Structures and hardness of ethyl halides and ethyl tosylate

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Ab initio calculations (RHF) of EtX molecules (X = F, Cl, Br, I, or OTs) were carried out with the use of different basis sets. Total charges on the atoms in the compounds under study were determined by Mulliken's, NPA, and Bader's methods, and a comparison of these values was performed. For all EtX compounds, a topological analysis of the electron density was carried out within the framework of Bader's theory, and the global and relative local hardnesses of the above-mentioned ethylating agents were estimated.

Key words: ethyl halides, electronic structure, *ab initio* calculations, hardness, softness.

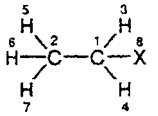
Alkylation of neutral (Nu:) and anionic (Nu^-) nucleophiles with alkyl halides RX (Eqs. (1) and (2)) are widely used in organic chemistry.[1,2] These reactions are often used in studies of the regioselectivity of alkylation at two different centers of ambident nucleophiles and carbanions.[3—5]

$$Nu: + \overset{\delta+}{R}\!-\!\overset{\delta-}{X} \longrightarrow \overset{+}{Nu}\!-\!R + X^- \qquad (1)$$

$$Nu^- + \overset{\delta+}{R}\!-\!\overset{\delta-}{X} \longrightarrow Nu\!-\!R + X^- \qquad (2)$$

The regioselectivity of alkylation of ambident anions can often be explained within the framework of the theory of hard and soft acids and bases (HSAB).[6—9] However, knowledge of the hardness of a particular reaction center, *i.e.*, of the local hardness, in complex molecules[9] rather than of their total (global) hardness is more important in considering their reactivity. It is known that the experimental determination or calculations of the local hardness is a rather complicated problem.[9] Because of this, the assignment of compounds to hard or soft acids or bases is often made based on the general concepts, for example, of the effect of substituents at the reaction center. Thus, the relative hardness of alkyl halides RX changes in the series RF > RCl > RBr > RI[3] due to a decrease in the hardness of the leaving group (F > Cl > Br > I).[6—9] However, when this approach is used, it is difficult to arrange exactly some compounds, for example, alkyl tosylates or triflates (which are much more commonly used for alkylation than alkyl fluorides), in the RX series.

In this work, the effects of the nature of the leaving X group on the distribution of the electron density of the C(1) reaction center of ethylating agents EtX (**1**) and on the hardness of this center were studied by *ab initio* quantum-chemical calculations.[10]



1a: X = F **1b:** X = Cl
1c: X = Br **1d:** X = I
1e: X = 4-$MeC_6H_4SO_2O$ (OTs)

The geometries of compounds **1a—e** were optimized using the GAMESS program[11] with different basis sets (Table 1). A topological analysis of the electron density

Table 1. Total energies (E), the global hardnesses (η), and the lengths (d) of the C(1)—C(2) and C(1)—X bonds in the EtX compounds calculated with different basis sets

X	Basis set	E	η	d/Å	
		/Hartree	/eV	C(1)—C(2)	C(1)—X
F	6-31G	−178.02187	3.58	1.509[a]	1.425[b]
	6-31G*	−178.07722[c]	3.39	1.512[a]	1.373[b]
OTs	6-31G*	−969.83280	3.42	1.512	1.442
Cl	6-31G	−538.08018	3.53	1.512[d]	1.885[e]
	6-31G*	−538.13152[f]	3.16	1.517[d]	1.799[e]
	6-311G**	−538.18160	3.89	1.516[d]	1.805[e]
	DH** [g]	−538.14168	3.06	1.520[d]	1.795[e]
Br	6-31G	−2648.38012	3.38	1.513[h]	2.015[i]
	6-31G*	−2648.57876	3.05	1.517[h]	1.958[i]
I	3−21G*	−6966.12323	3.14	1.532	2.193[j]

