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Synthesis on the basis of electrogenerated carbenes

9.* Quantum chemical investigation of S_N2 reactions of polyhalomethanes and their anions

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A series of S_N2 reactions with halomethanes as substrates and the corresponding anions as nucleophiles were studied by the semiempirical MNDO and AM1 methods, taking into account solvent effects. Analysis of the kinetics, structures of reagents, intermediates and products, and charge distribution in them allows one to draw the conclusion that the retardation of S_N2 reactions is stronger in solvents than in the gas phase, and the rates of reactions involving anions with a lower number of halogen atoms are higher.

Key words: semiempirical calculation, MNDO, AM1; S_N2 reactions, transition states, structure; chloro- and bromomethane anions, halomethanes; accounting for solvation, point dipole method.

Reactions of nucleophilic substitution (S_N2 reactions) in the aliphatic series can be attributed to processes that are being studied mostly theoretically (see Refs. 2—8). Results of various studies, including quantum chemical investigations, form a basis for many modern theories concerning mechanisms of organic reactions in solution and solvent effects on their character. For example, several programs that make it possible to take into account solvation effects determining rates of S_N2 reactions in the medium have appeared recently. They use various approaches for reproducing solvation effects: nonempirical (*e.g.*, Monte Carlo[9]), semiempirical (the Born—Kirkwood—Onsager model),[10] and combined approaches (for example, the method of Monte Carlo statistical mechanics with combined potential (quantum chemical and molecular mechanical), AM1/TIP3P).[11] One such approach based on the point dipole methods is used in this work for quantum chemical study of S_N2 reactions involving polyhalomethanes and anions generated from them.

We considered the following reactions of nucleophilic substitution:

$$CCl_3^- + CCl_4 \rightarrow Cl_3C—CCl_3 + Cl^-, \quad (1)$$

$$CCl_3^- + HCCl_3 \rightarrow HCl_2C—CCl_3 + Cl^-, \quad (2)$$

$$HCCl_2^- + HCCl_3 \rightarrow Cl_2HC—CHCl_2 + Cl^-, \quad (3)$$

$$HCCl_2^- + H_2CCl_2 \rightarrow Cl_2HC—CH_2Cl + Cl^-, \quad (4)$$

$$H_2CCl^- + H_2CCl_2 \rightarrow ClH_2C—CH_2Cl + Cl^-, \quad (5)$$

$$H_2CCl^- + H_3CCl \rightarrow ClH_2C—CH_3 + Cl^-, \quad (6)$$

$$H_3C^- + H_3CCl \rightarrow H_3C—CH_3 + Cl^-, \quad (7)$$

$$CBr_3^- + CBr_4 \rightarrow Br_3C—CBr_3 + Br^-, \quad (8)$$

$$CBr_3^- + HCBr_3 \rightarrow HBr_2C—CBr_3 + Br^-, \quad (9)$$

$$HCBr_2^- + HCBr_3 \rightarrow Br_2HC—CHBr_2 + Br^-, \quad (10)$$

$$HCBr_2^- + H_2CBr_2 \rightarrow Br_2HC—CH_2Br + Br^-, \quad (11)$$

$$H_2CBr^- + H_2CBr_2 \rightarrow BrH_2C—CH_2Br + Br^-, \quad (12)$$

$$H_2CBr^- + H_3CBr \rightarrow BrH_2C—CH_3 + Br^-, \quad (13)$$

$$H_3C^- + H_3CBr \rightarrow H_3C—CH_3 + Br^-. \quad (14)$$

These processes can be alternative reactions to α-elimination, forming halomethane anions under the conditions of both phase transfer catalysis and their electrochemical generation discussed in our previous publications. Therefore, in our opinion, the analysis of thermodynamic and structural parameters of reactions

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* For Part 8 see Ref. 1.

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(1)—(14), depending on electronic structures of halomethanes and anions and polar properties of the medium, is of general interest.

