



# On the origin of the enhanced reactivity of $\alpha$ -halocarbonyl compounds in $S_N2$ processes

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## Abstract

Bimolecular nucleophilic substitution ( $S_N2$ ) reactions of allyl halogenides ( $Z-C_\alpha H_2-HC_\beta=C_\gamma H_2$ ;  $Z = \text{Halogen}$ ) and of respective substituted ketones ( $Z-C_\alpha H_2-RC_\beta=O$   $R=CH_3, C_2H_5$ , etc.) are comparatively studied using the semilocalized quantum-chemical approach suggested previously [J. Mol. Struct. (Theochem) 541 (2001) 1] and based on the power series for the one-electron density matrix [J. Mol. Struct. (Theochem) 343 (1995) 183]. Contributions of the direct (through-space) interaction between the electron-donating orbital of nucleophile and the electron-accepting orbital of the nucleofuge-containing ( $Z-C_\alpha$ ) bond and of various indirect (through-bond) interactions between the same orbitals to the population acquired by the nucleofuge  $Z$  during the reaction process may be considered separately and explicitly in this approach. Moreover, orbitals of the nearest-neighborhood of the  $Z-C_\alpha$  bond play the role of the principal mediators in the indirect interactions. On this basis, the  $C_\beta=C_\gamma$  and  $C_\beta=O$  bonds are compared in respect of mediating abilities of their  $\pi$ -orbitals in the above-mentioned indirect interactions and thereby of their contributions to relative rates of  $S_N2$  processes. It is demonstrated that the indirect participation of the bonding  $\pi$ -orbital of the  $C_\beta=C_\gamma$  bond contributes to lowering of the total population acquired by the nucleofuge  $Z$  owing to the nucleophilic attack and thereby of the relative reaction rate, whereas the increment of the antibonding orbital gives rise to an opposite effect. For highly electron-donating (soft) nucleophiles, the second contribution predominates over the first one, and this fact serves to account for the known higher reactivity of allyl halogenides as compared to respective alkyl halogenides. Furthermore, passing from the  $C_\beta=C_\gamma$  to the  $C_\beta=O$  bond is shown to be accompanied by such changes in shapes and one-electron energies of bond orbitals that ensure a significant reduction of the absolute value of the negative increment of the bonding orbital and a simultaneous increase of the positive contribution of the antibonding orbital to the total population acquired by the nucleofuge. This principal result of the paper forms the basis for a new interpretation of the largely increased reactivity of  $\alpha$ -halocarbonyl compounds vs. their hydrocarbon analogues in terms of direct and indirect interactions of bond orbitals.

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## 1. Introduction

Studies of substituent effects upon relative reactivities of similar compounds is among the most

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popular approaches of organic chemistry [1–7]. The sets of experimental data embracing entire series of reactants containing various substituents along with respective theoretical interpretations largely contribute to our understanding of the reaction mechanism. The  $S_N2$  processes between halogenides and nucleophilic reagents serve as an excellent object of application of this classical approach [5–7].

In particular, the  $S_N2$  reactions between various chlorides (R–Cl) and iodide ions ( $I^-$ ) exhibit significant substituent effects [5]. Thus, relative reactivities of  $\pi$ -electron-system containing compounds (R = allyl, benzyl, etc.) are considerably higher as compared to respective rates for their saturated analogues (R = *n*-butyl, cyclohexyl, etc.). Such an enhanced reactivity in  $S_N2$  processes under influence of an unsaturated substituent has been easily rationalized by considering the intramolecular interactions in the supposed transition structures [5,8]: inasmuch as this structure is assumed to contain an  $sp^2$ -hybridized carbon atom within the reaction center, the remaining 2p orbitals of this atom are able to overlap with orbitals of the  $\pi$ -electron subsystem of the substituent and the relevant intramolecular interaction yields an additional stabilization of the whole reacting system.

The more intriguing phenomenon, however, consists in the further increase of reactivity when the C=C bond in the chloride molecule is replaced by a C=O bond. Indeed, ‘the much greater reactivity of  $\alpha$ -chloroacetone than of allyl chloride suggests that there is an additional rate accelerating factor in  $\alpha$ -halocarbonyl compounds [5]’. Accounting for such a hazy factor evidently offers a real challenge for theoretical chemistry.

The principal ways of interpretation of the enhanced reactivity of the  $\alpha$ -halocarbonyl compounds have been overviewed in detail [5]. As with the case of the hydrocarbon substituents, consideration of the hypothetical transition structure containing an  $sp^2$ -hybridized carbon atom forms the basis of the most reliable interpretation [9] of this outstanding fact. It should be noted, however, that an additional assumption was invoked in Ref. [9] about a greater ability of the carbonyl group to delocalize the acquired negative charge owing to the supposed increased polarizability of the C=O bond vs. that of the C=C bond. An alternative explanation of the same

phenomenon in terms of electrostatics also deserves mentioning here, namely by an additional electrostatic attraction of the carbonyl dipole for the approaching nucleophile [10] which is also called dual attraction [11]. This way of interpretation evidently refers to the very early stage of the reaction.

On the whole, analysis of contributions devoted to the enhanced reactivity of the  $\alpha$ -halocarbonyl compounds allows us to conclude that this phenomenon cannot be accounted for so straightforwardly as it was the case with an unsaturated hydrocarbon substituent vs. the saturated one.

A new theoretical approach to investigate chemical reactivity has been suggested recently [12–14] on the basis of power series for the one-electron density matrix (bond order matrix) [15–24]. Moreover, this approach has been successfully applied to study an  $S_N2$  process between a substituted alkane and nucleophile [12]. In particular, the well-known two-orbital model of the reaction (wherein only the direct interaction between the electron-donating orbital of nucleophile ( $\varphi_{(+N)}$ ) and the electron-accepting orbital of the nucleofuge-containing (Z– $C_\alpha$ ) bond of the reactant ( $\varphi_{(-a)}$ ) is taken into consideration) was shown to follow from the second order terms of the above-mentioned series. Again, taking into account the third order terms of the same series yielded an extended model of the same reaction, where the indirect interactions between orbitals  $\varphi_{(+N)}$  and  $\varphi_{(-a)}$  also were explicitly included. Moreover, orbitals of the nearest ( $C_\alpha$ – $C_\beta$  and  $C_\alpha$ –H) bonds with respect to the heteroatom-containing bond played the role of mediators in this indirect interaction. Finally, just this new type of intermolecular interaction was shown to contribute significantly to the greater efficiency of the back attack of nucleophile vs. the frontal one. It should be also noted here that significant values of definite overlap integrals were required for a non-negligible extent of the above-specified third order indirect interaction to arise, namely of integrals  $\langle \varphi_m | \varphi_{(+N)} \rangle$ ,  $\langle \varphi_m | \varphi_{(-a)} \rangle$  and  $\langle \varphi_{(+N)} | \varphi_{(-a)} \rangle$ , where  $\varphi_m$  stands for the mediating orbital.

