ORIENTAL JOURNAL OF CHEMISTRY
An International Open Free Access, Peer Reviewed Research Journal
www.orientjchem.org

ISSN: 0970-020 X
CODEN: OJCHEG
2017, Vol. 33, No. (3):
Pg. 1265-1275

Solvent Effects on the Mechanistic of Ketene and Halogenated Ketene Cycloadditions with Cyclopentadiene: A DFT Study

NASRIN FARAHANI[1] and SEYED MAJID MUSAVI[2]*

[1] Department of Chemistry, Buinzahra Branch, Islamic Azad University, Buinzahra, Iran.
[2]Department of Chemistry, Shahr-e- Qods Branch, Islamic Azad University, Tehran, Iran
*Corresponding author E-mail: moosavi_majid@yahoo.com

http://dx.doi.org/10.13005/ojc/330326

(Received: January 28, 2017; Accepted: March 19, 2017)

ABSTRACT

The energetic and activation barriers for 4 possible [2+2] and [4+2] cycloadditions of ketene and dihaloketenes with cyclopentadiene are investigated at B3LYP/6-31G* level of theory. Three solvents including DMSO, CCl$_4$ and water, using the CPCM model, are considered and their results are compared to those of gas phase. The entire studied cycloadditions take place *via* clear asynchronous TSs. For the parent ketene, all solvents stabilize the reactants within the range of 9.4-13.7 kcal/mol and reduce the thermodynamic achievability of this reaction (ΔE=-18.4, -10.9, -11.6 and -12.8 kcal/mol for gas phase, CCl$_4$, DMSO and H$_2$O, respectively, for [2+2] across C=C) and the energy barriers are increased to the maximum of 6.1 kcal/mol. In contrast, for dihaloketenes all solvents make the thermodynamics less favorite by decreasing the exoergicity (within 1-5 kcal/mol), however, most of reaction pathways become kinetically favored by lowering the energy barriers (within 1-7 kcal/mol) in the presence of polar solvents. The nonpolar solvent CCl$_4$ behaves like that of gas phase. Moreover, the preference of two-step cycloaddition *via* [3+3] sigmatropic rearrangement is reduced in the presence of solvents. The ultimate effect is pertaining to dichloroketen where it prefers the routine one-step cycloaddition pathway in H$_2$O like that observed for the parent ketene.

Keywords: Dihaloketene; Cycloaddition; Dielectric constant, Density functional theory, Dielse-Alder (Footnotes).

INTRODUCTION

Ketene chemistry started at the beginning of the previous century and subsequently it has extensively blossomed because of its theoretical significance as well as its utility in the organic synthesis[1,2]. The most characteristic reaction of ketenes is the cycloaddition, which is a powerful method to generate four membered ring heterocyclics. Ketenes mainly participate in [2+2] cycloadditions with a variety of dienophiles across the C=C, C=O, C=N, C=S, N=N, N=O, N=S, and P=N bonds[3]. Ketenes prefer to primarily form vinylcyclobutanone in the reaction with dienes which many reports argued their mechanisms by a single step [2+2] or by a [4+2] following a^{3,3} rearrangement[4,9]. Despite the large number of reports on the gas phase cycloadditions of ketenes[10] theoretical investigations on the roles of solvents in the reaction mechanisms appear to be limited. A general belief is that polar solvents stabilize the zwitterionic intermediates, consequently altering the mechanism from a concerted process in the gas phase to a stepwise one in solution via a more stable zwitterionic intermediate[11]. This is qualitatively in accord with experimental observations. However, quantitatively the magnitude of solvent effects on the free energy of activation has been a fundamental question[12]. Moreover, the accuracy of theoretical models in such reactions is a big problem for the computational study. for instance, SCRF and the more accurate self-consistent isodensity polarizable continuum model (SCIPCM) calculations at the HF/6-31G* and B3LYP/6-31G* levels predict the solvent effects lowering the activation energy of the cycloaddition of 1,1-dicyanoethylene (DCNE) and methyl vinyl ether (MVE) by 10-13 kcal/mol on going from CCl_4 to CH_3CN[13] which is substantially larger than the observed data of about 5 kcal/mol. Many researchers studied the stereo-divergent outcome of the cycloadditions of ketenes and imines theoretically and experimentally. Accordingly, Cossio *et al.,* stated that the solvent effects should be taken into account and suggested that the polarity of the solvent enhances the diastereomeric excess of the reaction[14]. Moreover, the reaction of ketene with formaldimine at the B3LYP/6-31G* level[15] showed a different reaction path compared to previous report of Sordo *et al.,*[16,17] where an intermediate was located when the solvent effect is added during the IRC calculation. This again confirms the significance of solvents in the reaction pathways of ketene cyclo additions.

As a consequence, it would be of interest to test the available solvation methodology on this inspiring reaction. For this purpose, we have investigated roles of three solvents on the structures and mechanisms of the [2+2] and [4+2] cyclo additions between ketene and dihalogenated ketene analogues with cyclopentadiene (cp) along four different reaction pathways previously outlined[18] (Figure 1).

