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[g020]

A COMPUTATIONAL STUDY OF THE MECHANISM OF THE UNIMOLECULAR ELIMINATION OF *α, β* - UNSATURATED ALDEHYDES IN THE GAS PHASE.

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INTRODUCTION

α,β-unsaturated aldehydes are versatile intermediates in organic synthesis. Due to the little information on the thermolysis of these compounds, recently Chaban et al. decided to carry out an experimental work aimed at examining the gas phase elimination kinetics of (*E*)-2-butenal (crotonaldehyde) and (*E*)-2-methyl-3-pheny-2-propenal (2-methylcinnamaldehyde).[1] One of their more important objectives was to find a rational mechanism for these elimination reactions. Finally, they found as the most reasonable hypothesis a concerted process with a semi-polar three-membered cyclic transition state structure (mechanism 1 in Figure 1). However, an alternative that Chaban et al. did not discard was a two-step reaction with a four-membered cyclic transition structure for the first stage. This implies the formation of a carbene type of intermediate and CO gas; such intermediate may undergo a 1,2-hydrogen migration to give the corresponding olefine (mechanism 2 in Figure 1). In order to try to elucidate the mechanism of these eliminations, in this work we carry out a comprehensive computational study. The complete reaction paths for these reactions were calculated and these results, together with the previous experimental findings, allow us to establish several interesting conclusions about the elimination reaction in these *α,β*-unsaturated aldehydes.

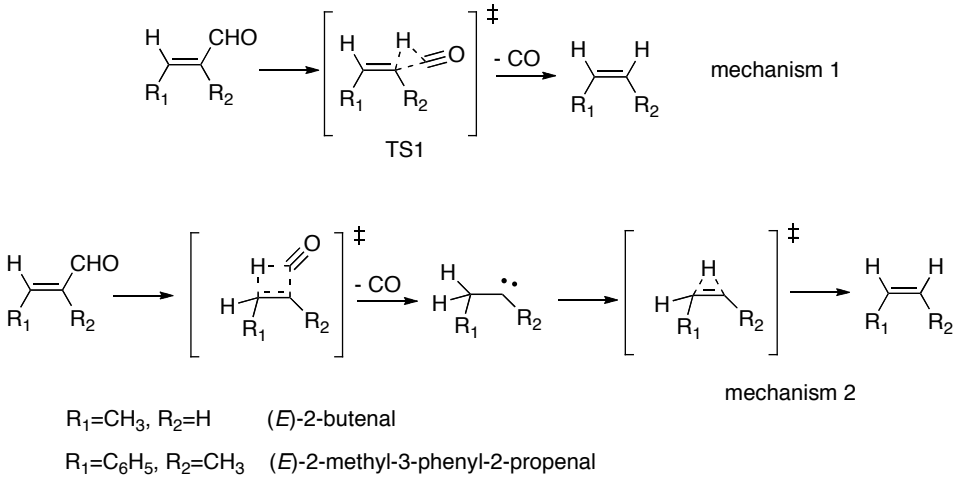


Figure 1. The two possible mechanisms proposed by Chaban et al for the elimination.[1]

COMPUTATIONAL DETAILS

All the stationary points (reactants, products, transition structures and intermediates) of the elimination reaction of crotonaldehyde were located by optimizing every degree of freedom (except one that is maximized for the transition states) via *ab initio* including electron correlation in the form of the second-order Møller-Plesset theory (MP2) and DFT using the B3LYP functional. For these calculations several basis sets of different size were used, ranging from 6-31G** to aug-cc-pVDZ. All the minima and transition states 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 the same levels of theory using analytical second derivatives. This allows us to obtain the complete profile for the Gibbs free energy including zero point energy (ZPE) and thermal correction (at the temperature of the experimental study). The pathway for each individual reaction was obtained by using the intrinsic reaction coordinate (IRC) with massweighted coordinates.[2-4] This allow to confirm the identity of all the transition states. From MP2 optimized geometries, single point calculations were performed at a higher correlated Møller-Plesset level (MP4SDTQ) with larger basis sets (up to aug-cc-PVTZ).

