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Application of the semilocalized approach to chemical reactivity of butadiene

V. Gineityte*

Institute of Theoretical Physics and Astronomy, Vilnius University, Gostauto 12, Vilnius 2600, Lithuania

Abstract

The semilocalized approach to chemical reactivity (J. Mol. Struct. (Theochem) 588 (2002) 99; Int. J. Quant. Chem. 94 (2003) 302) is applied to study the addition reaction of an electrophile or nucleophile to the butadiene molecule. In accordance with the classical concept of the reaction center and its neighborhood (substituent), only one of the two $H_2C=CH$-fragments of butadiene is supposed to be under a direct attack of the reagent, whereas the remaining $H_2C=CH$-group is assumed to play the role of the substituent and thereby to participate in the process indirectly by exerting certain electron-donating or accepting effect upon the former group and/or the reagent. The main aim of the study consists in revealing the role of the $H_2C=CH$-substituent in the formation of the known higher reactivity of the terminal carbon atom of the attacked $C=C$-bond (as compared to the internal atom) irrespective of the nature of the reagent. To this end, we seek to obtain an explicit algebraic representation of the interdependence between the direction and the extent of the total influence of the $H_2C=CH$-substituent, on the one hand, and the nature of the reagent, on the other hand. The expressions for electron density and bond order redistributions among separate fragments of contacting molecules derived previously in the form of power series are shown to yield the above-anticipated representation. On this basis, it is demonstrated that the electron-donating effect of the initially occupied (bonding) orbital of the substituent and the electron-accepting effect of its initially vacant (antibonding) orbital upon the remaining fragments of the whole reacting system may be considered independently whatever the nature of the reagent. However, a strong interdependence is established between the actual relative extents of these two components of the total effect of the $H_2C=CH$-group and the electron-donating (accepting) properties of the reagent. Moreover, this group of atoms is shown to manifest itself as an electron-donating (accepting) substituent under influence of an electrophilic (nucleophilic) attack. Using this principal result of the paper, the actual reactivity of butadiene with respect to electrophile (nucleophile) is interpreted by invoking a model system of a substituted ethene containing a simple (one-orbital) electron-donating (accepting) substituent, and a terminal addition easily follows for both types of the reagent.
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1. Introduction

Relative reactivities of the terminal and internal carbon atoms are known to differ significantly in the 1,3-butadiene molecule [1–5] in contrast to the two carbon atoms of ethene. Just this fact is among the principal arguments for the mutual interaction of the initially double ($C=C$) bonds usually referred to as conjugation [4–6]. The most surprising aspect of reactivity of butadiene, however, is that both an electrophilic and a nucleophilic reagent are primarily added to the same terminal carbon atoms C_1 and C_4.

Two principal ways of accounting for these intriguing properties of butadiene may be distinguished: the first one consists in relating the above-mentioned difference in reactivities of carbon atoms to certain characteristics of the initial (isolated) butadiene molecule. As for instance, the well-known classical concept of larger free valencies of terminal carbon atoms vs. those of the internal atoms suggested by Thiele may be mentioned [1,4,7] along with their quantum-chemical analogues in terms of bond orders [1,8,9]. The more modern approach based on consideration of constitution of the so-called frontier molecular orbitals (MOs) [3,10–13] also is among interpretations of the same type (The predominant direction of an electrophilic and nucleophilic attack may be successfully related to structures

* Tel.: +370-620-953; fax: +370-225-361.
  E-mail address: gineityt@mserv.itpa.lt (V. Gineityte).

of the highest-occupied MO (HOMO) and of the lowest-unoccupied MO (LUMO) of butadiene, respectively [3,11, 14,15]). It is also noteworthy in this context that populations of $2p_z$ AOs of carbon atoms of butadiene proved to be uniform in the framework of the simplest Hückel model [9]. As a consequence, these characteristics are traditionally omitted when discussing chemical reactivity of this molecule.

The second way of interpretation of the same reactivity consists in comparison of relative stabilities of the two possible intermediates of the addition process (carbenium ions). In particular, a more stable carbenium ion is expected to be formed as a result of addition of an electrophile to a terminal carbon atom as compared to an internal one, as a more extended π-electron system remains in the former case [2,4,5].

The above-discussed explanations of the observed chemical properties of butadiene are based on an implicit assumption that the system of two C=C bonds as a whole participates in the addition process (It is no surprise in this context that even a model of an one-dimensional potential well has been successfully used when discussing the same problem [4]). Thus, the term delocalized approaches will be exploited below instead of enumerating these traditional interpretations.

It should be emphasized, however, that the principal task of any theory of chemical reactivity consists not only in accounting for peculiarities of reactivity of a particular compound, but also in relating it to reactivities of other molecules, especially of those containing the same or a similar group of atoms (functional group) [16]. So far as delocalized approaches and models are concerned, these are orientated mainly towards solution of the first part of the problem.

Comparative studies of reactivities of similar molecules are usually based on the concept of the reaction center and its neighborhood. The point is that only certain fragment of an extended compound is supposed to be under attack of the reagent and thereby to participate in the process directly. This fragment is referred to as the reaction center [3]. Again, the rest of the molecule (especially a substituent) is considered as taking an indirect part in the same process by exerting certain electron-donating or accepting effect upon the reaction center. It is also essential that the extents of the above-mentioned effects are usually assumed to be quite different at various stages of the reaction [2,17,18].

Furthermore, this qualitative theory contains a hypothesis that the structures of the reaction center and of its neighborhood are of different importance in determining chemical reactivity of a particular compound. Indeed, the very mechanism of the reaction is assumed to be conditioned by the presence of the given reaction center, whilst an alteration in the relative rate of the whole process is expected to be the only consequence of an indirect influence of the neighborhood. This implies that molecules of similar structure undergo the same characteristic reactions. Such a principal conclusion complies with the whole complex of experimental facts and thereby forms

the basis of classification of both chemical compounds and their reactions [1,2,5,16,17].

Given that the above-described concepts are adequate for an electrophilic and/or nucleophilic attack upon the butadiene molecule, it appears that only one of the two C=C bonds forms the reaction center, whereas the remaining C=C bond plays the role of the substituent. Then a close analogy may be expected between the reactivity of butadiene and those of other substituted ethenes.

A predominant addition of an electrophilic agent to the terminal (C_β) carbon atom is peculiar to substituted ethenes (H_2C_β=C_αHX) containing an electron-donating substituent X (cf. the so-called Markovnikov rule [2–5,16,17]). On this basis, the H_2C=CH-substituent of butadiene was assumed to exert an electron-donating effect upon the reaction center of the Ad_E2 process [1]. To account for the addition of nucleophile to the same (terminal) carbon atom of butadiene, the H_2C=CH-substituent should be then considered as an electron-accepting group (Note that addition of nucleophile to an internal (C_α) atom is prevalent for substituted ethenes containing an electron-donating substituent, whist an addition of the same reagent to the C_β atom is observed when passing to the case of electron-accepting substituent [1,5,16,17]). Thus, the very direction of the charge transfer between the H_2C=CH-substituent and the reaction center is likely to depend upon the nature of the approaching reagent. The crucial role of the reagent in giving rise the above-mentioned charge transfer should be additionally emphasized here by the notation that it takes a zero value in an isolated butadiene molecule owing to its symmetry.

In this paper, we are about to verify the validity of the above-described concepts concerning the reactivity of butadiene. In other words, we pursue a goal to reveal the role of the H_2C=CH-substituent in the formation of the higher reactivity of the terminal carbon atom of the reacting C=C bond towards an electrophile (E^+) and a nucleophile (Nu^-).

To achieve this end, a quantum-chemical method is required wherein an analogue of the reaction center and its neighborhood may be formulated. The semilocalized approach to chemical reactivity suggested recently [19,20] seems to be promising here.

