Synthesis on the basis of electrogenerated carbenes
10.* Correlation of the energetics of α-elimination and nucleophilic substitution based on the results of quantum chemical calculations

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On the base of the semi-empirical MNDO, AM1, and PM3 methods of calculation, the reactivities of halomethane anions in α-eliminations and S_N2 reactions with participation of the initial polyhalomethanes have been compared and the dependence of the reactivity on the number of halogen atoms and solvent polarity has been investigated. The possibility of proton transfer when the initial polyhalomethane is C—H-acid has been also discussed.

Key words: polyhalomethanes, halomethane anions; reactivity, α-elimination, S_N2-reactions, proton transfer; quantum chemical calculation; MNDO, AM1, PM3 methods; solvation.

Competitive S_N2 reactions with participation of the carbanions formed and the initial halomethanes are possible in the process of generating halocarbenes from polyhalomethanes. On the base of data from quantum chemical calculations[1–3] we have tried to estimate the reactivity of the polyhalomethane anions. α-Elimination[2]:

$$CH_nHal_{3-n}^- \rightarrow :CH_nHal_{2-n} + Hal^-,$$

Hal = Cl, Br; n = 1...3,

and nucleophilic substitution reactions,[1] which may alternate with formation of halomethane anions under phase-transfer catalysis conditions and by electrochemical generation:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Comparing the previous results[1,2] it follows that the S_N2-reaction in the gas phase is thermodynamically preferable to the fragmentation of chloro- and bromomethane carbanions in every case under consideration. When fragmentation in the gas phase is too improbable, nucleophilic substitution, on the contrary, should proceed with a large energy advantage. In the framework of the solvent model[1,2] used the solvent polarity has an identical influence on the thermodynamics of the S_N2 reactions and the α-eliminations, since the charged particles are the same both in the initial mixture and in the products. Increasing the solvent polarity makes both reactions more thermodynamically profitable.

It should be noted that it is impossible on the base of the thermodynamical data only to conclude what of the transformations is preferable. Unlike the α-eliminations, the S_N2 reactions have a complicated potential energy profile and their reaction rates are determined by the difference between the energies of the ion-dipole complex (not of the reagents themselves) and the transition state. Therefore to find out what of the reactions under

* For 9 see Ref. 1.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 2155—2158, November, 1995.

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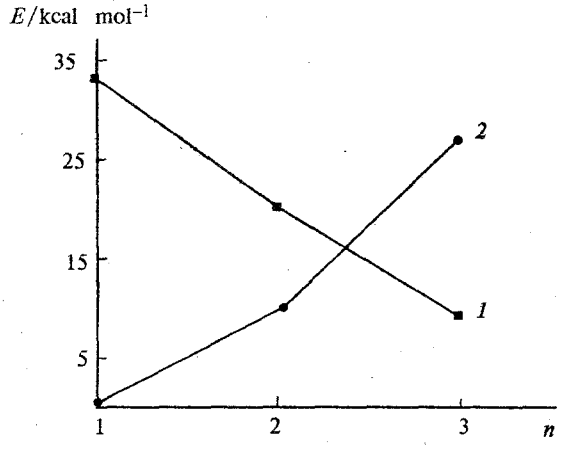


Fig. 1. Dependence of the activation energetics of α-elimination (*1*) and nucleophilic substitution (*2*) on the number of halogen atoms (*n*) in the initial anion.

consideration proceeds more easily it is necessary to know a contribution of the kinetical factors. Unfortunately, in this case too, a comparison of the absolute values of the activation energies for competitive of the α-elimination and the nucleophilic substitution processes is incorrect. It is true for reactions with the same stoichiometry, however, the first of the mentioned processes is monomolecular and the second is bimolecular one. That is why we have tried to clarify and to compare the trends on the changing reactivity of chloro- and bromomethane carbanions for two reaction rows and for either of these to know the dependence of equilibrium displacement upon the type of carbanion and solvent.

