Strain and Reactivity: Electrophilic Addition of Bromine and Tribromide Salts to Cyclic Allenes

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Abstract: The kinetics and the products of the bromination of several cyclic allenes, from C_9 to C_{13} (**1a**–**e**), with tetrabutylammonium tribromide (TBAT) and Br_2 have been investigated in 1,2-dichloroethane (DCE) and methanol. The first product of the interaction between the allene and Br_2 is a 1:1 π complex. The stability constant of this complex, determined at 25 °C for allene **1a**, is 7.4 M^{-1}. The comparison of this value with those reported for several alkenes and alkynes further support the hypothesis of the existence of sizeable structural effects on the stability of these complexes. The negative values of the apparent activation energy for the reaction of allenes **1a**–**e** with Br_2 in DCE demonstrate the involvement of these complexes as essential intermediates along the reaction coordinate. Different stereochemical behavior was observed in the bromine addition on going from the strained 1,2-cyclononadiene to the larger compounds. Furthermore, a solvent-dependent stereochemistry has been observed for each compound. The kinetic and product distribution data have been interpreted in terms of the influence of the strain on the nature of the intermediate and by considering the competition between pre-association and ion-pair pathways on going from aprotic to nuclophilic solvents or when nucleophilic bromide ions are added. Ab initio (MP2/6-311 + G**) and density functional (B3LYP/6-311 + G**) computations of 1:1 Br_2 complexes showed that the association energies of allene · Br_2 and ethene · Br_2 complexes are nearly the same but are greater than that of acetylene · Br_2 complexes. Allene · 2 Br_2 complexes are more stable than their ethene · 2 Br_2 counterparts. Br_2 · allene · Br_2 structures, in which the bromine molecules interact either with a single allene double bond or individually with both double bonds, are not preferred significantly over alternatives with $Br_2 \cdots Br_2$ interactions. As a result of the entropy, the association of bromine with unsaturated hydrocarbons is usually unfavorable in the gas phase (except at extremely low temperatures); complexes are observed in solution (under ambient conditions), since the entropy loss is reduced as a result of restricted translation and rotation and possible association to the solvent. The 1,2-cycloheptadiene · Br_2 > 1,2-cyclononadiene · Br_2 > 1,3-dimethylallene · Br_2 association energies increase with ring strain.

Keywords: allenes · bromination · charge-transfer complex · electrophilic addition · reaction mechanisms · steric strain

Introduction

The relationship between steric strain and chemical reactivity has been an important theme throughout chemistry. Strain often manifests itself with increased chemical reactivity.[1] However, despite the importance of strain in organic and biological chemistry, the quantitative relationship to chemical reactivity is only beginning to be understood.[1, 2]

The incorporation of multiple bonds into small cyclic compounds produces substantial strain energy. The limiting size in *trans*-cycloalkenes is seven carbon atoms[3] and, although for simple *cis*-cycloalkenes there is not a limiting ring size, cyclobutene and cyclopropene have high angle-strain energies. In contrast, no experimental proof for the intermediary existence of cyclobutyne has been found,[3a] and ab initio calculations revealed that cyclopropyne does not

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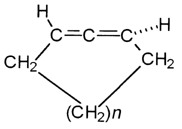
even possess a minimum on the energy hypersurface.[3b] As a result of the angle strain, simple cycloalkynes become isolable for rings with eight or more ring atoms. Though cyclic allenes with less than eleven carbon atoms are less strained than the isomeric acetylenes, the smallest isolable unsubstituted cyclic allene is 1,2-cyclononadiene. In consequence of the ring strain, a *cis* bending of the C−C≡C angles in cycloalkynes is observed, whereas strain in cycloallenes bends the cumulated double bond system ($\theta \neq 180°$) and/or twists ($\phi \neq 90°$) the two plains containing the double bonds.[4]

Recent work on bromine addition to alkenes showed that steric strain markedly affects the reactivity of the double bond.[5] The aim of the present study, therefore, was to quantitatively evaluate the kinetic and thermodynamic consequences of strain in cyclic allenes. Several cyclic allenes **1a–e** have been prepared and their bromination rates, both with bromine and a tribromide salt, have been measured.



1a-e

a: $n = 4$; **b**: $n = 5$; **c**: $n = 6$; **d**: $n = 7$; **e**: $n = 8$;

During the 1970s, the addition of bromine to allenes was studied intensively. On the basis of stereochemical results, a mechanism was proposed that was similar, at the time, to the mechanism reported for electrophilic bromination to olefins.[6] However, more recent studies on the electrophilic bromination of ethylenic compounds have shown that the bromine addition to double bonds is a more complex process than generally reported in organic text books. Important features about the early steps of the reaction, the formation of bromine · olefin complexes, the structure of the ionic intermediates, the role of the solvent, and the lifetime of the ionic intermediates have since been reported.[7–11]

In light of these newer aspects related to the bromine addition to isolated double bonds, taking into account our initial project aim, that is, the study of the correlation between steric strain and reactivity, we have reinvestigated the bromination of 1,3-disubstituted allenes. The relationship between steric strain and reactivity has been discussed in light of the mechanisms more recently proposed for Br_2 and Br_3^- addition to double and triple bonds.

Results and Discussion

Formation of a charge transfer complex between bromine and allene 1a: Compounds **1a–e** react quickly with Br_2 in 1,2-dichloroethane (DCE). In spite of this, the early stages of the reaction could be investigated when diluted solutions of Br_2 (around 1×10^{-4} M) were mixed with an excess of unsaturated compounds in a stopped-flow apparatus. Under these conditions the spectrum of the solutions at 25 °C showed, beyond the allene absorption region, a large differential absorption with respect to the reagents alone, interpreted as a charge-transfer band. The absorbances measured for the Br_2 absorption minimum (300–350 nm) immediately after mixing increased, at constant [Br_2], with increasing unsaturated compound concentration. Unfortunately, the strong absorbances of all the unsaturated compounds examined, probably owing to small amounts of impurities at least in some cases, did not allow us to establish the absorption maximum of the newly formed species and markedly reduced the chance to determine the formation constants and molar absorption coefficients of these complexes using Scott plots[12] or a multiwavelength fitting procedure.

Reliable spectrometric data for the evaluation of the formation constant and molar coefficient of the newly formed transient species were obtained only for **1a**; the moderate absorption above 320 nm allowed us to use an appropriate excess of allene. The initial absorbance-reagent concentration data measured at 25 °C and 320 nm were fitted to the Scott equation for 1:1 complexes. A satisfactory fitting ($r = 0.998$) was obtained, giving $K_f = 7.4(1)\,\mathrm{M}^{-1}$ and $\varepsilon_{320} = 2985\,\mathrm{M}^{-1}\mathrm{cm}^{-1}$ for the π complex at 25 °C.

It is noteworthy that although no data about the formation constant of charge transfer complexes between bromine and allenes have been reported, the value found in this work for the disubstituted allene **1a** is quite high, at least when it is compared with the values found for a disubstituted cyclic unstrained alkene (cyclohexene: $K_f = 0.47\,\mathrm{M}^{-1}$)[13] and a disubstituted cyclic unstrained alkyne (cyclododecyne: $K_f = 0.40(0.05)\,\mathrm{M}^{-1}$),[14] suggesting that the presence of the cumulated double bond and/or that the strain may affect the stability of these transient species. Structural data for 1,2-cyclononadiene predict[4] that the allene will be bent from linearity by 10° and that this bending, which will destroy the degeneracy of π and π* orbitals and affect the HOMO and LUMO energies, may influence the stability of the first-formed π complex. A very high stability constant for the π complex between bromine and an isolated double bond, which has been attributed to the steric strain present in the alkene, has been recently observed in the case of *trans*-(1-methyl-2-adamatylidene)-1-methyladamantane.[5b]

Kinetic measurements: The rates of bromination of compounds **1a–e** with Br_2 were first determined in DCE, the solvent in which the π complex had been investigated. For these measurements solutions of the reagents were mixed in a stopped-flow apparatus, both at identical concentrations and with a large excess of allene, while the disappearance of Br_2 at the visible absorption band was monitored. A third-order rate law [Eq. (1)] was always obeyed for at least two half-lives, as usually found for alkene[15] and alkyne[16] bromination in low-polar aprotic solvents, showing that two bromine molecules were involved in the rate determining step of the overall reaction.

$$-[Br_2]/dt = k_3[Br_2]^2[Al] \tag{1}$$

To determine the activation parameters, the kinetics were measured at three temperatures. The average third-order rate constants are reported in Table 1 together with the activation parameters obtained from the Arrhenius plots.

Rate constants for bromine addition to allenes have also been determined in methanol using a stopped-flow apparatus. At the Br_2 concentrations employed the reactions obeyed, up

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Table 1. Kinetic constants and apparent activation parameters for the reaction of Br_2 with allenes **1a**–**e** in DCE.