Computational Methods

The molecular orbital calculations were carried out using Gaussian 03 program package[19]. All geometry optimizations are performed at the B3LYP/6-31G* level (the hybrid three-parameter

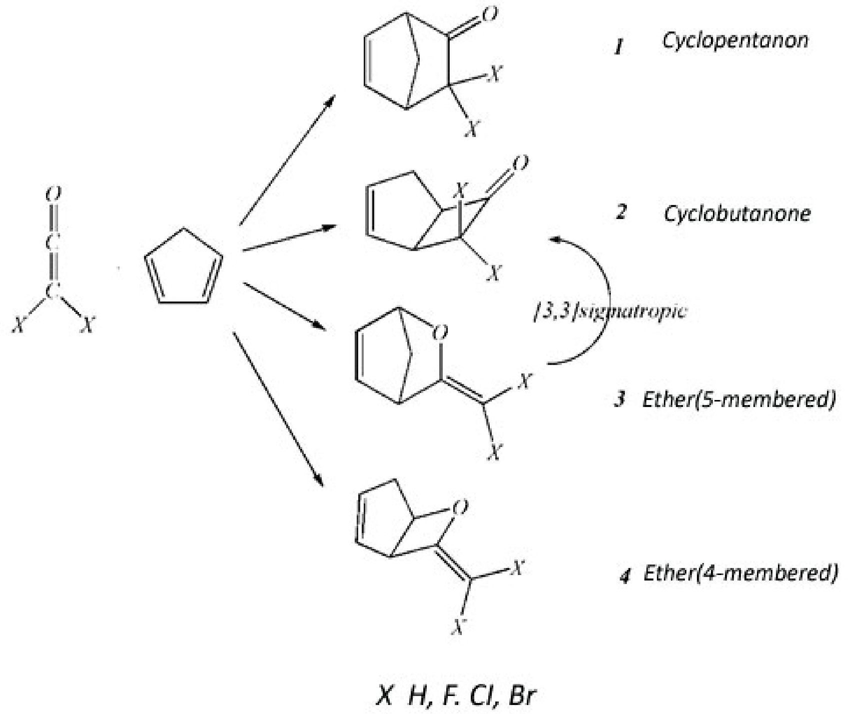

Fig. 1: Different pathways for [2+2] and [4+2] cycloadditions of ketene and dihaloketenes with cp

functional developed by Becke[20]) using the 6-31G* basis set[21]. Intrinsic reaction coordinate (IRC) calculations[22] are performed to connect the transition states to their respective minima in all cases. Frequency calculations verified the identity of each stationary point as a minimum or a transition state. Zero-point vibrational energies have been computed and have not been scaled. The polarizable continuum (PCM) and CPCM model[23] are employed to consider the effect of the solvent on the reactions of interest at the B3LYP/CPCM/6-31+G* level of theory using the optimized geometries along the minimum energy pathway. Natural bond orbital (NBO) calculations[24] have been done at B3LYP/6-311++G** level. The transition states (TSs) linking the initial and final structures found using the reactant products quasi synchronous transient (QST2) algorithm[25].

RESULTS AND DISCUSSION

In this section four different reaction pathways including [2+2] and [4+2] cycloadditions across the C=C and C=O bond of ketene and dihaloketenes with cp are considered. Besides, the sigmatropic rearrangements on the cycloadducts of [4+2] cyclo additions across the C=O bond of ketenes are inspected in the presence of three solvent environments of different dielectric constants (CCl_4: ε=2.2, DMSO: ε=46.8, and H_2O: ε=78.3). A general view on the optimized geometries of TSs

