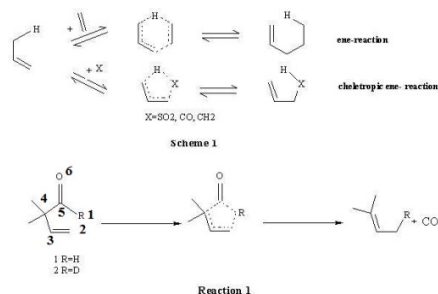


Kinetic isotope Effect on the Thermal Decomposition of DMB

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Three precyclic addition reactions i.e., the Diels-Alder reaction [1] including its 1,3-dipolar extensions [2], the cheletropic reaction [3] and the ene reaction [4] are well recognized and broadly used in their forward and reverse sense. A fourth reaction which can be considered to complete these kinds of reactions is the addition of a cheletropic reagent X to an ene (Scheme 1). Thermal decarboxylation of β -Ketoaldehydes [5] and, β,γ -unsaturated aldehydes [6] fall in this category. An example of the retro cheletropic reactions is the pyrolysis of 2,2-dimethyl but-3-enal (DMB) as described as Reaction 1. The experimental data show that the thermal decarboxylation of DMB and 1-d1-DMB are intermolecular, non-radical scavengable processes of highly reproducible rates. The molecular mechanisms involve the transfer of the aldehyde hydrogen and deuterium to γ -position. A complementary study with the aim of elucidating the molecular mechanism associated with these retro-cheletropic ene reactions is of importance in order to have a precise idea of the reactions pathways. The calculated kinetic parameters were obtained in characterizing the potential energy surfaces (PESs) to elucidate the nature of molecular mechanisms and investigation of kinetic isotope effects of the studied reactions. All calculations were performed using the Gaussian 03 computational package [7] with the ab initio and DFT methods. Optimized geometries of the stationary points on the PESs were obtained using the HF, MP2 and DFT calculations at the 6-31G(d) level. Vibrational frequencies for the points along the reactions paths were determined to provide an estimation of the zero point vibrational energies (ZPVEs). Activation parameters were also determined in the temperature ranges of pyrolysis reactions. The natural bond orbital (NBO) analysis of Reed and co-workers was used to determine the charge changes through the pyrolysis processes. Similar to our previous studies on the retro-ene reactions [8-11], theoretical studies of these kinds of the retro-cheletropic ene reactions show that the thermal decomposition occurs through a cyclic process. A five-membered ring with the R1-C2 bond formation and C4-C5 bond cleavage describes the TS for both reactions. Geometric parameters for the reactant and the TS were obtained. From these data one can

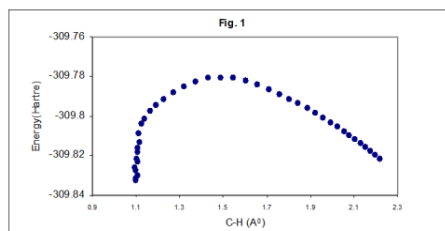


Fig.1. Reaction Path in IRC Calculations

understand that during the retro-cheletropic ene processes, when the reactants are transformed to the TSs, the R1-C5, C2-C3 and C4-C5 bond lengths increase, whereas the R1-C2, C5-O6 and C3-C4 bond lengths decrease. The B3LYP results for the reactions path is shown in Figure 1. Charge distribution at the TS shows that a small positive charge developed on R1 atom, while the C2 atom in the TS supports the electronic excess. The negative characters of C2 atom allow them to attract the positive characters in the TS. Thus the C2 atom increases their negative character, which supports the postulated cyclic transition state. There is one imaginary vibrational frequency in the TS for the studied reaction. The nearly high imaginary frequency at the three levels of the theory shows that this point is associated with the light atom movement of R1 in the TS. The activation parameters for the reaction 1 calculated at 563.15 K are shown in Table 1. These results are compared with the experimental values. The magnitude of the calculated kinetic isotope effects for the reaction 1 is 3.8, which indicates that the hydrogen is transferred extensively in the TS. Our results are similar to the other well-established precyclic reactions, which confirm the concertedness of the retro-cheletropic ene reaction. Finally, the calculated negative value of the activation entropy indicates that the reaction involves a cyclic TS.

