CHEMICAL BONDS AND THEIR TRANSFORMATIONS IN THE COURSE OF CHEMICAL REACTIONS

Robert PONEC and Martin STRNAD

Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague 6-Suchdol

The Julg's concept of chemical bond as a region of small charge fluctuation was generalized by incorporating into the framework of recently proposed overlap determinant method. The resulting generalization allowing a simple theoretical description of structural transformation in terms close to classical picture of disappearing and newly formed chemical bonds was applied to the analysis of several selected pericyclic reactions both allowed and forbidden. The forbidden reactions were shown to be accompanied by deeper charge fluctuations than the allowed ones.

One of the fundamental concepts of the whole modern chemistry is the concept of chemical bond[1]. Because of its immense impact to chemistry, this concept has become the subject of numerous theoretical investigations aiming at disclosure of expected parallel between the quantum chemical and classical Lewis's picture of bonding. The simplest situation is in the case of individual isolated molecules where such a parallel was indeed confirmed by a number of different techniques[2-12].

In spite of unquestionable importance of all these studies, the picture provided by the static analysis of chemical bonds for individual isolated molecules cannot be regarded as completely exhaustive since it says only little about what is the central topic of chemistry — the structural transformations accompanying chemical reactions. From that reason the above static techniques start to be complemented by various approaches attempting to analyse the destiny of chemical bonds in chemical reactions. The theoretical studies dealing with this problem can be roughly divided into two groups.

First of them is represented by the Bader's studies[13,14], in which the classification of structural changes and structural stability was elaborated on the basis of the analysis of density function $\varrho(r)$. Besides this approach is there another group of studies, the typical feature of which is the systematic investigation of the analogy between the chemical reaction and the classical "curved arrows" formalism of shifting electron pairs. As an example may serve, e.g., the study by Salem[15], in which the structural reorganization in pericyclic reactions was discussed in terms of pair density. Using this approach, the interesting differences were disclosed in the character of electron reorganization between the allowed and forbidden reaction.

Into the framework of this last category can be included also this our study, in which we propose a new alternative procedure of visualising the structural changes in chemical reactions. The basis of our approach is the Julg's concept of chemical bond as a region of small charge fluctuation[16]. This technique originally proposed only for the characterization of chemical bonds in isolated individual molecules was generalized by incorporating into the framework of the so-called overlap determinant method[17]. Using this approach the general expressions for the mean number of electrons $\bar{N}_{\mathcal{V}}$ and fluctuation of charge density $\tilde{N}_{\mathcal{V}}$ in individual orbital regions $\mathcal{V}$ (corresponding to classical chemical bonds) in dependence on the change of the variable φ playing the role of the generalized reaction coordinate were derived. The variation of corresponding fluctuations with the change of the reaction coordinate opens then the direct way to the visualization of structural transformations in terms close to classical chemical picture. The proposed formalism was applied to the analysis of several selected pericyclic reactions with the main interest concentrated to the differences in the character of electron reorganization between the allowed and forbidden reactions.

THEORETICAL

In an effort at finding the parallels between the quantum chemical and classical description of chemical bonding a new criterion of characterizing the chemical bonds in terms of charge fluctuation in certain, the so-called orbital regions, was proposed some time ago by Julg[16]. According to this criterion the fluctuations in the regions corresponding to classical chemical bonds are generally very small (the typical value being about 0·1), whereas for regions between the classically nonbonded atoms are much larger ($\approx 0.4 - 0.5$). The corresponding mean values of electron density $\bar{N}_{\mathcal{V}}$ and fluctuations $\tilde{N}_{\mathcal{V}}$ in individual regions are defined by the relations

$$\bar{N}_{\mathcal{V}} = \int_{\mathcal{V}} \varrho_1(1) \, \mathrm{d}v_1 \,, \tag{1}$$

$$\tilde{N}_{\mathcal{V}} = \bar{N}_{\mathcal{V}} - \bar{N}_{\mathcal{V}}^2 + 2 \iint_{\mathcal{V}} \varrho_2(1, 2) \, \mathrm{d}v_1 \, \mathrm{d}v_2 \,, \tag{2}$$

where the $\varrho_1(1)$ and $\varrho_2(1, 2)$ are spinless density matrices of the first and second order defined by usual relations

