Electron Reorganization along the Intrinsic Reaction Coordinate in 1,3-Dipolar Cycloaddition

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The population analysis along the intrinsic reaction coordinate (IRC) has been performed, taking 1,3-dipolar cycloaddition as an example. By calculating the derivatives of the Mulliken atomic charge and the Giambiagi bond order with respect to nuclear motions analytically, a decomposition of the derivatives into two components, the density derivative term and the overlap derivative term, has been demonstrated. The density derivative term represents the effect of redistribution of electrons due to the nuclear motion. By using this method, the electronic character of asynchronous bond formation in 1,3-dipolar addition between fluminic acid and acetylene has been revealed clearly.

1. Introduction

Quantum chemistry has developed remarkably and has become a useful method in various areas of chemistry. Not only the energies and structures of various molecular species but also reaction paths can easily be calculated with high accuracy, using recent powerful computers and many excellent methods of calculations.[1] Here, we should point out some problems that remain to be solved. The first point is that we have not established yet the method for a qualitative understanding of the wave function with high accuracy. The second point is that we do not know how to connect the change in wave function along the reaction coordinate with the enhancement or depression of chemical reactivity. To clarify these subjects, some attractive attempts, such as the valence bond (VB) type approach,[2−7] the density functional approach,[8] and the atoms in molecules (AIM) approach,[9] have been made.

An attempt in this line is the population analysis.[10−36] This concept was originally proposed by Mulliken[10] and has been generalized and developed by other groups. Wiberg introduced the bond order indices for the CNDO molecular orbital (MO) method,[11] and this concept has been generalized by Armstrong et al.[12,13] and independently by Borisova and Semenov.[14] Gopinathan and Jug also proposed the definition of valency of an atom within the framework of the zero-differential-overlap approximation.[15] On the other hand, Giambiagi et al.[16,17] proposed the bond order indices using the extended Hückel MOs, and Mayer[18−22] has extended this idea to the ab initio MOs. The multicenter bond indices have recently been proposed,[23−26] and their physical meanings and the relations among those quantities have also been discussed.[27−29]

The population analysis has an advantage of its easy treatment. Therefore, it is often used to describe the formation or cleavage of chemical bonds and the change in atomic charges along the reaction coordinate.[30−36] When a linear combination of atomic orbitals (LCAO) for MOs is used, both the gross atomic charge defined by Mulliken and the bond order suggested by Giambiagi et al. and Mayer are generally made up of the bond-order matrix[37] and the overlap matrix. The question we have to ask here is, what is the cause of the change in these quantities along the reaction coordinate? The change originates from two different contributions: the change in the bond-order matrix with keeping the overlap matrix unaltered and the change in the overlap matrix with keeping the bond-order matrix unaltered. The change in the bond-order matrix arises from the electron redistribution caused by nuclear motions. On the other hand, the change in the overlap matrix arises from the LCAO formalism. In usual quantum chemical calculations, each AO is centered on the nucleus of an atom, except for the cases with the floating orbital or the plane-wave basis set. These two contributions must be classified. These kinds of divisions have already been introduced in the force theory. Nakatsuji et al. investigated the analytical second derivative of the potential energy satisfying the Hellmann−Feynman theorem and discussed the role of each term in the second derivative of the Hartree−Fock energy.[38]

In the present study, the derivatives of the gross atomic charge, the bond order, and the atom valence with respect to the nuclear positions are calculated analytically along the intrinsic reaction coordinate (IRC). This method is applied to a simple 1,3-dipolar cycloaddition reaction between fulminic acid and acetylene. The 1,3-dipolar cycloaddition reactions not only are important from a synthetic viewpoint but also have attracted theoretical interests with respect to the reactivity and the regioselectivity. Some interesting studies have recently been done using the density functional theory (DFT) and a hard and soft acids and bases principle (HSAB) model for 1,3-dipolar cycloaddition reactions.[39,40] Chandra et al.[39] investigated the cycloaddition reactions between 1,3-dipoles and dipolarophiles and observed that the hardness went through a minimum along the reaction coordinate. Méndez et al.[40] have used the formalism of interaction energy in terms of the density functional theory and suggested that the electrophilic nature of the 1,3-dipole and the nucleophilic nature of dipolarophiles were important. Furthermore, they indicated that reshuffling of the charge distribution should be more important than charge-transfer processes. On the other hand, Karadakov et al. studied the mechanism of 1,3-dipolar cycloaddition in terms of the valence-bond theory.[41] They examined the spin-coupled wave function along the reaction coordinate around the transition state and

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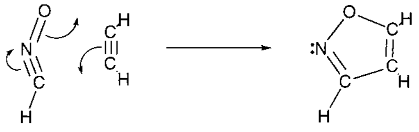
concluded that the following description I should be more plausible than II, by which the mechanism of 1,3-dipolar cycloaddition was usually represented. Having their discussion in mind, the reaction mechanism is investigated here by means of the population analysis using the Hartree−Fock electron density.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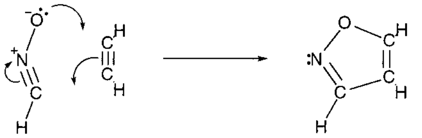
(II)

2. Methods of Calculation

In this study, the LCAO-MO approximation for the Roothaan−Hall equation[42] is used:

$$\phi_i(\mathbf{r}) = \sum_{\mu} c_{\mu i}\chi_\mu(\mathbf{r}) \tag{1}$$

where $c_{\mu i}$ is the coefficient of the AO $\chi_\mu(\mathbf{r})$ in the ith MO $\phi_i(\mathbf{r})$. Within this formalism, the bond-order matrix **P** consists of the elements $P_{\mu\nu}$ with respect to the atomic orbital:

$$P_{\mu\nu} = 2\sum_{i}^{\mathrm{occ}} c_{\mu i}c_{\nu i} \tag{2}$$

According to the Mulliken's population analysis,[10] the gross atomic charge of atom A, q_A, is

$$q_A = \sum_{\mu}^{A} (\mathbf{PS})_{\mu\mu} \tag{3}$$

where $\boldsymbol{S}$ is the overlap matrix composed with the elements $S_{\mu\nu}$:

$$S_{\mu\nu} = \int \chi_\mu(\mathbf{r})\,\chi_\nu(\mathbf{r})\,\mathrm{d}\mathbf{r} \tag{4}$$

