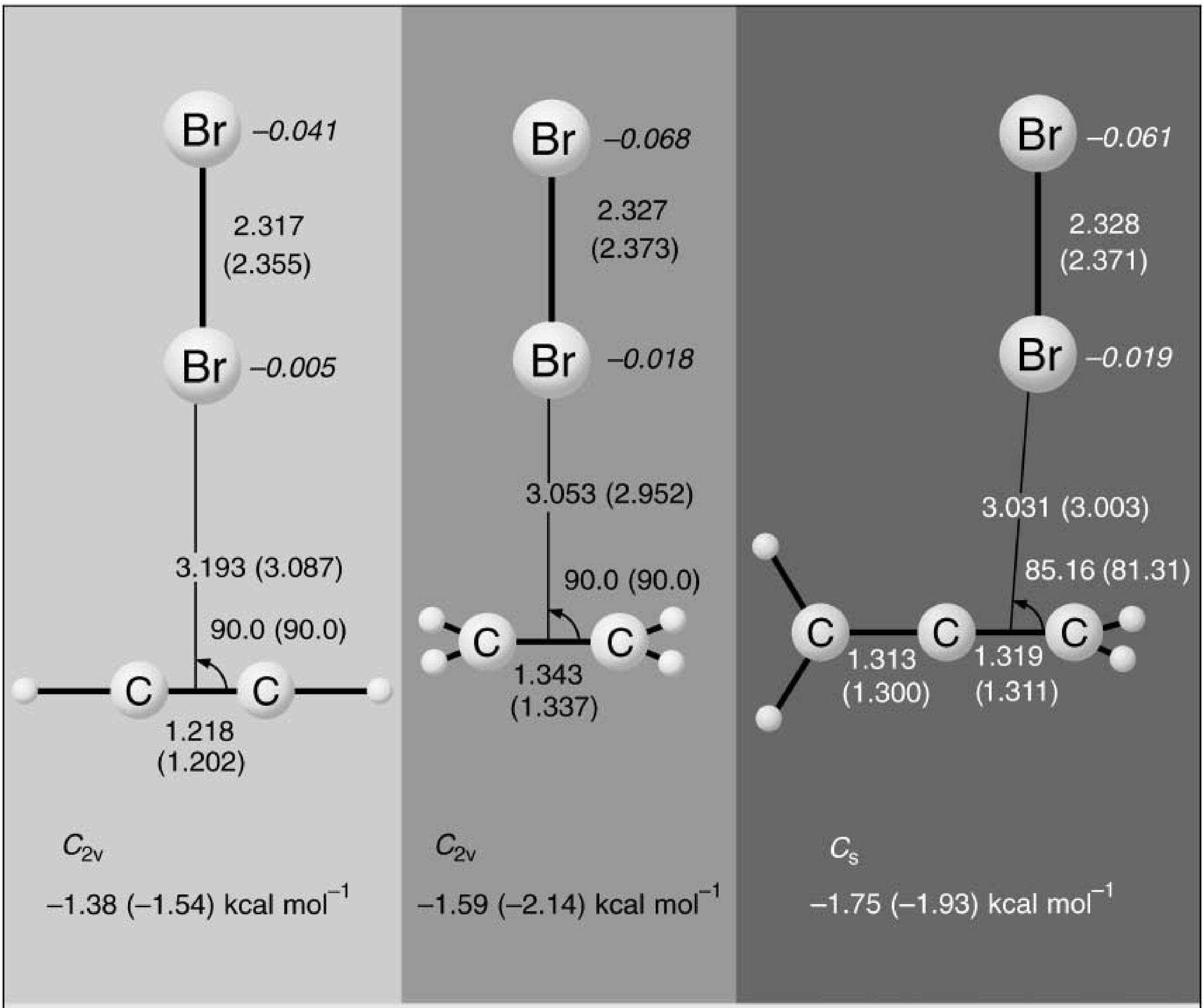

Charge-transfer complexes formed from alkenes, alkynes, and allenes with bromine have been studied experimentally and theoretically. These species have been shown to be very important on the overall reaction coordinate of brominations due to autocatalytic action of bromine.

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What is the Nature of the First-Formed Intermediates in the Electrophilic Halogenation of Alkenes, Alkynes, and Allenes?

