



Direct and indirect interactions of orbitals as an efficient tool for investigation of chemical reactivity. The Ad_E2 reaction of substituted ethenes

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Abstract

A new approach to investigate chemical reactivity is suggested on the basis of power series for the one-electron density matrix [J. Mol. Struct. (Theochem) 343 (1995) 183]. Electron density and bond order redistributions among separate fragments of contacting molecules are studied directly there without invoking the concept of delocalized molecular orbitals of respective isolated compounds. Direct and indirect interactions of fragmental orbitals serve as the principal terms for interpretation of the above-mentioned redistributions. To explore the possibilities of the approach, the electrophilic addition (Ad_E2) reaction of substituted ethenes $H_2C_\beta=C_\alpha HX$ is studied in a detail, where X is an electron-donating (accepting) substituent. Particular steps of the reaction are modeled, viz. an initial electrophilic attack upon individual carbon atoms, a middle attack upon the $C_\beta=C_\alpha$ bond resulting into a bridged electrophile-containing ion and a subsequent nucleophilic attack upon such an ion. A relation is established between different reactivities of the C_α and C_β atoms and different efficiencies of charge and bond order redistributions between the reagent, the $C_\beta=C_\alpha$ bond and the substituent X. It is shown that even in the hypothetical bridged ions of symmetrical spatial constitution there are some electronic factors that determine different abilities of carbon atoms to add a middle-positioned reagent. A concerted mechanism is predicted for the second step of the reaction, viz. for the addition of nucleophile to a bridged electrophile-containing intermediate. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Separate fragments of an extended organic compound are usually assumed to play different roles in chemical reactions. Indeed, certain fragments (functional groups) are supposed to participate in the given process directly and, as a consequence, their chemical nature undergoes a change. These fragments are

mostly referred to as the reaction center(s) (see Ref. [1]). Again, the remaining groups of atoms (especially the substituents) are considered as taking part in the reaction indirectly by exerting certain electron-donating (accepting) effects upon the reaction center(s). Moreover, the extents of these effects are expected to be quite different at various stages of the reaction [2–4].

The above-described traditional approach to chemical reactivity forms the basis of classification of both chemical compounds and reactions. The

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principal point here is that certain type of reactions is expected to be a distinctive feature of the whole class of compounds containing the same functional group able to play the role of the reaction center [4,5]. Similar concepts underlie the well-known powerful LFER method based on the Linear Free Energy Relationship [4–6].

These concepts, however, are not straightforwardly compatible with the majority of quantum chemical approaches to investigation of reactivity. Indeed, the latter are based on passing to the basis of delocalized canonical molecular orbitals (CMOs) either of isolated molecules or of a supposed transition state [1,7–10]. This makes it difficult to reveal different roles of separate groups of atoms in the given process and thereby to discuss the reaction mechanism in terms of molecular fragments and their interactions.

In this context, the direct way of obtaining the one-electron density matrix (bond order matrix) [11–13] in the form of power series seems to be promising. This expectation is based on the following points.

First, no passing into the basis of CMOs is required there. Moreover, basis orbitals localized on separate fragments of molecule(s) (e.g. the two-center bond orbitals [12–14], orbitals of the phenyl ring [15,16], etc.) meet the requirements underlying the relevant power series [12–16]. Hence, studies of redistributions among separate fragments of interacting molecules of both electron density and bond orders seems to be feasible. The resulting extents of intra- and intermolecular charge transfer, in turn, may be directly related to respective alterations in total energy as demonstrated recently [17].

Second, separate members of the power series for the bond order matrix have been expressed in terms of submatrices describing the direct and indirect interactions of basis orbitals [11]. This offers a possibility of interpretation of the electron density redistribution due to intermolecular contact in terms of above-mentioned interactions. The same evidently refers to the relevant redistributions of bond orders.

Thus, application of the above-specified approach is likely to yield a new interpretation of chemical reactivity, that is, more closely related to the above-described classical chemical concepts as compared to the usual quantum-chemical methods.

In this paper, we are about to demonstrate the above-outlined possibilities using the popular bimo-

lecular electrophilic addition ($\text{Ad}_{\text{E}2}$) reaction of substituted ethenes $\text{H}_2\text{C}_\beta=\text{C}_\alpha\text{HX}$ [1,2,4–8,18–29] as an example, where X stands either for an electron-donating substituent ($\text{X} = \text{D}$) or for an electron-accepting one ($\text{X} = \text{A}$). Specific aims of this study concerning the very $\text{Ad}_{\text{E}2}$ process also may be mentioned as follows:

(1) The C_α and C_β carbon atoms are known to be of different reactivity with respect to both the initially attacking electrophile (E^+) and the subsequently attacking nucleophile (Nu^-) (cf. the so-called Markovnikov rule [1,2,4–6]). Our aim here consists in relating this dissimilarity of carbon atoms to different efficiencies of charge and bond order redistributions among separate fragments of the system for different directions of the attack (to this end, the cases when the C_α and C_β atoms are under attack will be considered separately. The $\text{C}_\alpha=\text{C}_\beta$ bond, the substituent X and the attacking reagent(s) will play the role of fragments). We also are about to establish the place this new approach takes among the two traditional alternatives, namely (i) the perturbative methods based on CMOs and resolving themselves into studies of an isolated reactant molecule [1,8,18,20] (in particular, of constitution of the highest-occupied and lowest-vacant CMOs of initial substituted ethenes [1,8,18]), and (ii) studies of relative stabilities of the supposed transition states (e.g. of two possible carbenium ions [2,4,7]).

(2) Constitutions of intermediates of the $\text{Ad}_{\text{E}2}$ reactions are still under discussion [2,4,5,7,8,18,19,21,22,24–29]. The classical acyclic carbocation (carbenium ion) and the bridged non-classical (onium) ion are the extreme alternatives here. The latter has been suggested to play the role of the intermediate [22] in order to be able to account for the antiperiplanar addition peculiar to the majority of the $\text{Ad}_{\text{E}2}$ processes. For the electrophilic addition of bromine to alkenes, the intermediacy of bromonium ions has been supported later by several lines of evidence [5]. Under an assumption of a bridged ion as an intermediate, however, some difficulties arise [2,4] in the way of rationalizing the actual ratios between the two possible addition products (that are in accordance and against the Markovnikov rule for molecules containing an electron-donating and accepting substituent, respectively). In this paper, we are going to circumvent these difficulties on the

basis of investigation of the most probable subsequent rearrangement of the E^+ - and/or Nu^- -containing bridged ions. To this end, bond orders between the orbitals of a middle-positioned reagent and those of the C_α and C_β atoms will be studied.

We will start with a close analogy that may be traced between the problem to be solved here and that of the intersubstituent interaction [16] (Section 2). This analogy allows us to omit many details of derivation of expressions for occupation numbers of basis orbitals and to confine ourselves to a brief overview of the final formulae (Section 3). Derivation of expressions for newly formed bond orders (that are absent in the previous contributions) is discussed in a more detail.

Section 4 is entirely devoted to investigation of particular steps of the Ad_E2 process. We start with an initial electrophilic attack upon separate carbon atoms (Section 4.1). A middle attack upon the $C_\alpha=C_\beta$ bond resulting into a bridged E^+ -containing ion is studied in Section 4.2. Finally, a subsequent nucleophilic attack upon a bridged E^+ -containing ion is modeled in Section 4.3.