Therefore, the Mulliken gross atomic charge naturally corresponds to the partitioning of electron density $\rho(\mathbf{r})$ with respect to AO:[22]

$$\begin{aligned} N &= \int \rho(\mathbf{r})\,\mathrm{d}\mathbf{r} \\ &= \int \sum_{\mu}\sum_{\nu} P_{\mu\nu}\chi_\mu(\mathbf{r})\chi_\nu(\mathbf{r})\,\mathrm{d}\mathbf{r} \\ &= \sum_{\mu}\sum_{\nu} P_{\mu\nu}S_{\mu\nu} \\ &= \sum_{\mathrm{A}} q_A \end{aligned} \tag{5}$$

Another type of analysis was originally introduced by Wiberg and generalized by other groups. Giambiagi et al. and Mayer defined the bond-order index between the atom A and the atom B:

$$I_{AB} = \sum_{\mu\in A}\sum_{\nu\in B} (\mathbf{PS})_{\mu\nu}(\mathbf{PS})_{\nu\mu} \tag{6}$$

and the total valence of the atom A:

$$V_A = \sum_{B\neq A} I_{AB} \tag{7}$$

This corresponds to the partitioning of the exchange part of the second-order density matrix:

$$N = \frac{1}{2}\int \rho_1(\mathbf{r}_1,\mathbf{r}_2)\,\rho_1(\mathbf{r}_2,\mathbf{r}_1)\,\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2 \tag{8}$$

Therefore, the relation between the atom valence and Mulliken's gross atomic charge is given by

$$2q_A = V_A + \sum_{\mu\in A}\sum_{\nu\in A} (\mathbf{PS})_{\mu\nu}(\mathbf{PS})_{\nu\mu} \tag{9}$$

Although the population analysis by the partitioning of higher-order density matrices has been proposed,[23−28] it is beyond the scope of this paper.

Now, the derivatives of the Mulliken gross atomic charge, the Giambiagi bond order and the atom valence with respect to the Cartesian coordinates of the nucleus (X_i, Y_i, Z_i) (i = 1, 2, ..., N) are given by

$$\frac{\partial q_A}{\partial X_i} = \sum_{\mu}^{A}\left(\left(\frac{\partial \mathbf{P}}{\partial X_i}\mathbf{S}\right)_{\mu\mu} + \left(\mathbf{P}\frac{\partial \mathbf{S}}{\partial X_i}\right)_{\mu\mu}\right) \tag{10}$$

$$\begin{aligned} \frac{\partial I_{AB}}{\partial X_i} = {} & \sum_{\mu\in A}\sum_{\nu\in B}\left(\left(\frac{\partial \mathbf{P}}{\partial X_i}\mathbf{S}\right)_{\mu\nu}(\mathbf{PS})_{\nu\mu} + (\mathbf{PS})_{\mu\nu}\left(\frac{\partial \mathbf{P}}{\partial X_i}\mathbf{S}\right)_{\nu\mu}\right) + \\ & \sum_{\mu\in A}\sum_{\nu\in B}\left(\left(\mathbf{P}\frac{\partial \mathbf{S}}{\partial X_i}\right)_{\mu\nu}(\mathbf{PS})_{\nu\mu} + (\mathbf{PS})_{\mu\nu}\left(\mathbf{P}\frac{\partial \mathbf{S}}{\partial X_i}\right)_{\nu\mu}\right) \end{aligned} \tag{11}$$

The term which contains the derivative $\partial\mathbf{P}/\partial X_i$ is called the density derivative term, while the contribution from $\partial\mathbf{S}/\partial X_i$ is called the overlap derivative term. Moreover, we have

$$\frac{\partial V_A}{\partial X_i} = \sum_{B\neq A}\frac{\partial I_{AB}}{\partial X_i} \tag{12}$$

The derivative of the overlap matrix $\partial\mathbf{S}/\partial X_i$ consists of the elements $\partial S_{\mu\nu}/\partial X_i$:

$$\frac{\partial S_{\mu\nu}}{\partial X_i} = \frac{\partial}{\partial X_i}\int \chi_\mu(\mathbf{r})\,\chi_\nu(\mathbf{r})\,\mathrm{d}\mathbf{r} \tag{13}$$

and the derivative of the bond-order matrix $\partial\mathbf{P}/\partial X_i$ consists of the elements $\partial P_{\mu\nu}/\partial X_i$, which can be solved analytically:

$$\frac{\partial P_{\mu\nu}}{\partial X_i} = -2\sum_{l,m}^{\mathrm{occ}} c_{\mu l}c_{\nu m}S_{ml}^{(1)} + 2\sum_{l}^{\mathrm{occ}}\sum_{a}^{\mathrm{unocc}} {u_{al}}^{(1)}(c_{\mu l}c_{\nu a} + c_{\mu a}c_{\nu l}) \tag{14}$$

where $S_{ml}^{(1)}$ is the derivative of the MO overlap integral between the MOs ϕ_l and ϕ_m and ${u_{al}}^{(1)}$ is a mixing coefficient between the occupied and unoccupied MOs. The value ${u_{al}}^{(1)}$ is solved by the coupled-perturbed Hartree−Fock (CPHF) equation.[43−45] Nakatsuji et al. interpreted the physical meanings of each term in eq 14 as the renormalization term and the relaxation term in their force theory.[38] The first term on the right-hand side in eq 14, which is called the renormalization term, works to keep the total wave function normalized. The second term, which is called the relaxation term, shows the rearrangement of the charge distribution in the reaction system by mixing the occupied and unoccupied orbitals.