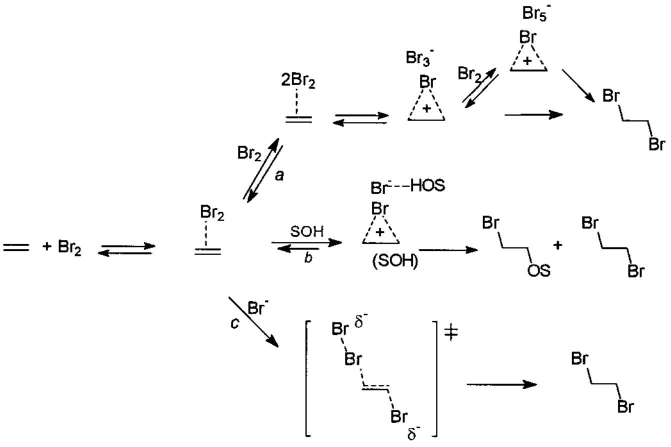
Dieter Lenoir*[a] and Cinzia Chiappe*[b]

Abstract: The π complexes first formed as essential intermediates from alkenes, alkynes, and allenes with bromine have been investigated in different solvents by UV-spectroscopy in combination with stopped-flow techniques allowing the determination of the equilibrium constants, K_f. Using alkenes with sterically protected double bonds, such as di-*tert*-butylstilbene and tetraneopentylethylene, the reaction stops at the stage of the 1:1 and 1:2 π complex of the alkene with bromine as persistent species in 1,2-dichlorethane as solvent. Calculations by state-of-art ab initio and DFT methods reproduces the experimentally determined thermodynamic values quite well, and reveal the preferred structures and nature of both complexes for ethene, ethyne, and allene. Consideration of the entropy term reveals that complexes are stabilized in solution owing to reduction of the entropy loss by restricted translations and rotation. According to calculations these species are Mulliken-outer-type complexes with no or little charge transfer from bromine to the double or triple bond, respectively. The 1:2 complex has a close structural relationship to the bromonium- or bromirenium ion, which is the subsequent intermediate on the reaction coordinate. Steric influences show a strong effect on the K_f value, which can be explained by the polarizibility of the parent system. Addition–elimination often occurs. In bromination of adamantylidenadamantane and its derivatives the reaction stops at the stage of the bromonium ion. The effect of various polar groups situated in equatorial homoallyl positions on the stability of corresponding π complex and bromonium ion has been studied in this series.

Keywords: alkenes · alkynes · allenes · bromination · electrophilic addition · molecular dynamics · pi interactions · reaction mechanisms

Introduction

Electrophilic halogenation like brominations of alkenes and alkynes performed in both protic and aprotic solvents have been extensively studied within the last decade; this has lead to a new view of the mechanism of this well-known and synthetically important reaction.[1–4] From these studies the following scheme (Scheme 1) has been developed as shown for bromination of alkenes.



Scheme 1. Detailed mechanistic scheme for bromination of alkenes, SOH represents a protic solvent.

In general, the reaction is stereoselective and leads to *trans* products. The first pathway (a, in Scheme 1) has been proposed for bromination in aprotic solvents,[4] of even modest polarity, and it is characterized by the cleavage of the bromine–bromine bond of the 1:2 complex to give an ionic intermediate, a bromonium (β-bromocarbenium) tribromide ion pair, which generally collapses to the dibromo adducts. The ionic intermediate, depending on bromine concentration, may be in equilibrium with species that have higher stoichiometry with respect to Br_2. In these solvents the reaction

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generally follows a third-order rate law (second-order in Br_2). A similar ionic mechanism, in which solvent-assisted bromine–bromine bond breaking occurs in a 1:1 olefin–Br_2 complex and in which the reaction is first-order in Br_2 (path b), has been established for bromination at low Br_2 concentration in protic solvents, which provide specific electrophilic solvatation by hydrogen bonding to the leaving bromide ion.[2] Depending on olefin structure bromination in nucleophilic solvents, for example, methanol, can occur also through a preassociation mechanism, in which the solvent on one side and bromine on the other side preassociate with the double bond before ionization within a ternary complex to generate a cationic intermediate formed in a sandwich between the leaving bromide and the entering solvent.[5]

Finally, in the presence of added bromide salts, which in low polarity nonprotic solvents bind Br_2 as a highly stable tribromide ion, bromination occurs through a rate- and product-determining nucleophilic attack by Br^- on the 1:1 olefin–Br_2 complex (path c), and the reaction follows a second-order rate law.[6]