[a] 1.502[12], 1.540[13], 1.505[14], and 1.5128[15]. [b] 1.397[12], 1.375[13], 1.398[14], and 1.3825[15]. [c] −178.07722[16]. [d] 1.5508[17], 1.5495[18], 1.520[19], and 1.526[16]. [e] 1.7770[17], 1.7785[18], 1.788[19], and 1.799[16]. [f] −538.13152 (6-31G*)[16]. [g] DH** is Dunning—Hay's basis set with the polarization functions on the atoms.[20] [h] 1.5495[21], 1.518[22]. [i] 1.9400[21], and 1.950[22]. [j] According to the results of X-ray and neutron diffraction studies, the average and maximum lengths of the C(sp^3)—I bonds are 2.162 Å and 2.179 Å, respectively.[23]

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distributions in the EtF, EtCl, EtBr, EtOTs, (6-31G* basis set), and EtI (3-21G* basis set) molecules was carried out within the framework of Bader's theory of atoms in molecules[12,24] with the use of the AIMPAC program package.[17]

For all the molecules under study, the results of the calculations predict that an eclipsed conformation (the X—C(1)—C(2)—H(6) torsion angle is 180°) is energetically most favorable. The preference of this conformation for the EtF [8] and EtCl [13,14] molecules is evidenced by the data of electron diffraction and microwave spectroscopy.

The total energies E of compounds **1a—e** and the C(1)—C(2) and C(1)—X bond lengths (d) are given in Table 1. A comparison of the experimental values of d in the EtF,[15,18,19,25] EtCl,[13,14,26,27] and EtBr [16,21] molecules with the corresponding theoretical values demonstrated that all the calculations reproduce reasonably well the lengths of the above-mentioned bonds. An increase in the size of the basis set by including diffuse and polarization functions[10] allows one to estimate more precisely the bond lengths. The results obtained for the EtF, EtCl, and EtBr molecules demonstrate that optimization even with the use of the 6-31G* basis set gave results that are in good agreement with the experimental data as well as with the results of RHF and MP2 calculations[28] of the EtF and EtCl molecules with the 6-31$^+$G* basis set.

The calculations also adequately describe the bond angles, which is evident from a comparison with the experimental data for EtF,[18,19,25,28] EtCl, [13,14,26—28] and EtBr[21,22,28] and with the results of the calculations of the EtF and EtCl molecules by the RHF, MP2, and B3LYP methods (6-31$^+$G* basis set).[29] The lack of experimental values for EtI and EtOTs makes it impossible to judge whether their geometries are adequately described by the calculations. However, the values of d(C—H) and d(C—C) in the ethyl fragments of EtOTs and EtF as well as in those of EtCl and EtBr have similar values, which is a strong argument in favor of the fact that the calculations also adequately reproduce the geometry of this fragment in EtOTs. The value of d(C(1)—C(2)) in EtI was overestimated compared to the other compounds under study, and the value of d(C(1)—I) was overestimated compared to the experimental data on C(sp^3)—I bond lengths,[23] which is, apparently, a consequence of the use of the 3-21G* basis set in the calculations. In this case, the use of larger basis sets is restricted because of the absence its reliable development for the I atom.

Although the calculations adequately describe the geometries of the EtX molecules under study, the electron density distributions, which were determined by different methods with the use of the same basis set for each compound, differ substantially (Table 2), and in many cases they are inconsistent with the lower electronegativity of the C atom compared to the X and O atoms.[9,33] Thus, in the EtCl, EtBr, and EtI molecules, the total charges q (hereinafter charges) on the C(1) and C(2) atoms, which were calculated by Mulliken's[30] and Weihold—Reed's (NPA-analysis)[31] methods, are substantially more negative than those on the halogen atoms (see Table 2). This feature remains virtually unchanged even when the basis set is substantially extended, which is seen most clearly from the data on the charges on the C(1), C(2), and Cl atoms in EtCl (see Table 2). The disagreement between the charges on the atoms of different elements calculated by Mulliken's and NPA methods and those expected taking into account the relative electronegativities of these elements, has also been observed in the case of acetonitrile, acetaldehyde, and some other compounds.[16] Compared to Bader's method,[12,24] the NPA scheme also substantially overestimates the electron density on the C atom when the transition states of degenerated S_N2 reactions of alkyl fluorides and chlorides with F^- and Cl^- or with LiF, NaF, and LiCl, respectively, were calculated by the RHF and MP2 methods.[29]

