

# Indirect electron-donating effects governing the concerted bimolecular elimination processes

V. Gineityte\*

*Institute of Theoretical Physics and Astronomy, Vilnius University, Gostauto 12, LT-01108 Vilnius, Lithuania*

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## Abstract

The concerted bimolecular  $\beta$ -elimination (E2) reaction of substituted alkanes ( $X-C_{\alpha}H_2-C_{\beta}H_2\dots$ ) is studied using the semilocalized quantum-chemical approach suggested previously (V. Gineityte, J. Mol. Struct. (Theochem), 588 (2002) 99; V. Gineityte, Int. J. Quant. Chem., 94 (2003) 302) and based on the power series for the one-electron density matrix. Electron density redistributions among separate bonds of both the reactant and the external base ( $B''$ ) are analyzed and interpreted in this approach in terms of direct (through-space) and indirect (through-bond) interactions of bond orbitals (BOs). The main aim of the study lies in revealing the principal ways of the indirect influence of the base  $B''$  upon characteristics of the heteroatom containing ( $X-C_{\alpha}$ ) bond (The direct interactions between respective orbitals are expected to be negligible in the E2 processes). The above-specified indirect influence is shown to consist of two components: First, of the additional indirect electron-donating effect of the initially occupied (bonding) orbital of the  $H-C_{\beta}$  bond upon the  $X-C_{\alpha}$  bond, wherein the orbital of the base participates as a mediator, and, second, of the indirect electron-donating effect of the base itself upon the same bond by means of orbitals of the  $H-C_{\beta}$  bond. The known predominance of the *trans*  $\beta$  elimination over the relevant *cis* process is accordingly related to higher efficiencies of the above-enumerated indirect electron-donating effects for the case of *trans*-arranged  $X-C_{\alpha}$  and  $H-C_{\beta}$  bonds. The results obtained along with those of an analogous investigation of the  $S_N2$  process (V. Gineityte, J. Mol. Struct. (Theochem), 541 (2001) 1) yield a unified description of both reactions, wherein the direct and indirect attacks of the reagent upon the  $X-C_{\alpha}$  bond underly the  $S_N2$  and E2 reactions, respectively. Consequently, the result of competition between these processes is expected to depend upon relative efficiencies of direct and indirect influences of the given reagent upon characteristics of the nucleofuge-containing ( $X-C_{\alpha}$ ) bond.

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## 1. Introduction

Search for unified descriptions of different organic reactions is among the principal goals of theoretical chemistry. Accordingly, good prospects for further development may be predicted for quantum- chemical theories that offer interpretation of a wide variety of processes in the same terms. The semilocalized approach to investigate chemical reactivity suggested recently [1,2] and based on the power series for the one-electron density matrix (DM) [3] seems to be promising in this respect. Electron density and bond order redistributions among separate fragments of

contacting molecules are studied directly in this approach 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 and thereby of the process under study. The approach has been successfully applied to the  $S_N2$  reactions of substituted alkanes [4] and of  $\alpha$ -halocarbonyl compounds [5], to the  $Ad_E2$  processes of substituted ethenes [1] and butadiene [6], as well as to some electrocyclic transformations [7]. This paper is devoted to application of the same approach for investigation of the concerted bimolecular  $\beta$ - elimination (E2) reaction between a substituted alkane ( $X-C_{\alpha}H_2-C_{\beta}H_2\dots$ ) and an external base ( $B''$ ) [8–11]. On the basis of comparison of the results obtained to those referring to the nucleophilic substitution ( $S_N2$ ) of the same compounds [4], a unified description of the  $S_N2$  and E2

\* Tel.: +370 5 262 0953; fax: +370 5 212 5361.

E-mail address: gineityte@mserv.itpa.lt.

reactions is expected to follow. The competitive nature of these two principal processes of organic chemistry [8] makes the above-anticipated description even more desirable.

The  $S_N2$  process between a substituted alkane and nucleophile (Nu) [4] was shown to be governed primarily by the direct interaction between the initially-occupied orbital of the reagent (Nu) and the antibonding orbital of the nucleofuge-containing ( $X-C_\alpha$ ) bond of the reactant and thereby by the direct electron-donating effect of nucleophile upon the  $X-C_\alpha$  bond. Contributions of the indirect interactions of the same orbitals by means of orbitals of the  $C_\alpha-C_\beta$  ( $C_\alpha-H$ ) bonds play the role of only additional corrections to charge redistribution in this case. In contrast to the nucleophilic substitution, the orbital of the external base ( $B^\cdot$ ) is unlikely to interact directly with orbitals of the nucleofuge-containing bond of the reactant in the  $\beta$ -elimination reaction (The  $H-C_\beta$  bond is actually under a direct attack in this case [8–10]). Again, the concerted E2 mechanism implies a simultaneous breaking of the  $X-C_\alpha$  and  $H-C_\beta$  bonds. Hence, a certain indirect influence of the base ( $B^\cdot$ ) upon characteristics of the  $X-C_\alpha$  bond may be expected to be the driving force of this reaction. The present contribution is aimed at revealing the principal ways of this indirect influence and representing them in terms of particular indirect interorbital interactions. Interpretation of stereoselectivity of the E2 reaction also is among the aims of our study (cf. the well-known predominance of the trans  $\beta$ -elimination [8–11]). To this end, the extents of the indirect influence of the base ( $B^\cdot$ ) will be compared for the cases of the cis- and trans-arranged  $X-C_\alpha$  and  $H-C_\beta$  bonds in the substituted alkanes.