The approach of Refs. [19,20] is based on the direct way of obtaining the one-electron density matrix (bond order matrix) by means of solution of the so-called commutation equation in the form of power series [21–28] without invoking the concept of delocalized (canonical) MOs. Orbitals localized on individual fragments of contacting molecules were chosen as initial basis functions there. Moreover, separate members of the above-mentioned series have been expressed in terms of submatrices describing the direct (through-space) and indirect (through-bond) interactions of these basis orbitals. Then, charge and bond order redistributions between fragments of both participants of the reaction (relatively to respective distributions in isolated compounds) may be studied for various directions of

the attack separately. As a result, dissimilar reactivities of particular atoms of the reactant have been accounted for by different efficiencies of the above-specified redistributions. It should be also noted here that electron density redistribution between fragments, in turn, has been related to respective alterations in total energy [29]. Finally, pairs of directly contacting fragments and of indirectly interacting ones may be easily distinguished in this approach in accordance with the concept of the reaction center and its neighborhood.

In the present study, the above-described approach will be applied to investigate the electrophilic and nucleophilic attacks upon butadiene. Our main aim consists in comparison of the relative extents of charge and bond order redistributions between the reagent (E^+ or Nu^-), the reacting $H_2C=CH$-group and the remaining $H_2C=CH$-fragment (substituent) for the cases of an internal and a terminal direction of the attack.

In Section 2, we start with a brief description of the model under study and with an overview of expressions for direct and indirect interorbital interactions. Thereupon, the expressions for occupation numbers of basis orbitals and bond orders are discussed in Section 3. Two important points are demonstrated later in Section 4, namely (i) additivity of the electron-donating effect of the initially occupied basis orbital (IOBO) of the $H_2C=CH$-substituent and of the electron-accepting effect of its initially vacant basis orbital (IVBO) upon the remaining fragments of the reacting system and (ii) similarity of these two effects to respective effects of the simple electron-donating (D) and electron-accepting (A) substituents in substituted ethenes $H_2C_\beta=C_\alpha HX$, $X = D,A$ under attack of the same reagent studied previously [19]. In connection with this similarity just the latter results are overviewed briefly on Section 5. The above-mentioned two conclusions, in turn, allow us to reduce the total influence of the $H_2C=CH$-substituent in the reacting butadiene to superposition of two components, viz. of an electron-donating effect of its IOBO and of an electron-accepting effect of its IVBO. Then no more is required as to look for a relation between relative extents of these elementary components of the total influence of the $H_2C=CH$-substituent and the nature of the approaching reagent. Just this relation is established in Section 6.

2. The model of butadiene under attack of electrophile or nucleophile. The expressions for direct and indirect interorbital interactions

As it was mentioned already, elements of the bond order matrix have been expressed in Refs. [21–28] in terms of those of certain principal matrices $G_{(k)}$ describing the direct and indirect interactions of basis orbitals, where k stands for the order parameter of the power series. To define the elements $G_{(k)ij}$, let us assume that our basis set $\{\varphi\}$ consists of I initially occupied orbitals ($\varphi_{(+)i}$, $i = 1, ..., I$) and of J initially vacant ones ($\varphi_{(-)j}$, $j = 1, ..., J$). Then the first order element $G_{(1)ij}$ may be expressed as follows [21]

$$G_{(1)ij} = -\frac{\langle \varphi_{(+)i}|\hat{H}|\varphi_{(-)j}\rangle}{E_{(+)i} - E_{(-)j}} \tag{1}$$

and describes the direct (through-space) interaction between orbitals $\varphi_{(+)i}$ and $\varphi_{(-)j}$. The numerator of the right-hand side of Eq. (1) contains the Hückel type Hamiltonian matrix element (resonance parameter) between basis orbitals indicated within the bra- and ket-vectors, and the denominator involves the relevant difference in one-electron energies.

Similarly, the second order element $G_{(2)ij}$ describes the indirect interaction between the same orbitals by means of a single mediator. This element takes the form

$$G_{(2)ij} = \frac{1}{E_{(+)i} - E_{(-)j}}$$

$$\times \left\{ \sum_m^{\text{IOBOs}} \frac{S_{im}R_{mj}}{E_{(+)m} - E_{(-)j}} - \sum_m^{\text{IVBOs}} \frac{R_{in}Q_{nj}}{E_{(+)i} - E_{(-)j}} \right\} \tag{2}$$

where the meanings of designations coincide with those of Eq. (1), and

$$S_{im} = \langle \varphi_{(+)i}|\hat{H}|\varphi_{(+)m}\rangle$$

$$R_{mj} = \langle \varphi_{(+)m}|\hat{H}|\varphi_{(-)j}\rangle \tag{3}$$

$$Q_{nj} = \langle \varphi_{(-)n}|\hat{H}|\varphi_{(-)j}\rangle$$

It is seen that both IOBOs and IVBOs play the role of mediators in the indirect interaction between orbitals $\varphi_{(+)i}$ and $\varphi_{(-)j}$. To be an efficient mediator, however, the orbital under consideration ($\varphi_{(+)m}$ or $\varphi_{(-)n}$) should overlap with both $\varphi_{(+)i}$ and $\varphi_{(-)j}$. Hence, orbitals situated in between the indirectly interacting orbitals meet this condition best of all.

The element $G_{(3)ij}$ describes the indirect interaction of the same orbitals $\varphi_{(+)i}$ and $\varphi_{(-)j}$ by means of two mediators. The relevant expression is as follows

$$G_{(3)ij}$$

$$= \frac{-1}{E_{(+)i} - E_{(-)j}} \left\{ \sum_n^{\text{IOBOs}} \sum_m^{\text{IOBOs}} \frac{S_{in}S_{nm}R_{mj}}{(E_{(+)n} - E_{(-)j})(E_{(+)m} - E_{(-)j})} \right.$$

$$- \sum_n^{\text{IOBOs}} \sum_r^{\text{IVBOs}} \left[\frac{S_{in}R_{nr}Q_{rj}}{(E_{(+)n} - E_{(-)j})(E_{(+)n} - E_{(-)r})} \right.$$

$$+ \frac{S_{in}R_{nr}Q_{rj}}{(E_{(+)i} - E_{(-)r})(E_{(+)n} - E_{(-)r})}$$

$$+ \frac{R_{ir}R_{rn}^+R_{nj}}{(E_{(+)n} - E_{(-)r})(E_{(+)r} - E_{(-)j})}$$

$$+ \left. \frac{R_{ir}R_{rn}^+R_{nj}}{(E_{(+)i} - E_{(-)r})(E_{(+)n} - E_{(-)r})} \right]$$

$$+ \left. \sum_p^{\text{IVBOs}} \sum_r^{\text{IVBOs}} \frac{R_{ir}Q_{rp}Q_{pj}}{(E_{(+)i} - E_{(-)p})(E_{(+)i} - E_{(-)r})} \right\} \tag{4}$$

Pairs of mutually overlapping orbitals situated in between the orbitals $\varphi_{(+)i}$ and $\varphi_{(-)j}$ are the most efficient mediators of this indirect interaction.

Let us turn now to the case of butadiene under attack electrophile. For an initial (isolated) butadiene molecule, the Hückel type model used in Ref. [25] will be invoked, as convergence of the resulting power series for the bond order matrix has been verified there. In particular, uniform values of Coulomb parameters are accepted for $2p_z$ AOs of carbon atoms χ_i, $i = 1–4$ and this parameter serves as the energy reference point. Resonance parameters between pairs of AOs (χ_1, χ_2), (χ_2, χ_3) and (χ_3, χ_4) also are of coinciding value and it is used as a (negative) energy unit. Bond orbitals (BOs) of the $C_1=C_2$ and $C_3=C_4$ bonds play the role of basis functions and these are defined as follows

$$\varphi_{(+)1}(\varphi_{(-)3}) = \frac{1}{\sqrt{2}}(\chi_1 \pm \chi_2);$$

$$\varphi_{(+)2}(\varphi_{(-)4}) = \frac{1}{\sqrt{2}}(\chi_3 \pm \chi_4) \tag{5}$$

The bonding BOs ($\varphi_{(+)1}$ and $\varphi_{(+)2}$) and the antibonding ones ($\varphi_{(-)3}$ and $\varphi_{(-)4}$) are additionally supposed to be initially occupied and initially vacant, respectively. It is evident that one-electron energies of the former are equal to one, whilst

those of the latter coincide with -1 in our negative energy units.