Calculation procedure

The calculations were performed by the MNDO[12] and AM1[13] semiempirical methods, which are somewhat less rigorous than *ab initio* methods, but allow one to consider a wide range of S_N2 reactions. In addition, a semiempirical method, in particular, MNDO, in terms of the point dipole model[14] makes it possible to qualitatively take into account solvation effects for the reactions considered with a low expenditure of computer time. Transition states were determined by the MNDO and AM1 methods, using the SADDLE procedure from the MOPAC program package followed by refinement of their geometry by minimization of the gradient norm. The calculation was performed by the previously described procedure.[15]

Cross sections of potential energy surfaces (PES) were developed in terms of MNDO by the reaction coordinate method. It should be mentioned, however, that nucleophilic substitution is one of the processes for which the choice of the reaction coordinate is not evident. If the length of the forming or breaking bond is chosen as such a coordinate (as recommended, *e.g.*, in Ref. 16), at small distances a slight change in any of them causes a strong change in another bond length.[17] Therefore, one can hardly expect to obtain the true PES cross section in this case, in particular, to correctly determine ion-dipole complexes on the PES. Therefore, the difference between the distances was chosen as a reaction coordinate

$$\Delta R = R_{X\cdots C} - R_{C\cdots Y}.$$

In fact, this calculation method means the search of a minimum on PES along the axes

$$R_{X\cdots C} = \Delta R + R_{C\cdots Y}$$

and allows one to find one point on the trajectory of the movement of reagents in the reaction course at the fixed value of ΔR. The energies of the transition states determined by this method coincide well with those obtained by the SADDLE procedure, which confirms the correctness of the choice of the reaction coordinate. The method suggested allows one to calculate the energy of the system in any point of the PES cross section along the reaction coordinate. In particular, energies of possible minima and, hence, true reaction barriers with complicated potential profiles with intrinsic activation barriers can be efficiently determined. Nucleophilic substitution belongs to such reactions.

Choice of solvents. In this work, the following solvents were chosen as models for estimation of the energy of the considered reactions in liquid media: high polar H_2O, medium polar dimethyl sulfoxide (DMSO), and low polar methylene chloride (CH_2Cl_2). This choice makes it possible to follow the change in thermal effects and activation energies of reactions as the polarity of a medium decreases. The corresponding parameters of the solvents are taken from Ref. 18.

Results and Discussion

Thermodynamics of reactions. The heats of reactions (1)—(14) were calculated by the MNDO and AM1 methods with complete optimization of their geometries. The results of the calculations and the experimental data are presented in Table 1. It can easily be seen that the values obtained by the MNDO method are closer to the experimental data except for reaction (1), whose strong divergence from the experiment is caused by the fact that the MNDO method overestimates the stability of the CCl_3^- carbanion. The AM1 method gives systematically decreased values of ΔH of the reactions (see Table 1) mainly due to its considerable underestimation of the stability of halogen anions.[19] Therefore, the positive values of ΔH of reactions (8) and (9) obtained by the AM1 calculation are obviously inflated and will not be taken into consideration.

The data in Table 1 allows one to draw a conclusion that the considered S_N2 reactions are thermodynamically favorable in the gas phase. Although the absolute values of ΔH obtained by the MNDO and AM1 methods sometimes strongly differ, both methods equally well reflect their relative changes. The following tendency is revealed: in the series considered the heats of reactions of nucleophilic substitution mainly depend on the number of Hal atoms in a carbanion and increase as their

Table 1. Thermal effects ($-\Delta H$, kcal mol^{-1}) of reactions (1)—(14) in the gas phase and solvents

Reaction	Gas phase			Solvent		
	Calculation		Experiment*	CH_2Cl_2	DMSO	H_2O
	MNDO	AM1		MNDO		
1	9.1	2.9	33.5	26	34	53
2	11.2	4.1		28	36	55
3	45.1	35.8		57	63	75
4	44.7	35.8		57	63	75
5	79.6	67.3	74.7	85	93	95
6	77.7	62.9	73.9	83	91	93
7	108.7	90.3	90.7	114	118	127
8	20.1	−3.9		39	46	59
9	22.2	−2.7		41	48	61
10	46.4	24.5		59	65	77
11	46.4	25.5		59	65	77
12	74.9	56.0		83	86	91
13	73.2	60.1	76.4	81	84	89
14	103.6	93.5	98.4	106	107	110