2. General discussion of the problem

Let us start with the analogy of our problem to that of intersubstituent interaction [16]. Different mutual spatial arrangements of two substituents (e.g. in *ortho*-, *meta*- and *para*-disubstituted benzenes) were shown to be accompanied by different extents of charge transfer both between the two substituents and between any substituent and the mediating hydrocarbon fragment [16]. A similar result may be expected also when studying the relative reactivities of the C_α and C_β atoms of substituted ethenes provided that an attacking nucleophilic (electrophilic) agent and an electron-donating (accepting) substituent may be modeled similarly.

The latter condition may be easily met in the approach of Refs. [11–16]. Indeed, both a substituent and a reagent may be represented by a single orbital [13,15,16,30], namely by an initially occupied (vacant) orbital for a donating (accepting) subsystem, respectively. Moreover, no specifying of the nature of an overlap integral

(resonance parameter) between two orbitals is required when constructing the Hückel type model Hamiltonian matrix of Refs. [11–16]. Thus, in this matrix, there is no qualitative difference between an interaction of the σ -type between an orbital of the attacking particle and a $2p_z$ AO of carbon atom and an interaction of the π -type between the latter and an orbital of a substituent.

The above-cited paper [16] was entirely devoted to the intersubstituent interaction in (D,A)-disubstituted benzenes. Nevertheless, the general expressions for elements of the bond order matrix responsible for intersubstituent effects refer to any hydrocarbon fragment provided that direct interactions between orbitals of different substituents may be ignored. After making the relevant assumption (see Eq. (6) given later), all the general expressions of Ref. [16] may be directly applied for investigation of substituted ethenes under attack of electrophile and/or nucleophile.

As it was mentioned already, elements of the bond order matrix have been expressed in Refs. [11–16] 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 ($\varphi_{(+)i}$, $i = 1, 2, \dots, I$) and of J initially vacant ones ($\varphi_{(-)j}$, $j = 1, 2, \dots, J$) that will be further abbreviated by IOBOs and IVBOs, respectively. Then, the first order element $G_{(1)ij}$ may be expressed as follows [11]:

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

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

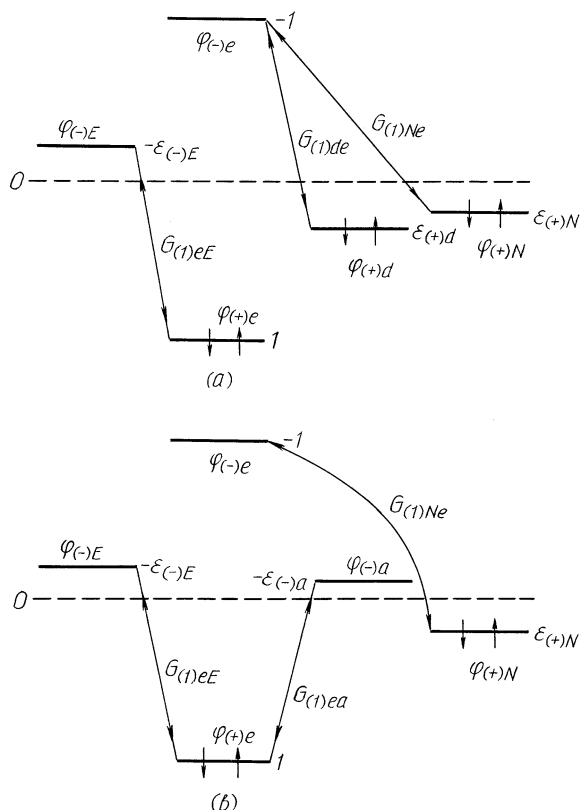


Fig. 1. Diagrams reflecting the relative positions of energy levels corresponding to fragmental orbitals of substituted ethenes $H_2C_B=C_AHX$ under attack of an electrophile and/or nucleophile, as well as the non-zero direct interactions between these orbitals. The first picture (a) refers to the system containing an electron-donating substituent ($X = D$) and the second one (b) corresponds to an analogous acceptor-containing system ($X = A$). Orbitals $\varphi_{(+),e}$ ($\varphi_{(-),e}$) and $\varphi_{(+),d}$ ($\varphi_{(-),a}$) coincide with the bonding (antibonding) orbital of the ethene fragment and those of substituents D(A), respectively. Similarly, orbitals $\varphi_{(-),E}$ and $\varphi_{(+),N}$ represent an approaching electrophile and nucleophile, respectively.

means of a single mediator. This element takes the form

$$G_{(2)ij} = \frac{1}{E_{(+),i} - E_{(-),j}} \left\{ \sum_m^{\text{IOBOs}} \frac{S_{im}R_{mj}}{E_{(+),m} - E_{(-),j}} - \sum_n^{\text{IVBOs}} \frac{R_{in}Q_{nj}}{E_{(+),i} - E_{(-),n}} \right\} \quad (2)$$

where the meanings of designations coincide with

those of Eq. (1), and

$$S_{im} = \langle \varphi_{(+),i} | \hat{H} | \varphi_{(+),m} \rangle, \quad R_{mj} = \langle \varphi_{(+),m} | \hat{H} | \varphi_{(-),j} \rangle, \quad (3)$$

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

It is seen that both IOBOs and IVBOs of the molecule 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:

$$G_{(3)ij} = \frac{-1}{E_{(+),i} - E_{(-),j}} \times \left\{ \sum_n^{\text{IOBOs}} \sum_m^{\text{IOBOs}} \frac{S_{in}S_{nm}R_{mj}}{(E_{(+),n} - E_{(-),j})(E_{(+),m} - E_{(-),j})} - \sum_n^{\text{IOBOs}} \sum_r^{\text{IVBOs}} \left[\frac{S_{in}R_{nr}Q_{rj}}{(E_{(+),n} - E_{(-),j})(E_{(+),n} - E_{(-),r})} + \frac{S_{in}R_{nr}Q_{rj}}{(E_{(+),i} - E_{(-),r})(E_{(+),n} - E_{(-),r})} + \frac{R_{ir}R_{rn}^+R_{nj}}{(E_{(+),n} - E_{(-),r})(E_{(+),r} - E_{(-),j})} + \frac{R_{ir}R_{rn}^+R_{nj}}{(E_{(+),i} - E_{(-),r})(E_{(+),n} - E_{(-),r})} \right] + \sum_p^{\text{IVBOs}} \sum_r^{\text{IVBOs}} \frac{R_{ir}Q_{rp}Q_{pj}}{(E_{(+),i} - E_{(-),p})(E_{(+),i} - E_{(-),r})} \right\} \quad (4)$$

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 dwell now on the D- or A-substituted ethenes under attack of electrophile (E^+) and/or nucleophile (Nu^-). The substituents D(A) will be represented by an IOBO(IVBO) $\varphi_{(+),d}$ ($\varphi_{(-),a}$), whereas the nucleophilic (electrophilic) agents will be accordingly described by an IOBO (IVBO) $\varphi_{(+),N}$ ($\varphi_{(-),E}$).

