



## Computational Studies on the Thermodynamic and Kinetic Parameters of Unimolecular and Bimolecular Dissociation of Propylene Glycol Ethyl Ether in Binary 1-Butanol and Isobutanol Solvent Mixtures



Rima H. Al Omari<sup>\*a,b</sup>, Khalidun M. Al Azzam<sup>a</sup>, Mansour H. Almatarneh<sup>\*b,c</sup>, Ahmad A. Ahmad<sup>d</sup>, Asma M. Ghazzy<sup>a</sup>, Asmaa Y. Alnajajrah<sup>b</sup>, Naeem M. Shalan<sup>a</sup>, Nida O. Karamah<sup>a</sup>, Lyazzat Bekbayeva<sup>e</sup>, and El-Sayed Negim<sup>f</sup>

<sup>a</sup> Pharmacological and Diagnostic Research Centre (PDRC), Faculty of Pharmacy, Al-Ahliyya Amman University, Amman 19328, Jordan.

<sup>b</sup> Department of Chemistry, University of Jordan, Amman 11942, Jordan.

<sup>c</sup> Department of Chemistry, Memorial University, St. John's, NL, A1B 3X7, Canada

<sup>d</sup> Department of Applied Physics, Faculty of Science and Arts, Jordan University of Science and Technology, Irbid-22110, Jordan.

<sup>e</sup> Asfendiyarov Kazakh National Medical University, Department of Engineering disciplines, 88 Tole bi St., Almaty, Kazakhstan

<sup>f</sup> School of Petroleum Engineering, Satbayev University, 22 Satpayev Street, 050013 Almaty, Kazakhstan

### Abstract

This study includes a theoretical investigation of Thermodynamic and kinetics of the unimolecular and bimolecular dissociation reaction of Propylene Glycol Ethyl Ether in the gaseous phase. A B3LYP functional with 6-31G(d) basis set was used to optimize all geometries of the stationary points. Potential-energy surface for various channels for the reaction of PGEE was studied at APFD/6-31G(d) and  $\omega$ B97XD/6-31G(d) levels of theory. The kinetic and thermodynamic parameters for nineteen reaction pathways are investigated. Most of the unimolecular dissociation mechanisms occur in a concerted transition state step endothermically. Our calculations proved that energy barriers for ethanol and acetone formation is the best reaction route with an activation barrier of 279 kJ mol<sup>-1</sup> at APFD/6-31G(d) level of theory. The PGEE bimolecular reaction with 1-butanol, the pathway which produces H<sub>2</sub> and butanal is more plausible to take place with a lower activation energy of 225 kJ mol<sup>-1</sup> at  $\omega$ B97XD/6-31G(d) level of theory.

**Keywords:** Binary mixtures; Carbene; Dissociation; 2-Methyloxirane; PGEE.

### 1. Introduction

Propylene glycol ethyl ether (PGEE) is a clear liquid with a sweetish odor, miscible with water, and reacts strenuously with strong oxidizing agents [1]. Glycol ethers are fine synthetic substances that join the best dissolvability plumes of alcohols and ethers [2,3]. They are broadly utilized as a significant solvent for oils and petrol and used in gasoline formulation [4,5]. Propylene glycol ether is considered as a substitute for ethylene glycol ether due to the lower toxicity [5-

7]. Binary mixtures containing alkoxypropanols and 1-alkanols probably create significant properties resulting from their complexity, the effect of hydrogen bond, specific interaction, etc [8-10]. There are different methods to prepare PGEE [11], and it could be produced by the reaction between propylene oxide and alcohol with the aid of a catalyst. This study was conducted to assess whether the kinetic and thermodynamic parameters of the PGEE+1-

\*Corresponding author e-mail: [r.alomari@ammanu.edu.jo](mailto:r.alomari@ammanu.edu.jo); (Rima H. Al Omari),

[m.almatarneh@ju.edu.jo](mailto:m.almatarneh@ju.edu.jo); (Mansour H. Almatarneh)

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butanol system resemble those of the PGEE+ isobutanol system. Theoretical systematic study of mixtures containing alkoxypropanols with linear alkanols has been investigated to better understand the molecular interactions of the alcohol and ether.