The approaching electrophilic and nucleophilic reagents will be modelled by a single initially vacant and initially occupied orbital, respectively, as it was done in Ref. [19]. These orbitals will be accordingly denoted by $\varphi_{(-)E}$ and $\varphi_{(+)N}$. The relevant one-electron energies will be designated by $-\varepsilon_{(-)E}$ and $\varepsilon_{(+)N}$, where $\varepsilon_{(-)E}$ and $\varepsilon_{(+)N}$ are positive parameters. Relative positions of energy levels of our system are shown on Fig. 1.

Let us assume now that the $C_1=C_2$ bond forms the reaction center of the addition process. This implies that the relevant carbon atoms, i.e. either C_1 or C_2, are under a direct attack of the reagent. To model this situation, the orbital of the latter ($\varphi_{(-)E}$ or $\varphi_{(+)N}$) will be situated either above the $2p_z$ AO χ_1 or above the $2p_z$ AO χ_2 (Fig. 2). To study the dependence of the charge and bond order redistributions only upon the spatial position of the attacking reagent, coinciding values of the intermolecular resonance parameters will be assumed for both directions of the attack, i.e.

$$\langle\varphi_{(+)N}|\hat{H}|\chi_1\rangle = \langle\varphi_{(+)N}|\hat{H}|\chi_2\rangle = \beta_N > 0$$

$$\langle\varphi_{(-)E}|\hat{H}|\chi_1\rangle = \langle\varphi_{(-)E}|\hat{H}|\chi_2\rangle = \beta_E > 0 \tag{6}$$
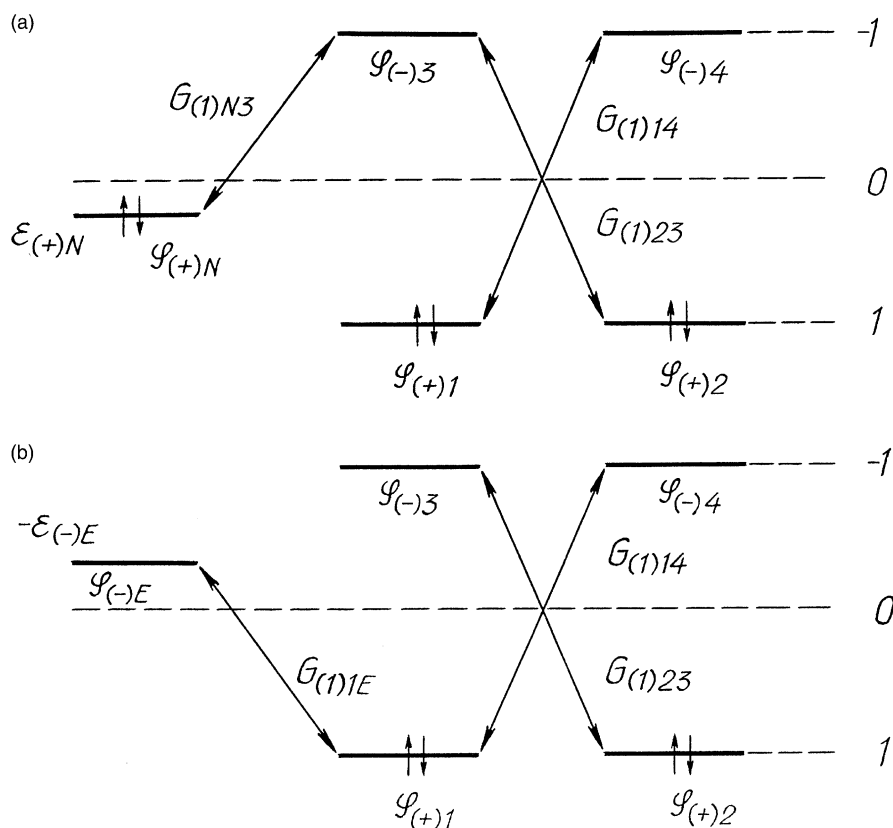

Fig. 1. Diagrams reflecting the relative positions of energy levels corresponding to fragmental orbitals of butadiene ($H_2C=CH–CH=CH_2$) under attack of nucleophile (a) and electrophile (b), as well as non-zero direct interactions $G_{(1)ij}$ between pairs of orbitals of opposite initial occupation ($\varphi_{(+)i}$) and ($\varphi_{(-)j}$). Orbitals $\varphi_{(+)1}(\varphi_{(-)3})$ and $\varphi_{(+)2}(\varphi_{(-)4})$ coincide with bonding (antibonding) orbitals of the $C_1 = C_2$ and $C_3 = C_4$ bonds, respectively. The basis functions $\varphi_{(+)N}$ and $\varphi_{(-)E}$ correspondingly represent an approaching nucleophile and electrophile. One-electron energies referring to the latter two orbitals are denoted by $\varepsilon_{(+)N}$ and $-\varepsilon_{(-)E}$, where $\varepsilon_{(+)N}$ and $\varepsilon_{(-)E}$ are positive parameters (negative energy units are used here).
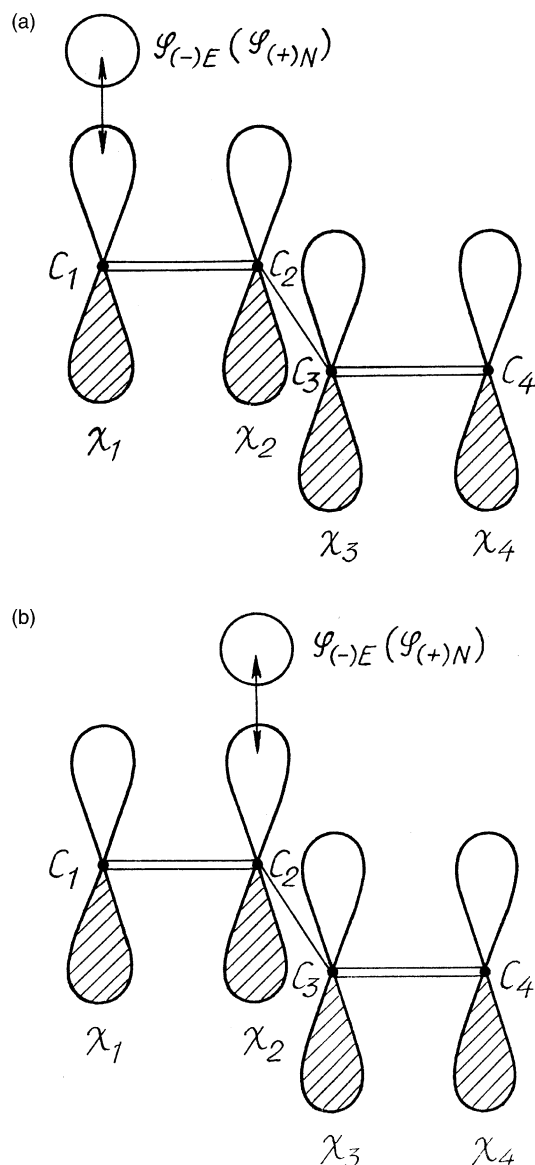
Fig. 2. Models of an electrophilic (nucleophilic) attack upon a terminal (a) and upon an internal (b) carbon atoms of butadiene. Intermolecular resonance parameters between orbitals of the electrophile (nucleophile) $\varphi_{(-)E}(\varphi_{(+)N})$, on the one hand, and the $2p_z$ AO of the carbon atom under attack, on the other hand, are indicated by double-headed arrows. Basis orbitals ($2p_z$ AOs) of carbon atoms $C_1 \cdots C_4$ are denoted by $\chi_1 \cdots \chi_4$. Dashed lobes of AOs are those corresponding to negative values of basis functions.

As a result, the following relations are valid

$$G_{(1)N3}^{(t)} < 0; \qquad G_{(1)N3}^{(i)} > 0;$$

$$|G_{(1)N3}^{(t)}| = |G_{(1)N3}^{(i)}| = \frac{\beta_N}{\sqrt{2}(1 + \varepsilon_{(+)N})}; \qquad (7)$$

$$S_{N1}^{(t)} = S_{N1}^{(i)} = \frac{\beta_N}{\sqrt{2}} > 0$$

and

$$G_{(1)1E}^{(t)} = G_{(1)1E}^{(i)} = -\frac{\beta_E}{\sqrt{2}(1 + \varepsilon_{(-)E})} < 0$$

$$\qquad (8)$$

$$Q_{3E}^{(t)} = \frac{\beta_E}{\sqrt{2}} > 0; \qquad Q_{3E}^{(i)} = -\frac{\beta_E}{\sqrt{2}} < 0$$

for the nucleophilic and electrophilic attacks, respectively, where the superscripts (*t*) and (*i*) here and below stand correspondingly for a terminal position of the reagent (i.e. above C_1) and for an internal one (above C_2). Eqs. (1) and (5) are used here to obtain the expressions for the direct interorbital interactions.

