1666 *Russian Chemical Bulletin, Vol. 47, No. 9, September, 1998*

MNDO/PM3 study of the mechanism of a model reaction between methane and Br^+ cation

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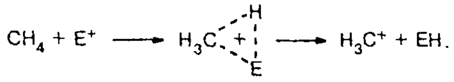
The structure of complexes formed in the $[CH_4+Br^+]$ system was simulated by the MNDO/PM3 method. Along with five local minima, a number of stationary points at which the Hessians have only one negative eigenvalue were found on the potential energy surface of this system. The results obtained were used for interpretation of the mechanisms of reactions occurring in the $[CH_4+Br^+]$ system.

Key words: superelectrophiles, methane, bromine; mechanism of electrophilic substitution; quantum-chemical calculations, MNDO/PM3 method.

Investigation of the nature of superelectrophiles and the mechanisms of their reactions with alkanes is one of the fundamental problems of organic chemistry. The classical mechanism of interaction between alkane and electrophilic reagents[1,2] includes the attack of electrophile (E^+) on the C—H bond with the formation of a three-center two-electron (3c-2e) intermediate or transition state according to the following scheme



This mechanism was convincingly proved for protolytic transformations of alkanes and in the case when the electrophile is a carbocation.

At the same time, it has been shown by *ab initio* quantum-chemical methods that reactions of methane[3] or ethane[4] with the nitrosonium cation NO^+ do not agree with this scheme. This cation attacks the carbon atom rather than the C—H bond to form a 3c-2e bond with H_2:

$$CH_4 + NO^+ \longrightarrow [CH_4 \cdot NO]^+ \longrightarrow$$
$$\longrightarrow [H_2C(H{-}H)NO]^+ \longrightarrow H_3C{-}NHO]^+.$$

However, a comparison[5] of methane reactions with various electrophilic agents confirmed the general character of the classical scheme suggested by Olah for electrophiles that are harder and stronger than NO^+. Thus, the mechanism of the reaction between electrophile and alkanes is dependent on the nature of cationic species.

In the last decade, new types of superelectrophilic complexes highly active in the reactions with alkanes have been found.[6—11] In a continuation of studies of the nature of active aprotic organic and inorganic superacids and mechanisms of their activating effect on alkanes,[12—14] in this work we analyze the potential energy surface (PES) of a system composed of a Br^+ cation and a methane molecule. We consider this investigation as the first step of studying the interaction of alkanes with superelectrophiles generated in $m\mathrm{Br}_2 \cdot n\mathrm{AlBr}_3$ systems.

Procedure for Calculations

The calculations were carried out by the MNDO/PM3 method[15] in the valence approximation with full optimization of geometric parameters using the MOPAC 5.10 and GAMESS [16] programs on a DEC 3000 AXP-400X workstation. The geometry of transition states was optimized by the Schlegel method.[17] Calculations of the potential curves were performed in the UHF approximation. The heats of formation (ΔH_f/kcal mol^{-1}) of certain species required for the determination of the energy effects of the reactions calculated by the MNDO/PM3 method are listed below.

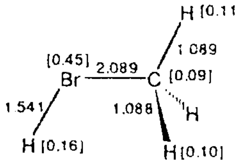
Species	$^3Br^+$	$^1Br^+$	H_2	HBr	CH_4	CH_3^+	$BrCH_2^+$
ΔH_f	284.6	300.7	−13.4	5.3	−13.0	256.6	259.1

Note that the calculated value of the energy of the singlet-triplet transition in the Br^+ cation (16.1 kcal mol^{-1})[18] differs substantially from the experimental value (32.6 kcal mol^{-1}).

Results and Discussion

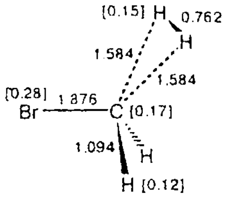
Local minima. Five local minima in the rather narrow energy interval from 235.6 to 248.0 kcal mol^{-1} were found on the potential energy surface (PES) of the $[CH_4+Br^+]$ system. The structures of intermediates corresponding to the minima are shown in Fig. 1. The major minimum corresponds to bromonium ion **1**, which

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 1715—1718, September, 1998.