It should be noted that the total of Mulliken gross atomic charges must be conserved,

$$\sum_{A}^{\text{all}} \frac{\partial q_A}{\partial X_i} = 0 \qquad (15\ )$$

As shown in eq 10, the derivative of the Mulliken gross atomic charge is given by two different contributions. The first term on the right-hand side represents the contribution from the change in the bond-order matrix without the change in the overlap matrix, that is to say, the redistribution of electrons due to the nuclear motion. This term is called the density derivative term. What is more, this term is able to be divided into two terms: the renormalization term and the relaxation term. On the other hand, the second term represents the contribution from the change in the overlap without the change in AO coefficients, and hence, this is called the overlap derivative term.

By transforming the derivatives with respect to the $3N$ Cartesian coordinates into those with respect to the $3N$ mass-weighted Cartesian coordinates x_i ($i = 1, 2, ..., 3N$), the derivative of the Mulliken gross atomic charge with respect to the IRC is given by

$$\frac{\mathrm{d}q_A}{\mathrm{d}s} = \sum_{i=1}^{3N} \frac{\partial q_A}{\partial x_i} \frac{\mathrm{d}x_i}{\mathrm{d}s} = \sum_{i=1}^{3N} \frac{\partial q_A}{\partial x_i} \frac{\partial V/\partial x_i}{\mathrm{d}V/\mathrm{d}s} \qquad (16)$$

where V is the adiabatic potential of the reaction system and where the IRC equation[46]

$$\frac{\mathrm{d}x_i}{\mathrm{d}s} = \frac{\partial V/\partial x_i}{\mathrm{d}V/\mathrm{d}s} \qquad (i = 1, 2, ..., 3N) \qquad (17)$$

has also been used. In the same way, the derivative of the bond order is given by

$$\frac{\mathrm{d}I_{AB}}{\mathrm{d}s} = \sum_{i=1}^{3N} \frac{\partial I_{AB}}{\partial x_i} \frac{\partial V/\partial x_i}{\mathrm{d}V/\mathrm{d}s} \qquad (18)$$

The derivatives of the atom valences are also defined in a similar fashion. These derivatives are divided into the redistribution part of the electron density $\rho(\mathbf{r})$ and the exchange part of the second-order density matrix along the IRC.

The restricted Hartree−Fock scheme with Pople's 6-31G** basis set[47] was used for calculations. The 6-31G** basis set is known to give reliable results for the population analysis. The geometry optimization and analytical frequency analysis with CPHF calculations were performed with the *Gaussian94* program package.[48] The IRC calculations by the Gonzalez−Schlegel algorithm[49] with the step size 0.01 amu$^{+1/2}$·bohr were done with the *GAMESS* program.[50]

3. Results and Discussion

Concerning the 1,3-dipolar cycloaddition reaction, Huisgen[51] proposed the concerted single step reaction mechanism, while Firestone[52] proposed that this reaction should take place in two steps via a biradical intermediate. Schlegel et al.[53] performed an MC−SCF study of three different 1,3-dipolar cycloaddition reactions and concluded that the concerted single step pathway was preferred to the biradical path. Therefore, the concerted single step reaction is considered here in our study.

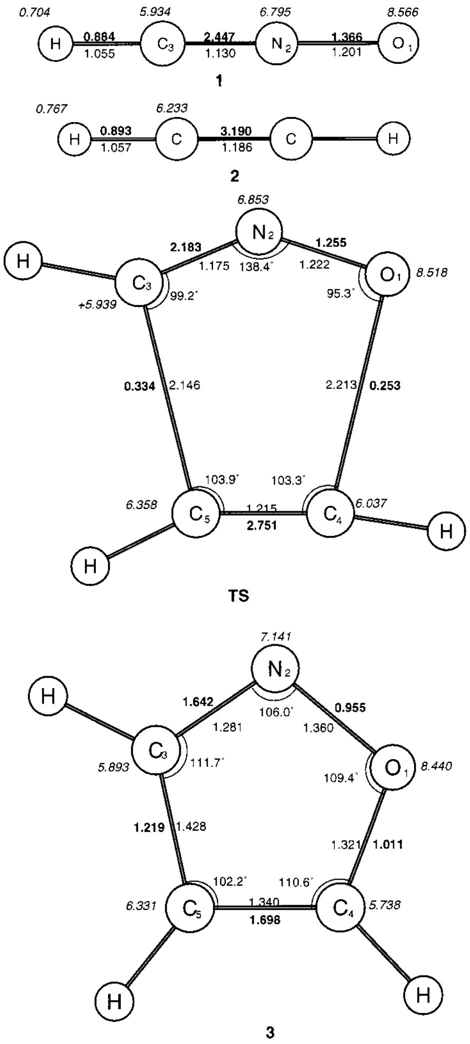

Figure 1. Optimized geometries. Bond lengths and bond angles are given in angstroms and degrees, respectively. The bond orders are represented in boldface, and the gross atomic charges are in italic.

TABLE 1: Total Energies at the HF/6-31G Level**

species	symmetry	total energy (au)	ZPE[a] (kcal/mol)
1 HCNO	$C_{\infty v}$	−76.82184	12.77
2 C_2H_2	$D_{\infty h}$	−167.63260	16.39
TS	C_s	−244.39925	29.84
3 isoxazole	C_s	−244.59419	35.20

[a] Zero-point energy (ZPE) scaled by a factor of 0.89.

