# Mechanisms of the reactions of propane with $CBr_3^+$ cation and superelectrophilic complex $CBr_4^+ \cdot AlBr_3^-$ containing a bromine-centered cationic center: a theoretical study*

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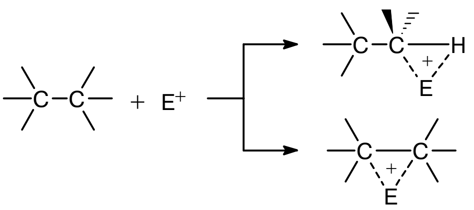
Fragments of the potential energy surfaces (PES) of the systems $[C_3H_8 + CBr_3^+]$ and $[C_3H_8 + Br_2CBr^+ \cdot Br_2AlBr_2^-]$ were simulated by the MNDO/PM3 method. Energy minima corresponding to weakly bound adducts of propane molecule with the $CBr_3^+$ cation or neutral complex $CBr_3^+ \cdot AlBr_4^-$ were found on the PES's of both systems. These are adducts with the coordination of a H atom of the methylene group of the propane molecule to the electrophile at the Br atom carrying the largest positive charge. As the fragments of the adducts are brought close together, the coordinated H atom migrates to the C atom of the $CBr_3^+$ fragment. The potential barriers of these migrations were found to be low for both systems. The reactions proceed without formation of cyclic intermediates or transition states typical of the Olah mechanism.

**Key words:** bromine, propane, aluminum bromide, complexes, superelectrophiles, mechanism of electrophilic activation of alkanes, quantum-chemical calculations, MNDO/PM3 method, potential energy surface.

In the last four decades, the mechanisms of electrophilic activation of alkanes have been the subject of thorough investigations.[1—3] The classical Olah mechanism (Scheme 1) involves the formation of cyclic three-center, two-electron (3c-2e) intermediates or transition states.

**Scheme 1**



Another mechanism (Scheme 2) proposed recently[4,5] for hypothetical nitrosation reactions of methane or ethane implies the formation of intermediates or transition states containing a $H_2$ quasi-molecule:

**Scheme 2**

$$CH_4 + E^+ \longrightarrow H_2C(H—H)E^+$$

Recent investigations in the chemistry of alkanes led to the discovery of active organic and inorganic superelectrophilic systems (see reviews[6—8]). Our theoretical studies[9—14] on the structure of possible active complexes in these systems and the mechanisms of their activating effect on alkanes revealed the formation of species which can be considered superelectrophiles that play the key role in the activation of alkanes. In the systems comprising aluminum halides and halogens,[11,13] these are mainly complexes with bidentate coordination of the $AlBr_4^-$ anion to the halogen atom carrying a large positive charge, while in the systems comprising aluminum halides and polyhalomethanes[9,10] these are polyhalomethyl cations constituting neutral complexes. Strictly speaking, these species as well as free cations cannot be considered as carbenium ions since the carbon atoms in the species are uncharged or even carry appreciable negative charges while the halogen atoms carry large positive charges (see Refs. 15—19 devoted to the structure of polyhalomethyl cations).

We began our investigations on the mechanisms of the reactions between alkanes and superelectrophiles found in the systems comprising aluminum halides and halogens with (i) calculations for the $Br^+ + CH_4$ model system[12] and (ii) consideration of the interaction of methane molecule with neutral electrophiles formed in the $AlBr_5$ system.[13,14] It was found that the addition of such a strong superelectrophile as "naked" $Br^+$ cation to a H atom of methane molecule proceeds barrierlessly and results in such a strong activation of the correspond-

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ing C—H bond that the $Br^+$ cation abstracts a hydride ion from the methane molecule when moving away from the latter (Scheme 3).

### Scheme 3

$$CH_4 + Br^+ \longrightarrow H_3CHBr^+ \longrightarrow H_3C^+ + HBr$$

It should be emphasized that transformation of $H_3CHBr^+$ into a methyl cation and HBr proceeds without formation of intermediates or transition states similar to those presented in Schemes 1 and 2.