An analysis of the calculation results[1–3] permits to ascertain the contrary trends of changing reaction rates of the anion fragmentation and the nucleophilic substitution (see Fig. 1). Increasing the number of halogen atoms in the anion and using more polar solvent promote the fragmentation. The same factors have contrary influence on the S_N2 reactions, while in this case the solvent polarity is not essential as was shown earlier.[2] It is known from experiments that the nucleophilic substitution rate changes slightly with the replacement of a highly polar solvent by one of medium polarity as compared to a change of 17—20 orders of magnitude upon transition from the gas phase to the solvent.

A quite curious result of calculations should be noted: the minimum on the PES of S_N2 reactions between $HCHal_3$ and $HCHal_2^-$ corresponds to an ion-dipole complex not of these but of other particles, resulting from receding proton transfer. So, instead of reaction (3), the following chain of transformations can be realized in fact:

$$HCCl_2^- + HCCCl_3 \longrightarrow H_2CCl_2 + CCl_3^- \qquad (3')$$

$$\downarrow$$

$$H_2CCl{-}CCl_3 + Cl^- \qquad (15)$$

The analogous chain may be assumed instead of reaction (10):

$$HCBr_2^- + HCBr_3 \longrightarrow H_2CBr_2 + CBr_3^- \qquad (10')$$

$$\downarrow$$

$$H_2CBr{-}CBr_3 + Br^- \qquad (16)$$

The formation of ion-dipole complex corresponding to another reagents results in an advantage of 34 kcal · mol^{-1} for reaction (3′) and 20 kcal · mol^{-1} for reaction (10′) according to the MNDO data. Reactions (3′) and (10′) are conceptually the proton transfer with the formation of the weaker acids. Sure, this pathway can be only realized for carbanions generated with the C—Hal-bond cleavage* (reactions (3), (5), (7), (10), (12), and (14)). Therefore, all possible processes of proton transfer:

$$H_2CCl^- + H_2CCl_2 \longrightarrow H_3CCl + HCCl_2^- \qquad (5')$$

$$\downarrow$$

$$H_3C{-}CHCl_2 + Cl^- \qquad (17)$$

$$H_2CBr^- + H_2CBr_2 \longrightarrow H_3CBr + HCBr_2^- \qquad (12')$$

$$\downarrow$$

$$H_3C{-}CHBr_2 + Br^- \qquad (18)$$

$$H_3C^- + H_3CCl \longrightarrow H_4C + H_2CCl^- \qquad (7')$$

$$H_3C^- + H_3CBr \longrightarrow H_4C + H_2CBr^- \qquad (14')$$

are worth consideration.

The heats of these reactions calculated by the MNDO, AM1[7] and PM3[8] methods for the gas phase and for solvents with different polarities in the framework of the MNDO technique (point dipole model[9]) as well as the experimental data are presented in Table 1. It follows that the processes under consideration are approximately equivalent in their thermodynamics. However comparing the results obtained with the data of Ref. 2, one can conclude that reactions (3) and (10), for which formation of pre-reaction complexes is unfavorable, can not compete with the thermodynamically favorable processes (3′) and (10′), respectively, which proceed with no barriers. On the contrary, demanding no activation energy and contributing 91 and 98 kcal · mol^{-1} of heat the S_N2 reactions with the participation of the CH_3^- anion are more preferable than proton transfer processes (7′) and (14′).

It is somewhat more difficult to estimate the competitive abilities of reactions (5), (5′) and (12), (12′). So,

* On the possibility of polyhalomethanes reduction by a C—H bond see Ref. 5, 6.