Energy and Geometries. The optimized structures of the reactants, fulminic acid **1** and acetylne **2**, the transition state **TS**, and the product, isoxazole **3**, are shown in Figure 1. The total energies are presented in Table 1. The activation energy of this reaction is 35.50 kcal/mol, and the reaction energy is exothermic by 81.65 kcal/mol (including zero-point energy correction). In literature, it has been reported that the activation energy is 26.0 kcal/mol and the reaction energy is 66.9 kcal/mol (exothermic) at the MRCI //MCSCF/4-31G level.[53] Another study[54] has shown that the activation energy is 11.0 kcal/mol and the reaction energy is 77.7 kcal/mol (exothermic) at the MP4(SDTQ)/6-311G(d,p)//HF/6-311G(d,p) level. More recently, it has been reported that the activation energy is 12.2kcal/mol at the CASPT2//CAS(6,6)/6-31G* level.[41]

Figure 2 shows the potential energy profile along the IRC. At the point $s = 5.9$, the IRC connects practically to the product. The changes in bond lengths and bond angles along the IRC

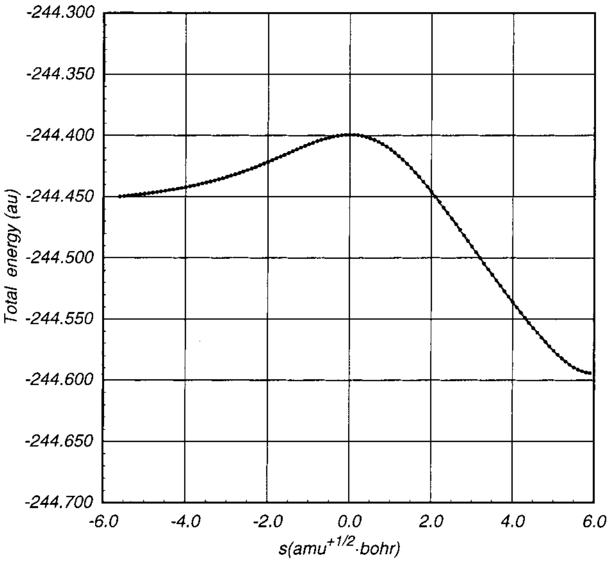

Figure 2. Potential energy curve along the IRC.

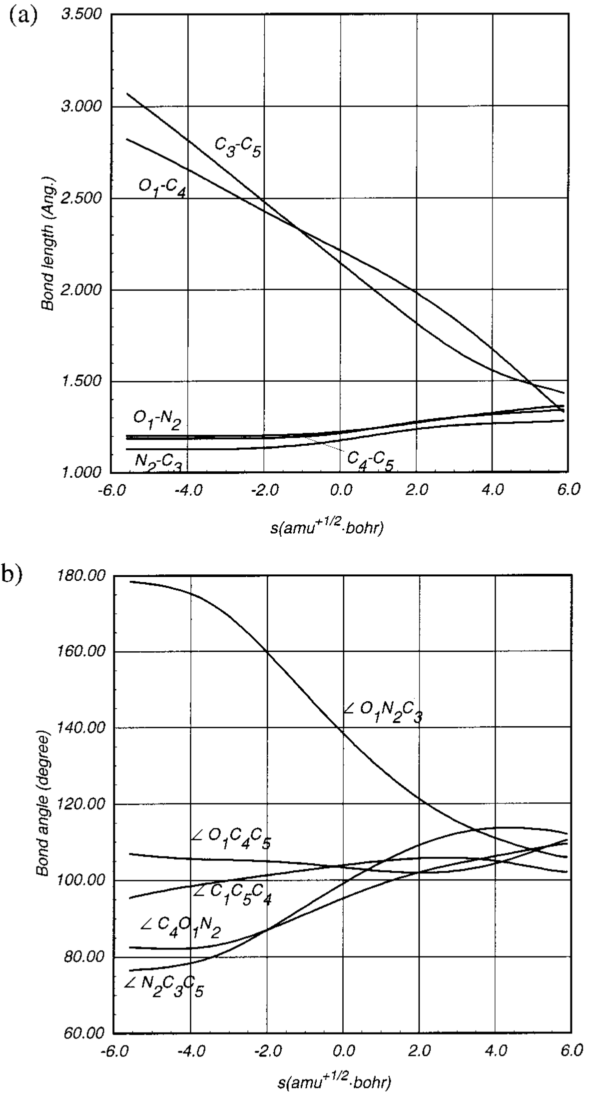

Figure 3. Geometrical changes along the IRC. The numbering of the atoms corresponds to those in Figure 1. The bond lengths are given in angstroms and the bond angles in degrees.

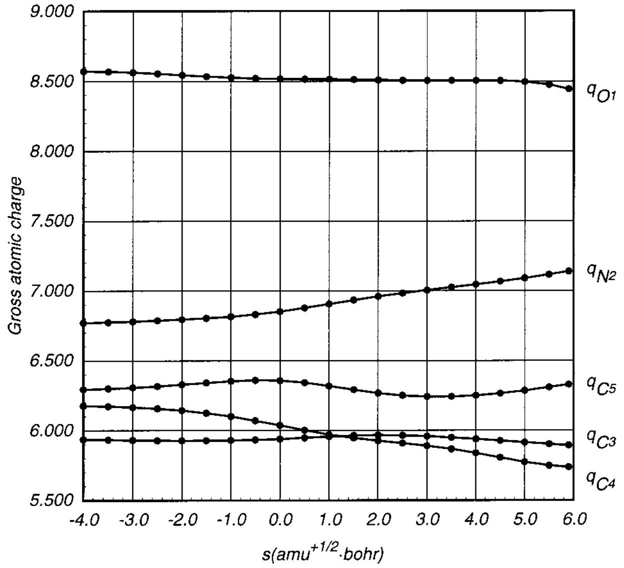

Figure 4. Gross atomic charge profile along the IRC.

are shown in Figure 3a,b, respectively. Here, the numbering of the atoms is the same as in Figure 1. Although the bond length of O_1-C_4 is shorter than that of C_3-C_5 in the initial reaction coordinate ($s < -1.5$), the bond length of C_3-C_5 is shortened rapidly, while the O_1-C_4 bond length does not become shorter rapidly until the coordinate reaches the transition state ($s > 2.0$). These different shapes reflect nonsynchronous bond formations. The bond angles of $\angle C_3C_5C_4$ and $\angle O_1C_4C_5$ do not change much along the IRC. Therefore, O_1 and C_3 atoms of fulminic acid attack the carbon atoms of the acetylene from the same directions, bending the $\angle O_1N_2C_3$ angle of the fulminic acid along the IRC, as shown in Figure 3b. On the other hand, the C_4-C_5 bond in acetylene and the O_1-N_2 and N_2-C_3 bond in fulminic acid are lengthened slightly after the transition state is reached.

