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A DFT Investigation of Alkyne Bromination Reactions

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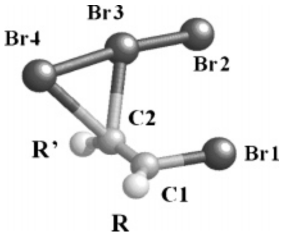

A DFT calculation study of the addition reaction between molecular bromine and the number of symmetrical or unsymmetrical substituted alkynes **1** (R−C≡C−R′), where R = R′ = H (**1a**), Me (**1b**), *t*-Bu (**1c**), or Ph (**1d**), or R = H and R′ = Me (**1e**), *t*-Bu (**1f**), or Ph (**1g**), was performed. Two possible reactions were checked: (a) the reactions suitable for the gas-phase interactions, which start from a 1:1 Br_2−alkyne π-complex and do not enter into a 2:1 Br_2−alkyne π-complex; and (b) the processes passing through a 2:1 Br_2−alkyne π-complex, which look more realistic for the reactions in solutions. The structures of the starting reactants and the final products as well as the possible stable intermediates have been optimized. The transition states of the predicted process have been found. Both *trans*- and *cis*-dibromoalkenes (**2** and **3**) may ensue without the formation of ionic intermediates from a π-complex of two bromine molecules with the alkyne (solution reactions). The geometry around the double bond forming in dibromoalkenes strongly depends on the nature of the substituents at the triple bond. The "cluster model" was also used for the prediction of solvent influence on the value of the activation barrier of the but-2-yne (**1b**) bromination reaction.

Introduction

The addition reactions of halogens to compounds containing multiple bonds were the focus of researchers' interest during the last century.[1,2] The first reason for this interest was the possibility of using the products of these reactions as reactants for further organic syntheses. On the other hand, these processes were very attractive for use in theoretical studies as the model reactions for mechanistic investigations. It should be noted that among the halogenation processes, the reactions with bromine were studied the most often, probably because of the comparative ease of experimental work and the ability of the reactions to proceed under mild conditions. Special attention was devoted to the bromination of alkenes, whereas the reactions of allenes and alkynes are still not as well studied.[3] According to the literature, different solvents have been used for alkyne bromination reactions, such as acetic acid,[4−7] alcohols,[8] $CHCl_3$,[9] and $ClCH_2CH_2Cl$.[10] The use of protic solvents leads to complicated mixtures of products, including ethers, esters, and ketones. Thus, the data obtained from the study of reactions in inert solvents such as haloalkanes are of great value for understanding the reaction pathways.

The concept of bromination reactions with different organic alkynes can be considered complete because of the brilliant combined theoretical and experimental investigations of Bianchini and co-workers.[10] In general, the reaction mechanism is similar to that for alkene bromination. The first step of the reaction is the formation of the Br_2−alkyne π-complex, which transforms into

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a 2:1 complex. The latter dissociates to a tribromide anion and one of two possible cationic intermediates, the cyclic bromirenium cation or the open bromovinyl cation. The attack of a $[Br_3]$ anion on cationic intermediates leads to the (*E*)-1,2-dibromoalkene or to the mixture of *E* and *Z* isomers. However, one question still remains undetermined: How do these cations form? In fact, according to data of the previous quantum chemical calculations,[10,11] the processes of these cation formations are energetically unfavorable, because these reactions require the rupture of a Br−Br bond to form two ions from one neutral molecule (π-complex). The usual explanation for the formation of these cations is connected to the presence of a solvent in the reaction mixture, which may decrease the activation barrier because of some specific interactions.[11] Although the latter suggestion is confirmed by the well-known fact that more polar solvents accelerate the reaction rate,[12] no firm evidence based on calculations has been found to date. However, it should be noted that several works dealing with simulation of the solvent influence have been published (see below).

The other problem still in question is which isomer, *E* or *Z*, will prevail in the concrete reaction. Very recently, we have studied the reactions of different element-substituted phenylacetylenes with bromine, where the element was silicon, germanium, or tin. The reactions were carried out in an aprotic solvent ($CHCl_3/CCl_4$), which led, in general, to the corresponding (*Z*)-1,2-dibromoalkenes.[13−15] This result cannot be explained on the basis of the generally accepted mechanism of alkyne bromination, in which appreciable amounts of *E* isomers should form. Thus, two open questions prompt us to find other possible pathways of the alkyne bromination. We have used the quantum chemical calculations for this purpose.

According to our literature search, there is only one computational study[16] of the bromination reaction of alkynes, which deals with calculations on the reaction products, transition structures, and intermediates of the bromination processes. Very recently, Herges et al. have published a study of the reaction of Br_2 with C_2H_2 in which a nonionic mechanism was suggested (B3LYP/6-31G*, see below).[16] Obviously, investigations of the mechanism of this process would be very important for understanding the bromination driving forces, including the reactions of alkynes with different structures. Modern quantum calculation methods, as well as the computer technique resources, enable us to examine the bromination reaction pathways in detail.

It should be noted that besides the communication of Herges et al.[16] several related works have been published to date. Yamabe et al.[17] have studied the electrophilic addition reactions of the molecular halogens (F_2, Cl_2, and Br_2) with ethene. They have found that the bromination of C_2H_4 proceeds through a zwitterionic three-centered transition state (cyclic bromonium ion plus Br^-) and leads to the anti addition product, with an activation barrier of 61.4 kcal mol^{-1}. Very recently, Kurosaki[18,19] suggested a radical mechanism of gas-phase ethylene chlorination. He has studied two different pathways of the reaction, i.e., direct Cl_2 addition to C_2H_4 and Cl abstraction from Cl_2 by C_2H_4. It has been found that in the gas phase, the $C_2H_4 + Cl_2 \rightarrow C_2H_4Cl + Cl$ (asymptote without undergoing a TS, 25.1 kcal mol^{-1} higher in energy than the reactants) $\rightarrow C_2H_4Cl_2$ pathway is energetically more feasible than the $C_2H_4 + Cl_2 \rightarrow$ TS (36.3 kcal mol^{-1}) $\rightarrow C_2H_4Cl_2$ pathway. De Almeida et al.[20] have found the activation barrier of the analogous acetylene reaction leading to *cis*- and *trans*-$C_2H_2Cl_2$ to be 22.6−41.8 kcal mol^{-1}, depending on the calculation method and basis set used. The reaction pathway includes the initiation step $C_2H_2 + Cl_2 \rightarrow C_2H_2Cl + Cl$, the isomerization step *trans*-$C_2H_2Cl \leftrightarrow$ *cis*-C_2H_2Cl, three different propagation steps, and three different termination steps. The analysis of the kinetics data gives 97.3% trans product and 2.7% cis product at room temperature. However, a radical mechanism of the halogenation of alkynes, obviously possible in the gas phase at high temperature or with UV irradiation, seems to be unlikely in solution.

