عنوان مقاله:

(Is single-reference calculation adequate to address kinetics of CH(X2Π)reaction with N2(1Σg

محل انتشار:

بیستمین کنگره شیمی ایران (سال: 1397)

تعداد صفحات اصل مقاله: 1

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خلاصه مقاله:

CH (X2Π) radical (methylidyne) is an omnipresent radical that plays an important role in atmospheric, interstellar and combustive systems [1]. This radical can interact with N2 and result into prompt NO formation and ozone layer depletion through production of HCN+N [2]. Though there are several experimental studies reported about this reaction, theoretical data are limited. Therefore, this study explores detailed mechanism of this reaction using singlereference calculations at CCSD(T)/aug-cc-pVTZ//M06/aug-cc-pVTZ level of theory (Fig. 1). According to the calculated reaction enthalpies, the results of CCSD(T)/aug-cc-pVTZ, G2M(RCC) [2] and multi-reference CASPT2/aug-cc-pVTZ [2] calculations are about 8.0 to 23.6, 0.5 to 9.2 and 38.1 kJ mol-1 different from the corresponding experimental values. Furthermore, there are three transition states that have been reported by G2M(RCC) and/or CASPT2 studies but cannot be found at the CCSD(T) level of theory. With respect to these observations, the related T1 diagnostic values were extracted, which suggested that, except TSn4, all transition states have strong multi-reference characters and should be treated with multi-reference calculations. The strong multi-reference character might be due to the presence of CH radical with the T1 diagnostic value of 0.108, at CCSD(T)/aug-ccpVTZ// M06/aug-cc-pVTZ level of theory. Meantime, the apparent activation energy of the overall reaction, 2H+3NCN formation and 2N+1HCN production were calculated as 90.2(81.6), 90.2 (73.3) and 56.9 kJ mol-1 at the CCSD(T) (CASPT2 [2]) level of theory, which can be compared with the experimental values of 92.7, 71.2 and 53.1 to 58.2 kJ mol-1,respectively. Therefore, both single and multi-reference calculations of this reaction might involve some discrepancies with respect to the experimental results. Regardless of the level of theory, 2N+1HCN, 2H+3NCN, 2N+1HNC, 2H+1Tri.CNN, 2H+3CNN and 3C+2HNN are the most to the least stable products of this reaction, along with 2HNCN, which is the most stable reaction intermediate. See Fig. 1 for more details.

کلمات کلیدی:

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