DFT Calculations on retro-ene reactions Part I: allyl *n*-butyl sulfide pyrolysis in the gas phase

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The mechanism and kinetic aspects of the retro-ene reaction of allyl *n*-butyl sulfide and its deuterated derivative were studied using four different types of density functional theory (DFT) methods with eight different levels of the basis sets. Vibrational frequency analysis confirmed that the stationary points include the transition state (TS) structure with only one imaginary frequency. Mechanistic studies on the retro-ene process rejected the step-wise mechanism and confirmed that the reaction proceeds through a six-centered cyclic transition state. Theoretical calculations show that propene elimination from the reactant can occur through an asynchronous concerted mechanism. A primary kinetic isotope effect of 2.21 for the reaction can be determined. Theoretical kinetics and activation energies especially at the B3LYP/6-31G* levels are in good agreement with the experimental values.

Keywords: allyl *n*-butyl sulfide, retro-ene reaction, asynchronous concerted mechanism, DFT calculations

Introduction

Among the great variety of ways of formation and chemical transformations of organic compounds of divalent sulfur, thermal reactions have a special place for the following reasons:[1] the utilisation of the sulfur containing wastes in oil-refining gas-coal and pulp-processing industries; the development of thermal methods for synthesis of organosulfur compounds which are difficult to obtain alternatively; the generation of labile sulfur containing intermediates, using the flash pyrolysis technique; and mechanistic studies.

The most important molecular mechanisms that are involved in the gas phase pyrolysis of organosulfur compounds include radical and concerted mechanisms. The kind of molecular mechanism depends on some different factors. The most important factors are: temperature, S-containing bond strength, electron donating and electron with- drawing properties of the substituents and interamolecular parameters. Many experimental and theoretical investigations have been carried out to determine the kinetics and mechanism of organosulfur compounds pyrolysis in both the gas and liquid phases.[2-8]

Faragher and co-workers[9] studied thermal decomposition of dialkyl sulfides in the gas phase at 400–800 °C. They proposed that the corresponding alkenes were produced by a free radical mechanism (Scheme 1).

Martin *et al*. studied the gas phase thermolysis of alkyl and cycloalkyl allyl sulfides at 400-500 °C.[10] A molecular rearrangement (retro-ene reaction), involving either a four or a six-membered cyclic TS, has been suggested.

Gas phase pyrolysis reactions of allyl *n*-butyl sulfide (ABS) and its deuterated derivative have been experimentally studied at temperatures between 262 and 293 °C.[11,12] According to Scheme 2, this reaction obeys a first order rate law and the elimination products are propene and *n*-butyl thioaldehyde.

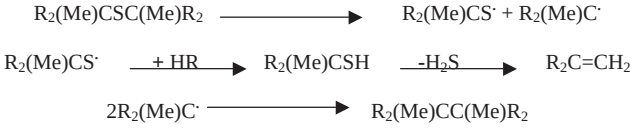
The experimentally obtained rate coefficients for the ABS and 1-d_1-ABS have been reported to fit the Eqns (1) and (2), respectively.

$$k_H(s^{-1}) = 10^{11.42 \pm 0.28} \exp[(-155 \pm 3)\ \text{kJ mol}^{-1}/RT] \quad (1)$$

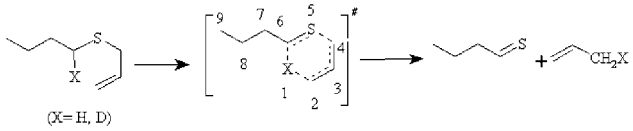
$$(k_H/k_D) = 2.6 \pm 0.2\ (T = 281\ ^\circ\text{C}) \quad (2)$$

The experimental results are interpreted in terms of a non-radical molecular mechanism involving a six-centre cyclic concerted TS. These unimolecular reactions proceed through hydrogen or deuterium transfer to the γ-position (Scheme 2).

The objective of this study is to provide a theoretical prediction of the kinetic and activation parameters. It is also important to elucidate the molecular mechanism associated with this retro-ene reaction in order to clarify the reaction pathway. Another aim of this survey is to obtain a more complete understanding of the performance of the DFT methods in the kinetic and mechanistic studies of organic reactions.



