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A MECHANISTIC STUDY ON THE REACTIONS OF VINYL CARBENE WITH HYDROGEN, CARBON MONOXIDE AND CARBON DIOXIDE: SHED LIGHT ON FURTHER MANIPULATIONS

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ABSTRACT

Density Functional calculations have been used to explore the potential energy profiles of H_2, CO, and CO_2 activation reactions by vinyl carbene structure **1**. The reactions of vinyl carbene **1** with CO_2 was proposed to yield a variety of possible products (**3**−**5**) depending on its selectivity. The density functional calculations established that the proposed reactions of **1** with CO_2 proceed in a *concerted* or *stepwise* manners to form **3** and **5**. However, that of CO reaction occur in only concerted fashion for the proposed products **15** and **16**. Furthermore, the compound **1** is found to be most reactive than **5** and **16** towards H_2 with the required lower energy barrier. Finally, the more dominant routes are determined to be formation processes of **3**, **4**, and **10**.

Keywords: Vinyl carbene, Small molecule activation, DFT, CO, CO_2

VİNİL KARBEN YAPISININ HİDROJEN, KARBON MONOKSİT VE KARBON DİOKSİT İLE TEPKİMELERİ ÜZERİNE MEKANİSTİK BİR ÇALIŞMA: İLERİ ÇALIŞMALARA BİR IŞIK

ÖZET

Yoğunluk fonksiyoneli teorisi H_2, CO ve CO_2 moleküllerinin vinil karben **1** bileşiği ile aktivasyonu sonucu oluşan enerji yüzeylerini incelemek için kullanılmıştır. Seçiciliğe bağlı olarak vinil karben **1** bileşiğinin CO_2 molekülü ile tepkimesi çeşitli muhtemel ürünlerin (**3**−**5**) oluşabileceğini önermektedir. Yoğunluk fonksiyoneli teorisi hesaplamaları **3** ve **5** numaralı ürünlerin oluşum tepkimelerinin *tek basamak* veya *basamak basamak* mekanizmalar üzerinden yürüyebileceğini göstermektedir. Buna karşın, **1** numaralı yapının CO ile tepkimesi sonucunda olası ürünler **15** ve **16** yalnızca tek basmak içermektedir. Dahası, H_2 aktivasyon tepkimeleri değerlendirildiğinde **1** numaralı yapının **5** ve **16** numaralı yapılara nazaran daha reaktif olduğu elde edilen enerji bariyerleri ile tespit edilmiştir. Sonuç olarak, en uygun mekanizmalar **3**, **4** ve **10** numaralı yapıların oluşumları için tespit edilmiştir.

Anahtar Kelimeler: Vinil karben, Küçük molekül aktivasyonu, DFT, CO, CO_2

1. INTRODUCTION

Alkylidene carbenes, alkenylidenes, have been known as highly reactive intermediates in organic chemistry [1−5]. Several methods have been improved to generate these highly reactive intermediates [6−13]. In the past few decades, the alkenylidenes have attracted considerable attention due to their role in many organic reactions. They play obvious roles in many organic synthesis with high levels of selectivity [14−25]. Furthermore, the cycloaddition of unsaturated carbenes can provide the synthesis of small ring, highly strained compounds by conventional ways. The 3−dimensional selectivity of substitute groups from the addition reactions of alkylidene carbene to olefins was exemplified in a collaboration of Apeloig and Fox [26,27]. As it can be seen from the literature, there are many reports and discussions on theoretical studies of alkylidene carbenes [28−32]. However, no scientific study has been reported on the activation of small molecules by alkylidene carbenes so far.