Again, the remaining $C_3=C_4$ bond will be supposed to form the $H_2C=CH$-substituent. The latter proves to be represented by two orbitals, namely by an initially occupied BO $\varphi_{(+)2}$ and an initially vacant BO $\varphi_{(-)4}$. It is evident that such a substituent may exert both an electron-donating and -accepting effects upon the remaining part of the whole reacting system in contrast to the simple substituents studied in Ref. [19] (The electron-donating substituent (X = D) and the electron-accepting one (X = A) in substituted ethenes $H_2C_\beta=C_\alpha HX$ were modelled in this contribution by a single IOBO and a single IVBO, respectively. Thus, these may be referred to as one-orbital substituents).

Definition of bond orbitals shown in Eq. (5) along with uniform Coulomb parameters for $2p_z$ AOs of carbon atoms $\chi_i, i = 1-4$ implies that no direct interactions take place between pairs of orbitals of the same C=C bond. We also will assume that the attacking reagent (Nu^- or E^+) does not interact directly with orbitals of the substituent, i.e. of the $C_3=C_4$ bond. We then obtain

$$R_{13} = R_{24} = R_{2E} = R_{N4} = 0;$$

$$\qquad (9)$$

$$G_{(1)13} = G_{(1)24} = G_{(1)2E} = G_{(1)N4} = 0$$

The expressions for the intramolecular interactions, viz.

$$S_{12} = R_{14} = \frac{1}{2}; \qquad R_{23} = Q_{34} = -\frac{1}{2};$$

$$\qquad (10)$$

$$G_{(1)23} = \frac{1}{4}; \qquad G_{(1)14} = -\frac{1}{4}$$

also easily follow from Eqs. (1) and (5). Finally, the definition of an indirect interaction $G_{(2)ij}$ shown in Eq. (2) along with Eqs. (6)−(8) yield the relations

$$G_{(2)N3} = G_{(2)1E} = 0; \qquad G_{(2)24} = 0 \qquad (11)$$

Zero values for both the direct and indirect interactions between orbitals of the $H_2C=CH$-substituent $\varphi_{(+)2}$ and $\varphi_{(-)4}$ (i.e. for $G_{(1)24}$ and $G_{(2)24}$) has important implications. In particular, vanishing of the first order interaction $G_{(1)24}$ allows a formal analogy to be traced between the $C_3=C_4$ bond and two directly non-interacting one-orbital substituents, namely an electron-donating substituent represented by the orbital $\varphi_{(+)2}$ and an electron-accepting one described

by the basis function $\varphi_{(-)4}$. Consequently, the system of butadiene under attack of electrophile or nucleophile actually differs from that of substituted ethenes [19] only in total numbers of simple directly non-interacting substituents. This, in turn, implies that the relevant expressions for occupation numbers of basis orbitals and those for bond orders also may be derived similarly [19,28]. These expressions will be discussed briefly in Section 3.

3. The expressions for partial transferred populations and bond orders

As it is shown in Ref. [19], peculiarities of charge redistributions between fragments of the reacting systems $[E^+(Nu^-)\cdots H_2C_\beta{=}C_\alpha HX]$ relatively to those in the isolated compounds responsible for different reactivities of the C_α and C_β atoms are described by fourth order corrections to occupation numbers (Corrections to within the third order inclusive are of coinciding values for both directions of the attack). Moreover, these charge redistributions have been conveniently represented in terms of partial populations $\delta x^{(4)}_{(+)i,(-)j}$ transferred between pairs of orbitals of opposite initial occupation ($\varphi_{(+)i}$ and $\varphi_{(-)j}$), where the superscript (4) indicates the order of the correction. Any partial transferred population $\delta x^{(4)}_{(+)i,(-)j}$, in turn, consists of three contributions that will be denoted by additional superscripts 1–3. For the butadiene molecule under attack of nucleophile, these contributions take the form

$$\delta x^{(4)1}_{(+)N,(-)3} = 2(G_{(1)N3})^4 + 2(G_{(1)N3})^2(G_{(1)23})^2$$

$$\delta x^{(4)1}_{(+)2,(-)3} = 2(G_{(1)N3})^2(G_{(1)23})^2 \tag{12}$$

$$\delta x^{(4)2}_{(+)N,(-)3} = 4G_{(1)N3}G_{(3)N3};$$

$$\delta x^{(4)3}_{(+)N,(-)4} = 2(G_{(2)N4})^2 \tag{13}$$

$$\delta x^{(4)2}_{(+)1,(-)4} = 4G_{(1)14}G_{(3)14};$$

$$\delta x^{(4)2}_{(+)2,(-)3} = 4G_{(1)23}G_{(3)23} \tag{14}$$

$$\delta x^{(4)3}_{(+)1,(-)3} = 2(G_{(2)13})^2 \tag{15}$$

For an electrophilic attack upon the same molecule, we obtain

$$\delta x^{(4)1}_{(+)1,(-)E} = 2(G_{(1)1E})^4 + 2(G_{(1)1E})^2(G_{(1)14})^2$$

$$\delta x^{(4)1}_{(+)1,(-)4} = 2(G_{(1)1E})^2(G_{(1)14})^2 \tag{16}$$

$$\delta x^{(4)2}_{(+)1,(-)E} = 4G_{(1)1E}G_{(3)1E};$$

$$\delta x^{(4)3}_{(+)2,(-)E} = 2(G_{(2)2E})^2 \tag{17}$$

instead of Eqs. (12) and (13), respectively, whereas Eqs. (14) and (15) do not change their form.

The partial transferred population $\delta x^{(4)3}_{(+)2,(-)4}$ between the two orbitals of the $C_3{=}C_4$ bond also is proportional to square of the relevant indirect interaction $G_{(2)24}$. This population, however, vanishes owing to the equality of $G_{(2)24}$ to zero as shown in Eq. (11). This implies that no charge redistribution takes place inside the $H_2C{=}CH$-substituent as a consequence of an electrophilic (nucleophilic) attack upon the reaction center.

Let us turn now to alterations of bond orders due to an attack of the reagent. Let us start with expressions for newly formed bond orders between the orbital of an approaching reagent and those of the attacked carbon atom. As it is shown in Ref. [19], differences in these bond orders for the internal and terminal directions of the attack are described by third order corrections $P_{(3)}[Nu^- - C_1]$, $P_{(3)}[Nu^- - C_2]$, $P_{(3)}[E^+ - C_1]$ and $P_{(3)}[E^+ - C_2]$, where the nature of the reagent and the attacked carbon atom are indicated within the square brackets. The relevant expressions take the form

$$P_{(3)}[Nu^- - C_1(C_2)]$$

$$= -\sqrt{2}[G_{(1)N3}G_{(2)13} + G_{(2)N4}G_{(1)14} \pm G_{(3)N3}] \tag{18}$$

$$P_{(3)}[E^+ - C_1(C_2)]$$

$$= -\sqrt{2}[G_{(3)1E} \mp G_{(1)23}G_{(2)2E} \mp G_{(2)13}G_{(1)1E}] \tag{19}$$

where the upper signs of the right-hand sides correspond to C_1, whereas the lower signs refer to C_2.

The expressions for the bond order alterations of the initially single $(C_2{-}C_3)$ bond due to an attack also may be derived similarly and take the form

$$P_{(3)}[Nu^-, C_2 - C_3] = G_{(3)23} - G_{(3)14} - G_{(1)N3}G_{(2)N4} \tag{20}$$

$$P_{(3)}[E^+, C_2 - C_3] = G_{(3)23} - G_{(3)14} - G_{(1)1E}G_{(2)2E} \tag{21}$$

where the nature of the reagent and the bond under consideration stand inside the square brackets.

