

Density Functional Study on the Bromination of Heteroelement-Substituted Acetylenes

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Abstract—The reactions of heteroelement-containing alkynes $\text{H}_3\text{SiC}\equiv\text{CH}$ and $\text{R}_3\text{MC}\equiv\text{CPh}$ [$\text{R}_3\text{M} = \text{H}_3\text{Si}$, Et_3Si , Et_3Ge , $(\text{MeO})_3\text{Si}$, $(\text{EtO})_3\text{Ge}$, $\text{N}(\text{CH}_2\text{CH}_2\text{O})_3\text{Si}$, $\text{N}(\text{CH}_2\text{CH}_2\text{O})_3\text{Ge}$, Bu_3Sn] with one and two bromine molecules were studied in terms of the density functional theory. Transition states along reaction channels leading to products of both addition at the triple bond (*cis*- and *trans*-dibromoalkenes and 1,1-dibromoalkenes) and cleavage of the $\text{M}-\text{C}\equiv$ bond were localized.

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Development of quantum chemistry methods provided the possibility of using computational technics for studying mechanisms of organic reactions. Analysis of papers published in 2005 in one of the leading organic chemistry journals, *Journal of Organic Chemistry*, showed that ~10% of the reported studies involve quantum-chemical calculations to greater or lesser extent. Quantum-chemical calculations make it possible to evaluate the possibility of each organic reaction to occur, find possible reaction paths, and (in some cases) predict the product ratio depending on the substrate nature. However, it is surprising that quantum-chemical studies on halogen addition to compounds possessing multiple bonds, specifically to alkynes, have not received due attention though such reactions have long been known and are widely used for the preparation of important intermediate products for organic synthesis [1–14].

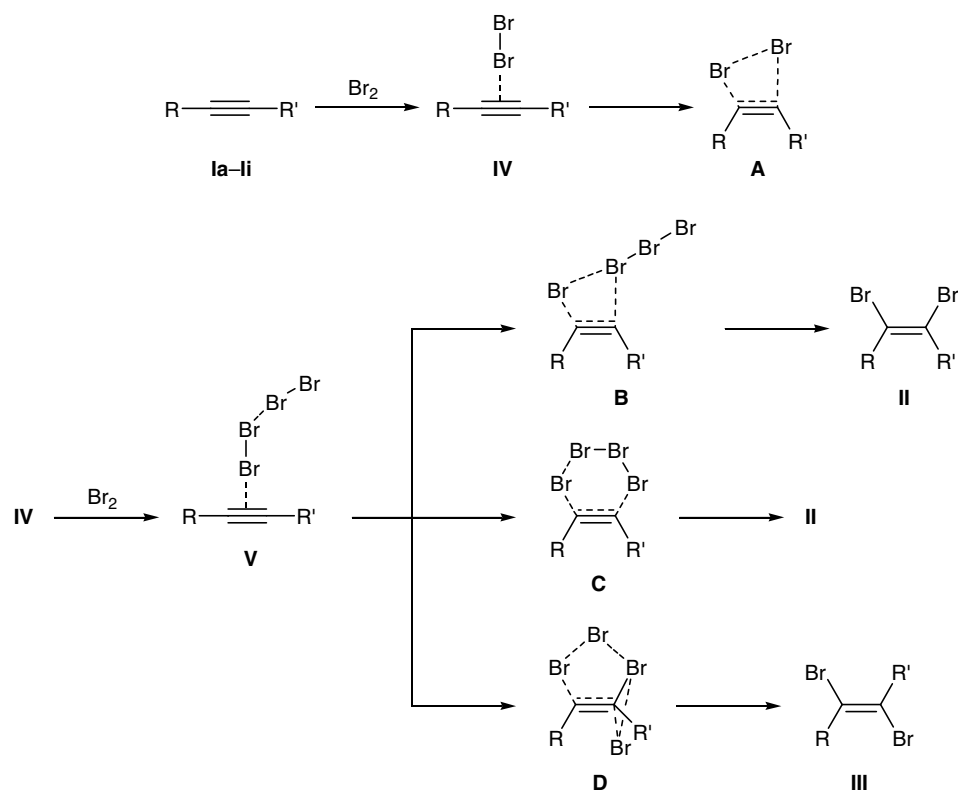
At present, the following mechanism of bromination of triple-bonded compounds is generally accepted [10, 15]. In the first step, a 1:1 Br_2 -alkyne π -complex is formed, and it is then transformed into 2:1 π -complex. The latter undergoes dissociation into tribromide anion and one of the two possible cationic intermediates: cyclic bromirenium ion or open-chain bromovinyl cation. Attack by Br_3^- on cyclic bromirenium ion leads to the formation of the corresponding *trans*-1,2-dibromoalkene, whereas attack by bromovinyl cation gives rise to a mixture of *cis*- and *trans*-alkenes. However, the formation of cationic intermediates has

never been proved experimentally, and the results of early quantum-chemical calculations showed that the formation of such charged species is unfavorable, for it requires heterolytic dissociation of the $\text{Br}-\text{Br}$ bond to produce ions from neutral π -complex [16]. Attempts were made to rationalize the formation of cationic intermediates in terms of the solvent effect which could reduce the activation barrier to cleavage of the $\text{Br}-\text{Br}$ bond via specific interactions stabilizing charged species [17]. This assumption is based on the known fact that polar solvents accelerate the bromination process [18]. Nevertheless, no rigorous proofs for the reduction of the activation barrier in solution were given so far, though some attempts to simulate effects of the medium were reported [19–21]. An obvious problem is also the lack of substantiation of the exclusive formation of *cis*-addition products in some experimentally studied alkyne bromination reactions [9, 22–24].

The existence of a concept implying radical mechanism of bromination should also be noted [14]. However, radical halogenation of alkynes is typical of gas-phase reactions at elevated temperature or under UV irradiation; in keeping with the latest experimental data, it is unlikely to operate in solution [10, 15].