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In the present computational study, we would like to distil a general message for the behavior of heavier vinyl carbenes towards hydrogen (H_2), carbon monoxide (CO), and carbon dioxide (CO_2). With this incentive, we started by calculations of the energy profiles for the oxidative addition reactions of the considered small molecules with vinyl carbene **1** on the basis of proposed mechanisms: The reactions may proceed in either *concerted* or *stepwise* fashion to yield variety of different possible products. As we show here, the ketene + CO complex **4** and a kind of cyclic carbene **5** can be generated from the proposed reaction of **1** with CO_2. Although formation process of **4** is determined to be exergonic, that of constitutional isomer **5** has an endergonic nature with nonspontaneous character. On the other hand, the proposed reaction of **1** with CO depict that the formation of proposed products **17** and **18** are strongly endergonic at the level of theories used herein. Furthermore, the H_2 activation by **1** is found to be more favored than **5** and **18** with the lower energy barriers.

2. COMPUTATIONAL DETAILS

Initially, all manipulations were performed using the Gaussian 09 suite of programs [33]. In order to optimize the structures on their potential energy surface in gas phase, Becke's three–hybrid method and the exchange functional of Lee, Yang, and Parr (B3LYP) theory was employed with the 6–311++G(d,p) basis set [34,35]. Further, the calculations were repeated with full geometry optimizations at newer theory level of WB97XD/6–311++G(d,p) [36]. The stationary points were characterized as minima or transition structures by vibrational frequency calculations, and all relative energies reported here are Gibbs free energies in kcal mol^{-1}. The intrinsic reaction coordinates (IRC) were also followed to verify the energy profiles connecting each transition state to the correct local minima, by using the second–order Gonzalez–Schlegel method [37,38]. The computed structures were visualized by using the GaussView 5.0 program [39].

3. RESULTS and DISCUSSION

From the theoretical calculations, vinylidene carbene **1** is known to be singlet ground state ($\Delta_{S\text{–}T}$ = 48 kcal mol^{-1}) [40]. Due to the high singlet−triplet energy separations, we consider only singlet state of **1** for oxidative addition of H_2, CO, and CO_2. Several conceptually different pathways have been proposed to explain the ability of vinylidene **1** to activate the related small molecules.

The reaction mechanisms of **1** with carbon dioxide (CO_2) was investigated in this part. The reaction can take place via **TS1**, **TS6**, and **TS7** which lead to diverse products such as **3**, **5**, and **4**, respectively. The [1+2] addition of **1** to CO_2 is found to be slightly exergonic to form proposed product **3** via **TS1** in a *concerted* manner by $\Delta G = -2.4$ kcal mol^{-1} and -5.6 kcal mol^{-1} at the B3LYP/6–311++G(d,p) and WB97XD/6–311++G(d,p) level of theories, respectively (Table 1 and Figure 1, black arrows). Then, the intramolecular rearrangement of **3** can be considered to form another possible products of **4** (ketene + CO) by the required energy barrier of $\Delta G^{\neq} = +5.9$ kcal mol^{-1}, so that the overall pathway for **4** starting from **1** is decidedly exergonic by $\Delta G = -36.1$ kcal mol^{-1} at the B3LYP/6–311++G(d,p) level of theory (Table 1 and Figure 1, red arrows). Moreover, the calculation at the WB97XD/6–311++G(d,p) level is very similar by $\Delta G = -35.4$ kcal mol^{-1}. Based on the theoretical results, the formation of **4** can also be evaluated with direct attack of **1** to oxygen atom of CO_2 via **TS7** by the required very high energy barrier of $\Delta G^{\neq} = +47.5$ kcal mol^{-1}, the overall pathway of *concerted* mechanism is determined to be also strongly exergonic by $\Delta G = -36.1$ kcal mol^{-1} (Table 1 and Figure 1, blue arrows). Next, we considered how to incorporate the product **5** from the reaction of **1** with CO_2 and intermolecular rearrangement of **4**. The [2+2] cycloaddition of **1** to CO_2 can also yield the product **5** by considerably high energy barrier of $\Delta G^{\neq} = +47.4$ kcal mol^{-1} (Table 1 and Figure 1, green arrows). In this case, the nature of the proposed reaction for **5** via **TS6** is found to be endergonic by $\Delta G = +18.2$ kcal mol^{-1}. The related energy barrier and overall pathway at the WB97XD/6–311++G(d,p) level are determined to be relatively lower by $\Delta G^{\neq} = +43.6$ kcal mol^{-1} and $\Delta G = +11.7$ kcal mol^{-1}, respectively. Similarly, the formation of **5** is also to be existed endergonic from intermolecular rearrangement of **4** (Table 1 and Figure 1, pink arrows).