On the other hand, despite the rather large positive charge of the attacking Br atom, activation of a C—H bond of the methane molecule upon barrierless addition of different isomers of neutral electrophile $AlBr_5$ to a H atom of methane is insufficient for a mechanism similar to that shown in Scheme 3 to be realized. Further transformations of the $H_3C—H \cdot BrAlBr_4$ complexes occur involving either the Olah transition states (see Scheme 1) or the formation of species containing the $H_2$ quasi-molecule (see Scheme 2). The potential barriers to these transformations were found to be rather high.

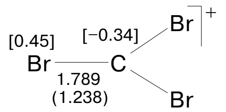
Embarking on an investigation of the interaction between alkanes and electrophiles formed from polyhalomethanes, in this work we studied the activation mechanism of C—H bonds at the secondary C atom of the propane molecule by two superelectrophiles, namely, a free $CBr_3^+$ cation and a neutral ionic complex $Br_2CBr^+ \cdot Br_2AlBr_2^-$. In the latter, the Br(1) atom coordinated to the $AlBr_4^-$ anion in a bidentate fashion carries a very large positive charge. We performed MNDO/PM3 simulations of those fragments of the potential energy surfaces (PES) of the $[C_3H_8 + CBr_3^+]$ (**I**) and $[C_3H_8 + Br_2CBr^+ \cdot Br_2AlBr_2^-]$ (**II**) systems, which were the most interesting for our purposes.

## Calculation Procedure

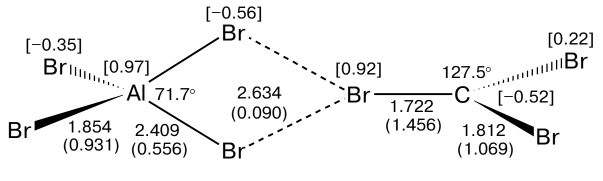
The PES fragments of systems **I** and **II** were studied by the UHF MNDO/PM3 method[20] using the GAMESS (US) program package[21] on a DEC 3000 AXP-400X workstation and the PC GAMESS program package[22] on a PC with a PENTIUM® III CPU. Different reaction coordinates were scanned. The geometries of transition states were optimized by the Schlegel method.[23] The characters of stationary points were refined by calculating the eigenvectors of the Hessian. Correspondence between particular local minima and each transition states was established in the intrinsic reaction coordinate (IRC) mode.

## Results and Discussion

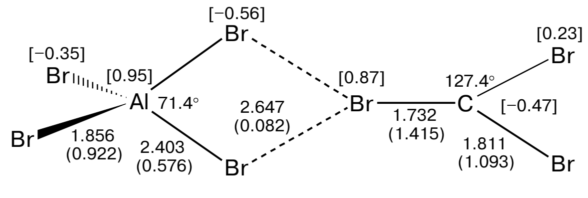
The geometries of the $CBr_3^+$ cation (**1**), the two isomers of the complex $Br_2CBr^+ \cdot Br_2AlBr_2^-$ (**2a**, **2b**), and the $C_3H_8$ molecule (**3**), as well as the corresponding heats of formation ($\Delta H_f$) and the effective atomic charges, are presented in Fig. 1. In rotamers **2a** and **2b**, the angles of rotation of the $CBr_3$ fragment with respect to the C—Br(1) bond differ by 90° and the Br(1) atoms have very large positive charges (0.92 (**2a**) and 0.87 (**2b**) au).



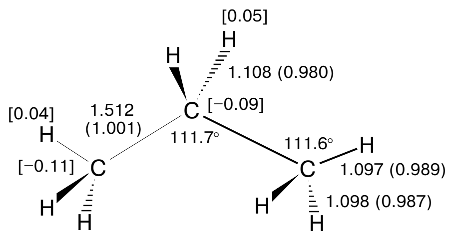
**1**, $D_{3h}$, $\Delta H_f$ = 272.1 kcal $mol^{-1}$



**2a**, $C_{2v}$, $\Delta H_f$ = −66.4 kcal $mol^{-1}$



**2b**, $C_{2v}$, $\Delta H_f$ = −62.5 kcal $mol^{-1}$



**3**, $C_{2v}$, $\Delta H_f$ = −23.6 kcal $mol^{-1}$

**Fig. 1.** The structures of initial systems corresponding to local minima of the total energy. The bond lengths (Å), bond orders (in au, figures in parentheses), and effective atomic charges according to Coulson (in au, figures in brackets) are shown.