It should be mentioned here that members of the power series for the one-electron DM (bond order matrix)  $P$  to within the fourth order inclusive proved to be essential when describing the electron density redistribution among localized orbitals [1,4,5,12–15], in contrast to the well-studied case of delocalized (canonical) orbitals of two interacting molecules or molecular fragments, where confinement to second order corrections proves to be sufficient [16,17]. Terms of this series to within the second order inclusive were derived in Ref. [3], whereas the expressions for the third and fourth order corrections may be found in Ref. [15]. When discussing the stereoselectivity of the E2 reaction, however, even the fifth order corrections were required. The relevant expressions have been additionally derived in the present study (Section 2). As with the  $S_N2$  reaction [4,5], individual chemical bonds play the role of elementary fragments in this study. Accordingly, two-center bond orbitals (BOs) are used as basis functions. Furthermore, a convenient representation of charge redistribution is invoked that is formulated in terms of partial transferred populations between pairs of initially-occupied and initially-vacant BOs [1,15]. Separate corrections to the latter, in turn, proved to be representable in terms of elements of certain principal matrices  $G_{(k)}$  [3,14,15]

describing various types of interorbital interactions. The relevant expressions are overviewed in Section 2.

Analysis of formulae for particular elements  $G_{(k)pl}$  carried out previously [14,15] showed that the higher is the order parameter ( $k$ ), the more cumbersome is the relevant expression. To circumvent difficulties when applying these expressions to the rather involved model of the E2 reaction, a way of their simplified evaluation is suggested in Section 3. The remaining sections of the paper are devoted to the very E2 reaction: Section 4 contains description of the employed model, whilst Section 5 consists of discussion of separate increments to charge redistribution.

## 2. The principal formulae for partial transferred populations

Charge redistributions between BOs of two contacting molecules may be conveniently represented [1,15] in terms of partial populations ( $q_{(-)l,(+)p}$ ) transferred between orbitals of opposite initial occupation, i.e. between an initially-occupied (bonding) BO  $\phi_{(+)p}$  and an initially-vacant (antibonding) BO  $\phi_{(-)l}$ . These populations, in turn, consist of sums of corrections  $q_{(-)l,(+)p}^{(k)}$  of various orders ( $k$ ). The expressions for the latter in terms of elements of the principal matrices  $G_{(k)}$  [3,14,15] take the form

$$q_{(-)l,(+)p}^{(2)} = 2(G_{(1)pl})^2, \quad (1)$$

$$q_{(-)l,(+)p}^{(3)} = 4G_{(1)pl}G_{(2)pl}, \quad (2)$$

$$q_{(-)l,(+)p}^{(4)} = 4G_{(1)pl} \left[ G_{(3)pl} + \frac{1}{2}(G_{(1)}G_{(1)}^+G_{(1)})_{pl} \right] + 2(G_{(2)pl})^2, \quad (3)$$

and

$$q_{(-)l,(+)p}^{(5)} = 4G_{(1)pl} \left[ G_{(4)pl} + \frac{1}{2}(G_{(1)}G_{(2)}^+G_{(1)})_{pl} \right] + 4G_{(2)pl} [G_{(3)pl} + (G_{(1)}G_{(1)}^+G_{(1)})_{pl}], \quad (4)$$

where the superscripts  $+$  are used here and below for Hermitian-conjugate (transposed) matrices. The first order increments to partial transferred populations ( $q_{(-)l,(+)p}^{(1)}$ ) always take zero values [1,15]. The principal matrices  $G_{(k)}$  were shown to meet matrix equations of the form [3]

$$E_{(+)}G_{(k)} + G_{(k)}E_{(-)} + W_{(k)} = 0, \quad (5)$$

where  $E_{(+)}$  and  $E_{(-)}$  stand for submatrices (blocks) of the zero order Hamiltonian matrix of our systems defined as follows

$$H_{(0)} = \begin{vmatrix} E_{(+)} & 0 \\ 0 & -E_{(-)} \end{vmatrix}. \quad (6)$$

The submatrices  $E_{(+)}$  and  $E_{(-)}$  refer to subspaces of bonding BOs (BBOs) and of antibonding BOs (ABOs), respectively, and contain intrasubspace resonance parameters along with one-electron energies of BOs. The minus sign in front of  $E_{(-)}$  is introduced for further convenience. The remaining matrices of Eq. (5) ( $W_{(k)}$ ) take the form

$$\begin{aligned} W_{(1)} &= R, & W_{(2)} &= SG_{(1)} - G_{(1)}Q, \\ W_{(3)} &= SG_{(2)} - G_{(2)}Q - (RG_{(1)}^+G_{(1)} + G_{(1)}G_{(1)}^+R), \\ W_{(4)} &= SG_{(3)} - G_{(3)}Q - [RG_{(1)}^+G_{(2)} + G_{(2)}^+G_{(1)}] \\ &\quad + (G_{(1)}G_{(2)}^+ + G_{(2)}G_{(1)}^+)R, \end{aligned} \quad (7)$$

where  $S, Q$  and  $R$  are submatrices of an analogous division of the first order Hamiltonian matrix  $H_{(1)}$ , viz.

$$H_{(1)} = \begin{vmatrix} S & R \\ R^+ & Q \end{vmatrix}. \quad (8)$$

Given that the blocks  $E_{(+)}$  and  $E_{(-)}$  of Eq. (6) are diagonal matrices containing elements  $E_{(+p)}$  and  $E_{(-l)}$  (these coincide with the relevant one-electron energies), the matrix problem of Eq. (5) may be solved algebraically [3]. As a result, separate elements  $G_{(k)pl}$  of matrices  $G_{(k)}$  may be expressed as follows

$$G_{(k)pl} = -\frac{W_{(k)pl}}{E_{(+p)} + E_{(-l)}}. \quad (9)$$

The matrix element  $W_{(1)pl}$  coincides with the respective resonance parameter  $R_{pl}$  as the first relation of Eq. (7) indicates. Consequently, the element  $G_{(1)pl}$  defined by Eq. (9) has been interpreted [3] as describing the direct (through-space) interaction of BOs  $\phi_{(+p)}$  and  $\phi_{(-l)}$ . Accordingly, the second order partial transferred population  $q_{(-)l,(+)p}^{(2)}$  shown in Eq. (1) represents the direct charge transfer between the above-indicated orbitals. Elements  $G_{(k)pl}$  corresponding to higher values of the order parameter ( $k=2,3,\dots$ ) proved to describe various types of indirect interactions of the same BOs [3,14,15], whilst the relevant corrections  $q_{(-)l,(+)p}^{(k)}$  of Eqs. (2)–(4) yield indirect charge redistributions of various orders.