	T [°C]	k_3 [$M^{-2}s^{-1}$]	$E_{a(app)}$ [kcal mol^{-1}]	$\Delta H^{\ddagger}$ [kcal mol^{-1}]	$\Delta S^{\ddagger}$ [eu]	k_{rel}[a]
1a	8	4.30 (0.3) × 10^7				
	21	3.35 (0.3) × 10^7				
	39	2.10 (0.2) × 10^7	– 4.4 (0.4)	– 5.0	– 41 (1)	200
1b	10	8.0 (0.3) × 10^5				
	25	5.8 (0.2) × 10^5				
	40	4.2 (0.2) × 10^5	– 3.8 (0.3)	– 4.4	– 47 (2)	1.1
1c	10	3.5 (0.2) × 10^5				
	25	2.5 (0.2) × 10^5				
	40	2.1 (0.2) × 10^5	– 3.3 (0.2)	– 3.9	– 46 (1)	0.5
1d	10	4.4 (0.2) × 10^5				
	25	3.3 (0.2) × 10^5				
	40	2.7 (0.2) × 10^5	– 2.7 (0.2)	– 3.3	– 44 (1)	0.65
1e	10	5.95 (0.2) × 10^5				
	25	5.1 (0.3) × 10^5				
	40	3.8 (0.2) × 10^5	– 2.6 (0.2)	– 3.2	– 44 (1)	1

[a] Relative rates of bromination of allenes at 25 °C.

Table 2. Kinetic constants and activation parameters for the reaction of Br_2 with allenes **1a**–**e** in methanol.

	T [°C]	k_2 [$M^{-1}s^{-1}$]	E_a [kcal mol^{-1}]	$\Delta H^{\ddagger}$ [kcal mol^{-1}]	$\Delta S^{\ddagger}$ [eu]	k_{rel}[a]
1a	5	1.77(0.05) × 10^4				
	25	2.60(0.05) × 10^4				
	40	3.68(0.05) × 10^4	3.55 (0.3)	2.95	– 28.2 (1)	11
1b	10	1.41(0.02) × 10^3				
	25	2.12(0.02) × 10^3				
	40	2.95(0.03) × 10^3	4.33 (0.15)	3.72	– 31 (1)	0.9
1c	10	7.20(0.20) × 10^2				
	25	1.17(0.02) × 10^3				
	40	1.84(0.10) × 10^3	4.45 (0.10)	3.86	– 37 (1)	0.5
1d	10	1.73(0.08) × 10^3				
	25	2.51(0.05) × 10^3				
	40	3.50(0.08) × 10^3	4.15 (0.15)	3.55	– 39 (1)	1.1
1e	10	1.77(0.08) × 10^3				
	25	2.34(0.10) × 10^3				
	40	2.75(0.10) × 10^3	4.59 (0.15)	3.99	– 36 (1)	1

[a] Relative rates of bromination of allenes at 25 °C.

to at least 80% conversion, the second-order rate law of Equation (2), as usually observed in bromine addition to isolated double bonds in this solvent.[7] Although the tribromide concentration[17] was not controlled by the addition of external bromide ions [Eq. (3)], Equation (2) was always followed, showing that the kinetic term related to bromide concentration [Eq. (4)] was not significant under these experimental conditions.[18]

$$-[Br_2]/dt = k_2[Br_2][Al] \qquad (2)$$

$$Br_2 + Br^- \Leftrightarrow Br_3^- \qquad (3)$$

$$k_{exp}(1 + K[Br^-]) = k + Kk_{Br_3^-}[Br^-] \qquad (4)$$

The average second-order rate constants and the activation parameters are reported in Table 2

It is noteworthy that negative values for the apparent activation energy were found for bromine addition to allenes **1a**–**e** in DCE, while positive values characterized the reactions of the same allenes in methanol. As it has been previously emphasized,[13, 16] a negative value of the apparent activation energy is considered to be conclusive evidence of the involvement of at least one complex between bromine and the unsaturated system on the reaction coordinate. Therefore, considering the above-reported results related to the formation of a charge-transfer complex, the reaction of allenes with Br_2 in chlorinated solvent is surely characterized by the initial formation of a 1:1 bromine- allene π complex. This behavior is in agreement with the proposed mechanism of bromine addition to isolated double bonds.[7–9] The positive activation parameters found for the reaction in methanol give no indication about the involvement of a π complex on the reaction coordinate; however, it is highly probable that, in analogy with isolated double bonds, a 1:1 π complex is involved even in this medium.

It is noteworthy that an increase in the relative rates of bromination on going from the cycloallenes **1b**–**e** to **1a** has been observed in the bromine addition both in DCE and methanol. Although this increase is moderate, at least in methanol, it can be ascribed to the higher strain energy of **1a**[4] and suggests that, in the strained 1,2-cyclononadiene, the rehybridization which occurs on going from reagents to products results in a partial strain relief in the rate-determining transition state. Analysis of the activation parameters gives further information about the transition state. For the reactions carried out in DCE the apparent activation energies ($E_{a(app)}$) vary uniformly. That is, on going from **1e** to **1a**, the apparent activation energies become more negative, while the entropy of activation ($\Delta S^{\ddagger}$) have little variation for allenes **1b**–**e**, $\Delta S^{\ddagger}$ values range from –44 to –47, while allene **1a** has a slightly lower $\Delta S^{\ddagger}$. Entropy differences between bromination of **1a** and those of the other allenes probably reflect greater ring flexibility in the transition state of **1a**, which may be related to the different nature of the intermediate having a more carbocation character (see below). A lower activation energy, as well as an entropy of activation, has been found also in the bromination of **1a** in methanol. In this case however, no trend was observed and the differences in the activation energies between **1a** and **1b**–**e** were lower than in DCE. This behavior may be related to the involvement of pre-association phenomena in the nucleophilic methanol in the reactions of **1b**–**e**, but not in that of **1a**. The relatively high values of activation entropies for these allenes in methanol were also in agreement with a pre-association mechanism for the reactions of **1b**–**e**. They are very similar to those found in DCE, a solvent in which bromination occurs through a termolecular transition state.

Finally, rate constants for the tetrabutylammonium tribromide (TBAT) addition to allenes **1a**–**e** in DCE were measured at three different temperatures. The reactions, monitored with a conventional spectrophotometer, followed the overall second-order rate law of Equation (5) (the kinetic constants and the activation parameters are reported in Table 3), which is similar to the rate law found for Br_3^- addition to alkenes[20] and alkynes.[16]

$$-[Br_3^-]/dt = k_2[Br_3^-][Al] \qquad (5)$$

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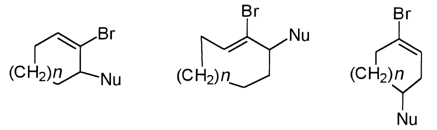
Table 3. Kinetic constants and activation parameters for the reaction of TBAT with allenes **1a**–**e** in DCE.

	T [°C]	K_2 [$\mathrm{M}^{-1}\mathrm{s}^{-1}$]	E_a [kcal mol^{-1}]	$\Delta H^{\neq}$ [kcal mol^{-1}]	$\Delta S^{\neq}$ [eu]
1a	10	0.17 (0.01)			
	25	0.32 (0.02)			
	40	0.53 (0.05)	6.73 (0.3)	6.13	– 40 (1)
1b	10	0.58 (0.05)			
	25	0.99 (0.08)			
	40	1.69 (0.10)	6.26 (0.3)	5.67	– 39.5 (1)
1c	10	0.06 (0.005)			
	25	0.16 (0.02)			
	40	0.26 (0.02)	8.63 (1.5)	8.05	– 35.5 (1)
1d	10	0.15 (0.01)			
	25	0.28 (0.02)			
	40	0.45 (0.05)	6.33 (0.3)	5.74	– 42 (1)
1e	10	0.06 (0.005)			
	25	0.15 (0.01)			
	40	0.30 (0.02)	9.45 (0.5)	8.85	– 33 (1)

Moreover, in analogy with the addition to isolated double or triple bonds, the reaction of Br_3^- with allenes is characterized, in contrast with the Br_2 addition in the same solvent, by a positive activation energy.[20]

It is noteworthy that, at variance with bromine addition, there is practically no correlation between the strain energy and reactivity in this reaction. 1,2-Cyclononadiene reacts at the same rate as all the other allenes and the activation parameters found for the bromination of **1a** with TBAT are very similar to those of other unstrained cycloallenes, showing that the strain energy present in the starting 1,2-diene is maintained in the transition state (TS).

Product analysis: (*E*)-2,3-Dibromocycloalkenes **2** or mixtures of (*E*)- and (*Z*)-2,3-dibromocycloalkenes **2** and **3** were obtained by reaction of allenes **1a**–**e** with TBAT in DCE. All compounds were identified by the NMR spectra of the reaction mixtures, from which the product distribution was also obtained (Table 4). The relative configurations of the two dibromo adducts were established for **2a**–**c**, **2e**, **3b**, **3c** and **3e** by comparison of the ^{1}H NMR signals with the reported data,[21–24] while for **2d** and **3d** it was assigned on the basis the allyl and vinylic hydrogen chemical shifts conforming to trends of the analogous dibromo adducts **2b**, **2c**, **2e** and **3b**, **3c**, **3e**.