The ethene fragment ($C_\beta=C_\alpha$), in turn, will be characterized by both an IOBO $\varphi_{(+e)}$ and an IVBO $\varphi_{(-e)}$. These will be defined as the bonding and the antibonding combinations, respectively, of $2p_z$ AOs of the C_α and C_β atoms denoted by χ_α and χ_β , i.e.

$$\varphi_{(+e)} = \frac{1}{\sqrt{2}}(\chi_\beta + \chi_\alpha), \quad \varphi_{(-e)} = \frac{1}{\sqrt{2}}(\chi_\beta - \chi_\alpha) \quad (5)$$

The initial Coulomb parameters of AOs χ_α and χ_β are assumed to be uniform and serve as the energy reference point, whereas the resonance parameter between AOs χ_α and χ_β coincides with the energy unit. Then one-electron energies of orbitals $\varphi_{(+e)}$ and $\varphi_{(-e)}$ equal to 1 and -1 , respectively. Energies corresponding to orbitals $\varphi_{(-E)}$, $\varphi_{(+N)}$, $\varphi_{(+d)}$ and $\varphi_{(-a)}$ will be designated by $-\varepsilon_{(-E)}$, $\varepsilon_{(+N)}$, $\varepsilon_{(+d)}$ and $-\varepsilon_{(-a)}$, where $\varepsilon_{(-E)}$, $\varepsilon_{(+N)}$, $\varepsilon_{(+d)}$ and $\varepsilon_{(-a)}$ are positive parameters (in our negative energy units). Relative positions of energy levels for the cases of D- and A-substituted ethene are shown in Fig. 1(a) and (b).

Definition of orbitals $\varphi_{(+e)}$ and $\varphi_{(-e)}$ of Eq. (5) along with uniform Coulomb parameters for AOs χ_α and χ_β imply that no direct interaction takes place between $\varphi_{(+e)}$ and $\varphi_{(-e)}$. Furthermore, the ‘external’ orbitals $\varphi_{(-E)}$, $\varphi_{(+N)}$, $\varphi_{(+d)}$ and $\varphi_{(-a)}$ are supposed to interact directly only with either $\varphi_{(+e)}$ or $\varphi_{(-e)}$ but not one with another. We then obtain

$$G_{(1)ee} = G_{(1)NE} = G_{(1)dE} = G_{(1)Na} = 0 \quad (6)$$

The non-zero direct interactions of our basis orbitals are shown in Fig. 1.

After accepting Eq. (6), our problem actually differs from that of intersubstituent effects [16] only in numbers of ‘surrounding’ electron-donating (D) and accepting (A) subsystems. On this basis, a similar nature of the relevant charge redistributions may be concluded. In particular, the second order transferred populations (that are proportional to squares of direct interactions between orbitals of two fragments [11–16]) describe local charge redistributions between pairs of directly contacting fragments, namely between the reagent and the $C_\alpha=C_\beta$ bond and between the latter and the substituent $X = D, A$. These redistributions evidently are independent of the spatial arrangement of the remaining fragment and thereby do not contribute to differences in reactivities

of the C_α and C_β atoms (see also Section 4.1). The third order corrections to populations transferred, in turn, take zero values under an assumption like that of Eq. (6) [16]. This implies that the fourth order contributions to occupation numbers should be considered when looking for differences in relative reactivities of carbon atoms. Just these are among the principal subjects of Section 3.

3. Expressions for occupation numbers of basis orbitals and for bond orders

Separate corrections to occupation numbers (including those of the fourth order) may be presented as sums of partial increments, each of them referring to an orbital of the opposite subset [16,17]. Then partial populations ($\delta x_{(+i),(-j)}$) transferred between pairs of orbitals of different initial occupation ($\varphi_{(+i)}$ and $\varphi_{(-j)}$) may be defined that offer a more convenient way of representation of charge redistribution. Each fourth order increment $\delta x_{(+i),(-j)}^{(4)}$ to the partial transferred population $\delta x_{(+i),(-j)}$, in turn, consists of three contributions, further denoted by additional superscripts 1, 2 and 3.

For a D-substituted ethene under attack of electrophile and/or nucleophile (Fig. 1(a)), the above-enumerated increments are

$$\delta x_{(+e),(-E)}^{(4)1} = 2(G_{(1)eE})^4; \quad \delta x_{(+N),(-e)}^{(4)1} = 2(G_{(1)Ne})^4 + 2(G_{(1)Ne})^2(G_{(1)de})^2; \quad (7)$$

$$\delta x_{(+d),(-e)}^{(4)1} = 2(G_{(1)de})^4 + 2(G_{(1)de})^2(G_{(1)Ne})^2$$

$$\delta x_{(+d),(-e)}^{(4)2} = 4G_{(1)de}G_{(3)de}; \quad \delta x_{(+d),(-E)}^{(4)3} = 2(G_{(2)dE})^2 \quad (8)$$

$$\delta x_{(+e),(-E)}^{(4)2} = 4G_{(1)eE}G_{(3)eE}; \quad (9)$$

$$\delta x_{(+N),(-e)}^{(4)2} = 4G_{(1)Ne}G_{(3)Ne}$$

$$\delta x_{(+N),(-E)}^{(4)3} = 2(G_{(2)NE})^2; \quad \delta x_{(+e),(-e)}^{(4)3} = 2(G_{(2)ee})^2 \quad (10)$$

For an analogous acceptor-containing system (Fig.

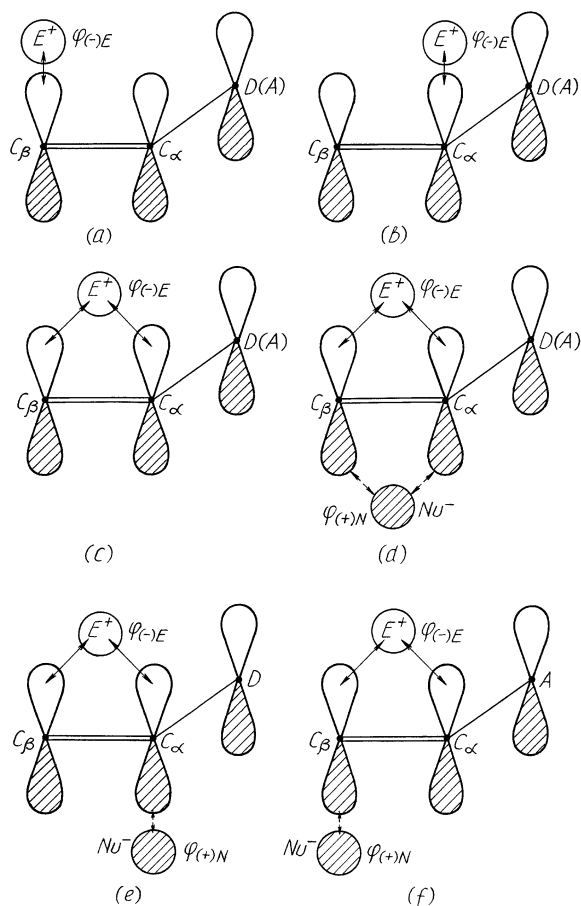


Fig. 2. Models of particular steps of the AdE_2 reaction studied in the article. The first two pictures (a) and (b) represent the initial electrophilic attacks upon the C_β and C_α atoms, respectively, while the third one (c) shows the model of a bridged electrophile-containing ion. The remaining pictures represent a hypothetical system containing two middle-positioned reagents (both E^+ and Nu^-) (d) and the models of the nucleophilic attack upon the C_α and C_β atoms of the bridged electrophile-containing ion. Dashed lobes of the atomic orbitals are those corresponding to negative values of basis functions. Intermolecular resonance parameters are indicated by arrows.

1(b)), we obtain

$$\begin{aligned} \delta x_{(+),e,(-)E}^{(4)1} &= 2(G_{(1)eE})^4 + 2(G_{(1)ea})^2(G_{(1)eE})^2; \\ \delta x_{(+),N,(-)e}^{(4)1} &= 2(G_{(1)Ne})^4; \\ \delta x_{(+),e,(-)a}^{(4)1} &= 2(G_{(1)ea})^4 + 2(G_{(1)eE})^2(G_{(1)ea})^2 \end{aligned} \quad (11)$$

and

$$\delta x_{(+),e,(-)a}^{(4)2} = 4G_{(1)ea}G_{(3)ea}; \quad \delta x_{(+),N,(-)a}^{(4)3} = 2(G_{(2)Na})^2 \quad (12)$$

instead of Eqs. (7) and (8), respectively, whereas the expressions of Eqs. (9) and (10) do not change their form.