Collectively, the dominant reaction route for the reaction **1** with CO_2 is determined to be formation process of **4** via **TS1** and **TS2** with the observed lower energy barriers. Another interesting point is that inclusion of dispersion by WB97XD, which uses a version of Grimme's D2, leads to negligible differences in terms of the energetics and nature of the proposed pathways. For this reason, the following discussions will be based on the results at the B3LYP/6–311++G(d,p) level of theory.

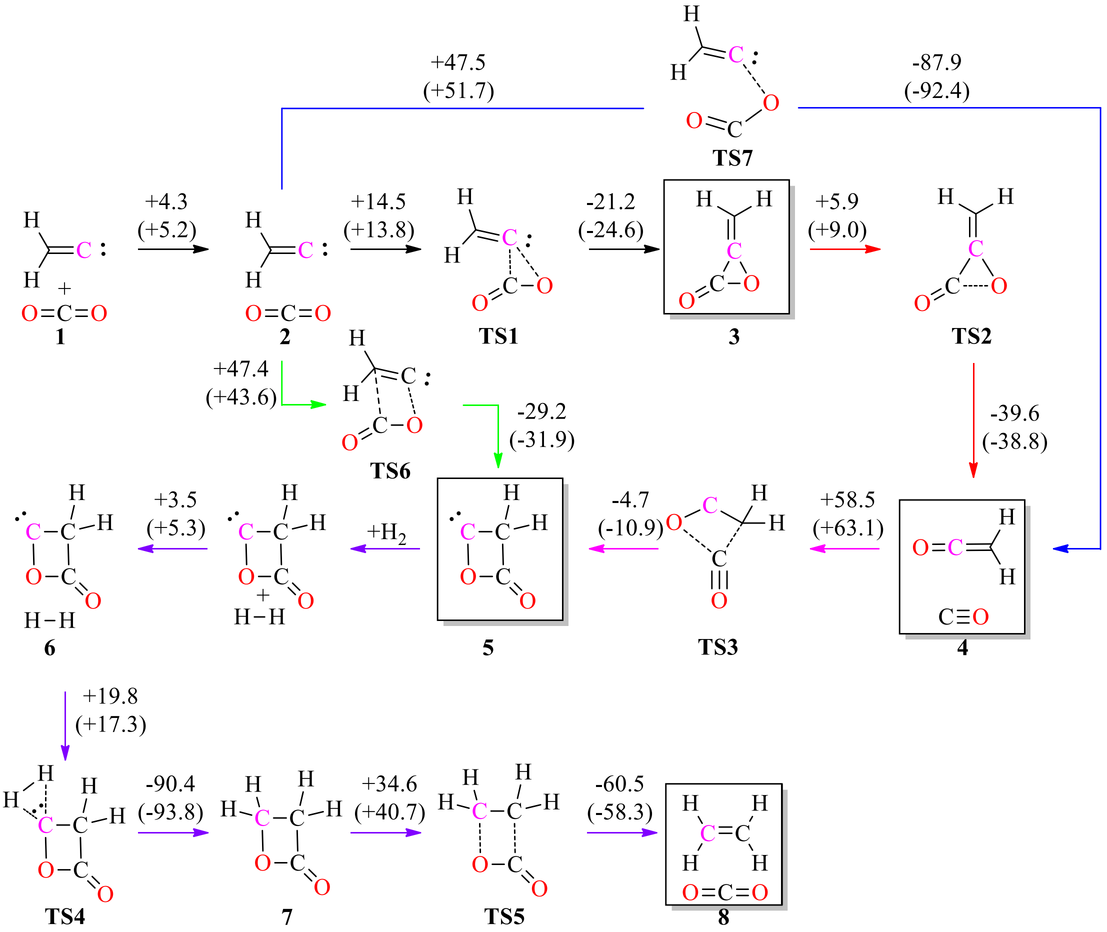

Figure 1. The proposed reaction mechanisms and energy channel for the reaction of vinyl carbene 1 with CO_2 and further H_2 activation at the B3LYP/6–311++G(d,p) and WB97XD/6–311++G(d,p) (in parentheses) level of theories (ΔG energies given in kcal mol^{-1})

We believe that it is possible to generate **5** from **1** + CO_2 at sufficiently high temperature. In this case, it can be designed the formation of ethylene from the hydrogenation of **5**. The addition of H_2 to the resulting product **5** begins with the formation of van der Waals complex **6** which is determined to be of higher in energy than the **5** + H_2 by $\Delta G = 3.5$ kcal mol^{-1}. Then, the required energy barrier to form **8** is to be existed $\Delta G^{\neq} = +19.8$ kcal mol^{-1} with strongly exergonic nature. The DFT calculations indicate that the liberation of CO_2 from the optimized structure **7** leads to the formation of **8** (ethylene + CO_2) by the considerably high energy barrier of $\Delta G^{\neq} = +34.6$ kcal mol^{-1}, so that the overall pathway for **8** starting from **6** is decidedly exergonic by $\Delta G = -96.5$ kcal mol^{-1} (Figure 1, purple arrows).

