Spectroscopic and Theoretical Investigations of Electrophilic Bromination Reactions of Alkynes: The First Evidence for π Complexes as Reaction Intermediates

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Abstract: A bromine–alkyne π complex ($\lambda_{max} = 294$ nm) of 1:1 stoichiometry has been observed for the first time in the course of the bromination of 1-phenylpropyne by means of a diode-array stopped-flow technique. The formation enthalpy and entropy ($\Delta H^{\circ} = -2.95\ \mathrm{kcal\,mol^{-1}}$, $\Delta S^{\circ}_{25} = -15.4$ eu) of this species are similar to those of charge-transfer complexes observed between bromine and alkenes. A negative apparent activation energy is found in the reaction of Br_2 with 1-phenylpropyne ($\Delta H^{\neq} = -0.61\ \mathrm{kcal\,mol^{-1}}$); this demonstrates that the complex is actually an essential intermediate on the reaction coordinate. The bromination of a series of nine alkynes has been studied. Bromination reactions with negative apparent activation parameters lead to mixtures of *E* and *Z* vinyl dibromides, whereas reactions with positive activation energy yield the *E* isomers exclusively. The reason for the difference in reactivity of these alkynes compared with structurally similar alkenes most likely lies in the stability of these 1:1 charge-transfer complexes. Usually open arylvinyl cations correspond to the energetically favored product-determining intermediates; bridged bromirenium ions are formed from deactivated alkynes and react to give *E* isomers. The kinetic effect of alkyl groups and of *p*-OCH_3, *p*-CN, and *p*-NO_2 substituents at the aryl group on the bromination of arylalkylacetylenes is discussed. Density functional calculations provide insight into the geometries, energies, and bonding of the intermediate 1:1 and 2:1 Br_2–acetylene complexes involved. These theoretical investigations demonstrate that the most stable trimolecular Br_2–Br_2–acetylene adduct possesses a structure very similar to a crystallographically characterized Br_2–Br_2–alkene species, which can directly yield the ionic products, Br_3^- and vinyl cation, driven by the heterolytic action of a solvent.

Keywords: alkynes · bromination · charge transfer · density functional calculations · electrophilic additions · reaction mechanisms

Introduction

Addition reactions of electrophiles to unsaturated molecules have been extensively studied, especially during the last 10–15 years. These investigations have significantly changed the hitherto accepted view of the mechanism of this reaction. Direct experimental evidence for the intermediacy of a 1:1 charge-transfer complex (Br_2–alkene π complex **I**) between bromine and an alkene during the bromination of olefins is now available,[1] and it is also generally accepted that the reaction proceeds with a third-order rate law (second-order with respect to the halogen concentration). Thus, a second halogen atom is necessary for the halogenation reaction to proceed. Some time ago such an intermediate structure was, in fact, directly observed in the reaction between two equivalents of bromine and the sterically hindered adamantylideneadamantane. This alkane cannot react to give the final 1,2-dibromide owing to steric crowding; however, the addition of halogen atoms leads to the formation of a solid adduct which has been amenable to crystallographic characterization. The structure of this compound ($(Br_2)_2$-adamantylidene-adamantane adduct **II**) is generally viewed as the first stable

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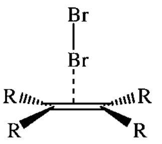

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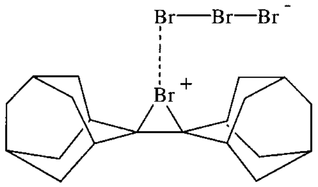


II

bromonium ion and regarded as an alkene–Br^+ species which is weakly coordinated to a Br_3^- counterion.[1]

Subsequent investigations successfully demonstrated the reversibility of this bromonium ion formation[2] and since then the influence of the nature of the nucleophile on the reaction path has been widely investigated.[3] Recently 1:1 adducts between alkenes and dihalogen molecules have been shown to be π complexes,[4] and during the bromination of another highly congested alkene, tetraneopentylethylene, the participation of a second species, a 2:1 complex between two halogen molecules and an alkene molecule, was observed directly.[5] This experimental work demonstrates that the 2:1 charge-transfer complex must be an intermediate between the π complex **I** and the charged bromonium ion. The influence of the solvent on the rate-limiting ionization that leads to these bromonium ions has been found to be especially pronounced in protic solvents[6] and updated general discussions of all these results, including the treatment of solvation effects on the bromination reactions according to the Winstein–Grunwald correlation, are available.[7]

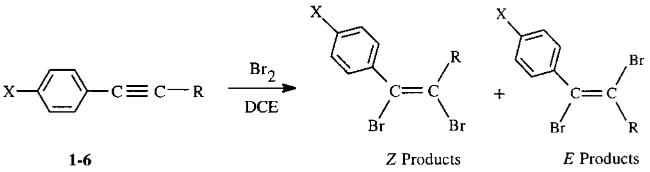
Abstract in German: *Zum ersten Mal konnte im Verlaufe der Bromierung von 1-Phenylpropinen ein intermediär gebildeter 1:1-π-Komplex zwischen einem Alkin und* Br_2 *(*$\lambda_{max} = 294$ *nm) durch Stopped-Flow-Technik direkt beobachtet werden. Die Werte für die Bildungsenthalpie und -entropie (*$\Delta H^{\circ} = -2.95$ *kcal mol*$^{-1}$*,* $\Delta S^{\circ}_{25} = -15.4$ *eu) dieser Spezies liegen in derselben Größenordnung wie die der bereits beschriebenen Charge-Transfer-Komplexe zwischen Brom und Alkenen. Für die Reaktion von* Br_2 *mit 1-Phenylpropin wurde eine scheinbare negative Aktivierungsenergie (*$\Delta H^{\neq} = -0.61$ *kcal mol*$^{-1}$*) bestimmt, die darauf hindeutet, daß der π-Komplex eine für die Produkte notwendige Zwischenstufe auf der Reaktionskoordinate ist. Die Bromierung von neun verschiedenen Alkinen wurde untersucht. Bromierungsreaktionen mit negativen Aktivierungsenergien liefern E- und Z-Gemische der entsprechenden vicinalen Dibromide. Dagegen führen Reaktionen mit positiven Aktivierungsenergien ausschließlich zu E-Isomeren. Der Grund für die im Vergleich zu strukturell ähnlichen Alkenen unterschiedliche Reaktivität der 1:1-Komplexe dieser Alkine liegt wahrscheinlich in deren verschiedenen Stabilitäten. Normalerweise sind Arylvinyl-Kationen die energetisch günstigeren, produktbestimmenden Zwischenstufen bei der Bromierung von Alkinen; verbrückte Bromirenium-Ionen bilden sich aus deaktivierten Alkinen und reagieren dann ausschließlich zum E-isomeren Dibromid. Der kinetische Einfluß von Alkylgruppen und p-*OCH_3*-, p-CN- sowie p-*NO_2 *Substituenten an der Arylgruppe auf die Bromierung von Arylalkylacetylenen wird erläutert. Dichtefunktionalrechungen werden herangezogen, um Einblicke in die Geometrien und Energien sowie die Bindungsverhältnisse der an den Reaktionen beteiligten* Br_2*-Acetylen Komplexe mit 1:1- und 2:1-Stöchiometrie zu erhalten. Wie die theoretischen Untersuchungen zeigen, besitzt das stabilste trimolekulare* Br_2*-*Br_2*-Acetylen-Addukt eine Struktur, die dem einzigen bisher kristallographisch charakterisierten* Br_2*-*Br_2*-Alken sehr ähnlich ist und aus der die im weiteren Verlauf der Reaktion durch heterolytischen Einfluß des Lösungsmittels gebildeten ionischen Folgeprodukte,* Br_3^- *und Carbokation, direkt entstehen können.*