It is evident that the direct overlap integrals between the orbital of nucleophile ( $\varphi_{(+N)}$ ) and those of more distant  $\sigma$  bonds (e.g. of the single  $C_\beta$ – $C_\gamma$  bond) take small values in substituted alkanes. An analogous conclusion also follows for intramolecular overlap integrals  $\langle \varphi_{(-a)} | \varphi_m \rangle$  between the orbital  $\varphi_{(-a)}$



## 2. The expressions for occupation numbers of basis orbitals of a heteroatom-containing bond

Let us consider a heteroatom-containing (Z–C) bond involved within any molecular system, including several interacting molecules. Let the bond under study coincide with the  $I$ -th bond of our system. An initially-occupied bonding orbital  $\varphi_{(+i)}$  and an initially-vacant antibonding orbital  $\varphi_{(-i)}$  defined below will correspond to this bond.

Furthermore, the  $sp^3$ -hybrid AOs (HAOs)  $\chi_{IZ}$  and  $\chi_{IC}$  will be ascribed to atoms Z and C of our bond and these will be directed along the bond. Let these orbitals be represented by Coulomb parameters  $\alpha_{IZ}$  and  $\alpha_{IC}$ , whereas the bond itself will be characterized by resonance parameter  $\beta_I$ . Then the above-mentioned bond orbitals (BOs)  $\varphi_{(+i)}$  and  $\varphi_{(-i)}$  will be defined as eigenfunctions of the respective two-dimensional Hamiltonian matrix block in the basis of HAOs  $\{\chi_{IZ}, \chi_{IC}\}$ , i.e.

$$\varphi_{(+i)} = a_I \chi_{IZ} + b_I \chi_{IC}, \quad \varphi_{(-i)} = b_I \chi_{IZ} - a_I \chi_{IC} \quad (1)$$

where the coefficients  $a_I$  and  $b_I$  are [17]

$$a_I = \cos(\gamma_I/2), \quad b_I = \sin(\gamma_I/2), \quad a_I > b_I \quad (2)$$

and

$$\gamma_I = \arctg[2\beta_I/(\alpha_{IZ} - \alpha_{IC})], \quad 0 \leq \gamma_I \leq (\pi/2) \quad (3)$$

More electronegative heteroatoms (Z) vs. carbon and hydrogen atoms are considered here and the ratio  $2\beta_I/(\alpha_{IZ} - \alpha_{IC})$  is a positive quantity. Let us also note that the particular case of a C–C bond may be described by equalities

$$\alpha_{IZ} = \alpha_{IC} \quad \gamma_I = \pi/2, \quad a_I = b_I = 1/\sqrt{2} \quad (4)$$

The general expression for occupation numbers  $X_{IZ}$  and  $X_{IC}$  of HAOs  $\chi_{IZ}$  and  $\chi_{IC}$ , respectively, has been derived in Refs. [12,17] and takes the form

$$X_{IZ}(X_{IC}) = 1 \pm \cos \gamma_I + \frac{1}{2}(\Delta X_{(2)I} + \Delta X_{(3)I}) \pm (d_{(2)I} + d_{(3)I}) \pm (p_{(2)I} + p_{(3)I}) + \dots \quad (5)$$

where the upper signs refer to the HAO  $\chi_{IZ}$  and the lower ones correspond to the orbital  $\chi_{IC}$ . The subscripts (2) and (3) denote here and below the second and the third order terms of power series, respectively.

The zero order term of Eq. (5) ( $1 \pm \cos \gamma_I$ ) describes the occupation numbers of HAOs  $\chi_{IZ}$  and  $\chi_{IC}$  of an isolated Z–C $_{\alpha}$  bond. The population of the HAO  $\chi_{IZ}$  of the more electronegative heteroatom Z proves to be increased, whereas that of the HAO of the carbon atom is reduced, and this result is not unexpected.

The next terms of Eq. (5) (placed within the first parentheses of the right-hand-side) coincide with halves of the second and third order contributions, respectively, to the population of the  $I$ -th bond lost (acquired) by this bond owing to the interbond charge transfer. Each of these contributions  $\Delta X_{(k)I}$ ,  $k = 2, 3, \dots$  contains a sum of two terms, the first one describing the increment of the bonding BO (BBO)  $\varphi_{(+i)}$  and the second one representing that of the antibonding BO (ABO)  $\varphi_{(-i)}$ , viz.

$$\Delta X_{(k)I} = \Delta X_{(k)I,(+i)} + \Delta X_{(k)I,(-i)} \quad (6)$$

The two components of Eq. (6), in turn, may be conveniently represented in terms of partial populations transferred between pairs of orbitals of opposite initial occupation, i.e.

$$\Delta X_{(k)I,(+i)} = \sum_{j \ni J} \delta x_{(+i),(-j)}^{(k)} \quad (7)$$

$$\Delta X_{(k)I,(-i)} = \sum_{j \ni J} \delta x_{(-i),(+j)}^{(k)}$$

where  $\delta x_{(+i),(-j)}^{(k)}$  stands for the  $k$ -th order partial population transferred between the BBO  $\varphi_{(+i)}$  of the  $I$ -th bond and the ABO  $\varphi_{(-j)}$  of the  $J$ -th bond. Similarly,  $\delta x_{(-i),(+j)}^{(k)}$  represents the analogous population transferred between orbitals  $\varphi_{(+j)}$  and  $\varphi_{(-i)}$ . For  $k = 2$ , the relevant expressions take the form

$$\delta x_{(+i),(-j)}^{(2)} = -2(G_{(1)ij})^2; \quad \delta x_{(-i),(+j)}^{(2)} = 2(G_{(1)ji})^2 \quad (8)$$

where  $G_{(1)ij}$  stands for an element of certain first order matrix [15] describing the direct (through-space) interaction between the BBO  $\varphi_{(+i)}$  and the ABO  $\varphi_{(-j)}$ .

As in Refs. [12,17,23], let us introduce the following notations for resonance parameters between various types of BOs, the latter being indicated within

the bra- and ket-vectors, viz.

$$S_{ij} = \langle \varphi_{(+i)} | \hat{H} | \varphi_{(+j)} \rangle, \quad R_{ij} = \langle \varphi_{(+i)} | \hat{H} | \varphi_{(-j)} \rangle, \quad (9)$$

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

and note that  $S_{ij} = S_{ji}$ ,  $Q_{ij} = Q_{ji}$  but  $R_{ij} \neq R_{ji}$ . Then the element  $G_{(1)ij}$  takes the form

$$G_{(1)ij} = -\frac{R_{ij}}{E_{(+i)} - E_{(-j)}} \quad (10)$$

where the denominator of Eq. (10) contains the difference in one-electron energies of BOs  $\varphi_{(+i)}$  and  $\varphi_{(-j)}$ .