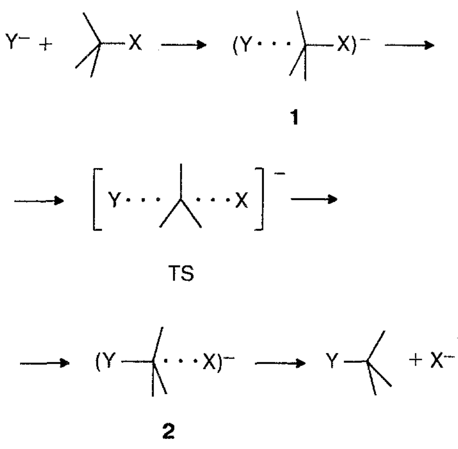
* The experimental values of the heats of formation of anions and neutral molecules for calculating reaction heats are taken from Ref. 20.

number decreases. The decrease in the number of Hal atoms by one in a substrate exerts almost no effect on the thermal effect of the reaction, while the same decrease in a carbanion results in the gain in energy of 20—30 kcal/mol.

The thermal effects of reactions (1)—(14) in the solutions are also presented in Table 1. It is seen that the reactions considered become more exothermic on going to solvents. The maximum thermal effects are observed in strongly polar solvents, although in this case the tendency described above (the dependence of ΔH of the reaction on the number of halogen atoms) is less pronounced. The matter is in the fact that only the solvation energy of the initial anion changes from one reaction to another; therefore, the lower the number of halogen atoms in it, the smaller the difference in solvation energies of the reagents and products (Table 2). At the same time, it is well known[21] that kinetic factors are determining for S_N2 reactions in liquid media, because nucleophilic substitution is assigned to the processes with complicated potential profiles.

Energies of transition states and intermediate complexes. The general scheme of the anionic S_N2 reaction (Scheme 1) corresponds to the typical shape of the PES cross section along the reaction coordinate (see Fig. 1).

Scheme 1



In fact, curves *b* and *c* (Fig. 1) are modifications of curve *a*. We considered only reactions with inversion of configurations of reaction centers. It is well known that for S_N2 reactions in the gas phase the energy level of the transition state (TS) is usually lower than the energy levels of reagents, and structural parameters of TS of these reactions to a greater extent depend on their exothermic natures.

Table 2. Solvation energies (kcal/mol) of halomethane anions in solvents of various polarities calculated in terms of the point dipole model

Anion	Solvent		
	High polar (H_2O)	Medium polar (DMSO)	Low polar (CH_2Cl_2)
CCl_3^-	44	42	39
$HCCl_2^-$	58	49	44
H_2CCl^-	73	53	49
H_3C^-	70	58	51
Cl^-	88	67	56
Br^-	76	61	53
CBr_3^-	37	35	34
$HCBr_2^-$	45	42	40
H_2CBr^-	60	50	45

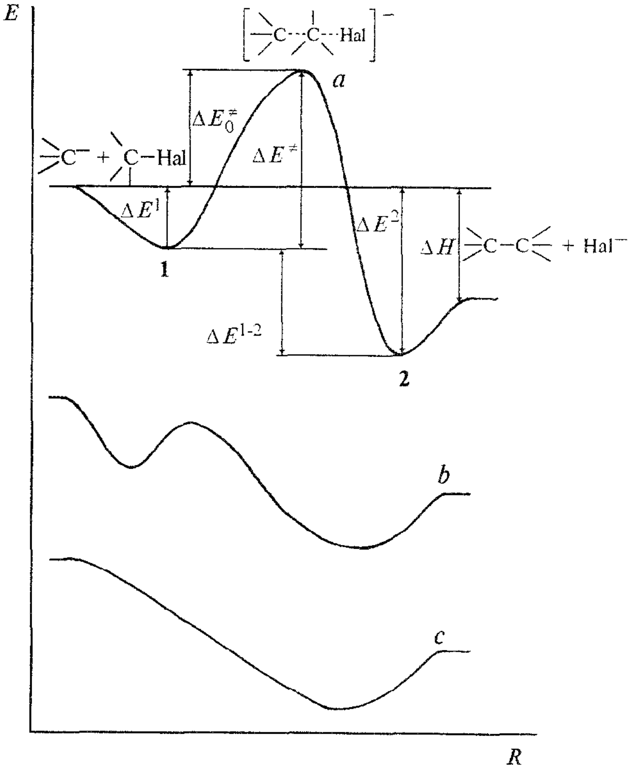
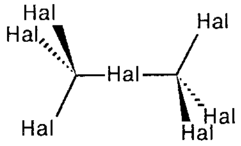