## 2. Computational Details

All calculations and mechanisms were performed using Gaussian-16W program [12]. Geometry optimizations of reactants, transition states, and products have been performed using Density function theory (DFT) with the 6-31G(d) p basis set. The calculations of vibrational frequency were carried out at the same level of theory to characterize the nature of those points as minima (no imaginary frequencies) or transition state (only one imaginary frequency) along the specified reaction pathway and to correct energies for zero-point (ZPE) and thermal contributions at 298K [13-15]. The optimization was carried out using Becke's three-parameter hybrid method (B3) using the LYP correlation functional (B3LYP) [16]. In this research, the reaction energies and enthalpies were determined using long-range-corrected functionals: APFD/6-31G(d) and  $\omega$ B97XD/6-31G(d) [17]. Additionally, the reactants connected with desired products minimum energy paths were computed through the intrinsic reaction coordinate (IRC) [18] procedure at the level of the theory of B3LYP/6-31G(d) to the assertive acquaintance of the reactants and products/intermediates on the potential energy curves (PECs).

## 3. Results and Discussion

Nineteen proposed mechanism pathways of PGEE were investigated via detailed quantum chemistry calculations. The pathways from **A** to **L** include unimolecular dissociation of PGEE, depicted in Figures 1 and 3, whereas pathways from **M** to **S** comprise the bimolecular reactions of PGEE with 1-butanol and isobutanol solvents, as shown in Figures 4 and 6, respectively. It is worth mentioning that all dissociation mechanisms take place, endothermically, in a concerted step, excluding pathways **F**, **H**, **J**, **M**, **N**, and **O** which are considered exothermic reactions. Tables 1-3 summarize energy barriers and reaction energies (activation energies ( $E_a$ ) and Gibb's energies of activation ( $\Delta G^\ddagger$ )), for the investigated pathways, were evaluated at different levels of theory. The calculated kinetic energies help in defining the most

plausible pathways; those with lower kinetic energy values are considered the most plausible. Furthermore, the stationary points are projected on the potential energy curves (PEC's) for analogs pathways to identify the kinetic energies of the most favorable pathways.

### 3.1. Unimolecular Dissociation of PGEE

The dehydration reaction of PGEE for two possible pathways has been symbolized as pathways **A** and **B**. In pathway **A**, the removal of H<sub>2</sub>O molecule is carried out from the carbon atom neighbouring to the etheric oxygen of PGEE to form an alkene (Figure 1). Conversely, the H<sub>2</sub>O is eliminated from the terminal carbon atom of PGEE to form an unsaturated bond via transition state (TSB), resulting in producing 3-ethoxypropene, as shown in pathway **B** (Figure 1). The optimized structures for reaction coordinates for all suggested unimolecular dissociation of PGEE are plotted on potential energy curves (PECs) at different levels of theory, depicted in Figures 1 and 2.

In Transition State A (TSA), a detectable geometric change can be observed. For instance, the bond lengths of C-O and C-H bonds are elongated by about 0.28 and 0.53 Å, respectively. Furthermore, the distance between H and O atoms decreases by about 1.73 Å by approaching each other. The unsaturated bond has been produced with a length of 1.34 Å. The Transition State B (TSB) denotes that the C-H and C-O bond lengths increase to 1.42 Å and 1.96 Å, respectively, while the H-O bond length decreases to 1.29 Å, and a double bond between C-C formed with 1.33 Å.