Let us turn now to expressions for bond orders between pairs of orbitals ($\varphi_{(-)E}$, χ_α), ($\varphi_{(-)E}$, χ_β), ($\varphi_{(+),N}$, χ_α) and ($\varphi_{(+),N}$, χ_β), representing the strengths of the newly formed bonds between an attacking reagent (Nu^- or E^+) and the $2p_z$ AOs of carbon atoms. Let these bond orders to be denoted by $P[\text{E}^+ - \text{C}_\beta(\text{C}_\alpha)]$ and $P[\text{Nu}^- - \text{C}_\beta(\text{C}_\alpha)]$. Using Eq. (5) we then obtain

$$P[\text{E}^+ - \text{C}_\beta(\text{C}_\alpha)] = \frac{1}{\sqrt{2}}(P_{(+),e,(-)E} \pm P_{(-),e,(-)E}) \quad (13)$$

$$P[\text{Nu}^- - \text{C}_\beta(\text{C}_\alpha)] = \frac{1}{\sqrt{2}}(P_{(+),e,(+)N} \pm P_{(-),e,(+)N}) \quad (14)$$

where the upper and lower signs here and below correspond to the C_β and C_α atoms, respectively. Expressions for intra- ($P_{(+),e,(+)N}$, $P_{(-),e,(-)E}$) and intersubset bond orders ($P_{(+),e,(-)E}$, $P_{(-),e,(+)N}$) may be taken from the off-diagonal elements of the respective submatrices of the total bond order matrix [16]. To discuss the results of substituting them into Eqs. (13) and (14), let us start with the bond order $P[\text{E}^+ - \text{C}_\beta(\text{C}_\alpha)]$.

The first order correction to this bond order is proportional to the direct interaction $G_{(1)eE}$ between orbitals $\varphi_{(+),e}$ and $\varphi_{(-)E}$ and does not contribute to differences under interest (see Section 4.1). The second order contribution to the same bond order is

$$P_{(2)}[\text{E}^+ - \text{C}_\beta(\text{C}_\alpha)] = -\sqrt{2} \left[G_{(2)eE} \mp \sum_i^{\text{IOBOs}} G_{(1)ei}^+ G_{(1)iE} \right] \quad (15)$$

After taking Eq. (6) into consideration, we then obtain

$$\begin{aligned} P_{(2)}^{(D)}[\text{E}^+ - \text{C}_\beta(\text{C}_\alpha)] &= P_{(2)}^{(A)}[\text{E}^+ - \text{C}_\beta(\text{C}_\alpha)] \\ &= -\sqrt{2}G_{(2)eE} = 0 \end{aligned} \quad (16)$$

where the superscripts (D) and (A) indicate the nature of substituents and the last equality is based on the

absence of an efficient mediator for the indirect interaction $G_{(2)eE}$ (see Fig. 1). Finally, the third order increment to the same bond order takes the form

$$P_{(3)}[E^+ - C_\beta(C_\alpha)] = -\sqrt{2} \left[G_{(3)eE} \mp \sum_i^{\text{IOBOs}} (G_{(1)ei}^+ G_{(2)iE} + G_{(2)ei}^+ G_{(1)iE}) \right] \quad (17)$$

and determines the difference between bond orders $P[E^+ - C_\beta]$ and $P[E^+ - C_\alpha]$. For a D-substituted ethene, we obtain

$$P_{(3)}^{(D)}[E^+ - C_\beta(C_\alpha)] = -\sqrt{2} [G_{(3)eE} \mp G_{(1)de} G_{(2)dE} \mp G_{(1)Ne} G_{(2)NE} \mp G_{(2)ee} G_{(1)eE}] \quad (18)$$

For an A-containing system, the relevant expression for $P_{(3)}^{(A)}[E^+ - C_\beta(C_\alpha)]$ follows from Eq. (18) after omitting the product $G_{(1)de} G_{(2)dE}$ from its right-hand side.

Analysis of Eq. (14) also yields similar results. Thus, the first order increments to bond orders $P[\text{Nu}^- - C_\beta(C_\alpha)]$ are of coinciding values for both carbon atoms, whereas the second order increments vanish. The third order contribution determining the difference being sought may be expressed as follows:

$$P_{(3)}[\text{Nu}^- - C_\beta(C_\alpha)] = -\sqrt{2} \left[\sum_j^{\text{IVBOs}} (G_{(1)Nj} G_{(2)je}^+ + G_{(2)Nj} G_{(1)je}^+) \pm G_{(3)Ne} \right] \quad (19)$$

and yields the following final expression

$$P_{(3)}^{(A)}[\text{Nu}^- - C_\beta(C_\alpha)] = -\sqrt{2} (G_{(1)Ne} G_{(2)ee} + G_{(1)eE} G_{(2)NE} + G_{(1)ea} G_{(2)Na} \pm G_{(3)Ne}) \quad (20)$$

The respective expression for $P_{(3)}^{(D)}[\text{Nu}^- - C_\beta(C_\alpha)]$ follows from Eq. (20) after omitting the product $G_{(1)ea} G_{(2)Na}$ from its right-hand side.

4. Studies of particular steps of the Ad_E2 reaction

4.1. Electrophilic attacks upon separate carbon atoms

An initial electrophilic attack upon the $C_\alpha(C_\beta)$ atom will be modeled by situating the relevant orbital $\varphi_{(-)E}$ above the AO χ_α (χ_β) as shown in Fig. 2(a) and (b) (nucleophile and thereby the orbital $\varphi_{(+)N}$ are absent in this model).

To study the dependence of charge redistribution only upon the spatial position of electrophile (E^+), the resonance parameters $\langle \varphi_{(-)E} | \hat{H} | \chi_\alpha \rangle$ and $\langle \varphi_{(-)E} | \hat{H} | \chi_\beta \rangle$ will be assumed to take coinciding values for both directions of the attack (that are positive in our negative energy units). As a result, the following inequalities

$$R_{eE}^{(\alpha)} = R_{eE}^{(\beta)} > 0; \quad G_{(1)eE}^{(\alpha)} = G_{(1)eE}^{(\beta)} < 0; \quad Q_{eE}^{(\alpha)} < 0; \quad Q_{eE}^{(\beta)} > 0; \quad |Q_{eE}^{(\alpha)}| = |Q_{eE}^{(\beta)}| \quad (21)$$

are valid whatever the nature of the substituent (definition of orbitals $\varphi_{(+)e}$ and $\varphi_{(-)e}$ of Eq. (5) is invoked here). Coincidence of direct interactions $G_{(1)eE}^{(\alpha)}$ and $G_{(1)eE}^{(\beta)}$ ensures coinciding extents of the direct (second order) charge transfer between the $C_\alpha=C_\beta$ bond and the electrophile for both directions of the attack (Section 2).

To study the indirect (fourth order) charge redistribution, let us start with the D-substituted ethene. Then the following relations

$$S_{ed} > 0; \quad R_{de} < 0; \quad G_{(1)de} > 0 \quad (22)$$

should be added to Eq. (21), and these do not depend on the direction of the attack. As a result, the increments to partial transferred populations defined by Eq. (7) do not contribute to differences being sought.