The third order analogue of Eq. (8) is [24]

$$\delta x_{(+i,(-j)}^{(3)} = -4G_{(1)ij}G_{(2)ij}; \quad (11)$$

$$\delta x_{(-i,(+j)}^{(3)} = 4G_{(1)ji}G_{(2)ji}$$

where  $G_{(2)ij}$  is an element of the second order matrix  $G_{(2)}$  defined as follows:

$$G_{(2)ij} = \frac{1}{E_{(+i)} - E_{(-j)}} \times \left( \sum_l^{\text{BBOs}} \frac{S_{il}R_{lj}}{E_{(+l)} - E_{(-j)}} - \sum_k^{\text{ABOs}} \frac{R_{ik}Q_{kj}}{E_{(+i)} - E_{(-k)}} \right) \quad (12)$$

The notations of Eq. (12) coincide with those of Eq. (10). It is seen that the element  $G_{(2)ij}$  describes the indirect (through-bond) interaction between the BBO  $\varphi_{(+i)}$  of the  $I$ -th bond and the ABO  $\varphi_{(-j)}$  of the  $J$ -th bond by means of other BBOs and/or ABOs.

The next parentheses of Eq. (5) contain terms  $d_{(2)I}$  and  $d_{(3)I}$  that also may be expressed in terms of transferred populations as follows:

$$d_{(k)I} = \frac{1}{2}(\Delta X_{(k)I,(+i)} - \Delta X_{(k)I,(-i)})\cos \gamma_I \quad (13)$$

and/or

$$d_{(k)I} = \frac{1}{2} \sum_{j \neq I} (\delta x_{(+i,(-j)}^{(k)} - \delta x_{(-i,(+j)}^{(k)})\cos \gamma_I \quad (14)$$

for both  $k = 2$  and  $k = 3$ . These corrections represent the second and third order increments to the so-called depolarization dipole moment of the  $I$ -th bond. This moment describes the reduction of the primary dipole of the given bond (equal to

$1 \pm \cos \gamma_I$ ) due to the dipole-like distribution of the additional population lost (acquired) by the  $I$ -th bond owing to the second order interbond charge transfer (substituting Eq. (8) into Eq. (14) indicates that  $d_{(2)I} < 0$  and thereby a reduction of the primary dipole follows).

The last two increments of Eq. (5) ( $p_{(2)I}$  and  $p_{(3)I}$ ) describe the corrections of the power series for the so-called induced dipole moment of the  $I$ -th bond arising under influence of the very presence of other bonds. These corrections are defined as follows:

$$p_{(k)I} = -2G_{(k)ii}\sin \gamma_I \quad (15)$$

where  $G_{(2)ii}$  should be taken from Eq. (12) for  $i = j$  and describes the indirect intrabond interaction between the BBO  $\varphi_{(+i)}$  and the ABO  $\varphi_{(-i)}$  of the  $I$ -th bond by means of orbitals of other bonds. The respective third order element  $G_{(3)ii}$  is defined as follows:

$$G_{(3)ii} = \frac{-1}{E_{(+i)} - E_{(-i)}} \times \left\{ \sum_j^{\text{BBOs}} \sum_m^{\text{BBOs}} \frac{S_{ij}S_{jm}R_{mi}}{(E_{(+j)} - E_{(-)}) (E_{(+m)} - E_{(-i)})} - \sum_j^{\text{BBOs}} \sum_r^{\text{ABOs}} \left[ \frac{S_{ij}R_{jr}Q_{ri}}{(E_{(+j)} - E_{(-i)}) (E_{(+j)} - E_{(-r)})} + \frac{S_{ij}R_{jr}Q_{ri}}{(E_{(+i)} - E_{(-r)}) (E_{(+j)} - E_{(-r)})} + \frac{R_{ir}R_{rj}^+R_{ji}}{(E_{(+j)} - E_{(-r)}) (E_{(+j)} - E_{(-i)})} + \frac{R_{ir}R_{rj}^+R_{ji}}{(E_{(+i)} - E_{(-r)}) (E_{(+j)} - E_{(-r)})} \right] + \sum_p^{\text{ABOs}} \sum_r^{\text{ABOs}} \frac{R_{ir}Q_{rp}Q_{pi}}{(E_{(+i)} - E_{(-p)}) (E_{(+i)} - E_{(-r)})} \right\} \quad (16)$$

and describes the indirect interaction between the BBO  $\varphi_{(+i)}$  and ABO  $\varphi_{(-i)}$  by means of two mediators.

### 3. Studies of the indirect participation of $\pi$ -orbitals of the $C_\beta=C_\gamma$ bond in the $S_N2$ reaction of allyl halogenide

Let us start with investigation of the intermolecular interaction between the allyl halogenide ( $Z-C_\alpha H_2- HC_\beta=C_\gamma H_2$ ) and nucleophile (Nu). The halogen atom (nucleofuge) Z will be represented by a single  $sp^3$ -hybrid orbital directed along the  $Z-C_\alpha$  bond as it was done previously [12,13,20,22,23]. Given that the number  $I = 1$  is ascribed to the  $Z-C_\alpha$  bond, the above-mentioned HAO acquires the subscript 1Z (Fig. 1(a)). The two BOs of the same bond ( $\varphi_{(+1)}$  and  $\varphi_{(-1)}$ ) will be defined in accordance with Eqs. (1)–(3). The relevant one-electron energies will be denoted by  $\epsilon_{(+1)}$  and  $-\epsilon_{(-1)}$  (Fig. 2(a)), where the minus sign in front of  $\epsilon_{(-1)}$  is introduced for further convenience. The attacking nucleophile (Nu) also is assumed to be representable by a single initially-occupied basis function  $\varphi_{(+N)}$  [12–14] and the corresponding energy level is designated by  $\epsilon_{(+N)}$ . Moreover, the reagent is placed in the back position with respect to the nucleofuge Z as it is usually supposed in the  $S_N2$  processes [2–7].