These recent investigations have dealt exclusively with the halogenation of alkenes; mechanistic investigations of the electrophilic addition of halogens to triple bonds have not been reported over the last two decades.[8] We were therefore interested as to whether these results were restricted to the chemistry of olefins, or whether they represented general characteristics for electrophilic additions of halogens to unsaturated systems. The participation of 1:1 π complexes in alkyne halogenation reactions has already been postulated in the case of ethyne,[9] and a number of π complexes between halogens and alkynes have been experimentally characterized in the gas phase and at low temperatures by matrix-isolation spectroscopy.[10] These species have also been proposed as reaction intermediates in general reaction schemes[11] and the significantly reduced reactivity of alkynes in bromination reactions, as compared to those of structurally similar alkenes, was explained by the different stabilities of the corresponding bimolecular π complexes.[9, 12]

In this study, we report the first direct detection of a 1:1 Br_2–alkyne complex as an intermediate during the addition reaction of Br_2 to alkynes. Spectroscopic, thermodynamic, and structural features of this charge-transfer complex are reported, and its occurrence on the reaction coordinate is demonstrated. The participation of either an open β-bromovinyl cation or a cyclic bromirenium cation as the intermediate in the addition reactions is discussed on the basis of product distributions and kinetic data. Furthermore, we report the results of density functional calculations for the parent acetylene–Br_2 system in order to elucidate the structural and energetic features along with the bonding in the experimentally observed bimolecular Br_2–HCCH and the trimolecular Br_2–Br_2–HCCH charge-transfer complexes.

Results and Discussion

Bromination of several alkynes, phenylacetylene (**1**), three phenylalkylacetylenes (**2**–**4**), four arylalkylacetylenes (**5a**–**d**), diphenylacetylene (**6**), and the dialkylacetylene 2-hexyne (**7**) was examined in 1,2-dichloroethane (DCE) (Scheme 1). We chose this solvent to enable direct comparison with the results for the bromination of alkenes. Most of the earlier studies of alkyne halogenation reactions have been conducted in protic solvents like water, methanol, or acetic acid, and only minimal kinetic data are available from a single study of a halogenation carried out in the chlorinated solvent 1,1,2-trichlorotrifluoroethane.[12] Since almost all measured stability constants for early 1:1 bromine–alkene complexes were



	1	2	3	4	5a	5b	5c	5d	6
X =	H	H	H	H	OCH_3	H	CN	NO_2	H
R =	H	Me	Et	*n*-Propyl	*n*-Butyl	*n*-Butyl	*n*-Butyl	*n*-Butyl	C_6H_5

Scheme 1. Bromination of several phenylalkynes **1**–**6**.

obtained in 1,2-dichlorethane,[13] a direct comparison with the 1:1 Br_2–alkyne case should be possible.

Br_2–alkyne 1:1 complexes: The bromination of **1**–**6** leads to the corresponding styrene or stilbene dibromides (with *E* or *Z* stereochemistry), which absorb much more strongly in the UV region than the starting materials. We therefore decided to use a diode-array stopped-flow apparatus to register the absorption spectra a few milliseconds after the start of the reaction and prior to the formation of the final products.[14] After 1-phenylpropyne (**2**) and Br_2 were mixed, we observed a differential absorbance in the range 290–390 nm. The results of two such experiments are shown in Figure 1. Solid lines represent the experimental spectra of 0.05 and 0.025 M solutions of **2** mixed with a 1×10^{-3} M solution of Br_2 (recorded 3 ms after mixing). The lower, dashed curves represent the result from the subtraction of the contributions of the spectra of alkyne and Br_2 from the experimental curves. We conclude that a new intermediate species is formed due to the appearance of a new UV band, centered at $\lambda_{max} = 294$ nm. Attempts to complex all the halogen with an appropriate excess of alkyne failed.[15] The strong absorbance of the unsaturated species prevented all attempts to obtain reliable spectrophotometric data for the evaluation of a formation constant and molar absorption coefficients of the newly formed transient species.

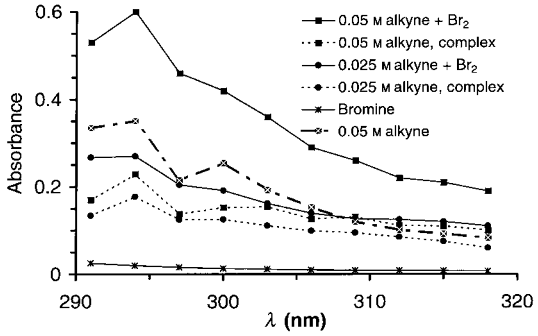


Figure 1. UV spectra of the alkyne–Br_2 π complex recorded with a diode-array stopped-flow apparatus. The spectra of the complex with a Br_2 concentration of 1×10^{-3} M and a concentration of alkyne **2** of 0.025 M (----, ●), and a concentration of 0.05 M alkyne **2** (----, ■), were obtained by subtraction of the contributions of alkyne (——, ●) and free Br_2 (——, *) from the experimental curves.

Therefore, we had to use a different approach: the stability constant of this complex was calculated from the concentration of free Br_2 at equilibrium measured at 560 nm. Since the concentration [complex] = $[Br_2]_T - [Br_2]_{free}$, where $[Br_2]_T$ is the total stoichiometric bromine concentration, it follows that $K_f = [\text{complex}]/([Br_2]_{free}[\text{alkyne}])$, on the basis of the plausible hypothesis that the complex has a 1:1 stoichiometry. In Table 1 the results of measurements obtained shortly after mixing the two reaction partners (3 ms elapsed time) in the stopped-flow apparatus are summarized. The alkyne does not absorb at this wavelength and the complex is also supposed to be transparent in the visible region, an assumption that is based on the similarity of λ_{max} in the complexes of Br_2 with alkenes and alkynes. The λ_{max} of the most bathochromically shifted 1:1 complex between an olefin and bromine is known to be centered at 272 nm and the absorption stops at 450 nm.[16]

On the basis of the linear van't Hoff plot of the data shown in Table 1 (Figure 2) we can calculate the enthalpy of formation for the charge-transfer complex as $\Delta H^{\circ} = -2.95$ kcal mol^{-1}, and an entropy value, $\Delta S^{\circ} = -15.4$ eu. These values are similar to those of a number of Br_2–alkene 1:1 charge-transfer complexes and are consistent with the results of our quantum-chemical calculations. The detailed structural and electronic features of this species are discussed below. From the K_f value at 25 °C (Table 1), the equilibrium concentration of the complex of **2** (0.05 M solution) is calculated to be 3.2×10^{-6} mol (Figure 1), so that an $\varepsilon_{max} = 7 \times 10^4$ mol^{-1} cm^{-1} can be estimated for the Br_2–alkyne charge-transfer complex. This value is slightly higher than that of the Br_2–adamantylideneadamantane complex ($\varepsilon_{max} = 2 \times 10^4$ mol^{-1} cm^{-1}).[16]

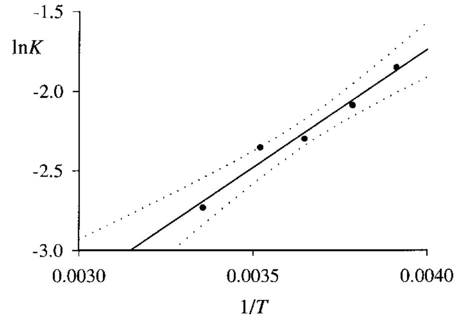


Figure 2. van't Hoff plot of the equilibrium constants reported in Table 1 (the dotted line corresponds to a confidence interval of 95 %).