The interaction between the propane molecule and electrophiles was simulated by bringing the reagents close together along three reaction coordinates:

$$R_c' = C(1)...H(1),\ R_c'' = C(1)...C(2) \text{ and } R_c''' = Br(1)...C(2)$$

(in each pair, the former atom belongs to the electrophile while the latter atom belongs to the propane molecule, Fig. 2). The interaction patterns were found to be of the same type, except for insignificant details. Therefore, hereafter we will use mainly the results obtained for the reaction coordinate $R'_c$ = C(1)...H(1).

**Interaction of propane with the $CBr_3^+$ cation.** Initial distances between the reagents were chosen to be rather long. By varying the initial arrangement of the $CBr_3^+$ cation relative to the propane molecule and using different reaction coordinates we found a number of local minima with very close energies. These minima are separated by low potential barriers and correspond to very weak adducts which are in essence the $CBr_3^+$ cations "solvated" by propane. The "solvates" differ from one another in mutual arrangement of the cation and propane molecule and in propane conformations. Electrostatic interaction between the positively charged Br(1) atom of the $CBr_3^+$ cation and the negatively charged C atoms of the propane molecule makes the major contribution to the rather low (~3 kcal $mol^{-1}$) "solvation" energy. In some of the adducts found the Br(1) atom of the $CBr_3^+$ cation was simultaneously "solvated" by the methylene group and both methyl groups of the propane molecule. In other adducts only one methyl group and the methylene group of propane were involved in the "solvation" of the Br(1) atom.*

The slight increase in energy due to repulsion of the fragments in "solvates" caused by bringing them close changes to a sharp decrease (by ~40 kcal $mol^{-1}$), which corresponds to transformation of the "solvates" into much more energetically favorable adducts of tribromomethane with the isopropyl cation (reaction (1)).