From Eq. (1) it is seen that the second order partial transferred populations are positive quantities whatever the signs of the relevant interorbital interactions  $G_{(1)pl}$ . By contrast, the signs of the higher order corrections of Eqs. (2)–(4) are not evident a priori. This implies that the population transferred between the given pair of BOs indirectly may be either added to or subtracted from that transferred directly. Hence, the actual extent of population transferred between the BBO  $\phi_{(+p)}$  and the ABO  $\phi_{(-l)}$  depends decisively upon signs of the higher order increments  $q_{(-)l,(+)p}^{(k)}$  ( $k > 2$ ). The latter, in turn, are determined by signs and absolute values of interorbital interactions  $G_{(k)pl}$  as Eqs. (2)–(4) indicate.

It is seen, therefore, that analysis of expressions for elements  $G_{(k)pl}$  of matrices  $G_{(k)}$  is required when looking for

charge redistributions among BOs of reacting molecules. The principal way of this procedure is outlined in Section 3.

### 3. Constitution of expressions for indirect interorbital interactions

In Refs. [3,14,15], the elements  $G_{(k)pl}$  have been interpreted as indirect interactions between BOs  $\phi_{(+p)}$  and  $\phi_{(-l)}$  by means of  $k$  mediators, the latter coinciding with the remaining orbitals of the system. In this Section, we are about to present a somewhat more formalized point of view to the same interactions. Use of Eqs. (7) and (9) allows the elements  $G_{(k)pl}$  to be expressed in terms of fractions, each of them containing products of  $k$  resonance parameters and of  $k$  energy intervals in its numerator and denominator, respectively. Let the resonance parameters (i.e. elements of matrices  $R, S$  and  $Q$ ) to be further denoted by  $\langle \phi_i | \hat{H} | \phi_j \rangle$ , where  $\phi_i$  and  $\phi_j$  stand for respective bond orbitals. We may notice immediately that products of these parameters always are of a cyclic constitution in the above-mentioned fractions, e.g.

$$\langle \phi_{(+p)} | \hat{H} | \phi_1 \rangle \langle \phi_1 | \hat{H} | \phi_2 \rangle \langle \phi_2 | \hat{H} | \phi_3 \rangle \cdots \langle \phi_k | \hat{H} | \phi_{(-l)} \rangle. \quad (10)$$

This implies that any of these products represents a pathway from the BBO  $\phi_{(+p)}$  to the ABO  $\phi_{(-l)}$  via a bridge of  $k$  mediators. In the case shown in Eq.(10), the bridge coincides with the set of BOs ( $\phi_1, \phi_2, \phi_3, \dots, \phi_k$ ). It is evident that both BBOs and ABOs are able to play the role of mediators. Moreover, the pathway under consideration actually contributes to the total element  $W_{(k)pl}$  and thereby to  $G_{(k)pl}$  only if all resonance parameters contained within the relevant product take non-zero values.

The above-outlined constitution of elements  $G_{(k)pl}$  may be illustrated by the second order element  $G_{(2)pl}$  which contains two types of fractions, viz.

$$\begin{aligned} G_{(2)pl} &= \sum_m^{\text{BBOs}} \frac{S_{pm}R_{ml}}{(E_{(+p)} + E_{(-l)})(E_{(+m)} + E_{(-l)})} \\ &\quad - \sum_n^{\text{ABOs}} \frac{R_{pn}Q_{nl}}{(E_{(+p)} + E_{(-l)})(E_{(+p)} + E_{(-n)})} \end{aligned} \quad (11)$$

where

$$\begin{aligned} S_{pm} &= \langle \phi_{(+p)} | \hat{H} | \phi_{(+m)} \rangle, & R_{ml} &= \langle \phi_{(+m)} | \hat{H} | \phi_{(-l)} \rangle, \\ Q_{nl} &= \langle \phi_{(-n)} | \hat{H} | \phi_{(-l)} \rangle \end{aligned} \quad (12)$$

as Eq. (8) indicates. It is seen that the fractions of the first sum of Eq. (11) correspond to various pathways from  $\phi_{(+p)}$  to  $\phi_{(-l)}$  via a BBO ( $\phi_{(+m)}$ ), whereas those of the second sum refer to analogous pathways via an ABO ( $\phi_{(-n)}$ ). Accordingly, the expression for  $G_{(3)pl}$  [13] contains four types of fractions corresponding to bridges of four possible constitution, namely ( $\phi_{(+m)}, \phi_{(+i)}$ ), ( $\phi_{(+m)}, \phi_{(-r)}$ ), ( $\phi_{(-r)}, \phi_{(+m)}$ ) and ( $\phi_{(-r)}, \phi_{(-n)}$ ). In the expression for the fourth order

element  $G_{(4)pl}$ , the number of different fractions is even higher. It is also noteworthy that several fractions containing the same numerator but different denominators emerge for some types of bridges in the expressions for  $G_{(3)pl}$  and  $G_{(4)pl}$ . This refers, for example, to bridges of the type  $(\phi_{(+m}, \phi_{(-r)})$  within the expression for  $G_{(3)pl}$  [13], each of them being represented by the sum of two fractions, viz.

$$\frac{S_{pm}R_{mr}Q_{rl}}{(E_{(+p)} + E_{(-l)})(E_{(+m)} + E_{(-l)})(E_{(+m)} + E_{(-r)})} + \frac{S_{pm}R_{mr}Q_{rl}}{(E_{(+p)} + E_{(-l)})(E_{(+p)} + E_{(-r)})(E_{(+m)} + E_{(-r)})} \quad (13)$$

By contrast, the pathways via two BBOs  $(\phi_{(+m}, \phi_{(+i)})$  are represented by a single fraction

$$\frac{S_{pm}S_{mi}R_{il}}{(E_{(+p)} + E_{(-l)})(E_{(+m)} + E_{(-l)})(E_{(+i)} + E_{(-l)})} \quad (14)$$

in the same expression for  $G_{(3)pl}$ .

