Application of Bond Energy Density Analysis (Bond-EDA) to Diels–Alder Reaction

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The bond energy density analysis (Bond-EDA), which can evaluate bond energies in molecules by using the results of theoretical calculations, is applied to investigate chemical bonds in Diels–Alder (DA) reaction. Evaluation of the bond energies confirms the bond alternation in the reactant and product quantitatively, and shows that the TS structure is close to the reactant. In the case of regioselective reaction, local stabilities in newly formed bonds in the TS show significant differences, which correspond to the relationship of the bond distances.

The evaluation of chemical bonds in molecules is essential for understanding chemical reaction involving bond formation and breaking. Electronic structure calculations give practical information such as total energies and optimized bond distances at transition states (TSs) as well as reactants and products. Furthermore, those calculations evaluate the bond order based on Mulliken population analysis (MPA).[1] However, it has been difficult to estimate the bond energies and their changes in the chemical reactions.

Recently, we have proposed analysis techniques termed energy density analysis (EDA)[2] and its extension for chemical bonds (Bond-EDA).[3] The Bond-EDA partitions the total energy of a molecule E, computed using Hartree–Fock (HF) or density functional theory (DFT), into atomic and bond energies, E^{A} and E^{AB}, as follows:

$$E = \sum_{A} E^{A} + \sum_{A>B} E^{AB}. \quad (1)$$

The scheme is analogous to MPA and the detailed formulations have been shown in Ref. 3. The Bond-EDA is capable of estimating bond energy quantitatively without significantly additional computation.

Similar techniques have been independently proposed by other groups.[4] Although they resemble each other in definition, the partitioning schemes such as exchange energy are slightly different. Note that we have to assess the validities of analyses in practical applications because the partitioned energies for atom and bond are not observable. However, to the best of our knowledge, their applications are very limited, i.e., only numerical tests for small molecules.

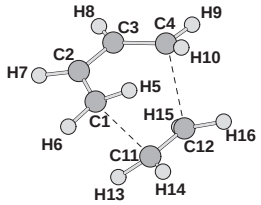

Figure 1. TS structure of the Diels–Alder reaction between butadiene and ethylene.

The aim of this letter is to analyze the chemical reactions based on the bond energies and their variations. For this purpose, we study well-known Diels–Alder (DA) reaction. The Bond-EDA calculations for optimized structures of reactants, TSs, products were performed by linking the original Bond-EDA code with the GAMESS program.[5] The optimized structures were obtained by the use of Gaussian 03 program.[6] All calculations were carried out with B3LYP[7]/cc-pVDZ[8] level.

First, we examine the fundamental DA reaction between *cis*-1,3-butadiene and ethylene. The optimized TS structure and atomic labels are shown in Figure 1. As is well known, the reaction occurs in concerted mechanism keeping C_s symmetry. The bond distances and bond energies for reactant, TS, and product as well as the total energies are summarized in Table 1 (See Supporting Information for the detailed data[10]). The calculated activation barrier and heat of formation are 20.07 and 38.17 kcal/mol, which reasonably match with the experimental ones, 25.1 ± 2 and 38.4 kcal/mol,[9] respectively. Negative values of the bond energies correspond to attractive interactions, namely, chemical bonds. In the reactant, the bond energies of C2–C3 is -149.03 kcal/mol, while those of (C1–C2, C3–C4) and C11–C12 are -206.65 and -212.28 kcal/mol, respectively. Thus, C–C single and double bonds have about -150 and -210 kcal/mol, respectively. These results correspond to bond distances between carbons and are consistent with the previous results.[3] The bond energies of C–H bond range from -105 to -115 kcal/mol.

Table 1. Bond distances and bond energies for reactants, TS, and products in the Diels–Alder reaction between butadiene and ethylene

	Bond distance/Å			Bond energy/kcal·mol^{-1}				
	Reactant	TS	Product	Reactant	TS[a]		Product[a]	
C1–C2, C3–C4	1.342	1.386	1.508	−206.65	−186.13	(+20.51)	−143.15	(+63.49)
C2–C3	1.472	1.407	1.340	−149.03	−166.05	(−17.01)	−188.50	(−39.47)
C1–H5, C4–H9	1.093	1.090	1.108	−107.06	−106.23	(+0.83)	−99.18	(+7.89)
C1–H6, C4–H10	1.092	1.093	1.101	−105.73	−108.11	(−2.39)	−104.68	(+1.05)
C2–H7, C3–H8	1.095	1.094	1.094	−115.62	−118.03	(−2.41)	−118.33	(−2.71)
C1–C11, C4–C12	∞	2.261	1.548	0.00	−33.16	(−33.16)	−147.40	(−147.40)
C11–C12	1.333	1.389	1.554	−212.28	−193.70	(+18.58)	−148.05	(+64.22)
C11–H13, C12–H15	1.094	1.090	1.102	−110.79	−111.33	(−0.54)	−104.69	(+6.11)
C11–H14, C12–H16	1.094	1.092	1.102	−110.79	−110.07	(+0.73)	−102.26	(+8.53)
Total				−147102.52	−147082.45	(+20.07)	−147140.68	(−38.17)

[a]Values in parentheses are differences from the reactant.