Nu = Br	**2**	**3**	**4**
Nu = OCH$_3$	**5**	**6**	**7**

The addition of bromine to allenes **1a**–**e** was carried out at 0 °C in DCE and in methanol with allene and Br_2 concentrations of 10^{-2} M. When the bromine addition to allenes was carried out in methanol to avoid possible solvolysis reactions, the reaction mixtures were diluted with water and the products were extracted with dichloromethane immediately after the end of the brominations. The (*E*)- and (*Z*)-methoxy bromides **5** and **6** were obtained by reaction of allenes **1a**–**e** with Br_2 in methanol. All compounds were identified by the NMR spectra of the reaction mixtures. The configurations of the methoxy bromides were assigned, for **5a**, **5b**, **5e** and **6e**, by comparison of the ^{1}H NMR signals with the reported data,[25, 26] while for **5c**, **5d** and **6c** assignments were made on the basis the allyl and vinylic hydrogen chemical shifts taking into account the observed trend in the analogous adducts. The formation of the 1,4-dibromo or 1,4-bromomethoxy adduct, arising by way of a transannular 1,5-hydride shift,[6] was observed only in the case of **1a**. Nevertheless, bromine addition in DCE to allenes **1b**–**e** always gave the two isomeric dibromo adducts **2** and **3** as the main products (80 %) and one or more byproducts.

The distribution of dibromides and methoxy bromides found for all allenes **1a**–**e** are reported in Tables 4 and 5.

Table 4. Product distribution for the bromination (Br_2 or TBAT) of allenes **1a**–**e** in DCE.

		Products [%]		
		2	**3**	**4**
1a	TBAT	100		
	Br_2	30		70
1b	TBAT	100		
	Br_2[a]	45	35	
1c	TBAT	23	77	
	Br_2[a]	36	47	
1d	TBAT	100		
	Br_2[a]	50	30	
1e	TBAT	22	78	
	Br_2[a]	33	57	

[a] Dibromides **2** and **3** were formed besides smaller amount of byproducts.

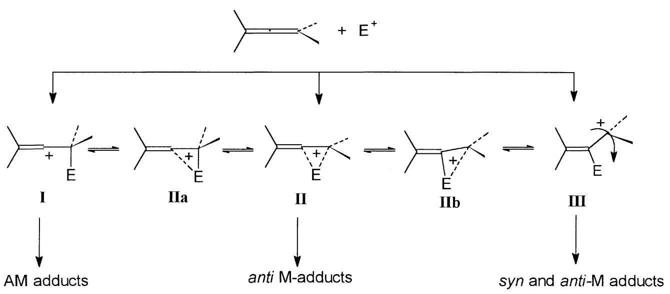
Table 5. Product distribution for Br_2 addition to allenes **1a**–**e** in MeOH.

	Products [%]		
	5	**6**	**7**
1a	30		70
1b	100		
1c	10	90	
1d	100		
1e	20	80	

Stereochemistry and chemoselectivity

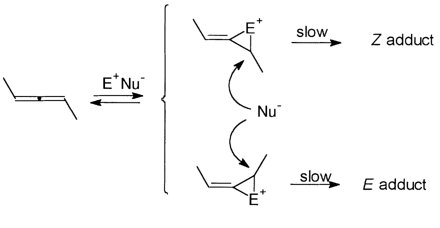
Br_2 addition: The electrophilic addition of a reagent (EN) to allenes can occur through three different pathways to give a larger number of intermediates: a) electrophilic attack at the terminal carbon atom leading to a vinylic carbocation (I) which subsequently provides an anti-Markovnikov (AM) addition product; b) electrophilic attack at the central carbon atom leading to a non-planar ethylenic carbocation (III) that is able, through isomerization to the corresponding allylic carbocation after a 90° rotation around the single C–C bond,

to form Markovnikov (M) *syn* and *anti* addition products; c) electrophilic attack at both carbons producing an onium species (II) from which the attack of the nucleophile must occur from the backside to give a Markovnikov *anti*-addition product. The species II may be a fully bridged (II) or a weakly bridged intermediate (IIa or IIb), as shown in Scheme 1. It is also noteworthy that, according to the nature of the reagents and solvent, a spectrum of intermediates between complete onium ion II (no rotation) and open carbocation (I or III) may exist (Scheme 1).



Scheme 1.

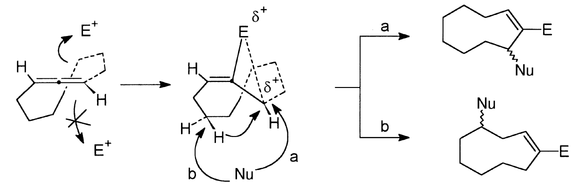
The stereochemical course of bromine addition to 1,3-disubstituted allenes was studied both in carbon tetrachloride and in methanol.[6, 27] On the basis of the *anti* stereoselectivity observed during the bromination of chiral 1,3-disubstituted allenes in both these solvents, the involvement of bridged bromonium ions was proposed.[27] Furthermore, on the basis of the mechanism reported in Scheme 1 the *Z* stereoselectivity which characterized the bromination and iodination reactions of acyclic 1,3-disubstituted allenes was explained on the basis of a reversible formation of these ionic intermediates.[6, 28] The nucleophilic attack by Y^- should be rate controlling and as it should occurs from the least hindered side of the double bond, should lead to the *Z* adduct (Scheme 2).



Scheme 2.

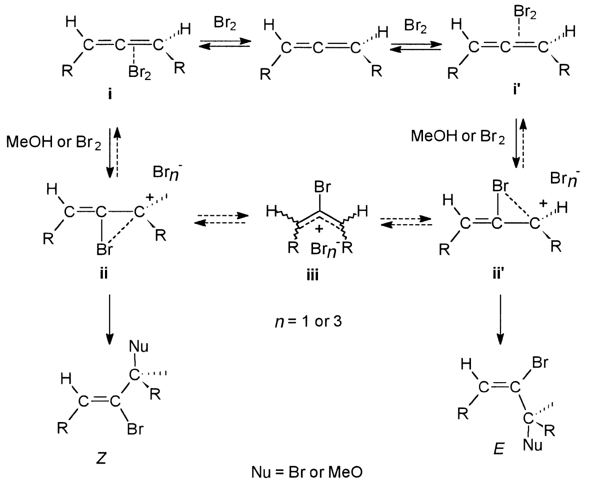
In contrast, the 100% *E* stereoselectivity encountered in the halogenation of 1,2-cyclonona- and 1,2-cyclodecadiene was attributed to the fact that in this case the electrophile enters from the less crowded face of the reacting double bond (Scheme 3).[6]

However, a more recent study using enantiomerically pure 1,3-dimethylallene has shown that at least for the addition of bromine in water, a significant loss in enantiomeric excess during the formation of the corresponding adducts occurs.[29] Open achiral cationic intermediates, formed either competitively with the chiral onium ion formation or by the partial opening of the initially formed onium ion intermediates, have therefore been invoked.[29]



Scheme 3.

On the basis of these data, kinetic measurements carried out in this work, and taking into account the product distribution, the following reaction scheme for bromine addition to allenes **1a–e** can be proposed. The reaction occurs through the initial formation of a 1:1 bromine allene π complex. Although direct evidence for its formation and involvement on the reaction coordinate have been obtained only in DCE, it is highly probable that the same complex is involved also in methanol. The initially formed complex (**i** or **i′**, in Scheme 4) evolves to the corresponding ionic intermediate and, in agreement with the reaction rate law, the ionization is electrophilically assisted by the solvent in the protic methanol (second-order reaction, first-order in bromine) and by a second molecule of bromine in DCE (third-order reaction, second-order in bromine). If bridged intermediates are involved, the formation of the *E* and *Z* adducts should arise exclusively by the *anti* collapse of the related intermediates **ii** and **ii′**. The stereochemical behavior of the reaction should be affected by steric and electronic factors during the electrophilic step if the formation of the ionic intermediate is an irreversible process, or during the electrophilic and nucleophilic steps when the ionic intermediates are able to return to reagents. However, if the reaction occurs through the formation of unsymmetrically bridged or open intermediates, represented as weakly bridged intermediates (**ii** or **ii′**) in Scheme 4, the product stereoselectivity is also affected by the rate of isomerization of the two intermediates **ii** and **ii′** through the delocalized allylic cation **iii**, and, when rotation is

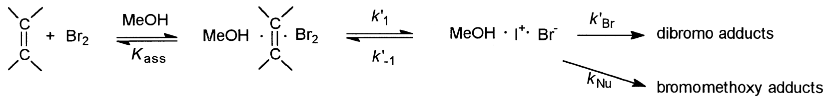


Scheme 4.