It is evident that the energy reference point and energy unit always may be chosen so that the intervals  $E_{(+m)} + E_{(-r)}$  are positive for any pair of orbitals. As a result, the signs in front of fractions and those of products of resonance parameters become of primary importance when looking for signs and absolute values of interorbital interactions  $G_{(k)pl}$ .

Therefore, the scheme of evaluation of a certain element  $G_{(k)pl}$  consists of two steps: First, the principal pathways from the BBO  $\phi_{(+p)}$  to the ABO  $\phi_{(-l)}$  should be revealed that contribute to the element under consideration most significantly. Second, the fractions representing the above-mentioned principal pathway(s) should be collected and evaluated in the relevant expression for  $G_{(k)pl}$ . Before passing to application of this procedure, we are about to describe the model of the E2 process.

#### 4. The model of the concerted E2 reaction between a substituted alkane and an external base

To construct the above-indicated model, we will employ our previous experience in studying the intramolecular charge distribution in substituted alkanes ( $X - C_{\alpha}H_2 - C_{\beta}H_2 - \dots$ ) [13]. Thus, bond orbitals will be defined as bonding and antibonding combinations of pairs of  $1s_H$  AOs of hydrogen atoms and of  $sp^3$ - hybrid AOs (HAOs) of the remaining atoms corresponding to separate bonds so that the intrabond resonance parameters and thereby the relevant direct interactions vanish. Moreover, we will confine ourselves to consideration of the fragment  $B^{\cdot\cdot} \dots H - C_{\beta} - C_{\alpha} - X$  of our reacting system (Contributions of the ‘side’ bonds to the indirect charge transfer between the  $C_{\beta}-H$  and  $X-C_{\alpha}$  bonds were shown to be negligible in substituted alkanes [13]. This primarily refers to increments of the  $C_{\alpha}-H$  bonds). Finally, the bonding orbital of the  $X-C_{\alpha}$  bond will be excluded from our model

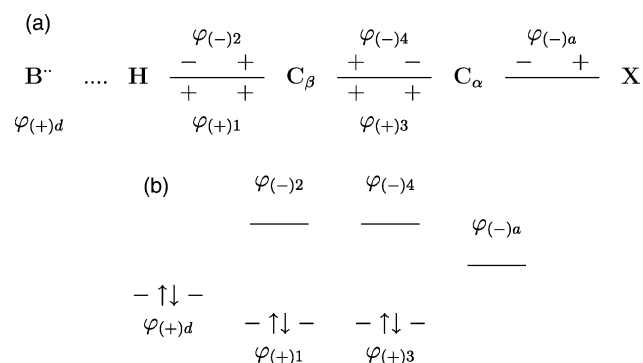


Fig. 1. The principal fragment ( $B^{\cdot\cdot} \dots H - C_{\beta} - C_{\alpha} - X$ ) and the relevant bond orbitals (BOs) included into the model of a substituted alkane ( $X - C_{\alpha}H_2 - C_{\beta}H_2 - \dots$ ) under attack of an external base ( $B^{\cdot\cdot}$ ). The initially-occupied (bonding) orbitals are supplied with subscripts (+) and shown below the respective bonds in the upper part of the picture (a), whilst the initially-vacant (antibonding) orbitals are accordingly denoted by subscripts (-) and indicated above the corresponding bonds. The signs of increments of the relevant  $sp^3$ -hybrid AOs and  $1s_H$  AOs contained within the definitions of BOs also are shown in the scheme (a). The diagram (b) reflects one-electron energies of the above-specified BOs.

owing to the relatively low one-electron energy. So far as the external base  $B^{\cdot\cdot}$  is concerned, it will be modelled by a single electron-donating orbital  $(\phi_{(+d)})$  as it was the case with other reagents studied previously [1,4–6]. The orbital  $\phi_{(+d)}$  will be assumed to interact (overlap) directly only with orbitals of the  $H-C_{\beta}$  bond. On the whole, six basis orbitals will be included into our model, namely, the BBO and the ABO of the  $H-C_{\beta}$  bond  $(\phi_{(+1)}, \phi_{(-2)})$ , the analogous two BOs of the  $C_{\alpha}-C_{\beta}$  bond  $(\phi_{(+3)}, \phi_{(-4)})$ , as well as the electron-donating orbital of the base  $(\phi_{(+d)})$  along with the electron-accepting (antibonding) orbital of the  $X-C_{\alpha}$  bond  $(\phi_{(-a)})$ . The signs of coefficients of these BOs at particular HAOs and  $1s_H$  AOs are shown in the upper part of Fig. 1(a), whereas the relevant one-electron energy levels are presented in its lower part (b).