Orbitals $\varphi_{(+)d}$ and $\varphi_{(-)e}$ play the role of mediators of the indirect $G_{(3)eE}$ (Fig. 1(a)). Then Eq. (4) yields the following expression

$$G_{(3)eE} = \frac{S_{ed} R_{de} Q_{eE}}{(1 + \varepsilon_{(-)E})(1 + \varepsilon_{(+)d})} \left[\frac{1}{2} + \frac{1}{\varepsilon_{(+)d} + \varepsilon_{(-)E}} \right] \quad (23)$$

After invoking Eq. (21), we obtain that

$$G_{(3)eE}^{(\alpha)} > 0; \quad G_{(3)eE}^{(\beta)} < 0 \quad (24)$$

Substituting Eqs. (21) and (24) into Eq. (9) results into relevant inequalities for partial transferred populations, viz.

$$\delta x_{(+),e,(-)E}^{(4)2(\alpha)} < 0; \quad \delta x_{(+),e,(-)E}^{(4)2(\beta)} > 0 \quad (25)$$

These relations indicate that more population is transferred from the $C_\alpha=C_\beta$ bond to electrophile if the C_β atom is under attack. This dissimilarity may be traced back to an opposite effect of indirect participation of the orbital of substituent D as mediator of the third order interaction $G_{(3)eE}$. Moreover, a direct relation between the above results and opposite signs of resonance parameters $Q_{eE}^{(\alpha)}$ and $Q_{eE}^{(\beta)}$ also may be concluded. This, in turn, implies a decisive role of constitution of the antibonding orbital $\varphi_{(-)e}$.

Opposite inequalities versus those of Eq. (24) may be easily obtained for the third order indirect interactions $G_{(3)de}^{(\alpha)}$ and $G_{(3)de}^{(\beta)}$. This, in turn, implies a positive correction $\delta x_{(+),d,(-)e}^{(4)2(\beta)}$ and a negative correction $\delta x_{(+),d,(-)e}^{(4)2(\alpha)}$. Thus, the electron-donating effect of the substituent D upon the $C_\alpha=C_\beta$ bond also proves to be strengthened under an indirect influence of the β -attacking electrophile, but it is suppressed in the case of the α -attacking one.

Orbitals of the $C_\alpha=C_\beta$ bond ($\varphi_{(+)e}$ and $\varphi_{(-)e}$) play the role of mediators for the second order indirect interaction $G_{(2)dE}$ and the relevant expression takes the form

$$G_{(2)dE} = \frac{1}{(\varepsilon_{(+)d} + \varepsilon_{(-)E})} \left[\frac{S_{de}R_{eE}}{1 + \varepsilon_{(-)E}} - \frac{R_{de}Q_{eE}}{1 + \varepsilon_{(+)d}} \right] \quad (26)$$

From Eqs. (21) and (22), it is seen that the two fractions within the brackets of Eq. (26) (describing the contributions of orbitals $\varphi_{(+)e}$ and $\varphi_{(-)e}$, respectively, to the total element ($G_{(2)dE}$) are added together for the β -attack of electrophile, but these are subtracted for its α -attack. This implies that the contribution $\delta x_{(+),d,(-)E}^{(4)3(\beta)}$ exceeds $\delta x_{(+),d,(-)E}^{(4)3(\alpha)}$ considerably and thereby a more significant population is transferred between the substituent (D) and the electrophile (E^+) if the latter attacks the C_β atom (as compared to the attack of the C_α atom).

The remaining intrabond second order interaction $G_{(2)ee}$ also may be expressed in terms of two fractions, the first one corresponding to the orbital of the substituent ($\varphi_{(+)d}$) and the second one referring to that of electrophile ($\varphi_{(-)E}$). Moreover, both fractions are added together in these expressions just for the β -attack of the reagent. Thus, the intrabond charge redistribution also proves to be more extended if the C_β atom is under attack.

Corrections to bond orders may be evaluated similarly. Analysis of Eq. (18) shows that all terms within the brackets are negative just for the β -attack. Thus, a significant positive correction $P_{(3)}^{(D)}[E^+ - C_\beta]$ follows in this case. Alternatively, separate increments are of different signs and the total correction $P_{(3)}^{(D)}[E^+ - C_\alpha]$ is of a small absolute value. As with Eq. (25), this result also may be traced back to the antibonding nature of the orbital $\varphi_{(-)e}$.

Therefore, it is the β -attack of electrophile, that is accompanied by more extended transferred populations between any two fragments of the system. At the same time, a larger bond order is formed between the orbital of electrophile $\varphi_{(-)E}$ and the $2p_z$ AO of the C_β atom if just the latter is under attack. This conclusion is in line with greater relative reactivity of the C_β atom as compared to that of the C_α atom (cf. the Markovnikov rule [1,2,4–6]).

Let us consider now the A-substituted ethene. Instead of Eq. (22), we then obtain

$$Q_{ea} < 0; \quad R_{ea} > 0; \quad G_{(1)ea} < 0 \quad (27)$$

for any direction of the attack. We may conclude immediately that the increments defined by Eq. (11) do not contribute to differences in charge redistribution under interest.

For the third order interaction $G_{(3)eE}$, the following expression results from Eq. (4)

$$G_{(3)eE} = - \frac{R_{ea}Q_{ae}Q_{eE}}{2(1 + \varepsilon_{(-)a})(1 + \varepsilon_{(-)E})} \quad (28)$$

Using Eqs. (21) and (27), we then obtain

$$G_{(3)eE}^{(\alpha)} < 0; \quad G_{(3)eE}^{(\beta)} > 0 \quad (29)$$

and

$$\delta x_{(+),e,(-)E}^{(4)2(\alpha)} > 0; \quad \delta x_{(+),e,(-)E}^{(4)2(\beta)} < 0 \quad (30)$$

if the definition of $\delta x_{(+),e,(-)E}^{(4)2}$ shown in Eq. (9) is used.

It is seen that the α -attacking electrophile (E^+) acquires more population from the $C_\alpha=C_\beta$ bond as compared to the β -attacking one. As with Eq. (25), this result may be traced back to an opposite effect of an indirect participation of the orbital $\varphi_{(-)a}$ of the substituent A as a mediator in the indirect third order interaction $G_{(3)eE}$. The principal role of signs of the overlap integrals Q_{eE} in the formation of the relations of Eqs. (29) and (30) also may be added here.

The relevant expression for $G_{(3)ea}$ is

$$G_{(3)ea} = - \frac{R_{eE} Q_{eE} Q_{ea}}{2(1 + \varepsilon_{(-)a})(1 + \varepsilon_{(-)E})} \quad (31)$$

and yields a negative value for $G_{(3)ea}^{(\alpha)}$ and a positive one for $G_{(3)ea}^{(\beta)}$. This result along with Eqs. (12) and (27) ensures that

$$\delta x_{(+)e,(-)a}^{(4)2(\alpha)} > 0; \quad \delta x_{(+)e,(-)a}^{(4)2(\beta)} < 0 \quad (32)$$

Hence, the electron-accepting effect of the substituent A upon the $C_\alpha=C_\beta$ bond becomes stronger under an indirect influence of an α -attacking electrophile as compared to the β -attacking one.

