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Ab Initio Studies of Thermal Syn-Elimination Reactions in Carbonates: Effect of Structure on Reactivity

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Thermal elimination reactions in carbonates are investigated from a theoretical point of view with density functional theory methods to obtain insight into the reaction mechanism and structural factors that influence the kinetics. Carbonate systems are good model systems for the kinetics of thermal degradable polycarbonates. Special attention is given to the influence of para-substituents placed either at C_α or C_β. The results enable prediction of ρ values of the Hammett equation and confirm earlier experimental data.

1. Introduction

Carbonates have the property of undergoing thermal decomposition upon heating to produce as major degradation products olefins, carbon dioxide, and methanol.[1] In a previous paper,[2] it was shown that carbonates are representative systems to model the chemically active area for thermal degradation processes in polycarbonates. For the latter materials, there exists a great interest due to their potential applications in electronics and lithography.[3] Up to now, the effect of a specific structural design of the polymer on the thermal degradation route was mostly obtained from experiment by measuring the thermal degradation temperature. This temperature is typically related to the polymer structure and can be measured by thermogravimetrical analysis (TGA) provided that the degradation products are sufficiently volatile.[4] In this case, the degradation temperature is an indication for the reaction rates. Modeling studies offer the advantage that the effect of structural parameters in the building blocks for the polymer can be predicted and hence provide a better rationale for new polymer synthesis strategies. In ref 2, the rate constants for thermal syn-elimination for a number of carbonates were calculated by means of density functional theory calculations and transition state theory. A good correlation was found between the barrier heights of carbonates and the thermal degradation temperature of corresponding polycarbonates. In this paper, further evidence is given for the proposed reaction mechanism by placing various functional groups at the para-position of a phenyl group attached at either the α or β carbon atom (as indicated in Figure 1. Thermal degradation is known to proceed by a β-H-elimination or syn-elimination with a cyclic transition structure (cf. Figure 1).[5] The reaction does not proceed fully concerted; a positive charge is developed at the α carbon atom in the transition state. Experimental substituent effect studies demonstrate that polar groups at the α and β position affect the reaction rate.[6,7] Hammett studies provided evidence that electron-withdrawing groups at the β position or electron-donating groups at the α position accelerate the reaction rates.[6,7] In this paper, the effect of substituents on the thermal degradation route in carbonates is studied in more detail. This is done in a scientifically straightforward way by varying the para-substituents and calculating the corresponding reaction rates. The relative rates enable us to predict the ρ values of the Hammett equation.

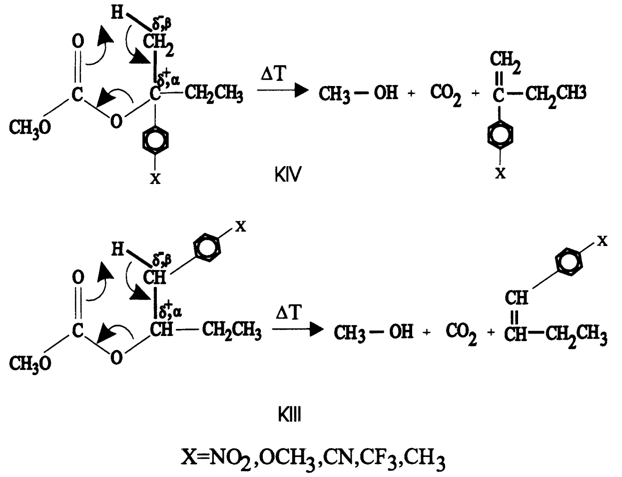

Figure 1. Schematic representation of β-elimination reactions.