Table 1. Calculated energy channel for the activation of CO_2 and H_2 by **1** and **5** at the B3LYP/6−311++G(d,p) and WB97XD/6–311++G(d,p) (in parentheses) level of theories (ΔG energies given in kcal mol^{-1})

CO_2 activation by **1**	Energy Channel	H_2 Activation by **5**	Energy Channel
1→2	+4.3 (+5.2)	**5→6**	+3.5 (+5.3)
2→TS1	+14.5 (+13.8)	**6→TS4**	+19.8 (+17.3)
TS1→3	−21.2 (−24.6)	**TS4→7**	−90.4 (−93.8)
3→TS2	+5.9 (+9.0)	**7→TS5**	+34.6 (+40.7)
TS2→4	−39.6 (−38.8)	**TS5→8**	−60.5 (−58.3)
4→TS3	+58.5 (63.1)		
TS3→5	−4.7 (−10.9)		
2→TS6	+47.4 (+43.6)		
TS6→5	−29.2 (−31.9)		
2→TS7	+47.5 (+51.7)		
TS7→4	−87.9 (−92.4)		

Additionally, the activation of H_2 by **1** is also considered in the presented theoretical study. The modelled mechanism for the direct addition of H_2 to **1** occurs in a *concerted* manner to yield ethylene **10** by the relatively lower energy barrier of $\Delta G^{\neq} = +12.6$ kcal mol^{-1} as compared to that of **5** (Table 2 and Figure 2, black arrows). Overall, the reaction is determined to be strongly exergonic by $\Delta G = -79.0$ kcal mol^{-1}. The activation of H_2 by **1** to generate an ethylene molecule is found to be slightly favorable than that of **5** with the lower energy barrier although the exergonic character of the pathway for **5** + H_2 is stronger. Furthermore, the mechanistic scenario for the activations of CO and CO_2 by ethylene molecule **10** were examined. As it can be seen from Figure 2, all the proposed mechanisms were determined to be strongly endergonic, showing that the reactions are nonspontaneous and not favorable (Table 2 and Figure 2, red, blue, and green arrows).