$$H_7C_3{-}H + CBr_3^+ \longrightarrow HCBr_3 \cdot C_3H_7^+ \qquad (1)$$

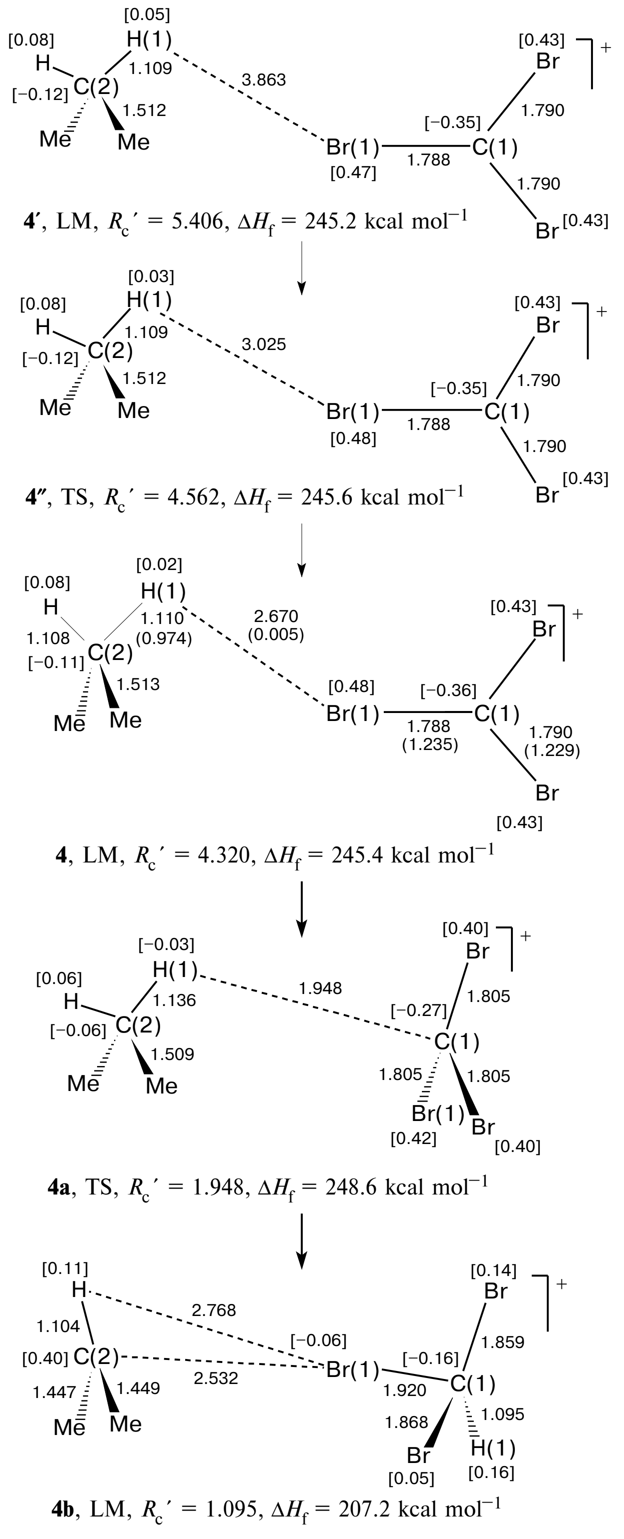
The course of this reaction is illustrated in Fig. 2 by the sequence of structures **4′** → **4″** → **4** → **4a** → **4b** corresponding to local minima (LM) and transition states (TS) found when moving along the reaction coordinate $R'_c$ = C(1)...H(1). The "solvation" energy of tribromomethane in **4b** is 7.6 kcal $mol^{-1}$. The major contribution to this value comes from the interaction between the Br(1) atom of tribromomethane carrying a small negative charge and the C atom which is the cationic center of the isopropyl cation.

Tracing the motion of the fragments of adduct **4** along the reaction coordinate $R'_c$ = C(1)...C(2) showed that, as the fragments approach each other, reductive alkylation of propane by $CBr_3^+$ cation (reaction (2)) proceeds along with reaction (1).

$$H_7C_3{-}H + CBr_3^+ \longrightarrow (CH_3)_2CHCHBr_2 \cdot Br^+ \qquad (2)$$

After overcoming a rather high barrier of 10.2 kcal $mol^{-1}$ (TS **5a**) this reaction results in complex **5b** of the $Br^+$ cation coordinated by two geminal Br atoms of dibromoisobutane in a bidentate fashion (Fig. 3).

As can be seen in Figs. 2 and 3, none of the reactions between propane and $CBr_3^+$ cation proceed with the



**4′**, LM, $R_c'$ = 5.406, $\Delta H_f$ = 245.2 kcal $mol^{-1}$

**4″**, TS, $R_c'$ = 4.562, $\Delta H_f$ = 245.6 kcal $mol^{-1}$

**4**, LM, $R_c'$ = 4.320, $\Delta H_f$ = 245.4 kcal $mol^{-1}$

**4a**, TS, $R_c'$ = 1.948, $\Delta H_f$ = 248.6 kcal $mol^{-1}$

**4b**, LM, $R_c'$ = 1.095, $\Delta H_f$ = 207.2 kcal $mol^{-1}$

**Fig. 2.** Abstraction of hydride ion from propane molecule in system **I** along the reaction coordinate $R'_c$ = C(1)...H(1) (LM denotes the local minimum and TS denotes the transition state). The bond lengths (Å), bond orders[24] (in au, figures in parentheses) and effective atomic charges according to Coulson (in au, figures in brackets).