Only in the EtF and EtOTs molecules are the charges on the X substituent calculated by Mulliken's[30] and NPA[31] methods more negative than those on the C(1) atom. However, in the above-mentioned cases, the negative charges on the C(2) atoms are also very large, and in the case of EtF this charge is even substantially larger

Table 2. Charges (q) on the C(1), C(2), and X atoms in the EtX compounds

X	Basis set	Method of calculations[a]	q/e		
			C(1)	X	C(2)
F	6-31G	M	0.126	−0.471	−0.495
	6-31G	NPA	0.049	−0.448	−0.725
	6-31G*	M	0.115	−0.412	−0.522
	6-31G*	NPA	0.107	−0.440	−0.683
	6-31G*	B	0.695[b]	−0.747[c]	0.073[d]
OTs	6-31G*	M	−0.032	−0.695	−0.496
		NPA	−0.044	−0.855	−0.657
		B	0.533	−1.394	0.095
Cl	6-31G	M	−0.420	−0.114	−0.454
	6-31G*	M	−0.375	−0.119	−0.483
		NPA	−0.382	−0.117	−0.653
		B	0.174[e]	−0.342	0.095[f]
	6-311G**	M	−0.204	−0.156	−0.238
	DH** [g]	M	−0.170	−0.168	−0.303
Br	6-31G	M	−0.496	−0.059	−0.439
	6-31G*	M	−0.340	−0.158	−0.481
		NPA	−0.450	−0.064	−0.652
		B	0.058	−0.241	0.099
I	3-21G*	M	−0.563	−0.020	−0.604
		NPA	−0.599	0.051	−0.680
		B	−0.166	−0.035	0.046

[a] M is Mulliken's method,[30] NPA is the natural population analysis,[31] and B is Bader's method.[12,24] [b] 0.795 (6-31G**, B)[16] and 0.69 (6-31G*, B)[32]. [c] −0.75 (6-31G*, B)[32]. [d] 0.235 (6-31G**, B)[16] and 0.06 (6-31G*, B)[32]. [e] 0.277 (6-31G**, B)[16]. [f] 0.254 (6-31G**, B)[16]. [g] See Note [g] in Table 1.

than that on the F atom (see Table 2). The charges on the H atoms in all the EtX compounds, which were calculated by both of the above-mentioned methods, are always positive. The charges on the H(3) and H(4) atoms vary (depending on the compound, the basis set, and the method) from 0.141 (EtCl, 6-311G**, according to Mulliken) to 0.258 (EtI, 3-21G*, according to Mulliken). The negative charges on the C(1) atom in the EtOTs, EtCl, EtBr, and EtI compounds (see Table 2) calculated by Mulliken's and NPA methods are inconsistent also with the electrophilic properties of the C(1) center of alkylating (including ethylating) agents[1,2] as evidenced by the schemes of reactions (1) and (2).

When the electron density ρ was analyzed by Bader's method,[12,24] a quite different situation was observed for the compounds under study. This analysis of the distribution of ρ (6-31G* basis set) in the EtF, EtOTs, EtCl, and EtBr molecules gave the positive charges on the C(1) and C(2) atoms (see Table 2). This is in complete agreement with the lower electronegativity of the carbon atom compared to the halogen and oxygen atoms as well as with the electrophilic properties of the EtX molecules. Only in the case of EtI did an analysis according to Bader give the negative charge on the C(1) atom (see Table 2), which is, most likely, due to the use of a too small basis set. The distributions of ρ in the EtF, EtCl, and EtBr molecules, which were calculated with alternative basis sets (see Tables 1 and 2), were not analyzed by Bader's method because it is known[34] that the results of this analysis are weakly sensitive to an increase in the size of the basis set (beginning from 6-31G).