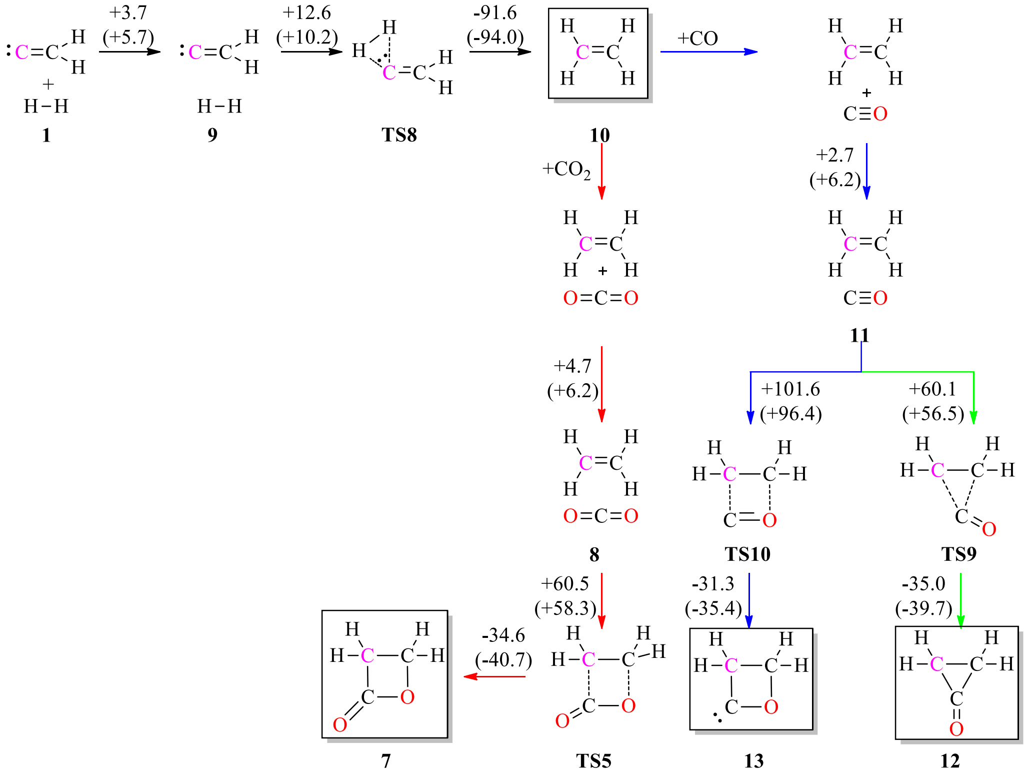

Figure 2. The proposed reaction mechanism for the reaction of vinyl carbene **1** with H_2 and further CO and CO_2 activations at the B3LYP/6–311++G(d,p) and WB97XD/6–311++G(d,p) (in parentheses) level of theories (ΔG energies given in kcal mol^{-1})

Table 2. Calculated energy channel for the activation of H_2, CO, and CO_2 by **1** and **10** at the B3LYP/6−311++G(d,p) and WB97XD/6–311++G(d,p) (in parentheses) level of theories (ΔG energies given in kcal mol^{-1})

H_2 activation by **1**	Energy Channel	CO and CO_2 Activation by **10**	Energy Channel
1→9	+3.7 (+5.7)	**10→8**	+4.7 (+6.2)
9→TS8	+12.6 (+10.2)	**8→TS5**	+60.5 (+58.3)
TS8→10	−91.6 (−94.0)	**TS5→7**	−34.6 (−40.7)
		10→11	+2.7 (+6.2)
		11→TS9	+60.1 (+56.5)
		TS9→12	−35.0 (−39.7)
		11→TS10	+101.6 (+96.4)
		TS10→13	−31.3 (−35.4)