Scheme 1



Scheme 2

Computational details

The structures corresponding to the reactant, transition state and products for the studied reaction were optimised using the Gaussian 98 computational package[13] with DFT methods. Optimised geometries of the stationary points on the potential energy surface (PES) were obtained using Becke's-three parameter hybrid exchange functional with the correlation functional of Lee-Yang-Parr (B3LYP),[14,15] the Becke and the correlation functional of Lee-Yang-Parr (BLYP), the Becke's-three parameter hybrid exchange functional with the Perdew 86 (B3P86)[16] and the Becke's-three parameter hybrid functional with the Perdew-Wang 91 (B3PW 91).[17] Basis sets were 6-31G*, 6-31G**, 6-31+G**, 6-31++G**, 6-311G*, 6-311G**, 6-311+G** and 6-311++G**.[18]

The corresponding TSs were calculated using the synchronous transit-guided quasi-Newton (STQN) method as implemented by Schlegel *et al.*[19] The IRC method[20] was also used to check the profiles connecting the TSs to the two associated minima of the proposed mechanism.

Vibrational frequencies for the points along with the reaction paths were determined to provide an estimation of the zero point vibrational energy (ZPVE). These calculations confirmed the nature of the stationary points as minima with the real frequencies and the TS with only one imaginary frequency.

Thermodynamic parameters (ΔH, ΔS, ΔG) for the reaction were calculated from the B3LYP/6-31G* data at 298.15K. Kinetic and activation parameters were also evaluated in the

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temperature ranges of the pyrolysis reaction. Activation energy, E_a, and Arrhenius factor were computed using the Eqns (3) and (4), respectively.[21]

$$E_a = \Delta H^{\neq}(T) + RT \quad (3)$$

$$A = (eK_B T/h) \exp(\Delta S^{\neq}(T)/R) \quad (4)$$

The natural bond orbital (NBO) analysis, suggested by Reed *et al.*,[22,23] was applied to determine the charges at the stationary points through the pyrolysis reaction.

Results and discussion

Propene and its deuterium-labelled elimination from the ABS and 1-d1-ABS may occur through the two probable mechanisms. The first one may be started by the cleavage of the C4–S5 bond (for atom numbering see Scheme 2), followed by a step-wise mechanism.

The second possibility is the interamolecular transfer of an X-atom to an unsaturated center via a six-centred cyclic TS, yielding propene and 3-d1-propene and *n*-butyl thioaldehyde. This can proceed through X1–C2 bond formation and C4–S5 bond cleavage.

The C4–S5 bond breaking is the rate-determining step in the former mechanism. Bond dissociation energy of the C4–S5 bond would be the main activation barrier of this process from the energy point of view (Scheme 3).

It has been reported that the unrestricted B3LYP remains fairly parallel to full configuration interaction potential energy curves for breaking bonds.[24] Therefore, the energies of the probable radicals were calculated after full geometry optimisation at the UB3LYP level of the theory using the 6-311++G** basis set. The results are shown in Table 1. It is obvious that the calculated activation energy is 306.00 kJ mol^{-1} for the ABS pyrolysis. The calculated activation energy is much greater than the experimental one; hence the radical mechanism is rejected. Therefore, the concerted mechanism was fully investigated.

During the reaction, the X1–C2, C3–C4 and S5–C6 bond lengths are decreased, while the X1–C6, C4–S5 and C2–C3 bond lengths are increased.

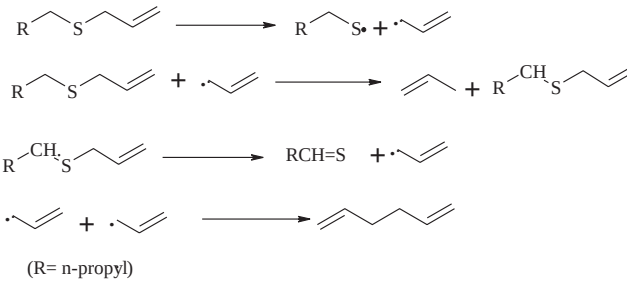
Geometric parameters for the reactant and the TS are reported in Table 2. Comparison between the H1–C2 and C4–S5 bond lengths in the TS with the same one in the reactant indicates that the H1–C2 bond formation occurs faster than the C4–S5 bond splitting. Therefore the new bond formation occurs by a slightly asynchronous mechanism in the concerted reaction.

The B3PW91/6-31G* results for the reaction path are shown in Fig. 1. This figure demonstrates the energy as a function of the reaction coordinate (H1–C2 bond length) and represents the minimum energy path, which connects the reactant to the products passing through the saddle point.

Table 1 Calculated total energies in Hartree for some probable radicals at the UB3LYP/6-311++G** level (T = 550.65K).

C_3H_5	C_3H_5S	C_4H_9	C_4H_9S
–117.266	–515.504	–157.828	–556.070

Total energy for the ABS in the ground state is –673.453 Hartree.