Table 1. Formation constants of the Br_2–1-phenylpropyne 1:1 complex determined at 560 nm by the stopped-flow measurements.

T [°C]	Abs. total Br_2	Abs. free Br_2	K_f [M^{-1}]
–17.5	0.700	0.475	0.157 (0.015)
–9.0	0.700	0.510	0.124 (0.015)
1.0	0.700	0.539	0.1 (0.01)
10.9	0.877	0.682	0.095 (0.02)
25.0	0.877	0.733	0.065 (0.015)
20.0 toluene 50 %	0.80	0.79	–

However, detection of a 1:1 complex with thermodynamic and spectroscopic properties similar to those of the corresponding complexes of alkenes with Br_2 and measured in the same solvent, does not automatically imply an involvement of this species along the reaction coordinate. To address this problem we studied the reaction kinetics of compounds **1**–**7** with molecular Br_2 in DCE. In principle, radical processes may compete with electrophilic addition; however, this should be detectable from deviations from a linear kinetic plot. To ensure linearity of the 1/absorbance versus time plots, an excess of isoamyl nitrite, a compound that is known to efficiently trap free radicals, was added to the solvent.[17]

Kinetics of the bromination reaction: All additions of Br_2 to alkynes were performed in DCE or in chloroform. The reactions follow an overall third-order kinetic law (second-order with respect to the bromine concentration), which is similar to the reaction order of alkene halogenations and demonstrates that two bromine molecules are involved in the process:

$$\frac{-\mathrm{d}[\mathrm{Br}_2]}{\mathrm{d}t} = k_3[\mathrm{Br}_2]^2[\mathrm{alkyne}]$$

The reactions were monitored either with a spectrophotometer or, in the case of fast-reacting alkynes, with a stopped-flow apparatus (see Experimental Section) and the kinetic parameters were calculated from the slope of 1/absorbance versus time. All the reactions were followed for at least two half-lives and the experiments were repeated three times at all indicated temperatures. Activation parameters were obtained from the Arrhenius equation. The kinetic constants (summarized in Table 2) indicate that the arylalkylacetylenes react considerably faster than the dialkyl derivatives, so the size and electronic nature of the alkyl group thus influences the reaction rate.

Substituent effects: A methyl group (in **2**) accelerates the bromination reaction by a factor of 1.6 relative to that in **1**. More pronounced acceleration (7 and 3.7 times, respectively) was found for the ethyl and propyl derivatives **3** and **4**. Since the effect of increased alkyl substitution, which is expected to inductively stabilize a neighboring cationic center, is smaller than one order of magnitude, it can be concluded that very little positive charge develops at the acetylenic carbon C2. This is consistent with an open-ion-like structure in addition reactions of **1**–**4**.[17] The observed acceleration is of the same order of magnitude as that found in α-arylvinyl cations generated by solvolysis of the corresponding bromides, which can be explained by a small stabilizing inductive effect of the β-methyl group on the vinyl cation.[18] Normal α-arylvinyl cations are stabilized by (α-aryl)-π-p^+ conjugation.[19] A similar trend has been observed in the bromination of alkyl-substituted phenylacetylenes in other solvents like methanol, acetic acid, and water–acetone mixtures; this demonstrates that the bromine in the β-position does not interfere with the stabilization of the phenyl group of the vinyl cation.[20] Furthermore, kinetic data for bromination reactions of α-methylstyrene derivatives in acetic acid have shown that the rate increases significantly only where the methyl and phenyl groups are geminal, while in the vicinal orientation no significant change is observed.[21] All these findings indicate that the positive charge has to develop mainly on the C1 carbon atom of the intermediate. This conclusion is also confirmed by the striking effect of the *p*-substituent in the arylpentylacetylene derivatives of type **5**: the methoxy group (in **5a**) causes an acceleration of the reaction of about six orders of magnitude with respect to the unsubstituted **5b**, while the cyano group (**5c**) depresses the rate constant by three orders of magnitude. This is underlined by the most negative apparent activation energy ($E_{a(obsd)}$) and $\Delta H^{\ddagger}$ for **5a** while positive values of both parameters were obtained for **5c**. An intermediate situation is found for the unsubstituted derivative **5b**. It is worth noting that the diphenyl derivative **6** reacts slowly compared with compounds **1**–**5**. This effect of the second phenyl group in tolane has already been noted and tentatively attributed to an inductive electron-withdrawing effect.[20] Bromination of **7** is slow as expected of a substrate in which

Table 2. Kinetic constants and activation parameters for the reaction of Br_2 with alkynes **1**–**7** in dichloroethane, DCE.

Alkyne	T [°C]	k_3 [mol^{-2} s^{-1}]	$E_{a(obsd)}$ [kcal mol^{-1}]	$\Delta H^{\ddagger}$ [kcal mol^{-1}]	$\Delta S^{\ddagger}$ [eu]
1	10	11.22			
1	25	11.10	−0.13 (0.02)	−0.73	−56
1	40	10.98			
2	10	19.25			
2	25	18.32	−0.61 (0.08)	−1.21	−56
2	40	17.35			
3	10	83.3			
3	25	78.7	−0.67 (0.09)	−1.27	−54
3	40	74.3			
3[a]	10	8.03			
3[a]	25	8.95	+1.17 (0.2)	+0.58	−52
3[a]	40	9.81			
4	10	42.5			
4	25	40.5	−0.55 (0.07)	−1.14	−55
4	40	38.7			
5a	12.5	1.44×10^7			
5a	26	1.26×10^7	−1.73 (0.3)	−2.32	−33.9
5a	35	1.15×10^7			
5b (*p*-H)	10	51.2			
5b	25	50.0	−0.28 (0.02)	−0.87	−53.7
5b	40	48.8			
5c	10	0.021			
5c	18	0.031	+8.71 (0.3)	+8.12 (0.3)	−37.3 (1)
5c	25	0.046			
6	10	0.4			
6	25	0.6	+4.34 (0.8)	+3.77	−47
6	40	0.84			
7	10	0.31			
7	25	0.63	+7.2 (1.0)	+6.6	−37.5
7	40	1.05			

[a] Reaction in $CHCl_3$.

no open, stabilized vinyl cation is formed. Here the bridged, unstable bromirenium ion is favored.