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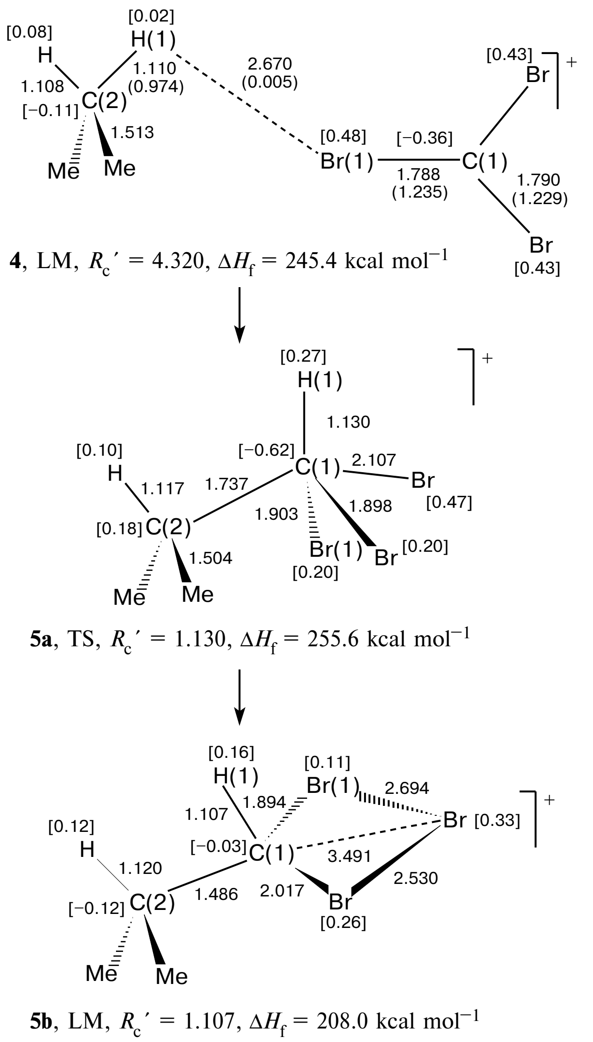
* In all structures, the methylene group is involved in "solvation"; this seems to be due to the choice of the initial arrangement of the reagents.



**4**, LM, $R_c' = 4.320$, $\Delta H_f = 245.4$ kcal mol$^{-1}$

**5a**, TS, $R_c' = 1.130$, $\Delta H_f = 255.6$ kcal mol$^{-1}$

**5b**, LM, $R_c' = 1.107$, $\Delta H_f = 208.0$ kcal mol$^{-1}$

**Fig. 3.** Reductive alkylation of propane by $CBr_3^+$ cation (reaction (2)) along the reaction coordinate $R'_c$ = C(1)...C(2)). For notations, see Fig. 2.

formation of cyclic intermediates or transition states similar to those proposed by Olah (see Scheme 1).

The energy diagrams of the reactions (1) and (2) are shown in Fig. 4, *a*.

**Interaction of propane with complex $Br_2CBr^+ \cdot Br_2AlBr_2^-$.** The structure of the adduct of propane with the neutral bromine-centered superelectrophile $Br_2CBr^+ \cdot Br_2AlBr_2^-$(**6**) is shown in Fig. 5. The energy of "solvation" of the electrophile by propane in adduct **6** is of course lower than in adduct **4** (1.4 and 3.1 kcal mol$^{-1}$, respectively). The fragments in adduct **6** approach each other more difficultly than in adduct **4**; however, after overcoming a barrier of 10.1 kcal mol$^{-1}$ corresponding to TS **6a** the energy also decreases substantially (by 39.5 kcal mol$^{-1}$) and complex **6b** is formed (see Fig. 5). In TS **6a**, the H atom of propane previously coordinated to the cationic center (the Br(1) atom of superelectrophile $Br_2CBr^+ \cdot Br_2AlBr_2^-$) appears to be coordinated to the C atom of the superelectrophile. In complex **6b**, the newly formed tribromomethane interacts (the interaction energy is 19 kcal mol$^{-1}$) with the isopropyl cation and $AlBr_4^-$ anion bound electrostatically (the interaction energy is 82.7 kcal mol$^{-1}$). Here, the interaction between the C atom (the cationic center of the isopropyl cation) and the Br atom of the $AlBr_4^-$ anion carrying the largest negative charge (reaction (3)) makes the major contribution. Multiple contributions also come from H atoms of the isopropyl cation.