2. Computational Details

All ab initio calculations are carried out with the Gaussian 98 software package.[8] Initial optimizations of the reactants and transition states are performed using the semiempirical PM3 method.[9] For all compounds, several stationary points are localized. For each compound, 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)[10] calculations. For the DFT calculations, Becke's three-parameter B3LYP functional is used.[11] The molecular orbitals are expanded in a triple-ζ 6-311G basis augmented with single first d and p polarization functions.[12] B3LYP functionals are known to give a reliable and quantitatively good description of geometries, frequencies, and reaction barriers for the studied systems.[13] Energy minima have been determined by full geometry optimizations with the Berny algorithm.[14] The transi-

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tion structures are determined according to the following procedure: At the first stage, all variables except 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).[14] 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,[15] while the zero-point vibrational energies are scaled with 0.9806.[15]

The reaction rates are determined by means of transition state theory (TST).[16,19] In TST, the rate equation for the reaction A → B + C is given by[17,18]

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

where k_B represents the 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 for the empirical kinetic parameters, namely, the activation energy, E_a, and the preexponential factor, A, defining the Arrhenius rate law:

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

with R being 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

Basically, two carbonate structures are considered with a phenyl group attached at the C_α or C_β. They will be referred to as KIV and KIII conform to the notations introduced in ref 2. Within each class five different complexes are studied that are obtained by substituting the functional group X by CN, NO_2, OCH_3, CH_3, and CF_3 (Figure 1).

Reactants. For all model compounds, several stable structures exist on the potential energy surface, which are principally related to each other by applying internal rotations of some main subgroups of the molecule. In principle, for an accurate determination of the kinetic parameters, especially the frequency factor, one should calculate the partition functions of all internal rotations on an exact basis as described in refs 20 and 21. In view of the final objective 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, the harmonic oscillator approximation is used for all internal motions of the molecule. The conformer corresponding to a minimal distance between the β hydrogen atom and the nearby oxygen atom is selected as the reference conformer for the final evaluation of the partition functions. The fully optimized reference structures at the B3LYP/6-311G** level of theory are shown in Figures 2 and 3.

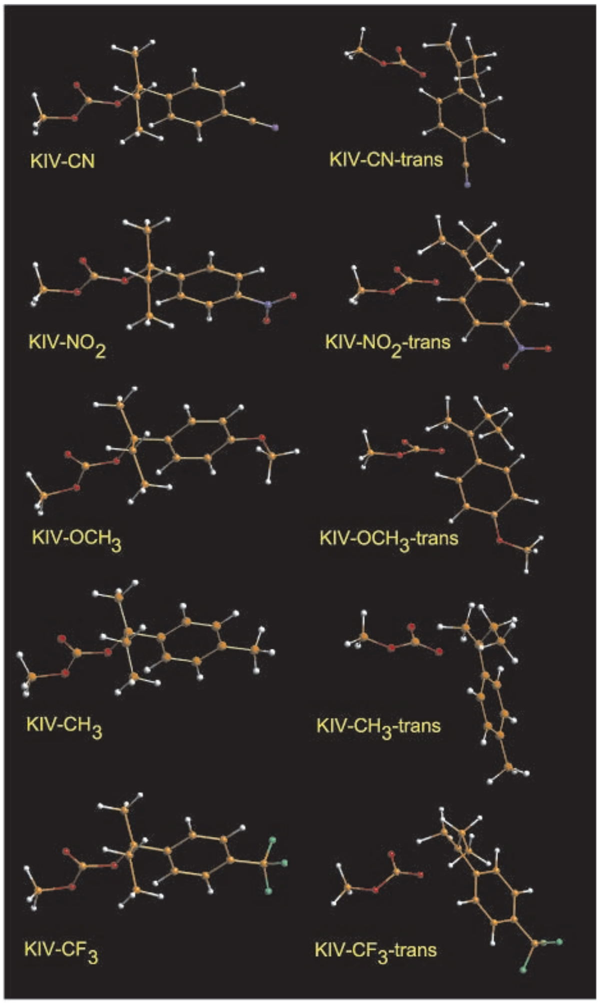

Figure 2. Conformations of reactants and transition states within class KIV.

The KIV reactant structures are characterized by a plane formed by the carbonate group and the phenyl group. The methyl group and ethyl group attached at the α carbon atom are oriented orthogonal toward this plane. In case of the KIV-CN and KIV-NO_2 compounds, the cyanide and nitro groups also are oriented in this plane because of resonance stabilization with the phenyl group. For the KIV-OCH_3 and KIV-CF_3, various orientations are possible for the para-substituent with respect to the phenyl group. In all cases, the most stable complex in terms of the specific internal rotation of the subgroup about the phenyl group was selected. The distance between the β hydrogen atom of the methyl group of the side chain and the nearby oxygen atom amounts to values between 2.65 and 2.70 Å for all KIV structures.