Let the  $C_\beta=C_\gamma$  bond to acquire the number  $I = 2$  and to be accordingly represented by  $2p_z$  AOs  $\chi_{2C_\beta}$

and  $\chi_{2C_\gamma}$  (Fig. 1(a)). Bond orbitals of this bond ( $\varphi_{(+2)}$  and  $\varphi_{(-2)}$ ) will be then defined by Eqs. (1) and (4), where  $\chi_{2C_\beta}$  and  $\chi_{2C_\gamma}$  stand for HAOs  $\chi_{1Z}$  and  $\chi_{1C}$  of Eq. (1), respectively. Moreover, the equalities  $\alpha_{2C_\beta} = \alpha_{2C_\gamma} = 0$  and  $\beta_2 = 1$  will be accepted for convenience. As a result of the above-specified choice of the energy reference point and energy unit, one-electron energies of BOs  $\varphi_{(+2)}$  and  $\varphi_{(-2)}$  coincide with 1 and  $-1$ , respectively, whilst  $\epsilon_{(+1)}$ ,  $\epsilon_{(-1)}$  and  $\epsilon_{(+N)}$  are positive parameters.

Let us introduce now the following notations for interbond resonance parameters

$$\langle \varphi_{(+N)} | \hat{H} | \chi_{2C_\beta} \rangle = \sigma; \quad \langle \varphi_{(+N)} | \hat{H} | \chi_{1C_\alpha} \rangle = \rho \quad (17)$$

$$\langle \chi_{2C_\beta} | \hat{H} | \chi_{1C_\alpha} \rangle = \tau$$

where

$$\sigma > 0; \quad \rho < 0; \quad \tau < 0 \quad (18)$$

Negative signs of parameters  $\rho$  and  $\tau$  follow from the definition of the HAO  $\chi_{1C_\alpha}$  so that the positive loop of this orbital is directed towards the heteroatom Z, whereas the negative one overlaps with the orbital of nucleophile.

As it was mentioned already, we will study the additional contribution to the total population  $X_{1Z}$  of

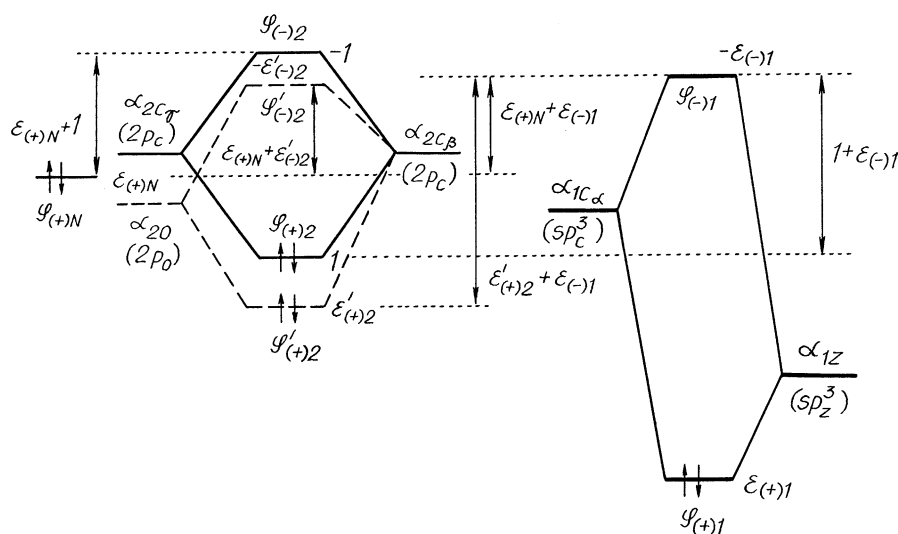


Fig. 2. Diagram reflecting the relative positions of energy levels corresponding to  $2p_z$  AOs,  $sp^3$ -hybrid AOs and bond orbitals of the allyl halogenide ( $Z-C_\alpha H_2- HC_\beta=C_\gamma H_2$ ) under attack of nucleophile (Nu) (solid lines), as well as alterations in one-electron energies when passing to the substituted acetone ( $Z-C_\alpha H_2- RC_\beta=O$ ) (dotted lines). Notations of basis orbitals coincide with those of Fig. 1, and the energy intervals involved within the expressions determining the additional population of the nucleofuge Z are indicated by double-headed arrows.

the HAO  $\chi_{1Z}$  of the nucleofuge Z which arises owing to the presence of the  $C_\beta=C_\gamma$  bond, including the population donated by the nucleophile indirectly by means of orbitals  $\varphi_{(+2)}$  and  $\varphi_{(-2)}$  playing the role of mediators. Let us start with the second order increments to the additional population of the HAO  $\chi_{1Z}$  shown in Eq. (5), viz.  $\frac{1}{2}\Delta X_{(2)1}$ ,  $d_{(2)1}$  and  $p_{(2)1}$ . From Eqs. (6), (7) and (14) it is seen that both  $\frac{1}{2}\Delta X_{(2)1}$  and  $d_{(2)1}$  are conditioned by the partial transferred populations of Eq. (8). The latter, in turn, describe the direct charge transfer between pairs of orbitals indicated within the respective subscripts. Additive form of Eqs. (6), (7) and (14), in turn, allows us to confine ourselves only to increments of orbitals under interest.

From the definition of BOs as eigenfunctions of respective intrabond Hamiltonian matrix blocks, it follows that the direct interactions  $G_{(1)11}$  and  $G_{(1)22}$  and thereby the relevant partial transferred populations  $\delta x_{(+1),(-1)}^{(2)}$  and  $\delta x_{(+2),(-2)}^{(2)}$  take zero values. Moreover, the partial transferred population  $\delta x_{(+1),(-2)}^{(2)}$  is of a small value owing to the large energy gap between BOs  $\varphi_{(+1)}$  and  $\varphi_{(-2)}$  (Fig. 2). We then obtain

$$\delta\left(\frac{1}{2}\Delta X_{(2)1} + d_{(2)1}\right) = \frac{1}{2}(\delta x_{(-)1,(+)N}^{(2)} + \delta x_{(-)1,(+2)}^{(2)})(1 - \cos \gamma_1) \quad (19)$$

where  $\delta$  of the left-hand side of Eq. (19) serves to denote that increment to the total sum  $\frac{1}{2}\Delta X_{(2)1} + d_{(2)1}$  which corresponds to orbitals considered in our model explicitly and shown in Fig. 2.

The first member of Eq. (19) ( $\delta x_{(-)1,(+)N}^{(2)}$ ) represents the direct charge transfer between nucleophile and the  $Z-C_\alpha$  bond which does not depend on the presence of the  $C_\beta=C_\gamma$  bond. Again,  $\delta x_{(-)1,(+2)}^{(2)}$  describes the additional electron-donating (hyperconjugative) effect of the  $C_\beta=C_\gamma$  bond upon the  $Z-C_\alpha$  bond which does not depend on the presence of nucleophile. Thus, the second order partial transferred populations and thereby the increment  $\delta(\frac{1}{2}\Delta X_{(2)1} + d_{(2)1})$  has nothing to do with the mediating ability of orbitals of the  $C_\beta=C_\gamma$  bond being sought.