$$H_7C_3{-}H + Br_2CBr^+ \cdot Br_2AlBr_2^- \longrightarrow [(CH_3)_2CH^+ \cdot AlBr_4^-] \cdot Br_2CHBr \qquad (3)$$

When moving along the reaction coordinate $R'_c$ = C(1)...H(1), one TS and two LM corresponding to reaction (3) were found. Their structures are shown in Fig. 5 and the energy diagram of reaction (3) is presented in Fig. 4, *b*.

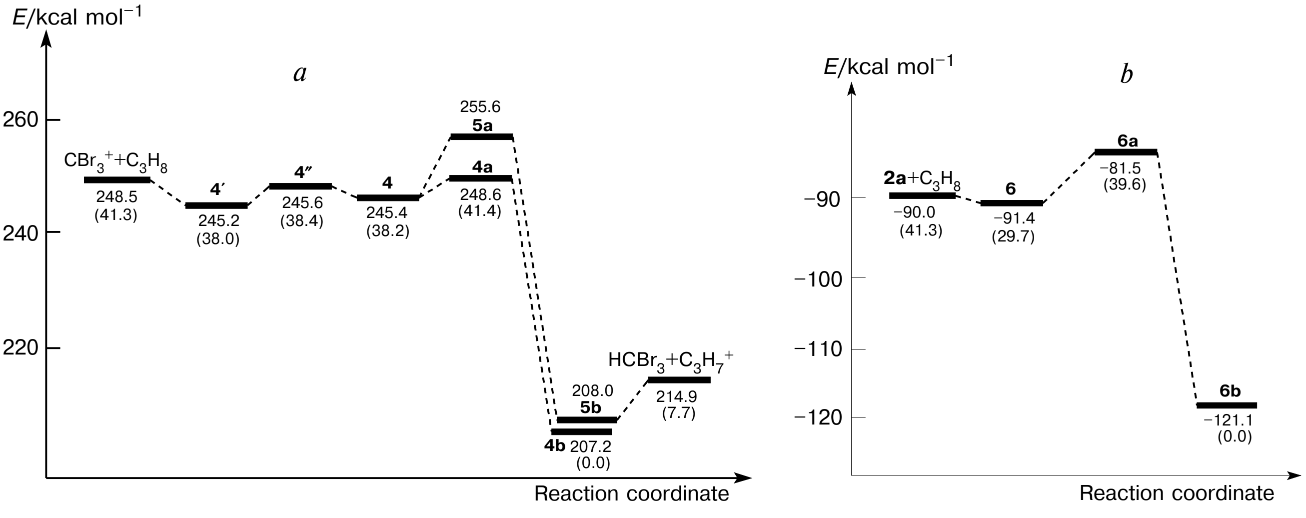
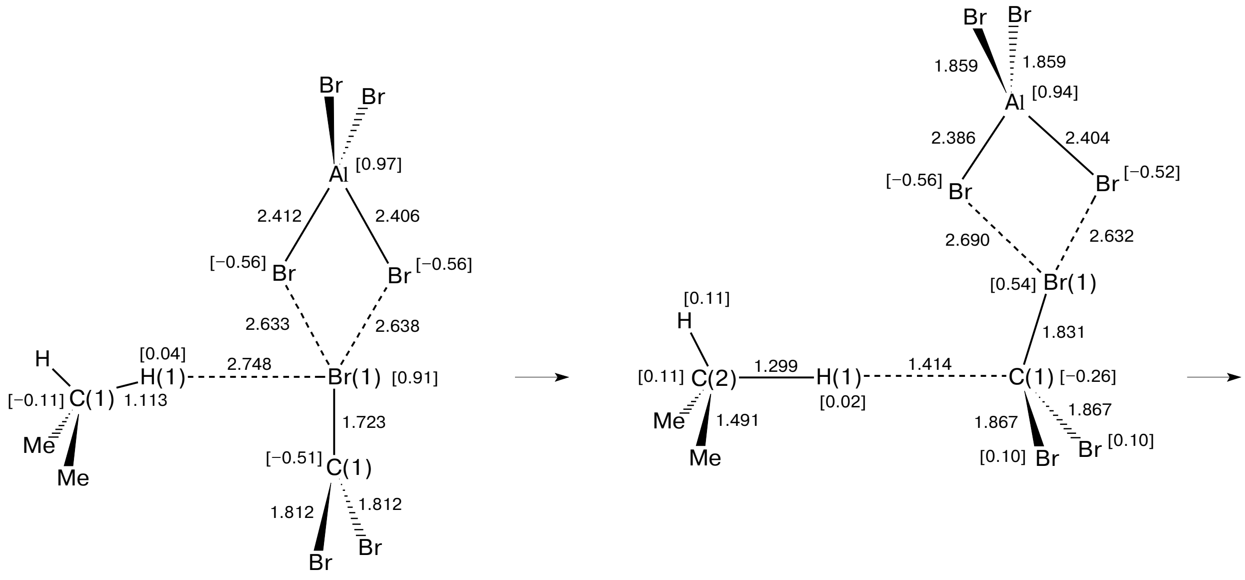
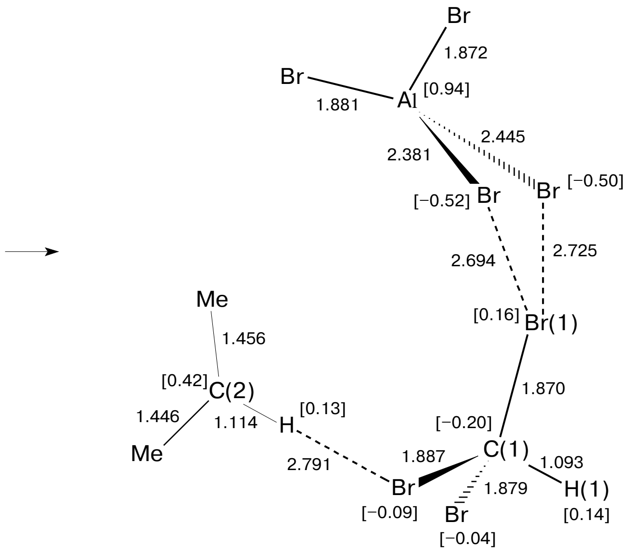