In the KIII complexes, the phenyl group is oriented almost orthogonal to the plane formed by the carbonate group. For the relative positions of the para-substituents with respect to the phenyl group, analogous considerations can be made as in the KIV class. For all KIII complexes, the distance between the β hydrogen atom and the nearby oxygen atom is nearly unaltered at a value of 2.40 Å.

Transition States. In this work, only thermal degradation routes for syn-elimination with a β hydrogen atom belonging

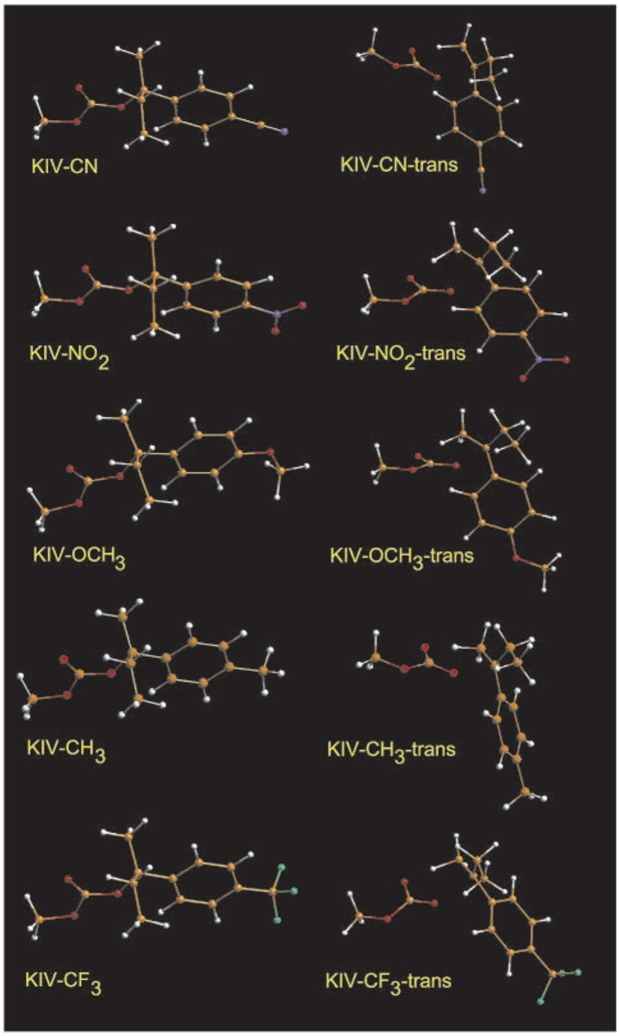

Figure 3. Conformations of reactants and transition states within class KIII.

to the side chain are considered. For all structures, alternative reaction pathways are possible in which syn-elimination occurs from the main chain. This research item, concerning the influence of competitive pathways on the reaction rates, is the subject of a forthcoming paper.[22] The optimized transition states for all model compounds are displayed in Figures 2 and 3. Their general characteristics are in line with previous studies.[2,23−25] All E_i transition states for syn-elimination consist of a characteristic six-membered ring, which is typical for the concerted transfer of a proton and the simultaneous cleavage of the oxygen−α carbon bond. In conformance with the literature,[4] it is also found here that the process is not fully concerted. This aspect can be studied in detail by comparing the relative lengthening of the two cleavage bonds in the transition state with respect to the reactant. These results are shown in Table 1. The relative lengthening of the C_α−O bond in the transition state is much more pronounced than the corresponding quantity of the C_β−H bond. This indicates that the C_α−O bond to a larger extent dissociates in the transition state and some carbocation character is developed on C_α. This is also confirmed by calculating atomic charges in the activated complex. These results are not explicitly taken up in this paper because a detailed explanation was already given in ref 2. The transition state for syn-elimination has a partial ionic character. All transition states show an 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, devoloping some sp^2 character for the C_α atom.