Herges et al. [11] used the density functional calculations (B3LYP/6-31G*) to localize a number of transition states involving two bromine molecules in the bromination of acetylene, leading to the *cis*-addition product; the authors showed that formation of

Scheme 1.



ionic intermediates is not necessary. The process leading to the *trans* isomer and side elimination reactions leading to bromoalkynes were not studied. More recently, we reported the results of our quantum-chemical study on the bromination of a series of alkyl- and phenyl-substituted acetylenes and proposed a mechanism involving no charged species [16]. We found transition states and determined activation energies for processes leading to the formation of both *cis*- and *trans*-1,2-dibromoalkenes, as well as transition states for possible further processes such as rearrangement into 1,1-dibromoalkenes and dissociation into bromoacetylenes and alkyl(phenyl) bromides (or HBr). We showed that the nature of substituents at the triple bond is the key factor responsible for the stereochemical structure of the resulting 1,2-dibromoalkenes.

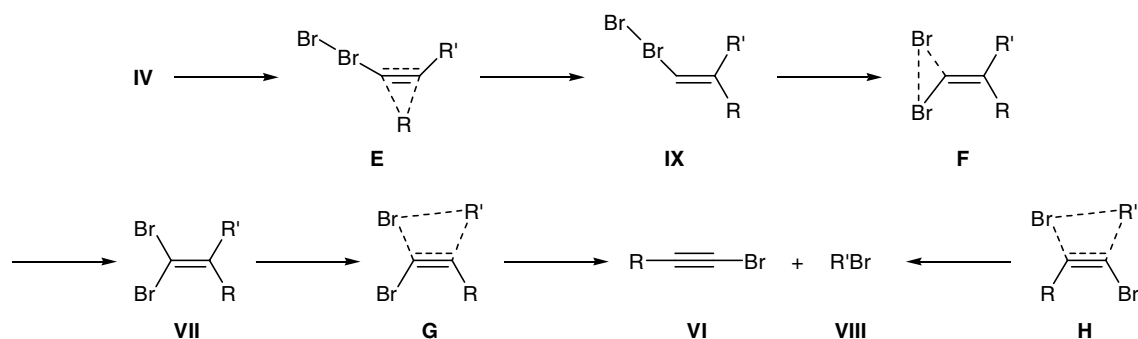
The present work continues our study on the bromination and bromodemetalation of heteroelement-substituted acetylenes in terms of the mechanism proposed by us in [16]. As model substrates we used silylacetylene (**Ia**), 1-silyl-2-phenylacetylene (**Ib**), and heteroelement-substituted phenylacetylenes $RC\equiv CR'$, where $R = Et_3Si$ (**Ic**), Et_3Ge (**Id**), $(MeO)_3Si$ (**Ie**), $(EtO)_3Ge$ (**If**), $N(CH_2CH_2O)_3Si$ (**Ig**), $N(CH_2CH_2O)_3Ge$ (**Ih**), Bu_3Sn (**Ii**); $R' = Ph$. Reactions of these com-

pounds with bromine were studied by us previously using experimental methods [22–24]. Our choice of model substrates was dictated by the possibility for concurrent bromodemetalation (according to the experimental data) [18, 22–24].

Theoretical studies were performed in terms of the density functional theory (DFT) using nonempirically generalized gradient approximation and PBE/TZ2P functional [25, 26] implemented in PRIRODA software [27]. Geometric parameters of all stable intermediates and saddle points (for transition states) were optimized. Stationary points were identified (as a minimum or saddle point) by calculating Hessian eigenvalues (matrices of the second derivatives of the energy with respect to coordinates of nuclei). Transition states were assigned to particular transformations by calculating the reaction coordinates. The energies were calculated with no correction for zero-point vibrations. Solvent effects were simulated according to the Onsager method implemented in GAMESS [28].

The general scheme for bromine addition to heteroelement-substituted alkyne **I** with formation of *cis*- and *trans*-dibromoalkenes **II** and **III** and their possible subsequent decomposition (Schemes 1, 2) is analogous to that proposed by us previously for the bromination

Scheme 2.



of alkyl- and phenylacetylenes [16]. In keeping with Schemes 1 and 2, we performed geometry optimization of possible addition products **II**, **III**, and **VII** and decomposition products **VI** and **VIII** and calculated the differences between the total energies of the products and between the sums of the total energies of the products (**VI**+**VIII**) and initial compounds (**I**+Br₂) (Table 1).*

The results showed that *cis*-dibromoalkene is the most thermodynamically favorable product for all the examined substituents. However, the difference in the energies of the respective *cis*- and *trans*-dibromoalkenes is not large (Table 6); therefore, the formation of both isomers is possible from the viewpoints of thermodynamics. On the other hand, the total energies of 1,1-dibromoalkenes **VII** and products resulting from cleavage of the heteroelement–carbon bond (**VI**+**VIII**) indicate that the processes leading to the formation of

these compounds are thermodynamically less favorable than the bromination process leading to 1,2-dibromoalkene **II** or **III**. All the examined products are more stable than the initial compounds (**I** and Br₂). The total energies of π -complexes **IV** and **V** with one and two bromine molecules, respectively, are also given in Table 1.

Complexes **IV** and **V** turned out to be more stable than the initial compounds, in keeping with the experimental data for analogous organic acetylene derivatives [10, 29]. The transformation of the initial compounds into π -complexes involves no activation barrier. The calculated structures of complexes **IV** and **V** are similar to those found previously for phenylacetylene [16]. Figure 1 shows typical structures of phenylsilylacetylene complexes **IVb** and **Vb**.

We calculated possible transition states **A–D** for all systems **I**–Br₂. The activation energies are given in

Table 1. Calculated ΔH values (kcal/mol) for bromination of alkynes and possible side processes relative to the sum of the energies of initial compounds **I** and Br₂, kcal/mol

Initial compound	R	R'	Products					
			II	III	VII	VI + VIII	IV	V
Ia	SiH ₃	H	–36.95	–35.62	–34.65	–14.72	–4.30	–8.70
Ib	SiH ₃	Ph	–28.01	–27.38	–24.78	–14.00	–5.74	–11.49
Ic	SiEt ₃	Ph	–24.35	–23.48	–18.74	–17.55	–5.40	–12.16
Id	GeEt ₃	Ph	–26.55	–25.62	–22.74	–21.14	–6.55	–13.92
Ie	Si(OMe) ₃	Ph	–24.98	–23.74	–21.47	–14.73	–5.03	–11.71
If	Ge(OEt) ₃	Ph	–27.22	–25.98	–25.69	–19.41	–4.71	–11.46
Ig	Si(OCH ₂ CH ₂) ₃ N	Ph	–26.05	–25.20	–22.91	–15.47	–7.71	–19.13
Ih	Ge(OCH ₂ CH ₂) ₃ N	Ph	–28.30	–27.00	–25.59	–18.44	–6.80	–17.49
Ii	SnBu ₃	Ph	–28.08	–27.10	–24.38	–26.19	–8.71	–16.90

* Despite one more decomposition process with formation of bromobenzene is obvious for the addition–elimination reaction, our previous studies showed [16] that it is unfavorable from the viewpoint of energy.

