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Ab Initio MP2 and DFT Study of the Thermal Syn Elimination Reaction in Ethyl Formate

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The thermal elimination reaction that appears in some polycarbonates has been studied by density functional theory (DFT) and ab initio methods of different levels. This work has been focused in the elimination process of ethyl formate, as a good model of this kind of reaction. Different minima and the transition state have been found to characterize the thermal elimination reaction, and the activation energy has been obtained. In this study, we have used different methods to calculate the contribution of the correlation energy; different basis sets were also employed. This will allow us to perform an analysis of the influence of the applied method in the obtained results to study the thermal elimination. The lengthening of the bonds has also been analyzed to shown how concerted the thermal elimination is in the ethyl formate. Three minima have been found for the ethyl formate, two of them are very close and the third is higher in energy. In general, the DFT method with a B3LYP functional gives a less concerted reaction. A nonplanar transition state is predicted by most of the methods used.

Introduction

The study of polycarbonates whose properties change very drastically upon heating is very important because of the possible industrial applications of these molecules.[1] Those polycarbonates belong to a type of molecule that contains a neighboring hydrogen and a proton abstracting group. When exposed to heat, a thermally induced elimination reaction appears. This process produces olefins and other low molecular weight products. The mechanism of this reaction is believed to be a single step elimination, where a cyclic transition state is involved, and it is called the E_i mechanism or internal elimination mechanism.[2] Figure 1 gives a representation of the E_i mechanism.

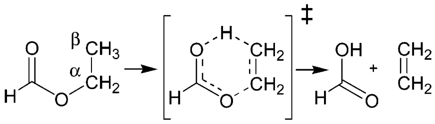

Figure 1. E_i mechanism of the 1,5 thermal elimination reaction.

Several ab initio and density functional theory (DFT) studies[3−6] have been performed to analyze the special characteristics of this reaction in different molecules. To carry out this task, analyses of the energies, atomic charges, kinetic parameters, and relative lengthening of the bonds have been done.

Erickson et al. studied this elimination process by performing Hartree−Fock calculations in ethyl formate, ethyl xanthate, and ethyl phosphinate.[3] In his work, Jursic performed the analysis in organic amine oxide, sulfoxide, and phosphoxide.[4] A theoretical study in phosphatoxy radicals is reported by Zipse.[5] Finally, Van Speybroeck et al. have extended the analysis to several models of polycarbonates.[6]

The above-mentioned studies have not been done at a very high level of theory, and a combination of a large basis set and a highly correlated ab initio method has not been used. We believe it is necessary to perform a systematic study that will provide us with clear information about the quality of the results obtained with different theoretical methods in the analysis of the thermal elimination mechanism. This knowledge will help us to further work in the task of understanding the process of thermal degradation that occurs in some polycarbonates. Using the data provided by this work will allow us to find the most suitable method for the studied problem. This study will also provide insight in the importance of the correlation contribution in the degradation properties of the polymers. There is a lot of interest in those properties because they can be the key for the design of new imaging systems. Those systems have several advantages, as the ability of working under daylight conditions or the absence of toxic solvent when they are used.

To perform this study, we have chosen as a working molecule the ethyl formate. On one hand, this molecule is big enough to provide results that will be useful in the prediction of properties for bigger polycarbonates, and on the other hand, it has a size that allows us to perform high level ab initio calculations.

In this study, we have used different methods to calculate the contribution of the correlation energy, and different basis sets were also employed. Energies, structures, and frequencies of the species involved in the reaction have been calculated. The lengthening of the bonds and the activation energy have also been analyzed.