The activation energies and Gibb's energies of activation for pathways from **A** to **F** shown in Table 1. The activation energy of TSA at the level of theory of APFD/6-31g(d) compatible with B3LYP/6-31G(d) with a value of 292 kJ mol<sup>-1</sup>. For the  $\omega$ B97XD/6-31G(d), the value obtained is 304 kJ mol<sup>-1</sup>, shown in Table 1. The TSB's activation energy is low in comparison to pathway **A** with no more than 5 kJ mol<sup>-1</sup> with a value of 289 kJ mol<sup>-1</sup> at APFD/6-31g(d) and has a high value of 307 kJ mol<sup>-1</sup> at  $\omega$ B97XD/6-31G(d) levels of theory.

Table 1. The kinetic parameters ( $E_a$  and  $\Delta G^\ddagger$ ) for the unimolecular dissociation of PGEE (in  $\text{kJ mol}^{-1}$ ) at 298.15 K.

Transition States	B3LYP/6-31G(d)		APFD/6-31G(d)		$\omega$ B97XD/6-31G(d)	
	$E_a$	$\Delta G^\ddagger$	$E_a$	$\Delta G^\ddagger$	$E_a$	$\Delta G^\ddagger$
TSA	285	283	292	290	304	302
TSB	280	281	289	290	307	307
TSC	292	293	293	296	303	305
TSD	360	360	359	360	373	373
TSE	308	308	319	318	336	335
TSF	289	291	284	287	298	300
TSG	293	290	299	297	312	309
TSH	273	273	279	281	286	287
TSI	359	357	356	356	372	371
TSJ	321	327	318	325	346	352
TSK	280	279	284	285	294	293
TSL	522	522	533	533	540	539

$E_a$ : Activation energy.

$\Delta G^\ddagger$ : Gibbs free energy.

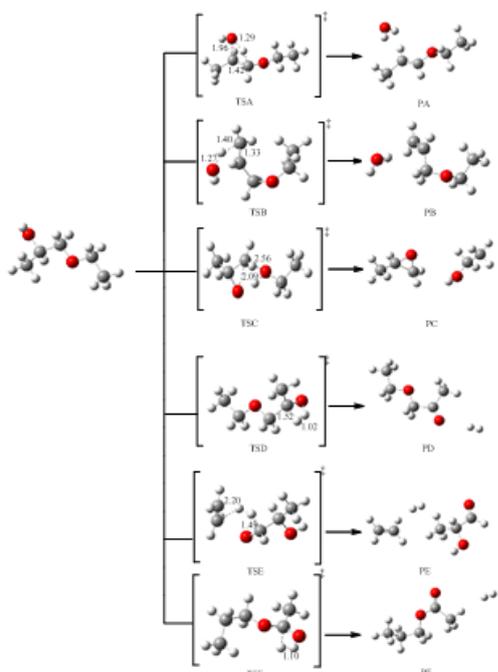


Fig.1 Suggested reaction mechanisms for the unimolecular reaction of PGEE (Pathways A→F).

There are several methods for the synthesis of propylene glycol. It could be produced by the unimolecular reaction of PGEE reaction, resulting in the formation of alcohol with propylene oxide (2-methyloxirane). It is worth noting that the epoxide ring of propylene oxide may open either at the C–O bond due to the asymmetry of propylene oxide. Therefore, the products are a mixture of secondary and primary alcohols [19]. Primary alcohols are among the products, it has a higher toxicity than

secondary alcohols; thus, the reaction must be highly selective [2].

The TSC indicates that the C–H and C–O bond lengths increase to 2.56 Å and 2.09 Å, respectively, while the H–O bond length decreases to 1.03 Å. A single bond between C–O is formed with 1.44 Å, which results in the formation of a three-membered ring (propylene oxide).

The thermodynamic parameters indicate that pathway A is endothermic by 59  $\text{kJ mol}^{-1}$  and by 48  $\text{kJ mol}^{-1}$  at APFD/6-31G(d) level of theory. It is worth mentioning that the formation of propylene oxide (pathway C) is a kinetically not favorable reaction. moreover, it was of interest to study it at different theory levels. For TSC the calculated activation energies are 293 and 303  $\text{kJ mol}^{-1}$  at ABFD/6-31G(d) and  $\omega$ B97XD/6-31G(d) levels of theory, respectively. The lower activation energies are accomplished at APFD/6-31G(d) level of theory.