Fig. 1. PES cross sections for reactions of nucleophilic substitution: *a*, 2, 3, 9—11 (MNDO, AM1), 4 (MNDO); *b*, 4 (AM1), 5, 6, 12, 13 (MNDO, AM1); *c*, 7, 14 (MNDO, AM1), *R* is the reaction coordinate.

The calculated PES cross sections in the gas phase correspond to the modern views about the shape of the potential curve for S_N2 reactions (see, for example, Ref. 21). The first minimum on the curve (Fig. 1, *a*, *b*) corresponds to the sufficiently stable ion-dipole (or prereaction) complex **1**, when the reagents form the associate almost without changes in geometry. After stabilization ion-dipole complex **1** undergoes the rearrangement to form a new complex **2** *via* the cleavage of the C—Hal bond and formation of the C—C bond. Complexes **1** and **2** are separated by the activation barrier ($\Delta E^{\#}$). The system passes through TS, overcoming the activation barrier.

The shapes of the potential curves of reactions (1), (7), (8), and (14) differ from those described above. CCl_4 and CBr_4, which cannot form ion-dipole complexes due to their nonpolar characters, act as substrates in reactions (1) and (8), respectively. According to the data of our calculations, the coupling appeared between the $CHal_3^-$ carbanion and Hal atom in $CHal_4$ results in the formation of the adduct, whose structure is shown in Scheme 2.

Scheme 2



These adducts were also predicted in the literature,[16] where they were called covalent complexes, and, according to the calculation, in the majority of cases they are less stable than ion-dipole complexes.

The reaction route calculated for reactions (7) and (14) in the gas phase and corresponding to the minimum of energy has the shape displayed in Fig. 1, *c*, when the only minimum exists on the PES cross section, *i.e.*, the reagents are combined without activation to form the stable adduct (both methods (MNDO and AM1) do not predict TS and, hence, intrinsic barrier $\Delta E^{\#}$). This result is expected, because, according to Jonston,[22] highly exothermic reactions in the gas phase can occur without a barrier. The thermodynamic parameters of the PES cross sections calculated by the MNDO method are presented in Table 3, and the values of $\Delta E_0{}^{\#}$ are also calculated in the AM1 approximation. It is noteworthy that, despite considerable differences between the ΔH values of the reactions calculated by these methods, the energies of TS coincide with the accuracy to 1—3 kcal/mol.

Reactions (5), (6) and (12), (13) are strongly exothermic, and the energy of TS is lower than the energies of the reagents. Therefore, the $\Delta E_0{}^{\#}$ values are negative (see Fig. 1, *b*). Such reactions are activationless in the gas phase. This conclusion is confirmed, in particular, by the experimental data for reactions of various anions with methyl chloride.[23]

Analysis of the results presented in Table 3 shows that for the reactions studied the value of the activation barrier $\Delta E_0{}^{\#}$, which determines the reaction rate in the gas phase, strongly depends on the natures of both the substrate and the nucleophile. Activation barriers $\Delta E_0{}^{\#}$ decrease as the number of Hal atoms in any of the reagents decreases. The same concerns intrinsic (true) barriers $\Delta E^{\#}$ in S_N2 reactions, which additionally depend on the depth of the potential well corresponding to the formation of the ion-dipole complex. As for ΔE^1 and ΔE^2 that are conceptually stabilization energies of ion-dipole complexes **1** and **2**, respectively, they remain almost unchanged on going from one reaction to another, *i.e.*, in the first approximation they are independent on the natures of the reagents (Table 3).