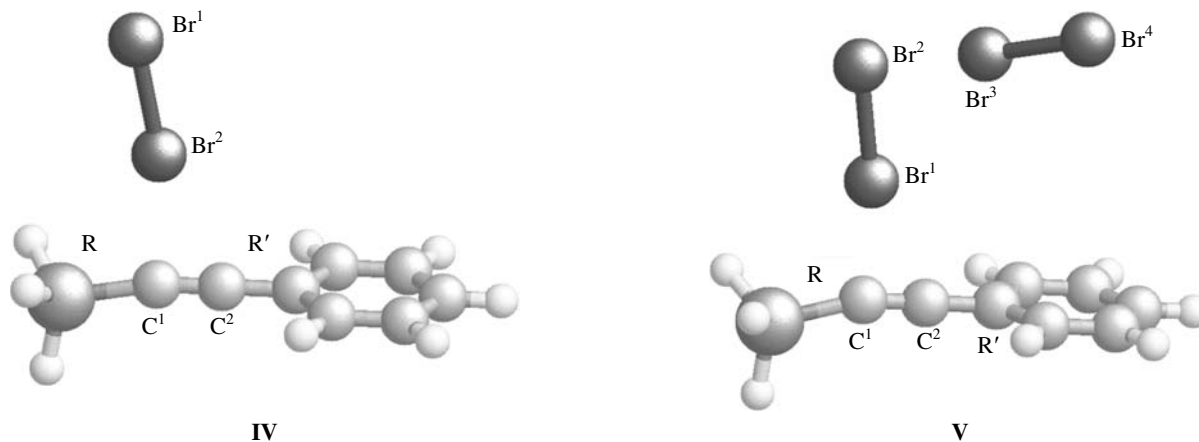


Fig. 1. Structures of typical π -complexes **IV** (C^1-Br^1 2.581–2.860, C^2-Br^1 2.839–2.974 Å) and **V** (C^1-Br^1 2.262–2.756, C^2-Br^1 2.706–2.892 Å). The complete sets of geometric parameters for all structures calculated in the present work are available from the authors.