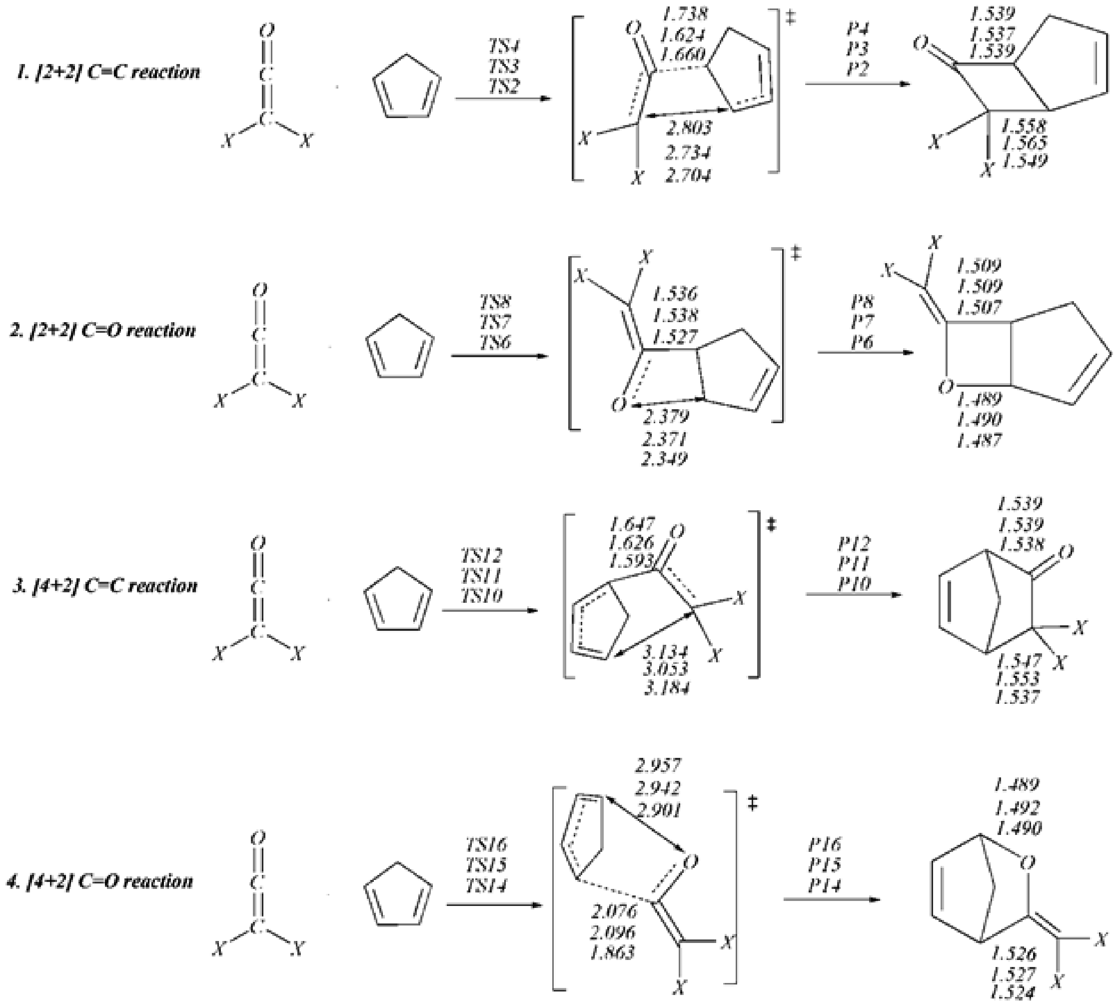

Fig. 2: Key bond lengths (in Å) of four cycloaddition pathways (1-4) of dihaloketenes with cp in the gas-phase (values from down to up denotes for F, Cl and Br, respectively).

of these concerted processes reveals that two new created C-C sigma bonds are clearly unsymmetrical and the linearity of ketenes is disappeared in a way that bond formation between the terminal carbon of diene moiety and central carbon of ketene is clearly more advanced (Figure 2). Hence, the cp and ketene reactions take place *via* asynchronous TSs.

Table 1: Calculated MO energies, au; as well as the differences between FMO energies, kcal/mol; for cycloadditions under studied

Interacting MOs	Phase	HOMO	LUMO	LUMO + 1	H- L	H-L+1
HOMO (cp)-LUMO (ketene)	Water	-0.22632	-0.04810	0.00148	111.8	142.9
	CCl4	-0.22338	-0.04968	0.00099	108.9	140.75
	DMSO	-0.22454	-0.04965	0.00110	109.7	141.5
	Gas	-0.222	-0.050	0.001	108.23	139.93
LUMO (cp)-HOMO (ketene)	Water	-0.25355	-0.02848	0.01565	141.2	168.9
	CCl4	-0.25378	-0.02708	0.01532	142.2	168.8
	DMSO	-0.25385	-0.02765	0.01590	141.9	169.2
	Gas	-0.253	-0.026	0.014	142.5	167.5
HOMO (cp)-LUMO (Difluoroketene)	Water	-0.22632	-0.10970	-0.00212	73.1	140.6
	CCl4	-0.22338	-0.11424	-0.00537	68.4	136.8
	DMSO	-0.22454	-0.11261	-0.00361	70.2	138.6
	Gas	-0.222	-0.116	-0.007	66.7	134.9
LUMO (cp)-HOMO (difluoroketene)	Water	-0.25107	-0.02848	0.01565	139.6	167.3
	CCl4	-0.25486	-0.02708	0.01532	142.9	169.5
	DMSO	-0.25334	-0.02765	0.01590	141.6	168.9
	Gas	-0.256	-0.026	0.014	144.4	169.4
HOMO (cp)-LUMO (Dichloroketene)	Water	-0.22632	-0.10558	-0.03492	75.7	120.1
	CCl4	-0.22338	-0.10796	-0.03682	72.4	117.0
	DMSO	-0.22454	-0.10746	-0.03604	73.4	118.2
	Gas	-0.222	-0.108	-0.037	71.3	116.0
LUMO (cp)-HOMO (Dichloroketene)	Water	-0.24929	-0.02848	0.01565	138.5	166.2
	CCl4	-0.25102	-0.02708	0.01532	140.5	167.1
	DMSO	-0.25048	-0.02765	0.01590	139.8	167.1
	Gas	-0.251	-0.026	0.014	141.3	166.2
HOMO (cp)-LUMO (Dibromoketene)	Water	-0.22632	-0.10777	-0.06087	74.3	103.8
	CCl4	-0.22338	-0.10928	-0.06299	71.5	100.6
	DMSO	-0.22454	-0.10906	-0.06226	72.4	101.8
	Gas	-0.222	-0.109	-0.063	70.8	99.7
LUMO (cp)-HOMO (Dibromoketene)	Water	-0.24553	-0.02848	0.01565	136.1	163.8
	CCl4	-0.24659	-0.02708	0.01532	137.7	164.3
	DMSO	-0.24637	-0.02765	0.01590	137.2	164.5
	Gas	-0.246	-0.026	0.014	138.3	163.1

On the other hand, for all ketene and halogenated ketenes the HOMO-LUMO gaps are smaller when HOMOs come from dienes while LUMOs come from ketenes (Table 1). All employed solvents stabilize these HOMO energies and destabilize these LUMO energies which in turn make the FMO interactions[26] to be more feasible.