$$\varrho_1(1) = N \int |\Phi|^2 \, \mathrm{d}v_2 \, \mathrm{d}v_3 \ldots \mathrm{d}v_N \, \mathrm{d}\sigma_1 \, \mathrm{d}\sigma_2 \ldots \mathrm{d}\sigma_N \,, \tag{3}$$

$$\varrho_2(1, 2) = N(N - 1)/2 \int |\Phi|^2 \, \mathrm{d}v_3 \, \mathrm{d}v_4 \ldots \mathrm{d}v_N \, \mathrm{d}\sigma_1 \, \mathrm{d}\sigma_2 \ldots \mathrm{d}\sigma_N \,. \tag{4}$$

Inspired by the simplicity and the elegance of this proposed criterion we have attempted at extending its applicability beyond the original scope of individual isolated molecules to the description of structural transformations accompanying the chemical reaction. Such an extension straightforwardly arises from incorporating
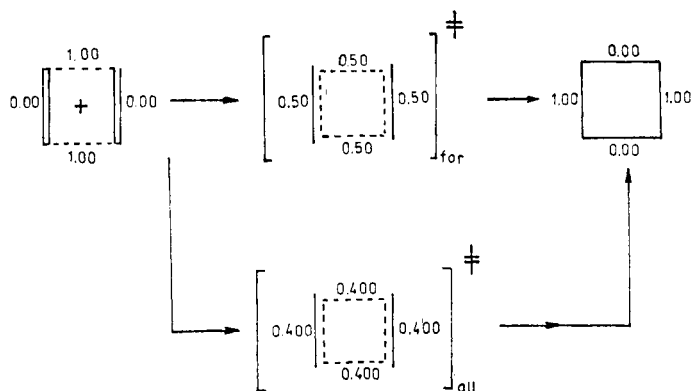
the original formalism into the framework of the so-called generalized overlap determinant method[18]. Since the formalism of this method is sufficiently described in the literature we consider it satisfactory to remind only some basic ideas to the extent necessary for the purpose of this study.

The method is based on a simple qualitative idea that chemical reaction is nothing but a specific transformation, converting the reactant into the product. Describing now the structure of the corresponding molecular species by the approximate wave functions Φ_R and Φ_P, the above idea can be realized by a mapping, converting in dependence on the continuous change of a certain parameter the function Φ_R into the wave function Φ_P. The detailed form of the corresponding mapping is not too important as long as it satisfies the requirement of continuity and mutual uniqueness (the more detailed discussion of this problem can be found in a study[19]). In previous study we used for this purpose a simple trigonometric formula describing the arbitrary transient species
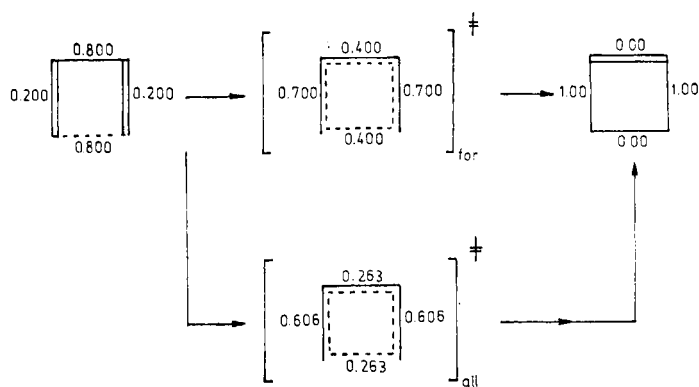
$$\Phi(\varphi) = \frac{1}{(1 + S_{RP} \sin 2\varphi)^{1/2}} (\Phi_R \cos \varphi + \Phi_P \sin \varphi) \tag{5}$$

