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Analysis of the electron density redistribution in the course of nucleophilic addition reactions of H^- and F^- to acetylene and methylacetylene molecules according to *ab initio* calculations

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Energy characteristics and peculiarities of variation of structural parameters along the minimum energy pathways (MEP) calculated earlier of six reactions of nucleophilic addition of H^- and F^- to acetylene and methylacetylene have been analyzed. The electronic mechanism of the reactions, the character of the electron density redistribution, and its relation with the changes in structural parameters have been discussed. It has been found for all six reactions that the structural reorganization of an alkyne + Nu system is completed before the barriers. However, the increase in the alkyne multiple bond length and changes in electronic characteristics for the reactions with F^- (endothermic reactions) take place before the barrier (late transition state) and for the reaction with H^- (exothermic reactions), after the barrier (early transition state).

Key words: nucleophile, alkyne, *ab initio* calculations, electron density, Markovnikov rule, chemical shifts, structure, minimum energy pathways, orbital and charge control.

The results of *ab initio* calculations of minimum energy pathways (MEP) of six nucleophilic addition reactions to alkynes (1)—(6) resulting in the formation of the vinyl anion (VA), fluorovinyl anion (FVA), propenyl anion (PA), and fluoropropenyl anion (FPA) have been described in previous publications.[1—3]

$$\mathrm{HC{\equiv}CH + H^- \rightarrow [HC{=}CH_2]^-\ (VA)} \quad (1)$$

$$\mathrm{HC{\equiv}CH + F^- \rightarrow [HC{=}CHF]^-\ (FVA)} \quad (2)$$

$$\mathrm{CH_3{-}C{\equiv}CH + H^- \rightarrow [CH_3{-}CH{=}CH]^-\ (1\text{-}PA)} \quad (3)$$

$$\mathrm{CH_3{-}C{\equiv}CH + H^- \rightarrow [CH_3{-}C{=}CH_2]^-\ (2\text{-}PA)} \quad (4)$$

$$\mathrm{CH_3{-}C{\equiv}CH + F^- \rightarrow [CH_3{-}CF{=}CH]^-\ (1\text{-}FPA)} \quad (5)$$

$$\mathrm{CH_3{-}C{\equiv}CH + F^- \rightarrow [CH_3{-}C{=}CHF]^-\ (2\text{-}FPA)} \quad (6)$$

The energy characteristics and peculiarities of variation of structural parameters along MEP of these reactions have been analyzed.[3]

In the present work, the electronic mechanism of the reactions, the character of the electron density redistribution, and its relation to the changes in structural parameters are discussed. In addition to the changes in effective atomic charges ($Z^*_{\mathrm{eff_A}}$) and overlapping populations (Q_{AB}) in the course of the reactions, we have also considered the calculated bond energies (or chemical shifts) of skeleton $1s_A$ electrons ($\Delta E1s_A$) determined as the difference in their one-electron energies in a molecule and in a separate atom:

$$\Delta E1s_A = -(\varepsilon 1s_A(\mathrm{mol.}) - \varepsilon 1s_A(\mathrm{at.}), \quad (7)$$

as has been done for reactions (1) and (2) in Ref. 4.

In terms of the electrostatic point charge model, the $\Delta E1s_A$ values can be approximately presented in the form[5]:

$$\Delta E1s_A = kZ^*_{\mathrm{eff_A}} + \sum \frac{Z^*_{\mathrm{eff_A}}}{r_{\mathrm{AX}}}, \quad (8)$$

where k is proportionality constant ($k = \langle 1/r_{\mathrm{VA}} \rangle$, r_{VA} is the mean radius of valent electrons of the A atom) and r_{AX} is the distance between the A and X atoms. The second term (the Madelung term, ΔE_{Mad}) in Eq. (8) reflects the dependence of the chemical shift $\Delta E1s_A$ of the given atom on the charges of all other atoms in the molecule.