The energy reference point and energy unit of our model will coincide with average values of Coulomb and intrabond resonance parameters, respectively, in the basis of HAOs and  $1s_H$  AOs. This implies a negative energy unit and thereby positive energy intervals within denominators of fractions in the expressions for  $G_{(k)pl}$  (Section 3). The same refers also to resonance parameters within the relevant numerators, provided that the respective overlap integrals are positive (The resonance parameters are assumed to be proportional to overlap integrals between the relevant pairs of basis orbitals [16]). Signs of resonance parameters between BOs referring to interactions inside the molecule  $X - C_{\alpha}H_2 - C_{\beta}H_2 - \dots$  have been established in Ref. [13]. The additional orbital  $\phi_{(+d)}$  of the external base included into our model is supposed to overlap with the  $1s_H$  AO of the hydrogen atom of the  $H-C_{\beta}$  bond, and, consequently, the resonance parameters  $S_{d1}$  and  $R_{d2}$  take a positive and a negative value, respectively (The negative sign of the contribution of the  $1s_H$  AO of the hydrogen atom in the definition of the ABO  $\phi_{(-2)}$  (Fig. 1(a))

should be also taken into consideration here). The final collection of resonance parameters and of direct interactions takes the form

$$S_{13} = S_{31} > 0, \quad R_{32} > 0, \quad R_{14} > 0, \quad Q_{24} > 0, \\ Q_{4a} > 0, \quad R_{3a} < 0, \quad S_{d1} = S_{1d} > 0, \quad R_{d2} < 0; \quad (15)$$

$$G_{(1)32} < 0, \quad G_{(1)14} < 0, \quad G_{(1)3a} > 0, \quad G_{(1)d2} > 0; \quad (16)$$

$$R_{1a}^{cis} < 0, \quad R_{1a}^{trans} > 0, \quad Q_{2a}^{cis} < 0, \quad Q_{2a}^{trans} > 0; \quad (17)$$

$$G_{(1)1a}^{cis} > 0, \quad G_{(1)1a}^{trans} < 0, \quad (18)$$

where the notations of Eq. (12) are used. As opposed to Eqs. (15) and (16), the last two relations contain conformation-dependent parameters corresponding to pairs of BOs of vicinal bonds H–C<sub>β</sub> and X–C<sub>α</sub>. Parameters referring to the cases of *cis*- and *trans*-arranged pairs of these bonds are supplied with the respective superscripts. The absolute values of resonance parameters  $R_{1a}^{cis}$  and  $R_{1a}^{trans}$  and thereby of the relevant direct interactions  $G_{(1)1a}^{cis}$  and  $G_{(1)1a}^{trans}$  were shown to fall close together and the equality

$$|G_{(1)1a}^{cis}| = |G_{(1)1a}^{trans}| \quad (19)$$

proved to be acceptable [13]. An analogous result was obtained also for  $Q_{2a}^{cis}$  and  $Q_{2a}^{trans}$ . On the whole, the relations of Eqs. (17)–(19) imply that opposite signs of matrix elements referring to pairs of BOs of vicinal bonds (H–C<sub>β</sub> and X–C<sub>α</sub>) make the only difference between the *cis*- and *trans*- conformations in our model. The relations of Eqs. (17)–(19) will be used in comparison of partial transferred populations for the cases of *cis*- and *trans*- arranged H–C<sub>β</sub> and X–C<sub>α</sub> bonds (Section 5).

## 5. Discussion of separate increments to partial transferred populations

Let us dwell now on the results of application of Eqs. (1)–(4), (7) and (9) to our six-orbital model of the concerted E2 reaction. Analysis of corrections to partial transferred populations and to interorbital interactions will be performed as described in Sections 2 and 3. We start with corrections of the second and third orders in Section 5.1. Thereupon, we will turn to increments of higher orders (Sections 5.2 and 5.3).

### 5.1. The second and third order increments

Let us start with the second order corrections  $q_{(-)l,(+)p}^{(2)}$  to partial transferred populations defined by Eq. (1). Non-zero values of these corrections may be expected if the relevant orbitals  $\phi_{(+)p}$  and  $\phi_{(-)l}$  interact directly and  $G_{(1)pl} \neq 0$ . In this context, the following increments are worth mentioning, viz.

$$q_{(-)2,(+)d}^{(2)} = 2(G_{(1)d2})^2, \quad q_{(-)a,(+)1}^{(2)} = 2(G_{(1)1a})^2 \quad (20)$$

and these describe the partial populations transferred directly from the external base (B<sup>⋅</sup>) to the H–C<sub>β</sub> bond and from the latter to the C<sub>α</sub>–X bond, respectively. Use of Eq. (19) allows us to conclude that

$$q_{(-)a,(+)1}^{(2)cis} = q_{(-)a,(+)1}^{(2)trans} > 0. \quad (21)$$

Thus, no dependence of the direct charge redistribution upon conformation of the molecule arises provided that Eq. (19) is accepted. Let us turn now to the third order corrections  $q_{(-)l,(+)p}^{(3)}$  defined by Eq. (2). It is seen that non-zero values of both  $G_{(1)pl}$  and  $G_{(2)pl}$  are imperative for a non-negligible value of this correction to arise. In particular, this condition proves to be met for the correction  $q_{(-)a,(+)1}^{(3)}$  describing the indirect charge transfer between the BBO  $\phi_{(+)1}$  of the H–C<sub>β</sub> bond and the ABO  $\phi_{(-)a}$  of the C<sub>α</sub>–X bond. As it is seen from Eq. (18), the direct interactions  $G_{(1)1a}^{cis}$  and  $G_{(1)1a}^{trans}$  contained within the definition of  $q_{(-)a,(+)1}^{(3)}$  are of opposite signs for *cis*- and *trans*- arranged vicinal bonds. So far as the signs of the relevant second order elements  $G_{(2)1a}$  are concerned, these are of negative signs whatever the conformation considered.