Independently of the nature of the solvent and of the presence of added bromide ions, all the reaction pathways shown in Scheme 1 involve the formation of bromine–alkene complexes as the first (and usually short-lived) intermediates. In the case of the reactions carried out in chlorinated solvents the intermediacy of a second bromine–alkene π complex with 2:1 stoichiometry has been inferred on the basis of thermodynamic and spectroscopic evidence. The two different π complexes can be recognized by their UV charge-transfer band: while the 1:1 complex is situated at about 270–280 nm the 1:2 complex shows its maximum at 310 nm.[7] As presented in Scheme 1, these complexes are essential intermediates in the overall reaction. This can be deduced, at least for the reactions in chlorinated solvents, from the negative apparent activation energy generally found in the bromination of alkyl- and aryl-substituted alkenes. Under the hypothesis that the 1:1 complex is a reactive intermediate, the the observed rate constant is described by Equation (1), and $E_{a(\mathrm{obsd})}$ is given by Equation (2).

$$-\mathrm{d}[Br_2]_{\mathrm{tot}}/\mathrm{d}t = k_2[Br_2]_{\mathrm{free}}[Br_2\text{–alkene}] \quad (1)$$

$$E_{\mathrm{a(obsd)}} = E_{\mathrm{a(2)}} + \Delta H[1/(1 + K_{\mathrm{f}}[\text{alkene}])] \quad (2)$$

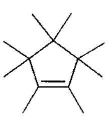
If ΔH (related to the π-complex formation) is negative, Equation (2) can give a negative value of $E_{\mathrm{a(obsd)}}$ provided that $|\Delta H|$ is larger that the true activation energy ($E_{\mathrm{a(2)}}$) and $K_{\mathrm{f}}[\text{alkene}] < |\Delta H|/E_{\mathrm{a(2)}}$; this is true for reactions carried out at not too low temperature (or high K_{f}) and not too high alkene concentration. Generally, however, the negative enthalpies found for the 1:1 π-complex formation do not fully account for the negative values of E_{a}, suggesting the occurrence on the reaction coordinate of a second bromine–alkene complex, probably the 2:1 stoichiometry complex characterized by the absorption maximum at 310 nm, which has once again a negative formation enthalpy.[8]

The spectroscopic, kinetic, and thermodynamic studies not only support the role of one or two π complexes as intermediates in bromine addition reactions, but they also indicate that some other complexes may present in solutions of alkenes and bromine. Through spectrophotometric measurements it has been established that the interaction of adamantylideneadamantane and bromine gives complexes of 2:1, 1:1, 1:2, and 1:3 stoichiometry. Conductimetric experiments reveal an ionic nature for the 1:2 and 1:3 complexes to which, supported also by NMR experiments, the structure of tribromide and pentabromide salts of the adamantylideneadamantane bromonium ion have been attributed.[9]

Influence of Steric and Polar Effects on Reaction Rates and Products formed in Bromination of Alkenes

The majority of alkenes, alkynes, and allenes react with bromine to give vicinal substituted products with *E* stereochemistry (see Scheme 1 for alkenes). It should be the mentioned that ethylene itself reacts very slowly with bromine in aprotic solvents like dichloroethane (DCE), when all components including the equipment are ultrapure. For example, an equimolar solution of ethylene and bromine in DCE stays brown due to unreacted bromine for several hours.[10] Steric effects at the double or triple bond can lead to substantional change relative to normal behavior as observed in the products obtained according to the statement “chemistry is an exercise of perturbation theory”. The results are first discussed below for steric effects after consideration of inductive effets.

Alkenes that lead to products resulting from addition–elimination: Steric bulk by alkyl groups in special tetrasubstituted alkenes like octamethylcyclopentene (**1**),[11] tetraisobutylethene (**2**),[12] (*E*)-2,2,3,4,5,5-hexamethylhex-3-ene (**3**),[13] and tri-*tert*-butylbuta-1,3-diene (**4**)[14] results in addition–elimination as a consequence of treatment with equimolar amounts of bromine; this is because the hypothetical 1,2-dibromide is sterically too strained to be formed.