With regard to the influence of a solvent, Rivail and co-workers[21] employed a continuum model for analysis of the bromination reaction of ethylene. They found a considerable decrease in the activation barrier when carried out in the solvent ($\epsilon_0 = 78.4$) in comparison with that in the gas phase. Similar results have been obtained by Cossi et al.[22] Kurosaki[23] has studied the charge-separation process of the $C_2H_4 + Cl_2$ reaction in water using a cluster model (four H_2O molecules). A very low activation barrier of such separation has been found. However, the final cluster still contained Cl···Cl contacts, and no IRC analysis leading to the chlorination products has been done. Additionally, the recent work of Coxon and Smith[24] examined the possible transition states of cyclopropane bromination. This process does not require the heterolytic cleavage of the bromine molecule during the course of the reaction.

Experimental results for acetylene (**1a**) bromination are ambiguous. Three different products were reported, but their structures were not determined. The authors only supposed the formation of *cis*- and *trans*-1,2-dibromoethylene as well as 1,1,2,2-tetrabromoethane at room temperature.[25] It is also known that the preparation of

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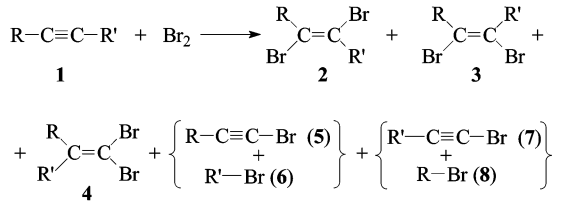
SCHEME 1. Possible Products of Alkyne Bromination



R = R' = H (**a**), Me (**b**), *t*-Bu (**c**), Ph (**d**);
R = H, R' = Me (**e**), *t*-Bu (**f**), Ph (**g**)

pure *trans*-1,2-dibromoethylene from bromine addition to acetylene requires the presence of $CuBr_2$ to prevent cis isomer formation.[26] Uemura et al.[9] have found the formation of both **2g** (see Scheme 1 for definitions) and **3g** (85/15 ratio) in the reaction of **1g** in chloroform (the kinetic control conditions: 20 °C, 0.5 h). The treatment of hexyne-1 (analogue of **1e**) and hexyne-3 (the analogue of **1b**) in the same conditions led to mixtures of corresponding *E* and *Z* isomers with 96/4 and 100/0 ratios, respectively. Bianchini and co-workers[10] have reported that bromination of **1d**, **1g**, and hexyne-2 (the closely related analogue of **1b**) in 1,2-dichloroethane at room temperature gave mixtures of corresponding *cis*- and *trans*-dibromides with *E*/*Z* ratios = 60/40, 57/43, and 100/0, respectively.

Thus, the publication of Herges' results[16] motivates us to report the results of our DFT study of the addition reaction between molecular bromine and a number of symmetrical or unsymmetrical substituted alkynes **1** (R−C≡C−R′), where R = R′ = H (**1a**), Me (**1b**), *t*-Bu (**1c**), or Ph (**1d**), or R = H and R′ = Me (**1e**), *t*-Bu (**1f**), or Ph (**1g**). The substituents were chosen for their different steric and electronic properties, as well as the opportunity to compare our calculated results with experimental data. Besides the bromination reactions leading to 1,2-dibromoalkenes, we also analyzed other possible processes, the formation of 1,1-dibromoalkenes and the cleavage of 1,2- and 1,1-dibromoalkenes. There are several previous theoretical works[27−32] that dealt with the elimination reactions of dihaloalkenes (see below).

We have studied two possible pathways: (a) reactions starting from a 1/1 Br_2−alkyne π-complex and not forming a 2/1 Br_2−alkyne π-complex and (b) processes passing through a 2/1 Br_2−alkyne π-complex. The first reaction is suitable for the gas-phase interactions, whereas the second looks more realistic for the processes in solutions. The structures of the reactants and the products, as well as the possible stable intermediates, have been optimized. The transition states of the predicted process have been found. The cluster model was also used for the prediction of solvent influence on the value of the activation barrier for the but-2-yne (**1b**) bromination reaction.

Methods of Calculations

Theoretical calculations were performed by the density functional theory (DFT) using the ab initio generalized gradient approximation and the PBE functional[33,34] implemented in the program "Priroda".[35] The one-electron wave functions were expanded in the extended TZ2P atomic basis sets of the contracted Gaussians (5s1p):[3s1p] for H, (11s6p2d):[4s3p2d] for C, and (19s16p9d):[6s5p3d] for Br. Full geometry optimization was performed for all stable compounds, and a saddle point search was performed for transition states. The type of stationary points was confirmed by vibrational frequency calculations; saddle points were confirmed also by the intrinsic reaction coordinate (IRC) calculation. The present method has been used and has given very useful results, including the study of bromine-containing molecules.[14,36−38]

Results and Discussion

Analysis of Final Product Structures. It is well-known that bromination reactions of alkyne with reagent ratio 1/1 may lead to (*E*)- or (*Z*)-dibromoalkenes (Scheme 1). One can expect that several other products may also form in the course of the reaction because of the rearrangement or cleavage processes.

We have calculated the sums of the total energies of the reactants (**1** + Br_2), and the differences between these values and the total energies of the optimized dibromoalkenes **2**−**4** or the cleavage products (**5** + **6**) and (**7** + **8**), which are summarized in Table 1 (see also Figure 1). Optimized structural parameters of **1**−**8** are available as Supporting Information. Their geometries are as expected, and are consistent with the available gas electron diffraction and microwave spectroscopy data.[39−42]

The most thermodynamically stable products for the bromination reaction of the alkynes **1d**, **1f**, and **1g** are the corresponding *cis*-dibromides **3d**, **3f**, and **3g**. However, *trans*-alkenes are the global minima for the bromination reactions of acetylenes (**1a**−**c**,**e**). It should be noted that the presence of one or two phenyl groups in the alkynes, as well as one bulky *t*-Bu group, stabilizes the cis geometry of dibromoadducts. However, the values of the total energy of corresponding cis and trans derivatives are similar (except **1c** and **1f**, in which the steric crowding of *t*-Bu groups strongly affects the total energy

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TABLE 1. Total Energies of the Reactants 1 + Br_2 (hartree), and the Relative Energies (kcal mol^{-1}) of the Possible Products[a]

	R	R′	**1** + Br_2 (E_{total})	**2** (ΔE)	**3** (ΔE)	**4** (ΔE)	**5** + **6** (ΔE)	**7** + **8** (ΔE)
a	H	H	−5224.89661	−44.06	−43.86	−41.85	−2.13[b]	−2.13[b]
b	Me	Me	−5303.46460	−38.18	−35.60	−33.73	6.54[b]	6.54[b]
c	*t*-Bu	*t*-Bu	−5539.10285	−16.65	−8.33	2.79	1.07[b]	1.07[b]
d	Ph	Ph	−5686.61052	−27.60	−28.13	−24.00	10.86[b]	10.86[b]
e	H	Me	−5264.18180	−41.31	−40.34	−37.84	−1.87	7.78
f	H	*t*-Bu	−5382.00087	−34.19	−38.28	−33.83	−2.02	2.40
g	H	Ph	−5455.75303	−37.01	−38.09	−35.74	−2.30	10.36

[a] The value of the relative energy is the corresponding difference: E_{total}(corresponding molecule) − E_{total}(**1** + Br_2). [b] Values for **5** + **6** and **7** + **8** are identical.

