



## A joint experimental and theoretical study of kinetic and mechanism of rearrangement of allyl *p*-tolyl ether

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### ABSTRACT

A joint theoretical and experimental study of the kinetic and mechanism of the rearrangement of allyl *p*-tolyl ether was performed in order to study the kinetic and mechanism of the reaction. Experimental studies were performed in gas phase over a temperature range of 493.15–533.15 K. The experimental Arrhenius parameters of this reaction were measured to be  $E_a = 36.08 \text{ kcal mol}^{-1}$ ,  $\Delta S^\ddagger = -7.88 \text{ cal mol}^{-1} \text{ K}^{-1}$ , and  $\text{Log } A = 11.74$ , experimentally. Using GC for the mixture of the reaction with and without cyclohexene demonstrated that the reaction is clean without any radical intermediates. The experimental results show that the studied reaction is unimolecular and proceeds through a concerted pathway. Theoretical calculation were performed at RHF and B3LYP levels of theory using 6-31G<sup>+</sup>, 6-31++G<sup>\*\*</sup> and 6-311G<sup>+</sup> basis sets. These calculations showed that the reaction proceeds through an asynchronous concerted mechanism. The calculated kinetics parameters especially at B3LYP/6-31G<sup>+</sup> level of theory are in good agreement with the experimental data. Also polarizable continuum model was used to study solvent effect on the reaction rate. These calculations indicated that the rate enhancement of the reaction in polar and protic solvents arise from specific solute–solvent interactions such as hydrogen bonding and the hydrophobic effects of solvent.

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### 1. Introduction

A typical organic reaction proceeds in a special mechanism. There may be many proposed mechanisms for a typical organic reaction. Experimental methods have many instrumental limitations such as trapping the intermediates or transition states (TSs) in confirming the mechanism that reactions proceed from it. Computational methods can make confirming the mechanism easier, cheaper and exacter. For example, the gas phase kinetics and mechanism of two retro-cheletropic ene reactions were studied by computational methods, therefore the stepwise mechanism was rejected and the concerted mechanism was fully investigated [1].

We solved such an example in order to confirm and detailed study of the rearrangement mechanism of allyl *p*-tolyl ether (Scheme 1). The rearrangement of allyl *p*-tolyl ether may proceed in two different mechanisms: (i) a concerted mechanism in which the transition state forms in one step (Claisen rearrangement) and (ii) a stepwise mechanism, involving forming a radical as the intermediate. The first one is one of the pericyclic mechanisms. Pericyclic

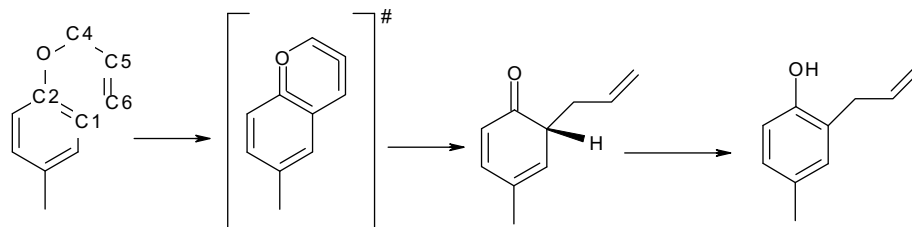
reactions have relatively nonpolar TSs with considerable cyclic delocalization referred to as aromatic character [2].

Substituent effect on the rate of Claisen rearrangement (Scheme 2) has extensively been investigated experimentally [3–5]. The origins of rate acceleration for this process were studied in order to show the dipolar character in the TS. However, the degree of charge separation in the TS has been debated [4–7]. It is proposed that electron donor groups at C1 and C2 accelerate the rearrangement. The methoxy groups as a substituent have a dual effect, the one at C4 and C6 accelerate the reaction while the one at C5 decelerates the reaction [6]. The majority of these studies were carried out in condensed phases [7], in which the solvent–solute interactions are strong. In order to study the mechanism of the reaction without such solvent interaction, the gas phase Claisen rearrangement of allyl *p*-tolyl ether was studied.