rapid, the product distribution is determined by the relative rate of collapse of these intermediates to products. The involvement of an intermediate having a considerable carbenium character has been suggested for bromine addition to **1a**.[6] In contrast with oxymercuration and sulfenylation, bromination of **1a** gives transannular addition as the main reaction pathway.[27b] This process, requiring a methylene hydrogen at C-5 (or C-8) of **1a** to be transferred to C-1 in a 1,5-shift, is probably favored by the development of positive charge at C-1. Nevertheless nucleophilic attack at C-5 (or C-8) to give the product may be synchronous or subsequent to the hydride-transfer step (Scheme 3). It is noteworthy that the formation of an intermediate having more carbenium character may remove, at least partially, the steric strain present in the starting allene. Furthermore, considering the recently reported stereochemical results on the bromination of 1,3-dimethylallene in water[29] and the low stereoselectivity observed in this work in the bromine addition to allenes **1b – e**, which always occurs with formation of byproducts, it is highly probable that at least partially bridged intermediates are involved in the bromination of these allenes in DCE. The moderate selectivity towards the *Z* isomer, observed in the reaction of **1c** and **1e**, but not in the case of **1d**, is not, therefore, to be interpreted in terms of reversible or irreversible formation of the bromonium ion intermediate, but, more likely, should be explained in terms of equilibration between open (or partially open) cationic intermediates and the rate of collapse to products.

Finally, the different stereoselectivity observed for bromine addition to allenes **1b – e** in DCE and methanol, which in principle may be related to the involvement of different intermediates, is probably due to different lifetimes of the same intermediates. On the basis of a recent kinetic and product study for stilbene bromination it was shown that, in contrast to the widely accepted postulate, bromine bridging, at least in alkenes, is not the sole stereochemistry-determining factor.[11] The stereochemical outcome is controlled also by the association of the ionic intermediate with its nucleophilic partners and its lifetime. A pre-association mechanism, of the type reported in Scheme 5, has been proposed to explain *anti* stereoselectivity observed for the bromine addition in methanol, but not in DCE, to some *para*-substituted stilbenes.[11] A pre-association mechanism of this type, depending on allene structure, could easily explain the high stereoselectivity and the absence of byproducts observed in the reaction of allenes **1b – e** in methanol, while the product distribution data for **1a** in the same solvent strongly suggest the involvement of the ion-pairs pathways, reported in Scheme 3.

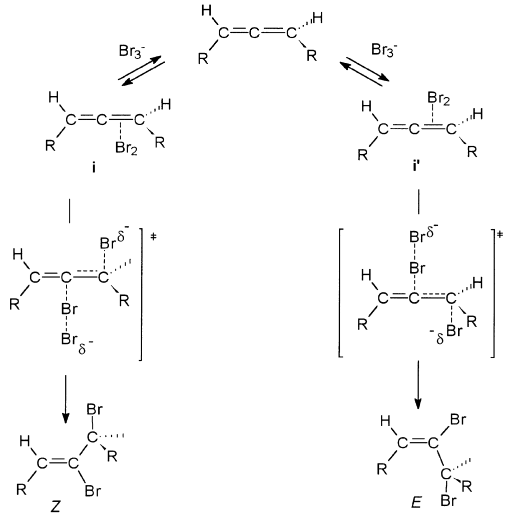
TBAT addition: It is known that in chlorinated solvents in the presence of added bromide salts, which in these media bind Br_2 as a highly stable Br_3^- ion, or when preformed Br_3^- salts are used as brominating agents, the bromination of alkenes proceeds through rate- and product-determining nucleophilic attack by Br^- on the 1:1 alkene · Br_2 π complex.[20] The same mechanism has been more recently proposed for the bromination of alkynes[30] and, on the basis of the presently reported kinetic and stereochemical results, it may be applied to the bromination of allenes. In agreement with a mechanism not involving ionic intermediates, only 1,2-addition products have been obtained from all allenes, including **1a**.



I^+ = cationic intermediate

Scheme 5.

A mechanism of the type reported in Scheme 6 can be therefore proposed and, taking into account that under the reaction conditions the two π complexes (**i** and **i′**) are in rapid equilibrium, the product distribution should depend—conforming to the Curtin – Hammett principle—exclusively on the rate of collapse of each complex to product. The energy of the two transition states should be, under these conditions, the factor determining the reaction stereoselectivity, and this is probably also affected by conformational features related to the ring size. It is noteworthy that the product stereoselectivity of this reaction (for compounds **1b – e**) is very similar to that observed for the methanolic bromination and is in agreement with a concerted mechanism for both reactions.



Scheme 6.

Theoretical investigation of charge transfer complexes:

The total energies[31] of the optimized complexes are compiled in Table 6: the association energies with and without zero-point energy (ZPE) corrections, the entropy change on complex formation, and the free-energy change of various complexes in the gas phase. The ZPE[32] correction changes the association energy (ΔE_{ZPE}) for the 1:1 complexes only to a small extent, whereas the correction is about 1.1 – 1.2 kcal mol^{-1} for the 2:1 complexes. Table 6 also gives the BSSE-corrected (BSSE = basis-set superposition effects) complexation energies ($\Delta E_{ZPE+BSSE}$).

Table 6. Total energies (E [au]), association energies (ΔE), ZPE-corrected association energies (ΔE_{ZPE}[kcal mol^{-1}]), BSSE correction computed by counter (CP) method (BSSE$_{CP}$ [kcal mol^{-1}]), ZPE and BSSE corrected association energies ($\Delta E_{ZPE+BSSE}$ [kcal mol^{-1}]), entropy changes on complexation ($\Delta(\Delta S)$ [kcal mol^{-1} K^{-1}]), and free-energy changes ($\Delta(\Delta G)$ [kcal mol^{-1}]) of acetylene · Br_2 complex **8**, ethylene · Br_2 complex **9**, allene · Br_2 complex **10**, and different allene · 2 Br_2 complexes **11**–**14** computed using ab initio (MP2) and density functional theory (B3LYP).

	Method	Symmetry	E[a]	ΔE[a]	ΔE_{ZPE}[b]	BSSE$_{CP}$[c]	$\Delta E_{ZPE+BSSE}$[d]	$\Delta(\Delta S)$[e]	$\Delta(\Delta G)$[f]
8	MP2	C_{2v}	– 5222.09006	– 2.80	– 2.49	1.11	– 1.38	– 18.72	4.44
	B3LYP	C_{2v}	– 5225.64494	– 2.16	– 1.68	0.14	– 1.54	– 21.56	5.01
9	MP2	C_{2v}	– 5223.32436	– 3.57	– 2.92	1.33	– 1.59	– 22.48	5.36
	B3LYP	C_{2v}	– 5226.90543	– 3.18	– 2.35	0.21	– 2.14	– 24.65	5.37
10	MP2	C_s	– 5261.28689	– 3.97	– 3.37	1.61	– 1.75	– 23.38	5.49
	B3LYP	C_s	– 5264.98477	– 2.87	– 2.16	0.23	– 1.93	– 23.75	5.37
11	MP2	C_2	– 10406.26608	– 8.25	– 7.18	3.58	– 3.57	– 52.46	12.75
	B3LYP	C_2	– 10413.27229	– 4.70	– 3.53	0.47	– 3.06	– 46.78	13.05
12	MP2	C_s	– 10406.26393	– 6.90	– 5.79	3.39	– 2.37	– 51.81	13.77
	B3LYP	C_s	– 10413.27212	– 4.44	– 3.24	0.34	– 2.90	– 51.77	13.19
13	MP2	C_1	– 10406.26278	– 6.18	– 5.31	2.73	– 2.55	– 41.48	10.69
	B3LYP	C_1	– 10413.27212	– 4.44	– 3.39	0.40	– 2.99	– 46.32	11.60
14	MP2	C_{2v}	– 10406.26543	– 7.85	– 6.90	3.24	– 3.63	– 49.85	12.01
	B3LYP	C_{2v}	– 10413.27253	– 4.55	– 3.54	0.43	– 3.11	– 51.20	11.49

[a] MP2/6–311 + G** and B3LYP/6–311 + G**. [b] MP2/6–311 + G** + ZPE (at MP2/6–31G*, 0.97 scaling factor) and B3LYP/6–311 + G** + ZPE (B3LYP/6–31G*, unscaled). [c] Counterpoise corrected at MP2/6–311 + G** and B3LYP/6–311 + G**. [d] Counterpoise corrected at MP2/6–311 + G** + ZPE (scaled by 0.97) and B3LYP/6–311 + G** + ZPE (unscaled). [e] MP2/6–31G* and B3LYP/6–31G* at 298.15 K. [f] ΔE (MP2/6–311 + G* * and B3LYP/6–311 + G**) + BSSE corrections (MP2/6–311 + G** and B3LYP/6–311 + G**) + thermal corrections (MP2/6–31G* and B3LYP/6–31G*).