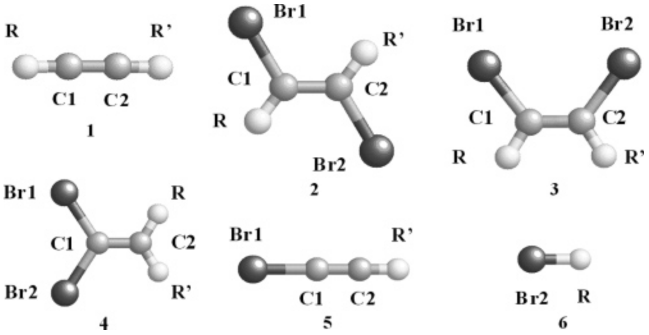


FIGURE 1. Calculated geometries of compounds **1**−**8** involved in the study (general view).

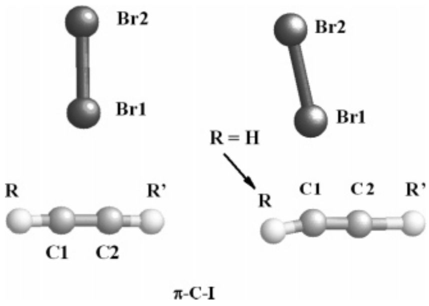


FIGURE 2. Calculated geometries of π-complexes π-**C**−**I** derived from symmetrical and unsymmetrical alkynes (general views).

of dibromoalkenes), and the formation of both isomers is thermodynamically expected. Thus, the kinetic factors probably determine the product distribution. The values of total energy of 1,1-dibromides **4** are, in general, slightly greater than those for both **2** and **3**. However, both possible cleavage processes (**5** + **6** and **7** + **8**) are strongly unfavorable.

Analysis of the Alkyne (1)−Br_2 One-Molecule System. According to both the experimental and calculated data,[10] it is generally accepted that the reaction of an alkyne molecule with bromine starts with the formation of a 1/1 Br_2−alkyne π-complex. We have optimized the structures of these complexes for studied systems **1a**−**g**. The general view of these complexes (π-**C**−**I**) is shown in Figure 2. Optimized structural parameters of these compounds are presented in Table 2 and in the Supporting Information. These species were assumed to have C_{2v} symmetry for the alkynes with the same substituents (**1a**−**d**), with the Br_2 molecule perpendicularly bound to the triple bond. Although the alkyne molecule is unsymmetrical (**1e**−**g**), the bromine atom attached to the triple bond (Br1) in π-**C**−**I** is shifted to the carbon atom bound to H. In all studied cases, the π-**C**−**I** complexes have considerably lower values of E_{total} than those for the reactants **1** + Br_2. The formation of π-complexes for **1b** and **1c** is the most favorable. This is in good agreement with the idea that the triple bond is the most electron-rich in these species. No transition states have been found by us for reactions **1** + Br_2 → π-**C**−**I**.

TABLE 2. Calculated Relative Energies (ΔE, kcal mol^{-1}) of Br_2−Alkyne π-Complexes (π-C-I)

	a	**b**	**c**	**d**	**e**	**f**	**g**
R	H	Me	*t*-Bu	Ph	H	H	H
R′	H	Me	*t*-Bu	Ph	Me	*t*-Bu	Ph
ΔE	−4.03	−7.89	−7.45	−5.09	−6.00	−6.21	−5.77

According to the established mechanism, the next stage of the alkyne bromination reaction should be the formation of a carbocation (**CC**) from the π-**C**−**I** complex. We have optimized the structures of target carbocations **CCa**−**CCg** (Figure 3, Table 3). Unfortunately, we have not been able to find any transition states for the decomposition process, but the activation barrier (if present) must be close to the value of ΔE [E_{total}(**CC** + $Br^{\ominus}$) − E_{total}π-**C**−**I**]. It should be noted that the relative energy of the calculated systems [**CC** + $Br^{\ominus}$] is very high in comparison with that for the related π-**C**−**I** complexes. Consequently, cleavage of the initially formed π-**C**−**I** complex with the formation of two charged fragments seems to be highly unrealistic, at least in the gas phase. However, as pointed out above, one can expect that these ions may form in solution. Thus, the analysis of the relationship of carbocation structures with R and R′ is required.

Species **CCa**, **CCb**, and **CCc** derived from ethyne and the symmetrical *bis*-alkylethynes are the cyclic bromirenium cations. On the contrary, the structures of the cations formed from the unsymmetrical alkynes (**CCe** and **CCg**) strongly depend on the nature of the substituents R and R′. When R′ is phenyl, which can effectively stabilize the α-carbocationic center, **CCg** possesses the structure of the pure open vinyl cation. The influence of the Ph group is so great that **CCd** is also the open cation. It should be noted that **CCf** is unstable, and rearranges to the allyl cation **CCf′** (Figure 3).

According to our investigations, besides the unfavorable formation process of the carbocations **CC** discussed above, two other reaction pathways beginning with the π-**C**−**I** complex are possible (Scheme 2).

Pathway I leads to the *cis*-dibromides, **3**, through the transition state **TS-1**, shown in Figure 4. The main geometric parameters of **TS-1** for the studied reactions