As discussed above, electronic effects of *p*-substituents strongly influence the rate of bromine addition in the series **5a–c**. A Hammett treatment of compounds **5a–c** with Brown's $\sigma^+(p)$ constants yields $\rho = -5.9$ as the reaction constant. The correlation ($R^2 = 0.99$) is quite good, although unfortunately only three points are available (a less pronounced linear correlation was found when the corresponding σ constants were used). This large, negative value confirms a developing positive charge on the intermediate.[8, 11] A possible change in the mechanism with increasing $\sigma^+(p)$ substituents, as has been postulated to occur in the bromination reactions of styrenes,[22] cannot be determined from the limited number of values. Reported reaction constants for substituents in solvolysis of α-arylvinyl derivatives lie in the order of -4 to -6.[19] In contrast to β-alkyl groups, which inductively stabilize the α-arylvinyl cation, β-bromo substitution destabilizes the positive charge and a possible stabilization by anchimeric formation of the bromirenium ion can thus be excluded. Therefore, the energy of the bromirenium ion is higher than that of the isomeric β-bromovinyl cation. Only in those cases where electron-withdrawing substituents on the aromatic moiety strongly destabilize the positive charge of the α-arylvinyl cation may the bromirenium ion possibly become the product-determining intermediate, especially in a non-ionizing solvent like DCE.

For the bromination of **1–4**, a small, negative value for the apparent activation energy was observed. This observation is new in alkyne bromination and similar to reports on electrophilic bromine additions to cyclohexene[1] and (*E*)-2,2,3,4,5,5-hexamethylhex-3-ene in DCE,[23] and provides conclusive evidence that the 1:1 charge-transfer complex between Br_2 and the alkyne is an essential intermediate.[24] As has been previously reported, the reaction of an olefin with Br_2 that involves a π complex as the reaction intermediate can be described by a bimolecular rate law as shown in Equation (1); the apparent activation energy $E_{a(obsd)}$ is related to the π-complex formation constant and enthalpy (K_f and ΔH^T) by Equation (2), where $E_{a(2)}$ is the true activation energy for the transformation of the π complex into the product.

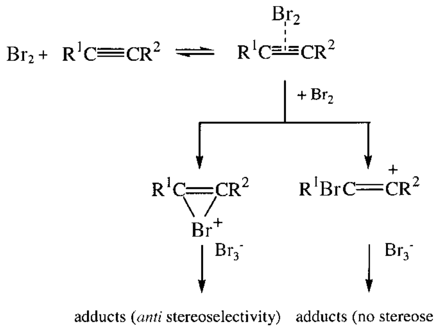
$$\frac{-d[Br_2]}{dt} = k_2[Br_2][Br_2-\text{alkyne}] \tag{1}$$

$$E_{a(obsd)} = E_{a(2)} + \Delta H^T\left(\frac{1}{1+K_f[\text{alkyne}]}\right) \tag{2}$$

Therefore, if $\Delta H < 0$, this equation can give a negative value of $E_{a(obsd)}$, provided that $|\Delta H| > E_{a(2)}$ and $K_f[\text{alkyne}] < |\Delta H|/E_{a(2)}$. These requirements are certainly met in the case described here, since the value of K_f is very low. The thermodynamic scheme and the energetics of the 1:1 species together with the reaction enthalpy suggest a second, 2:1 bromine–alkyne complex as an intermediate. This is quite similar to results obtained from bromination reactions of olefins, where the second bromine molecule helps in the formation of the charged intermediates by electrophilic catalysis.[5]

The behavior of alkyne **3** deserves a further remark. The measured rate constant k_3 in $CHCl_3$ is lower by one order of magnitude than in DCE. This, however, is not too surprising since the direct influence of the polarity of the chlorinated solvent on the reaction rate had already been noted and discussed in earlier studies.[25] In fact, the far less polar solvent chloroform probably decelerates the formation of the charged intermediate. $CHCl_3$ also leads to a significant change in the activation parameters. $E_{a(obsd)}$ is positive in this solvent, and 1.8 kcal mol^{-1} higher than in DCE.

The generally accepted mechanism of alkyne bromination involves the rate-determining formation of a cationic intermediate, which then reacts further with the nucleophile to give the final addition product, the more stable[26] (*E*)- and/or the (*Z*)-dibromo derivative. In chlorinated solvents and at moderate halogen concentrations, this nucleophile normally corresponds to a trihalide species.[3, 27] The cationic intermediate can be either a cyclic bromirenium or a β-bromovinyl cation as has been reported by Modena and co-workers (Scheme 2).[9, 11]



Scheme 2. The generally accepted mechanism of alkyne bromination: formation of a cationic intermediate (either a cyclic bromirenium or a β-bromovinyl cation), which then reacts further with the nucleophilic trihalide species to give the final addition product, the (*E*)- and/or (*Z*)-dibromo derivative.

The nature of the cationic intermediate can then be deduced from the stereochemical outcome of the reaction: the intermediacy of the bridged bromirenium ion can be reasonably assumed if the (*E*)-dibromo adduct is found, while a more or less pronounced formation of *Z* isomer will indicate an open-ion intermediate. Therefore we have also investigated the product distribution of the reaction of alkynes **1–7** with Br_2.

Study of the product distribution: (*E*)- or (*Z*)-dibromoalkene derivatives were identified by the use of the (*E*)-dibromoalkenes as reference compounds. These were synthesized selectively by reaction of alkynes with tetra-*n*-butylammonium tribromide (TBAT). The tribromide is known to react with alkenes through a concerted mechanism, and no charged intermediate like a bromonium ion or a β-bromo cation (see Scheme 2) occurs in this reaction. Products derived from stereoselective *anti*-addition are formed exclusively.[28] A similar mechanism has been demonstrated in the reaction of tribromide (and triiodide) with alkynes.[29] In the present investigation we actually obtained a single dibromo adduct by reaction of TBAT with each of the unsaturated compounds **1–7**. On the basis of these reference products, the ratio of *E* and *Z* products in the reaction mixtures was determined by GLC and NMR techniques (Table 3).

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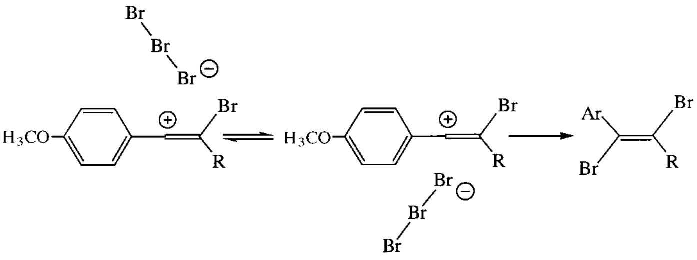
Table 3. Concentrations of reagents after mixing and product distribution (ratio of (*E*)- and (*Z*)-dibromoalkene) for the reaction of Br_2 with the alkynes **1**–**7** in DCE.

Alkyne	[Alkyne] [M]	[Br_2] [M]	*E*:*Z* [%]
1	0.1	0.1	57:43
2	0.2	0.2	78:22
3	0.07	0.07	70:30
4	5×10^{-3}	5×10^{-3}	66:34
4	5×10^{-2}	5×10^{-2}	67:33
4	5×10^{-2}	5×10^{-1}	70:30
4	5×10^{-2}	2.5×10^{-2}	66:34
4	0.5	0.5	77:23
5a	0.1	0.1	95:5
5b	0.5	0.5	72:28
5c	0.1	0.1	100:0
5d	0.1	0.1	100:0
6	0.1	0.1	60:40
7	0.1	0.05	100:0

Bromine adds stereospecifically to alkynes **5c**, **5d**, and **7**. For **5c** and **7**, positive activation parameters have been determined (Table 2); however, for **5d** no kinetic results could be obtained since an impurity underwent fast reaction with Br_2. Dependence of the product distribution on the concentration of the reagents, as is known to occur in the halogenation of stilbene derivatives,[30] can be ruled out on the basis of the results obtained for **4** since variation of reagent concentration by two orders of magnitude did not lead to any significant changes in the *E*:*Z* ratio.

