermal elimination of the six model compounds are displayed in Figure 4. All structures consist of an almost planar six-membered ring, in which hydrogen transfer is close to linear (i.e., $C_1-H_6-O_5$ angles of 167°−173°), in agreement with the reaction mechanism of syn elimination in formate and xanthate.[12] Furthermore, the E_i transition structures are consistent with the concerted transfer of a proton and the simultaneous breaking of the oxygen−α carbon bond, although previous studies of thermal decomposition on similar compounds[5,12] have shown that the reaction is not fully concerted (i.e., the two bonds do not dissociate at the same time). This feature is studied in a more extensive way by comparing the relative lengthening (in percent) of the two bonds in the transition state relative to the corresponding bond lengths in the reactant. These results are summarized in Table 1. The percent lengthening of the $C_\alpha-O$ bond is much larger than the corresponding value for the $C_\beta-H$ bond. This suggests that the $C_\alpha-O$ bond dissociates first and that the C_α carbon atom develops some carbocation character in the transition state [i.e., the ($C_\alpha^{\delta+}-O^{\delta-}$) is polarized in the direction shown]. Thus, transition states for thermal syn elimination of carbonate compounds show some E_1 characteristics (though they are still well removed from it). A similar conclusion is drawn when studying the charge shift in the transition state. For that purpose, atomic charges have been

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[31] Van Speybroeck, V.; Van Neck D.; Waroquier, M., submitted to *J. Chem. Phys.*, **2001**.

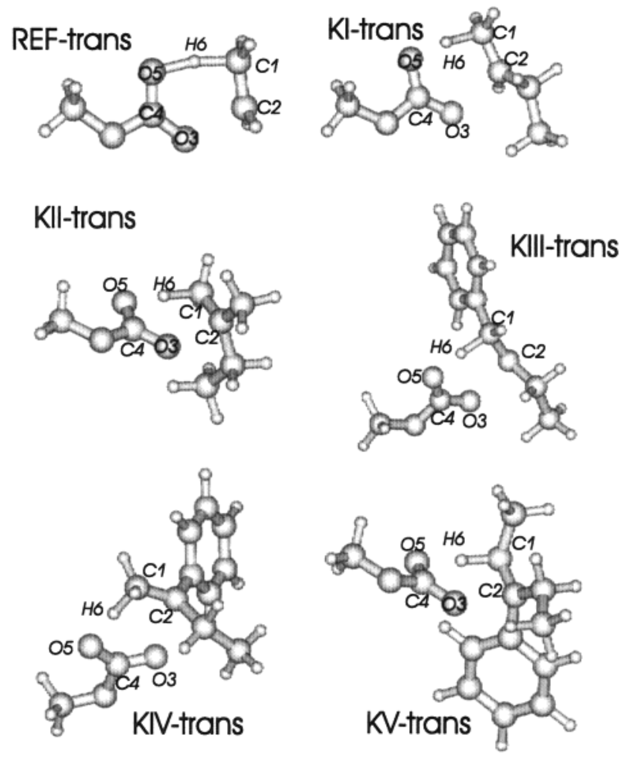

Figure 4. Conformations of the transition states.

Table 1. Bond Lengths of the C_α−O and C_β−H in the Transition Structures for Thermal Elimination[a]

	C_α−O	C_β−H	P(C_α−O) (%)	P(C_β−H) (%)
REF-1	1.44975	1.09113		
REF-trans	2.02515	1.32060	40	21
KI	1.46189	1.09097		
KI-trans	2.15658	1.28310	48	18
KII	1.47948	1.08885		
KII-trans	2.25826	1.25097	53	15
KIII	1.46007	1.09290		
KIII-trans	2.08824	1.29169	42	18
KIV	1.47120	1.08901		
KIV-trans	2.33906	1.22362	59	12
KV	1.46844	1.08941		
KV-trans	2.39411	1.21084	63	11

[a] Also given is the relative lengthening of the bonds on going from the stable conformer of the reactant to the transition state (expressed in percent): $P(l) = (l_{\mathrm{TS}} - l_{\mathrm{reactant}})/(l_{\mathrm{reactant}})$.