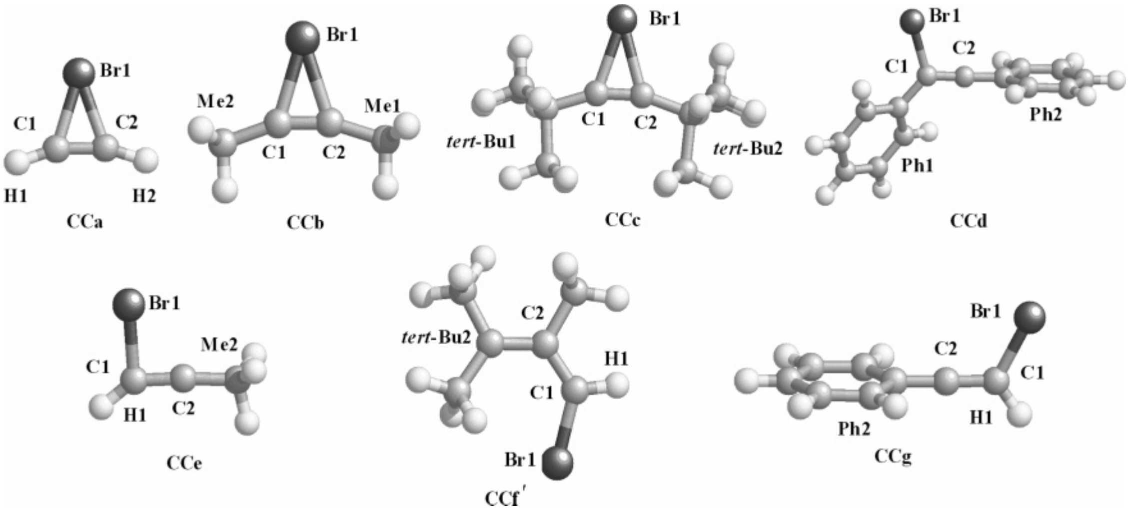


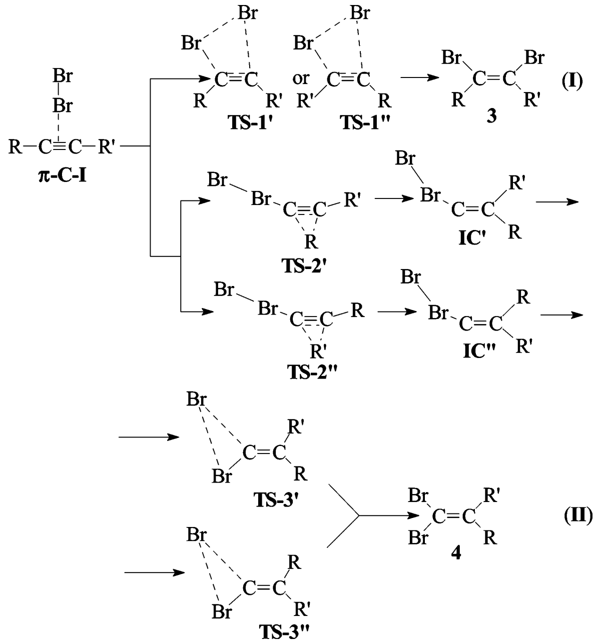
FIGURE 3. Calculated structures of carbocations **CCa**−**e**, **CCg**, and **CCf′**.

TABLE 3. Calculated Relative Energies (ΔE, kcal mol^{-1}) of the Carbocations (CC) Formed from π-Complexes (π-C−I), and Calculated Values of ΔE^a That Are Evaluative Values of E_{act} of π-C−I → CC + Br$^{\ominus}$ for the Decomposition Process

	a	b	c	d	e	f^b	g
R	H	Me	*t*-Bu	Ph	H	H	H
R′	H	Me	*t*-Bu	Ph	Me	*t*-Bu	Ph
ΔE	157.30	130.83	120.15	114.04	141.09		115.94
ΔE^a	161.33	138.73	127.60	119.13	147.10		121.71

[a] $\Delta E = E_{total}(\mathbf{CC} + \mathrm{Br}^{\ominus}) - E_{total}\pi$-**C**−**I**. [b] This cation is unstable (see discussion).

SCHEME 2. Possible Bromination Pathways Starting from π-Complex π-C−I



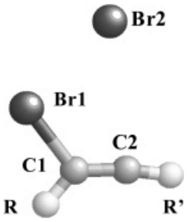


FIGURE 4. Calculated geometry of the found transition state in process I [**TS-1′** (**TS-1″**), general view].

are presented in the Supporting Information, and the energy barriers are listed in Table 4. There are two different pathways for pathway I in which the alkyne is unsymmetric, except the reaction π-**C**−**Ig** → **3g**. **TS-1′**s correspond to the process in which the carbon atom of C−R (i.e., C−H) is bound more closely to the Br atom than to the carbon atom of C−R′ (i.e., C−C) with the other bromine atom. Correspondingly, **TS-1**'s are the structures with the longer Br···C−H contact. For simplicity, the sole transition state for the symmetric alkynes was named **TS-1′**. In the case of phenylacetylene (**1g**), only **TS-1′** was found.

According to the obtained geometric parameters, **TS-1** possesses one sp^2 carbon atom of the former triple bond, whereas in π-**C**−**I** both carbons have sp hybridization. The Br−Br distances in **TS-1** (2.941−4.098 Å) are considerably longer than those in π-**C**−**I** (2.372−2.430 Å). One C−Br bond (1.943−2.094 Å) is noticeably shorter than the other C−Br distance (3.382−4.707 Å). These values allow **TS-1** to be considered as the contact ion pair. It should be noted that the values of E_{act} for process I are high, but the presence of Ph groups lightens the formation of *cis*-dibromides **3**. The activation barriers for the terminal alkynes in process I have lower values in comparison to those for the corresponding disubstituted alkynes. In the case of terminal alkynes, the reactions predominantly proceed through **TS-1′**, in which the stabilization of C$^{\delta+}$ by an alkyl or phenyl group occurs.

The second reaction is process II (in Scheme 2) that leads to 1,1-dibromides **4** through the transition state **TS-2**, the intermediate cation (**IC**), and the transition state **TS-3** (for the activation barriers, see Table 4). **TS-2** (Figure 5, see geometric parameters in the Supporting Information) differs considerably from **TS-1**, although both structures form from the same π-complex, π-**C**−**I**. **TS-2** is characterized by the shift of R (or R′) from one carbon atom of the former triple bond (C1) to the other (C2). At the same time, the Br−Br group is shifted from the center of the triple bond to the carbon atom (C1). The

TABLE 4. Activation Barriers for the Reactions of Processes I, II, and III (kcal mol^{-1})

process/compound	**a**	**b**	**c**	**d**	**e**	**f**	**g**
R	H	Me	*t*-Bu	Ph	H	H	H
R′	H	Me	*t*-Bu	Ph	Me	*t*-Bu	Ph
E(act) π-**C**−**I** → **3** (**TS-1′**)	45.43	47.35	48.40	44.90	40.42	42.10	34.69
E(act) π-**C**−**I** → **3** (**TS-1″**)					51.69	56.30	[a]
E(act) π-**C**−**I** → **IC′** (**TS-2′**)	37.99	50.58	60.90	45.66	37.46	39.44	42.51
E(act) π-**C**−**I** → **IC″** (**TS-2″**)					51.39	54.00	44.30
Δ*E* [E_{total}**IC′** − E_{total}π-**C**−**I**]	11.28	21.38	30.93	24.38	18.85	23.01	23.76
Δ*E* [E_{total}**IC″** − E_{total}π-**C**−**I**]					18.70	22.55	24.20
E(act)**IC′** → **4** (**TS-3′**)	19.63	19.82	26.86	28.62	18.13	22.47	24.92
E(act)**IC″** → **4** (**TS-3″**)					19.43	23.09	23.04
E(act) **3** → **2** (**TS-4′**)	73.47	62.75	37.38	51.76	66.36	65.58	58.08
E(act) **3** → **2** (**TS-4″**)					72.08	68.91	67.67
E(act) **2** → **3** (**TS-4′**)	73.67	65.33	45.69	51.22	67.33	61.49	57.00
E(act) **2** → **3** (**TS-4″**)					73.04	64.82	66.60

[a] **TS-1″** was not found for this process.