Note that the BSSE corrections, as expected,[33] are much smaller for the B3LYP (0.2–0.5 kcal mol^{-1}) than for the MP2 calculations (1.61–3.6 kcal mol^{-1}). Although the uncorrected association energies, ΔE in Table 6, for all the complexes are larger for MP2 than for B3LYP, the BSSE- and ZPE-corrected interaction energies ($\Delta E_{ZPE+BSSE}$) are in close agreement. This documents the validity of both methods. Note that the complexation energies for **8** and **9** are different to those reported earlier,[10, 16] since a larger basis set was used here.

As seen from Figure 1, the Br–Br bond lengths in all the structures are shorter at MP2 than at B3LYP. The multiple carbon–carbon bonds in ethyne and ethene change very little on Br_2 complexation: 0.002 Å for ethyne and 0.005 Å for ethene. This difference is shown internally by comparison of the two C=C bonds in allene · Br_2 complex **10**, in Figure 1.

Legon et al. have investigated experimentally the complex of ethylene with bromine by using nozzle expansion methods.[34] They reported a 3.068 Å separation of the nearest Br from the center of the C=C, $r(* \cdots Br_i)$. This distance agrees with our theoretical structures of ethylene · Br_2 complex **9** in Figure 1. If we constrain $r(* \cdots Br_i)$ to 3.068 Å and re-optimize the structures, the changes in the association energies are 0.00 kcal mol^{-1} at MP2/6-311 + G** and 0.09 kcal mol^{-1} at B3LYP/6-311 + G**. This documents the flatness of the potential-energy surfaces for these complexes.

Table 6 also summarizes the changes in entropy, $\Delta(\Delta S)$, and free energy, $\Delta(\Delta G)$, on complexation. $\Delta(\Delta S)$ and $\Delta(\Delta G)$ for the 2:1 associations are almost double those of the 1:1 complexes. The large negative entropies and positive free energies indicate that these complexes would not be bound in the gas phase at room temperature. However, under the experimental conditions (liquid phase) the entropy loss would be less. Typical reductions in entropy on going from the gas to the liquid phase are around 40 % ($\Delta(\Delta S)$ is 22.29 cal mol^{-1} K^{-1} for Br_2 and 24.27 cal mol^{-1} K^{-1} for ethylene)[35] as a result of the more restricted translational and rotational motions. Similar corrections, if applied to the entropies of complexes under investigation, would reduce the magnitude of $\Delta(\Delta S)$ of association considerably. Moreover, specific solvent interactions (e.g., the hydrogen bonding of protic solvents to the olefin or charge transfer solvent · Br_2 interactions) in solution will decrease the entropy and influence the free energies. As explicit computation of free energies in the solvents employed in the experimental work is beyond the scope of the methods available to us and since the computed free energies for the gas phase are misleading, we shall only discuss the interaction (association) energies, ($\Delta E_{ZPE+BSSE}$) in the text.

The most stable form of the 1:1 complex of allene with bromine, structure **10**, with Br_2 perpendicular to a C=C bond, is similar to the 1:1 bromine complexes of ethene (**9**) and acetylene (**8**) investigated previously.[10, 16, 34] Our stability order of the 1:1 complexes (Table 6), **9** ≅ **10** > **8**, can be attributed to decreasing Lewis basicity [as reflected by the IPs of allene (9.96 eV), ethene (10.51 eV) and acetylene (11.40 eV)].[36] The most stable structures of the 2:1 complexes of allene with bromine are **11** (C_2) and **14** (C_{2v}), but their preferences over **12** and **13** are small. In structure **11**, both the double bonds interact with two bromine molecules individually, whereas in **14** only one allene double bond interacts with both bromine molecules.

Table 6 also compares the stability of various possible 2:1 complexes. Earlier work found that complexes like **13** for ethylene and acetylene were slightly more stable than 2:1 complexes like **14**.[10, 16] Vibrational frequency analysis of the weakly bound complexes, **12** and **13**, indicated almost free rotation of the second bromine molecule around the approximate axis described by the midpoint of C=C and the first bromine molecule.

Since the energies of **11** through **14** are almost the same at the levels of theory employed (Table 6), all are suitable candidates for the allene · 2 Br_2 complex. Table 6 shows that

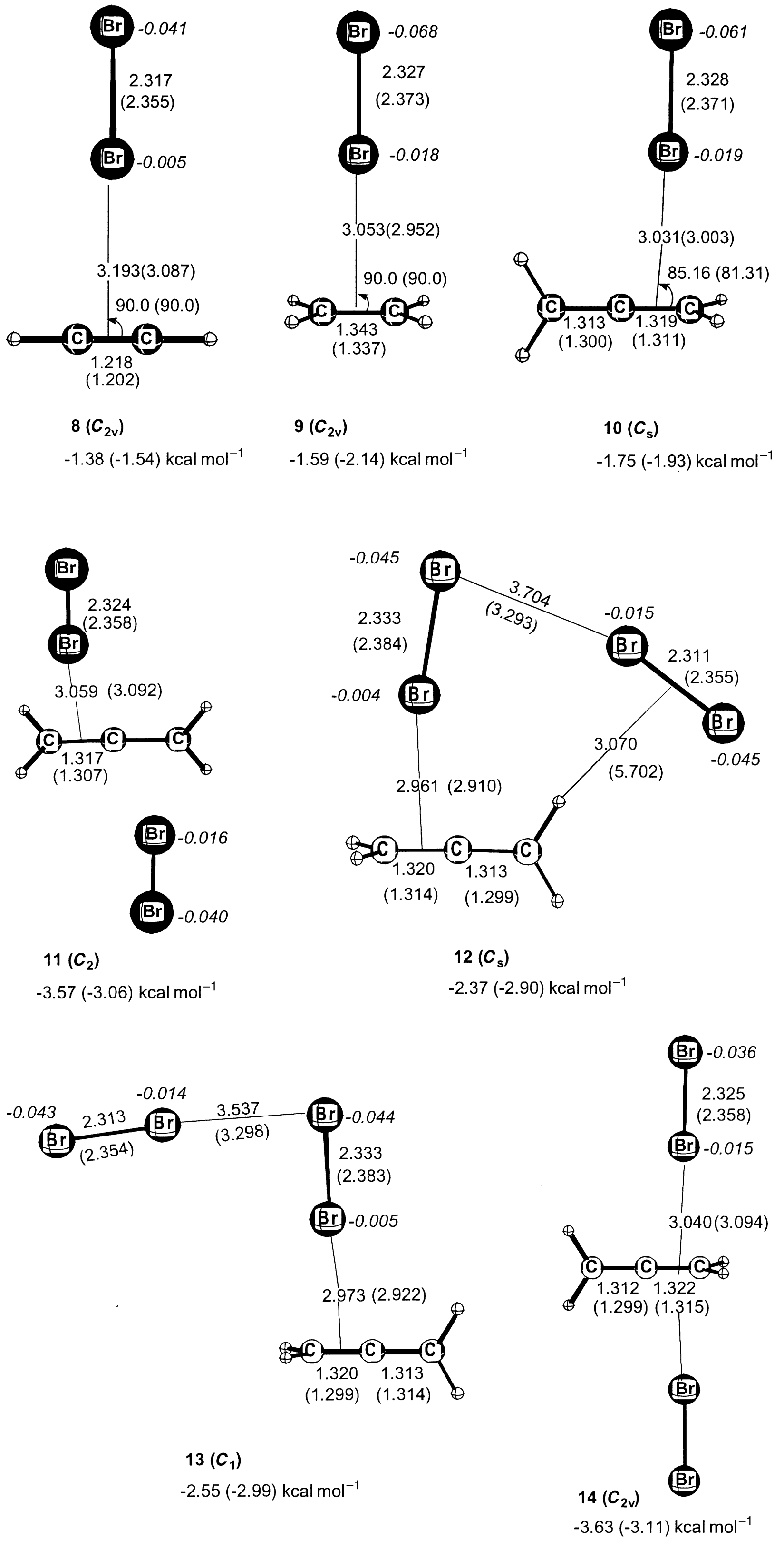


Figure 1. Geometries (at MP2/6–311 + G**) and complexation energies (at MP2/6–311 + G**, corrected for ZPE and BSSE) of 1:1 complexes of Br_2 with acetylene (**8**), ethylene (**9**), and allene (**10**), as well as the 2:1 complexes of bromine with allene (**11**, **12**, **13**, and **14**). Data in parentheses show the corresponding values at B3LYP/6–311 + G**. All the bond lengths are in Å. Data in italics denote the natural charges on the Br atoms from NBO analysis.

the formation of the 1:1 complex **10** is exothermic by -1.7 kcal mol^{-1} (MP2), whereas the exothermicity of 2:1 complex formation, -3.6 kcal mol^{-1} for both **11** and **14**, is almost twice as large. The same is true for free-energy changes, $\Delta(\Delta G)$, for allene · bromine (5.5 kcal mol^{-1}) and allene · $2Br_2$ (12.7 kcal mol^{-1}). The first Br_2 association does not influence the second olefinic π bond appreciably, as shown by the geometries of **10** and **11** (Figure 1). Note that although MP2 complexation energies (Table 6) are in favor of **11** and **14**, by around 1–1.2 kcal mol^{-1}, B3LYP complexation energies for all the allene · $2Br_2$ complexes **11**–**14** are in the same range.