A similar conclusion will be obtained also for the respective contribution to the second order induced dipole moment of the  $Z-C_\alpha$  bond ( $\delta p_{(2)1}$ ). Indeed,

from the definition of Eq. (15) for  $k = 2$  and Eq. (12) it follows that

$$\delta p_{(2)1} = \frac{-2 \sin \gamma_1}{\epsilon_{(+1)} + \epsilon_{(-1)}} \left[ \frac{S_{12}R_{21}}{1 + \epsilon_{(-1)}} - \frac{R_{12}Q_{21}}{\epsilon_{(+1)} + 1} \right] - \frac{2 \sin \gamma_1 S_{1N}R_{N1}}{(\epsilon_{(+1)} + \epsilon_{(-1)})(\epsilon_{(+1)N} + \epsilon_{(-1)})} \quad (20)$$

The first term of Eq. (20) containing the square brackets describes the contribution of orbitals of the  $C_\beta=C_\gamma$  bond to the total second order induced dipole of the  $Z-C_\alpha$  bond, which does not depend on the position of nucleophile. Thus, this term may be ascribed to an isolated reactant. Again, the last fraction of Eq. (20) represents an increment of nucleophile to the same dipole moment which does not involve the orbitals of the  $C_\beta=C_\gamma$  bond.

It is seen, therefore, that second order increments are insufficient when looking for an indirect participation of orbitals of the  $C_\beta=C_\gamma$  bond in the charge redistribution. Moreover, third order terms are likely to describe these effects adequately. Indeed, the third order partial transferred populations defined by Eq. (11) contain indirect interactions of participating orbitals along with the direct interactions in contrast to respective second order populations.

Thus, let us turn to analysis of third order increments to the total population  $X_{1Z}$  of the HAO  $\chi_{1Z}$ . Owing to zero values of direct intrabond interactions  $G_{(1)11}$  and  $G_{(1)22}$ , we may conclude immediately that

$$\delta x_{(+1),(-1)}^{(3)} = \delta x_{(+2),(-2)}^{(3)} = 0 \quad (21)$$

Furthermore, both the direct ( $G_{(1)12}$ ) and the indirect interaction ( $G_{(2)12}$ ) between orbitals  $\varphi_{(+1)}$  and  $\varphi_{(-2)}$  may be expected to take a small value owing to the large energy denominator  $\epsilon_{(+1)} + 1$ . This, in turn, implies an insignificant value of the respective partial transferred population  $\delta x_{(+1),(-2)}^{(3)}$ . Consequently,  $\delta x_{(-)1,(+)N}^{(3)}$  and  $\delta x_{(-)1,(+2)}^{(3)}$  are the most important increments of the final expression for  $\delta(\frac{1}{2}\Delta X_{(3)1} + d_{(3)1})$ . As a result, the sum  $\delta(\frac{1}{2}\Delta X_{(3)1} + d_{(3)1})$  may be written in the form of a single term as follows:

$$\delta\left(\frac{1}{2}\Delta X_{(3)1} + d_{(3)1}\right) = \frac{1}{2}(\delta x_{(-)1,(+)N}^{(3)} + \delta x_{(-)1,(+2)}^{(3)})(1 - \cos \gamma_1) \quad (22)$$

or

$$\delta\left(\frac{1}{2}\Delta X_{(3)1} + d_{(3)1}\right) = 2(G_{(1)N1}G_{(2)N1} + G_{(1)21}G_{(2)21})(1 - \cos \gamma_1) \quad (23)$$

if the definition of the third order partial transferred population of Eq. (11) is used.

The partial transferred population  $\delta x_{(-)1,(+)N}^{(3)}$  describes the alteration in the electron-donating effect of nucleophile to the Z–C $_{\alpha}$  bond owing to an indirect participation of orbitals of other bonds. Contributions, wherein orbitals of the C $_{\alpha}$ –C $_{\beta}$  (C $_{\alpha}$ –H) bonds played the role of mediators in the partial transferred population  $\delta x_{(-)1,(+)N}^{(3)}$ , have been considered in detail in Ref. [12]. Now, the analogous increments of  $\pi$ -orbitals of the C $_{\beta}$ =C $_{\gamma}$  bond will be analyzed (additivity of contributions of various mediators to the indirect interaction  $G_{(2)ij}$  is evident from the respective definition of Eq. (12). The mediating ability of the orbital  $\varphi_{(+1)}$  in the indirect interaction  $G_{(2)N1}$  turns to zero owing to the equality  $R_{11} = 0$ ). Similarly, the remaining partial transferred population  $\delta x_{(-)1,(+)2}^{(3)}$  represents an alteration in the electron-donating effect of the very C $_{\beta}$ =C $_{\gamma}$  bond upon the Z–C $_{\alpha}$  bond under an indirect participation of the orbital of the attacking nucleophile.

To establish the sign of the sum  $\delta(\frac{1}{2}\Delta X_{(3)1} + d_{(3)1})$  and thereby of the relevant contribution to the population of the HAO  $\chi_{1Z}$ , let us consider the right-hand side of Eq. (23) in more detail.

The direct interactions  $G_{(1)N1}$  and  $G_{(1)21}$  follow from Eq. (10) and take the form

$$G_{(1)N1} = -\frac{R_{N1}}{\epsilon_{(+N)} + \epsilon_{(-1)}}; \quad (24)$$

$$G_{(1)21} = -\frac{R_{21}}{1 + \epsilon_{(-1)}}$$

To derive the expressions for the indirect interactions  $G_{(2)N1}$  and  $G_{(2)21}$ , the definition of Eq. (12) should be used. Thus, the final expression for  $G_{(2)N1}$  takes

the form

$$G_{(2)N1} = \frac{1}{\epsilon_{(+N)} + \epsilon_{(-1)}} \times \left[ \frac{S_{N2}R_{21}}{1 + \epsilon_{(-1)}} - \frac{R_{N2}Q_{21}}{\epsilon_{(+N)} + 1} \right] \quad (25)$$

where the first and the second fractions inside the brackets represent the mediating abilities of orbitals  $\varphi_{(+2)}$  and  $\varphi_{(-2)}$ , respectively.