**Fig. 4.** Energy diagrams of reactions (1) and 2 (*a*), and 3 (*b*).



**6**, LM, $R_c' = 3.413$ Å, $\Delta H_f = -91.4$ kcal mol$^{-1}$

**6a**, TS, $R_c' = 4.414$ Å, $\Delta H_f = -81.5$ kcal mol$^{-1}$



**6b**, LM, $R_c' = 1.093$ Å, $\Delta H_f = -121.1$ kcal mol$^{-1}$

**Fig. 5.** Abstraction of hydride ion from propane molecule in system **II** along the reaction coordinate $R'_c$ = C(1)...H(1). For notations, see Fig. 2.

Transition state **6a** is similar to that of the propane reaction with $CBr_3^+$ cation. Thus, the bond between H atom and the secondary C atom of propane molecule can also be cleaved with ease under the action of a neutral superelectrophile $Br_2CBr^+ \cdot Br_2AlBr_2^-$. By and large, our calculations showed that the mechanism of hydrogen abstraction from the secondary C atom of propane remains unchanged upon replacement of the attacking cation by polar neutral electrophile. In both cases, migration of a H atom from the secondary carbon atom of propane molecule to the C atom of the superelectrophile occurs without formation of cyclic (3c-2e)-transition state or intermediate.