Scheme 3

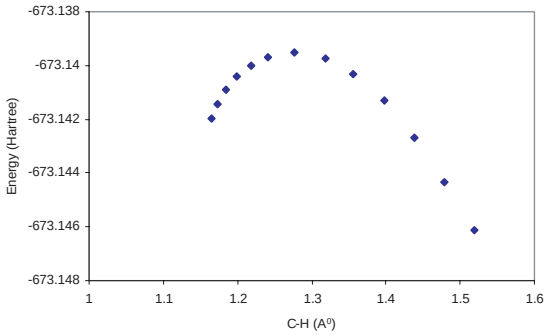


Fig. 1 Schematic energy profile of the PES for the ABS pyrolysis (X=H) at the B3PW91/6-31G* level.

Table 3 shows the charge distribution of the reactant and the TS in the gas phase using NBO analysis. Calculated values for the TSs indicate that a small positive charge developed on the H1 atom, while the C2 atom supported the electronic excess. The positive character of the H1 atom allows it to be attracted by the negative character of C2 atom. On the other hand the positive characters of the C3 and C4 atoms demonstrate that the H1–C2 bond formation is faster than the C4–S5 bond cleavage for the retro-ene reaction.

Imaginary vibrational frequencies for the TS were also obtained. High magnitudes of these frequencies show that these points are associated with the light atom movement of H1 in the TSs. It is obvious that the different basis sets in all methods do not show a proper effect on the obtained imaginary frequencies. The BLYP results are greater than other methods. Therefore, it can be concluded that the three-parameter hybrid functional of Becke has a major effect on the geometric parameters for the TS and calculated imaginary frequencies. Also dipole moments changes through the retro-ene reactions justify the greater polarity of the TS compared to the reactant, and it confirmed the cyclic structures for the TS.

Thermodynamic properties for the reaction using the B3LYP/6-31G* level of the theory are reported in Table 4. Calculated values show that the pyrolysis reaction is an endothermic process, the global process is spontaneous and the entropy change through the reaction is positive (ΔH>0, ΔG<0, ΔS>0).

Table 2 Main geometric parameters for allyl *n*-butyl sulfide (R) and the TS in the gas phase, using the 6-31G* basis set (distances in angstrom and dihedrals in degrees)

	B3LYP	BLYP	B3PW91	B3P86
Parameters	R/TS	R/TS	R/TS	R/TS
H1–C2	2.99/1.17	3.04/1.33	2.97/1.28	2.92/1.27
C2–C3	1.33/1.43	1.34/1.43	1.33/1.42	1.33/1.42
C3–C4	1.51/1.44	1.52/1.39	1.51/1.38	1.50/1.38
C4–S5	1.83/2.87	1.86/2.43	1.82/2.32	1.82/2.32
S5–C6	1.84/1.69	1.86/1.73	1.83/1.69	1.82/1.69
C6–C7	1.53/1.54	1.54/1.53	1.53/1.51	1.52/1.51
C7–C8	1.54/1.53	1.54/1.54	1.53/1.53	1.53/1.53
C8–C9	1.53/1.54	1.55/1.55	1.53/1.53	1.52/1.52
H1–C2–C3	80.41/101.75	80.15/99.27	80.09/99.56	80.71/99.71
C2–C3–C4	127.29/120.02	127.44/119.98	127.00/119.19	126.80/119.08
C3–C4–S5	117.62/95.32	117.77/97.69	117.44/98.30	117.24/98.31
C4–S5–C6	100.31/106.89	100.32/99.56	100.25/101.11	100.06/101.02
H1–C2–C3–C4	–50.82/53.23	–50.96/-63.27	–51.24/-62.35	–51.14/-62.43
C3–C4–S5–C6	73.56/-142.46	73.85/-43.64	73.68/-47.10	73.05/-47.68

Table 3 Distributed NBO charges on the ABS and the TS at the B3LYP/6-31++G** level

	H1	C2	C3	C4	S5	C6	C7
ABS	0.24	–0.44	–0.23	–0.62	0.19	–0.58	–0.46
TS	0.27	–0.73	0.01	–0.51	–0.20	–0.41	–0.45

Table 4 Thermodynamic parameters for the reaction using the B3LYP/6-31G* method (X=H)

ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	ΔG (kJ mol^{-1})
24.68	167.64	–25.30

Table 5 Calculated kinetic and activation parameters for the pyrolysis of ABS at 550.65 K, using the B3P86/B3PW91 methods (X=H, E_a, $\Delta H^{\neq}$ in kJ mol^{-1} and $\Delta S^{\neq}$ in J mol^{-1}K^{-1})