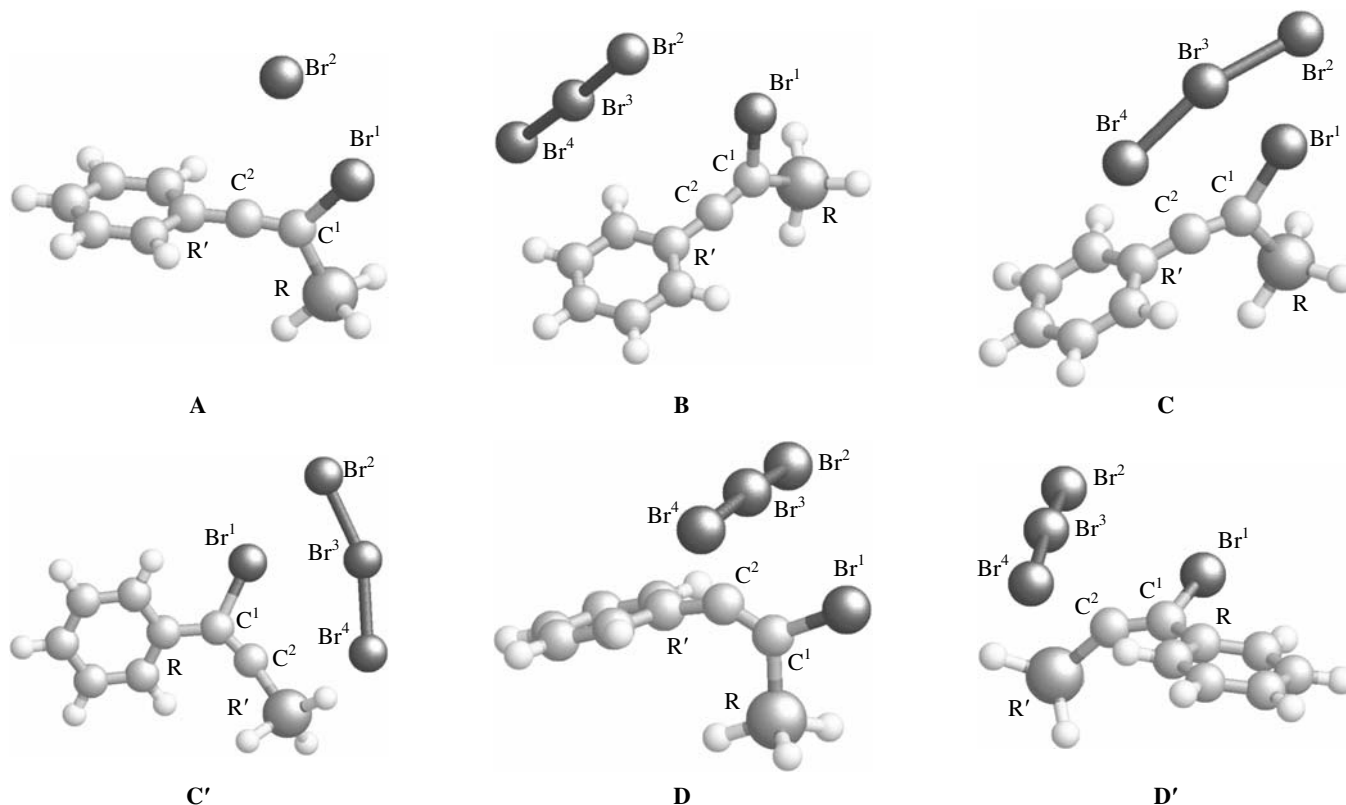


Fig. 2. Structures of typical transition states for the bromination reaction: **A**: Br^1-Br^2 3.006–3.310, Br^1-C^1 1.911–1.961, Br^2-C^2 3.853–4.404 Å; **B**: C^1-Br^1 1.871–1.961, Br^1-Br^2 3.471–4.749, C^2-Br^2 4.055–5.447 Å; **C**: C^1-Br^1 1.909–2.077, C^2-Br^4 3.194–3.439 Å; **C'**: C^1-Br^1 4.964–5.473, C^2-Br^4 3.262–3.602 Å; **D**: C^1-Br^1 1.879–1.920, C^2-Br^3 2.506–2.834, C^2-Br^4 2.601–3.013 Å; **D'**: C^1-Br^1 1.903–1.945, C^2-Br^3 2.349–2.870, C^2-Br^4 2.524–2.984 Å.

Table 2. Transition states **A** and **B** may be isomeric, depending on the addition sequence of bromine molecule fragments; nevertheless, only one of the two possible isomers is stable. Presumably, this is related to the nature of transition states **A** and **B** that resemble ion pairs. Obviously, the positive charge on the carbon

atom is stabilized by both α -phenyl and β -silyl (germyl or stannyl) groups. Correspondingly, processes involving increase of the positive charge on C^1 (Fig. 2) are unlikely to occur. By contrast, we succeeded in localizing both $Br^1-Br^2-Br^3-Br^4$ addition isomers for transition states **C** and **D**; their typical structures are

Table 2. Energies of activation for the bromination processes, calculated relative to the corresponding π -complexes, kcal/mol

Initial compound	Transition state			
	A	B	C (C')	D (D')
Ia	45.16	34.22	21.55 (20.32)	15.94 (14.86)
Ib	32.31	13.51	15.50 (26.01)	8.09 (21.01)
Ic	30.51	12.06	13.82 (25.71)	8.40 (21.57)
Id	28.11	9.00	12.34 (24.55)	7.01 (20.81)
Ie	29.71	8.99	15.14 (27.08)	8.34 (21.10)
If	27.75	9.22	12.91 (27.40)	6.25 (13.79)
Ig	29.58	12.03	17.98 (30.73)	12.94 (27.20)
Ih	27.70	11.62	15.49 (31.05)	10.43 (26.38)
Ii	27.78	7.45	11.86 (25.08)	6.79 (15.57)

shown in Fig. 2. In keeping with the calculated structures of transition states **A** and **B**, one originally triple-bonded carbon atom therein is sp^2 -hybridized, while both carbon atoms in initial complexes **IV** and **V** have sp hybridization. The Br–Br distance in transition state **A** (3.006–3.310 Å) is considerably longer than in complex **IV** (2.382–2.442 Å). Likewise, the Br¹–Br² bond in transition state **B** (3.471–4.749 Å) is longer than in complex **V** (2.408–2.581 Å). One C–Br distance in transition states **A** and **B** is appreciably shorter than the other (1.911–1.961 and 1.871–1.961 Å against 3.853–4.404 and 4.055–5.447 Å, respectively). These data led us to conclude that transition state **A** and especially **B** are contact ion pairs.

The energies of activation calculated for the bromination of **Ia** were much greater than those determined for all other examined compounds, i.e., the presence of a phenyl group favors the reaction. In addition, all processes involving two bromine molecules are more favorable than the reaction with one bromine molecule

through transition state **A**. For all compounds, except for **Ig**, the formation of *trans*-dibromide is preferred, though the difference in the activation energies for transition states **B** and **D** derived from compounds **Id**, **Ie**, and **Ig–Ii** does not exceed 2 kcal/mol (Table 1). Thus, the results of calculations lead us to expect formation of mixtures of *cis*- and *trans*-1,2-dibromides. Comparison of the data in Table 2 with the results of our previous calculations performed for the bromination of acetylenes with organic substituents, e.g., phenylacetylene [16], shows that the presence of a heteroelement-containing group in the β -position with respect to the carbocationic center destabilizes transition state like **A** but stabilizes transitions states **B–D**. The energies of activation for transition states **A**, **B**, **C**, and **D** in the bromination of phenylacetylene were estimated at 14.64, 14.61, 17.66, and 15.93 kcal/mol, respectively [16]. In almost all cases, the energy of activation decreases in the series of structurally related compounds with different heteroelements: **Ic** (Si) > **Id** (Ge) > **Ii** (Sn); **Ie** (Si) > **If** (Ge); **Ig** (Si) > **Ih** (Ge).

In the next stage of our study we examined attack by bromine molecule on silicon-, germanium-, or tin-containing substituent, followed by bromodemetalation. It is well known that halodemetalation processes are very characteristic of heteroelement-substituted β -haloalkyl and β -halovinyl derivatives and that such reactions have found synthetic applications [30]. On the basis of the experimental data it was presumed that steric effects of substituents force the reaction to follow a path involving one of the three transition states **J–L** [31–34].

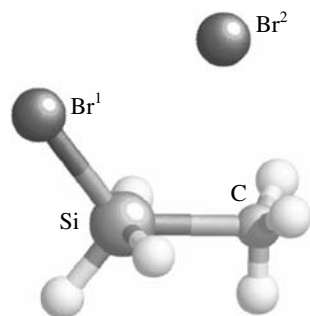
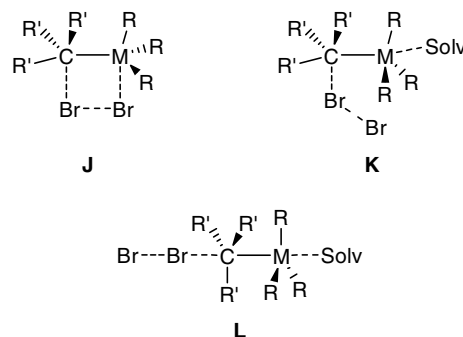


Fig. 3. Structure of type **J** transition state: Si–C 2.146, Si–Br¹ 2.283, C–Br² 3.168, Br¹–Br² 3.126, Br²–Si 3.396 Å; SiBr¹Br² 76.0, SiCBr² 76.8, Br¹Br²C 78.7, Br¹SiC 128.5°.