The second order indirect intrabond interaction $G_{(2)ee}$ determining the partial charge transfer $\delta x_{(+)e,(-)e}^{(4)3}$ may be expressed as follows:

$$G_{(2)ee} = - \frac{R_{eE} Q_{eE}}{2(1 + \varepsilon_{(-)E})} - \frac{R_{ea} Q_{ae}}{2(1 + \varepsilon_{(-)a})} \quad (33)$$

Using Eqs. (21) and (27), we then obtain that both increments to $G_{(2)ee}$ are positive for the α -attack. Consequently, a large positive value of $G_{(2)ee}^{(\alpha)}$ results. Alternatively, the two increments are of different signs for the β -attack and $G_{(2)ee}^{(\beta)}$ becomes of a small absolute value. Thus, a more efficient intrabond charge redistribution corresponds to the α -attack.

The newly formed bond orders between the orbital of electrophile $\varphi_{(-)E}$ and the $2p_z$ AOs of the carbon atoms under attack follow from Eq. (18), where the second and the third product within the brackets of the right-hand side should be omitted. Using Eqs. (21), (29) and (33), we then obtain a large positive correction $P_{(3)}^{(A)}[E^+ - C_\alpha]$ for the α -attack of electrophile but not for the β -attack.

It is seen that the electron-accepting effects upon the $C_\alpha=C_\beta$ bond both of electrophile and of the substituent A are more extended under an assumption of the α -attack of the former. At the same time, a

larger bond order is formed between the orbital $\varphi_{(-)E}$ and the $2p_z$ AO of the C_α atom. Thus, a predominant addition of electrophile to the C_α atom may be expected and this conclusion also is in line with experimental facts [2,4–6].

Therefore, different reactivities of the C_α and C_β atoms of substituted ethenes $H_2C_\beta=C_\alpha HX$ ($X = D, A$) may be successfully traced back to different efficiencies of charge redistribution between the electrophilic agent E^+ , the $C_\alpha=C_\beta$ bond and the substituent (D or A), as well as to dissimilar bond orders that are formed between the orbital of the reagent ($\varphi_{(-)E}$) and the $2p_z$ AO of the attacked carbon atom even if the relevant resonance parameters take coinciding values.

The above-mentioned distinct charge redistributions, in turn, are shown to originate from opposite signs of overlap integrals Q_{eE} between the orbital of reagent and the antibonding orbital of the $C_\alpha=C_\beta$ bond (overlap topology) for both directions of the attack. Consequently, an advantage of the $\beta(\alpha)$ -position of electrophile with respect to the substituent D(A) over its $\alpha(\beta)$ -position proves to be supported within a significant range of absolute values of intermolecular resonance parameters.

Finally, a direct relation between the above-established different extents of charge redistributions and dissimilar stabilization energies of the whole reacting system follows after invoking the results of Ref. [17]. (As it is shown in this contribution, the more extensive the partial transferred population $\delta x_{(+)i,(-)j}$ from the IOBO $\varphi_{(+)i}$ to an IVBO $\varphi_{(-)j}$ becomes, the larger the relevant increment to the total stabilization energy arises.) Such a relation makes our approach straightforwardly comparable to those based on consideration of total energy, in particular to the traditional quantum chemical approaches discussed in Section 1 (see also Section 5).

4.2. Studies of a bridged E^+ -containing ion

Let us assume now that the electrophilic agent (E^+) takes a middle position above the $C_\alpha=C_\beta$ bond as shown in Fig. 2(c). This model describes a hypothetical bridged E^+ -containing ion of a symmetric constitution. The intermolecular bonding will be represented in this case by two resonance parameters of coinciding values, viz. $\langle \varphi_{(-)E} | \hat{H} | \chi_\alpha \rangle$ and

$\langle \varphi_{(-)E} | \hat{H} | \chi_{\beta} \rangle$. Furthermore, Eqs. (22) and (27) keep to be valid also for a middle position of electrophile. Again, Eq. (21) becomes replaced by the following relations

$$R_{eE}^{(m)} > 0; \quad G_{(1)eE}^{(m)} < 0; \quad Q_{eE}^{(m)} = 0 \quad (34)$$

where the superscript (m) here and below serves to describe the middle position of the reagent. The resonance parameter Q_{eE} is contained within the principal expressions for indirect interactions of orbitals shown in Eqs. (23), (26), (28), (31) and (33). Thus, a zero value of this parameter seen from Eq. (34) is the most important peculiarity of a symmetric bridged E^+ -containing ion.

To study the consequences of this peculiarity upon the nature of charge redistribution, let us start with the partial transferred population between the electron-donating substituent D and the middle-positioned electrophile E^+ . The relevant expression for the second order interaction $G_{(2)dE}$ contains only the first fraction of the right-hand side of Eq. (26). This implies that the partial transferred population $\delta x_{(+d,(-)E}^{(4)3(m)}$ takes an intermediate value in between those for the α - and β -attacks (provided that the resonance parameters $R_{eE}^{(\alpha)}$ ($R_{eE}^{(\beta)}$) and $R_{eE}^{(m)}$ do not differ significantly). An analogous result may be obtained also for the partial intrabond transferred population $\delta x_{(+e,(-)e}^{(4)3(m)}$ whatever the nature of the substituent.

Furthermore, the following relations refer to the bridged ion containing an electron-donating substituent (D)

$$G_{(3)eE}^{(m)} = G_{(3)de}^{(m)} = 0; \quad \delta x_{(+e,(-)E}^{(4)2(m)} = \delta x_{(+d,(-)e}^{(4)2(m)} = 0 \quad (35)$$

Eq. (35) implies that the substituent D does not exert any influence upon the charge transfer between the $C_{\alpha}=C_{\beta}$ bond and the middle-attacking electrophile. Similarly, a zero influence of the latter upon the electron-donating effect of the substituent D towards the $C_{\alpha}=C_{\beta}$ bond may be concluded. For the acceptor-containing ion, the analogue of Eq. (35) takes the form

$$G_{(3)eE}^{(m)} = G_{(3)ea}^{(m)} = 0; \quad \delta x_{(+e,(-)E}^{(4)2(m)} = \delta x_{(+e,(-)a}^{(4)2(m)} = 0 \quad (36)$$

and implies a zero influence of the middle-attacking electrophile upon the electron-accepting effect of the substituent A and vice versa.

If we recall now that the same corrections were established to take non-zero values of opposite signs for the side attacks of electrophile (see Eqs. (25), (30), and (32)), the above results allow us to conclude that a middle attack of electrophile (E^+) has no advantages over its side attacks in respect of indirect influences of separate fragments. Thus, advantages of the central position of electrophile (if any) might be due only to possibility of larger direct interactions $G_{(1)eE}$ and thereby of a more significant second order charge transfer [11].

Studies of the newly formed bond orders between the orbital of the middle-positioned electrophile ($\varphi_{(-)E}$) and the $2p_z$ AOs of separate carbon atoms are of particular interest. Indeed, trends in the most probable subsequent rearrangement of our hypothetical bridged ion are expected to reveal themselves there.

For the donor-containing ion, the above-mentioned bond orders are determined by the third order corrections following from Eq. (18), viz.

$$P_{(3)}^{(D)}[E^+ - C_{\beta}(C_{\alpha})] = \pm \sqrt{2}[G_{(1)de}G_{(2)dE} + G_{(2)ee}G_{(1)eE}] \quad (37)$$

The second order intrabond interaction $G_{(2)ee}$ proves to be mediated here only by the orbital of the substituent $\varphi_{(+d)}$. Consequently, Eq. (22) yields a negative sign of this interaction. If we invoke Eq. (34) in addition, both factors of the right-hand side of Eq. (37) may be shown to be positive. Thus, a positive correction $P_{(3)}^{(D)}[E^+ - C_{\beta}]$ and a negative correction $P_{(3)}^{(D)}[E^+ - C_{\alpha}]$ result. Hence, the total bond order between orbitals $\varphi_{(-)E}$ and χ_{β} exceeds that between $\varphi_{(-)E}$ and χ_{α} despite coinciding values of the relevant resonance parameters. This result implies a trend towards formation of a stronger chemical bond between the electrophile and the C_{β} atom.