The [2+2] cycloadditions across the C=C and C=O bond of ketenes

The [2+2] cycloadditions of parent ketene with cp across the C=C bond of ketene leads to the cycloadduct P1 after passing thorough TS1 (Figure 3A). This is a moderate exoergic reaction (ΔE= -18.4 kcal/mol) with a high energy barrier ($\Delta E^{\ddagger}$=18.0 kcal/mol). All solvents stabilize the reactants within the range of 9.4-13.7 kcal/mol and reduce the thermodynamic achievability of this reaction (ΔE= -10.9, -11.6 and -12.8 kcal/mol for CCl_4, DMSO and H_2O, respectively). On the other hand, the energy barrier is increased to the maximum of 6.1 kcal/mol. Interestingly, the least polar solvent exerts the most unfortunate thermodynamic and kinetic conditions for this reaction.

In the other alternative pathway, the [2+2] cycloadditions of parent ketene with cp across the C=O bond of ketene leads to the cycloadduct P2 after passing thorough TS2 (Fig. 3B). This is a low exoergic reaction **(**ΔE**= -1**.8 kcal/mol) with a very high energy barrier ($\Delta E^{\ddagger}$=32.6 kcal/mol). Consequently, this path of reaction has a lower significance in the competition. Again, all solvents reduce the thermodynamic achievability of this reaction by switching the reactions to endoergic ones (ΔE= 5.7, 5.13 and 2.8 kcal/mol for CCl_4, DMSO and H_2O, respectively). On the other hand, the energy barrier is increased to 37.8 kcal/mol for CCl_4 and 34.7 kcal/mol for DMSO while decreased to 29.8 kcal/mol for H_2O. Again, the least polar solvent

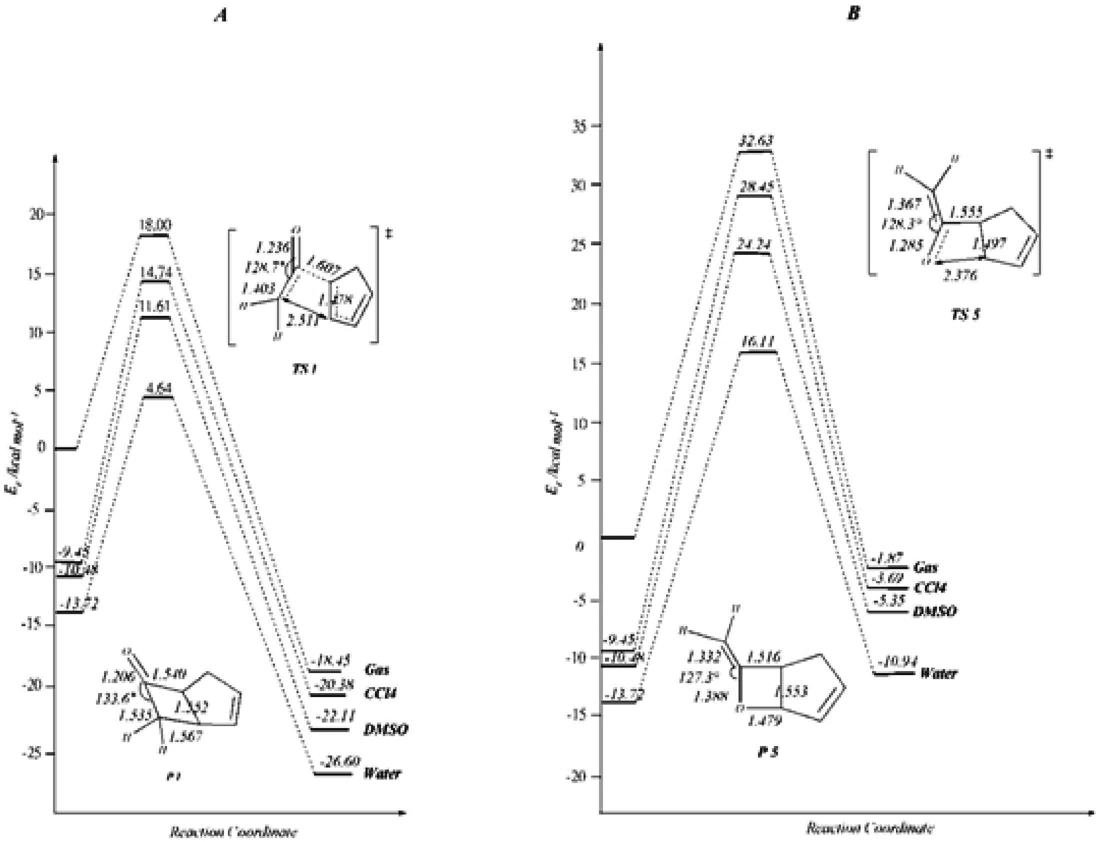

Fig. 3: Relative reaction energies of [2+2] cycloadition reaction across C=C bond of ketene (A) and [2+2] cycloadition reaction across C=O bond of ketene (B) in the gas phase and solvents

exerts the most unfortunate thermodynamic and kinetic conditions for this reaction. In general, the [2+2] cycloaddition across the C=C and C=O bond of ketene would be of less favorite in the solvents compared to gas phase.

The [4+2] cycloadditions across the C=C and C=O bond of ketene

The concerted [4+2] cycloaddition, namely Dielse-Alder reaction, across the C=C bond of the ketene with cp yields cyclopentanones P3 in one step after passing through the corresponding TS3 (Figure 4A).This is a moderate exoergic reaction (ΔE= -23.3 kcal/mol) with a high energy barrier ($\Delta E^{\ddagger}$=25.9 kcal/mol). All solvents reduce the thermodynamic achievability of this reaction (ΔE= -15.9, -16.8 and -18.2 kcal/mol for CCl_4, DMSO and H_2O, respectively). On the other hand, the energy barrier is increased to the maximum of 6.0 kcal/mol. Again, the least polar solvent exerts the most unfortunate thermodynamic and kinetic conditions for this reaction.