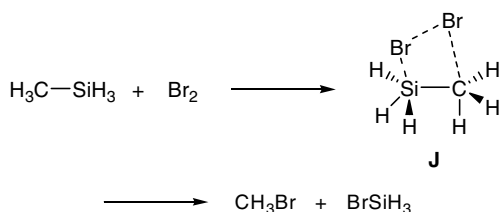


In addition, the reaction path is strongly affected by nucleophilic assistance by the solvent [31–34]. However, it is obvious that processes passing through transition states **K** and **L** should give rise to ionic intermediates like MR_3^+ –solvent, i.e., two charged species should be formed in these cases. As we showed

previously [16], such processes are unfavorable from the viewpoint of energy (at least in terms of the calculation schemes describing gas-phase reactions). Therefore, transition state **J** seems to be the most probable for the reaction of a heteroelement-substituted substrate with one bromine molecule.

Using silylmethane SiH_3CH_3 as model compound, we have revealed a transition state of type **J** (Fig. 3). Analysis of the corresponding reaction coordinate completely confirmed that the bromodemetalation process follows Scheme 3. Dissociation of the Si–C bond in transition state **J** and formation of C–Br² and Si–Br bonds occur synchronously. The energy of activation is 56.19 kcal/mol, and the heat effect, –27.40 kcal/mol.

Scheme 3.



We tried to localize an analogous four-membered transition state of type **J** for dissociation of the Si–C bond in silylacetylene molecule **Ia**. However, our attempts were unsuccessful. Instead, we revealed two other transition states with participation of one (**M**) and (later) two bromine molecules (**N**) for cleavage of heteroelement-substituted alkynes by the action of bromine. The structures of transition states **M** and **N** (Fig. 4) strongly differ from four-membered structure like **J** (Fig. 3). In fact, transition states for saturated compounds are planar, while in transition states for reactions of alkynes with bromine the Br² atom deviates from the plane formed by the three remaining atoms. Furthermore, initial addition of bromine through transition state **M** occurs at the triple-bonded carbon rather than at the heteroelement, as in transition state **J**. The energies of transition states **M** and **N** relative to the corresponding π -complexes are given in Table 3.

Thus transition state **J** is typical of only saturated systems, whereas coordination of bromine in reactions with alkynes always begins with addition at the triple bond. Analysis of the reaction coordinate shows that the addition of Br¹ to C¹ is followed by displacement of Br² toward the R substituent with simultaneous extension of the C¹–R bond, which finally leads to dissociation of that bond.

Table 3. Energies of activation of the bromodemetalation processes, kcal/mol

Initial compound	Transition state	
	M (M')	N (N')
Ia	51.23	37.43
Ib	31.69	22.40
Ic	24.86	16.14
Id	23.44	15.42
Ie	27.79	19.47
If	22.66	14.94
Ig	26.90	21.07
Ih	24.96	19.05
Ii	19.25	11.26

Comparison of the activation energies for the bromination (Table 2) and bromodemetalation processes (Table 3) shows that bromodemetalation can predominate over bromination in reactions of all the examined

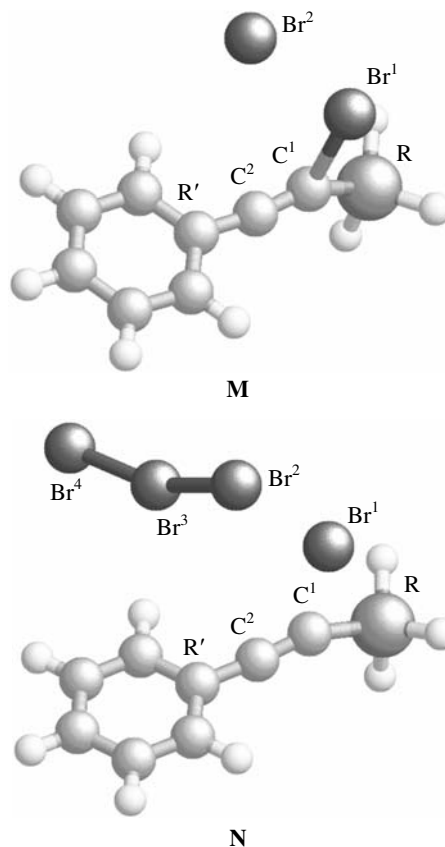


Fig. 4. Structures of typical transition states for halodemetalation of alkynes: **M**: C¹–Br¹ 2.128–2.342, C¹–Br² 3.211–3.400, Br¹–Br² 2.845–3.235, R–Br² 3.599–4.512 Å; **N**: C¹–Br¹ 2.310–2.550, C¹–Br² 3.477–3.640, Br¹–Br² 3.241–2.891, R–Br² 4.326–4.690 Å.

Table 4. Energies of activation of elimination processes (kcal/mol)

Initial compound	Transition states		$\Delta E(\text{IX})^a$	$\Delta E(\text{IX}-\text{IX}')^c$
	E (E') ^a	F (F') ^b		
Ia	24.00 (36.53)	18.19 (15.66)	15.32	0.87
Ib	27.22 (38.50)	17.30 (16.20)	22.29	-1.11
Ic	24.75 (35.51)	17.06 (16.52)	22.48	-0.69
Id	21.48 (35.25)	16.22 (15.50)	19.98	-0.42
Ie	26.04 (37.69)	16.70 (18.49)	20.88	-1.23
If	23.09 (38.19)	16.12 (18.08)	17.74	-1.79
Ig	26.82 (33.58)	16.34 (14.69)	21.25	2.59
Ih	23.11 (34.54)	16.14	18.19	1.76
Ii	(36.60)			

^a Calculated relative to π -complex IV.^b Calculated relative to complex IX (IX').^c Difference in the energies of isomeric complexes IX and IX'.**Table 5.** Energies of activation of elimination processes (kcal/mol)

Initial compound	Transition state			
	G ^a	H ^b	O ^c	P ^d
Ia	52.55	52.15		4.74 (5.61)
Ib	47.21	42.21		5.33 (4.22)
Ic	46.27	44.97		3.87 (3.18)
Id	43.90	42.16		2.96 (2.53)
Ie	46.96	42.12		4.58 (3.35)
If	42.92	36.49		5.37 (3.58)
Ig	50.94	47.59		2.82 (5.42)
Ih	45.82	40.34	11.42	3.38 (5.14)
Ii	32.40	29.75	2.67	

^a Calculated relative to compound VII.^b Calculated relative to compound III.^c Calculated relative to complex IX'.^d Calculated relative to complex IX (IX').