In order to test the possibility of the CO activation by vinyl carbene **1**, the DFT calculations were carried out for the modelled system. Two competitive *concerted* pathways can be considered from intermolecular rearrangement of **1** and CO to form the possible products of **15** and **16**. In accordance with the activation mechanism of CO_2, the CO included trends follow almost same order to form related proposed products with [1+2] and [2+2] cycloaddition steps via **TS11** and **TS12**, respectively. Although the possible [1+2] addition step of **1** to CO_2 for **3** needs lower energy barrier with exergonic nature, the overall pathway for **15** is determined to be strongly endergonic by ΔG = 17.1 kcal mol^{-1} in the case of CO, indicating that the reaction cannot occur spontaneously (Table 3 and Figure 3, black arrows). Based on the theoretical results, the formation of **16** is also plausible from the reaction of **1** with CO. For this reason, the formation mechanism of **16** was also designed. By this way, we can reach a dicarbene compound **16**. However, the calculations show that the formation of **16** is strongly endergonic and the required energy barrier is too high for a reaction at room temperature (Table 3 and Figure 3, blue arrows).

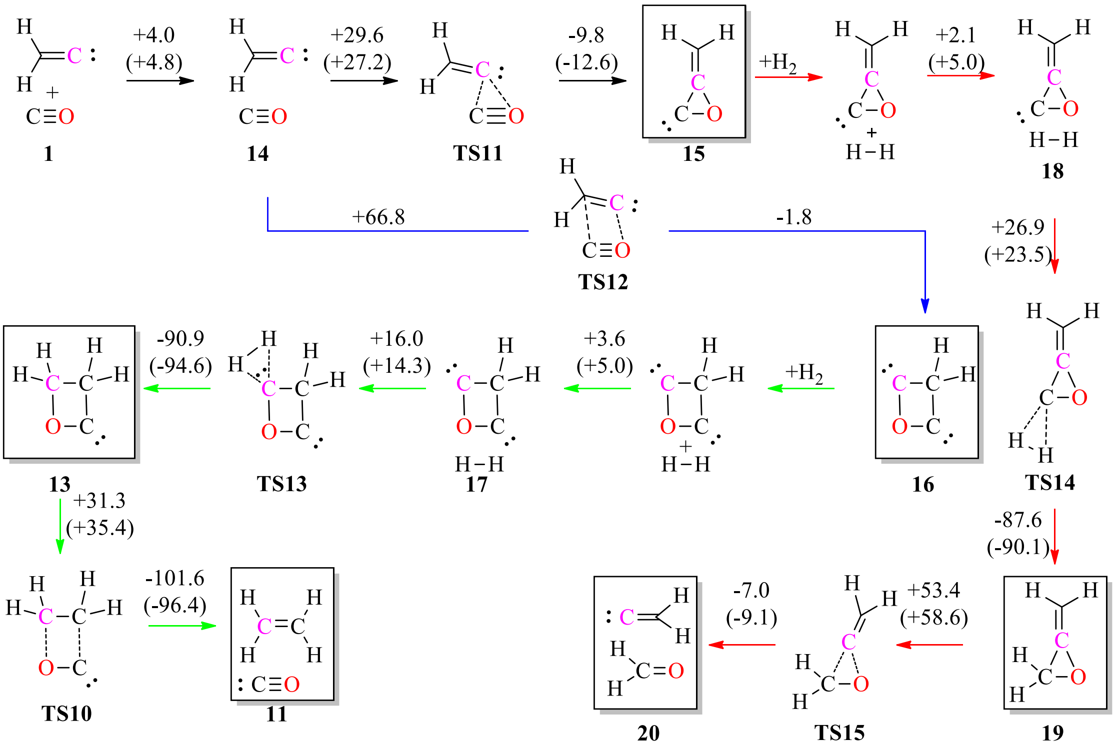

Figure 3. The proposed reaction mechanisms for the reaction of vinyl carbene **1** with CO and further H_2 activation at the B3LYP/6–311++G(d,p) and WB97XD/6–311++G(d,p) (in parentheses) level of theories (ΔG energies given in kcal mol^{-1}).