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## References

1. G. A. Olah, G. K. S. Prakash, and J. Sommer, *Superacids*, Wiley-Interscience, New York, 1985.

2. G. A. Olah, G. K. S. Prakash, R. E. Williams, L. D. Field, and K. Wade, *Hypercarbon Chemistry*, Wiley-Interscience, New York, 1987, Ch. 5.
3. G. A. Olah, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1393.
4. P. R. Schreiner, P. v. R. Schleyer, and H. F. Schaefer, III, *J. Am. Chem. Soc.*, 1993, **115**, 9659.
5. P. R. Schreiner, P. v. R. Schleyer, and H. F. Schaefer, III, *J. Am. Chem. Soc.*, 1995, **117**, 453.
6. M. Vol´pin, I. Akhrem, and A. Orlinkov, *New J. Chem.*, 1989, **13**, 771.
7. I. S. Akhrem, A. V. Orlinkov, and M. E. Vol´pin, *Usp. Khim.*, 1996, **65**, 920 [*Russ. Chem. Rev.*, 1996, **65**, 849 (Engl. Transl.)].
8. I. S. Akhrem and A. V. Orlinkov, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 771 [*Russ. Chem. Bull.*, 1998, **47**, 740 (Engl. Transl.)].
9. A. L. Chistyakov, I. B. Stankevich, I. S. Akhrem, N. P. Gambaryan, and M. E. Vol´pin, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 554 [*Russ. Chem. Bull.*, 1996, **45**, 514 (Engl. Transl.)].
10. I. S. Akhrem, A. L. Chistyakov, N. P. Gambaryan, I. V. Stankevich, and M. E. Vol´pin, *J. Organomet. Chem.*, 1997, 489.
11. A. L. Chistyakov, I. V. Stankevich, I. S. Akhrem, N. P. Gambaryan, and M. E. Vol´pin, *Mendeleev Commun.*, 1996, 175.
12. A. L. Chistyakov, I. V. Ctankevich, N. P. Gambaryan, and I. S. Akhrem, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 1715 [*Russ. Chem. Bull.*, 1998, **47**, 1666 (Engl. Transl.)].
13. A. L. Chistyakov, I. B. Stankevich, N. P. Gambaryan, and I. S. Akhrem, *Izv. Akad. Nauk, Ser. Khim.*, 2000, 802 [*Russ. Chem. Bull., Int. Ed.*, 2000, **49**, 799].
14. A. L. Chistyakov, I. B. Stankevich, N. P. Gambaryan, and I. C. Akhrem, *Tez. dokl. VII Vseros. konf. po metalloorg. khim. "Gorizonty organicheskoi i elementoorgnicheskoi khimii"* [*Abstrs. VIIth All-Russian Conf. on Metalloorg. Chem. "Horizons of Organic and Organoelement Chemistry"*], *Moscow, Sept. 6-11, 1999*, INEOS RAS, Moscow, 1999, **2**, p. 222 (in Russian).
15. G. A. Olah, L. Heiliger, and G. K. S. Prakash, *J. Am. Chem. Soc.*, 1989, **111**, 8020.
16. H. Vancik, C. Percas, and D.E. Sunko, *J. Am. Chem. Soc.*, 1990, **112**, 7418.
17. G. A. Olah, G. Rasul, A. K. Yudin, A. Burrichter, G. K. S. Prakash, A. L. Chistyakov, I. V. Stankevich, I. S. Akhrem, N. P. Gambaryan, and M. E. Vol´pin, *J. Am. Chem. Soc.*, 1996, **118**, 1446.
18. G. A. Olah, G. Rasul, L. Heiliger, and G. K. S. Prakash, *J. Am. Chem. Soc.*, 1996, **118**, 3580.
19. G. Franking, S. Fau, C. M. Marchand, and H. Grutzmacher, *J. Am. Chem. Soc.*, 1997, **119**, 6648.
20. J. J. P. Stewart, *J. Comput. Chem.*, 1989, **10**, 209, 221.
21. 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. Comput. Chem.*, 1993, **14**, 1347.
22. A. A. Granovsky, http://www.classic.chem.msu/gran/games/index.html.
23. H. B. Schlegel, *J. Comput. Chem.*, 1982, **3**, 214.
24. K. B. Wiberg, *Tetrahedron*, 1968, **24**, 1083.

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