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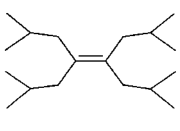

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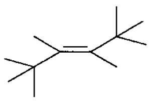

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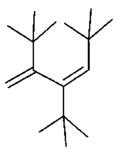

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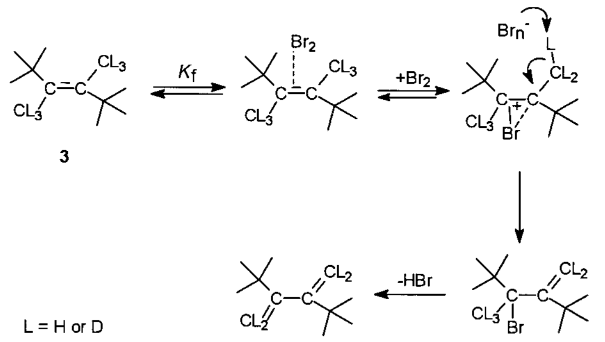
In any case sterically crowded, intermediate bromonium ions eliminate a proton either from the β-position, observed in alkenes **1**–**3**,[11–13] or from the α-position observed in compound **4**.[14]

The elimination of the proton is the rate-limiting step of the overall reaction, as shown by the value measured for primary kinetic isotope effect observed for alkene **3** (see Scheme 2: $k_{\mathrm{H}}/k_{\mathrm{D}} = 2.17$ in DCE at 25 °C. A strong temperature dependance of the effect was also observed: the value varies from 2.67 at 6.5 °C to 1.57 at 70 °C. An increase of strain in the ground state of the alkene reflects the strain of the bromonium ion as the rate- and product-determining intermediate; as consequence



Scheme 2. Products formed from the bromination of alkene **3** (equimolar amounts).

of the calculated increase of strain of 10.5 kcal mol^{-1} for alkene **3** relative to that of **4** the rate of **3** is faster by a factor of 2.4×10^4 at 25 °C in acetic acid.[13]

An alkene that results in formation of stable bromonium ion salts: The double bond in adamantylideneadamantane is unique, because the reaction of this alkene with bromine stops at the stage of the bromonium ion. This species was first observed by Wynberg in 1970 and isolated as salt with Br_3^- as the counterion.[15] A single-crystal X-ray structure has been obtained for this species, also with triflate as counterion.[16] The chemistry of this species has been extensively reviewed recently by Brown.[3] The rear of this bromonium ion is sterically strongly protected; therefore, the nucleophile cannot approach the reaction site of this species. The same behavior is observed for the epoxide of adamantylidenadamantane; this compound cannot be cleaved hydrolytically by treatment with strong bases or acids yielding the corresponding diol.[17] The rear of this cage molecule is protected by four axial hydrogen atoms held rigid by the cyclohexane moiety, see Figure 1; therefore, no reaction can occur. Surprisingly even small nucleophiles like fluoride anions do not attack the bromonium ion.[18]

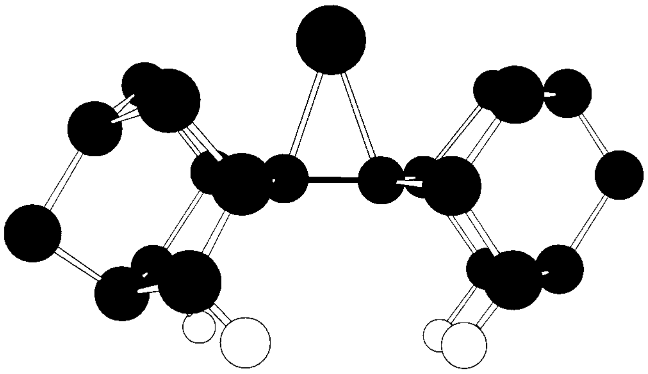
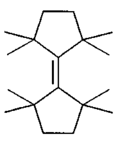


Figure 1. Structure of the halonium ion of adamantylideneadamantane with triflate as the anion, showing the steric protection of the rear of the molecule by four axial hydrogens, from ref. [3].

Persistent π complexes formed in equilibrium of sterically protected alkenes with bromine in solution: These species have been called charge-transfer complexes (CTC) in the past; a detailed discussion about their nature is given below.

Complexes of ethene and ethyne and halogens like chlorine and bromine have been investigated in the gas phase by Legon and his group by special techniques of rotational spectroscopy.[19] There are several recent studies of these species prepared in solid matrices at low temperature investigated by means of IR and Raman spectroscopy.[20]

As reported in literature and also studied by us some alkenes with sterically protected double bonds, such as octamethylcyclopentylidenecyclopentane (**6**),[21] polycyclic alkene (**7**),[22] (*E*)-di-tert-butylstilbene (**8**),[23] and tetraneopentylethylene (**9**),[7] do not react visually with bromine like normal alkenes. For alkenes **8** and **9** it was demonstrated that the reaction stops at the stage of π complexes: the existence of stable π complexes formed in equilibrium with the reagents in DCE was deduced from concentration-dependant UV spectra of these species.[7, 23]