Table 2. NPA Atomic Charges of the Transition Structures[a]

		C_β	C_α	O_3	H_6
REF-trans	q	−0.729	−0.0141	−0.630	0.405
	Δq	−0.130	0.0020	−0.080	0.197
KI-trans	q	−0.717	0.183	−0.669	0.398
	Δq	−0.121	0.035	−0.098	0.184
KII-trans	q	−0.724	0.379	−0.687	0.394
	Δq	−0.116	0.046	−0.101	0.168
KIII-trans	q	−0.554	0.191	−0.656	0.417
	Δq	−0.132	0.031	−0.088	0.195
KIV-trans	q	−0.699	0.364	−0.709	0.386
	Δq	−0.102	0.044	−0.125	0.161
KV-trans	q	−0.517	0.381	−0.697	0.389
	Δq	−0.108	0.062	−0.110	0.161

[a] Also given are the atomic charge differences between the transition state and the reactant (Δq).

calculated for all reactants and transition states. Among the various schemes available to extract atomic charge populations, the natural population analysis charges (NPA)[32] are selected. NPA charges at the B3LYP level of theory are known to be in excellent agreement with high-level post-Hartree−Fock ab initio treatments.[33] The results are listed in Table 2. In addition, the shift of the atomic charges in the transition state with respect to the reactant is given. In all compounds under study, the oxygen atom O_3 becomes more negative, while a positive charge transfer takes place toward the transferred hydrogen atom H_6. These results are in accordance with the enhancement of polarization of the $C_\alpha^{\delta+}$−$O^{\delta-}$ bond in the activated complex. Another similar feature observed in all transition-state geometries is the almost planar character of the α carbon atom. When going from reactant to product, the C_α carbon atom changes from sp^3 to sp^2 hybridization. The transition state shows some product-like characteristics, developing some sp^2 character for the C_α atom.

Although all transition states show some common features, some subtle but still significant differences in geometries and electronic properties exist, depending on the nature of the substituents attached. In the REF trans conformer, the ring structure is perfectly planar, while a small deviation from planarity is observed in the transition state of the other compounds. This is probably due to the groups attached at the α and β carbon atoms.

The degree of relative lengthening of the two dissociating bonds varies quite significantly from one compound to another (see Table 1). When more alkyl substituents are placed on the α carbon atom, the percent lengthening of the C_α−O bond increases (REF, KI, KII). This can be explained by the effect of hyperconjugation or inductive stabilization. Alkyl groups attached to the α carbon atom can help delocalize the positive charge and thus stabilize the carbocation character of the C_α atom in the transition state. When a phenyl group is placed at the α carbon atom, the degree of lengthening of the C_α−O bond in the transition state is even more increased (KIV, KV). In this case, the carbocation character is stabilized by resonance stabilization; the π electrons in the aromatic π cloud of the benzene ring help disperse the positive charge. The same feature cannot be extrapolated to the relative lengthening of the C_β−H bond. In contrast, the percent lengthening decreases in the sequence of conformers KI, KII, and KIV, while it seems not to be affected by the type of the R_1 substituent in conformers with the same R_2 substituent (KI and KIII; KIV and KV). This could be an indication that the breaking of the C_α−O bond is the rate-determining step for the elimination reaction. This aspect will be further explored in section 3.4.

3.3. Products. As a result of the thermal elimination reaction, monomethylcarbonate is formed together with an olefinic species. Experimentally, it is observed that the first product is not stable at the elevated temperature encountered during the thermolysis reaction and transforms directly into carbon dioxide and methanol. Theoretically, a stable minimum on the potential energy surface for the appropriate product is found. Further dissociation via an intramolecular process into carbon dioxide and methanol proceeds by a four-center transition state. The activation energy and pre-exponential factor are 158.8 kJ/mol and 2.2 × 10^{13} at the B3LYP/6-311G** level of theory, which are of the same order of magnitude as those corresponding to the dissociation of the former carbonate species (see Table 3). At low temperatures, monomethylcarbonate will reside in a