Mulliken Charges. Figure 4 shows the gross atomic charges calculated along the IRC. The gross charge of the O_1 atom, q_{O1}, does not change so much except for the final stage on the reaction coordinate ($s > 5.0$). The gross charge of the C_3 atom does not change much either. The largest change in the gross charge in the fulminic acid part is seen on the N_2 atom. The charge q_{N2} of the N_2 atom is 6.795 in fulminic acid and becomes 7.141 in the product. The C_4 and C_5 atoms of acetylene show different charge profiles. The charge q_{C4} of the C_4 atom decreases monotonically. In contrast, the charge q_{C5} of the C_5 atom increases both at the initial stage and at the final stage on the reaction coordinate.

To investigate the change in the gross charges of each atom in detail, the derivatives of these gross charges, q_{O1}, q_{N2}, and q_{C4} with respect to the IRC are shown in Figure 5a−c, respectively. In the case of the Mulliken gross charge, it is shown that the total derivative values behave in a way similar to the density derivative term. Moreover, it is seen that the two components of the density derivative term in the atomic charges exhibit different patterns. In the density derivative term of the N_2 atomic charge, both the relaxation term and the renormalization term make the N_2 atomic charge increase. On the other hand, the decrease in the density derivative term of the O_1 atom is dominated by the renormalization term. In the case of the density derivative term of the C_4 atomic charge, the renormalization term and the relaxation term have different effects from each other. That is to say, the relaxation term reduces the atomic charge, while the renormalization term increases slightly the atomic charge around the transition state. In addition, it should be noted that the trend of the charge redistribution in the final coordinate region is different from that around the transition state.

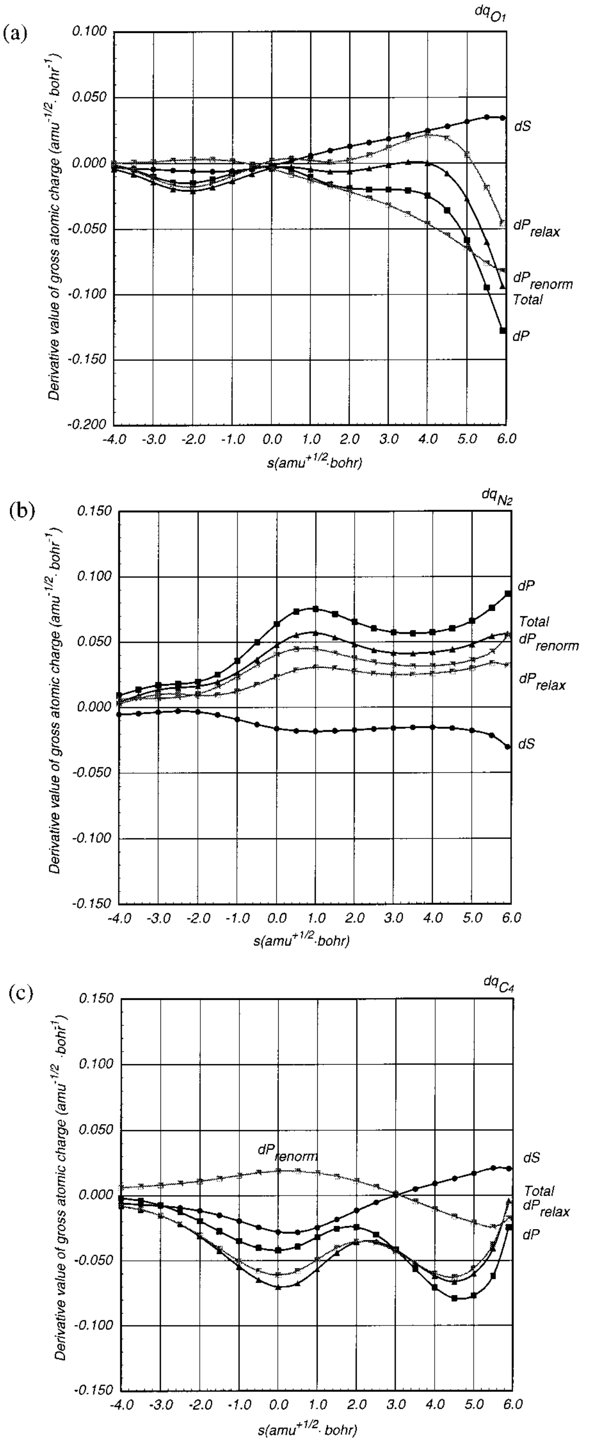

Figure 5. Derivatives of gross atomic charges (a) q_{O1}, (b) q_{N2}, and (c) q_{C4} with respect to the IRC, respsctively. The density derivative term, which consists of the renormalization term (dP_{renorm}) and the relaxation term (dP_{relax}), is plotted as ■. The overlap derivative term is plotted as ●, and the total derivative values as ▲.

Bond Orders and Atom Valences. Figure 6 shows the bond order profile along the IRC. In the fulminic acid part, the bond order between the O_1 atom and the N_2 atom, I_{O1N2}, is 1.366, and the bond order between the N_2 atom and the C_3 atom, I_{N2O3}, is 2.447. These values decrease gradually as the reaction proceeds and the bond orders I_{O1N2} and I_{N2C3} become 0.955 and 1.642 in the product, respectively. The bond order I_{C4C5}, which represents the triple bond in acetylene, is 3.190 initially and is 1.698 in the product. On the other hand, the bond orders I_{O1C4} and I_{C3C5}, which show the formation of new chemical bonds, increase along the IRC. It is found that I_{C3C5} increases more steeply than I_{O1C4}. As a result, the bond order I_{C3C5} is larger than I_{O1C4} in the product.