Table 7 and Figure 2 document that the association energies (ΔE_{ZPE}) of Br_2 complexation with 1,2-cycloheptadiene (**15** → **15a**), 1,2-cyclononadiene (**16** → **16a**/**16b**), and 1,3-dimethylallene (**17** → **17a**) decreases along this series. Figure 2 shows that there are two isomeric 1,2-cyclononadiene · Br_2 complexes, **16a** and **16b**, which differ in Br_2 placement. Complex **16a** is 1.5 kcal mol^{-1} more stable than the later (Table 7). As shown in Figure 2, **16a** is a "π complex" with the Br–Br axis perpendicular to a C=C bond. However, in the other isomer **16b**, the Br–Br axis is displaced sideways (twisted with respect to C=C; note the side views of **16a**′ and **16b**′ in Figure 2) with respect to allene double bond. The 1,2-cycloheptadiene · Br_2 complex prefers this twist form, owing to the strain in the cycloheptadiene ring, whereas 1,3-dimethyl allene · Br_2 favors a structure of type **16a**. An extensive search on the potential-energy surface showed that such a twisted isomer does not exist for the allene · Br_2 complex.[37] Greater ring strain not only increases the complexation energies, but

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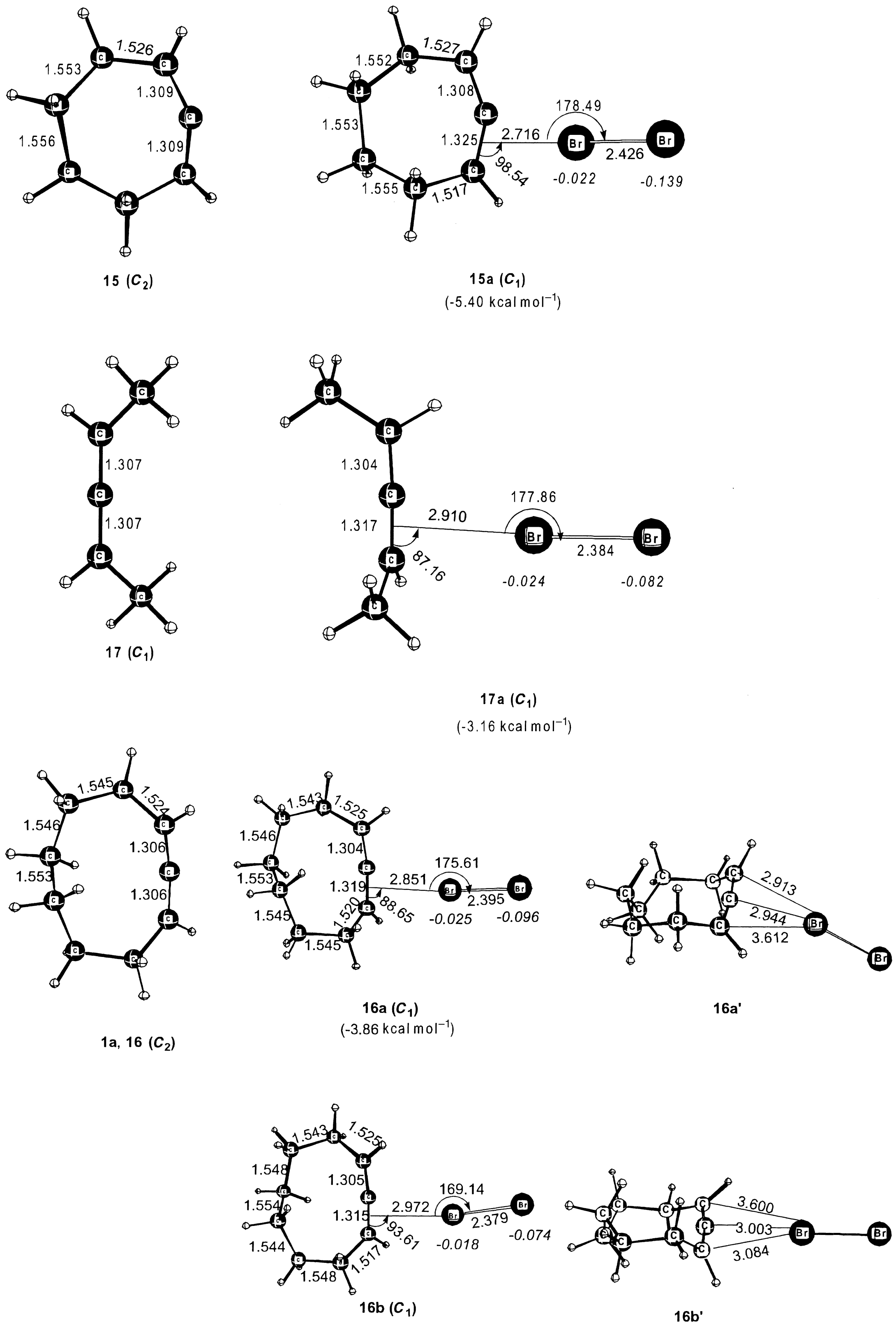

15 (C_2)

15a (C_1)
(-5.40 kcal mol^{-1})

17 (C_1)

17a (C_1)
(-3.16 kcal mol^{-1})

1a, **16** (C_2)

16a (C_1)
(-3.86 kcal mol^{-1})

16a'

16b (C_1)
(-2.32 kcal mol^{-1})

16b'

Figure 2. Geometries and energies (at B3LYP/6-311 + G**, corrected for ZPE) of 1:1 complexes of Br_2 with 1,2-cycloheptadiene (**15**), 1,2-cylononadiene (**16**), and 1,3-dimethylallene (**17**) yielding **15a**, **16** (**a** and **b**) and **17a** respectively. All bond lengths are in Å.

Table 7. Total energies (E [au]), association energies (ΔE [kcal mol^{-1}]), ZPE-corrected association energies (ΔE_{ZPE} [kcal mol^{-1}]), entropy changes on complexation, ($\Delta(\Delta S)$ [kcal mol^{-1}K^{-1}]), and free-energy changes ($\Delta(\Delta G)$ [kcal mol^{-1}]) of 1,2-cycloheptadiene · Br_2 complex **15a**, 1,2-cyclononadiene · Br_2 complexes **16a** and **16b**, and 1,3-dimethylallene · Br_2 complex **17a** computed using density functional theory (B3LYP).

	Symmetry	$E^{[a]}$	$\Delta E^{[a]}$	$\Delta E_{ZPE}{}^{[b]}$	$\Delta(\Delta S)^{[c]}$	$\Delta(\Delta G)^{[c]}$
15a	C_1	−5421.05247	−5.90	−5.40	−25.69	2.73
16a	C_1	−5499.71215	−4.44	−3.86	−27.07	4.65
16b	C_1	−5499.70966	−2.88	−2.32	−23.04	5.06
17a	C_1	−5343.64231	−3.77	−3.16	−27.04	5.27
cyclohexene · Br_2	C_1	−5383.00587	−4.94	−4.26	−28.31	4.51

[a] B3LYP/6-311+G**. [b] B3LYP/6-311+G**+ZPE (B3LYP/6-31G*, unscaled). [c] Electronic energies at B3LYP/6-311+G**+thermal corrections to free energies at B3LYP/6-31G* at 298.15 K.

the natural charges on the Br_2 moieties also become more negative. Thus the extent of charge transfer and the degree of carbocationic character of the allene increase with the ring strain.

Our computations on complexes of Br_2 with the parent allene and with the cyclic allenes give estimates of the association energies in the gas phase. Note that only the ΔE and ΔE_{ZPE} data in Tables 6 and 7 can be compared directly, since the other energies for the cyclic allenes are not BSSE-corrected. Computations on Br_2 complexes with two cyclic allenes, 1,2-cyclononadiene, 1,2-cycloheptadiene, and with unstrained allene, 1,3-dimethylallene, give an estimate of the difference in the complexation energies as a result of strain. Note that the structures of the type **11**–**14** are also probable candidates for the 2:1 complexes of cyclic allene · 2 Br_2 complexes.

The computations on the cyclohexene · Br_2 complex gave an association energy (ΔE_{ZPE}, Table 7) of −4.3 kcal mol^{-1}. The higher experimental formation constant of 1,2-cyclononadiene · Br_2 (7.4 M^{-1}) than cyclohexene · Br_2 (0.47 M^{-1}) is not, therefore, reflected by our computed association energies (−3.9 kcal mol^{-1} for 1,2-cyclononadiene · Br_2, Table 7).