The $Z^*_{\mathrm{eff_A}}$ and Q_{AB} values calculated in the biexponential Roos—Ziegbahn (DZRS) basis for the reagents of the transition state (TS) and the products of reactions (1)—(6) with the structural parameters obtained[1—3] with the geometry optimization in the

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Table 1. Electron density distribution in reactions (1)—(6) for reagents, transition state, and products

Reaction	Alkyne	Nu	Atom under attack	State	Atomic charges						Bond orders						
					C(1)	C(2)	H(1)	H(2) (C(3)H$_3$)	C(3)	Nu	C(1)—C(2)				C(1)——H(1)	C(2)——H(2) (C(2)——C(3))	C(attack)——Nu
											σ	π_x	π_y	Σ			
(1)	A	H^- (F^-)	—	Reagents	−0.19	−0.19	0.19	0.19	—	−1.00	0.74	0.57	0.57	1.88	0.80	0.80	—
		H^-	C(1)	TS	−0.09	−0.40	0.13	0.01	—	−0.73	0.75	0.32	0.55	1.62	0.85	0.79	0.14
				VA	−0.47	−0.42	0.00	−0.07	—	−0.03	0.60	0.04	0.48	1.13	0.76	0.51	0.69
(2)		F^-	C(1)	TS	−0.07	−0.46	0.07	0.06	—	−0.61	0.52	0.24	0.53	1.28	0.76	0.77	0.31
				FVA	−0.06	−0.46	0.03	−0.01	—	−0.50	0.50	0.14	0.50	1.14	0.77	0.63	0.35
(3)	MA	H^- (F^-)	—	Reagents	−0.33	−0.18	0.17	0.33	−0.15	−1.00	0.44	0.58	0.58	1.60	0.84	0.36	0.00
		H^-	C(2)	TS	−0.40	−0.03	0.09	0.02	−0.22	−0.72	0.85	0.40	0.57	1.82	0.81	0.64	0.18
				1-PA	−0.37	−0.42	−0.06	−0.12	−0.27	−0.02	0.58	0.09	0.51	1.18	0.54	0.54	0.73
(4)			C(1)	TS	−0.09	−0.29	0.12	−0.03	−0.30	−0.67	0.80	0.35	0.56	1.71	0.86	0.72	0.14
				2-PA	−0.44	−0.30	0.01	−0.27	−0.36	−0.03	0.64	0.05	0.49	1.18	0.79	0.46	0.66
(5)		F^-	C(2)	TS	−0.43	−0.03	0.06	0.01	−0.26	−0.60	0.80	0.28	0.54	1.58	0.80	0.60	0.30
				1-FPA	−0.40	−0.04	−0.01	−0.07	−0.28	−0.50	0.62	0.18	0.50	1.26	0.66	0.60	0.34
(6)			C(1)	TS	−0.05	−0.36	0.07	−0.08	−0.32	−0.58	0.62	0.22	0.54	1.38	0.78	0.76	0.32
				2-FPA	−0.01	−0.36	0.04	−0.17	−0.35	−0.49	0.53	0.12	0.50	1.15	0.80	0.61	0.36

Table 2. Values of $\delta(\Delta E1s_A)$* for transition states and products of reactions (1)—(6) calculated in the DZRS basis

Reaction	Alkyne	Nu	Atom under attack	State	$\delta(\Delta E1s_A)$/eV			
					C(1)	C(2)	C(3)	F
(1)	A	H^-	C(1)	TS	5.3	6.9	—	—
				VA	8.9	9.0	—	—
(2)	A	F^-	C(1)	TS	5.3	7.8	—	−8.1
				FVA	5.7	8.5	—	−11.5
(3)	MA	H^-	C(2)	TS	6.5	5.0	5.0	—
				1-PA	8.4	7.6	6.4	—
(4)	MA	H^-	C(1)	TS	5.0	6.8	5.1	—
				2-PA	7.5	8.4	6.9	—
(5)	MA	F^-	C(2)	TS	7.3	4.9	5.2	−8.3
				1-FPA	7.9	5.2	5.6	−11.7
(6)	MA	F^-	C(1)	TS	4.9	7.5	5.5	−8.6
				2-FPA	5.1	8.0	6.1	−11.9

* The differences in $\Delta E1s_A$ of TS or the product and reagent.