Computational Details

Different stationary points of the ethyl formate, the transition state, and the products geometry of the thermal elimination were located by optimizing every degree of freedom (except one that is maximized for the transition state) via ab initio calculations including electron correlation in the form of the second-order

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Møller−Plesset theory (MP2) or DFT using the B3LYP functional. Several explorations were conducted at the MP2/6-31G**and B3LYP/6-31G** levels. Those calculations were followed by optimizations with 6-311++G**, cc-pVDZ, and aug-cc-pVDZ basis sets and by single point calculations with cc-pVTZ and aug-cc-pVTZ basis sets for selected conformations. Calculations at the MP4 and QCISD levels were also done. Minima and transition state were characterized from harmonic frequencies and force constants (zero negative force constants at each minimum and one negative force constant for the transition state) calculated at several levels of theory. The activation energy (E_a) was also obtained by using the following equations:

$$E_a = \Delta H^{\ddagger} + RT$$

$$\boldsymbol{\Delta} H^{\ddagger} = \Delta H_{ts} - \Delta H_{react}$$

where ΔH_{ts} and ΔH_{react} are the enthalpies for the transition state and the reactant (in the most stable conformation), respectively. The enthalpies were determined from the expressions of the quantum statistical thermodynamics for ideal gases.[7] R represents the universal gas constant (1.9872 cal mol^{-1} K^{-1}), and T represents the temperature (we have used a value of 673 K, since at this temperature there are experimental kinetic data).[8] All computations were performed with the Gaussian98 software package.[9]

Results and Discussion

An exploration at MP2/6-31G** was performed to obtain the ethyl formate minima. Several optimizations were done at different starting points. These starting geometries were chosen by using chemical knowledge. Several stationary points were found, and three minima were detected. Figure 2 shows the geometry for the three located minima. It can be seen that only the minimum II has a planar skeleton; in the remaining minima, the molecule is twisted and the dihedral angle composed of C_β, C_α, the oxygen of the ether group, and the carbon of the carboxylic group is close to 90°. Minimum I is the most stable, but the energy of minimum II is less than 0.1 kcal/mol higher. A similar exploration was done at the B3LYP/6-31G** level. The obtained results are like those from the MP2/6-31G** level except that the minimum II is the most stable one (minimum I is about 1.3 kcal/mol higher). In both cases, minimum III is placed at much higher energy (between 5 and 6 kcal/mol). The transition state of the thermal elimination is obtained at MP2/6-31G** and B3LYP/6-31G** levels. For both levels, the transition state is the expected six-membered ring; however, with the MP2 method, it is not the planar structure predicted by Erickson et al. at the HF/6-31G* level.[3]

The previously found stationary points were used as starting points to new optimizations at the MP2/6-311++G** level. The obtained results seem to corroborate that there are only the three minima shown in Figure 2 and that minimum III has an energy much higher than minima I and II. Taking that into account, we decided to perform calculations only in minima I and II to describe the thermal elimination in ethyl formate. At the MP2/6-311++G** level, minimum II appears as the most stable one and minimum I is 0.21 kcal/mol higher. B3LYP/6-311++G** optimizations have been performed to compare with previous data. The results are similar to those provided by the MP2 method using the same basis set. For the DFT method, minimum II is 0.4 kcal/mol more stable than minimum I. For both methods, the transition state is a nonplanar six-membered ring.