Owing to the large size of 2-methylcinnamaldehyde, and taking into account quite reasonable DFT results for the elimination of crotonaldehyde, only calculations at the B3LYP/6-31+G** level were performed for the bigger compound.

All calculations were performed with the Gaussian03 software package.[5]

RESULTS AND DISCUSSION

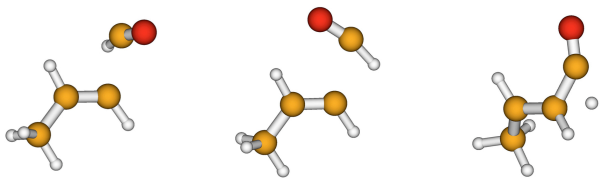
Elimination of (*E*)-2-butenal (crotonaldehyde). The s-*trans* conformation (referred to the orientation between the carbonyl double bond and the carbon-carbon double bond) of this aldehyde is more stable than the s-*cis* one, as expected. However, the energy difference is not very large: 1.3 kcal/mol at the B3LYP/6-31G* level, for example. Anyway, from here on, the s-*trans* conformation is considered the starting point of any energy scale (i.e. the reactant). The optimization of products (propene and carbon monoxide) allow us the calculation of the reaction enthalpy. Table 1 shows that B3LYP calculations lead to a slightly endothermic process. However, Møller-Plesset calculations indicate that reactant and products have a very similar enthalpy.

For three-membered cyclic transition state of mechanism 1 (Figure 1) three different structures were found (TS1a, TS1b and TS1c in Figure 2). All of them lead to products, but they present different characteristics. The only difference between TS1a and TS1b is the starting conformation of the reactant: s-*trans* for the former and s-*cis* for the latter. However, TS1c has a very different feature: it leads to a change in the configuration of the carbon-carbon double bond. The rotation of this double bond can be inferred from the animation of the imaginary frequency and it can be fully confirmed with the intrinsic reaction path. Anyway, for the elimination of crotonaldehyde the change of configuration

has not any consequence since the product does not change, because R_2=H. Table 2 shows that TS1a and TS1b lead to very similar activation Gibbs free energies, as expected. A priori TS1c could be supposed as the most expensive process since it implies a double bond rotation. However, on the contrary, it leads to a smaller activation Gibbs free energy (~ 4 kcal/mol at the Møller-Plesset level). This difference is enough to state that the three-membered cyclic transition state takes place mainly through TS1c.

Table 1. Enthalpy of reaction (kcal/mol) for the elimination of (*E*)-2-butenal calculated at several computational levels. It includes ZPE and thermal corrections to enthalpy (T=713.15 K).

	ΔH
B3LYP/6-31G**	8.20
B3LYP/6-31+G**	7.23
B3LYP/6-31++G**	7.27
MP2/6-31G**	1.78
MP4/6-31G**// MP2/6-31G**	-1.42
MP4/6-31++G**// MP2/6-31G**	-0.92
MP2/6-31++G**	2.06
MP4/6-31++G**//MP2/6-31++G**	-0.94
MP2/aug-cc-pVDZ	2.92
MP4/aug-cc-pVDZ// MP2/aug-cc-pVDZ	-0.14
MP4/aug-cc-pVTZ// MP2/aug-cc-pVDZ	1.64



TS1a TS1b TS1c

Figure 2. The three different structures found for the three-membered cyclic transition state of mechanism 1 (Figure 1). The MP2/aug-cc-pVDZ geometries are shown.

Table 2. Calculated activation Gibbs free energy ($\Delta G^{\ddagger}$, kcal/mol) for the three-membered cyclic transition structures of the elimination of (*E*)-2-butenal (Figure 2) at T=713.75 K.