The last possible reaction mode is the concerted [4+2] cycloaddition across the C=O bond of the ketene with cp which leads to a five-membered ring ether P4 after passing through the corresponding TS4 (Figure 4B). This is a low exoergic reaction (ΔE= -3.7 kcal/mol) with a high energy barrier ($\Delta E^{\ddagger}$=17.6 kcal/mol). All solvents reduce the thermodynamic achievability of this reaction by switching them to endoergic ones (ΔE= 4.1, 3.7 and 2.2 kcal/mol for CCl_4, DMSO and H_2O, respectively). On the other hand, the energy barrier is increased to nearly 6.0 kcal/mol. Again, the least polar solvent exerts the most unfortunate thermodynamic and kinetic conditions for this reaction.

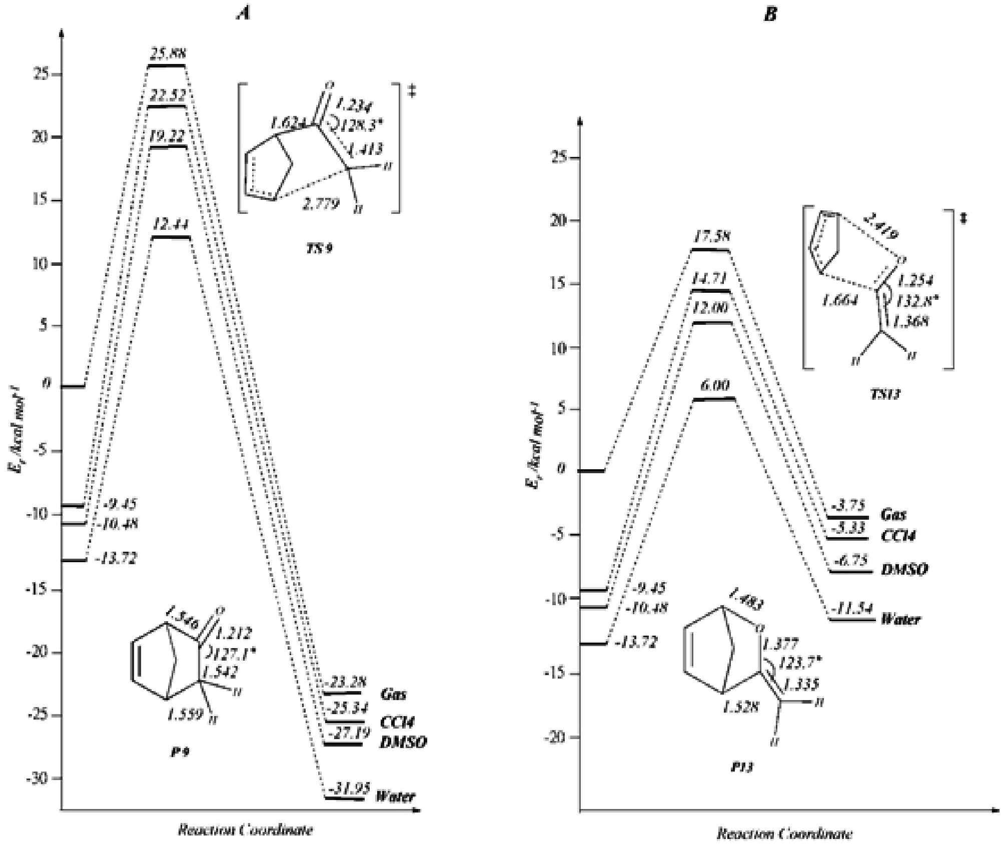

Fig. 4: Relative reaction energies of [4+2] cycloadition reaction across C=C bond of ketene (A) and [4+2] cycloadition reaction across C=O bond of ketene (B) in the gas phase (red line) and solvents

The [3,3] sigmatropic rearrangement of ketene

In this section, the possibility of $a^{3,3}$ sigmatropic rearrangement on the initially formed cycloadducts of [4+2] reaction across the C=O bond of the ketene[26] is considered. This rearrangement can result in a [2+2] product across the C=C bond of the ketene as the final transformation (Figure 5). Calculated data show that reactants convert to an unstable bicyclic six-membered ether (ΔE= -3.7 kcal/mol) after passing through a relatively high energy barrier ($\Delta E^{\ddagger}$=17.6 kcal/mol) which passes through the second barrier of 21.7 kcal/mol to generate the high stable cyclobutanone (ΔE= -18.4 kcal/mol). In a comparison with the one-step [2+2] cycloaddition, however it is apparent that for the parent ketene the one-step pathway is preferred over the mentioned two-step pathway due to the similarity of barrier heights. Again, all solvents increase the first barrier energies within the range of 1.1-6.5 kcal/mol ($\Delta E_1^{\ddagger}$=24.1, 22.4, and 18.7 kcal/mol for CCl_4, DMSO and H_2O, respectively) by stabilizing the corresponding reactants. Concurrently, the most polar solvent reduces the stability of intermediate by 5.9 kcal/mol and the second energy barrier somewhat increases by CCl4 and DMSO and slightly decreases