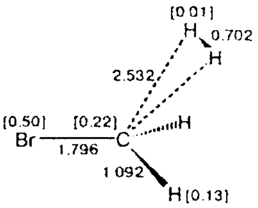
1 (C_s)

ΔH_f = 235.6 kcal mol^{-1}



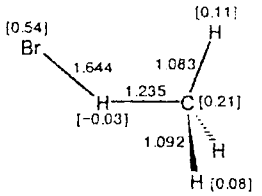
2 (C_s)

ΔH_f = 239.2 kcal mol^{-1}



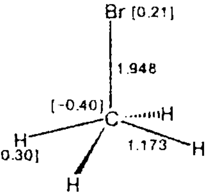
3 (C_s)

ΔH_f = 244.7 kcal mol^{-1}



4 (C_s)

ΔH_f = 242.8 kcal mol^{-1}



5 (C_{4v})

ΔH_f = 248.0 kcal mol^{-1}

Fig. 1. Structures of cationic complexes $BrCH_4^+$ corresponding to local minima on the PES. The bond lengths (in Å) are shown. Atomic charges (in au) are shown in brackets.

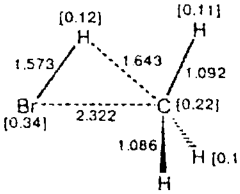
is the product of insertion of the Br^+ cation into the C—H bond. The lengths of the Br—C and Br—H bonds (2.09 Å and 1.54 Å, respectively) exceed the corresponding average values[19] by more than 0.1 Å. The major contribution to the positive charge of ion **1** comes from the Br atom (0.45 au).

The energy of complex **2** is higher (by 3.6 kcal mol^{-1}). In this complex, the three-center bond between the carbenium carbon atom of the $BrCH_2^+$ cation and the H_2 molecule is formed (the H...H distance is equal to 0.76 Å, while the distance from the C atom to the center of gravity of the H_2 fragment is equal to 1.54 Å). The positive charge is distributed over all atoms of the complex.

In addition to intermediate **2**, the loosely bound complex **3** with close structure was found, where the distance between two H atoms is equal to 0.70 Å. The H_2 fragment is rather distant from the C atom (2.53 Å), the positive charge is almost completely localized on the $BrCH_2$ group, and the energy of its bonding to the H_2 fragment is small (1 kcal mol^{-1}).

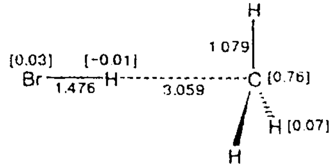
Two additional local minima correspond to the cations that can be considered as a result of an attack of the Br^+ ion on the CH_4 molecule in two alternative directions, namely, cation **4** formed upon the attack of Br^+ on the H atom and pyramidal carbonium ion **5** with C_{4v} symmetry formed upon the attack of Br^+ on the C atom; the latter is energetically less favorable by 5.2 kcal mol^{-1}. The 3c-2e Br—H—C bond with bridging hydrogen atom is formed in cation **4**. This cation is formed barrierlessly from isolated Br^+ and CH_4 species. The Br...H distance is equal to 1.64 Å, which is 0.2 Å longer than the length of the H—Br bond; the C...H distance is also increased. Most of the positive charge (0.54 au) remains on the bromine atom. On the contrary, considerable transfer of the positive charge from Br^+ to H atoms occurs in cation **5**, whereas a large negative charge is localized on the C atom. All bonds in cation **5** are lengthened as compared to the conventional ones.

Transition states. In addition to the local minima mentioned above (structures **1**—**5**), a number of critical points at which the Hessians have one negative eigenvalue were found on the PES of the $[CH_4+Br^+]$ system. The structures of the corresponding transition states between local minima **k** and **l** (TS(**k** ↔ **l**)) are shown in Fig. 2.