To show this, let us note that orbitals of the C<sub>α</sub>–C<sub>β</sub> bond (viz.  $\phi_{(+)3}$  and  $\phi_{(-)4}$ ) play the role of mediators in the indirect interaction  $G_{(2)1a}$ . From Eq. (11), we then obtain

$$G_{(2)1a} = \frac{1}{E_{(+1)} + E_{(-a)}} \left[ \frac{S_{13}R_{3a}}{(E_{(+3)} + E_{(-a)})} - \frac{R_{14}Q_{4a}}{(E_{(+1)} + E_{(-4)})} \right] \quad (22)$$

Use of Eq. (15) within Eq. (22) allows us to conclude that both fractions of this expressions are of negative signs and, consequently, build up a negative indirect interaction  $G_{(2)1a}$ . We then obtain

$$q_{(-)a,(+)1}^{(3)trans} > 0, \quad q_{(-)a,(+)1}^{(3)cis} < 0. \quad (23)$$

The above derivation of Eq. (23) shows that the orbital of the external base ( $\phi_{(+)d}$ ) participates neither in the indirect interaction  $G_{(2)1a}$  nor in the final correction  $q_{(-)a,(+)1}^{(3)}$ . Hence, the partial transferred populations of Eq. (23) actually are of intramolecular nature. After adding these third order increments to second order ones shown in Eq. (21), we obtain that more population is transferred between *trans*-arranged H–C<sub>β</sub> and C<sub>α</sub>–X bonds in substituted alkanes as compared to *cis*- arranged bonds. This result may be interpreted as non-equivalence of the *cis*- and *trans*-arranged H–C<sub>β</sub> bonds in respect of their electron-donating effects upon the C<sub>α</sub>–X bond. In Ref. [13], the same result has been alternatively considered as dissimilarity of electron-accepting effects of the heteroatom X upon the *cis*- and *trans*- arranged vicinal bonds. That is why the term ‘the *trans*-effect of heteroatom upon vicinal bonds in substituted alkanes’ was used to describe this dissimilarity. The present analysis of the effect yields an additional conclusion about its origin, namely the *trans*- effect originates from the conformation-dependent nature of the direct interaction

$G_{(1)1a}$  along with the conformation-independent character of the relevant indirect interaction ( $G_{(2)1a}$ ).

## 5.2. Studies of the fourth order corrections

As it was mentioned already, the number of terms to be considered grows dramatically when the order parameter  $k$  becomes higher. Thus, confinement to the most important increments seems to be advisable when studying the fourth and fifth order corrections to partial transferred populations. The intramolecular increments to the population of the  $C_\alpha$ -X bond were represented by the above-considered second and third order corrections (Section 5.1). In this connection, we will concentrate our attention here on terms representing the population acquired by the ABO  $\phi_{(-)a}$ , wherein the orbital of the external base  $\phi_{(+d)}$  participates explicitly or implicitly as mediator of a certain indirect interaction. These increments will be marked by the sign  $\sim$  and referred to as describing the base-assisted charge redistribution. Thus, let us turn to the definition of the fourth order partial transferred population  $q_{(-)l,(+)p}^{(4)}$  shown in Eq. (3) and confine ourselves to the case  $(-)l=(-)a$ . It may be easily seen that no base-assisted fourth order increments arise for  $(+)p=(+)3$ . Hence, the corrections  $\tilde{q}_{(-)a,(+)1}^{(4)}$  and  $\tilde{q}_{(-)a,(+)d}^{(4)}$  remain to be considered. Moreover, the base-assisted charge redistribution proves to be represented by the following terms denoted by additional superscripts 1 and 2, viz.

$$\tilde{q}_{(-)a,(+)1}^{(4)1} = 4G_{(1)1a}\tilde{G}_{(3)1a}, \quad (24)$$

$$\tilde{q}_{(-)a,(+)d}^{(4)2} = 2(G_{(2)da})^2 > 0. \quad (25)$$

Let us start with the correction shown in Eq. (24) and describing the fourth order indirect base-assisted charge transfer between orbitals  $\phi_{(+1)}$  and  $\phi_{(-)a}$ . The factor  $\tilde{G}_{(3)1a}$  of this expression corresponds to that part of the total third order indirect interaction  $G_{(3)1a}$ , wherein the orbital  $\phi_{(+d)}$  participates as mediator. This point deserves a somewhat more detailed discussion.

Indeed, the initially-occupied orbital of the external base ( $B''$ ) offers a new roundabout pathway from the BBO  $\phi_{(+1)}$  to the ABO  $\phi_{(-)a}$  via the orbitals  $\phi_{(+d)}$  and  $\phi_{(-)2}$  (Fig. 1(b)). This fact implies a new bridge ( $\phi_{(+d)}$ ,  $\phi_{(-)2}$ ) to arise between the above-mentioned orbitals after attack of the reagent that contributes to the indirect interaction  $G_{(3)1a}$ . The expression for the relevant increment ( $\tilde{G}_{(3)1a}$ ) to the total matrix element  $G_{(3)1a}$  follows from Eq. (13) and its sign proves to be determined by the sign of the product of three resonance parameters, viz.  $S_{1d}R_{d2}Q_{2a}$ . Using Eqs. (15) and (17) we then obtain

$$\tilde{G}_{(3)1a}^{trans} < 0, \quad \tilde{G}_{(3)1a}^{cis} > 0. \quad (26)$$

Thereupon, Eqs. (18), (19), (24) and (26) yield the final result

$$\tilde{q}_{(-)a,(+)1}^{(4)1,trans} = \tilde{q}_{(-)a,(+)1}^{(4)1,cis} > 0, \quad (27)$$

which resembles that of Eq. (21). The relation of Eq. (27) implies that an additional population is transferred from the H-C $_\beta$  bond to the C $_\alpha$ -X bond under an indirect influence of the external base ( $B''$ ) whatever the mutual arrangement of these bonds.