Table 2. Bond energies for reactant, TS, and product in the Diels–Alder reaction between methoxybutadiene and acrolein in kcal/mol

	Reactant	ortho isomer				meta isomer			
		TS[a]		Product[a]		TS[a]		Product[a]	
C1–C2	−209.17	−181.35	(+27.82)	−140.69	(+68.48)	−182.60	(+26.56)	−142.32	(+66.85)
C2–C3	−151.26	−165.57	(−14.31)	−180.12	(−28.86)	−165.67	(−14.41)	−179.53	(−28.27)
C3–C4	−174.17	−158.84	(+15.32)	−130.25	(+43.92)	−159.94	(+14.22)	−134.59	(+39.58)
C1–C11	0.00	−54.74	(−54.74)	−144.03	(−144.03)	−34.89	(−34.89)	−133.40	(−133.40)
C4–C12	0.00	−17.39	(−17.39)	−128.13	(−128.13)	−48.26	(−48.26)	−143.24	(−143.24)
C11–C12	−179.96	−162.55	(+17.41)	−135.66	(+44.30)	−161.59	(+18.37)	−129.16	(+50.80)
Total	−290021.08	−290006.60	(+14.48)	−290047.06	(−25.98)	−290000.37	(+20.70)	−290050.73	(−29.66)

[a]Values in parentheses are differences from the reactant.

In the product, the bond energies of C1–C2, C3–C4, and C11–C12 are close to −150 kcal/mol, which correspond to C–C single bond. That of C2–C3 is −188.50 kcal/mol, of which the absolute value is slightly smaller than those of C–C double bonds in the reactant. The changes of C–H bond are relatively small. The newly formed bonds, C1–C11 and C4–C12, have −147.40 kcal/mol, which correspond to C–C single bond. Thus, the variations of the bond energies are consistent with the bond alternation appeared in the reaction.

In the TS, the bond energies are closer to those of the corresponding bonds in the reactant than those in the product. It agrees with the resemblance of the bond distances between the TS and the reactant. The newly formed bonds, C1–C11 and C4–C12, have the bond energies of −33.16 kcal/mol of which the absolute values are considerably smaller than those of product. Those distances are 2.261 Å in the TS, which are significantly longer than those in the product, 1.548 Å. Therefore, the bond energy changes are also consistent with the geometrical changes.

Next, we investigate the DA reaction between 1-methoxy-1,3-butadiene and acrolein. This reaction is illustrative of regioselectivity, that is, yields ortho and meta isomer. The ortho isomer is known to be a main product despite of less thermodynamic stability. Figure 2 shows the TS structure of two isomers (See Supporting Information[10]). Since the reaction proceeds in asynchronous concerted mechanism due to the substituents, the geometries are asymmetric. In particular, the distortion in the ortho isomer is enormous.

Table 2 shows the bond energies of C–C bonds in the cyclo ring at product and total energies (See Supporting Information for the detailed data[10]). First, we focus on the products. The calculated heat of formation indicates that the ortho product is less stable than the meta one. Whereas the differences of bond distance between ortho and meta products are small, within 0.01 Å, the bond energies are somewhat different. For example, while the bond energy of C1–C11 in the ortho product is −144.03 kcal/mol, that in the meta product is −133.40 kcal/mol. The bond energies of C4–C12 in the ortho and meta products are −128.13 and −143.24 kcal/mol, respectively. These results might be related with the repulsion between bulky substituents.

Let us now discuss on the TSs. The calculated activation energy for the ortho isomer is lower than the meta one. The bond distances as well as the bond energies between two TSs show small differences except for newly formed bonds, C1–C11 and C4–C12. The bond energy of C1–C11 in the ortho TS is −54.74 kcal/mol, of which absolute value is larger than that in the meta TS, −34.89 kcal/mol. On the other hand, the bond energies of C4–C12 in the ortho and meta TSs are −17.39 and −48.26 kcal/mol, respectively. The absolute value of C4–C12 in the ortho TS is significantly smaller than that of meta TS. These results are correlated with bond distances.

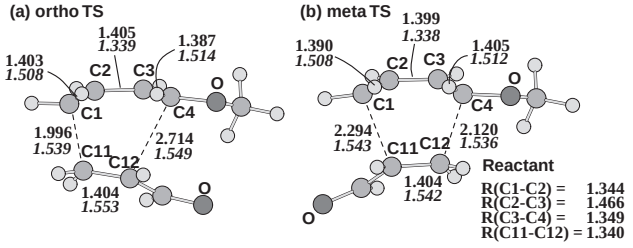

Figure 2. TS structure of the Diels–Alder reaction between methoxybutadiene and acrolein: (a) ortho and (b) meta isomer. The bond distances of TS (upper) and product (lower) are also shown in Å.

In conclusion, by investigating the bond energies that estimated by Bond-EDA, the DA reaction involving bond formation and alternation, and stabilities of the formed bonds in TS are understood quantitatively. In particular, the nature of regioselectivity is understood by the difference in newly formed bond energies at the TSs. Therefore, it is confirmed that the Bond-EDA provides valuable information for investigating a chemical reaction.

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10 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/.

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