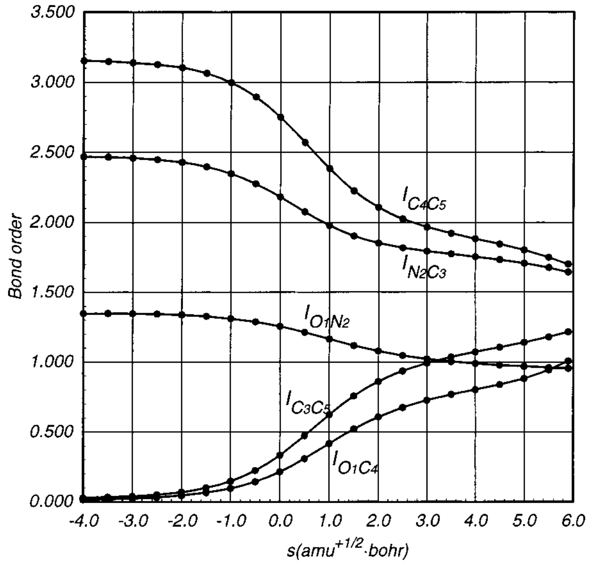

Figure 6. Bond order profile along the IRC.

The derivatives of the bond orders, I_{O1N2}, I_{N2C3}, I_{O1C4}, and I_{C3C5}, with respect to the IRC are shown in Figure 7a–d, respectively. First, we examine the derivatives of bond orders I_{O1N2} and I_{N2C3}, which decrease along the IRC. In these, the overlap derivative term dS contributes to the decrease in bond orders on the whole reaction stage. On the other hand, the density derivative term dP contributes to the decrease most around the transition state, although the two terms, dP_{renorm} and dP_{relax}, show different contributions. The renormalization term increases the bond orders slightly, while the relaxation term contributes intensely to a decrease in the bond orders. The derivative value of I_{O1N2} decreases and reaches the minimum at $s = 1.0$. On the other hand, the derivative of I_{N2C3} decreases more steeply than that of I_{O1N2} until the reacting system comes to the transition state and reaches the minimum at $s = 0.5$, since the large negative contribution of the relaxation term dominates the density derivative term. Consequently, the N_2-C_3 bond is more sensitive to the nuclear motion than the O_1-N_2 bond is around the transition state. This is connected with the π-electron state of the fulminic acid in the initial reaction coordinate. Namely, a part of electrons utilized to form the N_2-C_3 triple bond in the initial state should be converted to the lone pair of electrons on the N_2 atom in the product. After passing the minimum point, the derivative of I_{O1N2} comes close to zero in the product region, while that of I_{N2C3} comes close to zero at $s = 3.0$ and decreases again by the effect of the relaxation term dP_{relax}. The derivative of I_{C4C5} does not become zero in the final stage on the reaction coordinate either.

We compare next the derivatives of I_{O1C4} and I_{C3C5}. In both of the two terms, the overlap derivative term dS contributes to the increase in bond orders. As to the density derivative term, the relaxation term dP_{relax} increases these bond orders, while the renormalization term dP_{renorm} decreases these bond orders. As a result, the density derivative term dP causes these bond orders to increase. Before the transition state, the derivative of I_{C3C5} is larger than that of I_{O1C4} and I_{C3C5} increases more steeply than I_{O1C4}, as noted above. In the final stage, both of the derivatives also increase. It is interesting to note that the trend is different from that around the transition state. That is, although the density derivative term is a main component until the

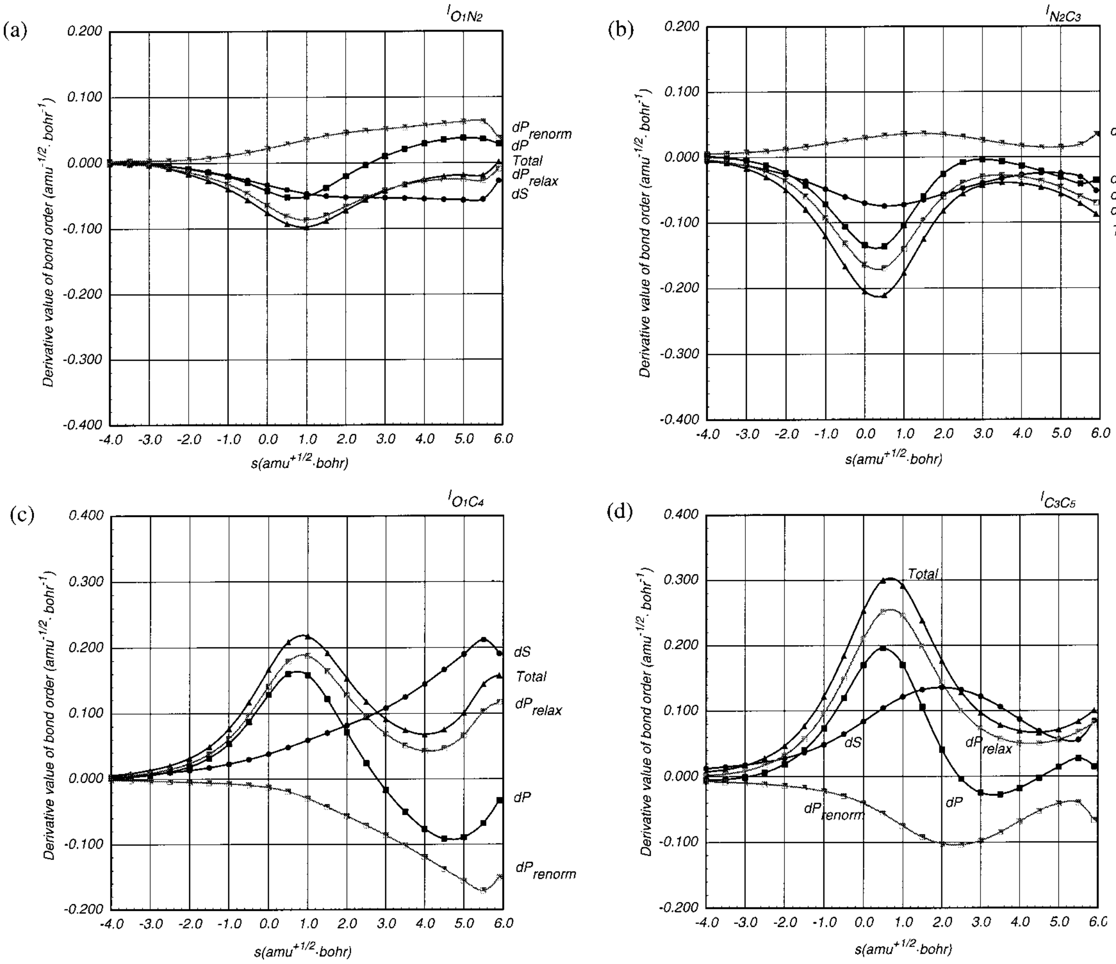

Figure 7. Derivatives of bond orders (a) I_{O1N2}, (b) I_{N2C3}, (c) I_{O1C4}, and (d) I_{C3C5} with respect to the IRC, respectively.

reacting system reaches the transition state, showing that the electron redistribution forms new bonds, the overlap derivative term is found to be the main part at the final stage. This shows that the nuclear motion is forced to complete the bond formation at the final stage.