TABLE 1: Relative Lengthening in the Transition State, Activation Energies, and Preexponential Factors[a]

	P1 (%)	P2 (%)	E_a (kJ/mol)	A (1/s)
KIV	59	12	138.99	2.0×10^{13}
KIV-CN	58	14	144.46	2.7×10^{13}
KIV-NO$_2$	56	13	145.64	3.1×10^{13}
KIV-OCH$_3$	69	10	132.03	3.2×10^{13}
KIV-CH$_3$	61	12	136.65	2.7×10^{13}
KIV-CF$_3$	56	13	143.52	6.9×10^{13}
KIII	43	18	154.48	1.2×10^{13}
KIII-CN	39	21	151.33	1.1×10^{13}
KIII-NO$_2$	38	22	150.21	1.0×10^{13}
KIII-OCH$_3$	44	17	155.83	1.7×10^{13}
KIII-CH$_3$	42	18	156.00	8.4×10^{13}
KIII-CF$_3$s	41	20	152.38	1.2×10^{13}

[a] P1 = $P(C_\alpha{-}O)$ and P2 = $P(C_\beta{-}H)$ with $P(l)$ defined as the relative bond lengthening in the transition state with respect to the reactant (expressed in percent): $P(l) = (l_{TS} - l_{reactant})/l_{reactant}$.

Reaction Products. As a result of the thermal elimination reaction, monomethyl carbonate is formed in addition with an olefinic species. Experimentally, it is observed that the first product is not stable at the elevated temperature encountered during the thermolysis reaction.[26,27] At low temperatures, monomethyl carbonate will reside in a stable minimum; however, at more elevated temperatures (600−700 K), at which the product is formed, it dissociated further 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. Depending on the reactant structures, various alkenes will be formed.

Reaction Rates. The activation energies and frequency factors for all model compounds are listed in Table 1. Previous studies have shown[20,21] that the frequency factor can be quite sensitive to the method of treating low vibrational modes. However, the changes turn out to be strongly dependent on the specific nature of the molecule under study. This aspect can be illustrated for compounds with a trifluoromethyl or methyl group as para-substituent, in which an internal rotation of the substituent about the phenyl group can take place. Such rotations can be identified by studying the low vibrational spectrum of the molecule. An exact treatment of the internal rotations will lead to an enhancement of the molecular partition function with respect to the harmonic oscillator treatment. The final effect on the reaction rates and the preexponential factor depends on a detailed balance of the partition functions of the transition states and reactants in the rate equation (eq 1). Because of the complexity of the considered species and the numerical algorithms to handle internal rotations in an exact way, all internal motions are treated in the harmonic oscillator approximation. The effects of substituents on the reaction rates will be mainly outlined on the basis of the activation energies rather than on the preexponential factors.

Activation Energies. The activation energies for KIV compounds are always smaller than those for KIII compounds. This is in line with the conclusions of ref 2, in which it was shown that the stabilizing effect of a phenyl group at C_α is larger than the anologous effect on C_β. The underlying reason is that the breakage of the C_α−O bond is the rate-determining step.

Effect of para-Substituents on E_a within Class KIV. It is seen that the activation energy is lowered with respect to the reference KIV without para-substituents, if the functional group is eletron-donating while the activation energy increases by placing an