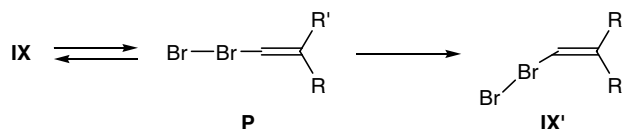
heteroelement-substituted alkynes with one bromine molecule (i.e., at a low concentration of bromine). When the concentration of bromine in solution is high (the reaction involves two bromine molecules per substrate molecule), bromine addition becomes the predominating process.

We also examined the possibility for various skeletal rearrangements to accompany reactions of substituted alkynes with bromine, as well as subsequent transformations of the bromination products. According to the calculations, decomposition of dibromo-

alkenes can also include formation of several intermediates and transition state according to the two-step addition–elimination pattern (Scheme 2) [16]. We have revealed two radically different and independent paths for the transformation of acetylenic substrates in reactions with bromine: (1) formation of 1,1-dibromo derivative like VII and its subsequent decomposition and (2) formation of *trans*-1,2-dibromide III (see above) and its subsequent decomposition (Scheme 2). We calculated the structures of all possible transition states and intermediates; the activation energies and energies of intermediates are collected in Tables 4 and 5, and typical transition state structures are shown in Fig. 5.

First, it was found that transition state E corresponds to migration of one substituent (R) with simultaneous displacement of the Br¹ atom relative the triple bond in π -complex IV toward C¹ with formation of intermediate IX; here, migration of heteroelement-containing group is always more favorable than migration of the phenyl substituent, except for compound IVi. Intermediate IX and isomeric structure IX' are neutral species in which one of the triple-bonded carbon atoms (C¹) has a positive charge, and one of the bromine atoms (Br²) has a negative charge. Second, transition state F is characterized by displacement of Br² toward C¹, leading to geminal dibromo derivative VII. The energies of formation of 1,1-dibromide VII from π -complex IV are given in Table 1. Third, decomposition of 1,1-dibromide VII and *trans*-dibromide III may involve two similar transition states G and H. These transition states may also have isomeric structures; however, our previous calculations showed that elimination of bromobenzene requires a high activation energy (82.49–93.87 kcal/mol [16]); therefore, this process is not considered here.

Apart from the transition states shown in Scheme 2, we have revealed two new transition states. The first of these (P) is responsible for the isomerization of intermediate IX (Scheme 4).

Scheme 4.

As follows from the data in Table 3, the difference in the energies of isomers IX and IX' is not large, and the energy of activation for their interconversion (P) ranges from 2.53 to 5.61 kcal/mol, i.e., both isomers

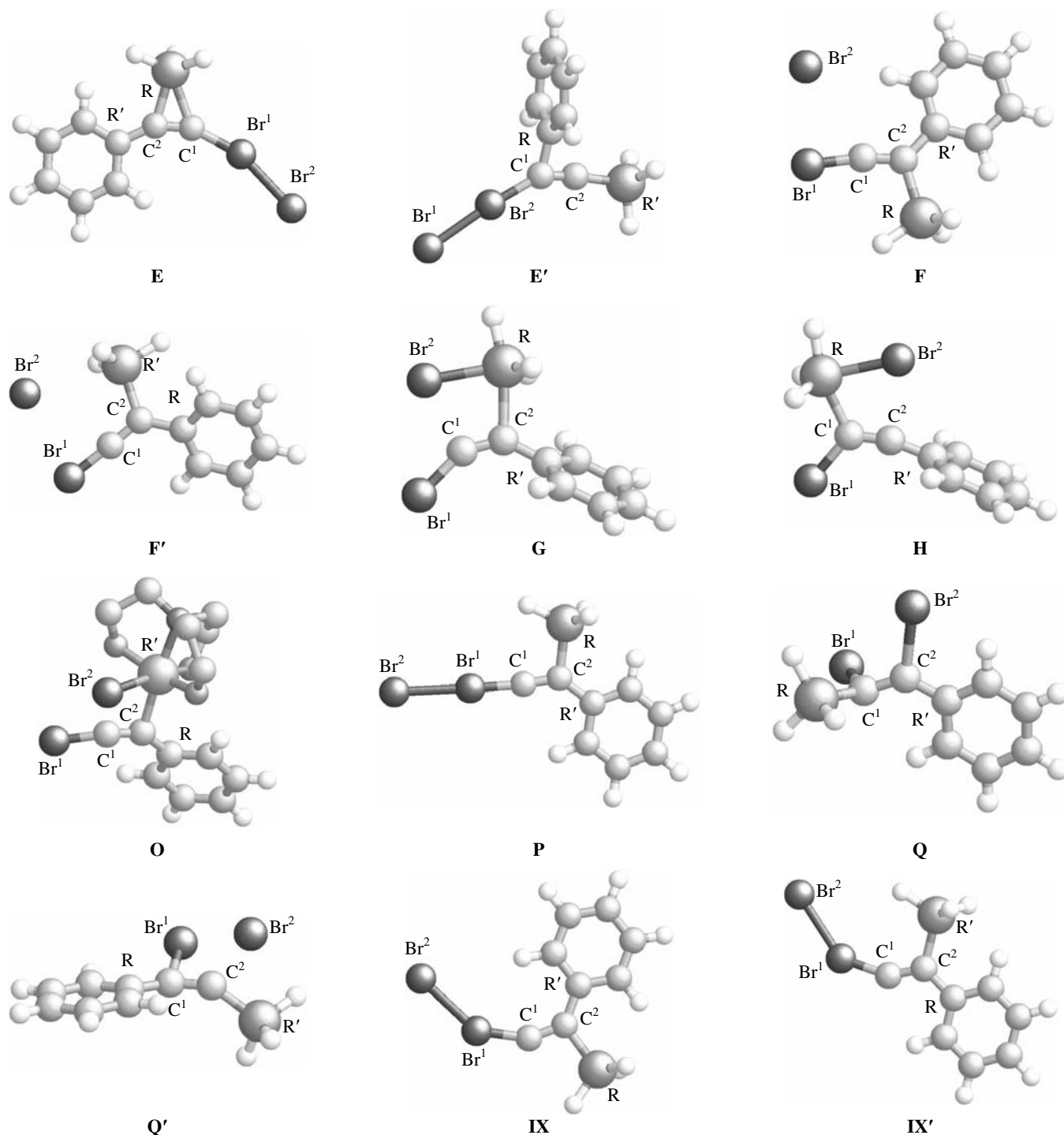
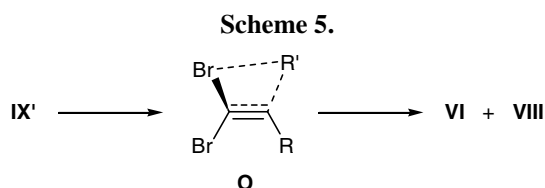