3-21+G and 3-21++G bases are presented in Table 1. The changes in the skeleton chemical shifts $\delta(\Delta E1s_A)$ calculated in the same approximation for TS and products are presented in Table 2 and compared with those of the corresponding separate reagents.

According to our calculations, H atoms have small positive charges (up to +0.2) and C atoms have small negative charges in the separate reagents, acetylene (A) and methylacetylene (MA). In a MA molecule, the methyl group is an electron donor ($Z^*_{\mathrm{eff}_{Me}} = +0.33$), according to the common concepts. The negative charge $Z^*_{\mathrm{eff}C(1)}$ on the terminal C(1) atom bound to the H atom is greater than that on the central atom C(2) bound to Me (see Table 1). It has already been mentioned[4] that this charge distribution (−0.33, −0.18, and −0.15 for C(1), C(2), and C(3), respectively) correlates with the $\Delta E1s_{C(i)}$ values (0.176, 0.159, and 0.140) in an assumption that $\Delta E1s_{C(i)} \approx kZ^*_{\mathrm{eff}C(i)}$, *i.e.*, without account for ΔE_{Mad}. No correlation between $Z^*_{\mathrm{eff}C(i)}$ and $\Delta E1s_{C(i)}$ is observed in the other bases used (3-21+G, 3-21++G, and 6-31+G), although the relationship $\Delta E1s_{C(1)} < \Delta E1s_{C(2)} < \Delta E1s_{C(3)}$ is remained in all cases.*

In terms of the Klopman concept,[6] the charge factor for the MA molecule indicates that the Markovnikov addition of Nu to the C(2) atom is preferable. The effect of the orbital factor is determined by the composition of LUMO (in this case, antibonding π^*-MO) of alkyne. The difference obtained in our calculations in the coefficients at $2p\pi_{C(1)}$- and $2p\pi_{C(2)}$-AO in π- and π^*-MO of the MA molecule is insignificant: the coefficient at the $2p\pi_{C(1)}$-AO for a more diffuse component of the bi-exponential function is only by several hundredth higher than that at the $2p\pi_{C(2)}$-AO. Therefore, although the attack of the C(1) atom (bound to H) is more preferable in the orbital control, the differences in the heats and barriers to the addition reactions of Nu to C(1) and C(2) atoms should be low.

The type of the control depends on the energy of the HOMO of a nucleophile. According to the results of calculations,[1—3] mild nucleophile H^- ($\varepsilon_{\mathrm{HOMO}} = -0.044$ au (3-21++G basis)) adds to the C(1) atom (anti-Markovnikov orbital control), and the hard nucleophile F^- ($\varepsilon_{\mathrm{HOMO}} = -0.178$ au (3-21+G basis)) adds to the C(2) atom (Markovnikov charge control). The differences in the heats and barriers to the Markovnikov and anti-Markovnikov addition of each of the nucleophiles, as it has been suggested, are low (2—5 kcal mol^{-1}), which correlates with the small difference in the Z^*_{eff} charges and coefficients at $2p\pi_{C(i)}$-AO in the π^*-MO of the multiple C(1)—C(2) bond.

As a whole, the electron density redistribution in the course of these reactions is similar to that described[1,2] for the addition of H^- to MA and of H^- and F^- to A. In the pre-barrier region, independent of alkyne, the site of the attack, and the type of Nu, the electron density is displaced from the C(attack.) to the adjacent C(ad.) atom of the multiple bond and to the H or Me atom bound to it. This results in transpolarization of the alkyne for the reactions with H^- and F^-, which occur contrary to the Markovnikov rule (the addition to the C(attack.) = C(1) in MA). Thus, for H^-, even at $r \approx 3$ Å the charges on C(ad.) and C(attack.) become equal, and at $r \approx 2$ Å, *i.e.*, long before TS, the electron density on C(ad.) becomes higher than on C(attack.). In TS of all reactions, the charge on C(attack.) is close to zero, and the negative charge on Nu decreases by ~0.3 for H^- and by ~0.4 for F^-.