Conclusion

Several conclusions arise from the present investigation. First, the steric strain affects the reactivity of cumulated double bonds. A significant increase in the bromine addition rate has been observed both in DCE and methanol on going from **1b**–**e** to **1a**. This effect, which is more moderate in methanol, may be related to the higher strain energy present in the smaller isolable cyclic allene, 1,2-cyclononadiene. Kinetic measurements and product distribution data show that, in analogy with the previously observed behavior of alkenes in bromine addition, the steric strain affects the reactivity by mainly changing the nature of the ionic intermediate which shifts from a partially bridged α,β-ethylenic carbocation to an open intermediate.

Secondly, the UV detection of a 1:1 complex of Br_2 and 1,2-cyclononadiene and the negative values of the apparent activation energy for the reaction of allenes **1a**–**e** with Br_2 in DCE have provided the first experimental evidence for the involvement of π complexes along the reaction coordinate for bromine addition to allenes, showing that the pre-equilibrium formation of these complexes among unsaturated compounds (alkenes, alkynes and allenes) and Br_2 is a general phenomenon. Furthermore, the value of the stability constant, K_f = 7.4 M^{-1} in DCE at 25 °C, found for the Br_2 · **1a** π complex and the comparison with the stability constants found for other 1:1 π complexes between Br_2 and an unsaturated compound (cyclohexene and cyclododecyne) in the same solvent, further support the hypothesis of the existence of sizable structural effects on the stability of these complexes.

The 2:1 bromine · allene complex has a gas-phase association energy ($\Delta E_{ZPE+BSSE}$) around −2.4 to −3.6 kcal mol^{-1} (Table 6) and may be formed with higher concentrations of bromine in solution. The association energy (−1.7 kcal mol^{-1}) of 1:1 complex **10** of allene (C_3H_4) with bromine, is almost the same as the ethene · bromine complex (−1.6 kcal mol^{-1}) **9**, whereas the 2:1 allene · 2 Br_2 complexes are more stable than those of the ethylene · 2 Br_2 analogues (not shown).[10] However, the much larger experimental formation constant of 1,2-cyclononadiene · Br_2 (7.4 M^{-1}; see above) than cyclohexene · Br_2 (0.47 M^{-1}) is not reflected by the computed association energies (ΔE_{ZPE}) for these species (−4.3 kcal mol^{-1} for cyclohexene · Br_2 and −3.9 kcal mol^{-1} for 1,2-cyclononadiene · Br_2). All the B3LYP structures of the allene · 2 Br_2 complex have nearly the same energies and free energies; however, MP2 predicts structures **14** and **11** to be somewhat more favorable. Although the entropies and hence the free energies do not favor complexation in the gas phase, these complexes might be formed under ambient experimental conditions in solution as a result of restricted translations and rotations as well as possible solvent associations. The stability order for the allenes, 1,2-cycloheptadiene · Br_2 > 1,2-cyclononadiene · Br_2 > 1,3-dimethylallene · Br_2, indicates the degree to which the strain of the cyclic allene affects the association energies.

Finally, the comparison of the kinetic and stereochemical behavior of bromine addition to allenes **1a**–**e** in DCE with that observed in methanol, as well as with the stereochemical behavior of the TBAT reaction, strongly suggests the involvement of a pre-association mechanism in the reaction of allenes **1b**–**e** with bromine in methanol showing that the competition among pre-association, free-ion, and ion-pair pathways is a general feature of the electrophilic bromination of unsaturated compounds.

Experimental Section

Instruments and materials: ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ with a Bruker AC200 instrument containing TMS as the internal reference. Kinetic measurements were performed with a Cary 2200 spectrophotometer or with a Tri-Tech stopped-flow instrument equipped with a diode-array detector. Bromine (1 mL sealed ampules, C. Erba > 99.5 %) and 1,2-dichloroethane (Fluka > 99.5 %) were used as supplied, methanol was treated as previously reported.[11]

1,2-Cyclononadiene, 1,2-cyclodecadiene, and 1,2-cycloundecadiene (**1a**–**c**) were synthesized in two steps, by dibromocarbene addition[24] and reaction with n-butyl lithium at −78 °C.[38] Allenes **1a** and **1b** were purified by distillation in vacuo and identified from IR and NMR data.[38] Allene **1c**

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was purified by column chromatography on silica gel using pentane as eluent. MS (EI): *m/z* (%): 150 (1) $[M]^+$, 135 (6) $[M-CH_3]^+$, 121 (8) $[M-C_2H_5]^+$, 107 (12) $[M-C_3H_7]^+$, 93 (36) $[M-C_4H_9]^+$, 79 (98) $[M-C_5H_{11}]^+$, 67 (100) $[M-C_5H_7]^+$. 1,2-Cyclotridecadiene (**1e**) was prepared in 68% yield following the Nozaki procedure[39] without adding sparteine to the reaction mixture. The product was identified on the basis of the ^{1}H NMR spectrum.[40]

Bromination procedure:

π Complex stability constants determination and kinetic measurements: Solutions of Br_2 in DCE or methanol were prepared shortly before use and were adjusted to twice the desired initial concentrations in the kinetic runs and protected from daylight. The same applied to solutions of TBAT in DCE. Aliquots of these solutions, thermostated at the temperatures reported in Tables 1, 2, and 3, were mixed with equal volumes of pre-thermostated solutions of allenes **1a–e** of suitable concentrations. The kinetic measurements for bromine addition in DCE and methanol were performed with a stopped-flow apparatus. All the kinetics of bromination with TBAT were achieved in the conventional spectrophotometer. The kinetic constants were calculated at several wavelengths on the basis of the disappearance of the free bromine absorption band in the 350–450 nm interval. The absorbance/time data were fitted to the appropriate third-order (pseudo second-order) rate equation or second-order (pseudo first-order) rate equation. All reactions were carried out at least in triplicate. The apparent activation parameters, reported in Tables 1, 2, and 3, were obtained from Arrhenius plots.

The measurements of K_f for the 1:1 π complex between **1a** and Br_2 were carried out by mixing in the stopped-flow apparatus solutions of Br_2 ($2-2.4\times10^{-4}$ M) with equal volumes of solution of **1a** ($6\times10^{-2}-1.0$ M) in the same solvent at 25 °C; the A_0 values were registered at 320 nm. Three independent determinations were carried out at each reagent concentration and the absorbance data were used to fit the Scott equation.[12]

Product distribution: Solutions (ca. 2×10^{-2} M) of Br_2 in DCE or methanol were rapidly mixed with equal volumes of solutions (ca. 2×10^{-2} M) of compounds **1a–e** in the same solvent and the reaction mixtures were then stored in the dark at 25 or 0 °C. At the end of the reactions the mixtures were washed with water (when carried out in DCE) or diluted with water and repeatedly extracted with dichloromethane (when carried out in methanol). After solvent removal in vacuo the reaction mixtures were analyzed by NMR spectroscopy. Each compound was also treated with TBAT by using the same procedure. The *Z*:*E* ratios were determined on the basis of the vinyl and/or allylic signals in the ^{1}H NMR spectra. All reactions were carried out at least in duplicate. The ratios reported in Tables 4 and 5 were reproducible within ±2%. All product ratios were independent of the degree of conversion. The stability of the reaction products in the presence of halogen was checked by exposing the reaction mixtures to Br_2 under conditions identical to those employed in the bromination reactions, followed by NMR analysis.

(*E*)-1,4-Dibromocyclononene (4a): ^{1}H NMR:[22] $\delta=5.83$ (t, ^3J(H,H) = 8.5 Hz, 1H), 4.10 (m, 1H), 2.9–1.4 (m, 12H).

(E)-2,3-Dibromocyclononene (2a): ^{1}H NMR:[21] $\delta=6.21$ (t, ^3J(H,H) = 9 Hz, 1H), 5.23 (dd, ^3J(H,H) = 5, 12 Hz, 1H), 2.5–1.2 (m, 12H); ^{13}C NMR: $\delta=135.4$ (C=), 50.74 (CHBr), 43.44, 37.75, 30.24, 28.89, 26.58, 25.86, 24.90.

(*E*)-2,3-Dibromocyclodecene (2b): ^{1}H NMR:[23] $\delta=5.88$ (dd, ^3J(H,H) = 5.8, 12 Hz, 1H), 5.44 (dd, ^3J(H,H) = 5.1, 12 Hz, 1H), 2.5–1.2 (m, 14H); ^{13}C NMR: $\delta=135.8$ (C=), 127.89 (=CBr), 50.78 (CHBr), 39.96, 28.14, 27.52, 25.31, 24.42, 22.80, 21.23.

(*Z*)-2,3-Dibromocyclodecene (3b): ^{1}H NMR:[23] $\delta=6.35$ (t, ^3J(H,H) = 7.5 Hz, 1H), 4.6 (t, ^3J(H,H) = 7.5 Hz, 1H), 2.5–1.2 (m, 14H).