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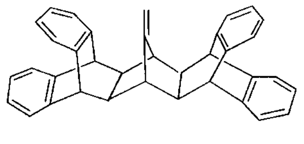

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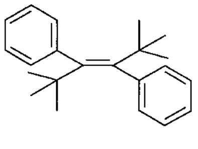

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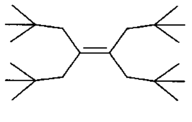

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The UV spectrum of the solution of tetraneopentylethylene, TNPE (**8**) with an equimolar amount of bromine is shown in Figure 2.[7]

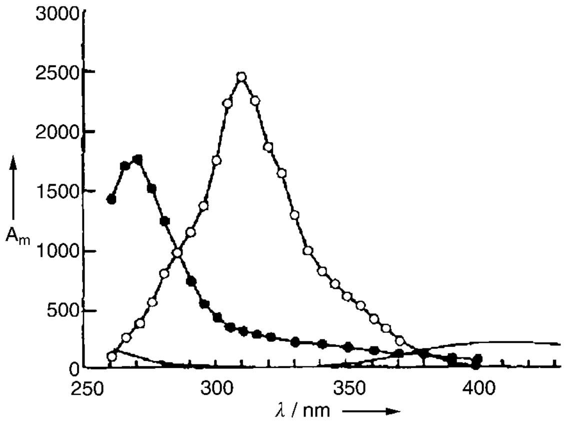


Figure 2. UV spectrum of the 1:1 (●) and 2:1 (○) complex of TNPE and bromine in DCE as compared with free bromine (–).

The structures of these complexes are known from calculations, which refer to the gas phase; see special section below. However, the structure of the bromonium ion salt of adamantylideneadamantane with Br_3^- as anion has been obtained by Brown et al., see Figure 3. This structure,

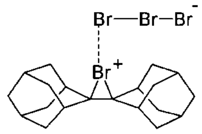


Figure 3. Structure of the solid salt of the bromonium ion of adamantylidenadamantane with Br_3^- as anion showing the close relationship to the calculated 1:2 π complex

although a bromonium ion salt, has a close resemblance to a 1:2 alkene bromine complex;[16] this is in agreement with the most stable structure calculated by ab initio methods, see below.

Influence of Steric Effects on the Equilibrium Constant K_f on the π Complex formed from Alkenes and Bromine

The π complexes formed reversibly from the reagents play an essential role on the hypersurface of this reaction; this leads further to the bromonium ion as a product-determining intermediate. This fact can be derived kinetically, as explained above, for bromination in chlorinated solvents. Table 1 summarizes the equilibrium constants for nine alkenes as 1:1 complexes measured in DCE. The values of the constants range from 0.47 for cyclohexene to 1850 for (*E*)-(1-methyl-2-adamantylidene)-1-methyladamantane.

Table 1. Equilibrium constants (K_f) for alkenes and bromine measured in DCE.

Alkene	σ_α	K_f (25 °C) [M^{-1}]	Ref.
cyclohexene (**10**)	− 0.96	0.47	[8]
(*E*)-di-*tert*-butylstilbene (**8**)	–	1.2	[23]
tetraneopentylethylene (**9**)	− 2.68	1.6	[7]
tetraisobutylethylene (**2**)	− 2.44	9.71	[12]
(*E*)-2,2,3,4,5,5-hexamethylhex-3-ene (**3**)	− 2.18	84	[13]
adamantylideneadamantane (**11**)	− 2.58	289	[24]
d,l-[D_3]-trishomocubyliden-[D_3]-trishomocubane (**12**)	− 2.88	768	[25]
E-(1-methyl-2-adamantyliden)-1-methyladamantane (**13**)	− 2.88	1850	[22]
tri-*tert*-butylethylene (**14**)	− 2.28	147	[27]