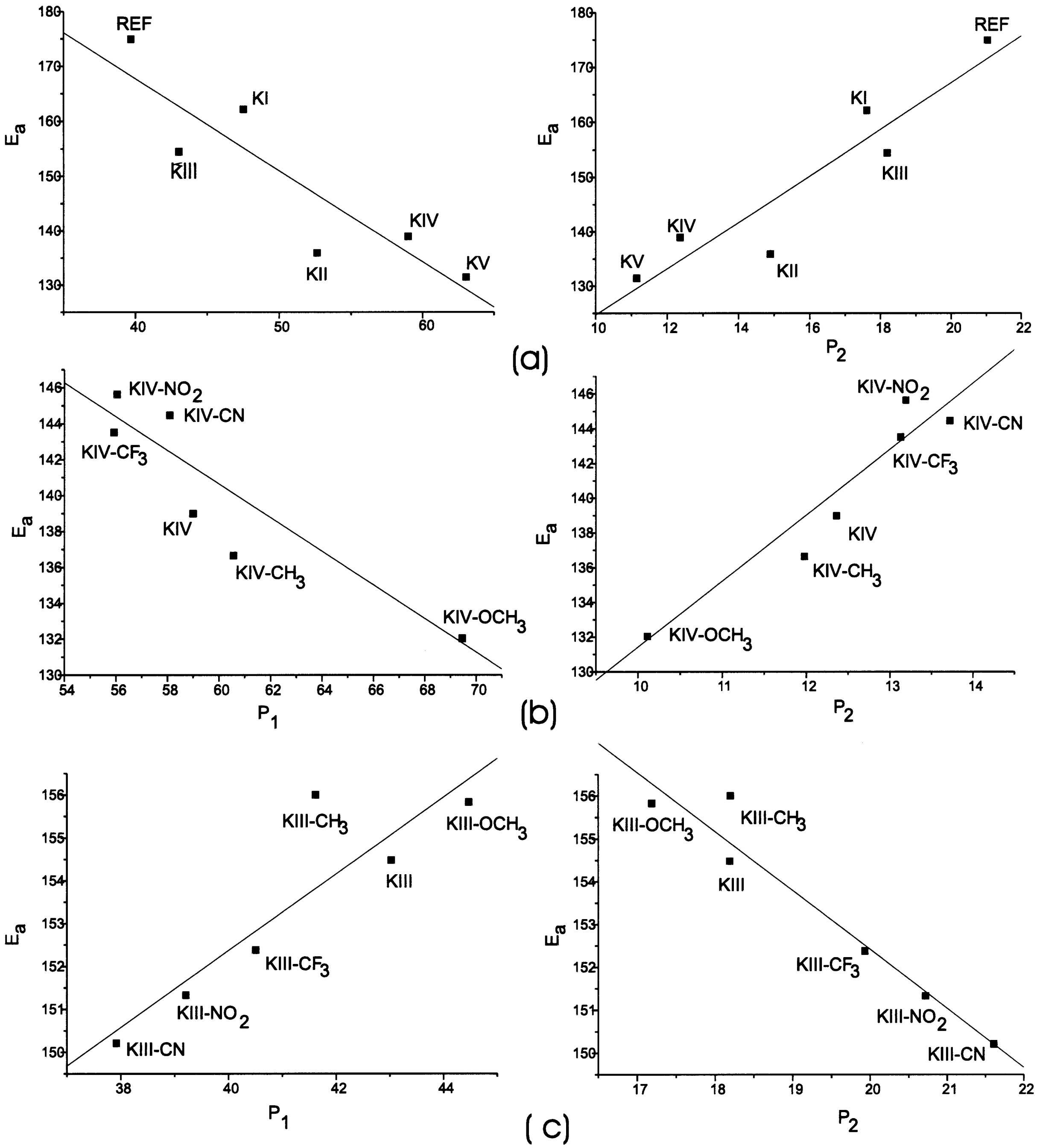

Figure 4. Linear correlations between activation energies and relative bond lengthenings in transition states.

electron-withdrawing group at the para position. Electron-donating groups such as OCH_3 and CH_3 further increase the carbocation character of C_α in the transition state. Moreover within class KIV, a good correlation exists between the activation energies and the relative lengthening of the two breaking bonds (P1 and P2). Para-substituents that enhance the value of P2, have a increasing effect on the activation energies. In addition, substituents that enlarge P1 decrease P2 (Figure 4b). This is a general conclusion for syn-elimination reactions in carbonates as can be illustrated by Figure 4a. The reaction barrier is proportional to the energy needed to break the two bonds during the reaction. In conclusion, electron-donating groups attached at the para position of the C_α atom accelerate thermal decomposition reaction in carbonates because they additionally stabilize the carbocation character in the transition state.

Effect of para-Substituents on E_a within Class KIII. Para-substituents within the KIII class have the opposite effect on the activation energies compared with those in the KIV class. In this case, electron-withdrawing groups stabilize the partial negative charge on C_β and thus lower the activation energies. A linear correlation can be found between the activation energies and the relative lengthening of P2 and P1 as illustrated in Figure 4c.