Then, we have investigated components of the bond order I_{O1C4} in detail. We divide the atomic orbitals of the O_1 and C_4 atoms into *s*-type atomic orbitals (*s*), σ-orbitals composed of the *p* and *d* atomic orbitals, which have extension in the C_s mirror plane (pd_σ), *p* and *d* orbitals which are perpendicular to the mirror plane (pd_π), and other orbitals. We decompose the bond order I_{O1C4} into AO bond orders. Figure 8 shows the main elements of I_{O1C4}. The major part of I_{O1C4} is $pd_\sigma{-}pd_\sigma$, $I_{\mathrm{pd\sigma-pd\sigma}}$, until the transition state is reached. This shows that the original $\pi{-}\pi$ interaction in the C_s plane initiates the bond formation at an early stage. On the other hand, the $pd_\pi{-}pd_\pi$ interaction which leads to formation of the π bond in the product is shown to occur at the final stage. The major derivative term is the density derivative of $I_{pd\sigma-pd\sigma}$ before the transition state. On the other hand, the overlap derivative terms having large values are not ascribed to some particular atomic orbital at the final stage.

We have analyzed the derivatives of the bond order by dividing them into the overlap derivative term and the density derivative term as mentioned above. We can discuss the bond formation also from another point of view. For the derivatives of bond orders presented in Figure 7, the overlap derivative term d*S* and the renormalization term dP_{relax} of the density derivative term exhibit the opposite behaviors, and they are nearly counterbalanced with each other along the IRC. Therefore, the total derivative value depends on the relaxation term of the density derivative term. That is, the change in bond orders originates from the relaxation of electron density.

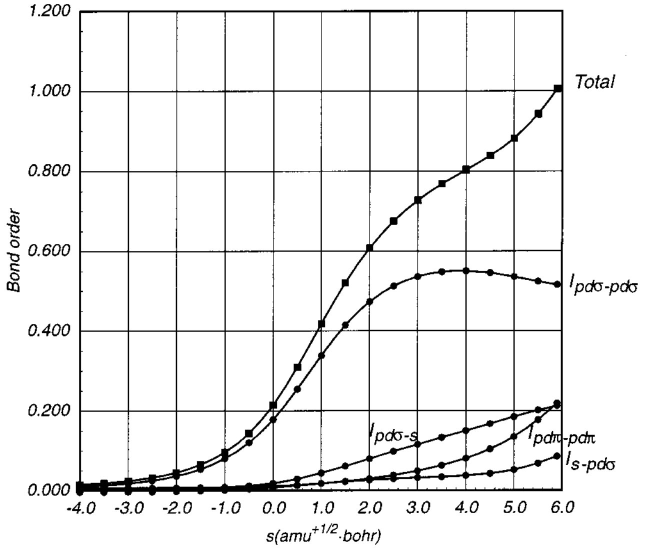

Figure 8. Elements of the bond order I_{O1C4} along the IRC.

The atom valences are shown in Figure 9. While the gross charge of the N_2 atom increases gradually with the progress of the reaction, as shown in Figure 4, the atom valence, V_{N2}, decreases around the transition state. This indicates that the second term of the right-hand side in eq 9 changes dynamically to break the $N_2{-}C_3$ triple bond and place a lone pair of electrons on N_2. The decrease in V_{N2} is caused both by the

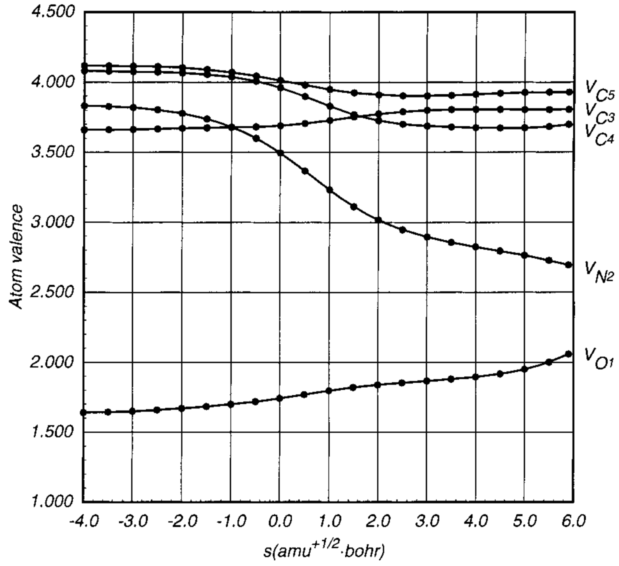

Figure 9. Atom valence profile along the IRC.

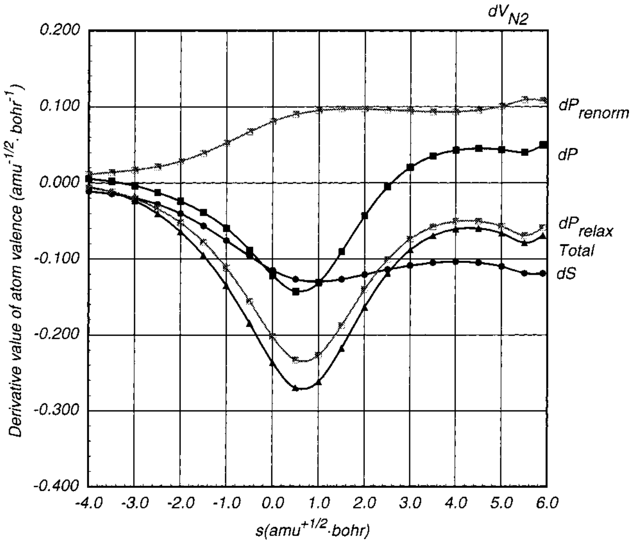

Figure 10. Derivative of N_2 atom valence with respect to the IRC, respectively.