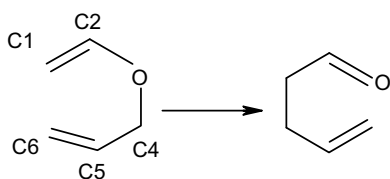
### 2. Experimental

Allyl *p*-tolyl ether was synthesized according to the literature [8,9]. The reactant was purified in the column of silica gel Merck 7733 as stationary phase and dichloromethane as mobile phase. Because the kinetic study was performed based on the phenoxide anion, the 2-allyl-4-methylphenol was synthesized and purified according to the literature [9]. Cyclohexene was synthesized

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Scheme 1. Claisen rearrangement of allyl *p*-tolyl ether.



Scheme 2. Typical Claisen rearrangement.

according to the literature [10] to be applied as a free radical inhibitor in the gas phase. The structures of allyl *p*-tolyl ether, 2-allyl-4-methylphenol and cyclohexene were confirmed by NMR spectrum that was obtained on the Bruker 500-Ultrashield instrument.

The rearrangement experiments were carried out in a vacuum vessel with a pressure of 1 mmHg. A gas chromatography oven with high insulation (stability  $\pm 0.2$  °C) was used to supply a constant temperature for the vessel of reaction at the desired conditions.

Kinetic measurements were done using UV–visible spectrophotometer. In this regard the reaction mixture was quenched after a while of initiation of the reaction (each run as independent run from beginning). Then a constant amount of petroleum ether was poured into the vessel to dissolve any obtained product or existing reactant. The solution was extracted with NaOH 10% for three times to convert the phenolic product of the reaction (see Scheme 1) to its phenoxide and transfer it to aqueous phase. This converted compound has a strong absorption in UV–visible spectra at 239 nm. So in this method the concentration of phenoxide or its equivalent product of the reaction was obtained as per usual absorption methods versus calibration curve of the sample.

The process mentioned above was repeated at a constant temperature and the reaction mixture was quenched at different times to determine the progress and therefore the rate of the reaction. Also to obtain Arrhenius parameters of the reaction, different temperatures were selected and the above-described method was repeated to determine the rate constant of the reaction for each temperature.

### 3. Computational details

The structures corresponding to the reactant, TS, intermediate and product were optimized, using the Gaussian 98 computational package [11] with *ab initio* and DFT methods. Optimized geometries of the stationary points on the potential energy surfaces were performed using Becke's three-parameter hybrid exchange functional with the correlation functional of Lee, Yang and Parr (B3LYP) [12,13] with the 6-31G\* [14,15], 6-31++G\*\* [14,15] and 6-311G\* [16,17] basis sets. The synchronous transit guided quasi-Newton (STQN) method [18] was used to locate the TS. The intrinsic reaction coordinate (IRC) method [13] was also applied in order to check and obtain the profiles connecting the TS to the two associated minima of the proposed mechanism. The natural bond orbital (NBO) analysis [19,20] was applied to determine the charge

changes occurring in the studied process. To take the solvent into account, some calculations were done using the polarizable continuum model (PCM) [21], specifically the integral equation formalism model, further referenced as IEFPCM.

The activation energies,  $E_a$  and the Arrhenius factors were computed using Eqs. (1) and (2), respectively, which were derived from the transition state theory [22,23]

$$E_a = \Delta H^\ddagger(T) + RT \quad (1)$$

$$A = (eK_B T/h) \exp(\Delta S^\ddagger(T)/R) \quad (2)$$

## 4. Results and discussion

### 4.1. Experimental results

The rate of Claisen rearrangement of allyl *p*-tolyl ether was determined in the temperature range of 493.15–533.15 K. Fig. 1 shows  $\ln k$  versus  $1/T$ ; a least square fit of the rate coefficients in the form of the Arrhenius equation produced the following relationship:

$$\ln k = 27.04 - (36.08 \pm 2)(\text{kcal mol}^{-1})/RT$$

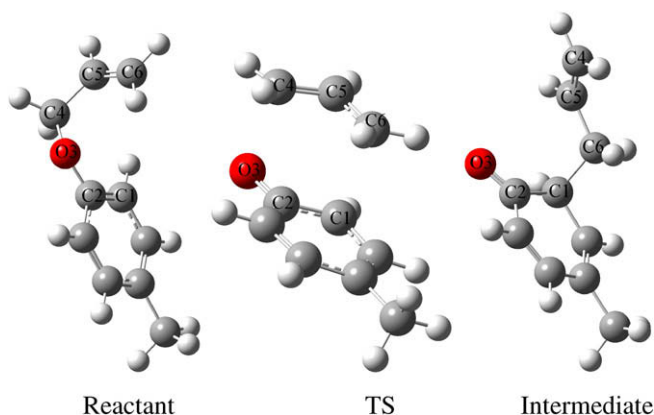
Also according to relation between Arrhenius and Eyring parameters,  $E_a$ ,  $\log A$ ,  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  of the reaction will be 36.08 cal mol<sup>-1</sup>, 11.74, 35.06 kcal mol<sup>-1</sup> and  $-7.88$  cal mol<sup>-1</sup> K<sup>-1</sup>, respectively (see Table 3).

To study the probability of existence of a radical mechanism for the reaction, the rate constant also had determined in presence of cyclohexene which acts as radical scavenger [24]. The results do not show any considerable changes in the rate of reaction to assign a radical mechanism for the reaction. On the other hand, a sample gas chromatography analysis of the reaction mixture shows only two peaks that belong to the reactant and product of reaction. These results and the obtained activated kinetic parameters suggest a tight activated complex with six-member cycle similar to the allyl vinyl ether claisen rearrangement [3,7,25–28]. Thus, the reaction proceeds through a non-radically concerted mechanism which was the reason to follow theoretical aspects of the reaction.

### 4.2. Theoretical results

Scheme 3 shows the optimized structures of reactants, TS, and intermediate with the selected geometrical parameters at the B3LYP/6-31G\* shown in Table 1.

The concerted mechanism is initiated with the O3–C4 bond cleavage and C6–C1 bond formation. According to Table 1 the transition structure of the allyl *p*-tolyl ether has a breaking O3–C4 bond distance of 2.12 angstrom and a forming C6–C1 bond distance of 2.2 angstrom. The Pauling relation [28] was used to determine the related partial bond orders and the values of 0.069 and 0.085 were obtained, respectively. The obtained partial bond orders indicate that 93.1% of etheric O3–C4 bond is broken, whereas C6–C1 bond has only 8.5% reaching to the transition state. The extent of



**Scheme 3.** The reactant, TS and the intermediate for the studied reaction.

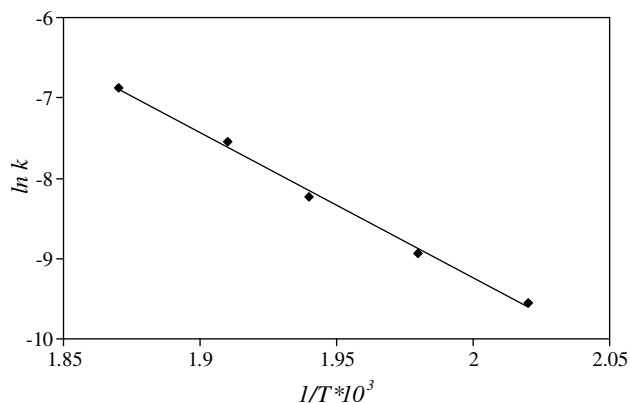
**Table 1**

Key geometrical parameters of the reactant, TS and intermediate at the B3LYP/6-31G<sup>\*</sup> level of theory (the numbering of atoms is like that in Scheme 3 and also distances in angstrom).