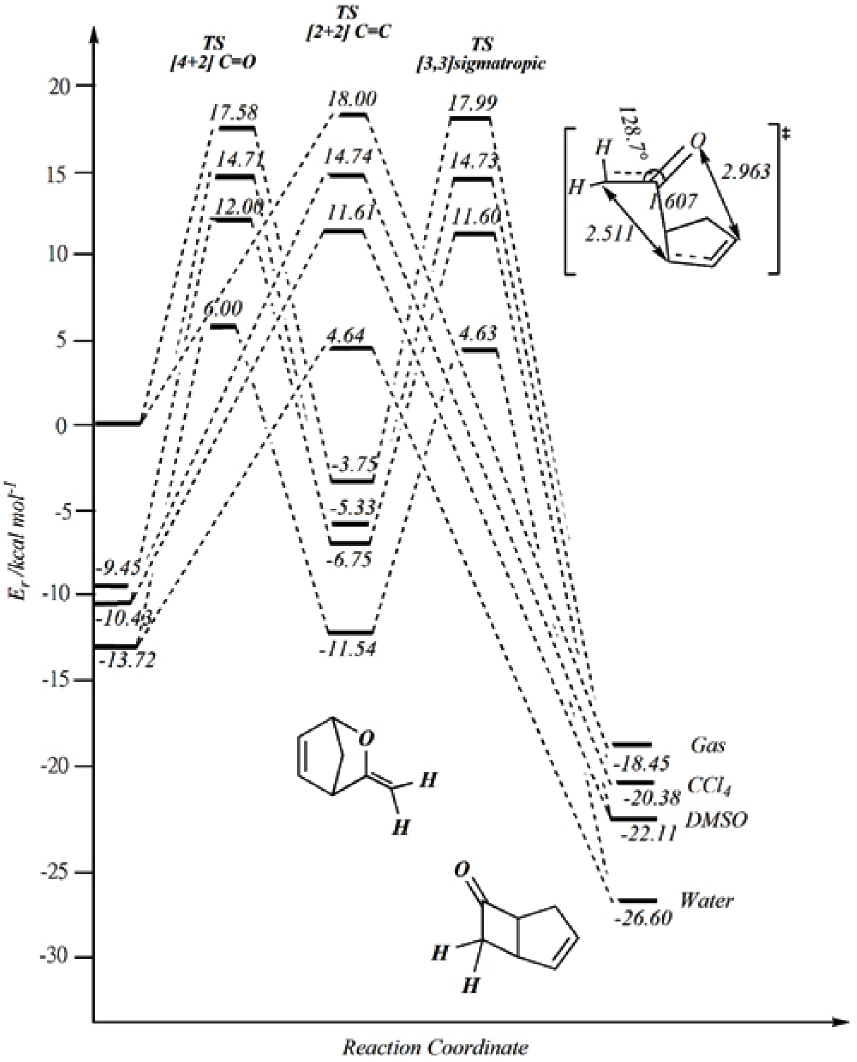

Fig. 5: Relative energies, kcal/mol; for the proposed [3,3] sigmatropic rearrangement of ketene and dihaloketenes with cp in the gas phase and solvents

by H_2O while all the exoergicities are reduced sharply by solvents (ΔE=-10.9, -11.7, and -12.9 kcal/mol for CCl_4, DMSO and H_2O, respectively). In other words, the preference of two-step cycloaddition is reduced in the presence of solvents.

Comparison to halogenated ketenes

Halogens, due to their electron withdrawing characters, considerably affect the thermodynamics and kinetics of these reactions in a way that they increase the exoergicity and reduce the energy barriers in the gas phase (Table 2).

On the other hand, solvent effects appear more pronounced and more divergent in halogenated ketenes compared to the parent ketene. As mentioned above, thermodynamic and kinetics of all the 4 mechanistic pathways of ketene are indigent in the presence of solvents. Similarly, for dihaloketenes all solvents make the thermodynamics less favorite by decreasing the exoergicity (within 1-5 kcal/mol). However, most of reaction pathways become kinetically favored by lowering the energy barriers (within 1-7 kcal/mol) in the presence of polar solvent, especially H_2O. This phenomenon may be

Table 2: The calculated energetics (total energy E and relative energy E_r/ kcal mol^{-1}) in the gas-phase and in different solvents for the cycloadditions of dihaloketenes with cp.