	TS1a	TS1b	TS1c
B3LYP/6-31G**	85.17	86.77	83.65
B3LYP/6-31+G**	84.57	86.77	83.88
B3LYP/6-31++G**	84.48	86.29	83.68
MP2/6-31G**	89.62	90.68	85.56
MP4/6-31G**// MP2/6-31G**	87.62	87.93	83.70
MP4/6-31++G**// MP2/6-31G**	86.78	87.76	83.04
MP2/6-31++G**	88.40	88.31	84.85
MP4/6-31++G**//MP2/6-31++G**	86.49	85.78	83.03
MP2/aug-cc-pVDZ	83.70	85.08	79.99
MP4/aug-cc-pVDZ// MP2/aug-cc-pVDZ	82.01	82.88	78.61
MP4/aug-cc-pVTZ// MP2/aug-cc-pVDZ	82.24	82.72	78.94

All attempts to find the first transition state of mechanism 2 (Figure 1) were unsuccessful. According to our calculations (with all the used levels), the simultaneous hydrogen atom migration and carbon monoxide elimination is not feasible. In all cases, the searching of this structure led to a transition state where only the hydrogen migration takes place. Therefore, we propose an alternative mechanism 2 (Figure 3). As in the original mechanism 2, in this case we did not find either a transition state where only the carbon monoxide elimination occurs. So, in this mechanism, the carbon monoxide elimination takes place not in the first step but in the second step. Figure 4 shows the geometry of the transition structures and reaction intermediate for this mechanism; Table 3 includes the energetic results. From the comparison between Table 2 and 3 it can be concluded that alternative mechanism 2 is more favorable than mechanism 1. Therefore, according to our calculations the elimination of (*E*)-2-butenal takes place mainly through a two-step reaction, being the second step (the simultaneous hydrogen migration and carbon monoxide elimination) the most energetically expensive process.

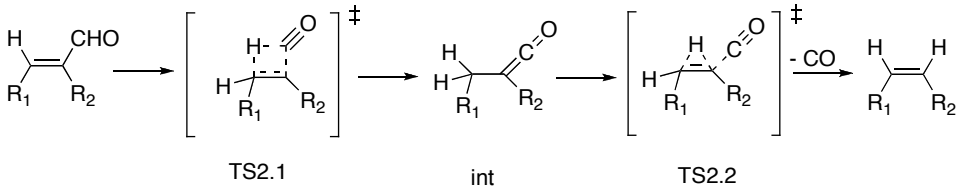


Figure 3. Alternative mechanism 2.

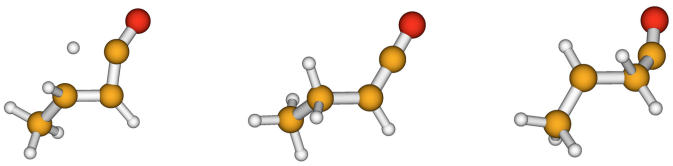


Figure 4. Transition structures and reaction intermediate for the alternative mechanism 2 (Figure 3). The MP2/aug-cc-pVDZ geometries are shown.

Table 3. Calculated relative Gibbs free energy (kcal/mol) for the transition structures and reaction intermediate of the alternative mechanism 2 of the elimination of (*E*)-2-butenal (Figure 3 and 4) at T=713.75 K.

	TS2.1	int	TS2.2
B3LYP/6-31G**	67.98	3.16	77.83
B3LYP/6-31+G**	68.12	4.61	77.40
B3LYP/6-31++G**	68.07	4.57	77.31
MP2/6-31G**	72.92	2.08	79.46
MP4/6-31G**// MP2/6-31G**	71.65	2.39	77.91
MP4/6-31++G**// MP2/6-31G**	71.29	4.21	77.33
MP2/6-31++G**	72.47	4.00	78.88
MP4/6-31++G**//MP2/6-31++G**	71.09	4.23	77.40
MP2/aug-cc-pVDZ	68.76	2.28	74.87
MP4/aug-cc-pVDZ// MP2/aug-cc-pVDZ	67.27	2.41	74.10
MP4/aug-cc-pVTZ// MP2/aug-cc-pVDZ	67.09	1.37	74.34