Thus, the following general tendency is observed for the series of chloro- and bromosubstituted methanes: activation barriers of nucleophilic substitution reactions increase (hence, rates decrease) as the number of Hal atoms in a carbanion and halomethane decreases. It should also be mentioned that the minima corresponding to prereaction complexes of the quite different process (involving hydrogen transfer) are observed on PES of reactions (3) and (10). This process will be discussed elsewhere.

On going to solvents, it should be taken into account that nucleophilic substitution reactions are strongly retarded in the liquid phase compared to those in the gas phase. Rates of S_N2 reactions between anionic nucleophiles and neutral substrates in solution are lower by many orders of magnitude than those in the gas phase. This means that kinetic factors are determining, and an increase in reaction enthalpies does not correlate with the change in activation barriers.

The intermediate ion-dipole complex **1** is formed with an excess of energy, whose relaxation in the gas phase is slow. Therefore, the rate of the S_N2 reaction in the gas phase is determined by the $\Delta E_0{}^{\#}$ value, while in solvents it is determined by the true barrier $\Delta E^{\#}$, which nicely confirms our calculations. In fact, the activation energy increases drastically (by ~18—30 kcal/mol) (see Table 3), when the effect of the medium (a water type strongly polar solvent) is taken into account. It should be mentioned that water was used here only as a model of the highly polar solvent, *i.e.*, the effects caused by the formation of hydrogen bonds were not taken into account.

Table 3. Calculated values of thermodynamic parameters* (kcal/mol) for reactions (1)—(14) in the gas phase and strongly polar solvent

Reaction	Gas phase						Solvent
	MNDO					AM1	$\Delta E^{\#}$
	ΔE^1	ΔE^2	ΔE^{1-2}	$\Delta E^{\#}$	$\Delta E_0{}^{\#}$	$\Delta E_0{}^{\#}$	
1	0	9.5	—	37.7	37.7	23.1	60
2	5.8	12.5	17.9	32.2	26.4	15.3	47
3	—	12.1	—	—	10.1	0.4	40
4	8.2	10.0	46.5	10.8	2.6	−4.4	32
5	10.8	4.7	73.6	2.0	−8.8	−16.1	36
6	8.2	6.9	86.2	0.1	−8.1	−12.2	33
7	0	0.4	109.1	0	—	—	
8	0	8.1	—	30.4	30.4	32.5	49
9	6.3	8.9	24.8	26.9	20.5	23.2	37
10	—	9.3	—	—	9.6	6.4	30
11	7.0	7.8	47.2	9.7	2.7	1.2	20
12	8.4	3.4	69.9	2.1	−6.3	−13.2	28
13	6.9	5.8	82.1	0.2	−6.7	−14.7	23
14	0	0.4	104.0	0	—	—	

* For designations see Fig. 1.

Table 4. Dependences of the charge (*e* u) on the C atom of the attacking anion and energies (eV) of BMO on the reaction coordinate ΔR (Å) for processes (2) and (12)

Reaction	ΔR	Charge		Energy of BMO	
		C	Cl	LUMO	HOMO
2	3.0	0.22	−0.13	1.63	−4.22
	1.9	0.17	−0.15	2.13	−4.34
	1.4	0.13	−0.16	2.52	−4.50
	1.0	0.09	−0.21	3.26	−4.85
	0.3	0.05	−0.46	2.77	−4.87
	0.0*	0.04	−0.62	3.12	−5.16
12	3.1	−0.59	−0.13	2.39	−0.64
	1.3	−0.55	−0.20	3.41	−1.23
	0.8	−0.52	−0.29	3.84	−1.64
	0.6	−0.49	−0.36	4.12	−1.96
	0.5	−0.46	−0.40	4.28	−2.16

* Transition state.