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Table 3. Energies, Activation Energies, and Frequency Factors[a]

	ΔE_o (kJ/mol)	E_a (kJ/mol)	A (s^{-1})	$E_{products} - E_{reactant}$ (kJ/mol)
REF	173.500	174.912	1.5×10^{13}	69.873
KI	160.503	162.149	2.4×10^{13}	68.958
KII	133.872	135.925	6.1×10^{13}	52.903
KIII	152.815	154.483	1.2×10^{13}	43.853
KIV	137.484	138.985	2.0×10^{13}	60.950
KV	129.661	131.452	1.9×10^{13}	20.443

[a] ΔE_0 is the molecular energy difference (from ab initio DFT) between the transition state and the reactant with inclusion of ZPE. E_a and A stand for the activation energy and pre-exponential factor for the forward reaction.

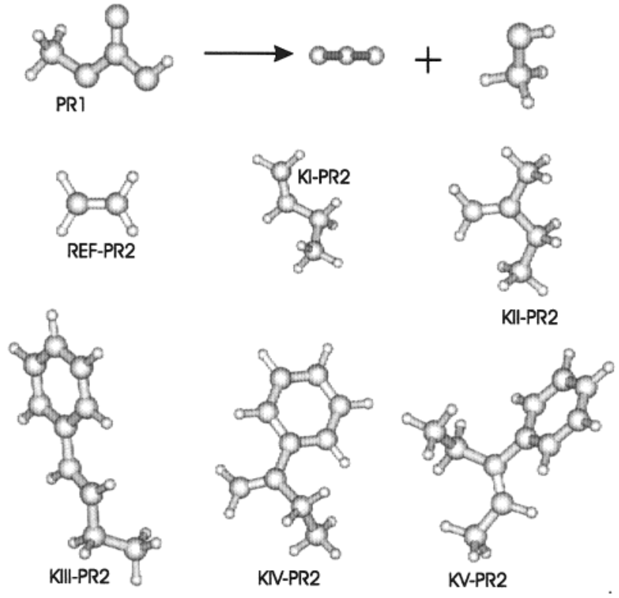

Figure 5. Conformations of the products.

stable minimum. However, at more elevated temperatures (600–700 K), at which this product is formed as evidenced by the experiment, the product further dissociates into methanol and carbon dioxide. It cannot be excluded that intermolecular processes occur as well. In the presence of a proton acceptor, the release of CO_2 will be promoted, so decomposition will occur more easily. This consideration only presents a sidelight and has no bearing on the essential part of this paper.

Depending on the choice of the reactant carbonate (REF, KI, KII, KIII, KIV, KV), the alkene formed is ethene, 1-butene, 2-methyl-1-butene,1-phenyl-1-butene, (1-methylenepropyl)benzene, and 3-phenyl-2-pentene, respectively. Only β elimination from the side chain is considered. Stable conformations of all products are shown in Figure 5.

3.4. Energies, Activation Energies, and Frequency Factors. Total binding energies, zero-point vibrational energies (scaled by 0.9806[30]) of all species, and total binding energy differences between product and reactants are tabulated in Table S1 of the Supporting Information. The kinetic parameters are calculated by the procedure described in section 2. For all considered syn eliminations, the critical energy, the kinetic parameters E_a and A, and the energy difference $E_{products} - E_{reactant}$ are taken up in Table 3. The parameters A and E_a deduced from TST are, in principle, temperature-dependent due to their construction by means of partition functions, although we found that for the reactions under study in the considered temperature range the Arrhenius rate law models very well the temperature dependence of the rate constant. The Arrhenius plots are shown in Figure 6. All reactions studied are endothermic, resulting from the positive energy difference $E_{products} - E_{reactant}$, as tabulated in Table 3. This is in accordance with previous studies.[34]