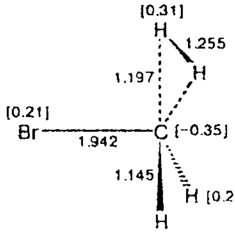
6 (C_s), TS(**1** ↔ **4**)

ΔH_f = 246.8 kcal mol^{-1}



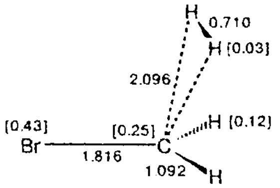
7 (C_{3v}), TS(**4** ↔ HBr + CH_3^+)

ΔH_f = 266.0 kcal mol^{-1}



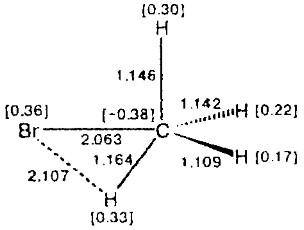
8 (C_s), TS(**2** ↔ **5**)

ΔH_f = 249.7 kcal mol^{-1}



9 (C_s), TS(**2** ↔ **3**)

ΔH_f = 245.8 kcal mol^{-1}



10 (C_1), TS(**4** ↔ **5**)

ΔH_f = 252.4 kcal mol^{-1}

Fig. 2. Transition states in the $[Br^++CH_4]$ system. The bond lengths (in Å) are shown. Atomic charges (in au) are shown in brackets.

Structure **6** can be considered as a transition state for the transformation of complex **4** into bromonium cation **1**. The energy of transition state **7** of the reaction of HBr abstraction from complex **4** with the formation of methyl cation is considerably higher (by about 20 kcal mol^{-1}). The C...H distance in structure **7** is equal to 3.06 Å and the H—Br bond lengths in structure **7** and in HBr molecule are close. The CH_3 fragment has a pronounced carbocationic character, since its total positive charge is equal to 0.97 au.

Transition state **8** for transformation **2** → **5** has also been found. Though structure **8** is analogous to system **2**, its geometric parameters are different: the distance between the hydrogen atoms of the H_2 fragment is increased to 1.25 Å, whereas the distance between these H atoms and the C atom is shortened to 1.20 Å.

A critical point on the PES, at which the Hessian has two negative eigenvalues, corresponds to structure **9**. However, this structure can be considered as a transition state of the reaction **2** → **3**, since a local maximum on the potential curve along the reaction coordinate (R_c) corresponds to structure **9** (the distance from the C atom to the center of gravity of the H_2 fragment was taken as the reaction coordinate). The C...$H(H_2)$ distance at this point (2.10 Å) is intermediate between analogous values for compounds **2** and **3** (1.58 Å and 2.53 Å, respectively). The bond length in the H—H quasi-molecule also appeared to be intermediate between the H...H distances in systems **2** and **3** (0.76 Å and 0.70 Å, respectively).

Structure **10** corresponds to the transition state of transformation **4** → **5**. In this structure, the Br...H and Br...C distances and charges q_{Br} and q_C are intermediate between those obtained for cations **4** and **5**.

Possible reaction channels in the $[CH_4+Br^+]$ system. The results of our calculations make it possible to describe several reactions that can occur in this system. Thus, the abstraction of the hydride ion from methane can be described by the following overall equation

$$CH_4 + Br^+ \longrightarrow CH_3^+ + HBr + 9.7 \text{ kcal mol}^{-1}. \qquad (1)$$

This exothermic reaction can occur *via* two channels, the first of which involves the stage of barrierless addition of Br^+ to the H atom of methane with the formation of cation **4**:

$$Br^+ + CH_4 \longrightarrow \underset{\mathbf{4}}{BrHCH_3^+} \xrightarrow{7} CH_3^+ + HBr.$$

The abstraction of the HBr molecule from cation **4** occurs through transition state **7** with a potential barrier of 23.2 kcal mol^{-1} (Fig. 3).