in a general point of the concerted reaction coordinate by the generalized wave function $\Phi(\varphi)$. On the basis of this wave function the bonding fluctuations can be calculated not only for the isolated molecules of the reactant and the product but along the whole reaction path (the detailed derivation of the corresponding expressions is given in the Appendix). The knowledge of the detailed form of the dependencies $\overline{N}_{\mathscr{V}}$ and $\tilde{N}_{\mathscr{V}}$ vs φ for properly defined orbital regions $\mathscr{V}$ opens then the possibility of simple visualization of the process of bond reorganization in terms close to classical chemical picture of dissappearing and newly formed chemical bonds. Thus, e.g., restricting ourselves to orbital regions $\mathscr{V}$ associated with two (orthogonal) atomic orbitals χ_a, χ_b contributing to either dissappearing or newly formed bonds, the resulting dependencies $\overline{N}_{ab}$ and $\tilde{N}_{ab}$ vs φ describe the gradual bonding reorganization analogously as the classical chemical formalism of "curved arrows".
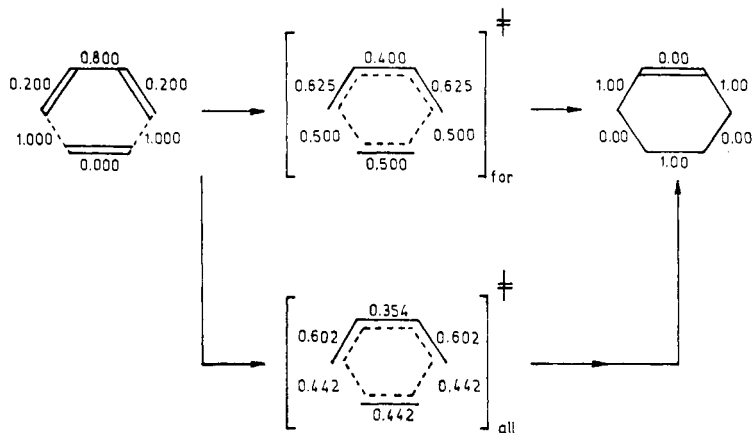
In the following part the practical application of the proposed formalism will be demonstrated on a concrete example of several selected pericyclic reactions. Since the first step of the analysis, the construction of the generalized wave function (5) is sufficiently discussed in previous studies[17,18], we consider it possible not to repeat these technical data here and to skip directly to the presentation of the final results. For the sake of completeness we remind only that the wave functions of the reactant and the product appearing in the formalism of the overlap determinant method were obtained by simple Hückel method. The calculated values of bonding fluctuations for both the starting reactants, final products and transient species corresponding to critical structure $X(\pi/4)$ (the specific properties of this structure were detected already in previous studies[18,19]) are collected in the Schemes 1−4.
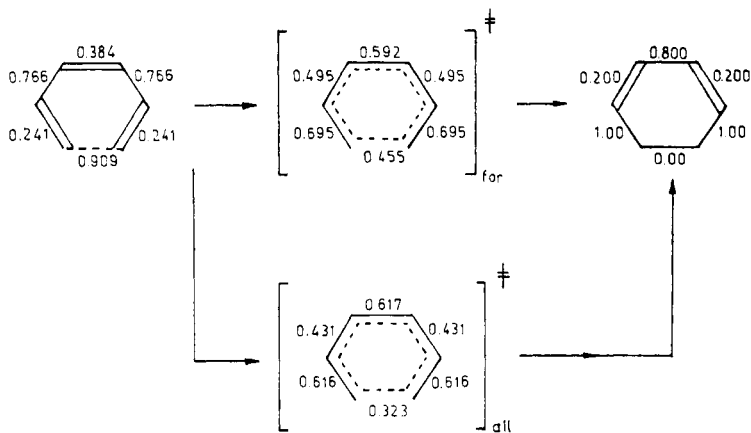
SCHEME 1

SCHEME 2

SCHEME 3

SCHEME 4

RESULTS AND DISCUSSION

Let us discuss now some general conclusions suggested by the above schemes. The first most important result concerns the comparison of bonding fluctuations $\tilde{N}_{ab}$ in isolated molecules of the reactant and the product. The corresponding values demonstrate, in harmony with the conclusions of original Julg's formalism, that the resulting picture of bonding fluctuations corresponds closely to classical chemical formulae — the fluctuations in the regions corresponding to classically localized bonds are considerably smaller indeed than in the nonbonded ones. On the basis of this positive result it is then possible, in the second step, to start with the analysis of bonding fluctuations accompanying the continuous change of the reaction coordinate φ. The simplest situation is in the case of ethene dimerization where the general expression for the bond fluctuations (12) can be reduced to trivial analytic relations given for the allowed $s + a$ cycloaddition by Eqs $(6a, 6b)$