In the post-barrier region of the reactions with H^-, the electron transfer from Nu mainly to C(attack.) and atoms bound to it continues, and the charge of the added H atom in the products is close to zero. In the reactions with F^-, the process of the transfer of the electron density in TS is almost completed ($Z^*_{\mathrm{eff}_F} \approx -0.50$ in the products of FVA and FPA), the charge on C(attack.) and C(ad.) for the both types of Nu remains almost unchanged.

In the products, the negative charge is approximately equally distributed between two groups of the atoms, each of them has one of the atoms (C(attack.) or C(ad.)) of the multiple bond and the atoms bound to this atom (along with Nu). Thus, independent of the charges of these groups in the initial alkyne and the type of Nu, about a half electron charge of Nu transfers to the group containing C(ad.). The second half transfers to the group containing C(attack.) in the reactions with H^- and remains on Nu in the reactions with F^-. It can be supposed that this charge distribution is also typical of other Nu that are intermediate in the degree of hardness (HOMO energies) between H^- and F^-. In the products of their reactions with alkyl-substituted alkynes, the electron density will be distributed between a nucleophilic species and the group of atoms with C(attack.), depending on the HOMO energy of the nucleophile.

Of course, this consideration is too rough. As can be seen from Table 1, in all of the cases, somewhat more than a half electron density transfers to the group of the atoms including Me, independent of to what atom Me is bound, C(attack.) or C(ad.). In general, Me is an electron donor in alkynes and an acceptor in the products (PA and FPA): the substitution of H for Me in VA and FVA decreases (to a lesser extent than in alkynes) the electron population on the adjacent group and on the C atom directly bound to Me. It can be supposed that an increase in the length of the substituent (alkyl radical) results in an increase in the portion of the electron density transferred onto it. It should be also mentioned

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* It is likely that this correlation shows the real electron distribution in MA with the maximum negative charge Z^*_{eff} on C(1) and the minimum one on C(3) in Me. This correlation cannot be caused by the contribution of ΔE_{Mad} (Eq. (8)) to the chemical shift $\Delta E1s_{C(i)}$, because for positive $Z^*_{\mathrm{eff}H(i)}$ and negative $Z^*_{\mathrm{eff}C(i)}$ the maximum negative value of ΔE_{Mad} should be associated with the central C(2) atom.

that in the products the H atom or Me group bound to C(attack.) in the majority of cases have lower negative charge than those bound to C(ad.). Negative charges on all of the atoms of the former alkyne are always higher in the products of the reactions with H^- than in the products of reaction with F^-.

The changes in the chemical shifts of the skeleton $1s_{C(i)}$-levels on going from the reagents *via* TS to the products (see Table 2), as for the reactions (1) and (2) described,[4] in general correlate well with the corresponding increments of effective charges. As the calculations show, at large distances (r > 5 Å), the changes in $\delta(\Delta E1s_{C(i)})$ in the alkyne + Nu system, by contrast to separate neutral alkyne, are independent of the type of Nu and are described with the 10—12 % accuracy by the Madelung term in Eq. (8) related to the point negative charge of the Nu anion. The $\delta(\Delta E1s_{C(ad.)})$ deviation from ΔE_{Mad} for the C(ad.) atom increases abruptly as r decreases, which corresponds to the polarization of alkyne, *i.e.*, to an increase in the negative charge on C(ad.).

The curves $\Delta E1s_{C(attack.)}$ and $\Delta E1s_{C(ad.)}$ in Fig. 1 diverge for the reactions obeying the Markovnikov rule, and for the anti-Markovnikov reactions they approach and intersect even before reaching TS, which corresponds to transpolarization of the C(attack.) and C(ad.) atoms, *i.e.*, to the changes in their charges described above. The $\Delta E1s_{C(attack.)}$ curves have extremes at the points of TS corresponding to the minimum negative charges $Z^*_{effC(attack.)}$. On going from TS to the products, the absolute values $|\delta(\Delta E1s_{C(attack.)})|$ increase by more than 2 eV for the reactions with H^- (see Table 2) and only by 0.2 eV for the reactions with F^-. $Z^*_{effC(attack.)}$ change similarly.