It is reasonable that solvents with lower polarities to a lesser extent affect the change in the value of the activation barrier. For example, the *ab initio* calculations for the reaction

$$Cl^- + CH_3Cl \rightarrow ClCH_3 + Cl^-$$

show that the rate of this S_N2 reaction increases by 10^5 times on going from an aqueous medium[24] to DMF,[25] and it is established that there are no ion-dipole complexes in H_2O. It is noteworthy that the solvent effects on nucleophilic substitution processes can be estimated only knowing geometric structures of transition states and intermediate ion-dipole complexes and the charge distribution in them.

Structures of TS and ion-dipole complexes. The profile of the PES cross section along the reaction coordinate is mainly determined by interactions of three types: electrostatic, orbital, and steric. The interactions of the first two types cause the attraction of reagents, facilitate the formation of prereaction complex **1**, and stabilize TS. The steric interaction destabilizes these structures. It is rather important to elucidate which of the interactions mentioned dominate at each region of the PES cross section, because these are the interactions on which specific features of the structure of the corresponding intermediate depend.

Let us consider this question by the example of reactions (2) and (12), whose reagents differ in number and nature of halogen atoms. It is seen from Table 4 that in these reactions a considerable decrease in the negative charge on the C atom of the attacking anion and leaving group occurs only in the immediate vicinity of TS due to the charge transfer to the C—Hal bond of a substrate. Molecular orbitals (MO) of reagents are overlapped and noticeably mixed at such distances, *i.e.*, the orbital interaction plays a substantial role.

Energies of boundary molecular orbitals (BMO) begin to change at very large distances $R_{X...C}$, when the overlapping of MO of reagents is negligible and can be caused only by the Coulombic attraction between the negatively charged nucleophile and substrate. The nature of bonding in such prereaction complexes is pure electrostatic and caused by the ion-dipole interaction of the corresponding anion and polar bonds in halomethanes. The role of the steric repulsion decreases in these series of the reactions as the number of Hal atoms decreases.

The main structural parameters of ion-dipole complexes **1** and **2** and TS are presented in Table 5. The analysis of these data shows that on going to weaker nucleophiles, *i.e.*, when H is substituted for Hal in the carbanion, the charge on the carbon atom of the

Table 5. Main structural parameters* of ion-dipole complexes and the transition state

Reaction	Complex **1**				Transition state				Complex **2**			
	$R_{X...C}$	$R_{C...Y}$	Charge		$R_{X...C}$	$R_{C...Y}$	Charge		$R_{X...C}$	$R_{C...Y}$	Charge	
			C	Y			C	Y			C	Y
1	—	—	—	—	2.09	2.04	0.09	−0.51	—	—	—	—
2	3.37	1.79	0.15	−0.16	2.07	2.08	0.04	−0.63	1.55	3.10	0.26	−0.90
3	—	—	—	—	2.24	1.98	−0.13	−0.52	1.54	3.23	0.20	−0.97
4	3.32	1.80	−0.09	−0.23	2.21	1.98	−0.14	−0.55	1.52(9)	3.37	0.21	−0.98
5	3.07	1.81	−0.43	−0.27	2.46	1.90	−0.38	−0.46	1.52(6)	3.52	0.12	−0.99
6	2.98	1.84	−0.42	−0.37	2.65	1.88	−0.41	−0.45	1.51(9)	3.80	0.17	−1.00
7	—	—	—	—	—	—	—	—	1.52(2)	4.38	0.13	−1.00
8	—	—	—	—	2.19	2.06	−0.19	−0.41	1.51	4.16	0.10	−0.59
9	2.82	1.87	−0.23	−0.13	2.12	2.10	−0.23	−0.51	1.52	3.22	0.05	−0.91
10	—	—	—	—	2.27	2.04	−0.30	−0.44	1.51(9)	3.28	0.06	−0.97
11	3.38	1.89	−0.35	−0.16	2.24	2.04	−0.32	−0.49	1.51(8)	3.45	0.06	−0.97
12	3.16	1.90	−0.55	−0.20	2.49	1.98	−0.46	−0.40	1.52(0)	3.68	0.03	−1.00
13	—	—	—	—		1.96	−0.52	−0.38	1.51(7)	3.90	0.01	−1.00
14	—	—	—	—	—	—	—	—	1.52(2)	4.41	0.01	−1.00

* Bond lengths are presented in Å; charges on atoms in *e u*; C is the carbon atom of the nucleophile; $R_{X...C}$ is the distance between carbon atoms; $R_{C...Y}$ is the distance between the C atom and the leaving Hal atom.