$$\tilde{N}_{12}(\varphi) = \tilde{N}_{34}(\varphi) = \frac{\sin^2 \varphi}{1 + \frac{1}{2} \sin \varphi \cos \varphi}, \tag{6a}$$

$$\tilde{N}_{23}(\varphi) = \tilde{N}_{14}(\varphi) = \frac{\cos^2 \varphi}{1 + \frac{1}{2} \sin \varphi \cos \varphi} \tag{6b}$$

and for the forbidden $s + s$ one by Eqs $(7a), (7b)$

$$\tilde{N}_{12}(\varphi) = \tilde{N}_{34}(\varphi) = \sin^2 \varphi , \tag{7a}$$

$$\tilde{N}_{23}(\varphi) = \tilde{N}_{14}(\varphi) = \cos^2 \varphi . \tag{7b}$$

Visualizing the corresponding dependencies graphically the final picture (**Fig. 1**) is obtained. Let us discuss now the general conclusions arising from this figure. First what can be deduced from the corresponding curves is, that the resulting picture of varying bond fluctuations is in complete harmony with what can be expected on the basis of classical chemical considerations regarding the reaction as a process of gradual scission of old bonds and the formation of new ones. Thus, e.g., the gradual scission of π_{12} and π_{34} bonds in the ethene molecules is reflected by the increase in the corresponding fluctuations whereas the formation of new σ_{23} and σ_{14} bonds in the product corresponds, on the other hand, to the decrease of fluctuations. Analogous picture then holds also for the reactions displayed in Schemes 2 – 4.

Such a simple straightforward parallel with the classical picture of bonding is not, however, the only result. Another interesting conclusions which can be extracted from the calculated data concern the systematic trends in the values of bonding fluctuations which are generally higher in forbidden reactions than in the allowed ones. This confirms that the tendency to conserve the electron pairing is in allowed reactions greater than in the forbidden ones. This result is not of course too surprising since the similar conclusions can be intuitively expected already on the basis of Woodward–Hoffmann rules but the theoretical confirmation in terms of quantities directly reflecting the behaviour of electron pairs is in this case certainly valuable.

Besides this trivial conclusion based on the differences in the individual bond fluctuations another interesting information about the differences between the allowed and forbidden reactions can be obtained also from the global characterization of the fluctuations represented by the dependence $\sum \tilde{N}_{ab}$ vs φ where the summation runs only over the newly formed or disappearing bonds. For the specific case of butadiene to cyclobutene cyclization such a dependence is shown in Fig. 2 but analogous picture holds for other reactions as well.
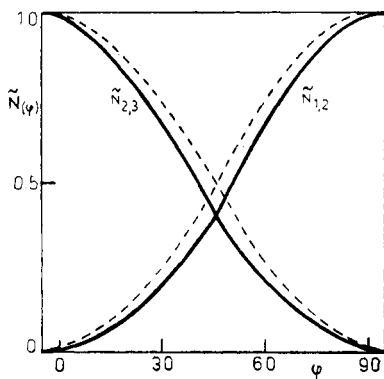

Fig. 1

Calculated values of charge fluctuation for disappearing ($\pi_{12} = \pi_{34}$) and newly appearing ($\sigma_{23} = \sigma_{14}$) bonds for the ethene dimerization, in dependence on the change of the reaction coordinate φ (full line corresponds to allowed and broken one to forbidden reaction mechanism)

The most interesting feature that can be seen from these dependencies is the sharp qualitative difference in the overall trend of corresponding curves. This difference can be the most simply demonstrated on the existence of certain critical structures, for which the total fluctuations are either maximal (for forbidden reactions) or minimal (for the allowed ones). This result is very interesting since similar qualitative differences were already reported in related study by Salem[15].

Summarizing the above results it is possible to say that the proposed generalization of the Julg's concept of chemical bond provides a new, perhaps interesting attempt at the qualitative visualization of structural changes in terms of close to classical chemical thinking and contributes thus to the elucidation of old but still living problem of destiny of electron pairs in chemical reactions[15].