The reaction mechanisms of loss hydrogen process have been investigated via three pathways, denoted as pathways D, E and F. All transition states are performed by two protons removable from different sites in PGEE. The highest activation energy of TSD is 373  $\text{kJ mol}^{-1}$  at the WB97XD. In contrast, the results of the B3LYP/6-31G(d) level of theory are similar to APFD/6-31G(d) level of theory. For TSE, the activation energy is 319  $\text{kJ mol}^{-1}$  at APFD/6-31G(d) level of theory. Furthermore, using  $\omega$ B97XD/6-31G(d) led to an increase in the energy barrier's calculated value by no more than 17  $\text{kJ mol}^{-1}$ . The same pattern of increasing the energy barrier was found with TSF (Table 1). The PED using APFD/6-31G(d) level of theory for pathways from A to L is depicted in Figure 2.

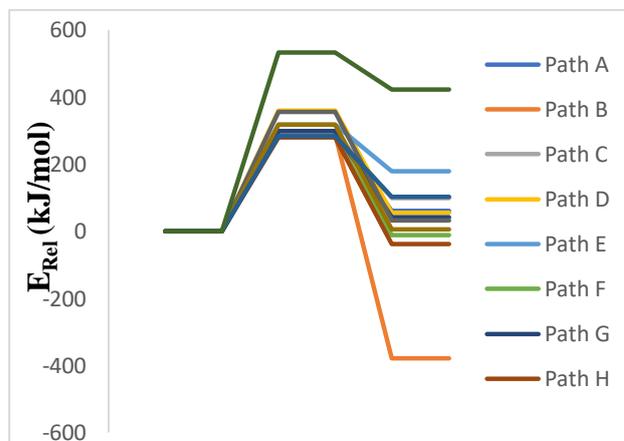


Fig.2 The PEC of the unimolecular reactions of PGEE, pathways A→L, calculated at APFD/6-31G(d) level of theory.

The thermodynamic parameters of pathways **D** and **E** were found to be endergonic, and the reaction prefers the reversible direction at all levels of theory. Otherwise, pathway **F** was exothermic and exergonic and favor the forward direction.

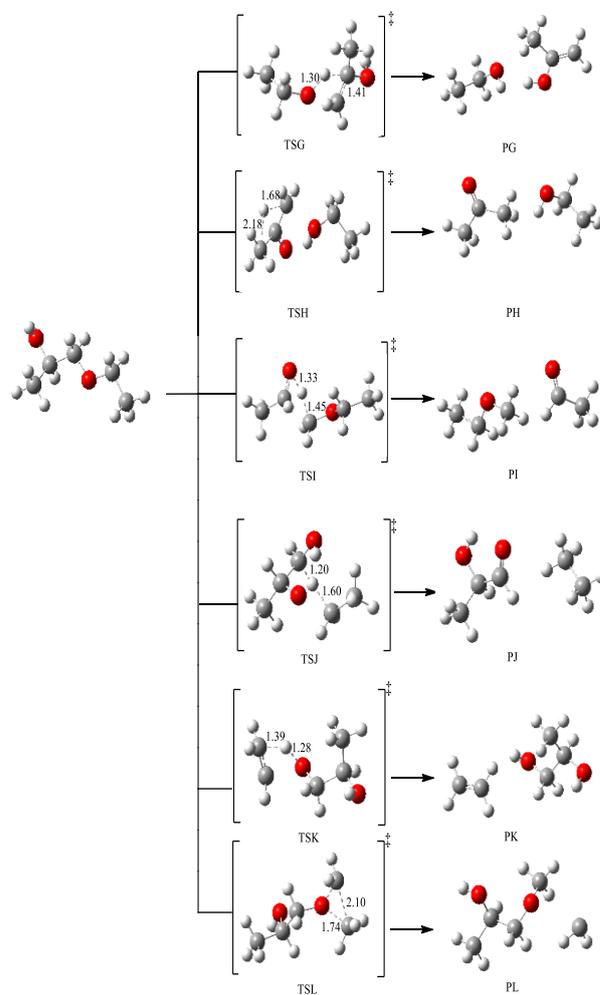
The formation of ethanol and acetone happens through the transition state TSG and TSH, as shown in Figure 3. In pathway **G**, the H atom gradually draws near the etheric oxygen atom, the C-O and C-H bonds are further extended. As a result, the strength of these bonds is extremely weakened. On the other hand, the O...H bond interaction is strengthened. The distance between the C-O bond is increased to 1.98 Å, and it is broken, and a double bond is formed with a bond distance of 1.41 Å. Finally, ethanol is formed by decreasing the distance between O-H to 1.30 Å. On the other hand, several decomposition reaction mechanisms can produce different products through TSI, TSJ, and TSK, as shown in Figure 3.