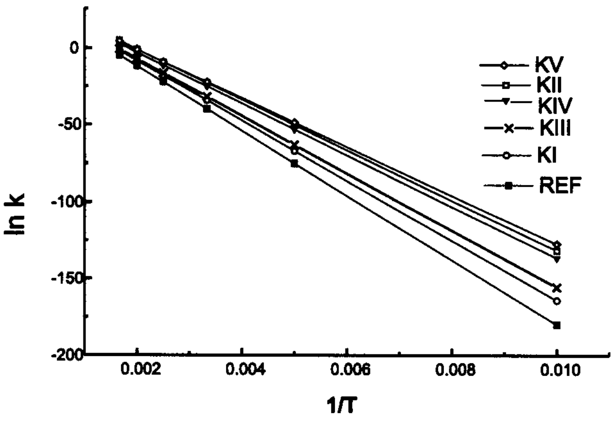

Figure 6. Arrhenius plots of ln k versus $1/T$ for the β-elimination reactions.

The values for the frequency factor, A, all lie in the same order of magnitude; slight differences are noticed when going from one compound to another. The accuracy of the method is not of that level to stress the importance of the absolute values of these frequency factors. Due to the complexity of the considered species and the numerical algorithms to handle internal rotations in an exact way,[22,31] all low vibrational modes are treated here in the harmonic oscillator approximation, even those that can rather be identified with a hindered rotor motion. The activation energy is only slightly affected by this approach, while the effects on the frequency factor may be substantial.[22] However, the changes turn out to be strongly dependent on the specific nature of the molecule under study. Therefore, attention is focused on activation energies to explain effects of substituents, rather than on pre-exponential factors.

Effects of Substituents on the Activation Energies. A comparitive study of the activation energies reveals the following sequence of reaction rates: REF < KI < KIII < KIV < KII < KV. This sequence indicates that the presence of alkyl groups on the α carbon atom substantially increases the reaction rates. The more substituted the α carbon atom, the lower the activation energy. This specific feature is not surprising and agrees with previous observations on the relative increase of the C_α–O bond length in the transition state with respect to the reactant (section 3.2). These trends can be explained by the effect of inductive stabilization of the carbocation character of the C_α carbon atom in the transition state by the alkyl groups. The activation energy also decreases substantially by placing aromatic groups on the α carbon atom. This is due to the resonance stabilization of the carbocation in the transition state, in accordance with the results on bond lengthening in the activated complexes (section 3.2). Comparison of the activation energies obtained for the compounds KI with respect to KIII and KIV with respect to KV shows that aromatic groups and alkyl substituents on the β carbon atom accelerate the rates for thermal elimination. This result agrees with that found by Louw et al.,[35] who performed experimental studies on alkyl acetates. The KIV and KV compounds differ only by an additional alkyl group at the C_β carbon atom. This would principally reduce the stability of the negatively charged C_β atom. The global effect is an increase of the reaction rate, which is an indication that the breaking of the CH bond is of secondary importance. The primary effect of

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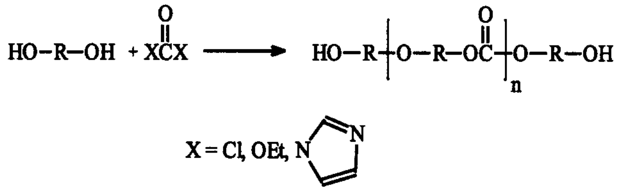

Figure 7. Schematic representation of the polycondensation.

placing substituents on the C_β atom is the remote effect on the C_α—O bond: C_β and its substituents stabilize the carbocation character of C_α in the transition state. The appearance of more subtle differences between the reaction rates, e.g., between KII and KIV, might be due to other factors of secondary importance. In principle, barrier formation can be ascribed to one or a combination of the following factors: (i) the inductive and mesomeric effects of the substituents, (ii) the effect of the substituent upon the breakage of the C_β—H or C_α—O bond, (iii) the effect of the substituent on the stability of the forming alkene, and (iv) the possibility of steric acceleration through a decrease in steric hindrance between substituents in the product alkene and the starting carbonate. Hence, relief of steric hindrance along the reaction pathway might contribute to the reaction rate.[36]

Based on the relative lengthening of the C_α—O/C_β—H bond, the dissociation process for KIV is expected to be faster than for KII, although the calculated reaction rates predict a slight lower activation energy for KII. This is an indication that effects (iii) and (iv) may contribute to the reaction rates.