Z adducts were formed (22 to 43%) from the bromination of all the other alkynes, with the exception of **5a** where, surprisingly, the reaction was stereoselective (95% *E* adduct). The presence of both diastereoisomeric products from the bromination of **1**, **2**, **3**, **4**, and **5b** indicates that open vinyl cations must therefore occur as the product-determining reaction intermediates. Interestingly, these product mixtures are in accord with the calculated negative activation parameters (see Table 2). The assumption that aryl acetylenes react via β-bromovinyl cations parallels previous results obtained in acetic acid and other protic solvents.[31] It is known that both the benzylic and the vinylic nature of the intermediate allows efficient delocalization of the positive charge over the phenyl ring through allenic conjugation.[32] This finding also explains the lower energy of this intermediate with respect to the bridged bromiranium ion, whose presence is indicated by the exclusive stereospecific formation of the *E* dibromides during bromination of dialkylacetylenes[9] and arylalkynes with electron-withdrawing substituents, such as in **5c** and **5d**. Positive activation parameters were found only in these latter derivatives. But a further factor exists that may influence the product distribution: according to the above interpretation it is not clear why bromination of **5a** leads to 95% of the *E* product. Here a very stable open ion must be involved, as can be concluded from recently reported NMR spectroscopic measurements of similar vinyl cations[33] and the formation of significant amounts of *Z* isomer would be expected as a consequence of *syn* attack of the tribromide (the nucleophile) on the β-bromo cation. This unexpected behavior is most likely due to the stability of the charged intermediate. The nucleophile can probably undergo a favorable translation process prior to attack that leads to *trans* stereochemistry, as depicted in Scheme 3.



Scheme 3. Favorable translation of the nucleophile prior to attack, resulting in *trans* stereochemistry.

The bromination of alkyne **6** gives rise to a mixture of *E* and *Z* products, which indicates an open intermediate, but with a positive activation energy. Besides the electronic and steric effect of the second phenyl substituent, two further factors may be responsible for this nonselective addition. Firstly there will be considerable steric repulsion between the geminal phenyl ring and the bromine substituents at C2. The second factor, probably much more important, is the stabilization of **6** due to conjugation of the two phenyl rings with the tolane triple bond. During the development of the charge on C1, this conjugation will be lost, and the step therefore requires additional energy.

Finally, we propose a reaction profile for the bromination reactions of alkynes as shown in Figure 3. The reaction starts with the exothermic formation of the reactive, essential 1:1 Br_2–alkyne complex, which is lower in energy than the reagents. This leads to a second 2:1 complex, from which a trihalide anion and two different cationic intermediates can form, depending on alkyne structure: aryl-substituted acetylenes most likely give rise to an open β-bromovinyl cation[32] at an energy comparable to that of the reactants, whereas the deactivated phenylacetylenes and the dialkyl derivatives probably form the irenium species. Final attack of the nucleophilic trihalide anion then leads to the formation of (*E*)- or, alternatively, (*Z*)-1,2-dibromoalkenes.

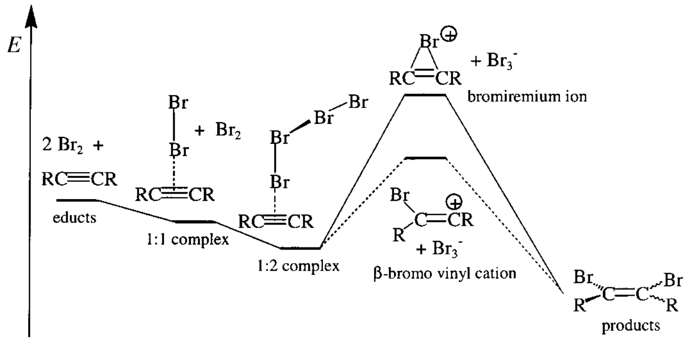
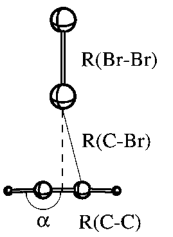


Figure 3. Proposed reaction profile for the electrophilic addition of bromine to alkynes.

The question of reversibility of the formation of the charged intermediate cannot be answered in the present investigation and further investigations are also required to show whether the positive charge can lie on the bridging bromine atom, as found in the case of the bromirenium ion[34] in these solution reactions. Investigations carried out so far[34, 35] do not tackle this problem. However, it seems reasonable to assume that the reversible steps in this reaction can only be restricted up to the formation of the irenium intermediates.

Theoretical analysis of the bonding in the charge-transfer complex Br_2–HCCH and trimolecular complexes $(Br_2)_2$–HCCH: To probe the nature and energetics of the experimentally observed complexes of Br_2 and alkynes, we have investigated the parent system HCCH–Br_2 as well as the trimolecular $(Br_2)_2$–HCCH complexes invoked in the addition reactions by means of hybrid (B3LYP) and pure density functional calculations (BLYP) (see Computational Methodology in the Experimental Section for details). The reliability of density functional calculations for the elucidation of such weak charge-transfer complexes has recently been demonstrated.[5, 36] We started with an analysis of the bonding in the T-shaped complex Br_2–HCCH (structure **III**) and then proceeded to analyze the geometrical and electronic features of the trimolecular complexes $(Br_2)_2$–HCCH.



III

Table 4 shows the results of the B3LYP and BLYP calculations for the axial-perpendicular 1:1 complex **III** between Br_2 and HCCH (C_{2v} symmetry). The Br_2–HCCH complex can be regarded as an archetypal charge-transfer complex. The nature of these weak intermolecular complexes was described qualitatively a long time ago by Mulliken in his seminal contributions on the interactions of electron donors and acceptors.[37, 38] In Mulliken's classification scheme, these halogen π complexes are generally termed weak *outer* complexes, since the interactions do not involve a significant amount of charge transfer.[39] However, it should be noted here that the distinction between *inner* and *outer* complexes is often used in a confusing manner in the current literature. As Mulliken stated,[37] formation of a strong *inner* complex will generally require a dissociative action that usually occurs only with environmental assistance, that is in a solvent that will lead to dissociation of the complex into two ionic entities. Use of the terms *outer* or *inner* complex for a gas-phase system can thus be misleading.

Table 4. Results for the density functional calculations on the Br_2–HCCH species **III**. Bonding energy E corresponds to the zero-point energy corrected ΔE values between the separate Br_2 and HCCH molecules and the charge-transfer complex, Br_2–HCCH. Occ(LUMO) of Br_2 is the calculated occupation of the LUMO of the Br_2 fragment; $Q(Br_{cent})$ and $Q(Br_{term})$ correspond to the calculated charges on the terminal (Br_{term}) and central Br atom (Br_{cent}), respectively. The reported charges are natural (B3LYP) and Hirshfeld charges (BLYP), respectively.