The effect of photochemical reactions on the barrier heights is investigated in pathway **L**. The chemical reactions that involve alkyl radicals have a significant impact on the dissociation of organic compounds [20]. Due to the instability and activity of alkyl radicals [21,22] monitoring of their experimental methods does not occur easily.

The formation of carbene is studied through TSL. A hemolytic cleavage of the weak PGEE bond via ultraviolet light to generate 1-methoxy-2-propanol and carbene [23]. The activation energies are calculated to be 533 and 540 kJ mol<sup>-1</sup> at the APFD/6-31G(d) and ωB97XD/6-31G(d) levels of theory, respectively (Table 1). These values are also in good agreement with the B3LYP results. Moreover, the high activation energies indicate that it is not preferred to occur. Among the thermodynamic and kinetic parameters, the most favorable reaction mechanism through the dissociation mechanism is pathway **H**. The calculated energy barrier value at the APFD/6-31G(d) is 279 kJ mol<sup>-1</sup>, within a ± 7 kJ mol<sup>-1</sup> difference from other levels of theory. It should be noted that carbene formation in pathway **L** is not a plausible channel, neither thermodynamically nor kinetically (Table 1).

Depending on the energy values in Table 1, the activation energies indicate that the least cost computational method, B3LYP/6-31G(d), is a

suitable method for alike reactions. The activation energies calculated by B3LYP are within a 1-20 kJ mol<sup>-1</sup> difference for most pathways compared to the activation energies values calculated utilizing the more expensive computational methods such as APFD/6-31G(d) and ωB97XD/6-31G(d).



**Fig.3** Suggested reaction mechanisms for the unimolecular reaction of PGEE (Pathways **G**→**L**).

### 3.2. Bimolecular Reaction of PGEE

The strong dipole-dipole interactions were produced due to the presence of high dipole moments of alkoxyethanols compared with *n*-alkanols [24,25]. In addition to substantial intermolecular effects generated by the presence of hydroxy ether make mixtures containing it more significant [26]. Studying the binary liquid mixtures aims to understand the nature of molecular interactions between the component molecules [27,28]. According to this work, we expanded our studies to the binary mixtures

formed by PGEE with two mono-alcohols comprising 1-butanol and isobutanol at 298.15 K. Both thermodynamic functions ( $\Delta H$  and  $\Delta G$ ), and kinetic parameters (activation energies  $E_a$  and Gibb's energies of activation  $\Delta G^\ddagger$ ) were calculated for all pathways studied.