The second (less favorable) channel is due to the possibility of transforming cation **4** into bromonium cation **1** through transition state **6**:

$$Br^+ + CH_4 \longrightarrow \underset{\mathbf{4}}{BrHCH_3^+} \xrightarrow{6} \underset{\mathbf{1}}{HBrCH_3^+} \xrightarrow{7}$$
$$\longrightarrow CH_3^+ + HBr.$$

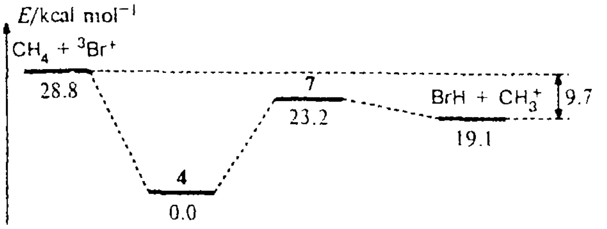


Fig. 3. The energy diagram of the most favorable channel of the reaction $CH_4 + Br^+ \rightarrow CH_3^+ + HBr$. Relative energies (in kcal mol^{-1}) are shown.

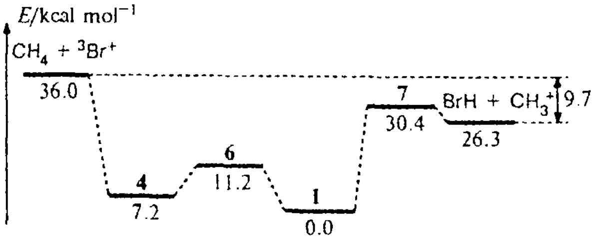


Fig. 4. The energy diagram of the second channel of the reaction $CH_4 + Br^+ \rightarrow CH_3^+ + HBr$. Relative energies (in kcal mol^{-1}) are shown.

In fact, the potential barrier of this reaction is small (only 4 kcal mol^{-1}). The abstraction of the HBr molecule from bromonium cation **1** also occurs through transition state **7**; however, the potential barrier is equal to 30.4 kcal mol^{-1} (Fig. 4).

Consider now the abstraction of a hydrogen molecule with the formation of the CH_2Br^+ cation as an example of much more favorable process:

$$CH_4 + Br^+ \longrightarrow CH_2Br^+ + H_2 + 25.9 \text{ kcal mol}^{-1}. \qquad (2)$$

The barrierlessly formed complex **4** can be transformed into the pyramidal cation **5** through transition state **10**. Let us take the distance from the C atom to the center of gravity of any two H atoms in structure **5** as the reaction coordinate R_c assuming that the corresponding line is perpendicular to the line connecting these atoms. An analysis of the potential curve calculated taking into account these restrictions in the interval $0.8 \text{ Å} \le R_c \le 1.9$ Å showed that there are a maximum at $R_c = 1.0$ Å and a minimum at $R_c = 1.537$ Å. The minimum corresponds to structure **2** discussed above and found with full optimization of geometric parameters. Transition state **8** between complexes **5** and **2** was found in the vicinity of the maximum when minimizing the norm of the gradient. Further passage from structure **2** to a system of noninteracting fragments $BrCH_2^+$ and H_2 requires only 6.5 kcal mol^{-1}. This transformation can occur through transition state **9** and local minimum **3**.

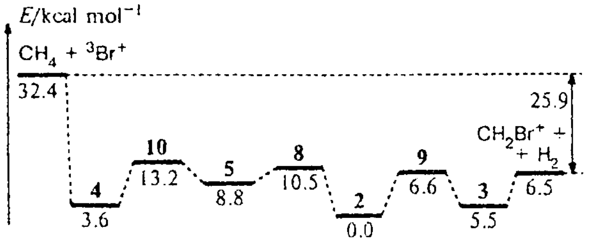


Fig. 5. The energy diagram of the channel of the reaction $CH_4 + Br^+ \rightarrow BrCH_2^+ + H_2$. Relative energies (in kcal mol^{-1}) are shown.

The scheme of this multistage reaction can be depicted as follows:

$$Br^+ + CH_4 \longrightarrow \underset{\mathbf{4}}{BrHCH_3^+} \xrightarrow{\mathbf{10}} \underset{\mathbf{5}}{BrCH_4^+} \xrightarrow{\mathbf{8}}$$

$$\longrightarrow \underset{\mathbf{2}}{H_2C(H{-}H)Br^+} \xrightarrow{\mathbf{9}} \underset{\mathbf{3}}{H_2C(H_2)Br^+} \longrightarrow$$

$$\longrightarrow BrCH_2^+ + H_2.$$

Its energy diagram is shown in Fig. 5.