4. Additivity of the electron-donating and -accepting effects of the $H_2C{=}CH$-substituent

In this section, we are about to demonstrate that terms of Eqs. (12)–(21) describing the electron-donating effect of the orbital $\varphi_{(+)2}$ upon the remaining fragments of the whole reacting system may be studied independently from those representing the electron-accepting effect of the orbital $\varphi_{(-)4}$. Let us start with partial transferred populations defined by Eqs. (12)–(15) and corresponding to an attack of nucleophile. It is seen that only the IOBO $\varphi_{(+)2}$ participates in the partial transferred populations $\delta x^{(4)1}_{(+)N,(-)3}$ and $\delta x^{(4)1}_{(+)2,(-)3}$ of Eq. (12), whilst the IVBO $\varphi_{(-)4}$ is not involved there. Thus, these populations may be traced back to the influence of the electron-donating orbital $\varphi_{(+)2}$ upon the charge redistribution. Moreover, the same conclusion also refers to the partial transferred population $\delta x^{(4)2}_{(+)2,(-)3}$

(The IVBO $\varphi_{(-)4}$ is not able to play the role of mediator in the third order interaction $G_{(3)23}$ owing to the zero value of the resonance parameter R_{24} as shown in Eq. (9)). Similarly, the partial transferred populations $\delta x^{(4)3}_{(+)N,(-)4}$ and $\delta x^{(4)2}_{(+)1,(-)4}$ contain the IOBO $\varphi_{(+)2}$ neither directly nor indirectly as a mediator. Thus, these populations may be entirely ascribed to the electron-accepting influence of the orbital $\varphi_{(-)4}$. Given that the orbital $\varphi_{(+)N}$ plays the role of mediator in the second order interaction $G_{(2)13}$ (otherwise, the influence of the reagent upon the final charge redistribution cannot be described), the partial transferred population $\delta x^{(4)3}_{(+)1,(-)3}$ does not involve the orbitals of the substituent $\varphi_{(+)2}$ and $\varphi_{(-)4}$.

Therefore, only the partial population $\delta x^{(4)2}_{(+)N,(-)3}$ defined by Eq. (13) remains to be considered. Two pairs of orbitals, namely $(\varphi_{(+)1}, \varphi_{(+)2})$ and $(\varphi_{(+)1}, \varphi_{(-)4})$ play the role of mediators in the indirect interaction $G_{(3)N3}$, the first one describing the participation of the electron-donating orbital $\varphi_{(+)2}$ and the second one representing that of the electron-accepting orbital $\varphi_{(-)4}$. Additivity of the relevant two increments to the total matrix element $G_{(3)N3}$ easily follows from the definition of the third order interaction $G_{(3)ij}$ of Eq. (4), viz.

$$G_{(3)N3} = G^{(D)}_{(3)N3} + G^{(A)}_{(3)N3} \tag{22}$$

where

$$G^{(D)}_{(3)N3} = -\frac{S_{N1}S_{12}R_{23}}{4(1 + \varepsilon_{(+)N})}; \qquad G^{(A)}_{(3)N3} = \frac{S_{N1}R_{14}Q_{43}\lambda}{2(1 + \varepsilon_{(+)N})} \tag{23}$$

are the contributions of the electron-donating orbital $\varphi_{(+)2}$ and of the electron-accepting orbital $\varphi_{(-)4}$, respectively, and

$$\lambda = \frac{1}{2} + \frac{1}{1 + \varepsilon_{(+)N}} > 1 \tag{24}$$

is an $\varepsilon_{(+)N}$-dependent parameter ($\varepsilon_{(+)N} < 1$ as shown in Fig. 1).

For the partial transferred population $\delta x^{(4)2}_{(+)N,(-)3}$ we accordingly obtain

$$\delta x^{(4)2}_{(+)N,(-)3} = \delta x^{(4)2(D)}_{(+)N,(-)3} + \delta x^{(4)2(A)}_{(+)N,(-)3} \tag{25}$$

where

$$\delta x^{(4)2(D)}_{(+)N,(-)3} = 4G_{(1)N3}G^{(D)}_{(3)N3}$$
$$\delta x^{(4)2(A)}_{(+)N,(-)3} = 4G_{(1)N3}G^{(A)}_{(3)N3} \tag{26}$$

When applied to bond orders $P_{(3)}[\text{Nu}^- - \text{C}_1(\text{C}_2)]$ of Eq. (18), the same partition of the indirect interaction $G_{(3)N3}$ yields the following increments

$$P^{(D)}_{(3)}[\text{Nu}^- - \text{C}_1(\text{C}_2)] = \mp\sqrt{2}G^{(D)}_{(3)N3}$$
$$P^{(A)}_{(3)}[\text{Nu}^- - \text{C}_1(\text{C}_2)] = -\sqrt{2}[G_{(2)N4}G_{(1)14} \pm G^{(A)}_{(3)N3}] \tag{27}$$

(Note that the first product of the right-hand side of Eq. (18), viz. $G_{(1)N3}G_{(2)13}$, does not depend on the orbitals of the substituent). For the alteration of the bond order of

the C_2-C_3 bond, we obtain

$$P^{(D)}_{(3)}[\text{Nu}^-, \text{C}_2 - \text{C}_3] = G_{(3)23}$$
$$P^{(A)}_{(3)}[\text{Nu}^-, \text{C}_2 - \text{C}_3] = -G_{(3)14} - G_{(1)N3}G_{(2)N4} \tag{28}$$

Comparison of these results to the relevant expressions of Ref. [19] allows us to conclude that the collection of terms of Eqs. (12)–(15), (18) and (20) related to the orbital $\varphi_{(+)2}$ and denoted by the superscript (D) in Eqs. (26)–(28) coincides with the respective collection for substituted ethenes containing a simple (one-orbital) electron-donating substituent D, whereas terms originating from the orbital $\varphi_{(-)4}$ and denoted by the superscript (A) do not differ from those of substituted ethenes $\text{H}_2\text{C}_\beta=\text{C}_\alpha\text{HA}$, where A stands for a simple (one-orbital) electron-accepting group. Moreover, the above-specified two sets of increments contribute additively to both the charge redistribution and alterations in bond orders of butadiene due to an attack of the reagent.

Therefore, the entire pattern of charge and bond order redistributions between the three fragments of the system $[\text{Nu}^- \cdots \text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2]$ results from superposition of two independent patterns corresponding to systems $[\text{Nu}^- \cdots \text{H}_2\text{C}=\text{CHD}]$ and $[\text{Nu}^- \cdots \text{H}_2\text{C}=\text{CHA}]$. For further simplicity, the latter will be referred to as elementary subsystems of our reacting system.

The case of an electrophilic attack upon the same butadiene molecule may be treated similarly. To this end, the third order indirect interaction $G_{(3)1E}$ should be accordingly partitioned as follows

$$G_{(3)1E} = G^{(D)}_{(3)1E} + G^{(A)}_{(3)1E} \tag{29}$$

where

$$G^{(D)}_{(3)1E} = \frac{S_{12}R_{23}Q_{3E}\mu}{2(1 + \varepsilon_{(-)E})}; \qquad G^{(A)}_{(3)1E} = -\frac{R_{14}Q_{43}Q_{3E}}{4(1 + \varepsilon_{(-)E})} \tag{30}$$

describe the increments of orbitals $\varphi_{(+)2}$ and $\varphi_{(-)4}$, respectively, and

$$\mu = \frac{1}{2} + \frac{1}{1 + \varepsilon_{(-)E}} > 1 \tag{31}$$

is an $\varepsilon_{(-)E}$-dependent parameter ($\varepsilon_{(-)E} < 1$, Fig. 1). For the partial transferred population $\delta x^{(4)2}_{(+)1,(-)E}$ we then obtain an additive form like that of Eq. (25).

The final result of analysis of Eqs. (16), (17), (19), (21) and (29)–(31) also completely resembles that obtained above: The total charge and bond order redistribution between fragments of the system $[\text{E}^+ \cdots \text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2]$ follows from superposition of two independent redistributions corresponding to respective elementary subsystems, viz. $[\text{E}^+ \cdots \text{H}_2\text{C}=\text{CHD}]$ and $[\text{E}^+ \cdots \text{H}_2\text{C}=\text{CHA}]$.