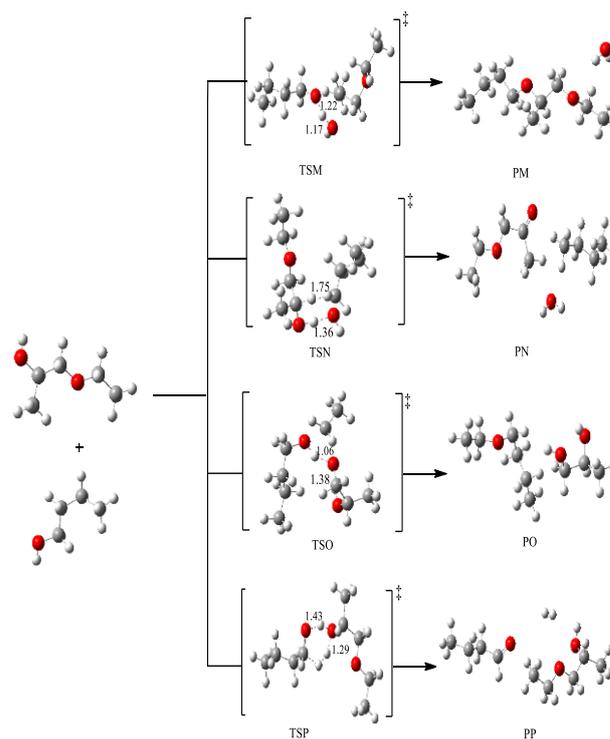
### 3.2.1. Reaction of PGEE with 1-Butanol (Pathways M $\rightarrow$ P)

The bimolecular reaction of PGEE with 1-butanol were investigated via four pathways, which are designated as pathways **M**, **N**, **O** and **P**. Figure 4 emphasize the equilibrium geometries of all the stationary points that are plotted on the PED for pathways from **M** to **P**. The energy barriers for these mechanisms are listed in (Table 2). Pathways **M** and **N** investigate the dehydration reaction mechanism. Pathway **O** yields butyl ethyl ether and 1,2-propandiol, also hydrogen is removed in pathway **P**. In TSM the activation energies at APFD/6-31g(d) and  $\omega$ B97XD/6-31G(d) are 293 and 314 kJ mol<sup>-1</sup>, respectively. APFD/6-31g(d) activation energies agree with the B3LYP/6-31G(d) level of theory differing by no more than 10 kJ mol<sup>-1</sup>. Furthermore, the activation energies for TSN, and TSO, and TSP at the  $\omega$ B97XD/6-31G(d) method are 362, 301, and 235 kJ mol<sup>-1</sup>, respectively. Among these proposed pathways for the bimolecular reactions of PGEE, pathway **P** is the most favorable reaction. It has lower energy barriers at APFD/6-31g(d). Moreover, the activation energies at the B3LYP/6-31G(d) level of theory is 206 kJ mol<sup>-1</sup>, which is comparable with the corresponding value deduced at the  $\omega$ B97XD/6-31G(d) level of theory (Table 2).

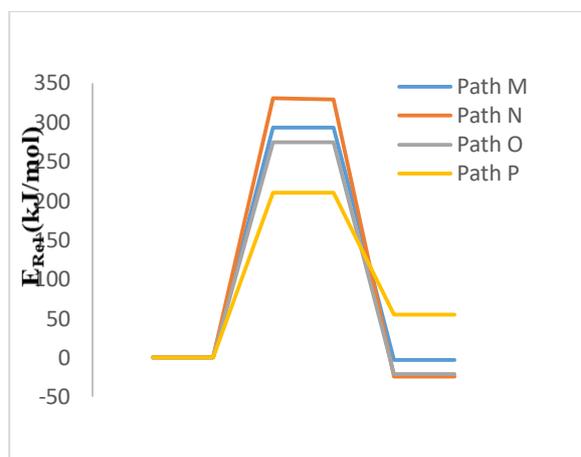
**Table 2.** The kinetic parameters ( $E_a$  and  $\Delta G^\ddagger$ ) for the bimolecular reaction of PGEE with 1-butanol (in kJ mol<sup>-1</sup>) at 298.15 K.