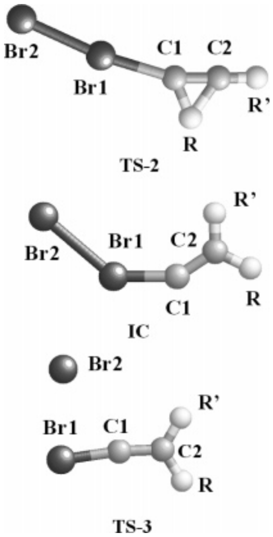
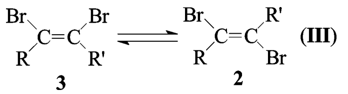


FIGURE 5. Calculated geometries of the found transition states and the intermediate in process II [**TS-2′** (**TS-1″**), **IC′** (**IC″**), and **TS-3′** (**TS-3″**), general view].

migration of the H atom (**TS-2′**) is more favorable in comparison to the shift of R′ (Me, *t*-Bu, Ph) (**TS-2″**) for all three studied substrates. The intermediate cation **IC** (Figure 5, see geometric parameters in the Supporting Information) is the local minimum on the potential energy surface (PES) for all studied cases, and represents a neutral particle in which one carbon atom of the former triple bond (C1) possesses a positive charge, whereas the bromine atom (Br2) is negatively charged. **TS-3** (Figure 5, see geometric parameters in the Supporting Information) is characterized by the shift of the long bromine atom (Br2) toward the C1 atom of the former triple bond. **IC′** and **IC″**, as well as **TS-3′** and **TS-3″**, possess very similar geometries for the unsymmetrical alkynes. Unfortunately, we have not found any processes leading to *trans*-dibromides **4** (except the possibility of carbocation **CC** formation which should be ruled out). However, the cis ↔ trans isomerization is a suitable source of *trans*-dibromides **2** (process III, Scheme 3).

It should be noted that the process of the cis ↔ trans isomerization of alkenes is actually complicated, and still not fully understood.[43−45] We have analyzed process III by the DFT method, and found the ground-state saddle point on PES of this reaction; the found transition state

SCHEME 3. Cis−Trans Rearrangement of Dibromoalkenes



is consistent with the theory of this process,[43−45] and corresponds to an ionic and highly polarizable zwitterionic state. As it was previously found by us for other transition states, there are two isomers for unsymmetric alkenes **e**, **f**, and **g**.

The structures of **TS-4** possess the dihedral angle Br1−C1−C2−Br2, which is close to 90°. One carbon atom of the former double bond (C2) is sp^2 hybridized. The extent of pyramidalization of the other carbon of the former double bond (C1) strongly depends on steric factors, and correlates with the strength of the C2−Br bond. Thus, for species **TS-4′a** and **TS-4′e** (see Figure 6) with a strong C2−Br bond (2.104−2.179 Å), a significant pyramidalization of C1 was found; compound **TS-4′d** with a weak C2−Br bond (3.309 Å) possesses an almost planar C1 atom. It should be especially noted that, in contrast to previous investigations (see, for example, the study of ethylene ($CH_2{=}CH_2$) and stilbene (PhCH=CHPh isomerization[44])), the transition states **TS-4** are the saddle points on PES.

The comparison of the activation barrier values for processes I and II allows one to make some remarks on the gas-phase bromination of the alkynes. The presence of at least one hydrogen atom on the C≡C bond, and the absence of a Ph group in alkynes **1**, leads to formation of *cis*-dibromides **3b**, **3c**, **3d**, and **3g** as kinetically favorable products in the **1**−Br_2 system; in cases **1c** and **1d**, *trans*-dibromides are also expected. However, the presence of an H atom in alkynes **1a**, **1e**, and **1f** promotes the formation of 1,1-dibromides because of the ease of the migration of hydrogen in comparison to the other studied substituents. This migration is necessary in this reaction pathway. The peculiar behavior of alkynes with Ph groups is probably related to its well-known ability to stabilize the positive charge on the α-carbon atom.

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(44) Han, W. G.; Lovell, T.; Liu, T.; Noodleman, L. *ChemPhysChem* **2002**, *3*, 167−178.

(45) Viel, A.; Krawczyk, R. P.; Manthe, U.; Domcke, W. *Angew. Chem.* **2003**, *115*, 3556−3559; *Angew. Chem., Int. Ed.* **2003**, *42*, 3434−3436.

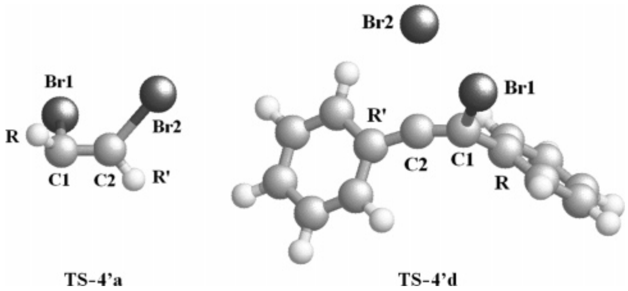
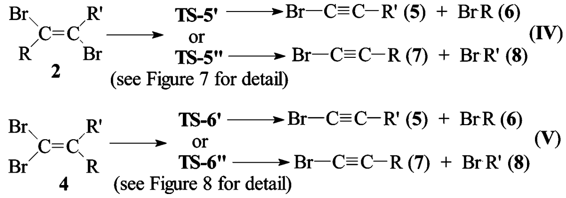


FIGURE 6. Calculated geometries of the found transition states in process III [**TS-4′** (**TS-4″**), **TS-4′a**, and **TS-4′d** are presented as examples].

SCHEME 4. Cleavage Processes for Dibromoalkenes 2 and 4



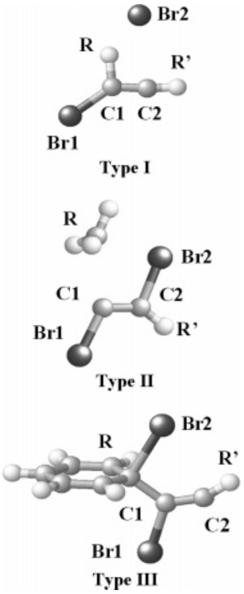


FIGURE 7. Calculated geometries of the found transition state in process IV [three different types of **TS-5′** (**TS-5″**), general view].

Thus, in general, three different addition products may form in the gas phase for the **1**−Br_2 system. Computational works based on the experimental data confirm the possibility of haloolefins (such as vinyl chloride, vinyl fluoride, 1,1-, *cis*-, and *trans*-1,2-difluoroethylenes) dissociating to give HHal as one of the products.[28−32] The dissociation process of 1,1-dichloroethylene leading to Cl_2 and C_2H_2 was also studied.[27] Different pathways for dissociation processes were found, but all of them possess relatively high activation barriers (>90 kcal/mol).