Elimination of (*E*)-2-methyl-3-pheny-2-propenal (2-methylcinnamaldehyde). In this case, the considerable size of this system prevents the use of high-level Møller-Plesset calculations. However, the previous study of the elimination of (*E*)-2-butenal showed that B3LYP results were reasonably good both for geometries and energies: no substantial differences were found for all the geometries of transition states and reaction intermediate and the energetic conclusions coming from DFT and Møller-Plesset were basically the same. Moreover, it could be observed that the basis set has an almost negligible influence for all the B3LYP calculations. For these reasons, the elimination of (*E*)-2-methyl-3-pheny-2-propenal was only studied at the B3LYP/6-31+G** level.

The two possible products of the elimination are (*Z*)-*β*-methylstyrene and (*E*)-*β*-methylstyrene. The alternative mechanism 2 can lead both to (*Z*)-*β*-methylstyrene and to (*E*)-*β*-methylstyrene, since rotation around the middle C-C single bond is possible for the reaction intermediate. However, mechanism 1 only leads to a specific product depending on the transition structure. So, (*Z*)-*β*-methylstyrene is the product of TS1a and TS1b, whereas (*E*)-*β*-methylstyrene is the product of TS1c. The experimental study showed that two other products were obtained too: *α*-methylstyrene and indan (Figure 5).[1] This fact was interpreted by means of a very rapid isomerization of the *β*-methylstyrene products.

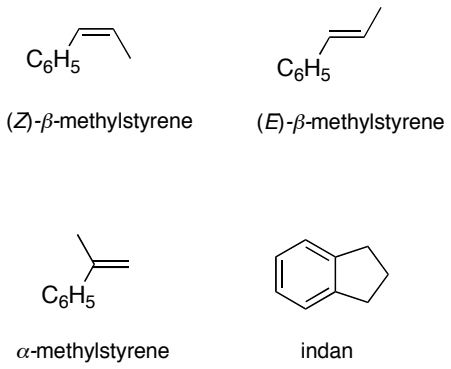


Figure 5. Experimental products of the elimination of (*E*)-2-methyl-3-pheny-2-propenal.

All the singular points of the mechanism 1 and the alternative mechanism 2 were optimized at the B3LYP/6-31+G** level. According to values of table 4, the elimination of (*E*)-2-methyl-3-pheny-2-propenal takes place mainly through TS1c, and to a lesser extent through the alternative mechanism 2. So, from a kinetic point of view, formation of (*E*)-*β*-methylstyrene will be favored since the main channel (TS1c) only give rise to the (E) product and the secondary channel give rise to a (E)/(Z) mixture. This agrees rather well with the experimental results since the obtained distribution was 42.7 % of (*E*)-*β*-methylstyrene and 13.7 % of (*Z*)-*β*-methylstyrene. Chabán et al. suggested that the distribution of products is a consequence of thermodynamic considerations.[1] However, in our opinion, several signs point to a kinetic control for the elimination. Firstly, the product distribution almost does not change over time and it only changes slightly with temperature. Moreover, according to our results (Table 4) the energetic difference between the two isomers should lead to a larger difference between

the amount of each one. Table 4 also shows that both isomers give rise to exothermic and very exergonic processes.

Apart from the two *β*-methylstyrene isomers, the experimental work showed that two other products were produced: *α*-methylstyrene (29.4 %) and indan (14.4 %). Evidently, this fact cannot be explained either from a thermodynamic point of view since *α*-methylstyrene is clearly the less stable product (actually, its formation is the only endothermic process). In general, from the results of Table 4, it is clear that the experimental distribution of the products has not any relation with the energetic stability of them; this is another argument against thermodynamic control.

Table 4. Calculated relative enthalpy and Gibbs free energy (kcal/mol) for the singular points of the elimination of (*E*)-2-methyl-3-pheny-2-propenal at T=743.35 K.