Previous results provide further evidence for the general picture given by August et al.[37] concerning E_i elimination reactions. Within the spectrum of E_i transition states for six-center eliminations, there are two broad mechanistic categories, both depending on the atoms comprising the ring and the groups attached at various points.

The first class is composed of compounds with a very polar $C^{\delta+}$—$D^{\delta-}$ bond, as indicated in the general scheme in Figure 1a, which can readily polarize in the direction shown. The associated transition states have E_1-like characteristics, and breaking of the C—D bond is the most important step. The carbonates studied in this work can be classified into this group. In contrast, the second category of compounds does not exhibit a pronounced polar C—D bond but rather a very polar B—H bond. For these compounds the nucleophilic attack by F (or E═F bond) on hydrogen is the most important step of the reaction. Examples within this class have been thoroughly studied by August et al.[37]

3.5. Experimental Results: Thermogravimetric Analysis of Polycarbonates. In this part, it is investigated whether a correlation can be found between the calculated rates for the model compounds and the degradation temperatures for the polycarbonates. The polycarbonates are prepared by a polycondensation reaction,[39] where a diol is converted into a polymer as schematically depicted in Figure 7. A detailed description of the synthesis of the polycarbonates is reported elsewhere.[38] Three commercially available 1,4-diols were used for the polycondensation reaction (Figure 8) in order to obtain polycarbonates with a structure similar to those of the model compounds (Figure 2). The polycarbonates are analyzed by thermogravimetric analysis (TGA). The results are shown in Figure 9. The degradation temperature, T_d, is defined as the maximum of the first derivative of the weight loss curve. The degradation temperature decreases from 330° to 198° when the substituents R_1 and R_2 are varied, as defined by the classes REF, KI, and KII. This demonstrates that a variation of the substituents on the α and β carbon atoms significantly influences the degradation temperature. Next, the activation energies obtained from the ab initio calculations on the model carbonates are compared with the degradation temperature of the polycarbonates. The results are listed in Table 4. A good correlation is observed between the barrier heights for decomposition of the carbonates and the degradation temperatures of the polycarbonates. Substituents on the α and β carbon atoms of the carbonate that lower the activation energy for the thermal decomposition also lower the thermal stability of the corresponding polycarbonate.

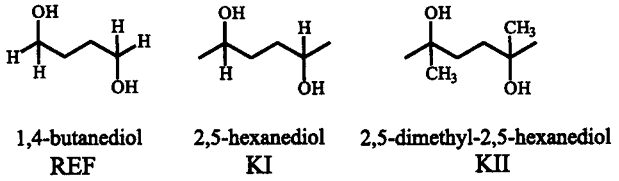

Figure 8. Diols used for the preparation of the polycarbonates.

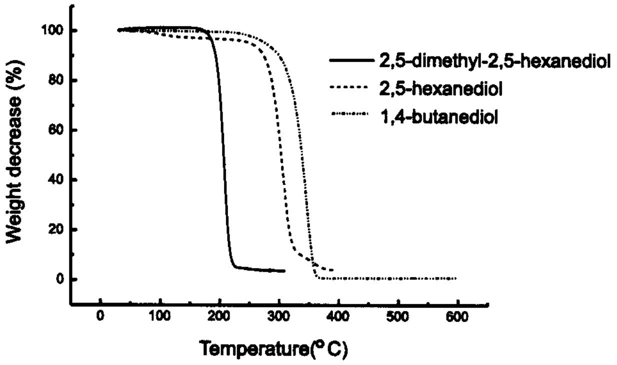

Figure 9. Weight decrease measured as a function of temperature for a series of polycarbonates.