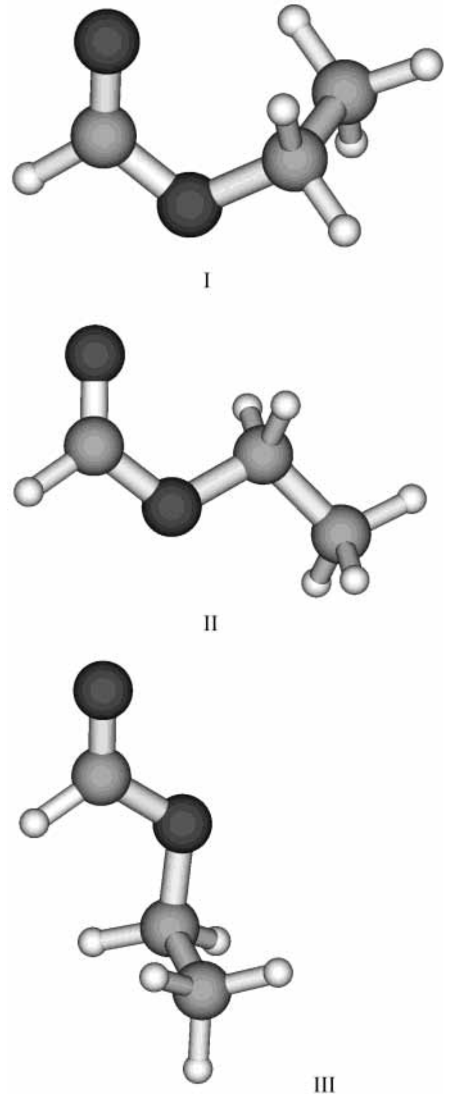

Figure 2. Geometry of the ethyl formate minima at the MP2/6-31G**.

Several different methods have been used to study the barrier of the thermal elimination. A list of the employed methods and the predicted values is given in Table 1.

Previously to the discussion of the barrier results, there are two facts that are worth mentioning. First, we must point out that the relative stability of minima I and II is not clear and that the different methods predict one or another as the most stable minimum. Even though most methods predict minimum II as the most stable one, optimizations with a rather high level as MP2/aug-cc-pVDZ give minimum I as the most stable. Except for DFT calculations, the energy difference between both minima is 0.2 kcal/mol or smaller, which gives an idea of the difficulty in predicting the relative stability of these minima. To calculate the value of the barrier (given in Table 1), the minimum with a lower enthalpy has always been used for each method. It must be noted that this minimum does not always correspond with that of lowest energy, because the inclusion of the thermal correction to the enthalpy always produces an extra stabilization of the minimum II. The second observation that must be done is that except for B3LYP/6-31G**, all methods (including B3LYP/6-311++G**) predict a transition state very distant from the planarity (see Table 3). For instance, at the MP2 level and depending on the employed basis set, the dihedral angles vary as follows: $C_\alpha - C_\beta$- - -H- - -O from 23 to 29°, C_α- - -O−C−O from 20 to 33°, and O−C−O- - -H from

TABLE 1: Activation Energy (kcal/mol) at 673 K and Enthalpy Difference (kcal/mol) between Minimum I and Minimum II at Different Calculation Levels

geometry and vibrational calculation	single point energy	E_a	$\Delta H_I - \Delta H_{II}$
B3LYP/6-31G**	B3LYP/6-31G**	47.41	0.26
B3LYP/6-311++G**	B3LYP/6-311++G**	46.07	0.48
MP2/6-31G**	MP2/6-31G**	55.58	0.00
	MP4SDTQ/6-31G**	54.78	−0.03
	QCISD(T)/6-31G**	54.96	0.01
	MP2/6-311++G**	52.97	0.29
MP2/6-311++G**	MP2/6-311++G**	51.62	0.27
	MP4SDTQ/6-311++G**	51.08	0.23
	MP2/cc-pVTZ	50.00	0.12
	MP4SDTQ/cc-pVTZ	49.40	0.08
MP2/cc-pVDZ	MP2/cc-pVDZ	52.56	0.04
	MP2/cc-pVTZ	51.56	0.11
	MP4SDTQ/cc-pVTZ	50.91	0.07
MP2/aug-cc-pVDZ	MP2/aug-cc-pVDZ	49.76	0.03
	MP4SDTQ/aug-cc-pVDZ	49.14	−0.01
	QCISD/aug-cc-pVDZ	52.87	0.16
	MP2/cc-pVTZ	51.52	0.08
	MP4SDTQ/cc-pVTZ	50.85	0.05
	MP2/aug-cc-pVTZ	50.59	0.10
experimental[a] (673 K)		48.25	

[a] Ref 8.