Bearing in mind the possibility of decomposition processes in the gas phase for dibromides **2**−**4**, we have investigated PESs for these compounds (Scheme 4). It has been determined that there is no direct pathway from *cis*-dibromides **3** to the decomposition products **5**−**8**. We have found processes IV and V that lead to **5**−**8**, from **2** and **4**, respectively (Table 5). The details of structures of **TS-5** and **TS-6** are shown in Figures 7 and 8. For the unsymmetrical dibromides **2** and **4**, **TS-5′** and **TS-6′** led to the elimination of H−Br, whereas **TS-5″** and **TS-6″** led to the corresponding Alk(Ph)−Br. The main geometric parameters are listed in the Supporting Information. It should be noted that the nature of the substituents at the double bond governs the type of transition state structures, which are noticeably different. Thus, the dissociation process of *trans*-dibromoalkenes with a =C−H fragment (**2a**, **2e**−**g**) leading to H−Br is characterized by the weakening of the C−Br bond in **TS-5′** (type I, Figure 7), whereas the same processes leading to formation of Alk−Br pass through **TS-5′** (**2a**−**c**) or **TS-5″** (**2e** and **2f**), which possess a weak C−C= contact (type II, Figure 7). The formation of Ph−Br from **2d** (**TS-5′**) and **2g** (**TS-5″**) is characterized by type III of **TS-5**, in which very close contact of Ph−Br was found (Figure 7). The same trends were also detected for **TS-6** (Figure 8). We propose that the main reason for the possible existence of transition states **TS-5** and **TS-6** is the energetics of the process of the $H^{\delta+}$ formation in comparison with the $C^{\delta+}\equiv$ formation in the gas phase. Both of these processes (IV and V) require very high energy inputs. Formation of H−Br is considerably more favorable in comparison to the formation of Alk(Ph)−Br for both processes IV and V. Thus, the dissociation processes of **2** and **4** leading to Alk(Ph)−Br look physically unreal.

Analysis of the Alkyne (1)−Br_2 System in Chloroform Solution (as a Supermolecule). To estimate the solvent effects on the bromination process of alkynes, we studied the bromination reaction of **1b** (π-**C**−**Ib** → **3b**) in chloroform. The solvent influence was simulated by the addition of six molecules of $CHCl_3$ to the system (cluster model). The found transition state (process I, Scheme 2) **TS-1′b***6$CHCl_3$ with the starting π-complex π-**C**−**Ib***6$CHCl_3$ and the product **3b***6$CHCl_3$ are shown

TABLE 5. Activation Barriers for the Reactions of Processes IV and V (kcal mol^{-1})

process/compound	a	b	c	d	e	f	g
R	H	Me	*t*-Bu	Ph	H	H	H
R′	H	Me	*t*-Bu	Ph	Me	*t*-Bu	Ph
E(act) **2** → **5** + **6** (**TS-5′**)	type I 64.18	type II 110.21	type II 70.04	type III 89.76	type I 63.94	type I 61.34	type I 65.51
E(act) **2** → **7** + **8** (**TS-5″**)					type II 111.27	type II 98.88	type III 84.82
E(act) **4** → **5** + **6** (**TS-6′**)	type I 72.71	type II 106.69	type II 87.74	type III 82.49	type I 63.78	type I 56.53	type I 55.79
E(act) **4** → **7** + **8** (**TS-6″**)					type II 106.24	type II 92.27	type III 93.87

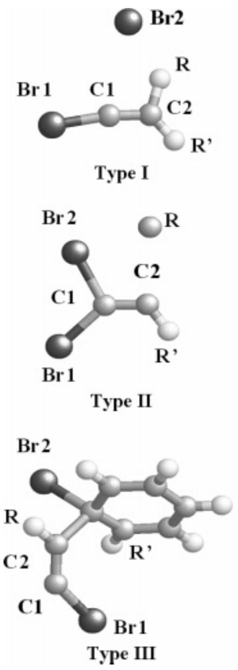


FIGURE 8. Calculated geometries of the found transition state in process V [three different types of **TS-6′** (**TS-6″**), general view].

in Figure 9. The structure of this transition state is close to that found for the gas-phase reaction (**TS-1′b**), with a minor elongation of Br1–Br2 (0.15 Å), Br2–C1 (0.10 Å), and Br2–C2 (0.08 Å); i.e., in chloroform solution the proposed process passes through a slightly more ionic transition state than that for the gas phase (**TS-1′b**). It should be noted that, as expected, the activation barrier was found to be considerably lower for the bromination reaction leading to *cis*-dibromoethylene (**3b**) in $CHCl_3$ solution (supermolecule procedure, 23.57 kcal mol^{-1}) than that in the gas phase (47.35 kcal mol^{-1}). However, the calculated barrier (23.57 kcal mol^{-1}) is higher than that found for the bromination process with two bromine molecules (see below).

Analysis of the Alkyne (1)–2Br$_2$ Two-Molecule System. As stated above, the examination of alkyne bromination with one bromine molecule and one molecule of the organic substrate is suitable for the description of the processes in the gas phase. However, the generally accepted mechanism of these reactions in solution involves the formation of a π-complex of the alkyne molecule with two molecules of bromine. This was confirmed by both experimental and calculated data for C_2H_2 (**1a**).[10,16] Herges et al. have found that three different types of such complexes derived from **1a** may exist.[16] We have optimized the structures of **1**–$2Br_2$ π-complexes and found only one type of structure as local minima. The general view of these complexes (π-**C**–**II**) is shown in Figure 10. The structural parameters of these compounds are presented in the Supporting Information; relative energies are presented in Table 6. The geometry data verify the nature of these species as π-**C**–**I** complexes, with an additional bromine molecule that is weakly bound to the triple-bonded bromine atom (Br2). In all studied cases, π-**C**–**II** complexes have considerably lower values of E_{total} than those for starting **1** + $2Br_2$ and π-**C**–**I** + Br_2. No transition states have been found for reactions π-**C**–**I** + $Br_2 \rightarrow$ π-**C**–**II**. It should be noted that although the formation of the carbocation (**CC**) with $Br_3^{\ominus}$ from the π-**C**–**II** complex is more favorable than the dissociation of π-**C**–**I** (**CC** + $Br^{\ominus}$), the activation barrier is very high (Table 7). No transition states for this type of process were found.

TABLE 6. Calculated Relative Energies (ΔE, kcal mol^{-1}) of 2:1 Br$_2$–Alkyne π-Complexes (π-C–II)

	a	**b**	**c**	**d**	**e**	**f**	**g**
R	H	Me	*t*-Bu	Ph	H	H	H
R′	H	Me	*t*-Bu	Ph	Me	*t*-Bu	Ph
ΔE	−8.11	−13.61	−13.77	−10.94	−11.08	−11.58	−11.71
ΔE^{a}	−4.08	−5.71	−6.32	−5.85	−5.08	−5.37	−5.94

[a] $\Delta E = E_{total}$π-**C**–**II** − E_{total}π-**C**–**I**.