A topological analysis according to Bader[12,24] makes it also possible to reveal other very important peculiarities of the distribution of ρ. At the critical points (3,−1)[12,24] on all the C—H bonds in the EtX molecules, the values of the Laplacian, $\nabla^2\rho_c$, and the densities of the local electron energy,[12,14] $H(r_c)$, are negative. Therefore, both these parameters indicate that the electron density is concentrated about the above-mentioned critical points[12,24,35,36] on the C—H bonds. An analogous situation is also observed for the C(1)—C(2) bonds in all the EtX molecules and for the C(1)—X bonds in the EtCl, EtBr, and EtI molecules (Table 3), whereas the values of $\nabla^2\rho_c$ are positive at the critical points (3,−1) on the C—F and C—O bonds in EtF and EtOTs, respectively. However, this is not evidence for the fact that in the two last-mentioned compounds the C—F and C—O bonds are noncovalent or unstable because it is impossible to unambiguously determine the character of the chemical bond from the sign of $\nabla^2\rho_c$.[12,24,35] According to the modern concepts,[12,24,35,36] the character of the chemical bond can be determined only from the sign of $H(r_c)$.

For the covalent bonds, the values of $H(r_c)$ are negative because at the critical points (3,−1) the potential energy of electrons predominates, which favors their localization on the bond line. At analogous critical points on ionic, hydrogen, and van der Waals bonds, the kinetic energy of electrons predominates, and the values of $H(r_c)$ at these points are positive.[12,24,35–37]

Taking into account the topological characteristics, the C—O bond in methanol can serve as the simplest analog of the C(1)—O bond in EtOTs. However, the published data[12,35] and the results of calculations, which we have carried out by the RHF/6-31G* method, demonstrate that not only $H(r_c)$ but also $\nabla^2\rho_c$ has the negative value at the critical point (3,−1) on the C—O bond in methanol. The positive value of $\nabla^2\rho_c$ for the C—O bond in EtOTs may be a result of the substantially higher electronegativity of the OTs group than that of OH. It should also be noted that in many other molecules with covalent bonds the $\nabla^2\rho_c$ values are also positive at the critical points (3,−1), and $H(r_c)$ are negative.[37]

In the EtX molecules, the length of the r_{1-H} vector from the C(1) nucleus to the critical point (3,−1) on the C(1)—H(3) or C(1)—H(4) bond line depends only slightly on the nature of the X substituent (1.306 (F), 1.317 (OTs), 1.313 (Cl), 1.312 (Br), and 1.299 (I) au). The length of the r_{1-2} vector from the C(1) nucleus to the critical point (3,−1) on the C(1)—C(2) bond line also depends only slightly on the nature of the X substituent (see Table 3). The electron density ρ_c at the critical points on the above-mentioned bond lines changes only slightly in the series of the EtX compounds under study. This is evidenced, for example, by the values of ρ_c for the C(1)—C(2) bond (see Table 3). The value of r_{1-X}, *i.e.*, the distance from the C(1) atom to the critical point (3,−1) on the C(1)—X bond line, increases in the series F < OTs < Cl < Br < I (Fig. 1) by a factor of more than

Table 3. Lengths of the (r_{1-2} (au)) and (r_{1-X} (au)) vectors from the C(1) atom to the critical points (3,−1) on the C(1)—C(2) and C(1)—X bond lines, the electron density (ρ_c/e · (au)$^{-3}$), the Laplacian ($\nabla^2\rho_c$/e · (au)$^{-5}$), and the electron energy density ($H(r_c)$/Hartree · (au)$^{-3}$) at these points in the EtX compounds calculated with the use of the 6-31G* basis set (3-21G* for EtI)