	B3LYP/6-31 + G*	BLYP/triple-ζ
bonding E [kcal mol^{-1}]	− 4.1	− 3.3
R (Br-Br) [Å]	2.353	2.386
R (C-Br) [Å]	3.001	2.981
R (C–C) [Å]	1.210	1.195
α [°]	179.0	178.5
Occ(LUMO of Br_2)	0.07	0.08
$Q(Br_{cent})$	0.0	− 0.01
$Q(Br_{term})$	− 0.06	− 0.07

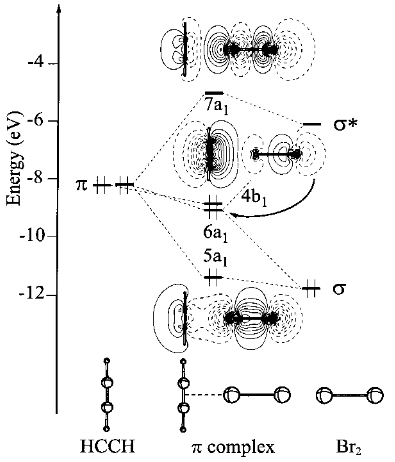


Figure 4. FMO diagram of the interaction of a Br_2 molecule with acetylene to give the charge-transfer complex **III** (only the important orbital interactions are shown).

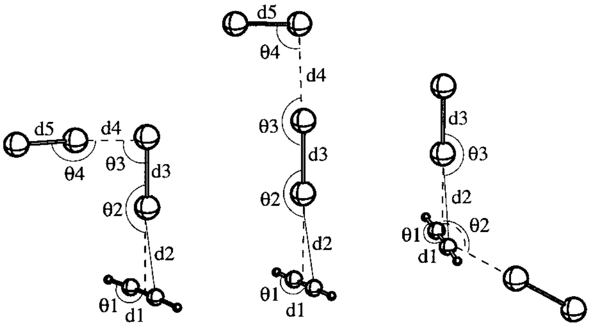
We found that in the Br_2–HCCH charge-transfer complex both the Br–Br distance and the C–C distance are slightly elongated compared to the separate molecules. Using BLYP, the C–C distance of 1.195 Å is stretched by a marginal 0.004 Å compared to acetylene, and the Br–Br bond is 0.038 Å longer than in free Br_2 (2.348 Å). This can be readily understood by taking a closer look at the orbital interactions that are responsible for holding the complex together. Figure 4 shows a fragment molecular orbital (FMO) interaction diagram for Br_2–HCCH. This donor–acceptor interaction corresponds to a typical three-level system, similar to that found in the classically hypervalent trihalides, X_3^- (X = F, Cl, Br, I),[40] and other molecular complexes.[41] The three orbitals are formed by the interaction of one of the corresponding π levels of the HCCH fragment, the bonding σ orbital and the low-lying, antibonding σ* level of the Br_2 fragment. The lower orbital of the set ($5a_1$) of three is maximally bonding, the central orbital ($6a_1$) is practically nonbonding, and the unoccupied high-lying orbital, $7a_1$, is antibonding. The calculated charges on the Br_2 fragment serve as a good measure of the actual strength of the interaction between the two molecules. The BLYP results indicate that − 0.08 electrons have been transferred from the acetylene molecule to the two bromine atoms in the complex. The central and terminal Br atoms have charges of − 0.01 and − 0.07, respectively. This charge transfer arises from the mixing of the unoccupied σ* orbital of Br_2 into the central orbital $6a_1$. The occupation of this σ* orbital is exactly 0.08 (BLYP result), which indicates that other interactions between the two closed-shell Br_2 and HCCH fragments must be very weak. Table 4 shows the corresponding bonding energies (B3LYP/6-31 + G* and BLYP(triple-ζ) calculations). The temperature-corrected bond enthalpy (at 298 K) amounts to 2.6 kcal mol^{-1} at the BLYP level of theory. This value is in very good agreement with the experimentally determined value of 2.95 kcal mol^{-1} for the phenylpropyne–Br_2 complex (see above). We do not expect this number to change dramatically

Table 5. Bond lengths [Å] and angles [°] for the optimized $(Br_2)_2-HCCH$ complexes corresponding to structures **IV**, **V** and **VI**.

	d1	d2	d3	d4	d5	θ1	θ2	θ3	θ4
IV (BLYP)	1.195	2.935	2.403	2.988	2.401	179.2	176.4	101.9	178.8
IV (B3LYP)	1.211	2.921	2.362	3.170	2.347	178.8	179.2	90.12	177.2
V (BLYP)	1.193	3.050	2.400	3.197	2.350	179.3	178.9	176.7	100.8
V (B3LYP)	1.210	3.031	2.359	3.324	2.321	179.3	180.3	178.8	88.8
VI (BLYP)	1.198	3.077	2.374	–	–	178.7	126.2	180.0	–
VI (B3LYP)	1.212	3.05	2.344	–	–	179.5	95.2	179.7	–

from acetylene to phenylpropyne; however, π conjugation may increase the bonding energy slightly.

The analysis of the kinetic results points to a reactive complex that consists of two Br_2 molecules and one HCCH molecule. What are the structures of these experimentally predicted trimolecular $(Br_2)_2HCCH$ complexes? We located three weakly bound charge-transfer minima, structures **IV**, **V**, and **VI**, on the Br_2-Br_2-HCCH surface (see Table 5 for distances and bond lengths).



IV (C_s) **V** (C_s) **VI** (C_{2v})

Structures **IV** and **V**[42] both possess C_s symmetry while species **VI** corresponds to a C_{2v}-symmetric structure. Qualitatively, they are all donor–acceptor complexes of the T-shaped Br_2-HCCH complex **III**, with a second Br_2 molecule. All three structures are stationary points on the potential energy surface and can be readily understood by taking a closer look at the levels in the T-shaped complex **III**. This π complex can act as both an acceptor (through the only slightly populated σ* orbital of the weakly coordinated Br_2 entity) or as a donor, either using the remaining, unperturbed π-levels of the acetylene moiety or the lone pairs of the Br_2 unit. In structures **IV** and **VI**, the bimolecular $HCCH-Br_2$ complex acts as a donor, while the second Br_2 molecule is the acceptor. Structure **V**, however, corresponds to a species where the central Br_2 molecule acts as a double acceptor: on one end for the HCCH π electrons and on the other end for a lone pair from the second Br_2 molecule. We find that the structure **IV** is the most stable complex, at both levels of theory employed (Table 6). The bond energy of a Br_2-HCCH complex that reacts with a further Br_2 molecule amounts to −4.8 (BLYP) and 4.0 kcal mol^{-1} (B3LYP). This can be rationalized by the better donor ability of Br_2, as compared to the HCCH π orbitals and the fact that the σ* system in the Br_2 entity of complex **III** is already slightly populated. Thus the second Br_2 molecule acts as an acceptor, rather than further populating this orbital. In line with this argument, we find that both Br_2 units in complex **IV** are elongated by 0.017 (d3) and 0.021 Å (d4) compared to the bimolecular π complex **III** and free Br_2.

Table 6. Relative energies [in kcal mol^{-1}, ZPE-corrected] of the trimolecular $(Br_2)_2HCCH$ species with respect to formation of Br_2 and the π complex Br_2-HCCH (**III**).

	B3LYP	BLYP
2	−4.0	−4.8
3	−1.4	−3.7
4	−2.3	−3.5
$Br_2 + HCCH-Br_2$ (**1**)	0.0	0.0

Figure 5 shows the fragment molecular orbital diagram for the interaction of a Br_2 molecule with π complex **III**, corresponding to structure **IV**. As we can see, the picture is slightly more complicated than in the simple bimolecular charge-transfer complex. The Br_2-HCCH system actually donates electron density into the empty σ orbital of the second Br_2 molecule through the π and π* orbitals. Thus, we obtain a four-level scheme. However, the fundamental features of the donor–acceptor scheme remain unchanged and arise from population of the σ* level of Br_2. The important orbitals (4a′, 5a′, 9a′, and 12a′) are shown in Figure 6. 4a′ is the bonding orbital, 5a′ and 9a′ are now essentially nonbonding between the Br_2 and $HCCH-Br_2$, and 12a′ is the antibonding combination.