As stated above, the main question in the mechanism of the alkyne bromination that is still unresolved is how *cis*- and *trans*-dibromoalkenes are formed from the π-**C**–**II** complex if the formation of the carbocation (**CC**) is disadvantageous. Herges et al. suggested that in nonpolar solvent, the reaction may proceed without the formation of a cationic intermediate: "The Br_3 anion forms a covalent bond with the cationic center. This tribromide adduct forms from a π-complex, and rearranges directly to the product (dibromide) without passing through a cationic intermediate."[16] However, only *cis*-dibromides

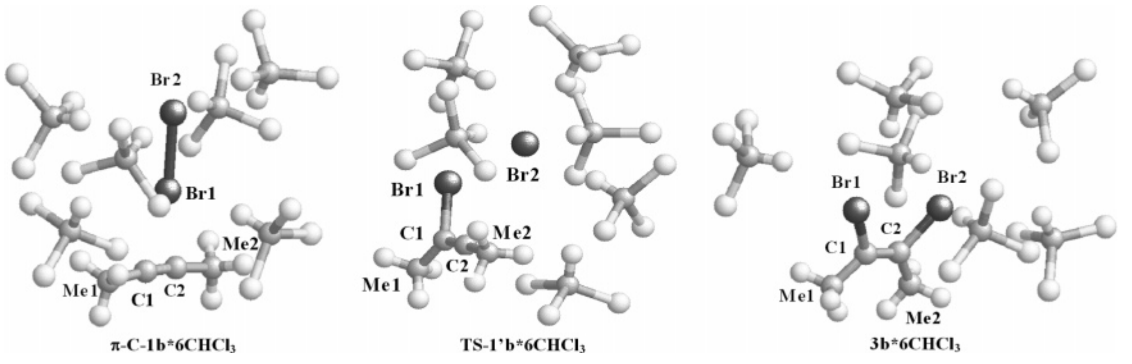


FIGURE 9. Results of the study of the bromination reaction as a supermolecule calculation. The found transition state (process I, Scheme 2) **TS-1b′**$*6CHCl_3$, the starting π-complex π-**C**–**Ib**$*6CHCl_3$, and the product **3b**$*6CHCl_3$. The main geometrical parameters for **TS-1b′**$*6CHCl_3$ (bond lengths, Å; angles, deg): Br1–Br2 = 3.106, Br1–C1 = 2.001, Br1–C2 = 2.755, Br2–C1 = 4.150, Br2–C2 = 3.859, C1–C2 = 1.281, C1–R = 1.501, C2–R′ = 1.418; Br1–Br2–C2 = 45.0, Br1–C1–C2 = 112.3, Br1–C1–R = 116.0, Br2–Br1–C1 = 106.7, Br2–C2–C1 = 94.0, Br2–C2–R′ = 89.1, C1–C2–R′ = 176.6, C2–C1–R = 131.7.

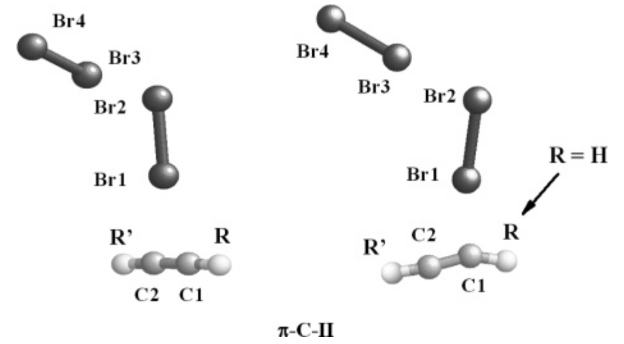


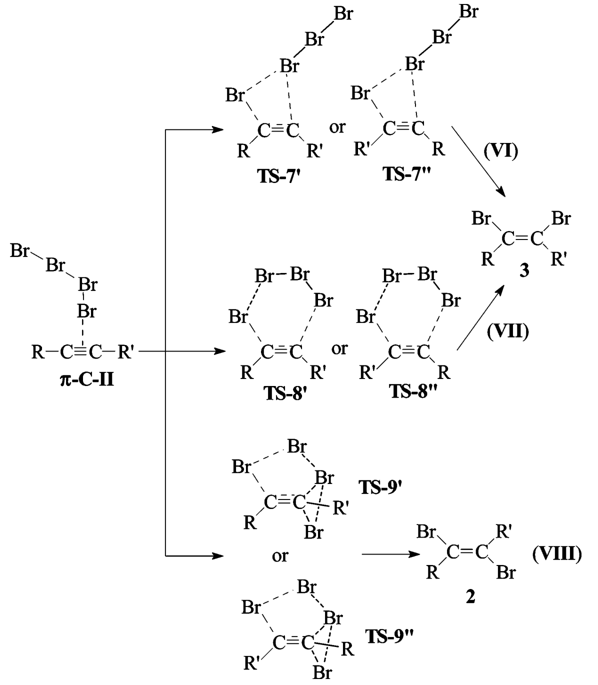
FIGURE 10. Calculated geometries of π-complexes π-**C**−**II** derived from symmetrical and unsymmetrical alkynes (general views).

TABLE 7. Relative Energies (ΔE, kcal mol^{-1}) of [CC + $Br_3^{\ominus}$] Systems, and Calculated Values of ΔE^a that Are Evaluative Values of E_{act} of the π-C−II → CC + $Br_3^{\ominus}$ Rupture Process

	a	b	c	d	e	f^b	g
R	H	Me	*t*-Bu	Ph	H	H	H
R′	H	Me	*t*-Bu	Ph	Me	*t*-Bu	Ph
ΔE	114.94	88.47	77.79	71.69	98.74		73.59
ΔE^a	123.06	102.08	91.56	82.63	109.82		85.29

[a] $\Delta E = E_{total}(CC + Br_3^{\ominus}) - E_{total}\pi$-**C**-**II**. [b] This cation is unstable (see discussion).

SCHEME 5. Bromination Pathways Starting from π-Complex π-C−II



may form in this way. The formation of *trans*-dibromides was still in question. It should be noted (see Introduction) that these species at least form from sterically nonhindered alkynes during bromination. We have studied the possible pathways from π-**C**−**II** complexes to the dibromoalkenes, and three different processes were found (Scheme 5). Two of them (VI and VII) led to *cis*-derivatives **3**, but one (VIII) led to *trans*-dibromoalkenes **2**.

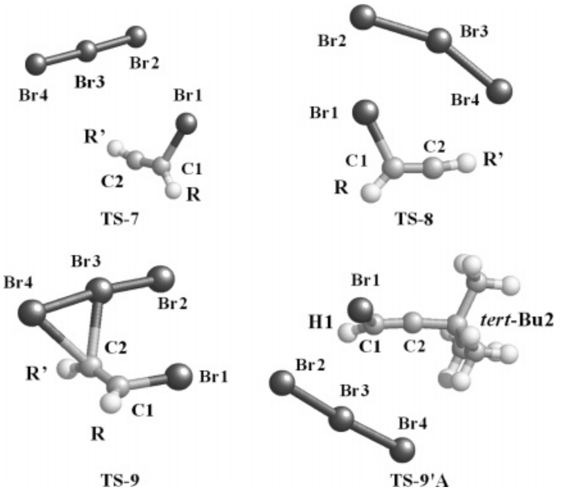


FIGURE 11. Calculated geometries of the found transition states in processes VI, VII, and VIII [**TS-7′** (**TS-7″**), **TS-8′** (**TS-8″**), and **TS-9′** (**TS-9″**), as well as **TS-9′A**, general views]. The main geometrical parameters for **TS-9′A** (bond lengths, Å): Br1−Br2 = 3.520, Br1−Br3 = 3.723, Br1−Br4 = 5.235, Br1−C1 = 1.949, Br1−C2 = 2.663, Br2−Br3 = 2.588, Br2−Br4 = 5.154, Br2−C1 = 4.215, Br2−C2 = 5.281, Br3−Br4 = 2.569, Br3−C1 = 3.426, Br3−C2 = 4.087, Br4−C1 = 4.232, Br4−C2 = 4.186, C1−C2 = 1.280, C1−R = 1.087, C2−R′ = 1.429; for angles see Supporting Information.