Phase	**Gas**		**DMSO**		**CCl_4**		**Water**	
Reaction mode	**E**	**Er**	**E**	**Er**	**E**	**Er**	**E**	**Er**
Diflouroketene + Cp	-342082.8	0	-342090.7	-7.86	-342089.8	-7.00	-342095.9	-13.05
TS[2+2] C=C	-342078.9	3.89	-342084.9	-2.07	-342082.0	0.83	-342091.0	-8.24
P[2+2] C=C	-342131.9	-49.07	-342136.2	-53.39	-342134.1	-51.33	-342140.9	-58.14
TS[2+2] C=O	-342076.1	6.74	-342085.0	-2.14	-342080.4	2.35	-342092.9	-10.06
P[2+2] C=O	-342106.3	-23.50	-342110.5	-27.67	-342108.5	-25.68	-342116.1	-33.34
TS[4+2] C=C	-342074.4	8.39	-342082.6	0.19	-342078.4	4.36	-342091.4	-8.57
P[4+2] C=C	-342136.6	-53.75	-342141.6	-58.76	-342139.2	-56.36	-342146.5	-63.65
TS[4+2]C=O	-342082.7	0.13	-342089.1	-6.27	-342086.0	-3.15	-342095.4	-12.57
P[4+2] C=O	-342109.4	-26.58	-342113.2	-30.36	-342111.4	-28.57	-342118.0	-35.23
Dichloroketene + Cp	-794339.0	0	-794346.6	-7.58	-794345.8	-6.83	-794349.6	-10.57
TS[2+2] C=C	-794329.3	9.72	-794336.2	2.76	-794332.8	6.21	-794343.3	-4.31
P[2+2] C=C	-794370.9	-31.88	-794374.9	-35.93	-794373.0	-33.95	-794380.1	-41.06
TS[2+2] C=O	-794324.5	14.49	-794333.7	5.32	-794329.0	10.01	-794342.4	-3.43
P[2+2] C=O	-794354.1	-15.10	-794358.3	-19.29	-794356.3	-17.27	-794363.7	-24.71
TS[4+2] C=C	-794320.0	19.03	-794326.9	12.10	-794323.4	15.59	-794333.4	5.64
P[4+2] C=C	-794373.1	-34.05	-794377.5	-38.54	-794375.4	-36.36	-794382.6	-43.61
TS[4+2] C=O	-794333.3	5.73	-794337.7	1.25	-794335.6	3.40	-794342.1	-3.07
P[4+2] C=O	-794355.8	-16.82	-794359.7	-20.67	-794357.8	-18.83	-794364.6	-25.63
Dibromoketene + Cp	-3444306.2	0	-3444313.9	-7.65	-3444313.1	-6.87	-3444316.9	-10.68
TS[2+2] C=C	-3444297.1	9.13	-3444303.8	2.45	-3444300.5	5.78	-3444311.1	-4.89
P[2+2] C=C	-3444345.1	-38.88	-3444349.1	-42.86	-3444347.2	-40.95	-3444354.1	-47.89
TS[2+2] C=O	-3444294.3	11.95	-3444303.6	2.63	-3444298.8	7.41	-3444313.0	-6.80
P[2+2] C=O	-3444323.6	-17.40	-3444327.7	-21.46	-3444325.8	-19.52	-3444333.0	-26.75
TS[4+2] C=C	-3444291.6	14.64	-3444298.9	7.34	-3444295.2	11.02	-3444306.6	-0.38
P[4+2] C=C	-3444347.4	-41.15	-3444351.8	-45.50	-3444349.7	-43.42	-3444356.8	-50.57
TS[4+2]C=O	-3444303.2	2.99	-3444308.1	-1.89	-3444305.8	0.46	-3444313.6	-7.38
P[4+2] C=O	-3444325.5	-19.29	-3444329.3	-23.05	-3444327.5	-21.26	-3444334.3	-28.07
[3,3] sigmatropic	-3444306.7	-0.43	-3444312.6	-6.33	-3444309.7	-3.43	-3444319.3	-13.08

Table 3: The B3LYP/6-31G(d,p) calculated energetic data for one-step and two-step [3,3] sigmatropic rearrangements of ketene and dihaloketenes with cp at four media

	ΔE/kcal mol^{-1}			
	Ketene	**Diflouroketene**	**Dichloroketene**	**Dibromoketene**
R→TS	18.0	3.9	9.7	9.1
	24.2	7.8	13.0	12.6
	22.0	5.8	10.3	10.0
	18.4	4.8	6.2	5.8
R→TS1	17.6	0.1	5.7	3.0
	24.1	3.8	10.2	7.33
	22.4	1.6	8.8	5.7
	19.7	0.5	7.5	3.3
R→Int	-3.7	-26.6	-16.8	-19.3
	4.1	-21.5	-12.0	-14.4
	3.7	-22.5	-13.1	-15.4
	2.2	-22.2	-15.0	-17.4
Int→TS2	21.7	18.1	20.5	19.7
	20.0	17.1	19.2	17.8
	18.3	15.9	18.0	16.7
	16.2	14.1	15.9	15.0
R→P	-18.4	-49.1	-31.9	-38.9
	-10.9	-44.3	-27.0	-34.1
	-16.7	-45.5	-28.3	-35.2
	-12.9	-15.5	-30.4	-37.2

valuable in the desired regioselectivity among four different cycloaddition pathways. The nonpolar solvent CCl_4 behaves like that of gas phase by destabilizing the TSs in halogenated ketenes, which is an indicative of the polar (but not zwitterionic) character of TS structures. Moreover, in contrast to the parent ketene, dihaloketenes strongly prefer the two-step pathways by lowering the first step energy barriers while increasing the energy barrier of one-step pathways (Table 3).

Interestingly, all solvents again reduce the preference of two-step pathways by destabilizing the corresponding intermediates and increasing the energy barriers concerning to the first step. This is in a way that for dichloroketene the single-step cycloaddition appears as the preferred path in H_2O, as solvent, like that observed for the parent ketene.