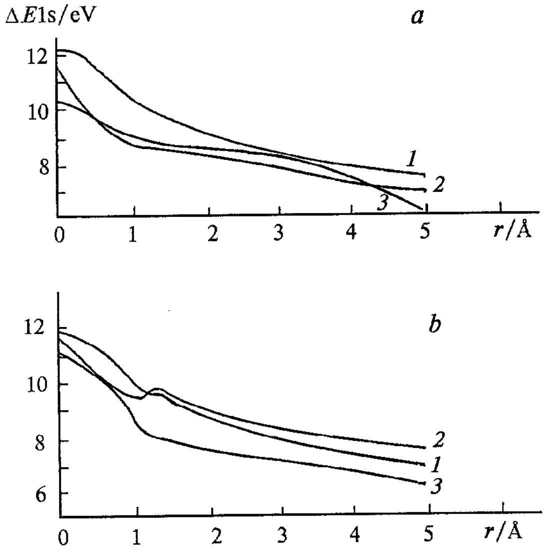

Fig. 1. Changes in $\Delta E1s_{C(i)}$ along the reaction coordinate r for the Markovnikov addition of H^- to MA (*a*) and for the anti-Markovnikov (*b*) for C(ad.) (*1*), C(attack.) (*2*), and C(Me) (*3*) atoms.

Certain disagreements are also observed. For example, the difference in $\Delta E1s_F$ of TS and products is high, although the corresponding Z^*_{effF} differ only slightly. In the products of reactions (3)—(6), $\Delta E1s_{C(Me)}$ is always lower than $\Delta E1s_{C(ad.)}$ and $\Delta E1s_{C(attack.)}$, while $Z^*_{effC(Me)} > Z^*_{effC(ad.)}$ for the charges in the product of reaction (3). It is substantial that for all of six reactions $|\Delta E1s_{C(ad.)}| > |\Delta E1s_{C(attack.)}|$. This corresponds to a higher negative charge on C(ad.), which agrees with the common concept about its concentration precisely on C(ad.) upon addition of a nucleophilic species. However, this is valid for Z^*_{eff} only in the case of the reactions with F^-. It is likely that the electron density distribution in the reaction products is more adequately reproduced by the $\Delta E1s_{C(i)}$ values.

As r decreases, the population of the overlap (Q_{C-Nu}) for C(attack.) and Nu increases continuously from 0 to ~0.70 in the reactions with H^- (passing through a shallow minimum of ~−0.06 at $r \approx 1.2$ Å) and to ~0.35 in the reactions with F^-. It is likely that this difference is the result of the more ionic character of the C—F bond compared to the C—H bond. The Q_{C-Nu} population in TS is equal to 0.14—0.18, *i.e.*, ~20 % of $Q_{C-H(Nu)}$ in the products, and for the C—F bonds it is 0.30—0.32, *i.e.*, 90 % of that inherent in the product.

All three components of the multiple C(1)—C(2) bond weaken in the course of the reaction: π_y weakens inconsiderably (~0.1), and the monotonic decrease from ~0.6 almost to 0 in the reactions with H^- and to 0.14—0.18 for those with F^- is observed for π_x. This difference is probably associated with the difference in the β angles in the products (~120° in hydrocarbons and ~130° in fluoro-substituted derivatives) and is determined[2] by the hybridization of C(1) and C(2) atoms. The population of the σ component decreases before the beginning of the bending of alkyne (especially strongly in the reactions with F^-), then increases reaching the maximum value in the region of TS, and then decreases slightly in the products. This is likely caused by the fact that one of the occupied MO of the σ-system of linear alkyne has a negative overlapping population of the C(1) and C(2) atoms of the multiple bond (small (−0.06) in A and considerable (−0.32) in MA, due to which the total overlapping population $Q_{C(1)-C(2)}$ in MA is lower than in A).

When a nucleophilic species approaches alkyne at an angle of 180°, the negative population of the C(1)—C(2) σ-bond increases, while it decreases, when a molecule is bent and the attacking angle changes, owing to which the total population $Q_{C(1)-C(2)}$ increases. On going from the reagents to the products, the overall decrease in $Q_{C(1)-C(2)}$ is equal to ~0.7 and ~0.4 for derivatives of A and MA, respectively.