APPENDIX

Let the structure of the reactant and the product of a given reaction be described by approximate wave functions Φ_R, Φ_P constructed in the form of standard Slater determinant: $(n = N/2)$,

$$\Phi_R = \left| r_1 \bar{r}_1 r_2 \bar{r}_2 \dots r_n \bar{r}_n \right| , \qquad (8a)$$

$$\Phi_P = \left| p_1 \bar{p}_1 p_2 \bar{p}_2 \dots p_n \bar{p}_n \right| , \qquad (8b)$$

where the individual molecular orbitals r_i, p_j are transformed in harmony with the philosophy of overlap determinant method into the common basis of atomic orbitals χ:

$$r_i = \sum_\mu \varrho_{\mu i} \chi_\mu , \qquad (9a)$$

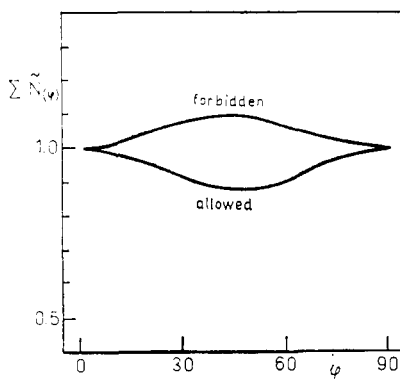$$p_i = \sum_\mu \pi_{\mu i} \chi_\mu . \qquad (9b)$$

FIG. 2

Calculated dependence of total charge fluctuations $\sum \tilde{N}_{ab}$ on the change of the reaction coordinate φ for the allowed conrotatory and forbidden disrotatory cyclization of butadiene to cyclobutene

This transformation described by the so-called assigning tables is sufficiently reported in the literature[17,18] and need not be therefore repeated. We recall only that the form of these tables depends on the actual mechanism of the transformation $R \rightarrow P$. In this way the possibility to discriminate between the allowed and forbidden processes thus enters into the formalism. Having performed the required transformation, the whole following procedure is entirely straightforward and consists in the direct combination of Eq. (5) for the generalized wave function with the definition Eqs (1)−(4) and the Julg-like approximation[16]

$$\int_{\mathscr{V}} \chi_\mu \chi_\nu \, dv \approx \tfrac{1}{2}\delta_{\mu\nu}\eta_{\mu\nu}(\mathscr{V}),\tag{10}$$

where $\delta_{\mu\nu}$ is Kronecker symbol and $\eta_{\mu\nu}(\mathscr{V})$ denotes a number of orbitals χ_μ a χ_ν contributing to an orbital region $\mathscr{V}$. The resulting final expressions for mean number of electrons and the fluctuation in a region $\mathscr{V}$ are given by Eqs (11) and (12):

$$\overline{N}_{\mathscr{V}} = \frac{2}{1 + S_{RP}\sin 2\varphi} \cdot \left(\sum_{\mu}^{\mathscr{V}}\sum_{i=1}^{occ} \varrho_{\mu i}^2 \cos^2\varphi + \sum_{\mu}^{\mathscr{V}}\sum_{i=1}^{occ} \pi_{\mu i}^2 \sin^2\varphi + \right.$$

$$\left. + 2D_{RP}\sum_{\mu}^{\mathscr{V}}\sum_{i=1}^{occ}\sum_{j=1}^{occ} \varrho_{\mu i}\pi_{\mu j}A_{ij}\sin\varphi\cos\varphi\right),\tag{11}$$

$$\tilde{N}_{\mathscr{V}} = \overline{N}_{\mathscr{V}}(1 - \overline{N}_{\mathscr{V}}) + \frac{2}{1 + S_{RP}\sin 2\varphi}\left\{\left[2\left(\sum_{\mu}^{\mathscr{V}}\sum_{i=1}^{occ}\varrho_{\mu i}^2\right)^2 - \sum_{\mu}^{\mathscr{V}}\sum_{\nu}^{\mathscr{V}}\left(\sum_{i=1}^{occ}\varrho_{\mu i}\varrho_{\nu i}\right)^2\right]\cos^2\varphi + \right.$$

$$+ \left[2\left(\sum_{\mu}^{\mathscr{V}}\sum_{i=1}^{occ}\pi_{\mu i}^2\right)^2 - \sum_{\mu}^{\mathscr{V}}\sum_{\nu}^{\mathscr{V}}\left(\sum_{i=1}^{occ}\pi_{\mu i}\pi_{\nu i}\right)^2\right]\sin^2\varphi +$$