In the case of an A-substituted ethene, the bond orders between pairs of orbitals ($\varphi_{(-)E}$, χ_{α}) and ($\varphi_{(-)E}$, χ_{β}) are determined by Eq. (37), where the product $G_{(1)de}G_{(2)dE}$ is absent. The second order interaction $G_{(2)ee}$ is mediated in this case by the orbital of the substituent A. Thus, this interaction is determined by the last fraction of Eq. (33) and proves to be positive. This, in turn, implies a positive correction $P_{(3)}^{(D)}[E^+ - C_{\alpha}]$ and a negative correction

$P_{(3)}^{(D)}[E^+ - C_\beta]$. Hence, the total bond order between orbitals $\varphi_{(-)E}$ and χ_α exceeds that for the another pair of orbitals ($\varphi_{(-)E}$, χ_β), and the electrophile is likely to approach the C_α atom in this case.

It is seen, therefore, that bond orders between the orbital of electrophile and the $2p_z$ AOs of carbon atoms are dissimilar even if a symmetric spatial position of the reagent and thereby coinciding values of the relevant two resonance parameters are assumed. Moreover, the middle-attacking electrophile tends towards formation of a stronger chemical bond with the C_β atom of the molecule $H_2C_\beta=C_\alpha HD$ and with the C_α atom of the system $H_2C_\beta=C_\alpha HA$ in accordance with the relative reactivities of the C_β and C_α atoms with respect to side-attacking electrophiles (Section 4.1). This result indicates that even in the hypothetical bridged ion of symmetric constitution there are some electronic factors that determine different abilities of carbon atoms to add the initially middle-positioned electrophile. Thus, the actual ratios between two alternative addition products may be rationalized on the basis of our results no matter if a symmetrical bridged E^+ -containing ion is assumed to play the role of intermediate. In this context, the quite common assumption about steric effects being the only factor determining the final products in the case of a bridged intermediate [4] should be revised. On the other hand, the above-obtained results support the recent hypothesis about a non-symmetric (partially bridged) constitution of intermediates of some Ad_E2 reactions of substituted ethenes [4,5] (the latter was based on the results of MNDO studies of methyl-substituted bromonium ions [27,28], where structures corresponding to energy minima were found with a longer distance from the bromine atom to the more substituted carbon atom).

4.3. Models of the subsequent nucleophilic attack upon the bridged E^+ -containing ions

In this subsection, we are about to reveal the role of the subsequently attacking nucleophile in further rearrangement of the bridged E^+ -containing ions into final reaction products. To this end, we will look for alterations in bond orders between pairs of orbitals ($\varphi_{(-)E}$, χ_α) and ($\varphi_{(-)E}$, χ_β) under influence of a nucleophilic attack. The newly formed bond orders

between the orbital $\varphi_{(+)N}$ and the AOs χ_α and χ_β also will be considered.

In accordance with the most probable antiperiplanar addition process [2,4,18], the nucleophilic agent will be assumed to be situated below the triangle $C_\alpha E^+ C_\beta$ (Fig. 2(d)–(f)). Moreover, a negative sign will be ascribed to the orbital $\varphi_{(+)N}$ for convenience, so that the overlap integrals $\langle \varphi_{(+)N} | \chi_\alpha \rangle$ and $\langle \varphi_{(+)N} | \chi_\beta \rangle$ are positive. Then, the following systems of relations

$$R_{Ne}^{(m)} = 0; \quad G_{(1)Ne}^{(m)} = 0; \quad S_{Ne}^{(m)} > 0 \quad (38)$$

$$R_{Ne}^{(\alpha)} < 0; \quad G_{(1)Ne}^{(\alpha)} > 0; \quad S_{Ne}^{(\alpha)} > 0 \quad (39)$$

$$R_{Ne}^{(\beta)} > 0; \quad G_{(1)Ne}^{(\beta)} < 0; \quad S_{Ne}^{(\beta)} > 0 \quad (40)$$

describe the middle-, α - and β -positions of nucleophile, respectively (Fig. 2(d)–(f)). Eq. (34) representing the middle position of electrophile will be used here as well.

Let us start with the middle position of nucleophile with respect to a bridged E^+ -containing ion of the D-substituted ethene (Fig. 2(d)). To study the bond orders between pairs of orbitals ($\varphi_{(+)N}$, χ_α) and ($\varphi_{(+)N}$, χ_β), Eq. (20) will be used after omitting the third product of its right-hand side. The first product also vanishes there if Eq. (38) is taken into consideration. The indirect interaction $G_{(2)NE}$ between orbitals of the middle-positioned reagents proves to be mediated only by the orbital $\varphi_{(+)e}$ and acquires a positive sign. Similarly, $\varphi_{(+)e}$ and $\varphi_{(+)d}$ is the only pair of mediators of the remaining interaction $G_{(3)Ne}^{(m)}$ and the latter also is positive. As a result, we obtain a large positive correction $P_{(3)}^{(D)}[Nu^- - C_\alpha]$. At the same time, its counterpart $P_{(3)}^{(D)}[Nu^- - C_\beta]$ is likely to take a small value.

It is seen, therefore, that a middle-positioned nucleophile trends towards formation of a stronger chemical bond with the C_α atom as it may be expected on the basis of final reaction products [1,2,4–6].

Let us turn now to Eq. (18) and consider the alterations in the corrections $P_{(3)}^{(D)}[E^+ - C_\beta(C_\alpha)]$ (if any) owing to the emergence of the new orbital $\varphi_{(+)N}$. It may be easily seen that only the third order interaction $G_{(3)eE}$ is able to contribute to this alteration. The zero value of $Q_{eE}^{(m)}$, however, ensures a zero value of this contribution. Hence, a middle-attacking nucleophile exerts no influence upon bond

orders between pairs of orbitals ($\varphi_{(-)E}$, χ_α) and ($\varphi_{(-)E}$, χ_β).

Let us assume now that the C_α atom of our bridged E^+ -containing ion of molecule $H_2C_\beta=C_\alpha HD$ is under a nucleophilic attack (Fig. 1(e)). Then Eq. (38) will be replaced by Eq. (39). Let us consider again the alterations in bond orders between the orbital $\varphi_{(-)E}$ and AOs χ_α and χ_β under the influence of nucleophile. As with the middle attack of the latter, the zero value of the resonance parameter $Q_{eE}^{(m)}$ ensures a zero contribution of the orbital $\varphi_{(+N)}$ to the third order interaction $G_{(3)eE}$. For the α attack, however, the last two products of Eq. (18) also are able to contribute to the alteration under interest.

The second order indirect interaction $G_{(2)NE}$ is mediated by the bonding orbital $\varphi_{(+e)}$ of the $C_\alpha=C_\beta$ bond. Using Eqs. (2), (34), and (39), a positive sign of $G_{(2)NE}$ may be obtained. Contribution of the orbital $\varphi_{(+N)}$ to the indirect intrabond interaction ($G_{(2)ee}$) also easily follows from Eqs. (2) and (39) and proves to be negative.

Substituting these results along with Eqs. (34) and (39) into Eq. (18) yields the following relations

$$\Delta P_{(3)}^{(D)}[E^+ - C_\beta] > 0; \quad \Delta P_{(3)}^{(D)}[E^+ - C_\alpha] < 0 \quad (41)$$

for alterations in bond orders being sought.