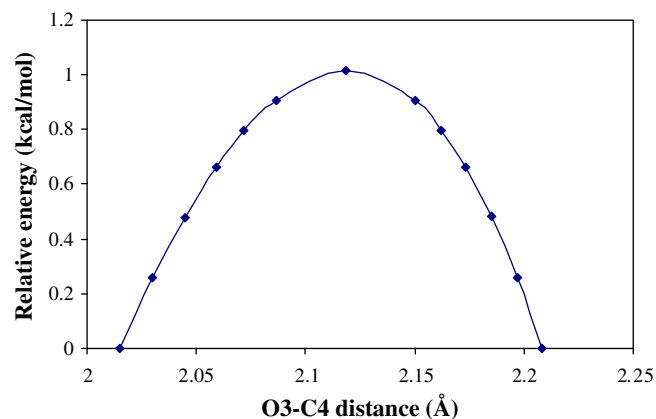
	Reactant	TS	Intermediate
C1–C2	1.397	1.446	1.532
C2–O3	1.373	1.277	1.225
O3–C4	1.421	2.118	–
C4–C5	1.507	1.382	1.333
C5–C6	1.332	1.399	1.503
C6–C1	–	2.202	1.571

broken and formed bonds in transition state shows that an asynchronous concerted mechanism had occurred for the allyl *p*-tolyl ether rearrangement. As a result the carbonyl group was formed which has an important role in accelerating the reaction in hydrogen bond donor solvents observed with alcohol and water solvents [8]. B3LYP/6-31G<sup>\*</sup> results for the reaction paths are shown in Fig 2. This figure demonstrates the energy as a function of the reaction coordinate, O3–C4, and represents the minimum energy paths which connect the reactant to the intermediate through the saddle points.

Table 2 shows the charge distribution in the reactant, TS and the charge difference between TS and reactant ( $\Delta$ charge) by means of NBO analysis. The results at the TS indicate that a small negative charge developed on O3 and C4 atoms which demonstrate that the O3–C4 bond cleavage is faster than C6–C1 bond formation. The charge difference shows that electron donor groups at C1, C2



**Fig. 1.** Temperature dependency for the rate constant of the gas phase Claisen rearrangement of allyl *p*-tolyl ether.



**Fig. 2.** Schematic energy profile of the potential energy surface for the studied reaction at B3LYP/6-31G level of theory.

**Table 2**

Distributed NBO charges on the reactant and TS at the B3LYP/6-31G<sup>\*</sup> level of theory (the numbering of atoms is like that in Scheme 3).

	C1	C2	O3	C4	C5	C6
Reactant	–0.3085	0.3081	–0.5337	–0.2653	–0.1287	–0.4229
TS	–0.2937	0.3878	–0.5647	–0.3145	–0.2712	–0.3654
$\Delta$ charge	–0.0148	–0.0797	0.031	0.0492	0.1425	–0.0575

and C6 accelerate the reaction. However, at C5 position opposite result is observed, which is in accordance with the experimental results for allyl ether Claisen rearrangement [6]. The same substituent effect can be concluded in gas and solution phases for these types of reactions. It is obvious that the strength of the hydrogen bonding is sensitive to a small shift in charge [29], therefore charge difference on O3 shows that hydrogen bond donor solvents stabilize the TS of the reaction more than the reactant, and therefore the reaction rate should increase with the presence of hydrogen bond donor solvent which has previously been reported with alcohols and water solvents [8].

In addition, calculated kinetic and activation parameters for the reaction at 513.15 K are listed in Table 3. From Table 3,  $E_a$  obtained from B3LYP/6-31G<sup>\*</sup> is in good agreement with experimental value. Therefore, we concluded that the studied reaction in the gas phase is a clean unimolecular reaction with a six-member cyclic activated complex. Also this reaction proceeds through an asynchronous concerted mechanism which is similar to allyl vinyl ether Claisen rearrangement.