Table 1. Heats (kcal · mol^{-1}) of the reactions of proton transfer

Hal	Reaction	Gas phase				Solvent[a]		
		Calculation			Experiment[b]	*1*	*2*	*3*
		MNDO	AM1	PM3				
Cl	3′	−24.1	−26.9	−23.5	−18	−23	−25	−32
	5′	−29.5	−30.7	−27.2	−22	−27	−27	−37
	7′	−29.7	−22.4	−28.3	−22	−24	−27	−25
Br	10′	−20.0	−24.0	−25.5	−15	−21	−22	−23
	12′	−24.4	−40.7	−27.5	−13[c]	−18	−25	−38
	14′	−29.3	−31.6	−35.4	−26	−32	−34	−36

[a] Reaction heats in solvents (*1*, slightly-polarity solvent; *2*, medium-polarity solvent; *3*, highly-polarity solvent) have been obtained taking into account the values of the solvation energies of anions (A^-)[2] calculated by the point dipole method[9] and the gas phase experimental heats of formation A^-.[10]

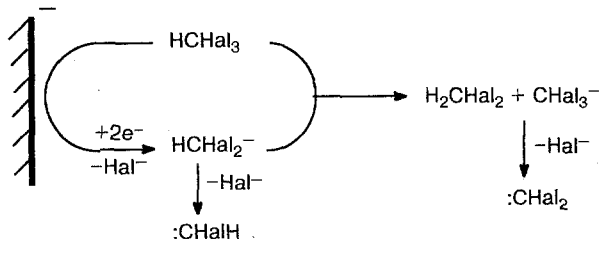
[b] Heats of formation of anions from Ref. 10.

[c] For calculation the corrected value of $\Delta H_f(CHBr_2^-)$ has been used.[1]

too small activation barriers (2.1 and 1.5 kcal · mol^{-1}) were calculated for processes (5′) and (12′). This does not allow a well-defined conclusion on the preference of one or another process pathway. In fact, this method is well-known (see Ref. 11, for example) to be usually incorrect at reproducing activation energies of reactions with proton transfer.

On the basis of the data given, one can conclude that in these cases, when in the reaction mixture the carbanions resulted in the electrochemical reduction of the respective halomethanes by C—Hal-bond are present, the reaction of proton transfer may be also competitive. Simultaneously, the carbanions more substituted by halogen atoms will be accumulated in the system that in turn has to promote α-elimination. The latter means that $HCHal_2^-$ anion, electrochemically generated from $HCHal_3$, can not serve as a source of monohalocarbene, through this fact does not seem to be evident. Scheme 1 clearly demonstrates that dihalocarbene is to be formed actually. This conclusion is indirectly confirmed by the fact, that the monohalocarbenes were obtained electrochemically so far.

Scheme 1



The results presented induce us to discuss the earlierly published data,[12] in accordance with those the formation of ethylene, 1,2-dichloroethane, and cyclopropane by the CH_2Cl_2 cathodic electrolysis is explained by the dimerization of intermediate methylene and also its introduction by the C=C- and C—H-bonds, respectively. On the basis of structures of the electrolysis products, authors[12] concluded that the electrochemical reduction of dichloromethane proceeds through the $:CH_2$ carbene formation. This conclusion seems to be ambogous. According to our calculations (see above and Ref. 2) a quite possible reaction of nucleophilic substitution (5) should be taken into account. This is especially right as $ClCH_2CH_2Cl$ formed in this reaction is reduced by approximatelly the same potentials like CH_2Cl_2 to give ethylene.

Thus, one can assume another mechanism for the formation of the products observed by authors[12] on the cathodic reduction of CH_2Cl_2 (Scheme 2).

Scheme 2

$$CH_2Cl_2 \xrightarrow{e^-} ClCH_2^{\cdot} + Cl^-$$

$$ClCH_2^{\cdot} \xrightarrow{e^-} ClCH_2^-$$

$$ClCH_2^- + CH_2Cl_2 \xrightarrow[-Cl^-]{} ClCH_2CH_2Cl \xrightarrow[-2Cl^-]{2e^-} CH_2{=}CH_2$$

$$CH_2{=}CH_2 + ClH_2C^- \xrightarrow[-Cl^-]{} \triangle$$

Unfortunately, there is in the literature only limited information about the regularities of electrochemical reduction of halosubstituted methanes. This circumstance does not allow us to pursue a more detailed discussion of this problem as compared to the quantum chemical data.

This work was partially supported by the International Science Foundation (Grant No. MHYOO).

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Received February 1, 1995