In other terms, a base-assisted indirect electron-donating effect of the H-C $_\beta$  bond upon the nucleofuge-containing (C $_\alpha$ -X) bond takes place during the elimination process. This new effect evidently is added to the relevant intramolecular effects discussed in the previous subsection. The increment of Eq. (25) represents the indirect charge transfer from the orbital  $\phi_{(+d)}$  to the ABO of the C $_\alpha$ -X bond ( $\phi_{(-)a}$ ). From Eq. (17) and the diagram of Fig. 1(b) it is seen that orbitals of the H-C $_\beta$  bond (viz.  $\phi_{(+1)}$  and  $\phi_{(-)2}$ ) play the role of mediators there. The positive sign of the correction  $\tilde{q}_{(-)a,(+)d}^{(4)2}$  also is evident. For further purposes, however, let us note that contributions of the BBO  $\phi_{(+1)}$  and of the ABO  $\phi_{(-)2}$  are added together in the expression for  $G_{(2)da}$  shown in Eq. (11) and this matrix element meets the following relations

$$G_{(2)da}^{trans} > 0, \quad G_{(2)da}^{cis} < 0, \quad |G_{(2)da}^{trans}| = |G_{(2)da}^{cis}|. \quad (28)$$

The final result of this consideration takes the form

$$\tilde{q}_{(-)a,(+)d}^{(4)2,cis} = \tilde{q}_{(-)a,(+)d}^{(4)2,trans} > 0. \quad (29)$$

Therefore, the external base  $B''$  exerts an indirect electron-donating effect upon the C $_\alpha$ -X bond by means of orbitals of the H-C $_\beta$  bond whatever the spatial arrangement of these bonds.

On the whole, the above-studied fourth order corrections exhibit no dependence upon conformation of the reactant. This implies that the fifth order terms should be additionally analyzed when looking for such a dependence, and this is undertaken in the next Subsection.

## 5.3. Consideration of the fifth order corrections to partial transferred populations

Analysis of Eq. (4) for  $(-)l=(-)a$  and  $(+)p=(+)1$  shows that the increment of Eq. (24) becomes supplemented with two fifth order corrections

$$\tilde{q}_{(-)a,(+)1}^{(5)1,1} = 4G_{(1)1a}[\tilde{G}_{(4)1a} + (G_{(1)}G_{(2)}^+G_{(1)})_{1a}], \quad (30)$$

$$\tilde{q}_{(-)a,(+)1}^{(5)1,2} = 4G_{(2)1a}[\tilde{G}_{(3)1a} + (G_{(1)}G_{(1)}^+G_{(1)})_{1a}]. \quad (31)$$

Accordingly, the following fifth order contribution should be added to the correction of Eq. (25)

$$\tilde{q}_{(-)a,(+)d}^{(5)2} = 4G_{(2)da}[G_{(3)da} + (G_{(1)}G_{(1)}^+G_{(1)})_{da}]. \quad (32)$$

Let us consider these increments separately. Let us start with the notation that the term  $(G_{(1)}G_{(2)}^+G_{(1)})_{1a}$  of Eq. (30) contains the orbital  $\phi_{(+d)}$  neither explicitly nor implicitly and thereby it does not contribute to the base-assisted charge redistribution. Again, emergence of the following pathways

$(\phi_{(+d}), \phi_{(-)2}, \phi_{(-)4})$  and  $(\phi_{(+d)}, \phi_{(-)2}, \phi_{(+3)})$  ensures participation of the orbital  $\phi_{(+d)}$  in the fourth order interaction  $G_{(4)1a}$ . The signs of the relevant contributions to the total matrix element  $G_{(4)1a}$  are determined by signs of products  $S_{1d}R_{d2}Q_{24}Q_{4a}$  and  $-S_{1d}R_{d2}R_{23}^+R_{3a}$ , respectively (the minus sign in front of the second product arises because of negative sign in front of the relevant fraction within the expression for  $G_{(4)pl}$ ). Employment of Eq. (15) allows us then to conclude that  $\tilde{G}_{(4)1a}$  is a negative quantity within Eq. (30) whatever the conformation considered. If we recall now the conformation-dependent nature of the first order interaction  $G_{(1)1a}$  seen from Eq. (18), we obtain

$$\tilde{q}_{(-)a,(+)1}^{(5)1,1,trans} > 0, \quad \tilde{q}_{(-)a,(+)1}^{(5)1,1,cis} < 0. \quad (33)$$

The correction of Eq. (31) may be analyzed similarly. First, the term  $(G_{(1)}G_{(1)}^+G_{(1)})_{1a}$  may be ignored as it was the case with the increment  $(G_{(1)}G_{(2)}^+G_{(1)})_{1a}$  of Eq. (30). Second, the matrix element  $G_{(2)1a}$  is a negative quantity (Section 5.1), whereas  $\tilde{G}_{(3)1a}$  is shown in Eq. (26). On this basis, we obtain

$$\tilde{q}_{(-)a,(+)1}^{(5)1,2,trans} > 0, \quad \tilde{q}_{(-)a,(+)1}^{(5)1,2,cis} < 0. \quad (34)$$