The transition states **TS-7**, **TS-8**, and **TS-9** sufficiently differ from each other (Figure 11, see Supporting Information for geometric parameters). **TS-7** structures may be considered as the analogues of **TS-1** in which the additional bromine molecule stabilizes the $Br^{\ominus}$ to form according to the geometrical parameters of the $Br_3^{\ominus}$ ion. Correspondingly, the new Br−C bond forms between the C2 atom and the Br2 atom, which is the nearest atom to the Br1 bound with C1. In contrast to **TS-7**, **TS-8** possesses the Br−Br−Br fragment, which may not be considered as $Br_3^{\ominus}$ ion due to its nonlinearity. This fragment also attacks the cationic carbon center as it was found for **TS-7**, but the bond forms between the long bromine atom (Br4) and C2. Both processes VI and VII led to *cis*-isomers **3**.

According to the IRC analysis results, process VIII, which passed through **TS-9** and led to the trans isomers **2**, is characterized by the linear transfer of the Br−Br−Br fragment with regard to the C2 atom. This transfer is accompanied by the rotation of the C2−R(R′) fragment around the C1−C2 bond.

In general, there are not remarkable differences between the structures of **TS-7′** and **TS-7″**, **TS-8′** and **TS-8″**, and **TS-9′** and **TS-9″**. It should be also noted that for *tert*-butylacetylene, the additional transition state (**TS-9′A**) was also found (Figure 11).

The comparison of activation barrier values for processes VI, VII, and VIII (Table 8) allows one to make several conclusions on the bromination of alkynes. The terminal alkynes **1a**, **1f**, and **1g** react more easily with the bromine than do their disubstituted analogues. This conclusion is supported by the experimental data that show slow reaction rates for these reactions for sterically hindered derivatives.[16] According to our data, phenylacetylene (**1g**) and diphenylacetylene (**1d**) give mixtures of the corresponding **2** and **3** products. This fact is

TABLE 8. Activation Barriers for Processes VI, VII, and VIII (kcal mol^{-1})[a]

process/compound	**a**	**b**	**c**	**d**	**e**	**f**	**g**
R	H	Me	*t*-Bu	Ph	H	H	H
R′	H	Me	*t*-Bu	Ph	Me	*t*-Bu	Ph
E(act) π-**C**−**II** → **3** (**TS-7′**)	32.68	30.26	29.28	22.87	27.34	28.04	14.64
E(act) π-**C**−**II** → **3** (**TS-7″**)					35.75	38.64	41.91
E(act) π-**C**−**II** → **3** (**TS-8′**)	21.27	26.01	27.91	26.97	21.65	24.65	17.66
E(act) π-**C**−**II** → **3** (**TS-8″**)					25.89	28.52	32.62
E(act) π-**C**−**II** → **2** (**TS-9′**)	13.54	19.90	27.91	23.67	16.45	23.40	25.60
E(act) π-**C**−**II** → **2** (**TS-9″**)					19.42	21.07	15.93
E(act) π-**C**−**II** → **2** (**TS-9A′**)						24.80	

[a] The DFT study of the bromination of various alkynes gave values of activation barriers for processes leading to *cis*-, *trans*-, and 1,1-dibromoalkenes without ionic intermediates.

consistent with the data of Uemura et al. and of Bianchini and co-workers.[9,10] As expected, the reaction of sterically hindered **1c** may lead to **3c** (cis product) or **2c** (trans product). The mixture of *cis*- and *trans*-dibromides may also form in the case of *t*-Bu-acetylene, but the trans derivative predominates. The other studied systems, i.e., dimethylacetylene (**1b**), methylacetylene (**1e**), as well as acetylene itself (**1a**), have to form the trans isomers **2** as a single product of the bromination reaction. This behavior also corresponds with experimental data.[9,10] It should be noted that the values of the activation barriers found by Herges et al.[16] for acetylene (**1a**) bromination resulting in **3a** are 23.72 and 28.43 kcal mol^{-1} (depending on the type of starting π-complex). These magnitudes are sufficiently larger than those found by us (Table 8).

Conclusions

We have carried out the theoretical analysis of the bromination of various substituted alkynes. According to our calculation data, the gas-phase bromination of alkynes **1** leads, in general, to three different products: *cis*-dibromoalkenes **3**, 1,1-dibromoalkenes **4**, and *trans*-dibromoalkenes **2** (as a result of isomerization of **3**). The process of formation of **3** prevails for phenylacetylene (**1g**) and disubstituted alkynes (**1b**−**d**). The presence of a hydrogen atom in the alkynes **1a**, **1e**, and **1f** promotes the formation of 1,1-dibromides **4**. The pathway for the bromination of dimethylacetylene (**1b**) with one bromine molecule in chloroform (the supermolecule approach) is more favorable than the reaction in the gas phase, but is still high in comparison with that found for the bromination reaction with two bromine molecules. Dibromoalkenes **2** and **4** may decompose, resulting in bromoacetylenes and alkylbromides (phenylbromide or HBr) **5**−**8**. The formation of HBr is the most favorable among possible cleavage processes. With regard to solution reactions, we have found that both *trans*- and *cis*-dibromoalkenes (**2** and **3**) may ensue without the formation of ionic intermediates from a π-complex of two bromine molecules with the alkyne. The geometry around the forming double bond in dibromoalkenes strongly depends on the nature of the substituents at the triple bond. Among studied compounds, the formation of trans derivatives **2** is favorable for acetylene (**1a**), methylacetylene (**1e**), and dimethylacetylene (**1b**); sterically hindered alkynes **1c**, **1d**, **1f**, and **1g** may lead to a mixture of **2** and **3**. In general, the terminal alkynes, as well as acetylene, undergo bromination more easily than their disubstituted analogues. These results are in good agreement with available experimental data.

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Supporting Information Available: Calculated main geometric parameters of starting alkynes (**1**), *trans*-dibromides (**2**), *cis*-dibromides (**3**), 1,1-dibromides (**4**), bromoacetylenes Br−C≡C−R(R′) (**5**, **7**) and R(R′)−Br (**6**, **8**), and their energies. Calculated main geometric parameters of **TS-1**−**TS-9.** Cartesian coordinates of transition states and stable compounds together with the total energies and numbers of imaginary frequencies. This material is available free of charge via the Internet at http://pubs.acs.org.

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