X	C(1)—C(2)				C(1)—X			
	r_{1-2}	ρ_c	$\nabla^2\rho_c$	$H(r_c)$	r_{1-X}	ρ_c	$\nabla^2\rho_c$	$H(r_c)$
F	1.470	0.269	−0.757	−0.240	0.819	0.231	0.506	−0.304
OTs	1.491	0.266	−0.744	−0.238	0.856	0.220	0.138	−0.305
Cl	1.495	0.261	−0.711	−0.230	1.391	0.178	−0.279	−0.125
Br	1.497	0.260	−0.707	−0.229	1.599	0.150	−0.209	−0.093
I	1.529	0.222	−0.536	−0.195	1.929	0.106	−0.040	−0.047

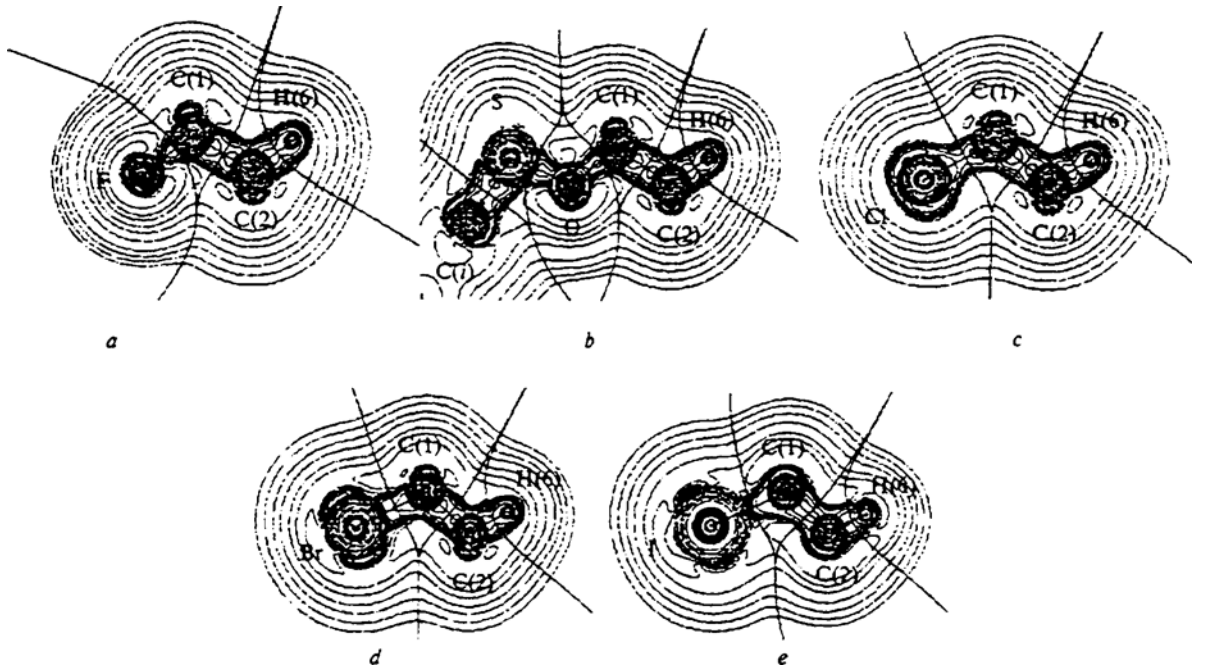

Fig. 1. Contour maps of the distribution of the Laplacian of the electron density $\nabla^2\rho$ (RHF/6-31G*) in the X—C(1)—C(2)—H(6) planes of the EtF (*a*), EtOTs (*b*), EtCl (*c*), EtBr (*d*), and EtI (*e*) molecules. The solid lines connect the points with $\nabla^2\rho < 0$, the dashed lines connect the points with $\nabla^2\rho > 0$. Contours correspond to the following values of $\nabla^2\rho$: $\pm1 \cdot 10^{-3}$, $\pm2 \cdot 10^{-n}$, $\pm4 \cdot 10^{-n}$, $\pm8 \cdot 10^{-n}$, where n changes from -3 to $+2$.

two, and ρ_c decreases in the series F > OTs > Cl > Br > I by a factor of almost 2.2 (see Table 3). The increase in r_{I-X} is clearly seen in Fig. 1.