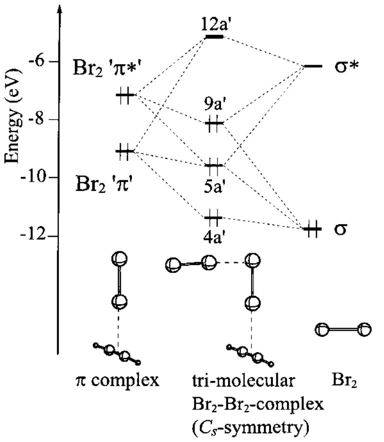


Figure 5. FMO diagram of the interaction of a Br_2 molecule with the Br_2-HCCH π complex **III** to give rise to species **V** (only the important orbital interactions are shown).

Interestingly, structure **IV** is very similar to the trimolecular complex between two Br_2 molecules and the sterically hindered alkene adamantylidene-adamantane (**II**) which was structurally characterized by Brown et al.[43] This species is generally viewed as a bromonium ion, but in the 2:1 complex

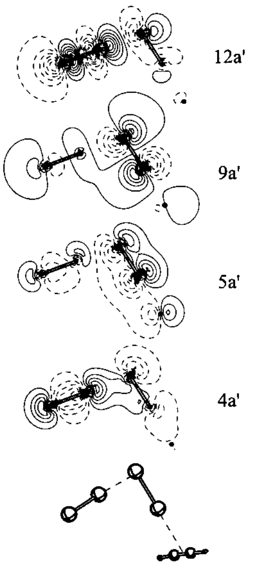


Figure 6. The MOs of $(Br_2)_2-HCCH$ (**V**) involved in the donor-acceptor interaction of a Br_2 molecule with the charge-transfer complex Br_2-HCCH (**III**).

IV we have no charge separation. In fact, heterolytic bond cleavage is extremely unlikely to be observed in these gas-phase calculations. This might indicate that Brown's 2:1 alkene-bromine complex is really much more closely related to a donor-acceptor species than to the actual bromonium ion, which is readily formed in an ionizing solvent.

Still we need to ask why such trimolecular complexes are involved in electrophilic bromination reactions? If we assume that the electrophilic addition in solution proceeds by a nonconcerted, ionic mechanism that involves a solvated bromirenium ion $Br-HCCH^+$, the calculated heterolytic dissociation energy of the Br_2-HCCH π complex that forms the bromirenium ion and a Br^- anion has to be compensated by the solvation energy of the resulting Br^- and cyclo-$BrHCCH^+$ ions. The energy for this heterolytic bond cleavage in the gas phase is 161.4 $kcal\,mol^{-1}$ (BLYP results). However, the enthalpy of formation of Br_3^- from Br^- and Br_2 lies around 40 $kcal\,mol^{-1}$,[43] which reduces the energy required for heterolytic dissociation significantly. Thus, the formation of the classically hypervalent trihalide anions X_3^- via such trimolecular complexes lowers the barrier for the ionic pathways in electrophilic halogenation reactions significantly.

Conclusions

A 1:1 complex of Br_2 and phenylmethylacetylene was detected in DCE by UV spectroscopic measurements of halogen and alkyne reaction mixtures by means of diode-array stopped-flow methods. The stability of this complex has been determined and its thermodynamic data measured. The λ_{max} of this species is red-shifted by 15–25 nm with respect to similar π complexes formed by alkenes, while ε_{max} is slightly increased.

The present investigation furnishes the first direct kinetic evidence for the intermediacy of an early 1:1 Br_2–alkyne complex in the reaction profile. This is consistent with results from quantum-chemical calculations. The negative apparent activation energies which have been measured in the bromination reactions of arylalkylacetylenes in DCE are only compatible with the formation of a reactive complex that precedes the rate-determining step.

A tribromide salt, TBAT, was used to obtain reference (*E*)-dibromoalkenes. Comparison of these species with the mixtures from the reactions of molecular bromine with the alkynes enabled reliable product distributions to be determined. We have found that the reactions with negative activation energies lead to *E*:*Z* mixtures. In these cases, it can be concluded that the ionic intermediate corresponds to an open β-bromovinyl cation. For reactions that possess positive activation energies, the *E* isomer is obtained stereospecifically, and a bridged bromirenium ion appears to be the intermediate. A consistent reaction profile for these reactions has been proposed.

On the basis of the present results, the question of the possible influence of the stability of the 1:1 π complex on the low reactivity of alkynes compared with alkenes[8, 12] can be addressed as follows: We believe that the bromination of arylalkylacetylenes, which possess negative apparent activation energies, most likely passes through an open intermediate. The difference in the stability of the early 1:1 complexes may account for the different reactivities. The formation constant of the Br_2-**2** complex ($K_f = 0.065\ L\,mol^{-1}$) is lower, by orders of magnitude, than for all Br_2–alkene complexes reported so far. Also, in these cases, the difference in reactivity is relatively small, quite in contrast to dialkylacetylenes, or deactivated aryl substrates. With regard to these latter alkynes, the low stability of the complex can contribute to, but not fully explain, the difference. So a decisive contribution must come from bromirenium intermediates which lie higher in energy and whose formation is accompanied by high, positive activation energies.[44]

Detailed density functional calculations yield further insight into the structures and energetics of these charge-transfer complexes. We find that the Br_2 entity in the bimolecular halogen–acetylene charge-transfer complex preferably functions as a donor for a second Br_2 molecule, which gives rise to a trimolecular complex that is structurally very similar to a stable Br_2-Br_2–alkene adduct that was reported some time ago.

Experimental Section

Instruments and materials: Melting points were determined on a Kofler apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ with TMS as the internal reference on a Bruker AC200 instrument. Kinetic measurements were performed with a Cary 2200 spectrophotometer or with a previously described[14] stopped-flow instrument equipped with a parallel diode-array detector. GLC analyses were carried out with a DANI 3800HR instrument equipped with a 30 m DB17 megabore column under the following conditions: nitrogen flow 1 $mL\,min^{-1}$, evaporator and detector 240 °C, column temperature 130 °C. Bromine (1 mL sealed ampoules, C. Erba, >99.5%) and 1,2-dichloroethane (Fluka, >99.5%) were used as supplied.

Compounds **5a–d** were prepared by palladium-mediated coupling of appropriate aryl halides and 1-heptyne.[45] The preparation of **5a** by this procedure, however, led to a mixture of isomers. Reaction of heptynyl zinc reagent with *p*-iodo anisole in analogy to ref. [46] gave rise to a uniform product. All products were purified by flash chromatography and subsequently by kugelrohr distillation. However, **5d** could not be separated from a brownish impurity, which was not visible in the NMR spectra. (The NMR data of compounds **5a–d**, along with their boiling points and yields, are available as supporting information on the WWW under http://www.wiley-vch.de/home/chemistry/ or from the author.)