Fig. 5. Structures of typical transition states and intermediates for the bromination reaction: **H**: R–C¹ 2.135–2.376, R–C² 2.021–2.200, C¹–Br¹ 1.921–2.017 Å; **H'**: R–C¹ 1.219–1.648, R–C² 1.378–1.899, C¹–Br¹ 1.993–2.138 Å; **J**: C–Br 1.733–1.752, C¹–Br² 3.317–3.507, Br¹–Br² 3.080–3.219 Å; **J'**: R'–Br² 3.362–4.330, C¹–Br¹ 1.739–1.768, C¹–Br² 3.314–3.507, Br¹–Br² 3.151–3.584 Å; **K**: C¹–Br² 2.164–2.557, C²–R 2.181–2.669, Br²–R 2.415–2.755 Å; **L**: C¹–R 2.088–2.454, C²–Br² 2.433–2.771, R–Br² 2.410–2.783 Å; **O**: R'–C² 2.206–2.554, R'–Br² 2.775–2.961, C¹–Br² 2.637–2.881 Å; **P**: Br²–Br¹ 2.647–2.700, Br¹–C¹ 1.846–1.886, C¹–C² 1.281–1.297 Å; **Q**: C¹–Br¹ 1.897–2.018, C²–Br² 2.119–3.310, R–C¹ 1.857–2.282, R'–C² 1.092–1.425; C¹C²Br² 89.2–129.8, C¹C²R' 129.4–164.4, C²C¹Br¹ 88.1–130.8, C²C¹R 111.9–136.8, RC¹Br¹ 114.9–118.1, R'C²Br² 100.6–110.5°; **Q'**: C¹–Br¹ 1.931–1.985, C¹–C² 1.305–1.340, C²–Br² 2.342–2.920, R–C¹ 1.086–1.453, R'–C² 1.878–2.199 Å; C¹C²Br² 114.2–123.3, C¹C²R' 134.9–171.1, C²C¹Br¹ 88.6–110.5, C²C¹R¹ 130.9–143.2, RC¹Br¹ 116.8–125.3, R'C²Br² 74.5–102.7°; **IX** (**IX'**): Br¹–Br² 2.630–2.687, C¹–Br¹ 1.790–1.863, C¹–C² 1.280–1.313 Å.

could exist in equilibrium. A specific feature of transition state **P** is linear structure of the $\text{Br}^2\text{-Br}^1\text{-C}^1\text{-C}^2$ fragment (Fig. 5). An exception was compound **II** for which only one intermediate **IX'** was found. Another specific feature of that process is the existence of only one isomer of transition state **F** for compound **Ih** and the lack of transition state **F** for compound **II**. The absence of isomeric structure of transition state **F** for compound **II** may be related to instability of intermediate **IX**, i.e., it is impossible to localize a saddle point in the corresponding potential energy surface region.

Instead of missing transition states **F'** for **Ih** and **II** we found a new transition state (**O**) which is responsible for one-step elimination from intermediate **IX'**, bypassing the stage of formation of 1,1-dibromide (Scheme 5). Unlike transition states **F'**, the $\text{Br}^2\text{-R}$ distance in structure **O** is shorter (Fig. 5). The difference between transition states **O** and **G** is that the $\text{Br}^2\text{-R-C}^2\text{-C}^1$ fragment in the latter is planar (the Br^2 atom in **O** deviates from the plane formed by the three other atoms).

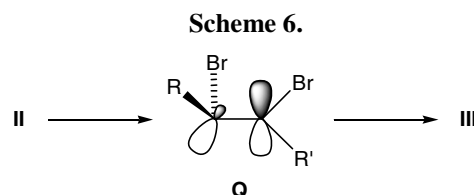


Taking into account that no possible paths for decomposition of *cis*-dibromide **II** were found, we examined one more process which may occur in parallel with the bromination process and lead to accumulation of one or another dibromoalkene isomer

Table 6. Energies of activation of the *cis-trans* isomerization process, calculated relative to compounds **II** (**III**) and energy differences between compounds **II** and **III** (kcal/mol)

Initial compound	ΔE (III-II)	Transition states	
		Q	Q'
Ia	1.33	65.98 (64.66)	70.66 (69.33)
Ib	0.63	49.24 (48.61)	61.81 (61.18)
Ic	0.87	45.75 (44.88)	55.64 (54.77)
Id	0.93	45.63 (44.70)	55.66 (54.73)
Ie	1.23	45.55 (44.32)	59.63 (58.40)
If	1.24	46.30 (45.06)	61.89 (60.65)
Ig	0.85	46.52 (45.67)	58.37 (57.52)
Ih	1.30	47.95 (46.65)	60.74 (59.44)
Ii	0.98	41.07 (40.09)	54.01 (53.02)

in the reaction mixture, namely *cis-trans* isomerization (Scheme 6). As we showed in [16], two isomeric transition states **Q** and **Q'** are possible for unsymmetrically substituted dibromoalkenes (transition state **Q'** in Scheme 6 corresponds to the presence of a lone electron pair on the neighboring carbon atom). Table 6 contains the activation energies calculated relative to the *cis* (*trans*) isomer, and the structures of typical transition states are shown in Fig. 6. It is seen that the activation energies (**Q**, **Q'**) for heteroelement-substituted phenylalkenes are considerably lower than those found for most alkenes with organic substituents. The energies of activation for the *cis-trans* isomerization of organic alkenes were 51.22–73.67 kcal/mol [16], except for 3,4-dibromo-2,2,5,5-tetramethylhex-3-ene; the energy of activation for the latter was comparable with the values calculated for heteroelement-containing systems, 37.38 (45.69) kcal/mol [16]. Nevertheless, the isomerization barrier remains fairly high.