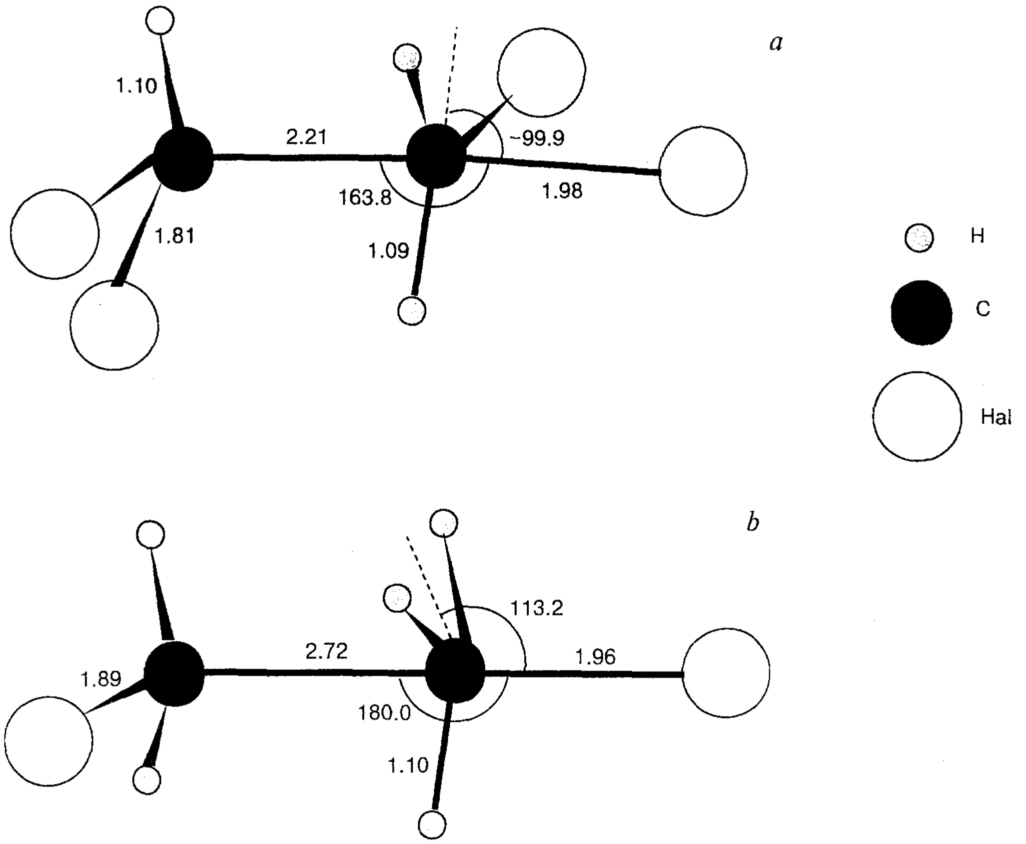


Fig. 2. Structures of TS of reactions 4 (*a*) and 13 (*b*) (the distances are presented in Å and the angles in deg).

nucleophile in prereaction complex **1** increases, which is likely caused by a decrease in the Coulombic attraction and steric hindrances. The charge on the leaving Hal atom and distance $R_{C...Y}$ remain almost unchanged, because (see above) the orbital interaction does not play a substantial role at such distances $R_{X...C}$.