Therefore, additivity of the electron-donating and electron-accepting effects of the $\text{H}_2\text{C}=\text{CH}$-substituent upon the remaining fragments of the whole reacting system proves to be supported whatever the nature of the attacking reagent. This non-trivial result (it concerns third and fourth

order corrections of power series that are generally non-additive) may be traced back both to zero values of the direct and indirect interactions between orbitals of the $H_2C=CH$-substituent and to the additive nature of the third order interorbital interaction $G_{(3)ij}$ with respect to separate pairs of mediators (just the latter peculiarity makes partitions of Eqs. (22) and (29) possible).

5. Discussion of electron density and bond order redistributions for elementary subsystems

From the results of Section 4 it may be expected that the extent and the direction of the total influence of the $H_2C=CH$-substituent upon the remaining fragments of the reacting system depend on the relative ratio between the electron-donating effect of the orbital $\varphi_{(+)2}$ and the electron-accepting effect of the orbital $\varphi_{(-)4}$ for a particular type of the attacking reagent. In as much as the predominant direction of the addition process is unambiguously related to the electron-donating (accepting) properties of the substituent [2,5,16,17], competition of opposite trends may be anticipated also in respect of contributions of orbitals $\varphi_{(+)2}$ and $\varphi_{(-)4}$ to the relative reactivities of the internal and terminal carbon atoms of butadiene. Thus, relative increments of alternative elementary subsystems into the total electron density and bond order redistributions should be compared for systems $[Nu^-\cdots H_2C=CH-CH=CH_2]$ and $[E^+\cdots H_2C=CH-CH=CH_2]$ separately. Before turning to such a comparison, however, certain discussion of the nature of the electron density and bond order redistributions in individual elementary subsystems along with corresponding trends in relative reactivities of carbon atoms is required.

Let us start with the notation that the increments to the partial transferred populations denoted by the superscript 1 and described by Eqs. (12) and (16) do not contribute to differences in relative reactivities of the internal and terminal carbon atoms of both D- and A-substituted ethene (this may be easily seen after substituting Eqs. (7) and (8) into Eqs. (12) and (16)). The same evidently refers to relative reactivities of carbon atoms in butadiene. Thus, only the increments of Eqs. (13)–(15) and (17) should be considered. These yield the patterns of charge redistributions shown in Fig. 3.

To comment these pictures, let us start with the case of an electrophilic attack upon the D-substituted ethene studied in Ref. [19] in a more detail. As it is seen from the respective diagram 3a, the additional electron-donating influence of the orbital $\varphi_{(+)2}$ upon the charge redistribution due to electrophilic attack actually consists of three contributions, viz. (i) of the alteration in the electron-donating effect of this orbital upon the reacting $C_1=C_2$ bond under an indirect participation of electrophile represented by the partial transferred population $\delta x_{(+)2,(-)3}^{(4)2}$ (Note that the orbital $\varphi_{(-)E}$ is among the mediators of the indirect interaction $G_{(3)23}$),

(ii) of the indirect charge transfer between the electron-donating orbital $\varphi_{(+)2}$ and that of electrophile ($\varphi_{(-)E}$) by means of orbitals of the $C_1=C_2$ bond described by the increment $\delta x_{(+)2,(-)E}^{(4)3}$, and (iii) of the alteration in the electron-donating effect of the $C_1=C_2$ bond towards electrophile under an indirect participation of the orbital $\varphi_{(+)2}$ represented by the remaining partial transferred population $\delta x_{(+)1,(-)E}^{(4)2(D)}$. Accordingly, the most efficient way of addition of an electrophile to a D-substituted ethene coincides with that direction of the attack, which ensures larger extents of the above-enumerated three additional effects.

Comparative studies of these increments for an internal and a terminal position of electrophile with respect to the substituent in a D-substituted ethene [19] showed that positive (negative) corrections $\delta x_{(+)2,(-)3}^{(4)2}$ and $\delta x_{(+)1,(-)E}^{(4)2}$ and a large (small) positive value of the remaining correction $\delta x_{(+)2,(-)E}^{(4)3}$ are peculiar to a terminal (internal) position of the reagent E^+. Thus, it is the terminal attack of electrophile E^+ upon the molecule $H_2C=CHD$ that is accompanied by more extended transferred populations between any two fragments of the system $[E^+\cdots H_2C=CHD]$ and thereby by a larger stabilization energy (As it is shown in Ref. [29], the more extensive the partial transferred population $\delta x_{(+)i,(-)j}$ from the IOBO $\varphi_{(+)i}$ to the IVBO $\varphi_{(-)j}$ becomes, the larger the relevant increment to the total stabilization energy arises). At the same time, a larger bond order proves to be formed between the orbital $\varphi_{(-)E}$ and the $2p_z$ AO of the terminal carbon atom if just the latter is under attack [19]. These predictions of our approach, in turn, are in line with experimental facts [2,5,16,17].

On the whole, the above results along with coincidence between the system $[E^+\cdots H_2C=CHD]$ and an elementary subsystem of our reacting system $[E^+\cdots H_2C=CH-CH=CH_2]$ allow us to conclude that it is the electron-donating influence of the orbital $\varphi_{(+)2}$ that provides for a terminal addition of electrophile to the butadiene molecule.

For an electrophilic attack upon the A-substituted ethene (Fig. 3b), two partial transferred populations determine the difference in relative reactivities of carbon atoms, namely $\delta x_{(+)1,(-)E}^{(4)2(A)}$ and $\delta x_{(+)1,(-)4}^{(4)2}$. The first of these increments describes the alteration in the electron-accepting effect of electrophile upon the $C_1=C_2$ bond owing to the presence of the electron-accepting orbital $\varphi_{(-)4}$, whereas the second one represents an analogous alteration in the electron-accepting effect of the orbital $\varphi_{(-)4}$. Moreover, an internal (terminal) attack of electrophile was shown to be characterized by a positive (negative) values of both corrections and thereby by more (less) extended electron-accepting effects of both acceptors. Hence, the presence of an electron-accepting orbital $\varphi_{(-)4}$ contributes to an ability of butadiene to add an electrophile to its internal carbon atom.