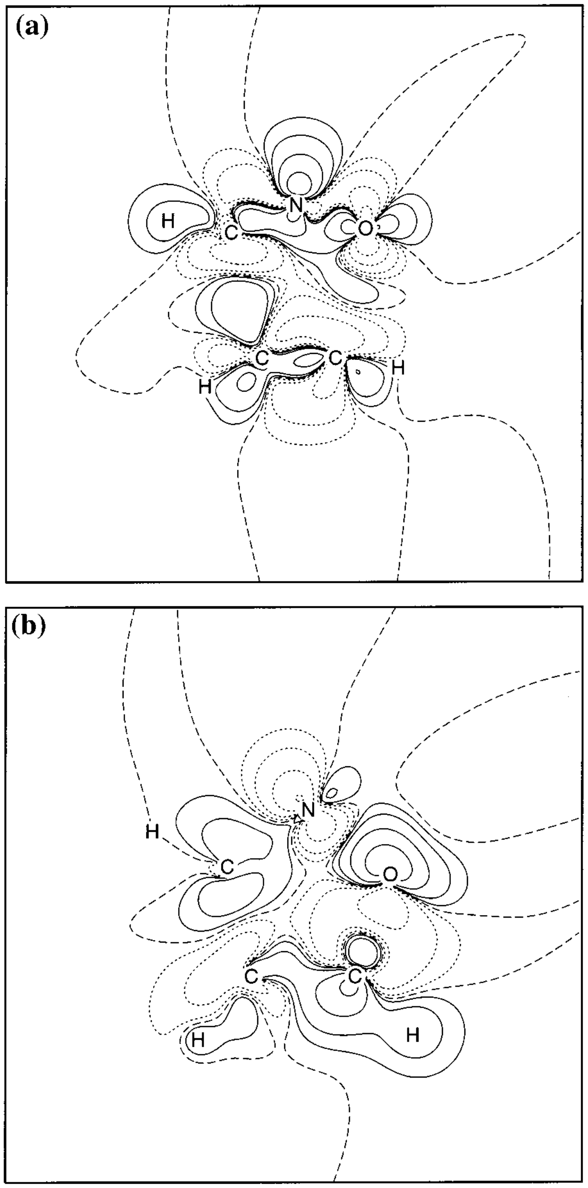

Figure 11. Contour maps of the density differential with respect to the IRC $\Sigma_{r,s}(dP_{rs}/ds)\chi_r(\mathbf{r})\ \chi_s(\mathbf{r})$ in (a) TS and (b) $s = 5.5$ on the C_s plane. Contours are drawn by (—) 0.3, 0.1, 0.03, 0.01, 0.003, and 0.001; (--) 0.0; and (···) −0.001, −0.003, −0.01, −0.03, −0.1, and −0.3.

density derivative term and by the overlap derivative term, as shown in Figure 10. The O_1 atom valence, V_{O1}, increases gradually along the IRC. Because the gross charge of this atom changes little, the electron population of the lone-pair orbital decreases gradually. This gives rise to the electronic mechanism as described by II of the transition state, within the Hartree−Fock scheme of electron density.

We also compare aspects of derivative values of bond orders to the contour map of $\Sigma_{r,s}(dP_{rs}/ds)\chi_r(\mathbf{r})\chi_s(\mathbf{r})$, which is called the density differential.[38] It corresponds to the density derivative term in the present approach. In Figure 11a,b, the contour maps of the density differential with respect to the IRC at TS and at $s = 5.5$ are shown, respectively. At the final stage around $s = 5.5$, the decrease in electron density around the O_1-C_4 bond area of I_{O1C4} arises from the decrease in the density derivative term. In the present method, it is also possible to describe the bond formation or cleavage in terms of the change in bond orders between some particular pair of atomic orbitals.

Finally we refer to the other relevant study and mention a limitation of the method used in this study. Balawender et al.[55] have studied the derivatives of the molecular valence in order to measure the aromaticity of five-membered heterocycles recently. They treated the derivatives of the molecular valence, which consists of the sum of each atom valences, with respect to the electron number N. The derivatives with respect to the IRC are investigated in the present study. We believed that analysis of the variation in the electronic structure along the reaction coordinate is also important.[56,57] It is well-known that Mulliken's population analysis gives strange results when diffuse functions are applied in the calculation of the wave function. Some useful localization methods have been introduced to overcome this problem.[58−60] These localization methods may describe the variation of bonds along the reaction coordinate suitably. Extension of the present approach to multicentered bond-order indices which has been proposed recently is straightforward.[23−26] The present calculation has been performed within the Hartree−Fock formalism. It is sometimes mentioned that the effect of electron correlation may play an important role in 1,3-dipolar cycloadditions. Therefore, it is desirable in our future study to express the electron reorganization in the course of reactions using the correlated wave functions. This extension is worthwhile, but may encounter some difficulties because the generation of the bond-order indices for correlated wave functions is not yet completely clear.[61]

4. Conclusion

The population analysis along the IRC has been investigated. The derivatives of the Mulliken atomic gross charge and the Giambiagi bond order with respect to the nuclear motion along the IRC have been calculated analytically. These derivatives have been divided into two components: the derivative term of the density matrix and the derivative term of the overlap matrix. Furthermore, the density derivative term has been shown to be divided into two parts, namely, the renormalization term and the relaxation term. The method has been applied to the 1,3-dipolar cycloaddition reaction between fulminic acid and acetylene using the Hartree−Fock electron density. Concerted but nonsynchronous bond formation has been described clearly in this analysis.

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