	H	*G*
reactant	0.00	0.00
TS1a	86.79	84.18
TS1b	90.20	85.85
TS1c	75.97	76.99
TS2.1	63.26	64.83
int	9.86	8.01
TS2.2	77.32	77.77
(*E*)-*β*-methylstyrene + CO	-5.20	-32.04
(*Z*)-*β*-methylstyrene + CO	-2.44	-28.89
α-methylstyrene + CO	7.97	-17.75
indan + CO	-5.19	-24.65

The most stable of the three methylstyrene products is the isomer (*E*)-*β*-methylstyrene. This fact is easily explained from the optimized geometry: only this isomer can adopt a fully planar disposition where the external CC double bond get the highest delocalization with the π cloud of the phenyl group. However, in (*Z*)-*β*-methylstyrene and, especially in α-methylstyrene, the steric repulsion prevents a planar disposition (figure 6). Indan is enthalpically a product as favored as (*E*)-*β*-methylstyrene, but it is entropically penalized.

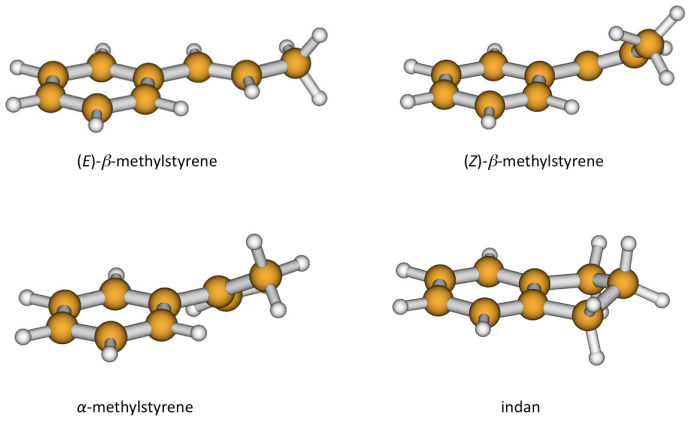


Figure 6. Products optimized geometry of the elimination of (*E*)-2-methyl-3-pheny-2-propenal.

According to Table 4, α-methylstyrene is considerably the less stable product. However, a significant amount (29.4 %) of this product is found experimentally. A plausible explanation of this fact could be that α-methylstyrene came from isomerization of the main product, (*E*)-*β*-methylstyrene. Recently, Lin *et al* have proposed a mechanism for the dimerization of (*E*)-*β*-methylstyrene at a temperature about 100º C, in which 1,4-diphenylcyclohexane could be involved (figure 7).[6] If 1,4-diphenylcyclohexane can be present, then it is not difficult to postulate the mechanism for the α-methylstyrene formation; so, only depending on the C-C single bonds which break, (*E*)-*β*-methylstyrene or α-methylstyrene can be produced (in both cases, the reaction is basically the formation of two molecules of propene from cyclohexane).

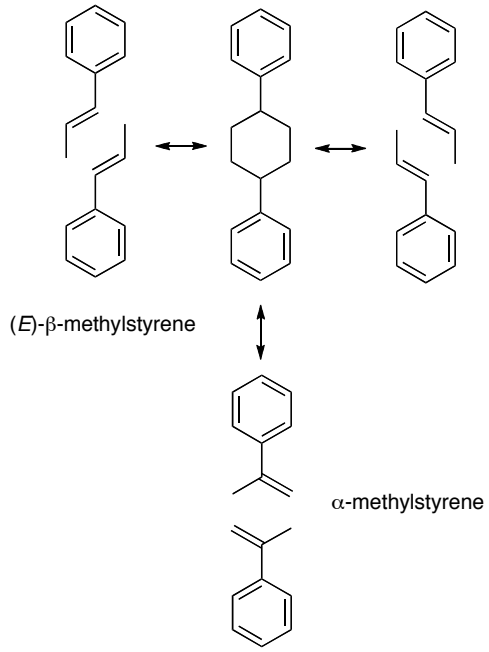


Figure 7. A possible path for the formation of α-methylstyrene.

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