The population densities of the other bonds (C—H and C(2)—C(3)) also decrease in the course of the reaction, and some of them decrease nonmonotonically. It is likely that the nonmonotonic character of the change in the population densities of σ-bonds in alkyne

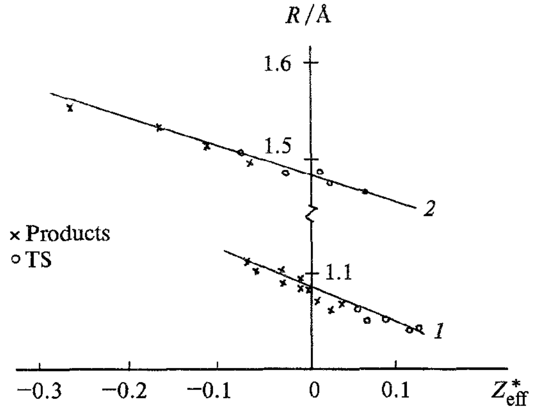

Fig. 2. Dependences of lengths of the C—H and C—C bonds adjacent to the multiple bonds on effective charges ($Z^*_{\rm eff}$) of the terminal H atom r(C(i) – H(i)) = f($Z^*_{\rm H}$) (*1*) and Me group r(C(2) – C(3)) = f($Z^*_{\rm Me}$) (*2*).

is determined by the strong electron density redistribution and by the fact that a molecule remains linear for some time in the course of the reaction, when the transfer has already begun, which results in the appearance of negative population densities of overlapping in some MO of the σ-system.

There is a definite correlation between the electron density distribution and the geometry of TS and the products. Although, as a whole, none of the reactions considered exhibit a distinct dependence of the bond length on its population, in each of the products, the lower population always corresponds to the longer bond adjacent to the multiple bond, and the maximum negative charge of the terminal H atom or CH_3 group corresponds to the minimum population. According to the results of the calculations for all of the reactions considered altogether, the C—H and C(2)—C(3) bond lengths in the products and TS depend almost linearly on the effective charges on the H atom and CH_3 group (Fig. 2). The lengthening of the bond as the negative charge is accumulated is likely caused by the character of antibonding MO. Thus, the C—H and C—C bonds at the C atom adjacent to the attacked atom are always longer than those in the attacked one, and the terminal bonds in the products are longer in the case of addition of H^- than for addition of F^-.

The correlation between the lengths and charges is observed only for terminal bonds, but not for multiple bond, because the charges on C(1) and C(2) depend noticeably on the substituent at the bond and the nucleophile attached, and its length is determined, in fact, only by the nucleophile. It is likely that the difference in the α and β angles of nonsubstituted and fluoro-substituted anions can also be explained by the differences in the charges of terminal atoms (H or Me, see Ref. 2).

The length and population of the multiple bond do not correlate, because the length changes monotonically along the MEP, and the population passes through a minimum and a maximum. The products also do not exhibit this correlation. However, in all fluoro-substituted derivatives the multiple bond is a little shorter than in nonsubstituted VA, 1-PA, and 2-VA, which can be explained by the existence of a slight triple-bonding due to the π_x-component.

Thus, the energy and structural values and the character of the electron density redistribution in the reactions of alkynes (A and MA) with soft and hard nucleophiles differ noticeably. The effect of substituents at the multiple bond, such as weak donor Me, and of the site of the attack is less significant. Only a smoother change in the structural and electronic parameters in the reactions of the Markovnikov addition of H^- and F^- can be mentioned.

For all of the six reactions, the structural rearrangement of the alkyne + Nu system (bending of alkyne, a decrease in the angle of the Nu attack from 180 to 120°) is completed in the pre-barrier region. However, lengthening of the multiple bond of the alkyne, transfer of electron density from Nu to alkyne, decomposition of the π_x-component of the bond, and formation of a new C(attack.)—Nu bond in reactions with F^- (endothermic) occur before the barrier (late TS) and in the reactions with H^- (exothermic) after it (early TS). This corresponds to the Hammond postulate that the TS is closer to the reagent with higher energy.

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