The structures of transition states **Q'** are consistent with the up-to-date *cis-trans* isomerization theory [35–37] and are strongly polar zwitterionic systems where one of the double-bonded carbon atoms has a positive charge, and the other, a negative charge. The dihedral angle $\text{Br}^1\text{C}^1\text{C}^2\text{Br}^2$ in transition state **H** approaches 90° . One carbon atom (C^2) at the originally double bond has sp^2 hybridization. The degree of pyramidity of the other carbon atom (C^1) depends on the strength of the $\text{C}^2\text{-Br}^2$ bond and steric factors, being approximately similar for all transition states **Q** and **Q'**, except for that derived from compound **Ia**: the degree of pyramidity of C^1 in **Qa** ($\text{R} = \text{SiH}_3$) is greater than in **Q'a** ($\text{R} = \text{Ph}$).

Finally, we examined solvent effect on transition state **A** involving one bromine molecule in terms of a *supermolecule* approach using compound **Ib** as an example. The reaction center was assumed to be surrounded by six chloroform molecules. Further increase in the number of solvent molecules was restricted by the performance of computational equipment. The calculated structures of complex **IVb** and transition state **Ab** are shown in Fig. 6. The results obtained using the above approach were compared

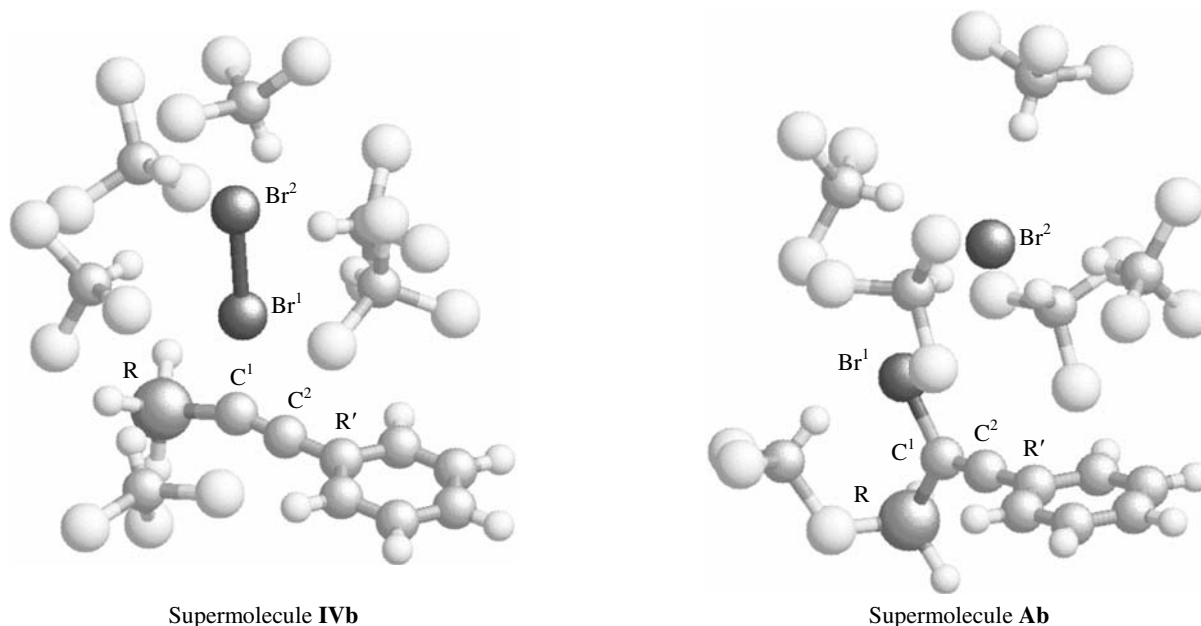


Fig. 6. Structures of transition states and intermediates for the bromination process with account taken of solvent effect: **IVb**: supermolecule: C¹–Br¹ 2.421, C²–Br¹ 2.826, Br¹–Br² 2.512 Å; Onsager: C¹–Br¹ 2.842, C²–Br¹ 3.086, Br¹–Br² 2.396 Å; **Ab**: supermolecule: C¹–Br¹ 1.931, C²–Br² 4.884, Br¹–Br² 3.541 Å; Onsager: C¹–Br¹ 1.922, C²–Br² 4.218, Br¹–Br² 3.564 Å.

with those found by the traditional Onsager solvent model. The energies of the transition state were 31.74 (Onsager) and 16.98 kcal/mol (supermolecule). The latter value is considerably smaller than that found for gas-phase reaction through transition **A** (32.31 kcal/mol⁻¹, Table 2), while the Onsager model gave a fairly similar value. This means that the results obtained by more expensive supermolecule method are more appropriate than the Onsager data. Comparison of the calculated data for the bromination of **IVb** (Table 2) with the results of supermolecule calculations shows that the bromination process involving one bromine molecule can compete with the process involving two bromine molecules (transition states **B–D**) in such weakly polar solvents as chloroform. It should be noted that solvent effect on the bromination of heteroelement-containing alkynes is stronger as compared to purely organic acetylenes [16]. Radically different results were obtained by us previously when the bromination of organic alkynes was simulated by the supermolecule method. The energy of activation of but-2-yne, calculated by the supermolecule method, considerably exceeded the energy of activation calculated for processes passing through transition states **B–D** [16].

Thus, the results of our theoretical study showed that bromination of heteroelement-substituted alkynes should give mixtures of the corresponding *cis*- and *trans*-1,2-dibromo derivatives. At low concentration of

bromine (reaction of alkyne with one bromine molecule), bromodemetalation may predominate over bromination for all the examined heteroelement-substituted alkynes.

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