Similar anticipations refer to a nucleophilic attack upon butadiene, only the directions of the favoured attacks traced back to influences of orbitals $\varphi_{(+)2}$ and $\varphi_{(-)4}$ are opposite to those obtained above. The relevant diagrams of charge redistributions are shown in Fig. 3c and d.
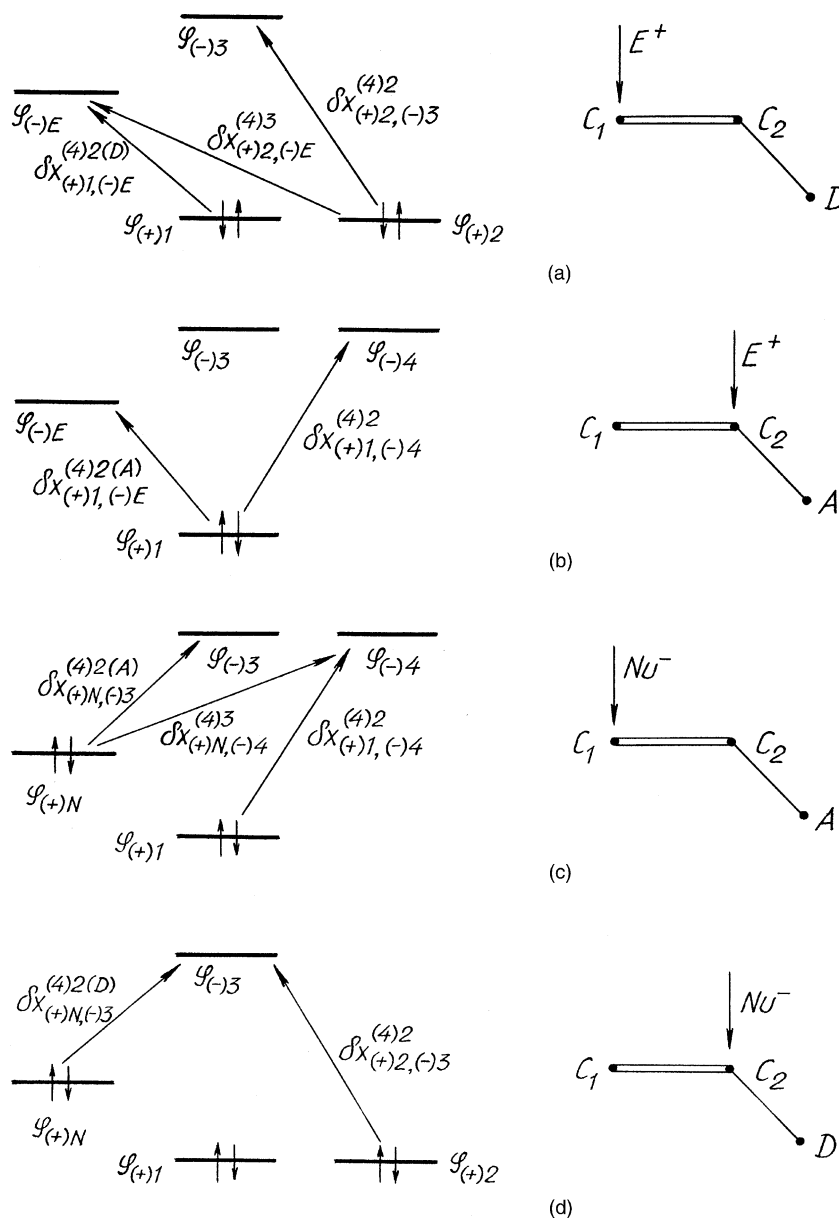
Fig. 3. Diagrams representing the electron density redistributions in elementary subsystems of systems [E$^+$···H$_2$C=CH–CH=CH] (a and b) and [Nu$^-$···H$_2$C=CH–CH=CH$_2$] (c and d). Notations of fragmental orbitals coincide with those of Fig. 1, whereas the partial populations $\delta x_{(+)i,(-)j}$ transferred between orbitals of opposite initial occupation ($\varphi_{(+)i}$ and $\varphi_{(-)j}$) are indicated by arrows (Definitions of these populations are given in Eqs. (12)–(17)). Substituted ethenes under attack of the same reagent corresponding to these elementary subsystems are shown in the right part of the diagram along with the predominant directions of the attack that are indicates by arrows.

Owing to similarity of models for reagents Nu$^-$ and E$^+$ and for substituents D and A, respectively [19], the elementary subsystems [Nu$^-$···H$_2$C=CHA] and [E$^+$···H$_2$C=CHD] also are similar so far as the nature of the electron-density redistribution is concerned. Thus, the approaching nucleophile (Nu$^-$) gives rise to additional electron-accepting effects of the substituent A both upon the C$_1$=C$_2$ bond and upon the reagent itself (Fig. 3c). Moreover, the orbital of the substituent A ($\varphi_{(-)4}$) participates in an additional charge transfer from nucleophile to the reaction center. Finally, an increased relative reactivity of the terminal position also will be obtained. This result, in turn, implies

that the influence of the electron-accepting orbital $\varphi_{(-)4}$ provides for a terminal addition of nucleophile to the butadiene molecule.

For a nucleophilic attack upon the D-substituted ethene (Fig. 3d), two partial populations represent the mutual influence of the electron-donating fragments Nu$^-$ and D, namely $\delta x_{(+)N,(-)3}^{(4)2(D)}$ and $\delta x_{(+)2,(-)3}^{(4)2}$. Studies of these increments shows that an internal attack of nucleophile is favoured.

It is seen, therefore, that the influences of orbitals $\varphi_{(+)2}$ and $\varphi_{(-)4}$ provide for opposite directions of the attacks of both E$^+$ and Nu$^-$ in accordance with our expectations.

Thus, the final result of this competition becomes of particular importance in determining the actual relative reactivities of the two carbon atoms in butadiene. In Section 6 we are going to compare the relevant contributions for a nucleophilic and an electrophilic attacks separately.

6. Dependence of the relative extents of the electron-donating and accepting effects of the H₂C=CH-substituent upon the nature of the attacking reagent

Let us deal first on the butadiene molecule under attack of nucleophile (Fig. 3c and d). Using Eqs. (6), (7), (10) and (23), we obtain that

$$G_{(3)N3}^{(D)} = \frac{\beta_N}{16\sqrt{2}(1 + \varepsilon_{(+)N})};$$

$$G_{(3)N3}^{(A)} = -\frac{\beta_N \lambda}{8\sqrt{2}(1 + \varepsilon_{(+)N})} \qquad (32)$$

and

$$|G_{(3)N3}^{(A)}| > |G_{(3)N3}^{(D)}| \qquad (33)$$

where the definition of λ Eq. (24) also is taken into consideration. As a result, Eqs. (7), (26) and (33) yield the following relation

$$|\delta x_{(+)N,(-)3}^{(4)2(A)}| > |\delta x_{(+)N,(-)3}^{(4)2(D)}| \qquad (34)$$

(Owing to opposite signs both of direct interaction $G_{(1)N3}^{(t)}$ and $G_{(1)N3}^{(i)}$ as shown in Eq. (7) and of two components of the third order interaction seen from Eq. (32), comparison of absolute values of partial transferred populations is appropriate here). The result shown in Eq. (34) implies that the role of the electron-accepting orbital $\varphi_{(-)4}$ predominates over that of the electron-donating orbital $\varphi_{(+)2}$ in the formation of the final extent of the charge transfer between nucleophile and the reaction center. A similar conclusion refers also to relative contributions of orbitals $\varphi_{(+)2}$ and $\varphi_{(-)4}$ to the newly formed bond orders between the orbital of nucleophile $\varphi_{(+)N}$ and those of the C₁=C₂ bond. Indeed, substituting Eq. (32) into Eq. (27) yields the relation

$$|P_{(3)}^{(A)}[\text{Nu}^- - \text{C}_1(\text{C}_2)]| > |P_{(3)}^{(D)}[\text{Nu}^- - \text{C}_1(\text{C}_2)]| \qquad (35)$$

(A considerable positive value of the second order indirect interaction $G_{(2)N4}$ and a small value of the same interaction for a terminal and an internal direction of the nucleophilic attack, respectively, should be taken into consideration here [19]).

The origin of the principal relation shown in Eq. (33) and thereby of its consequences represented by Eqs. (34) and (35) also deserves mentioning here. Indeed, this origin consists in a larger mediating ability of orbitals of opposite initial occupation ($\varphi_{(+)1}, \varphi_{(-)4}$) as compared to those of the same initial occupation ($\varphi_{(+)1}, \varphi_{(+)2}$) in the third order indirect interaction $G_{(3)N3}$ (The contribution $G_{(3)N3}^{(A)}$ contains

two increments that yield the factor λ, whilst $G_{(3)N3}^{(D)}$ consists of a single increment). The above-mentioned different mediating abilities, in turn, are determined by the structure of the right-hand side of Eq. (4).

Let us compare now the relative values of populations redistributed between orbitals of butadiene under attack of nucleophile and corresponding to participation of orbitals $\varphi_{(+)2}$ and $\varphi_{(-)4}$, namely $\delta x_{(+)2,(-)3}^{(4)2}$ and $\delta x_{(+)1,(-)4}^{(4)2}$, respectively. The first order interactions $G_{(1)23}$ and $G_{(1)14}$ contained within the definition of these populations (Eq. (14)) are of coinciding absolute values as shown in Eq. (10). Again, the third order interaction $G_{(3)14}$ is mediated by two orbitals of different initial occupation ($\varphi_{(+)N}$ and $\varphi_{(-)3}$), whereas the remaining one $G_{(3)23}$ contains orbitals of the same initial occupation ($\varphi_{(+)1}$ and $\varphi_{(+)N}$) in the same role. Consequently, a smaller absolute value of $G_{(3)23}$ is obtained, viz.

$$|G_{(3)14}| = \left| \frac{S_{1N}R_{N3}Q_{34}\lambda}{2(1 + \varepsilon_{(+)N})} \right| = \frac{\beta_N^2 \lambda}{8(1 + \varepsilon_{(+)N})}$$

$$|G_{(3)23}| = \left| -\frac{S_{21}S_{1N}R_{N3}}{4(1 + \varepsilon_{(+)N})} \right| = \frac{\beta_N^2}{16(1 + \varepsilon_{(+)N})} \qquad (36)$$

and

$$|G_{(3)14}| > |G_{(3)23}| \qquad (37)$$

The final result of our comparison is as follows

$$|\delta x_{(+)1,(-)4}^{(4)2}| > |\delta x_{(+)2,(-)3}^{(4)2}| \qquad (38)$$

This relation indicates that the assistance of nucleophile in the charge transfer between orbitals $\varphi_{(+)1}$ and $\varphi_{(-)4}$ proves to be more efficient as compared to the charge transfer between $\varphi_{(+)2}$ and $\varphi_{(-)3}$.