$$\left. + 2\left[\left(\sum_{\mu}^{\mathscr{V}}\sum_{i=1}^{occ}\sum_{j=1}^{occ}\varrho_{\mu i}\pi_{\mu j}A_{ij}\right)^2 + D_{RP}\sum_{\mu}^{\mathscr{V}}\sum_{\nu}^{\mathscr{V}}\sum_{i=1}^{occ}\sum_{j=1}^{occ}\sum_{k=1}^{occ}\sum_{l=1}^{occ}\varrho_{\mu i}\pi_{\mu j}\varrho_{\nu k}\pi_{\nu l}A_{ij,kl}\right]\sin\varphi\cos\varphi\right\}.$$

$$\tag{12}$$

In these expressions representing the generalization of original Julg's expressions D_{RP} denotes the overlap determinant related to the overall overlap S_{RP} by the relation

$$S_{RP} = D_{RP}^2,\tag{13}$$

A_{ij} represents the corresponding minor and $A_{ij,kl}$ the minor of this minor resulting from further elimination of k-th row and l-th column $(i \neq k, j \neq l)$ and the symbol $\mathscr{V}$ in the summations denotes that these summations run only over the indices of such AO contributing to a given orbital region.

The close correspondence with Julg's expressions can be easily demonstrated for $\varphi = 0$ and $\varphi = \pi/2$, i.e. for the isolated reactant and the product where for the orbital regions formed by two contributing orbitals χ_a, χ_b the above equations identically reduce to formulae given by Julg.

REFERENCES

1. Pauling L.: *The Nature of Chemical Bond*. Cornell University Press, Ithaca 1960.
2. Lennard-Jones J.: Proc. Roy. Soc. *38*, 433 (1942).
3. Millié P., Levy B., Berthier G. in: *Localization and Delocalization in Quantum Chemistry* (O. Chalvet, R. Daudel, S. Diner and J. P. Malrieu, Eds), Vol. 1. Reidel, Dordrecht 1975.
4. Leroy G., Peters D., Tihange M.: J. Mol. Struct., Theochem *123*, 243 (1985).
5. Goddard III W. A., Dunning T. H., Hunt W. J., Hay P. J.: Acc. Chem. Res. *6*, 368 (1973).
6. Hiberty P. C.: Int. J. Quantum Chem. *19*, 259 (1981).
7. Cooper D. L., Gerratt J., Raimondi M.: Adv. Chem. Phys. *69*, 319 (1987).
8. Bader R. F. W., Stephens M. E.: J. Am. Chem. Soc. *97*, 7391 (1975).
9. Aslangul C., Kottis P., Constanciel R., Daudel R.: Adv. Quantum Chem. *6*, 93 (1972).
10. Bader R. F. W. in: *Chemical Applications of Topology and Graph Theory, Studies in Physical and Theoretical Chemistry* (R. B. King, Ed.), Vol. 28. Elsevier, Amsterdam 1984.
11. Cremer D. in: *Modelling of Structure and Properties of Molecules* (Z. B. Maksič, Ed.). Ellis Horwood Ltd., Chicester 1987.
12. Cooper D. L., Allan N.: J. Chem. Soc., Faraday Trans. 2 *83*, 449 (1987).
13. Bader R. F. W., Tal Y., Anderson S. G., Tung Nguyen-Dang T.: Isr. J. Chem. *19*, 8 (1980).
14. Tal Y., Bader R. F. W., Tung Nguyen-Dang T., Ojha M., Anderson S. G.: J. Chem. Phys. *74*, 5162 (1981).
15. Salem L.: Nouv. J. Chim. *2*, 559 (1978).
16. Julg A., Julg P.: Int. J. Quantum Chem. *13*, 483 (1978).
17. Ponec R.: Collect. Czech. Chem. Commun. *49*, 455 (1984).
18. Ponec R.: Collect. Czech. Chem. Commun. *50*, 1121 (1985).
19. Ponec R., Strnad M.: J. Phys. Org. Chem., *4*, 701 (1991).

Translated by the author (R.P.).