In the remaining second order interaction  $G_{(2)21}$ , it is the orbital  $\varphi_{(+N)}$  that plays the role of the principal mediator (orbitals of the C $_{\alpha}$ –C $_{\beta}$  bond are not able to play this role owing to their orthogonality to the BO  $\varphi_{(+2)}$ . The same refers also to the orbital  $\varphi_{(-2)}$ ). We then obtain

$$G_{(2)21} = \frac{S_{2N}R_{N1}}{(1 + \epsilon_{(-1)})(\epsilon_{(+N)} + \epsilon_{(-1)})} \quad (26)$$

The resonance parameters contained within Eqs. (25) and (26) equal to

$$S_{2N} = S_{N2} = R_{N2} = \frac{\sigma}{\sqrt{2}}; \quad R_{21} = Q_{21} = -\frac{a_1\tau}{\sqrt{2}}; \quad (27)$$

$$R_{N1} = -a_1\rho \quad (28)$$

Substituting Eqs. (24)–(28) into Eq. (23) yields

$$\delta\left(\frac{1}{2}\Delta X_{(3)1} + d_{(3)1}\right) = \frac{a_1^2\rho\sigma\tau(1 - \cos \gamma_1)}{(\epsilon_{(+N)} + \epsilon_{(-1)})} \times \left[ -\frac{1}{(\epsilon_{(+N)} + \epsilon_{(-1)})(1 + \epsilon_{(-1)})} + \frac{1}{(\epsilon_{(+N)} + \epsilon_{(-1)})(\epsilon_{(+N)} + 1)} - \frac{1}{(1 + \epsilon_{(-1)})^2} \right] \quad (29)$$

It is seen that the sign of the right-hand side of Eq. (29) and thereby of the relevant alteration in the population of the HAO  $\chi_{1Z}$  depends on the relative values of fractions inside the square brackets. The latter, in turn, are determined by the relative positions of one-electron energies of basis orbitals (the absolute values of interbond resonance parameters  $\rho$ ,  $\sigma$  and  $\tau$  are irrelevant here). As a result, the positive sign of the total sum inside the brackets is ensured provided



that the energy levels satisfy the following relation

$$\epsilon_{(+N)} + \epsilon_{(-1)} < \epsilon_{(+N)} + 1 < 1 + \epsilon_{(-1)} \quad (30)$$

This condition may be easily met for highly electron-donating (soft) nucleophiles characterized by sufficiently high energy  $\epsilon_{(+N)}$  of its initially-occupied orbital  $\varphi_{(+N)}$  (Fig. 2).

It should be also mentioned here that individual fractions of the right-hand side of Eq. (29) may be interpreted separately. For example, the most important second (positive) fraction inside the brackets may be traced back to that part of the partial transferred population  $\delta x_{(-1, (+N))}^{(3)}$ , which is mediated by the antibonding orbital  $\varphi_{(-2)}$  of the  $C_\beta=C_\gamma$  bond. Again, the contribution of the BBO  $\varphi_{(+2)}$  to the same partial transferred population gives rise to the first (negative) fraction and thereby to certain reduction of the total sum  $\delta(\frac{1}{2}\Delta X_{(3)1} + d_{(3)1})$ . Under condition of Eq. (30), however, the indirect contribution of the ABO  $\varphi_{(-2)}$  predominates over that of BBO  $\varphi_{(+2)}$  and an increase of the total population of the HAO  $\chi_{1Z}$  due to indirect charge transfer is obtained.

Let us consider now the last increment ( $\delta p_{(3)1}$ ) to the total population  $X_{1Z}$  of the HAO  $\chi_{1Z}$ . Two pairs of orbitals, viz.  $(\varphi_{(+2)}, \varphi_{(+N)})$  and  $(\varphi_{(+N)}, \varphi_{(-2)})$  should be considered as possible mediators of the third order intrabond interaction  $G_{(3)11}$  determining the induced dipole  $p_{(3)1}$  as shown in Eq. (15). Additivity of contributions to  $G_{(3)ii}$  and thereby to  $G_{(3)11}$  originating from different pairs of mediators follows from the definition of Eq. (16). The pair of orbitals of the  $C_\beta=C_\gamma$  bond ( $\varphi_{(+2)}$  and  $\varphi_{(-2)}$ ), as well as other pairs containing either the BBO or the ABO of the  $C_\alpha-C_\beta$  bond do not play the above-expected role because of zero values of overlap integrals between orbitals inside these pairs. As a result, the total dipole  $\delta p_{(3)1}$  consists of two additive parts.

Let the increment to the induced dipole  $\delta p_{(3)1}$  traced back to mediators  $(\varphi_{(+2)}, \varphi_{(+N)})$  to acquire the superscript (1). This contribution proves to be determined by the first double-sum of Eq. (16). Moreover, two cases should be considered here, namely  $j = (+)N$ ,  $m = (+)2$  and  $j = (+)2$ ,  $m = (+)N$ . We then obtain

$$\delta p_{(3)1}^{(1)} = \frac{2(S_{1N}S_{N2}R_{21} + S_{12}S_{2N}R_{N1})\sin \gamma_1}{(\epsilon_{(+1)} + \epsilon_{(-1)})(\epsilon_{(+N)} + \epsilon_{(-1)})(1 + \epsilon_{(-1)})} \quad (31)$$

The remaining contribution to the total dipole  $\delta p_{(3)1}$  traced back to the mediating ability of orbitals  $(\varphi_{(+N)}, \varphi_{(-2)})$  will be denoted by the superscript (2). It originates from the second double-sum of Eq. (16) and takes the form

$$\delta p_{(3)1}^{(2)} = \frac{-2(S_{1N}R_{N2}Q_{21} + R_{12}R_{2N}^+R_{N1})\sin \gamma_1}{(\epsilon_{(+1)} + \epsilon_{(-1)})(\epsilon_{(+N)} + 1)} \times \left[ \frac{1}{\epsilon_{(+N)} + \epsilon_{(-1)}} + \frac{1}{\epsilon_{(+1)} + 1} \right] \quad (32)$$

After summing up the increments  $\delta p_{(3)1}^{(1)}$  and  $\delta p_{(3)1}^{(2)}$  and substituting Eqs. (27) and (28) along with the following expressions for the remaining resonance parameters

$$S_{1N} = b_1\rho; \quad S_{12} = R_{12} = \frac{b_1\tau}{\sqrt{2}} \quad (33)$$

we obtain

$$\delta p_{(3)1} = \frac{2a_1b_1\rho\sigma\tau\sin \gamma_1}{\epsilon_{(+1)} + \epsilon_{(-1)}} \left[ -\frac{1}{(\epsilon_{(+N)} + \epsilon_{(-1)})(1 + \epsilon_{(-1)})} + \frac{1}{(\epsilon_{(+N)} + 1)(\epsilon_{(+N)} + \epsilon_{(-1)})} + \frac{1}{(\epsilon_{(+N)} + 1)(\epsilon_{(+1)} + 1)} \right] \quad (34)$$

It is seen that  $\delta p_{(3)1}$  is a positive quantity under condition of Eq. (30). Moreover, the positive fractions of the right-hand side of Eq. (34) are traced back to mediating contributions of the ABO  $\varphi_{(-2)}$  of the  $C_\beta=C_\gamma$  bond along with the orbital of nucleophile  $\varphi_{(+N)}$ , whereas the only negative fraction originates from the mediating contribution of orbitals  $(\varphi_{(+2)}, \varphi_{(+N)})$ . Hence, contributions of the BBO  $\varphi_{(+2)}$  and of the ABO  $\varphi_{(-2)}$  of the  $C_\beta=C_\gamma$  bond to the third order induced dipole of the  $Z-C_\alpha$  bond also are of opposite signs as it was the case with the sum  $\delta(\frac{1}{2}\Delta X_{(3)1} + d_{(3)1})$ .