Hence, the initially larger bond order between the orbital $\varphi_{(-)E}$ and the $2p_z$ AO of the C_β atom becomes even more increased under influence of the α -attacking nucleophile, whereas the initially weaker bond order between $\varphi_{(-)E}$ and χ_α is additionally reduced. This implies that an α -attacking nucleophile is able to contribute essentially to further rearrangement of the E^+ -containing ion, namely it is likely to push the middle-positioned electrophile towards the C_β atom of the molecule $H_2C_\beta=C_\alpha HD$.

A nucleophilic attack upon the bridged E^+ -containing ion of the molecule $H_2C_\beta=C_\alpha HA$ also may be studied similarly.

For the middle position of nucleophile, the bond orders between its orbital $\varphi_{(+N)}$ and the AOs χ_α and χ_β may be evaluated using Eqs. (20), (27), (34) and (38). The indirect interaction $G_{(2)NE}$ between the two middle-positioned reagents does not depend on the nature of substituent and keeps to be positive. The second order interaction $G_{(2)Na}$ is mediated only by the bonding orbital $\varphi_{(+e)}$ and also is positive. Again,

the orbitals $\varphi_{(+e)}$ and $\varphi_{(-)a}$ play the role of the only pair of mediators for the third order interaction $G_{(3)Ne}$. From Eq. (4), we then obtain

$$G_{(3)Ne} = \frac{S_{Ne}R_{ea}Q_{ae}}{(1 + \varepsilon_{(+N)})(1 + \varepsilon_{(-)a})} \left[\frac{1}{2} + \frac{1}{\varepsilon_{(+N)} + \varepsilon_{(-)a}} \right] \quad (42)$$

and a negative sign of $G_{(3)Ne}$ follows. Substituting these results into Eq. (20) allows us to conclude that $P_{(3)}^{(A)}[Nu^- - C_\beta]$ is a positive correction, whereas $P_{(3)}^{(A)}[Nu^- - C_\alpha]$ is a negative one. This, in turn, implies a trend towards formation of a stronger chemical bond between the middle-positioned nucleophile and the C_β atom.

Let us turn now to alterations in bond orders between orbitals ($\varphi_{(-)E}$, χ_α) and ($\varphi_{(-)E}$, χ_β) under influence of nucleophile. For the middle position of the latter, zero values of the above-expected alterations and thereby no influence of nucleophile upon bond orders $P^{(A)}[E^+ - C_\beta(C_\alpha)]$ follows from Eq. (18) if Eq. (38) is taken into account.

Let our nucleophile to be situated below the C_β atom (Fig. 2(f)) and described by Eq. (40). As with the respective donor-containing ion, the zero value of the resonance parameter $Q_{eE}^{(m)}$ (see Eq. (34)) ensures a zero increment of the orbital $\varphi_{(+N)}$ to the third order interaction $G_{(3)eE}$. Finally, the second order interaction $G_{(2)NE}$ is mediated by the orbital $\varphi_{(+e)}$ and remains positive. Contribution of the orbital $\varphi_{(+N)}$ to the second order intrabond term $G_{(2)ee}$ follows from Eq. (2) and also is a positive quantity.

Substituting these results into Eq. (18) yields a positive alteration of $P_{(3)}^{(A)}[E^+ - C_\alpha]$ and a negative one of $P_{(3)}^{(A)}[E^+ - C_\beta]$. Hence, the initially larger bond order between the orbital of the middle-positioned electrophile and the $2p_z$ AO of the C_α atom is even more increased under influence of the β -attacking nucleophile, whereas the lower bond order $P^{(A)}[E^+ - C_\beta]$ is additionally reduced. This implies that the middle-positioned electrophile is likely to be pushed towards the C_α atom in this case.

Conclusions that may be drawn here are as follows:

First, bond orders between the orbital of a middle-positioned nucleophile and the $2p_z$ AOs of carbon atoms are dissimilar as it was the case with a middle-positioned electrophile (Section 4.2). Moreover, bond orders of larger values correspond to those carbon

atoms, where the future chemical bonds are expected to be formed in the final addition products. Thus, the conclusion of Section 4.2 about the presence of electronic factors determining different abilities of carbon atoms to add a middle-positioned electrophile refers to a middle-positioned nucleophile as well.

Second, an essential role of a side-attacking nucleophile in further decay of a bridged E^+ -containing ion follows from our results. Thus, an initially middle-positioned electrophile is likely to be pushed towards the $C_\beta(C_\alpha)$ atom of the molecule $H_2C_\beta=C_\alpha$ -HD(A) under attack of nucleophile upon the $C_\alpha(C_\beta)$ atom and this trend is in accordance with the predominant final addition products. Weakening of the $E^+ - C_\alpha(E^+ - C_\beta)$ bond of a bridged E^+ -containing ion under influence of an $\alpha(\beta)$ -attacking nucleophile is usually predicted also on the basis of the well-known octet rule [5,29]. Along with supporting this prediction, our results additionally indicate that breaking of the above-specified bond always is accompanied by strengthening of its counterpart (i.e. of the $E^+ - C_\beta$ and $E^+ - C_\alpha$ bond, respectively). This, in turn, implies a concerted mechanism of the second step of the whole addition process, i.e. of the addition of nucleophile to a bridged E^+ -containing ion (provided that just the latter plays the role of intermediate).

5. Concluding remarks

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

(1) The assumption of the classical chemistry about either a direct or an indirect participation of certain fragment of reacting molecules in a chemical process is corroborated: the direct participation is shown to be accompanied by a second order (local) charge transfer between the reagent and a given fragment, whereas an indirect participation is represented by fourth order (non-local) charge redistributions embracing several fragments.

(2) An additional insight is given into the nature of an indirect participation of a neighboring fragment (e.g. of a substituent) in a chemical process. Three aspects reveal themselves there: first, this fragment exerts an indirect influence upon the charge redistribution between the reaction center of its own

molecule and the approaching reagent. Second, an additional electron-donating or accepting effect of this fragment upon the reaction center of its own molecule is induced by the reagent. Third, an indirect charge transfer takes place between the substituent and the reagent by means of orbitals of the reaction center playing the role of mediators.

(3) The scope of applicability of the very concept of direct (through-space) and indirect (through-bond) interactions of orbitals is extended. This concept has been originally suggested in Refs. [31–34] and used for interpretation of photoelectron spectra of molecules [31–40] and of localized molecular orbitals [11,41–44]. Now the same concept is applied for investigation of chemical reactions.

(4) The role of signs of overlap integrals between orbitals of the reaction center and those of the reagent (i.e. of the overlap topology) in the formation of the predominant direction of a chemical process is revealed. On this basis, an invariance of the above-mentioned direction within an extended range of the reaction coordinate may be expected.

The scope of validity of the approach suggested is determined by the range of convergence of the applied power series for the bond order matrix [11–14]. The small value condition underlying this series concerns interfragmental resonance parameters versus the energy differences between IOBOs and IVBOs. Thus, applicability of the approach is primarily ensured for reactant molecules consisting of quasi-transferable fragments, e.g. substituted alkanes [13, 30], aliphatic conjugated hydrocarbons of a small and medium size [14] along with their derivatives, as well as substituted benzenes [15,16]. It should be emphasized that weak intermolecular interactions versus the intramolecular ones are not required here in contrast to the usual perturbative approaches based on canonical MOs of isolated molecules [1,8,18,20]. Hence, the approach suggested is not limited to the early stages of the reaction.

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