TABLE 2: Bond Lengths (Å) of the C_α−O and C_β−H in the Reactant and the Transition State of the Thermal Elimination at Different Calculation Levels[a]

		C_α−O	C_β−H	$P(C_\alpha$−O)	$P(C_\beta$−H)
B3LYP/6-31G**	react	1.45024	1.08762	39.0	22.7
	TS	2.01610	1.33500		
B3LYP/6-311++G**	react	1.45385	1.09212	40.7	19.8
	TS	2.04552	1.30852		
MP2/6-31G**	react	1.45170	1.08678	34.4	22.9
	TS	1.95097	1.33574		
MP2/6-311++G**	react	1.45024	1.08762	33.8	21.8
	TS	1.94085	1.32485		
MP2/cc-pVDZ	react	1.44895	1.10031	32.3	25.6
	TS	1.91706	1.35681		
MP2/aug-cc-pVDZ	react	1.46109	1.09888	32.8	20.6
	TS	1.94049	1.32485		

[a] Percent of lengthening between the transition state and the reactant bond length, P (%).

19 to 30°. In general, the distortion from the planarity increases with the size of the used basis set. A representation of the nonplanar transition state is given in Figure 3. This result disagrees with the fully planar transition state obtained by Erickson et al.,[3] showing that the level of theory used by these authors is not good enough to give a proper description of the transition state of the thermal elimination in the ethyl formate molecule.

Several observations can be extracted from the energy values given in Table 1. Possibly the most surprising result is that obtained at B3LYP/6-31G** level: the value is only 1.7% lower than the experimental result. To check the quality of this value and the behavior of the DFT method, new calculations were done at the B3LYP/6-311++G** level. At this level, the result gets worse with a difference of 4.5% as compared to the experimental value. This result suggests that the good value obtained at the B3LYP/6-31G** level could be the consequence of an error cancellation: on one hand, the error due to the small basis set employed and, on the other hand, the problem of the B3LYP functional to treat long range interactions. This problem appears more clearly when intermolecular interactions are considered, but it could affect the calculation of the transition state energy due to the already large distances that appear in the transition state geometry.[10]

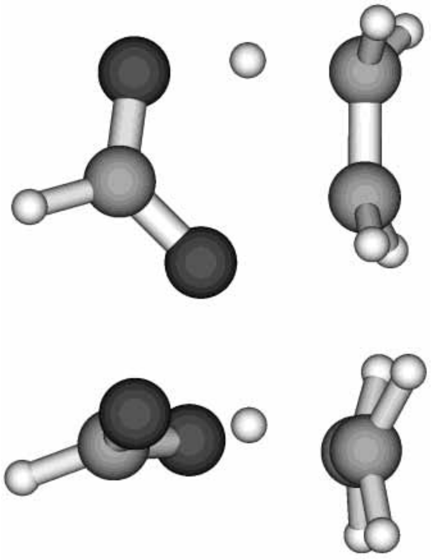

Figure 3. MP2/aug-cc-pVDZ geometry of the transition state; front and top view.

The obtained result at MP2/6-31G** is very poor, with an important error as compared to the experimental value. When the basis set is increased and diffuse functions are added, there is a significant improvement in the result. Using the cc-pVDZ basis set, the obtained energy is considerably better than with the 6-31G**, although the size of both basis sets is very similar. The energy value at MP2/aug-cc-pVDZ is significantly closer to the experimental result than the MP2/cc-pVDZ value. This fact confirms the importance of including diffuse functions in the calculation of the barrier for this kind of reaction.

It can be seen that including high order terms with MP4 calculations improves the MP2 results by 0.6−0.8 kcal/mol. However, it is different when the QCISD method is used, because in one case the result gets better but in another it gets worse. In general, to increase the size of the basis set in the single point calculations gives a better result than to increase the level of the method. The improvement of the values is larger for the first modification than for the second one. However, there is an important exception to that statement at the MP2/aug-cc-pVDZ level. When bigger basis sets are used to obtain the energy of the structures predicted at this level, the agreement with the experimental result gets worse. It may be due to the fact that the size of the basis set at MP2/aug-cc-pVDZ is already big enough, and other elements of the calculation (to obtain the real geometry of the stationary point for the used level, the influence of the high order terms, etc.) are more important to get the correct result.