Bromination procedure: measurement of the kinetics and stability of the π complexes: Br_2 solutions in 1,2-dichloroethane with a fivefold excess of isoamyl nitrite were prepared shortly before use, and were adjusted to twice the initial concentrations in the kinetic runs and protected from daylight. Aliquots of these solutions, kept at the temperatures reported in Table 1, were mixed with equal volumes of thermally equilibrated solutions of alkynes **1**–**7** of suitable concentration. The kinetic measurements for the bromination of alkynes **1**–**4**, **5c**–**d**, and **3**–**7** were carried out with the conventional spectrophotometer, those of **5a** and **b** with the stopped-flow apparatus. All the kinetics of bromination with TBAT were determined in the conventional spectrophotometer. Temperature control was ensured by a mixing device, a Sf-3L Hi-Tech support unit. The kinetic constants were calculated at several wavelengths from 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. All reactions were carried out a minimum of three times. The kinetic constants are reported in Table 2. The apparent activation parameters, also reported in Table 2, were obtained from Arrhenius plots. The initial absorbance at 560 nm of 7×10^{-2} M solutions of Br_2 and 3 M (after 1:1 mixing) in the unsaturated species was measured in triplicate at different temperatures (see Table 1). At the end of the reactions, the solvent was evaporated, and the reaction mixtures were analyzed by GLC.

Product distribution: 1,2-Dichloroethane solutions of Br_2 were rapidly mixed with equal volumes of solutions of alkynes **1**–**7** in the same solvent. The reaction mixtures were maintained in the dark until colorless and, after solvent removal, analyzed by NMR in $CDCl_3$, and eventually by GLC. The concentrations of reagents after mixing are reported in Table 3. Each alkyne was also treated with TBAT by the same procedure. In this case, the residual bromide was washed out from the solution before solvent removal. The *E*:*Z* ratios were determined on the basis of the allylic signals in the ^{1}H NMR spectra (except for products **1**$+Br_2$ and **6**$+Br_2$). All reactions were carried out in duplicate. The ratios reported in Table 3 were reproducible within ±2%. All product ratios were independent of conversion. The stability of dibromides in the presence of halogen was checked by exposure of the dibromide mixtures to Br_2 under conditions identical to those employed in the bromination reactions, followed by NMR analysis.

From alkyne 1: The *E:Z* ratio was determined from the signals of the vinyl protons. *(Z)*-1,2-dibromostyrene: ^{1}H NMR: $\delta = 7.02$ (6.98)[46] 3%; (*E*)-1,2-dibromostyrene: $\delta = 6.77$ (6.75)[46] 93%.

From alkyne 2: (*E*)-1,2-dibromo-1-phenylpropene. ^{1}H NMR: $\delta = 7.50$ (m, 5 aromatic protons), 2.60 (s, 3H, CH_3); *(Z)*-1,2-dibromo-1-phenylpropene; $\delta = 7.35$ (m, 5 aromatic protons); 2.26 (s, 3H, CH_3).

From alkyne 3: *(E)*-1,2-dibromo-1-phenylbutene: ^{1}H NMR: $\delta = 7.35$ (m, 5 aromatic protons), 2.84 (q, 2H, CH_2), 1.22 (t, 3H, CH_3); *(Z)*-1,2-dibromo-1-phenylbutene: $\delta = 7.35$ (m, 5 aromatic protons), 2.40 (q, 2H, CH_2), 1.10 (t, 3H, CH_3).

From alkyne 4: *(E)*-1,2-dibromo-1-phenylpentene: ^{1}H NMR: $\delta = 7.16$ (m, 5 aromatic protons), 2.80 (m, 2H, CH_2), 1.70 (m, 2H, CH_2), 1.00 (t, 3H, CH_3); *(Z)*-1,2-dibromo-1-phenylpentene: $\delta = 7.16$ (m, 5 aromatic protons), 2.32 (m, 2H, CH_2), 1.55 (m, 2H, CH_2), 0.77 (t, 3H, CH_3).

From alkyne 5a: *(E)*-1,2-dibromo-1-(*p*-methoxyphenyl)heptene: ^{1}H NMR: $\delta = 7.30$–6.87 (AA′BB′ system, 4 aromatic protons), 3.80 (s, 3H, CH_3O), 2.82 (m, 2H, CH_2), 1.70 (m, 2H, CH_2), 1.38 (m, 2H, CH_2), 0.94 (t, 3H, CH_3); *(Z)*-1,2-dibromo-1-(*p*-methoxyphenyl)heptene: $\delta = 2.38$ (m, 2H, CH_2).

5b: *(E)*-1,2-dibromo-1-phenylheptene: ^{1}H NMR: $\delta = 7.33$ (m, 5 aromatic protons), 2.84 (m, 2H, CH_2), 1.70–0.85 (m, 9H, alkyl protons); *(Z)*-1,2-dibromo-1-phenylheptene: $\delta =$ 2.37 (m, 2H, CH_2).

From alkyne 5c: *(E)*-1,2-dibromo-1-(*p*-cyanophenyl)heptene: ^{1}H NMR: $\delta = 7.66$–7.46 (AA′BB′ system, 4 aromatic protons), 2.84 (m, 2H, CH_2), 1.74–0.94 (m, 9H, alkyl protons); *(Z)*-1,2-dibromo-1-(*p*-cyanophenyl)heptene: $\delta = 2.36$ (m, 2H, CH_2).

From alkyne 5d: *(E)*-1,2-dibromo-1-(*p*-nitrophenyl)heptene: ^{1}H NMR: $\delta = 8.22$–7.52 (AA′BB′ system, 4 aromatic protons), 2.85 (m, 2H, CH_2), 1.74–0.94 (m, 9H, alkyl protons); *(Z)*-1,2-dibromo-1-(*p*-nitrophenyl)heptene: $\delta = 2.38$ (m, 2H, CH_2).

From alkyne 6: *(E)*-1,2-dibromo-1,2-diphenylethene: ^{13}C NMR: $\delta = 125.66$ (CBr=C); *(Z)*-1,2-dibromo-1,2-diphenylethene: $\delta = 118.05$ (CBr=C).

From alkyne 7: *(E)*-1,2-dibromo-2-hexene: ^{1}H NMR: $\delta = 2.42$ (s, 3H, $C{=}CCH_3$), 2.64 (t, 2H, $C{=}CCH_2$), 1.60 (m, 2H, CH_2), 0.94 (t, 3H, CH_3).

Computational methodology: The quantum mechanical calculations were carried out with the Amsterdam Density Functional (ADF) program[47–49] and the Gaussian94 suite of programs.[50] Within ADF the gradient corrections were performed with the Becke (exchange)[51] and Lee–Yang–Parr (correlation)[52–54] formulations (commonly known as BLYP functional). A triple-ζ basis set with one polarization function was employed for bromine and triple-ζ basis sets with two added polarization functions were used for carbon and hydrogen atoms. The core orbitals of the atoms were frozen out to 1s (C), and 3p (Br), respectively.[55] The charges reported for the ADF results were calculated with the Hirshfeld analysis.[56] Contour plots of orbitals from ADF were generated with the YAeHMOP progam.[57] The B3LYP results were obtained with the GAUSSIAN94 program with the standard 6–31+G* basis set. For these results, the reported charges correspond to natural charges obtained within the natural bond orbital scheme (NBO).[58] All reported structures were fully optimized and characterized as local minima on the corresponding surfaces by frequency analysis. The reported energy values are all corrected for zero-point energy (ZPE).

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