In order to study solvent effect on the studied reaction, we performed the PCM calculations in water, ethanol, DMSO, heptane and cyclohexane solvents. These calculations were performed in B3LYP/6-31G<sup>\*</sup> level of theory. Furthermore, to investigate hydrogen bonding effects, the calculations were performed by considering one water molecule near the hydrogen bonding site (oxygen atom). The results are summarized in Table 4.

According to White and Wolfarth [30] it is expected that the rate of the studied reaction should increase in polar and protic solvents. The PCM model could not predict the accurate sequence of reaction rates in solution phase (see Table 4). This discrepancy is due to the fact that the use of non-specific interactions, incorporated in this model, is not sufficient. From Table 4 the rate of the reaction strongly increased by considering one water molecule in reaction media, and inferred that the rate enhancement of the reaction in polar and protic solvents arise from specific solute–solvent interactions such as hydrogen bonding and the hydrophobic effect. This discussion says that solvent effect on this reaction is

**Table 3**Theoretical and experimental kinetic and activation parameters for the rearrangement of allyl *p*-tolyl ether in gas phase ( $T = 513.15$  K).

	6-31G <sup>*</sup>		6-31++G <sup>**</sup>		6-311G <sup>*</sup>		Exp
	RHF	B3LYP	RHF	B3LYP	RHF	B3LYP	
$E_a$ (kcal mol <sup>-1</sup> )	54.50	34.69	53.46	33.23	54.22	33.62	36.08 ± 2
Log <i>A</i>	11.71	11.81	11.72	11.86	12.01	12.43	11.74 ± 0.2
$\Delta H^\ddagger$ (kcal mol <sup>-1</sup> )	53.48	33.67	52.44	32.21	53.20	32.60	35.06 ± 2
$-\Delta S^\ddagger$ (cal mol <sup>-1</sup> K <sup>-1</sup> )	8.00	7.58	7.99	7.33	6.36	4.69	7.88 ± 2

**Table 4**Theoretical kinetic and activation parameters for rearrangement of allyl *p*-tolyl ether, calculated by PCM model at the B3LYP/6-31G<sup>\*</sup> level of theory ( $T = 298.15$  K).

	Non (1H <sub>2</sub> O)	Water	Ethanol	DMSO	Heptane	Cyclohexane
$E_a$ (kcal mol <sup>-1</sup> )	10.60	34.02	34.46	33.27	33.91	34.02
Log <i>A</i>	12.75	12.13	12.85	11.96	11.78	12.13
$\Delta H^\ddagger$ (kcal mol <sup>-1</sup> )	10.01	33.43	33.87	32.68	33.31	33.43
$-\Delta S^\ddagger$ (cal mol <sup>-1</sup> K <sup>-1</sup> )	2.19	5.01	1.75	5.82	6.64	5.01

similar to the other type pericyclic reactions (Diels–Alder reactions) [31].

## 5. Conclusion

The rate of studied reaction does not show any considerable change in presence of cyclohexene as a radical scavenger. This result and the obtained experimental kinetic parameters suggest a tight activated complex with six-member cycle and a non-radically concerted mechanism.

The extent of broken and formed bonds in transition state shows that an asynchronous concerted mechanism had occurred for the allyl *p*-tolyl ether rearrangement. The charge analysis shows that electron donor groups at C1, C2 and C6 accelerate the reaction. However, at C5 position opposite result is observed, which is in accordance with the experimental results for allyl vinyl ether Claisen rearrangement in the solution phase. The same substituent effect can be concluded in gas and solution phases for these types of reactions. The rate enhancement of the reaction in polar and protic solvents arises from specific solute–solvent interactions such as hydrogen bonding and the hydrophobic effect.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.theochem.2008.09.030.

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