Even though the transition state structure points to a concerted thermal elimination, a previous study predicts a non-fully concerted reaction.[3] This feature is studied by comparing the degree of lengthening of the two bonds that are breaking in the reaction. It is done by obtaining the percent of lengthening between the transition state and the reactant bond length. Table 2 lists the percent bond lengthening obtained with the different methods used. Erickson et al.[3] by performing calculations at the HF level predict that the C_α−O bond is lengthened by 47% and the C_β−H bond is lengthened by 21%. It can be seen in Table 2 that the introduction of the correlation decreases this difference and, consequently, predicts a more concerted reaction. These data show that the difference between the lengthening

TABLE 3: Six Dihedral Angles (Degrees) around the Six-Membered Ring in the Transition State

	$C_\beta C_\alpha OC$	$C_\alpha OCO$	OCOH	$COHC_\beta$	$OHC_\beta C_\alpha$	$HC_\beta C_\alpha O$
B3LYP/6-31G**	0.7	−2.9	2.7	1.0	−2.8	0.8
B3LYP/6-311++G**	4.3	−17.6	16.7	4.1	−15.2	4.8
MP2/6-31G**	6.3	−25.7	23.2	12.3	−27.8	7.6
MP2/6-311++G**	7.0	−31.9	30.1	7.2	−27.4	9.4
MP2/cc-pVDZ	3.2	−20.4	19.3	9.2	−23.1	7.6
MP2/aug-cc-pVDZ	8.1	−32.7	30.2	9.5	−29.3	8.9

values is about 10% larger in the B3LYP results as compared to the MP2 values. Taking into account the lack of ability of B3LYP to treat long range interactions, it seems that this method overestimates the length of the Ca−O bond in the transition state geometry.

Conclusions

In the present work, ab initio and DFT calculations at different levels of theory have been performed to study the elimination process in ethyl formate. For each level, several stationary points and the transition state have been found for this compound.

The calculations predict three minima, two of them very close in energy, minima I and II. The different methods predict one or another as the most stable one, and the third minimum (minimum III) is placed at much higher energy.

Except for B3LYP/6-31G**, a clearly nonplanar transition state is obtained by all applied methods. This geometry disagrees with the planar transition state predicted by Erickson,[3] and the disagreement is probably due to the role of the correlation energy. This also is an indication of the poor description offered by the B3LYP/6-31G** level, which probably will produce lack of precision in the description of the studied process.

The B3LYP/6-31G** level gives an activation energy very close to the experimental value. This fact could appear as a consequence of an error cancellation because of the small employed basis set and the problems of the B3LYP functional to describe long range interactions. Those interactions may be important to define the structure of the transition state. When the size of the basis set is increased (at the B3LYP/6-311++G** level) the difference respect to the experimental value also increases. This seems to corroborate the previous hypothesis about the error cancellation.

The closest value to the experimental result, apart from the B3LYP/6-31G** level, is at the MP4SDTQ/aug-cc-pVDZ//MP2/aug-cc-pVDZ level. From the obtained results, it can be seen that in general to increase the basis set produces more similar results to the experimental value than to increase the level of the calculation method.

The calculations give a degree of lengthening predicted that the thermal elimination in the ethyl formate is more concerted than the results given by Erickson.[3] In general, the DFT methods point to a less concerted reaction of elimination.

In general terms, and from the results obtained in the present work, it can be inferred that it is necessary to use a method including the electronic correlation for a good description of the studied systems. Moreover, our results also point out that the lack of ability of the B3LYP functional to treat long range interactions leads to several deviations: to increase the stability of the planar conformations with respect to spacial configurations, to overestimate the length of the C_α−O bond in the transition state geometry, and to predict a less concerted reaction. Those problems can be aggravated if a small basis set is used and if diffuse functions are not included. Thus, in calculations performed in thermally degradable polycarbonates with substituents, like π rings, that increase the importance of the dispersion interactions, diffuse basis functions should be used to give a good description of long range forces. Those terms can change the relative stability of two different conformations or vary the energy of the transition state giving noticeable changes in the activation energy of the reaction.

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Supporting Information Available: Table containing the Cartesian coordinates and harmonic frequencies of the optimized geometries of reactants and transition states. This material is available free of charge via the Internet at http://pubs.acs.org.

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