Finally, comparison of Fig. 3c and d shows that only the accepting orbital $\varphi_{(-)4}$ offers a possibility of an indirect charge transfer from nucleophile to the substituent (cf. the positive correction $\delta x_{(+)N,(-)4}^{(4)3}$). This fact also contributes to the conclusion about the more important role of the orbital $\varphi_{(-)4}$ as compared to that of $\varphi_{(+)2}$ in the charge redistribution under influence of a nucleophilic attack. Substituting Eq. (36) into Eq. (28), in turn, yields the relation

$$|P_{(3)}^{(A)}[\text{Nu}^-, \text{C}_2 - \text{C}_3]| > |P_{(3)}^{(D)}[\text{Nu}^-, \text{C}_2 - \text{C}_3]| \qquad (39)$$

It is seen that the orbital $\varphi_{(-)4}$ contributes more essentially to the increase of bond order of the initially single (C₂−C₃) bond due to the attack of nucleophile.

Therefore, it is the electron-accepting ability of the antibonding orbital $\varphi_{(-)4}$ of our H₂C=CH-substituent that manifests itself more extensively under influence of a nucleophilic attack upon butadiene as compared to the electron-donating ability of the bonding orbital $\varphi_{(+)2}$. Consequently, the entire H₂C=CH-group may be considered as an electron-accepting substituent in this case. It is no surprise that a terminal addition of nucleophile to the butadiene molecule actually predominates over an

internal one as it was the case with an A-substituted ethene [1–5,16,17,19].

Let us turn now to the electrophilic attack. Instead of Eqs. (32)–(34), we then obtain

$$|G_{(3)1E}^{(D)}| = \frac{\beta_E \mu}{8\sqrt{2}(1 + \varepsilon_{(-)E})};$$

$$|G_{(3)1E}^{(A)}| = \frac{\beta_E}{16\sqrt{2}(1 + \varepsilon_{(-)E})}, \tag{40}$$

$$|G_{(3)1E}^{(D)}| > |G_{(3)1E}^{(A)}| \tag{41}$$

and

$$|\delta x_{(+)1,(-)E}^{(4)2(D)}| > |\delta x_{(+)1,(-)E}^{(4)2(A)}| \tag{42}$$

Hence, contribution of the electron-donating orbital $\varphi_{(+)2}$ exceeds that of the electron-accepting orbital $\varphi_{(-)4}$ in the charge transfer between the $C_1{=}C_2$ bond and electrophile. This result may be traced back to a larger mediating ability of orbitals $(\varphi_{(+)2}, \varphi_{(-)3})$ as compared to that of orbitals $(\varphi_{(-)4}, \varphi_{(-)3})$ in the third order interaction $G_{(3)1E}$. It is also seen that the electron-donating level $\varphi_{(+)2}$ offers its electrons to electrophile by means of orbitals of the $C_1{=}C_2$ bond and thereby contributes additionally to the total stabilization of the system.

To make a comparison of the partial transferred populations inside the butadiene molecule ($\delta x_{(+)1,(-)4}^{(4)2}$ and $\delta x_{(+)2,(-)3}^{(4)2}$), Eqs. (10) and (14) should be used. As opposed to the case of a nucleophilic attack, it is the third order interaction $G_{(3)23}$ that is mediated by two orbitals of different initial occupation (viz. $\varphi_{(+)1}$ and $\varphi_{(-)E}$) but not $G_{(3)14}$. We then obtain

$$|G_{(3)23}| > |G_{(3)14}| \tag{43}$$

and

$$|\delta x_{(+)2,(-)3}^{(4)2}| > |\delta x_{(+)1,(-)4}^{(4)2}| \tag{44}$$

The latter relation implies that the role of the initially occupied orbital $\varphi_{(+)2}$ predominates over that of the initially vacant orbital $\varphi_{(-)4}$ in the intramolecular charge redistribution under influence of an electrophilic attack. The same conclusion refers also to alterations in bond orders defined by Eqs. (19) and (21).

Hence, it is the electron-donating ability of the bonding orbital $\varphi_{(+)2}$ of the $H_2C{=}CH$-substituent that primarily manifests itself under influence of an electrophilic attack. Consequently, the entire substituent may be considered as an electron-donating one in this system. This conclusion, in turn, proves to be in line with a terminal addition of electrophile to the butadiene molecule.

It is seen, therefore, that the $H_2C{=}CH$-substituent always acquires opposite electron-donating (accepting) properties relatively to those of the approaching reagent, and thereby a terminal addition of the latter predominates over an internal one for both electrophile and nucleophile.

7. Concluding remarks

The principal achievements of the above study may be summarized as follows:

1. A new way of accounting for the known higher reactivity of the terminal carbon atoms of butadiene as compared to the internal ones is suggested in terms of charge and bond order redistributions between separate fragments of both participants of the reaction. These redistributions, in turn, are directly related to respective alterations in total energy [29]. As opposed to traditional ways of interpretation of the same reactivity, delocalized (canonical) MOs of butadiene are not invoked here.
2. The charge and bond order redistributions determining different reactivities of carbon atoms of butadiene, in turn, are related to definite peculiarities of indirect interactions between fragmental orbitals. This result demonstrates the efficiency and fruitfulness of the concept of direct (through-space) and indirect (through-bond) interactions, which was originally suggested for interpretation of photoelectron spectra of molecules [30–33].
3. Adequacy of the classical concepts of the reaction center and its neighborhood is verified for the case of an addition reaction to butadiene. It is shown that neither the formal equivalence of the $H_2C{=}CH$-fragments in an isolated butadiene molecule nor their mutual interaction (conjugation) is likely to run counter to an assumption about distinct roles of these fragments in the addition process.
4. As opposed to the traditional delocalized approaches and models, reactivity of butadiene is considered in the context of those of other substituted ethenes. In particular, a direct relation is established between the reactivity of butadiene with respect to electrophile and nucleophile and those of D- and A-substituted ethenes, respectively.
5. A decisive dependence of the electron-donating (accepting) ability of the $H_2C{=}CH$-group upon the nature of the approaching reagent is demonstrated. This example serves as an additional argument for certain limitations of the usual classification of substituents into electron-donating and electron-accepting ones irrespective of the whole system under study.

The direct way of obtaining the one-electron density matrix by means of solution of the commutation equation underlying the above-enumerated achievements was shown to be a part of the so-called non-canonical method of MOs (NCMO method) [21,24]. Another part of the same method coincides with the Brillouin theorem used to derive non-canonical one-electron orbitals (NCMOs). Moreover, both the bond order matrix and the relevant NCMO representation matrix proved to yield a localized description of electronic structures. In this context, the above study may be considered as an application of the NCMO method to chemical reactivity

of butadiene, and a localized description of this reactivity is actually obtained.

The NCMO method and the canonical MO method have been considered as complementary approaches to investigate electronic structures including that of butadiene [25]. The same conclusion is likely to refer to their applications to reactivity of this molecule with respect to an electrophile or nucleophile: In the standard perturbative approaches based on the HOMO/LUMO concept [3,11,14,15], emphasis was laid on properties of the initial butadiene molecule as a whole that determine its further reactivity (cf. coefficients of the HOMO and LUMO at the $2p_z$ AOs of the internal and terminal carbon atoms). In our approach, however, emphasis is replaced on roles of separate $H_2C=CH$-fragments in the addition process.

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