Transition States	B3LYP/6-31G(d)		APFD/6-31g(d)		$\omega$ B97XD/6-31G(d)	
	$E_a$	$\Delta G^\ddagger$	$E_a$	$\Delta G^\ddagger$	$E_a$	$\Delta G^\ddagger$
TSM	283	284	293	295	314	313
TSN	331	336	329	333	362	365
TSO	279	286	275	286	301	309
TSP	206	213	210	216	225	229

$E_a$ : Activation energy.  
 $\Delta G^\ddagger$ : Gibbs free energy.



**Fig.4** Suggested reaction mechanisms for the bimolecular reaction of PGEE with 1-butanol (Pathways **M** $\rightarrow$ **P**).

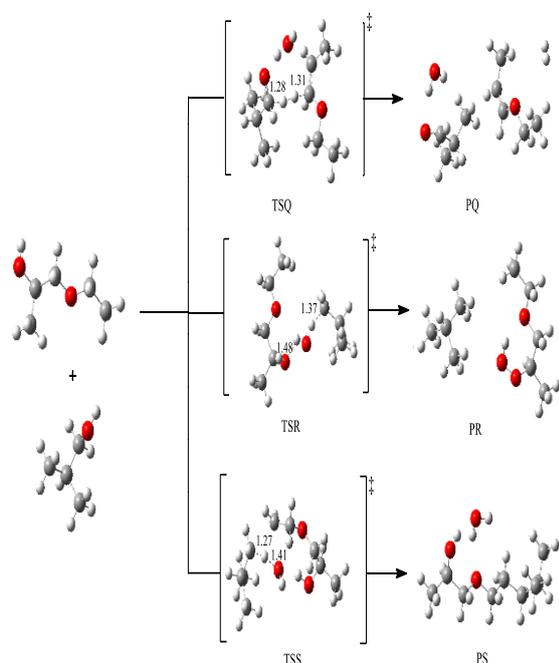


**Fig.5** PEC for the bimolecular reactions of PGEE for pathways **M** $\rightarrow$ **P**, calculated at APFD/6-31G(d) level of theory.

### 3.2.2. Reaction of PGEE with Iso-butanol (Pathways Q $\rightarrow$ S)

The reactions between PGEE and isobutanol were also calculated computationally. Figure 6 indicates the proposed mechanism for pathways **Q**, **R**, and **S**. Figure 7 illustrates the PECs for pathways from **Q** to **S**. Two proposed pathways (**Q** and **S**) study the PGEE dehydration reaction. Table 3 reports the energy barriers for pathways from **Q** to **S**.

For TSQ, the lowest activation energy is  $341 \text{ kJ mol}^{-1}$  calculated at the B3LYP/6-31G(d). The activation energy of TSR at  $\omega$ B97XD/6-31G(d) method is  $477 \text{ kJ mol}^{-1}$ . The lowest activation energy among other transition states for TSQ is  $341 \text{ kJ mol}^{-1}$  at the B3LYP/6-31G(d) level of theory. The activation energies of TSR and TSS at the APFD/6-31G(d) level of theory are  $465$  and  $449 \text{ kJ mol}^{-1}$ , respectively, and are  $477$  and  $472 \text{ kJ mol}^{-1}$  at  $\omega$ B97XD/6-31G(d) level of theory. It should be mentioned here that the activation energies of the bimolecular reaction PGEE with isobutanol (The higher barrier is  $477 \text{ kJ mol}^{-1}$  at  $\omega$ B97XD/6-31G(d) level of theory) are higher than those of the bimolecular reaction with I-butanol (The higher barrier is  $363 \text{ kJ mol}^{-1}$  at  $\omega$ B97XD/6-31G(d) level of theory).



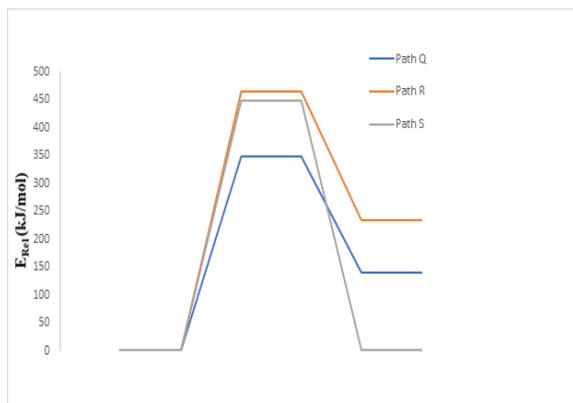
**Fig.6** Suggested reaction mechanisms for the bimolecular reaction of PGEE with isobutanol (Pathways  $Q \rightarrow S$ ).