The conformation-dependent fifth order increments of Eqs. (33) and (34) should be then added to respective fourth order terms of Eq. (27) as it was the case with the third and second order increments of Eqs. (23) and (21), respectively. As a consequence, an analogous non-equivalence of the *cis*- and *trans*-arranged H–C $_{\beta}$  bonds arises in respect of efficiencies of their indirect base-assisted electron-donating effects upon the C $_{\alpha}$ –X bond, namely a more efficient electron-donating effect is obtained for the *trans* H–C $_{\beta}$  bond as compared to the *cis* bond. This result may be alternatively interpreted also as a base-assisted *trans*-effect of the heteroatom X upon the H–C $_{\beta}$  bonds in substituted alkanes. Hence, the intramolecular (primary) *trans*-effect of this atom [13] proves to be strengthened under influence of the approaching base. It is also noteworthy that the primary *trans*-effect in an initial reactant and its new base-assisted component are determined by signs of the same overlap integrals between orbitals of vicinal bonds, i.e. by the so-called overlap topology of BOs (see Ref. [13] for details). Let us consider finally the correction of Eq. (32). As it is seen from the Figure, four different pathways are possible between orbitals  $\phi_{(+d)}$  and  $\phi_{(-)a}$ . Accordingly, four pairs of orbitals are able to play the role of mediators in the indirect interactions  $G_{(3)da}$ , viz.  $(\phi_{(+1)}, \phi_{(+3)})$ ,  $(\phi_{(-)2}, \phi_{(-)4})$ ,  $(\phi_{(+1)}, \phi_{(-)4})$  and  $(\phi_{(-)2}, \phi_{(+3)})$ . The signs of contributions of these pairs of mediating orbitals to the total interaction  $G_{(3)da}$  are correspondingly determined by signs of the following products, viz.  $-S_{d1}S_{13}R_{3a}$ ,  $-R_{d2}Q_{24}Q_{4a}$ ,  $S_{d1}R_{14}Q_{4a}$  and  $R_{d2}R_{23}^+R_{3a}$ . From Eqs. (15) and (17), we obtain the positive signs of these products whatever the spatial arrangement of the C $_{\alpha}$ –X and H–C $_{\beta}$  bonds. This, in turn, implies that

$$G_{(3)da}^{cis} = G_{(3)da}^{trans} > 0. \quad (35)$$

The remaining term of Eq. (32) takes the form

$$(G_{(1)}G_{(1)}^+G_{(1)})_{da} = G_{(1)d2}G_{(1)23}^+G_{(1)3a} \quad (36)$$

and proves to be small as compared to  $G_{(3)da}$  of Eq. (35) as the relevant evaluations show. After a recall of Eq. (28), the final result is obtained, viz.

$$\tilde{q}_{(-)a,(+)d}^{(5)2,trans} > 0, \quad \tilde{q}_{(-)a,(+)d}^{(5)2,cis} < 0. \quad (37)$$

It is seen that the fifth order corrections to the partial populations transferred between orbitals  $\phi_{(+d)}$  and  $\phi_{(-)a}$  also are of opposite signs for the cases of *cis*- and *trans*-arranged vicinal bonds. Moreover, summing up the corresponding corrections of Eqs. (29) and (37) shows that more population is transferred between the external base and the nucleofuge-containing bond under an assumption of *trans*-conformation of the participating fragment. In other terms, the *trans*-arranged bridge mediates the indirect electron-donating effect of the base (B $^{\cdot\cdot}$ ) upon the C $_{\alpha}$ –X bond more efficiently as compared to the *cis*-arranged bridge.

## 6. Summarizing discussion and conclusions

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

1. The indirect influence of the external base (B $^{\cdot\cdot}$ ) upon characteristics of the nucleofuge-containing (C $_{\alpha}$ –X) bond of substituted alkanes is shown to consist of two indirect electron-donating effects upon this bond, namely of the base-assisted electron-donating effect of the H–C $_{\beta}$  bond and of the indirect electron-donating effect of the base itself by means of orbitals of the H–C $_{\beta}$  bond. These effects may be considered as the driving force of the concerted bimolecular  $\beta$ -elimination reaction of substituted alkanes.
2. Non-equivalence of the *trans*- and *cis*- conformations of the fragment B $^{\cdot\cdot}$ ...H–C $_{\beta}$ –C $_{\alpha}$ –X is established in respect of relative efficiencies of the above-enumerated electron-donating effects, namely both effects prove to be more efficient under an assumption of the *trans*-arrangement of the H–C $_{\beta}$  and C $_{\alpha}$ –X bonds. This result is in line with the well-known predominance of the *trans*- $\beta$ -elimination over the relevant *cis*-process [8–11], thereby yielding an interpretation of stereoselectivity of the E2 reactions.

Let us turn now to the joint discussion of the above-obtained results and those of an analogous investigation of the S $_N$ 2 process of the same compounds [4]. The following points deserve mentioning here:

1. The S $_N$ 2 reaction between a substituted alkane and nucleophile has been modelled by the direct attack of the latter upon the nucleofuge-containing bond [4] and thereby it was shown to be governed by the respective

direct electron-donating effect. The relevant  $\beta$ -elimination process is considered as a consequence of an indirect influence of the external base upon the same bond in the above study. In summary, these processes are expected to be governed by direct and indirect electron-donating effects of the reagent upon the nucleofuge-containing ( $C_{\alpha}$ -X) bond.

- Application of the semilocalized approach developed previously [1,2] to models representing the direct and indirect attacks of the reagent upon the  $C_{\alpha}$ -X bond shows that the relevant electron-donating effects are representable by members of the same power series for occupation numbers. The latter, in turn, are interpretable in terms of direct (through-space) and indirect (through-bond) interactions of bond orbitals. Hence, a unified quantum-chemical description of the  $S_N2$  and E2 processes is actually obtained.
- In the above-outlined context, competition between the  $S_N2$  and E2 reactions [8,11] may be considered as being based on choice between the direct and indirect attacks of the reagent upon the  $C_{\alpha}$ -X bond. Consequently, the actual way of reaction between a certain pair of molecules is likely to be determined by relative efficiencies of the direct and indirect influences of the given reagent upon characteristics of the  $C_{\alpha}$ -X bond of the reactant.
- Predictions of our approach concerning the dependence of the actual way of reaction upon properties of the reagent are as follows: For reagents of high electron-donating ability described by efficient direct interactions of its orbital with the antibonding orbital of the  $C_{\alpha}$ -X bond, the direct attack is likely to predominate over

the indirect one and an  $S_N2$  process is more probable. Again, possibility of an indirect attack remains for reagents of lower electron-donating ability and thereby predominance of an E2 reaction is expected in this case. These predictions are in line with those based on the concept of soft and hard nucleophiles as well as with experimental facts [11,18].

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