Structural Effects on Reactivity Treated by the Hammett Equation. In an attempt to quantify the effects of structure on the reactivity, one can use the Hammett equation:[28]

$$\log \frac{k}{k_0} = \sigma\rho \qquad (3)$$

where k_0 is the rate constant for X = H, k is the rate constant

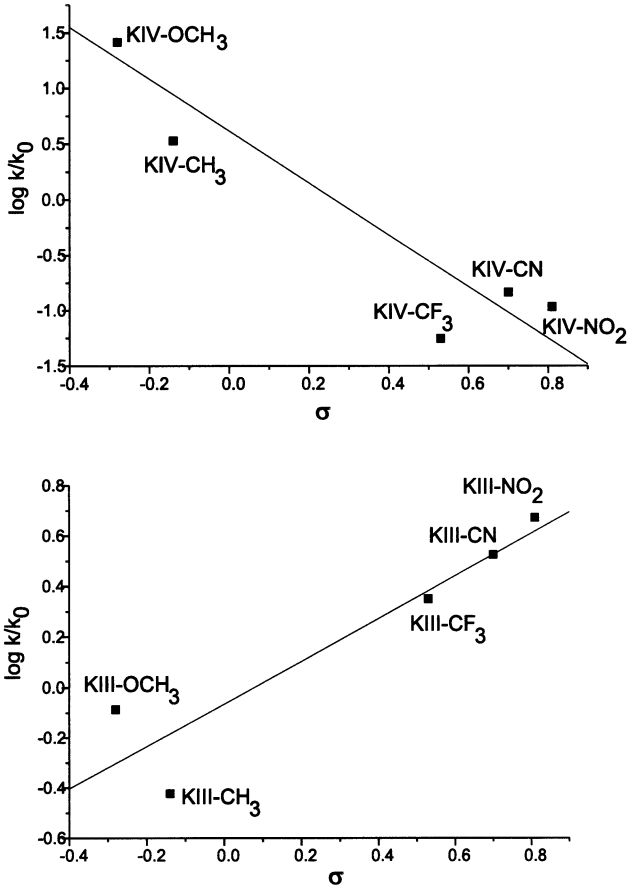

Figure 5. Hammett plots for thermolysis reactions of KIII and KIV compounds. The solid regression line is given for KIV and KIII compounds, respectively, by log $k/k_0 = -2.1409\sigma + 0.4713$ with $R^2 = 0.8754$ and log $k/k_0 = 0.8452\sigma - 0.068$ with $R^2 = 0.8694$.

for the group X, σ is a constant characteristic for the group X, and ρ is a constant for a given reaction under a given set of conditions. The resulting plots are given in Figure 5 for the KIII and KIV compounds. A ρ value of 0.8452 and −2.1409 for compounds within, respectively, KIII and KIV class is found. The sign and the magnitude of the ρ-factor of a reaction is considered to be a measure of the charge separation in the rate-determining transition state. The larger value of ρ for substituents at C_α confirms that the cleavage of the C_α−O bond is the rate-determining step and that substituents on this center have a larger impact on the reaction rates than those placed at C_β. This confirms the early results of Taylor et al. on syn-elimination reactions.[6]

A positive value of ρ for KIII compounds confirms that the reaction rates are enhanced by electron-withdrawing groups, while a negative value for KIV compounds indicates that electron-donating groups are stimulating the reaction rates. On the basis of the limited number of data points, only a qualititative Hammett relation can be established. One must be careful when extrapolating the quantitative values in a more general context. The discrepancies from the linear fit must be explained in terms of inaccuracies in the reaction rates due to the specific treatment of the preexponential factor on the basis of partition functions determined in the harmonic oscillator approximation.[29]

4. Conclusions

The results reported in this paper are in line with the proposed reaction mechanism of thermal syn-elimination reactions in carbonates.[2] The C_α−O bond dissociates before the C_β−H bond, and the cleavage of the C_α−O bond is the rate-determining step. Furthermore, electron-withdrawing groups and electron-donating groups, respectively, placed at the para position of a phenyl group at C_α and C_β enhance the reaction rates because they further stabilize the partial charges of these atomic centers in the transition state. Our results enable us to predict quantitative values for ρ of the Hammett equation. The sign of ρ confirms the proposed reaction mechanism. Moreover, larger values for ρ are obtained for substituents at C_α than for those on C_β confirming that the cleavage of the C_α−O bond is the rate-determining step.

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Supporting Information Available: A table containing the Cartesian coordinates of the optimized geometries of all studied species, reactants, and transition states. This material is available free of charge via the Internet at http://pubs.acs.org.

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