In case of any possible synthesis of **15** and **16** at sufficiently high temperature, we also designed their H_2 activation mechanisms to generate **11** (ethylene + CO) and **20** (Vinylidene carbene + formaldehyde). The direct addition of H_2 to the proposed product **15** can form the related van der Waals complex of **18** which is more stable than **15** + H_2 by $\Delta G = -2.1$ kcal mol^{-1} (Table 3 and Figure 3, red arrows). Clearly, the hydrogenation of the **15** can proceed by direct addition of H_2 to the carbenic center of **15** via **TS14**. This process requires 26.9 kcal mol^{-1} energy barrier to overcome for the formation of **19**. Then, the decomposition of **19** to form **20** can be activated with the cleavage of C−C and C−O bonds in a *concerted* manner by the very high energy barrier of $\Delta G^{\neq} = +53.4$ kcal mol^{-1} (Table 3 and Figure 3, red arrows). Separately, the calculations indicate that the addition of H_2 can be feasibly binded to the one of the carbenic centers in **16**, forming possible compound **13** by the required relatively lower energy barrier of $\Delta G^{\neq} = +16.0$ kcal mol^{-1} (Table 3 and Figure 3, green arrows). We found that the formation processes of **13** from the van der Waals complex of **17** is strongly exergonic by $\Delta G = -74.9$ kcal mol^{-1}. Additionally, the subsequent CO elimination from the structure **13** was also investigated. In the following rearrangement, it is possible to yield the ethylene + CO mixture **11** via the transition state of **TS10** and the process is exergonic by $\Delta G = -70.5$ kcal mol^{-1}. (Figure 3). Overall, the reaction starting from **17** is determined to be strongly exergonic by $\Delta G = -145.4$ kcal mol^{-1}.

Table 3. Calculated energy channel for the activation of CO and H_2 by **1**, **15** and **16** at the B3LYP/6−311++G(d,p) and WB97XD/6–311++G(d,p) (in parentheses) level of theories (ΔG energies given in kcal mol^{-1}).

CO activation by **1**	Energy Channel	H_2 Activation by **15** and **16**	Energy Channel
1→14	+4.0 (+4.8)	**15→18**	+2.1 (+5.0)
14→TS11	+29.6 (27.2)	**18→TS14**	+26.9 (+23.5)
TS11→15	−9.8 (−12.6)	**TS14→19**	−87.6 (−90.1)
14→TS12	+66.8 (+62.4)	**19→TS15**	+53.4 (+58.6)
TS12→16	−1.8 (−2.7)	**TS15→20**	−7.0 (−9.1)
		16→17	+3.6 (+5.0)
		17→TS13	+16.0 (+14.3)
		TS13→13	−90.9 (−94.6)
		13→TS110	+31.3 (+35.4)
		TS10→11	−101.6 (−96.4)

4. CONCLUSION

Using B3LYP theory with 6–311++G(d,p) basis set, the activation reaction mechanism of H_2, CO, and CO_2 by **1**, **5**, **10**, **15**, and **16** were studied. The calculations depict that the reactions may proceed in either *concerted* or *stepwise* fashion to yield a variety of different possible products. The proposed reactions can occur in *concerted* and *stepwise* manners to generate **3**, **4**, or **5** from **1** + CO_2. The nature of the formation process of **4** is strongly exergonic, whereas that of constitutional isomer **5** is determined to be endergonic with the proposed mechanisms. Additionally, the activation of H_2 by **5** was also considered in the presented theoretical study. The computed relative ΔG energies indicated that the formation of **8** (ethylene + CO_2) is exergonic with energy of −96.5 kcal mol^{-1} at the B3LYP/6–311++G(d,p) level of theory. In the case of CO activation by **1**, the proposed reactions is strongly endergonic for both products **15** and **16**. In spite of this, however, the required energy for the activation of H_2 by **16** is relatively lower with $\Delta G^{\neq} = +16.0$ kcal mol^{-1}. Overall, the formation process of **11** starting from **17** is determined to be strongly exergonic by $\Delta G = -145.4$ kcal mol^{-1}. Collectively, the formation processes of **3**, **4,** and **10** are found to be favorable with the obtained facile energy values.

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