CONCLUSIONS

Dielse-Alder [4+2] and Staudinger [2+2] reactions between ketene and dihaloketenes with cyclopentadiene are studied in four different reaction pathways and four different media (gas phase, CCl_4, DMSO and H_2O) at B3LYP/6-31G* level. For the parent ketene, [2+2] across the C=C and [4+2] across the C=C bond of ketene are high exoergic *(*Δ*E*=-23.2 kcal/mol and -18.4 kcal/mol, respectively) while the two other pathways including [2+2] across the C=O and [4+2] across the C=O bond of ketene are somewhat endoergic. The activation barriers for these reaction modes change in the range of 17.5- 32.6 kcal/mol. Halogens substitution facilitates the cycloadditions by increasing the exoergicity and reducing the activation barriers. All cycloadditions take place *via* clear asynchronous TSs. For the parent ketene, all solvents stabilize the reactants by 9.4-13.7 kcal/mol and reduce the exoergicity (*e.g.* ΔE=-18.4, -10.9, -11.6 and -12.8 kcal/mol for gas phase, CCl_4, DMSO and H_2O, respectively, for [2+2] across C=C) and the energy barriers are increased to the maximum of 6.1 kcal/mol. In contrast, for dihaloketenes all solvents make the thermodynamics less favorite by decreasing the exoergicity (within 1-5 kcal/mol), however, most of reaction pathways become kinetically favored by lowering the energy barriers (within 1-7 kcal/mol) in the presence of polar solvents. The nonpolar solvent CCl_4 behaves like that of gas phase. Furthermore, the preference of two-step cycloaddition *via* the [3+3] sigmatropic rearrangement is reduced in the presence of solvents. Finally, for dichloroketene the routine single-step cycloaddition appears as the preferred pathway in H_2O like that observed for the parent ketene. Our findings denote the polar, but not zwitterionic, cycloadditions in this study.

ACKNOWLEDGEMENTS

The research supported by the Research Council of the Islamic Azad University Buinzahra Branch.

REFERENCES

.

1. Beaker, P.; Bittman, R.; Ciganek, E.; Curran, D.; Hegedus, L.; Joyce, R. M.; Kelly, R.C.; Ov.erman, L. E.; Paquette, L.A.; Press, J.B.; Poush, W.; Smith, A.B.; Uskokovic, M.; Wiley, J.D. Organic Reactions, , John Wiley and Sons, Inc., New York. **1994**, *45*
2. Tidwell, T.T. Ketenes, John Wiley and Sons, Inc., New York. **1995**,
3. Ulrich, H. Cycloaddition Reactions of Heterocumulenes, , Academic Press Inc., New York. **1967**
4. Holder, R.W.; Graf, N.A.; Duesler, E.; Moss, J.C. *J. Am. Chem. Soc.* **1983**, *105,* 2929-2931.
5. Schmittel, M.; Von Seggern, H. *J. Am. Chem. Soc.* **1993**, *115*, 2165-2177.
6. Yamabe, S.; Dai, T. *J. Am. Chem. Soc.* **1996**, *118*, 6518-6519.
7. Machiguchi, T.; Hasegawa, T.; Ishiwata, A.; Terashima, S.; Yamabe, S.; Minato, T. *J. Am. Chem. Soc.* **1999**, *121,* 4771-4786.
8. .Mayr, H.; Heigl, U.W. *J. Chem. Soc. Chem. Commun.* **1987**, 1804-1805.
9. Rubio, M.F.; Cruz, F.J.; Galicia, G. R. *J. Mex. Chem. Soc.* **2010**, *54*, 209-215.
10. Allen, A.D.; Tidwell, T.T. *Chem. Rev.* **2013**, *113,* 7287-7342.
11. Visser, P.; Zuhse, R.; Wong, M.W.; Wentrup, C. *J. Am. Chem. Soc.* **1996**, *118***,** 12598-12602.
12. Truong, T.N. *J. Phys. Chem. B* **1998**, *102*, 7877-7881.
13. Lim, D.; Jorgensen, W.L. *J. Phys. Chem.* **1996**,*100,* 17490-17500.
14. Arrieta, A. Lecea, B.; Cossio, F.P. *J. Org. Chem.* **1998**, *63*, 5869-5876.
15. Zhou, C.; Birney D.M. *J. Am. Chem. Soc.* **2002**, *124*, 5231-5241.
16. Sordo, J. A.; Gonzalez, J.; Sordo, T.L. *J. Am. Chem. Soc.* **1992**, *114*, 6249-6251.
17. Lopez, R.; Sordo, T.L.; A. Sordo, J.; Gonzalez, J. *J. Org. Chem.* **1993**, *58*, 7036-7037.
18. Musavi, S.M.; Amani, J.; Omidian, N. *Tetrahedron* **2014**, *70*, 708-719.
19. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-

Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. **2004**, Gaussian, Inc., Wallingford CT, Gaussian, Inc., Gaussian 03, Revision C.02, Wallingford CT.

20. Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648-5652.
21. Hariharan, P.C.; Pople, J.A. *Theor. Chim. Acta.* **1973***, 28,* 213-222.
22. Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523-5527.
23. Peng, C.; Ayala, P.Y.; Schlegel, H.B.; Frisch, M. J. *J. Comp. Chem.* **1996**, *17*, 49-56.
24. Weinhold, F.; Carpenter, J.E. The Natural Bond Orbital Lewis Structure Concept for Molecules, Radicals, and Radical Ions, in, Naaman R.; Vager Z. (eds.), The Structure of Small Molecules and Ions. Plenum, New York, **1988**, 227-236.
25. Miertus, S.; Scrocco, E.; Tomasi, J. *J. Chem. Phys.* **1981**, *55,* 117-129.
26. Fukui, K.; Yonezawa, T.; Shingu, H. *J. Chem. Phys.* **1952**, *20*, 722-725.