Basis set	E_a	$\Delta H^{\neq}$	Log A	$-\Delta S^{\neq}$
6-31G*	150.53/152.45	145.95/147.87	12.03/11.93	19.66/21.70
6-31G**	148.79/150.60	144.21/146.02	12.11/12.03	18.27/19.77
6-31+G**	149.44/150.15	144.86/145.57	12.04/11.95	19.51/21.16
6-31++G**	149.38/151.33	144.80/146.75	12.05/11.95	19.38/21.17
6-311G*	150.23/152.14	145.65/147.56	12.19/12.14	16.56/17.71
6-311G**	148.31/150.08	143.73/145.50	12.20/12.14	16.47/17.64
6-311+G*	148.64/151.17	144.06/146.59	12.17/12.11	17.00/18.25
6-311++G*	148.67/150.44	144.09/145.86	12.18/12.11	16.93/18.20

Experimental values for the ABS pyrolysis reaction taken from ref. 12: E_a =152.6 ± 0.7 kJ mol^{-1}, log A = 11.16 ± 0.06 and ref. 11: E_a =155 ± 3 kJ mol^{-1}, log A = 11.42 ± 0.28 (R=H).

Table 6 Calculated kinetic and activation parameters for the pyrolysis of ABS at 550.65 K using the BLYP/B3LYP methods, respectively (X=H, E_a, $\Delta H^{\neq}$ in kJ mol^{-1} and $\Delta S^{\neq}$ in J mol^{-1}K^{-1})

Basis set	E_a	$\Delta H^{\neq}$	Log A	$-\Delta S^{\neq}$
6-31G*	126.77/155.19	122.19/150.61	12.24/12.21	15.76/16.32
6-31G**	125.00/153.45	120.42/148.88	11.66/12.18	26.77/16.92
6-31+G**	126.27/154.54	121.69/149.96	11.87/12.15	22.87/17.44
6-31++G**	126.11/154.43	121.53/149.85	11.87/12.16	22.70/17.32
6-311G*	127.27/154.69	122.69/150.12	12.16/12.12	17.23/18.02
6-311G**	124.88/152.74	120.30/148.16	12.17/12.13	17.01/17.89
6-311+G**	125.71/153.61	121.13/149.03	12.14/12.21	17.61/16.30
6-311++G**	125.75/153.63	121.17/149.05	12.14/12.21	17.56/16.23

Experimental values for the ABS pyrolysis reaction taken from ref. 12: E_a =152.6 ± 0.7 kJ mol^{-1}, log A = 11.16 ± 0.06 and ref. 11: E_a =155 ± 3 kJ mol^{-1}, log A = 11.42 ± 0.28 (R=H).

Calculated kinetic and activation parameters for the reaction at 550.65K are listed in Tables 5 and 6, using eqns (3) and (4).

We can conclude that the B3LYP and B3PW91 results are the best ones from the activation energy point of view. If the calculation time is included, the best DFT method for calculation of the activation energy will be the B3LYP/6-31G* method. This is in accordance with the previous studies.[2-5,25] The BLYP results differ extensively from the other DFT methods. It can be interpreted by the effects of the three-parameter hybrid functional of Becke on the calculated energies, which arise from the TS geometry optimisation.

A value of 156.77 kJ.mol^{-1} for deuterium derivative of the ABS pyrolysis is calculated at the B3LYP/6-31++G** level. A calculated kinetic deuterium isotope effect of 2.21 at 550.65K indicates that the reaction displays a primary kinetic isotope effect. These values for activation energy and kinetic isotope effect justify the proposal that hydrogen and deuterium are transformed extensively in the TS.

For some organic compounds such as acetates[26] and isopropyl carbonate[27] which decompose thermally and proceed through the six-centred cyclic TS, the deuterium kinetic isotope effect posses a value of 2.7±0.2 at 554.15K and 2.6 at 673.15K, respectively. The value of 2.21 in this study can be another reason for hydrogen migration in the TS and confirmed the proposed molecular mechanism.

The calculated activation energy is also low in comparison with the expected value for the pyrolysis of All$SC_3H_6CH_2$–H (E_a=155 kJ mol^{-1} for the ABS pyrolysis, bond dissociation energy is, however, 464 kJ mol^{-1}) suggesting that the reaction is concerted.

The negative calculated activation entropies show that ABS pyrolysis proceeds through a concerted cyclic TS, which has been confirmed experimentally.[11,12]

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