It has already been mentioned that knowing the structure of TS and its position in the reaction coordinate makes it possible to predict the solvation effect on reactions of nucleophilic substitution. The results of the calculations by the MNDO and AM1 methods show that the charge distribution in TS and its geometry also depend on the composition of the reagents. It is seen from Fig. 2 (the TS structure) and Table 5 that the C—Hal bond length ($R_{C...Y}$) weakly changes on going from one reaction to another. The change in the C—C bond length ($R_{X...C}$) is most substantial, and the substitution of H for Hal in the nucleophile noticeably shifts the position of TS on PES toward the formation of products (the ΔR values are presented in Table 6). A similar substitution in the neutral substrate results in an opposite, but weakly pronounced effect: ΔR is almost unchanged for the same nucleophile in accordance with the Hammond rule (see also Table 1).

The charge on the attacking center behaves similarly: the total tendency to a decrease in the charge as the number of Hal atoms decreases exhibits a stronger drop, when Hal is substituted for H in the nucleophile. This substitution results in the shift in the electron density from the carbanionic center to Hal atoms. The more Hal atoms, the smaller negative charge on the carbon

Table 6. Dependence of the reaction coordinate (ΔR/Å) on the structures of reagents

Reaction	Reagents	Complex **1**	TS	Complex **2**
1	$CCl_3^- + CCl_4$	—	0.047	−2.431
2	$CCl_3^- + HCCl_3$	1.580	−0.016	−1.550
3	$HCCl_2^- + HCCl_3$	—	0.253	−1.694
4	$HCCl_2^- + H_2CCl_2$	1.518	0.231	−1.838
5	$H_2CCl^- + H_2CCl_2$	1.259	0.560	−1.991
6	$H_2CCl^- + H_3CCl$	1.132	0.767	−2.283
7	$H_3C^- + H_3CCl$	—	—	−2.490
8	$CBr_3^- + CBr_4$	—	0.129	−2.648
9	$CBr_3^- + HCBr_3$	0.944	0.020	−1.701
10	$HCBr_2^- + HCBr_3$	—	0.232	−1.756
11	$HCBr_2^- + H_2CBr_2$	1.490	0.200	−1.928
12	$H_2CBr^- + H_2CBr_2$	1.266	0.505	−2.108
13	$H_2CBr^- + H_3CBr$	1.102	0.762	−2.378
14	$H_3C^- + H_3CBr$	—	—	−2.888

atom, while it is positive in the case of reactions (1) and (2), according to our calculation.

It is reasonable that the position of TS should strongly shift toward the formation of reaction products. The approach of reagents occurring in this case requires large energy expenditure, and, hence, the activation barrier of the reaction should increase, which is confirmed by the data of our calculations. The shift of ion-dipole complexes and TS along the reaction coordinate, depending on the structure of reagents and strength of a nucleophile, can be more clearly characterized, if compare the ΔR values for the considered reactions of nucleophilic substitution presented in Table 6.

The data of Ref. 26 allows one to draw a conclusion that almost no shifts of TS and intermediate complexes occur along the reaction coordinate on going to solvents. This allows the effect of the medium polarity on the considered nucleophilic substitution reactions to be predicted on the basis of the results obtained. In this case, a larger TS with the considerably delocalized charge is formed, and the delocalization decreases as the number of halogen atoms in reagents decreases. Therefore, it can be asserted that weakening of the solvent polarity results in a decrease in the activation barriers, which can be noticeable due to a large size of TS.

The calculations performed confirm the current concepts on the mechanism of S_N2 reactions in the gas phase based on experimental data and results of quantum chemical studies. In all cases considered, nucleophilic substitution is thermodynamically favorable. Its easiness and low activation energies in the gas phase are explained by the formation of intermediate ion-dipole complexes.

The calculation shows that the charge distribution in TS and its geometry depend on the structures of reagents. A considerable decrease in the negative charge on the attacking anion and leaving Hal atom occurs only in the immediate vicinity of TS. The position of TS on PES mainly depends on the number of halogen atoms in the nucleophile and to a lesser extent in the substrate. Structures of TS and intermediate complexes determine the solvation effect on the thermodynamics of S_N2 reactions.

The introduction of solvents increases thermal effects of nucleophilic substitution reactions, although they are strongly retarded, because initial anionic particles are considerably stronger solvated than intermediate ion-dipole complexes and TS. It is very substantial that the rates of reactions involving anions with a lower number of halogen atoms are considerably higher.

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