The above-considered data demonstrate that the volume of the atomic basin of the C(1) atom in which its electron density is located increases substantially in the series EtF < EtOTs < EtCl < EtBr < EtI,[12,24,32,36] which is mainly due to an expansion of the atomic basin of the C(1) atom toward the X substituent. The volumes V_1 of the atomic basins of the methylene C(1) atom of the EtX compounds, which are limited by surfaces of the zero flux and the shell (0.001 au) of the electron density in the open portions of the surface of the C(1) atom (see Fig. 1), were calculated by Bader's method.[17,24,38] These values are 49.97 (EtF), 52.35 (EtOTs), 60.23 (EtCl), 63.39 (EtBr), and 72.72 (EtI) (au).[3] Note that the corresponding volume of the methylene C atom in normal alkanes is ~53.9 (au)[3].[38] The calculations demonstrated that in each of the above-mentioned EtX derivatives, the volumes accommodate no less than 99.9% of the electron density that is assigned to the C(1) atom.

The volumes of the atomic basins adequately reflect the sizes of the atoms, which are characterized by the van der Waals radii,[38] just as the spherical shell, which includes 98% of the electron density of the free atom, adequately describes its size.[39] Because for 75% of elements from Li to Xe (including C), 97% of the total volume of the atom falls on its outer shell, the polarizabilties of the spherical atoms correlate well with the electron densities of their outer electron shells, whose sizes are described by the radii of the above-mentioned spheres.[40]

It is reasonable to assume that most of the total volume of the atom of the molecule also belongs to the outer electron shell. Then, the above-mentioned values of V_1 adequately reproduce the volume of the outer shell of the C(1) atom in the EtX molecules. Because the inner shell of this atom contains 2 electrons, it is easy to determine the population $n_1 = N_1 - 2$ of its outer shell in the compounds under study from the total population N_1 calculated, for example, according to Bader. Then, the electron density ρ_1^s per unit volume of the outer shell of the C(1) atom can be readily calculated by dividing n_1 by V_1. The specific electron densities ρ_1^s of the outer shell of the C(1) atom in the EtX compounds under study, which were calculated according to the above-described procedure, are 0.0661 (EtF), 0.0662 (EtOTs), 0.0635 (EtCl), 0.0622 (EtBr), and 0.0573 (EtI) $e \cdot (au)^{-3}$. As mentioned above, the charge on the C(1) atom in EtI, which was determined according to Bader, is negative, which is inconsistent with the relative electronegativities of the C and I atoms as well as with the electrophilic properties of the C(1) atom in EtI. This indicates that the population N_1 calculated for EtI is substantially overestimated, and therefore, the

corresponding value of ρ_1^s should be even lower than the given value (0.0573 e · (au)$^{-3}$).

The smaller the volume of the atom and the larger the specific electron density on it, the larger its chemical hardness.[6—9] The above-mentioned estimates of ρ_1^s demonstrate that the hardness of the C(1) reaction center (to put it differently, the local hardness[9]) of the ethylating agents under study decreases in the order EtF ≈ EtOTs > EtCl > EtBr > EtI. It should be emphasized that the hardness of the reaction center of ethyl halides changes in the order identical to that obtained previously[3] based on a decrease in the hardness of the leaving X^- anion (F^-, Cl^-, Br^-, or I^-)[6—9] and a decrease in the electronegativity of the X atom. The global hardnesses of the EtX compounds,[6,7] $\eta = (E_{HOMO} - E_{LUMO})/2$, which were determined by *ab initio* calculations (see Table 1) with the use of the same basis set, change in the same order. Only the hardness calculated for EtI with the small basis set does not exactly fit in with this series. To put it differently, the orders in which the total and local hardnesses change in the series of the ethylating agents under study coincide. The hardnesses of EtOTs and EtF are very close to each other, but they are substantially lower than that of EtCl.

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