Table 4. Activation Energies and Degradation Temperatures for Different Compounds[a]

		E_a (kJ/mol)	T_d (°C)
REF		175	330
KI	$R_1 = H, R_2 = H$	162	300
KII	$R_1 = H, R_2 = CH_3$	136	198

[a] E_a are the activation energies as obtained from ab intio calculations on the modelstructures. T_d are the degradation temperatures of the corresponding polymers as obtained from TGA experiment.

Where possible, the theoretically predicted Arrhenius plots are compared with the experimental kinematics. This is realized by conducting an isothermal TGA experiment. The weight change of the polymer was measured as a function of time at several temperatures. The rate constant of the degradation at a given temperature can be calculated by assuming that the fragmentation process is a first-order reaction. This procedure was successful only for the copolymer based on 2,5-dimethyl-2,5-hexanediol and 1,4-benzenedimethanol (KII). The following kinetic parameters were obtained: $E_a = 144.02 \pm 8$ kJ/mol and $A = 6.53 \times 10^{13} \pm 8.96\ s^{-1}$. For this case the theoretical predicted values are in close agreement with the experimental

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values taking into account the experimental errors. For the other polymers corresponding to the model structures REF and KI, a kinematic analysis was not possible due to the occurrence of a subsequent degradation process.

In conclusion, the selected carbonates are representative models for understanding the miscroscopic structural effects of side-group substituents on the thermal degradation of polycarbonates. Ab initio calculations cannot predict a priori a quantitative value for the degradation temperature. However, by modeling small systems that are representative of the chemical active sites of the decomposition process, one can understand the reaction mechanism of the thermal degradation process and the structural parameters that influence the reaction rates. Such calculations can help the experimentalist, interested in designing new polymers with specific thermal behavior, to understand the microscopic aspects that are responsible for the experimental results and to predict a priori qualitatively the impact of varying the chemical structure of the polymer backbone on the thermal behavior.

4. Conclusions

In this paper, model compounds were used to gain insight into the structural effects that influence the thermal elimination reactions of polycarbonates.

First, DFT calculations were performed on a set of carbonates differing from each other by the groups attached at the α and β carbon atoms. Kinetic parameters were calculated for the E_i elimination reaction by means of TST. The microscopic partition functions are the principal quantities in this theory, and they depend on the geometries and vibrational frequencies as obtained from the ab initio calculations.

The optimized transition structures reveal information on the order of bond dissociation in syn elimination reactions for carbonates. It was observed that the C_α−O bond dissociates first, while the C_α atom develops some carbocation character in the transition state. This is followed by the abstraction of the β hydrogen atom. These results are in good agreement with previous studies.[12,40]

The degradation products are olefinic species, carbon dioxide, and methanol. For a first approximation, only syn elimination of a β hydrogen of the side chain was taken into consideration. The study of possible competing pathways is currently under investigation.[41]

The results of this work allow us to draw some general conclusions about the effect of substituents on the thermal decomposition process:

(i) Alkyl and aromatic groups on C_α accelerate the reaction rate. This is due to a stabilization of the carbocation character in the transition state caused by hyperconjugation and resonance stabilization.

(ii) Alkyl and aromatic groups on the C_β carbon further increase the rate constant. Carbonates are compounds with a very polar C_α−O bond. The cleavage of this bond is the rate-determining step.

In the experimental part, we synthesized the polycarbonates corresponding to the model compounds and determined the degradation temperatures by TGA. The ab initio calculations were compared with the experimental data for a series of C_α- and C_β-substituted polycarbonates in order to investigate whether the carbonate systems are representative of the microscopic aspects of decomposition. The degradation temperatures are indeed influenced by the nature of substituents in the polymer backbone. A good correlation is observed between the activation energies calculated for the model compounds and the thermal degradation temperatures of the polycarbonates. A lower activation energy corresponds with a decreased thermal stability of the polymer.

In this paper we were able to show that ab initio calculations can provide a fundamental understanding of the reaction mechanism and the structural parameters that govern the reaction rates.

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Supporting Information Available: Cartesian coordinates, ground-state energies, and zero-point vibrational energies of the optimized geometries of all studied species, reactants, and transition states (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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