Table 1. Calculated and experimental kinetic and activation parameters

Parameter	RHF	MP2	B3LYP	Experimental
Ea (kcal mol ⁻¹)	58.05	37.61	35.99	41.25/44.2
Log A	13.4	13.09	13.10	12.38/132.40
ΔH^\ddagger (kcal mol ⁻¹)	56.94	36.49	34.89	-----/43.1
ΔG^\ddagger (kcal mol ⁻¹)	57.38	37.74	36.07	-----/-----
ΔS^\ddagger (cal mol ⁻¹ K ⁻¹)	-0.79	-2.21	-2.13	-----/2.0

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Effect of two ionic liquids on the structure of adenosine deaminase enzyme

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In this study, effect of two ionic liquids of 1-allyl 3-methylimidazolium [amim]Cl, (allyl) and 3-methyl-3-octylimidazolium chlorides, [omim]Cl, (octhyl) in various concentrations on the adenosine deaminase enzyme (ADA) was investigated by molecular dynamics simulations. At first step, the structures of ionic liquids were drawn using (Hyperchem 7 software) and optimized with the semi-empirical AM1 method. Then 5, 10, 15 and 20% concentrations of the ionic liquids were prepared and inserted into a box of $7 \times 7 \times 7$ nm³. Protein and water molecules were randomly added into the simulation box and the system was equilibrated for 20000 ps at constant pressure (1 atm) and temperature (300 K). After simulation, we surveyed changes of protein area (SAS), Radius gyration (Rg), Radial Distribution Function (RDF), Root Mean Square Deviation (RMSD) and Hydrogen bonds (Hbond) around the protein, solvent and ionic liquid in various concentrations. By studying the changes in protein surface area, it was observed that the surface area is increased by increasing concentration. The same trend is observed in the radius gyration analyses. It was also observed from hydrogen bond analyses that the number of hydrogen bond between solvent and protein is decreased by increasing concentration of ionic liquids. In RDF diagrams, we have increasing trend for solvent-ligand and decreasing trend for ligand-ligand and ligand-protein by increasing concentration. Totally in these diagrams, RDF value for octhyl is more than allyl, which represent more interaction of octhyl than allyl. Reaching the system to equilibrium is observed from constant curves of RMSD diagrams. In conclusion octhyl interaction is more than the allyl which is proved in above result.

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Complexation of dimethyltin(IV) dichloride with tryptophan

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Organotin(IV) compounds have long been characterized to exhibit relatively high antitumour activity. The structures adopted by di- and trialkyltin(IV) ions in aqueous solutions appear to have linear C-Sn-C and planar skeletons, respectively. Information pertaining to the structure and behavior of these ions in solution at different pH has been the subject of many recent papers.¹⁻³ These ions have rather unusual effects on the structure in water as solvent. There should be particularly pronounced ordering of water molecules in the equatorial plane of the dialkyltin(IV) ions because of the strong electrostatic field near the tin atom. In addition, the hydrophobic nature of the alkyl groups will tend to force more hydrogen bonding in the solvent around the axial positions. All measurements were carried out at 25 °C. The ionic strength was maintained to 0.1 mol dm⁻³ with sodium perchlorate. The pH-meter was calibrated for the relevant H⁺ concentration with a solution of 0.01 mol dm⁻³ perchloric acid containing 0.09 mol dm⁻³ sodium perchlorate (for adjusting the ionic strength to 0.1 mol dm⁻³).

For this standard solution, we set $-\log[H^+] = 2.00$. Junction potential corrections calculated from eq 1

$$-\log[H^+]_{\text{real}} = -\log[H^+]_{\text{measured}} + a + b[H^+]_{\text{measured}}$$

a and b were determined by measuring of hydrogen ion concentration for two different solution of HClO₄ with sufficient NaClO₄ to adjust the ionic media. In all cases, the procedure was repeated at least three times and the resulting average values and corresponding deviations from the average are shown in the text and Tables. Using a combination of spectrophotometric and potentiometric methods different models including ML and MHL and several polynuclear and protonated species were tested by the computer program. As expected, polynuclear complexes were systematically rejected by the program, as also were MH₂L₂, MHL₂, and ML₂, (the charges were omitted for simplicity). A value for the MH₂L species was also calculated by the program, but the species was not considered further, because the estimated error in its formation constant was unacceptable, and its inclusion does not improve the goodness of the fit. The models finally chosen, formed by MHL and ML for the ligands, besides the hydrolysis products of Me₂Sn(IV)²⁺ resulted in a satisfactory of numerical and graphical fitting.

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