As was expected for the gas phase, no reactions of electrophilic substitution of hydrogen by the Br^+ cation occur:

$$Br^+ + CH_4 \not\longrightarrow BrCH_3 + H^+.$$

Calculations of the potential curve along the R_c = C...H variable taken as the reaction coordinate showed that the abstraction of hydrogen atom from cations **5** and **2** (the H...H distances of 1.57 Å and 1.86 Å, respectively) results in elimination of the H_2 molecule, while the abstraction of the hydrogen atom bonded to the bromine atom from complex **4** results in elimination of the HBr molecule.

In conclusion we note that cations **1**—**4** and transition states **6**, **8**, and **9** can be considered as analogs of certain structures in the $[CH_4+NO^+]$ system found by the *ab initio* MO LCAO method using different basis sets taking into account correlation corrections.[3]

This work was financially supported by the Russian Foundation for Basic Research (Project Nos. 96-03-33255a and 98-03-32274a) and Civil Research and Development Fund of the USA (CRDF, Grant RC1-274;506).

References

1. G. A. Olah, G. K. S. Prakash, R. E. Williams, L. D. Field, and K. Wade, *Hypercarbon Chemistry*, Wiley-Interscience Publ.—J. Wiley and Sons, New York, 1987, Ch. 5.
2. G. A. Olah, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1393.
3. P. R. Schreiner, P. v. R. Schleyer, and H. F. Schafer, III, *J. Am. Chem. Soc.*, 1993, **115**, 9659.
4. P. R. Schreiner, P. v. R. Schleyer, and H. F. Schafer, III, *J. Am. Chem. Soc.*, 1995, **117**, 453.
5. G. A. Olah, N. Hartz, G. Rasul, and G. K. S. Prakash, *J. Am. Chem. Soc.*, 1995, **117**, 1336.
6. I. S. Akhrem, A. V. Orlinkov, E. I. Mysov, and M. E. Vol'pin, *Tetrahedron Lett.*, 1981, **22**, 3891.
7. M. Vol'pin, I. Akhrem, and A. Orlinkov, *New J. Chem.*, 1989, **13**, 771.
8. I. S. Akhrem, A. V. Orlinkov, and M. E. Vol'pin, *Usp. Khim.*, 1996, **65**, 920 [*Russ. Chem. Rev.*, 1996, **65**, 849 (Engl. Transl.)].
9. I. Akhrem, A. Orlinkov, and M. Vol'pin, *J. Chem. Soc., Chem. Commun.*, 1993, 67.
10. I. Akhrem, L. Afanas'eva, A. Orlinkov, and M. Vol'pin, *Mendeleev Commun.*, 1994, 131.
11. I. Akhrem, S. Gudima, and M. Vol'pin, *Chem. Eur. J.*, 1996, **2**, 812.
12. A. L. Chistyakov, I. V. Stankevich, I. A. Akhrem, N. P. Gambaryan, and M. E. Vol'pin, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 554 [*Russ. Chem. Bull.*, 1996, **45**, 514 (Engl. Transl.)].
13. A. L. Chistyakov, I. V. Stankevich, I. S. Akhrem, N. P. Gambaryan, and M. E. Vol'pin, *Mendeleev Commun.*, 1996, 175.
14. I. S. Akhrem, A. L. Chistyakov, N. P. Gambaryan, I. V. Stankevich, and M. E. Vol'pin, *J. Organomet. Chem.*, 1997, 489.
15. J. J. P. Stewart, *J. Comp. Chem.*, 1989, **10**, 209.
16. M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis, and J. A. Montgomery, *J. Comp. Chem.*, 1993, **14**, 1347.
17. H. B. Schlegel, *J. Comp. Chem.*, 1982, **3**, 214.
18. C. E. Moore, *Atomic Energy Levels*, National Bureau of Standarts of U.S., 1952, **II** 161.
19. J. E. Huheey, *Inorganic Chemistry. Principles of Structure and Reactivity*, 3rd Ed., Harper and Row Publisher, New York, 1983.

Received March 23, 1998