It is seen, therefore, that the indirect participation of the bonding  $\pi$ -orbital of the  $C_\beta=C_\gamma$  bond contributes to lowering of the total population of the nucleofuge Z and thereby of the relative rate of the reaction, whereas that of the antibonding orbital gives rise to an increase of the same population and thereby to acceleration of the whole process. For highly

electron-donating (soft) nucleophiles, the second effect predominates over the first one, and this conclusion serves to account for the increased reactivity of allyl halogenides vs. that of respective alkyl halogenides [5].

#### 4. Comparison of mediating abilities of orbitals of the $C_{\beta}=C_{\gamma}$ and $C_{\beta}=O$ bonds

To make the above-indicated comparison easier, let us retain the energy reference point and the energy unit defined in Section 3. This implies that  $\alpha_{2C_{\beta}} = 0$  for the  $C_{\beta}=O$  bond as well, whereas  $\alpha_{2O}$  is a positive parameter (note that the electronegativity of the oxygen atom exceeds that of the carbon atom [5,6]). In connection with dissimilar values of Coulomb parameters of  $2p_z$  AOs  $\chi_{2C_{\beta}}$  and  $\chi_{2O}$ , the bond orbitals of the  $C_{\beta}=O$  bond will be defined as shown in Eq. (1) and denoted by  $\phi'_{(+2)}$  and  $\phi'_{(-2)}$ . The relevant coefficients  $a'_2$  and  $b'_2$  are related to parameters of the  $C_{\beta}=O$  bond ( $\alpha_{2O}$  and  $\beta'_2$ ) as shown in Eqs. (2) and (3). However, the sign of the ABO  $\phi'_{(-2)}$  will be chosen so that similarity of this orbital to the ABO  $\phi_{(-2)}$  of the  $C_{\beta}=C_{\gamma}$  bond is retained, viz.

$$\phi'_{(+2)} = a'_2\chi_{2O} + b'_2\chi_{2C_{\beta}}, \quad (35)$$

$$\phi'_{(-2)} = -b'_2\chi_{2O} + a'_2\chi_{2C_{\beta}}$$

where  $a'_2 > b'_2$  as shown in Fig. 1(b) and thereby

$$2(a'_2)^2 > 1; \quad 2(b'_2)^2 < 1 \quad (36)$$

One-electron energies corresponding to orbitals  $\phi'_{(+2)}$  and  $\phi'_{(-2)}$  will be accordingly designated by  $\epsilon'_{(+2)}$  and  $-\epsilon'_{(-2)}$ , where  $\epsilon'_{(+2)}$  and  $\epsilon'_{(-2)}$  are positive parameters. Moreover, the relations

$$\epsilon'_{(+2)} > 1, \quad \epsilon'_{(-2)} < 1 \quad (37)$$

are assumed to be met owing to the larger electronegativity of the oxygen atom vs. that of the carbon atom. The resonance parameters  $\rho$ ,  $\sigma$  and  $\tau$  between AOs (HAOs)  $\phi_{(+N)}$ ,  $\chi_{1C_{\alpha}}$  and  $\chi_{2C_{\beta}}$  are assumed to take the same values for both allyl halogenide and substituted acetone under attack of nucleophile (see Eqs. (17) and (18)). Such a transferability, however, does not refer to resonance parameters involving BOs  $\phi'_{(+2)}$  and  $\phi'_{(-2)}$ . Instead of Eqs. (27) and (33) we then

obtain

$$S'_{N2} = S'_{2N} = b'_2\sigma; \quad R'_{N2} = a'_2\sigma; \quad (38)$$

$$R'_{21} = -b'_2a_1\tau$$

$$Q'_{21} = Q'_{12} = -a_1a'_2\tau; \quad S'_{12} = S'_{21} = b_1b'_2\tau;$$

$$R'_{12} = b_1a'_2\tau$$

Using these new parameters within Eqs. (23)–(26), an analogue of Eq. (29) for the substituted acetone may be easily derived, viz.

$$\begin{aligned} \delta\left(\frac{1}{2}\Delta X'_{(3)1} + d'_{(3)1}\right) &= \frac{a_1^2\rho\sigma\tau(1 - \cos\gamma_1)}{(\epsilon_{(+N)} + \epsilon_{(-1)})} \\ &\times \left[ -\frac{2(b'_2)^2}{(\epsilon_{(+N)} + \epsilon_{(-1)})(\epsilon'_{(+2)} + \epsilon_{(-1)})} \right. \\ &+ \frac{2(a'_2)^2}{(\epsilon_{(+N)} + \epsilon_{(-1)})(\epsilon_{(+N)} + \epsilon'_{(+2)})} \\ &\left. - \frac{2(b'_2)^2}{(\epsilon'_{(+2)} + \epsilon_{(-1)})^2} \right] \quad (39) \end{aligned}$$

Let us compare this expression to that of Eq. (29). As it is seen from the relation of Eq. (36), the numerator of the second (positive) fraction inside the square bracket of Eq. (39) is increased as compared to the respective numerator of Eq. (29), whereas those of the first and third fractions are accordingly reduced. On the other hand, the following interrelations between energy intervals

$$\epsilon_{(+N)} + \epsilon'_{(-2)} < \epsilon_{(+N)} + 1; \quad (40)$$

$$\epsilon'_{(+2)} + \epsilon_{(-1)} > 1 + \epsilon_{(-1)}$$

ensure a reduction of the denominator of the second fraction along with an increase of their values for the first and the second fractions vs. the relevant denominators of Eq. (29) (the relation of Eq. (40) easily results from Eq. (37) and Fig. 2). The final conclusion of this analysis is as follows: the second (positive) increment to the population alteration of the HAO  $\chi_{1Z}$  due to indirect charge transfer proves to be increased for the substituted acetone vs. that of allyl halogenide, whilst the remaining (negative) increments are accordingly reduced. This evidently implies a larger positive value of the total sum  $\delta(\frac{1}{2}\Delta X'_{(3)1} + d'_{(3)1})$  vs. that of  $\delta(\frac{1}{2}\Delta X_{(3)1} + d_{(3)1})$ .