(*E*)-2,3-Dibromocycloundecene (2c): ^{1}H NMR:[24] $\delta=6.05$ (dd, ^3J(H,H) = 5.5, 11 Hz, 1H), 5.20 (dd, ^3J(H,H) = 4.6, 11 Hz, 1H), 2.6–1.2 (m, 16H); ^{13}C NMR: $\delta=138.5$ (C=), 49.21 (CHBr).

(*Z*)-2,3-Dibromocycloundecene (3c): ^{1}H NMR:[24] $\delta=6.25$ (dd, ^3J(H,H) = 5.6, 10 Hz, 1H), 4.68 (dd, ^3J(H,H) = 5, 10Hz, 1H), 2.5–1.2 (m, 16H); ^{13}C NMR: $\delta=133.3$ (C=), 59.21 (CHBr).

(*E*)-2,3-Dibromocyclododecene (2d): ^{1}H NMR: $\delta=5.9$ (dd, ^3J(H,H) = 6, 12 Hz, 1H), 5.38 (dd, ^3J(H,H) = 4.6, 12 Hz, 1H), 2.6–1.2 (m, 18H); ^{13}C NMR: $\delta=135.2$ (C=), 127.2 (=CBr), 50.1 (CHBr), 39.26, 27.44, 26.81, 24.61, 23.72, 22.10, 20.53.

(*Z*)-2,3-Dibromocyclododecene (3d): ^{1}H NMR: $\delta=6.25$ (t, ^3J(H,H) = 7.5 Hz, 1H), 4.68 (t, ^3J(H,H) = 7.5 Hz, 1H), 2.5–1.2 (m, 18H); ^{13}C NMR: $\delta=133.3$ (C=), 57.21 (CHBr).

(*E*)-2,3-Dibromocyclotridecene (2e): ^{1}H NMR:[24] $\delta=5.90$ (dd, ^3J(H,H) = 5, 11 Hz, 1H), 5.10 (dd, ^3J(H,H) = 5.0, 10 Hz, 1H), 2.5–1.2 (m, 20H); ^{13}C NMR: $\delta=138.7$ (C=), 49.4 (CHBr).

(*Z*)-2,3-Dibromocyclotridecene (3e): ^{1}H NMR:[24] $\delta=6.10$ (dd, ^3J(H,H) = 5, 10 Hz, 1H), 4.70 (dd, ^3J(H,H) = 4.5, 12 Hz, 1H), 2.5–1.2 (m, 20H); ^{13}C NMR: $\delta=135.6$ (C=), 58.16 (CHBr).

(*E*)-1-Bromo-4-methoxycyclononene (7a): ^{1}H NMR:[25] $\delta=5.85$ (t, ^3J(H,H) = 9 Hz, 1H), 3.22 (s, OCH_3), 3.2 (m, CH), 2.7–1.4 (m, 12H).

(*E*)-2-Bromo-3-methoxycyclononene (5a): ^{1}H NMR:[25] $\delta=6.25$ (t, ^3J(H,H) = 9 Hz, 1H), 4.2 (dd, ^3J(H,H) = 4.5, 9 Hz, 1H), 3.12 (s, 3H, OCH_3), 2.5–1.2 (m, 12H).

(*E*)-2-Bromo-3-methoxycyclodecene (5b): ^{1}H NMR:[21] $\delta=6.10$ (dd, 1H,*J* = 5.6, 12.6 Hz), 4.34 (m, 1H), 3.25 (s, 3H, OCH_3), 2.5–1.2 (m, 14H); ^{13}C NMR: $\delta=136.6$ (C=), 127.53 (=CBr), 77.37 (CHO), 55.80 (OCH_3).

(*E*)-2-Bromo-3-methoxycycloundecene (5c): ^{1}H NMR: $\delta=6.25$ (dd, 1H), 4.15 (dd, ^3J(H,H) = 6, 12 Hz, 1H), 3.29 (s, 3H, OCH_3), 2.5–1.2 (m, 16H).

(*Z*)-2-Bromo-3-methoxycycloundecene (6c): ^{1}H NMR: $\delta=6.18$ (dd, ^3J(H,H) = 5.6, 9.5 Hz, 1H), 3.61 (dd, ^3J(H,H) = 4.8, 8.7 Hz, 1H), 3.28 (s, 3H, OCH_3), 2.5–1.2 (m, 16H); ^{13}C NMR: $\delta=133.5$ (C=), 87.37 (CHO), 55.80 (OCH_3).

(*E*)-2-Bromo-3-methoxycyclododecene (5d): ^{1}H NMR: $\delta=6.14$ (dd, ^3J(H,H) = 5.8, 12.5 Hz, 1H), 4.35 (dd, ^3J(H,H) = 5, 10.7 Hz, 1H), 3.25 (s, 3H, OCH_3), 2.6–1.2 (m, 18H); ^{13}C NMR: $\delta=136.6$ (C=),127.53 (=CBr), 77.37 (CHO), 55.80 (OCH_3).

(*E*)-2-Bromo-3-methoxycyclotridecene (5e): ^{1}H NMR: $\delta=6.18$ (dd, ^3J(H,H) = 4, 10 Hz, 1H), 4.05 (dd, ^3J(H,H) = 5, 12 Hz, 1H), 3.25 (s, 3H, OCH_3), 2.5–1.2 (m, 20H).

(*Z*)-2-Bromo-3-methoxycyclotridecene (6e): ^{1}H NMR:[26] $\delta=6.00$ (dd, ^3J(H,H) = 5, 9.5 Hz, 1H), 3.58 (dd, ^3J(H,H) = 4.4, 10 Hz, 1H), 3.23 (s, 3H, OCH_3), 2.5–1.2 (m, 20H); ^{13}C NMR: $\delta=134.5$ (C=H), 85.7 (CHO), 55.80 (OCH_3).

Computational methodology: Theoretical investigations on the isomeric 1:1 allene·Br_2, and 1:2 allene·2Br_2 complexes provide details of the structure and bonding. While the preferred orientation of the former, as expected, is that of a π complex, different spatial arrangements are possible for complexation of two Br_2 molecules with allene. Exhaustive searches of the potential-energy surfaces were performed at the ab initio (MP2) and density functional theory (B3LYP) levels with the Gaussian 98[41] program. The nature of stationary points (minima or transition states) were confirmed by computing the vibrational frequencies at both MP2/6–31G* and B3LYP/6–31G* levels. The minima were then re-optimized at MP2/6–311+G** and B3LYP/6–311+G** with the larger basis set for all the atoms as implemented in Gaussian 98. Zero-point energy corrections (ZPE, with 0.97 scaling for MP2[42] and no scaling for B3LYP) from the frequency calculations were applied. The entropies in the isolated state were computed at 298.15 K by using the 6–31G* basis set data. The 6–311+G** MP2 and B3LYP complexation energies were corrected for basis-set superposition effects (BSSE) by the counterpoise method (CP).[43] For 2:1 complexes, the BSSE corrections were applied by considering each monomeric unit as a separate identity.[44] The free energies were based on the higher level BSSE-corrected electronic energies (MP2/6–311+G** and B3LYP/6–311+G**) and applying lower level thermal corrections (MP2/6–31G* and B3LYP/6–31G*). B3LYP/6–311+G** computations of the 1:1 Br_2 complexes of 1,2-cycloheptadiene (**15**) 1,2-cyclononadiene (**1a**; **16**), and 1,3-dimethylallene (**17**) probed the effects of strain on the association energies. Natural charges on the atoms at B3LYP/6–311+G** were computed using natural bond orbital analysis (NBO).[45]

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[31] Absolute energies at B3LYP/6–311 + G** (in a.u.): −5148.28485 (Br_2), −77.35665 (C_2H_2), −78.61551 (C_2H_4), −116.69535 (allene), −272.75822 (1,2-cycloheptadiene), −351.42022 (1,2-cyclononadiene), −195.35144 (1,3-dimethylallene), and −234.71315 (cyclohexene). Energies at MP2/6–311 + G** (in a.u.): −5144.97237 (Br_2), −77.11323 (C_2H_2), −78.346303 (C_2H_4), and −116.30820 (allene).

[32] ZPE corrections (in kcal mol^{-1}) with scaling of 0.97 at MP2/6–31G* (B3LYP/6–31G*): bromine 0.47 (0.47), acetylene 15.50 (16.72), ethylene 31.68 (32.15), allene 34.25 (34.81), **2** 16.45 (17.66), **3** 32.80 (33.44), **4** 35.32 (35.98), **5** 36.27 (36.90), **6** 36.30 (36.93), **7** 36.07 (36.78), **8** 36.15 (36.74), **9** (94.85), **9a** (95.82), **10** (132.43), **10a** (132.46), **10b** (132.43), **11** (71.03), and **11a** (72.11).

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