**Table 3.** The kinetic parameters ( $E_a$  and  $\Delta G^\ddagger$ ) for the bimolecular reaction of PGEE with isobutanol (in  $\text{kJ mol}^{-1}$ ) at  $298.15 \text{ K}$ .

Transition States	B3LYP/6-31G(d)		APFD/6-31G(d)		$\omega$ B97XD/6-31G(d)	
	$E_a$	$\Delta G^\ddagger$	$E_a$	$\Delta G^\ddagger$	$E_a$	$\Delta G^\ddagger$
TSQ	341	339	406	395	373	371
TSR	439	436	465	460	477	468
TSS	445	454	449	453	472	473

$E_a$ : Activation energy.

$\Delta G^\ddagger$ : Gibbs free energy.



**Fig.7** The PEC for the bimolecular reactions of PGEE for pathways  $Q \rightarrow S$ , calculated at APFD/6-31G(d) level of theory.

#### 4. Thermodynamic Parameters of the Unimolecular and Bimolecular Reactions of propylene glycol ethyl ether

The study of thermodynamic parameters ( $\Delta H$  and  $\Delta G$ ) for the proposed unimolecular and bimolecular reactions of PGEE are at all the levels of theory determined in Table S1 in the Supporting Information (SI). Among the unimolecular reactions of PGEE (Pathways **F**, **H**, and **J**) are exothermic and exergonic at all levels of theory. The dissociation reactions of PGEE are mostly endothermic and endergonic at all levels of theory. Based on the results, we conclude that pathway **H** has the lowest thermodynamic parameter values; therefore, they are more spontaneous and favorable reactions.

#### 5. Conclusion

A quantum chemical calculation has been used to investigate the reaction of propylene glycol ethyl ether. Twelve significant pathways for the unimolecular reaction of PGEE and seven for the bimolecular reactions with butanol and iso-butanol were studied, with a total of 19 pathways. The optimized geometries of R's, TS's, I's, and Ps were performed. As well, the potential energy curves (PECs) were described using the APFD/6-31G(d) and  $\omega$ B97XD/6-31G(d) levels of theory. The thermodynamic parameters ( $\Delta H$  and  $\Delta G$ ) and the kinetic properties ( $E_a$  and  $\Delta G^\ddagger$ ) were calculated using the DFT theories for each proposed pathway. It is worth mentioning that all dissociation mechanisms take place, endothermically, in a concerted step, excluding pathways **F**, **H**, **J**, **M**, **N**, and **O** which are considered exothermic reactions.

The PGEE dissociates to produce several products. Conformational changes were performed during the first TS's. Kinetically, the formation of carbene is not preferred in comparison to all other pathways. Pathway **L** has the highest overall activation energy of 540 kJ mol<sup>-1</sup> at ωB97XD/6-31G(d) level of theory. The formation of acetone and ethanol (Pathway **H**) was found likely to occur for the unimolecular dissociation reactions of PGEE as it has the lowest activation energy of 279 kJ mol<sup>-1</sup> at APFD/6-31G(d). Pathway **P** is more likely to occur for the bimolecular dissociation reactions with 1-butanol with the lower activation energy of 210 kJ mol<sup>-1</sup> at APFD/6-31G(d).

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### Conflict of Interest

The authors declare no competing financial interests.

### Supporting Information

The thermodynamic parameters for all proposed pathways were calculated at APFD/6-31G(d) level of theory. The cartesian coordinates for all optimized structures of all pathways to facilitate reproducibility of the results.

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NA

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