It is also evident that the first and the second fractions of Eq. (39) may be traced back to mediating contributions of orbitals  $\phi'_{(+2)}$  and  $\phi'_{(-2)}$ , respectively, to the partial transferred population  $\delta x_{(-)1,(+)N}^{(3)}$ , as it was done when analysing Eq. (29). Accordingly, the increase (reduction) of the absolute values of the second (first) fraction of Eq. (39) vs. those of Eq. (29) implies an increased (reduced) mediating ability of the ABO  $\phi'_{(-2)}$  (BBO  $\phi'_{(+2)}$ ) of the  $C_\beta=O$  bond as compared to respective abilities of orbitals of the  $C_\beta=C_\gamma$  bond in the indirect charge transfer from nucleophile to the  $Z-C_\alpha$  bond.

The expression for the third order induced dipole moment of the  $Z-C_\alpha$  bond due to the presence of the  $C_\beta=O$  bond may be derived and analysed similarly. The final expression for this moment takes the form

$$\delta p'_{(3)1} = \frac{2a_1 b_1 \rho \sigma \tau \sin \gamma_1}{\epsilon_{(+1)} + \epsilon_{(-1)}} \times \left[ -\frac{-2(b'_2)^2}{(\epsilon_{(+N)} + \epsilon_{(-1)})(\epsilon'_{(+2)} + \epsilon_{(-1)})} + \frac{2(a'_2)^2}{(\epsilon_{(+N)} + \epsilon'_{(-2)})(\epsilon_{(+N)} + \epsilon_{(-1)})} + \frac{2(a'_2)^2}{(\epsilon_{(+N)} + \epsilon'_{(-2)})(\epsilon_{(+1)} + \epsilon'_{(-2)})} \right] \quad (41)$$

and it should be compared to Eq. (34). It is seen that the positive  $(a'_2)^2$ —containing contributions to the total induced dipole  $\delta p'_{(3)1}$  are increased in Eq. (41) as compared to respective contributions of Eq. (34), whereas the absolute value of the remaining  $(b'_2)^2$ —containing fraction is accordingly reduced. This evidently implies a larger positive value of  $\delta p'_{(3)1}$  for substituted acetone vs. that of allyl halogenide ( $\delta p_{(3)1}$ ). Finally, this result may be traced back to an increased (reduced) mediating ability of the ABO (BBO) of the  $C_\beta=O$  bond as compared to respective values for the  $C_\beta=C_\gamma$  bond in the formation of the third order induced dipole of the  $Z-C_\alpha$  bond.

On the whole, the increased relative reactivity of the substituted acetone vs. that of the allyl halogenide proves to be related to the larger indirect contribution of orbitals of the  $C_\beta=O$  bond vs. those of the  $C_\beta=C_\gamma$  bond to the total increase of population of nucleofuge Z. The immediate reason of this effect consists in lowering of the negative increment of the BBO of the mediating bond and in a simultaneous increase of

the positive contribution of the ABO of the same bond when passing from the allyl halogenide to the substituted acetone. These alterations in relative mediating abilities of the above-mentioned BOs, in turn, may be traced back to respective changes in their shapes and relative positions. Indeed, comparison of Fig. 1(a) and (b) shows that the ‘center of gravity’ of the BBO is shifted away from the reacting carbon atom ( $C_\alpha$ ), whilst that of the ABO becomes nearer to this atom, when passing from the allyl halogenide to the substituted acetone (the BBO  $\phi'_{(+2)}$  acquires an increased coefficient at the  $2p_z$  AO of the oxygen atom, whereas the ABO  $\phi'_{(-2)}$  becomes primarily localized on the  $2p_z$  AO of the  $C_\beta$  atom). An analogous effect is observed also in respect to one-electron energies of BOs of mediating bonds, namely the position of the BBO becomes more remote from the relevant electron-accepting orbital ( $\phi_{(-)1}$ ), whilst the ABO comes nearer in energy to the electron-donating orbital of nucleophile.

## 5. Concluding remarks

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

1. A new way of accounting for highly increased reactivities of substituted acetones as compared to allyl halogenides, as well as of the latter vs. the respective alkyl halogenides is suggested in terms of direct (through-space) and indirect (through-bond) interactions of orbitals of separate bonds.
2. Demonstration of efficiency and fruitfulness of the concept of direct and indirect interorbital interactions to investigate chemical reactivity carried out previously [12–14] is supplemented with a new outstanding example.
3. The decisive role of characteristics of nucleophile in determining the relative reactivities of different reactants is revealed on the basis of comparison of allyl and alkyl halogenides. Indeed, an increased reactivity of the former vs. that of the latter is shown to follow under certain conditions that refer to relative positions of one-electron energies of nucleophile as compared to those of orbitals of the reactant.

Interpretation of the enhanced reactivity of  $\alpha$ -halocarbonyl compounds suggested in this paper corresponds to an intermediate region of the reaction coordinate in between the very early stage of the process (usually discussed in terms of electrostatics [10]) and the transition state [9]. On the other hand, our interpretation is valid within an extended interval of intermolecular resonance parameters. It may be concluded on this basis that even in the rather early stage of the  $S_N2$  reaction of  $\alpha$ -halocarbonyl compounds the interorbital interactions ensure their enhanced reactivity vs. that of allyl halogenides.

Comparison of the above-obtained results referring to the  $S_N2$  reaction of allyl halogenides to the results of Ref. [14] concerning the addition reaction between nucleophile and the butadiene molecule also causes an interest in respect of the influence of the  $H_2C=CH$  substituent upon the relative rate of reaction. Although these reactions are described by terms of different orders within the power series for the one-electron density matrix (viz. by the third and fourth order terms, respectively), common aspects of the indirect influences of the  $H_2C=CH$ -substituents also reveal themselves here. These aspects are as follows:

- (1) Orbitals of the substituent play the role of mediators in the electron-donating effect of nucleophile towards the reacting bond;
- (2) Influences of the bonding  $\pi$ -orbital and of the antibonding  $\pi$ -orbital of the substituent upon the relative rate of reaction are representable by additive contributions to total populations acquired by orbitals of the reacting bond;
- (3) The above-specified contributions are of opposite signs and thereby the relevant influences are in a mutual competition;
- (4) Under a nucleophilic attack, the effect of the antibonding orbital has a tendency to predominate over that of the bonding orbital.

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