The values increase with the size of the specific compounds. There is no correlation of measured K_f values with the ionization potential (I) of the alkenes expressed by the calculated HOMO value by means of PM3 calculations. A fairly good correlation has been found between the K_f values of six alkenes and the substituents' polarizability effects introduced by Taft and Topson.[28] Figure 4 reports the K_f values versus the σ_α value. Alkyl substituents that are not conjugated exert essentially only this kind of effect, since electronegativity (ρ_X), field (ρ_F) and resonance (ρ_R) effects are generally all negligible, as discussed by Tafts and Topson. It is however noteworthy that, although the number of the K_f values is quite limited, all the alkenes that have a significant strain energy (compounds **3**, **13**, and **14**) are characterized by slighly higher K_f values than those of the unstrained olefins. At variance, the K_f values found for the two highly congested alkenes **2** and **9**, bearing flexible alkyl chains that are able to shield the double bond and to exert the above explained entropic contributes, are very low and do not fit with this correlation; see Figure 4. This result shows that polarizibility effects play a major role in stability of these complexes; this is also in agreement with the ab initio calculations as discussed below. Calculated dispersion interaction values (interaction of induced dipoles with induced dipoles) can be correlated with K_f values showing the dominance of this effect.[27]

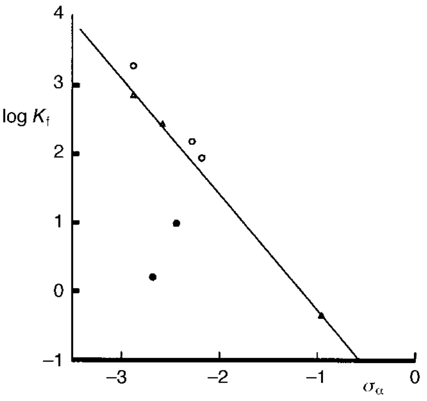


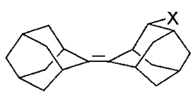
Figure 4. Correlation of the 1:1 Br_2–alkene π-complex equilibrium constants with σ_α parameters. △ for alkenes **10**, **11**, **12**; ○ for **3**, **13**, **14**; and ● for alkenes **2** and **9**.

It should be mentioned that higher chlorinated ethenes (di-, tri- and tetrachloro compounds) do not add bromine in DCE, but we could detect and measure very weak π complexes of these species. All results we have discussed are solely related to bromine as halogen. For the gas phase other halogens have been investigated by Legon resulting the following stability order for either formed complex: Cl_2, Br_2, BrCl, ICl.[19d]

Influence of Polar Groups on the Equilibrium Constant K_f on π Complexes and Bromonium Ions

Studies of polar effects on stability of π complexes are rare. The double bond of crotonic acid has a low K_f value of 0.08 in DCE at 25 °C, probably due to the negative inductive effect of the carboxyl groups.[29] Recently the reaction of 4-equatorial homoallylderivatives of adamantylideneadamantane (**15**: X = F, Cl, Br, OH, OEt, OAc) with bromine were studied.[30]

Analogously to the parent olefin, these compounds are characterized by an unstrained but highly congested double bond; however, the presence of the substituent (X) at the homoallylic position markedly af-



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fects the stability of the 1:1 π complexes and of the related ionic intermediates. When X is a halogen (F, Cl, or Br), as previously observed in the case of the unsubstituted olefin, reaction with bromine in 1,2-dichloroethane results in an equilibrium among the free olefin, free Br_2, the 1:1 π complex, and bromonium tri- and pentabromide ion pairs. The values of the formation constants of the 1:1 π complexes of the Cl and F derivatives ($K_f = 44$ and $123\,\text{M}^{-1}$, respectively at 25 °C) are, however, somewhat lower than that of adamantylideneadamantane ($K_f = 289\,\text{M}^{-1}$), while that of the Br-derivative is slightly higher ($K_f = 492\,\text{M}^{-1}$) at 25 °C. All three halogen compounds give a stable bromonium ion in CD_2Cl_2, the ion of the Cl compound has been fully characterized by ^1H and ^{13}C spectroscopy. It shows that the ionic isomer with *syn* stereochemistry is formed preferentially due to *syn* faciality of this unsaturated system. The introduction of a hydroxy, acetoxy, or ethoxy group in the same position determines a drastic variation in reactivity; these olefins react quickly with Br_2 to give a substitution product. The reaction occurs, however, through the initial formation of a 1:1 olefin–Br_2 π complex, which, in the case of the OH derivative, is characterized by an unusually high formation constant, $K_f = 2274\,\text{M}^{-1}$ at 25 °C (ca. one order of magnitude higher than the corresponding formation constant of the unsubstituted olefin). In contrast, the formation constant of the 1:1 π complex of the EtO and OAc derivatives with Br_2 is of the same order of magnitude as the unsubstituted olefin, $K_f = 134$ and $173\,\text{M}^{-1}$, respectively, at 25 °C. For the OAc compound the stability of the bromonium ion depends on the reagent concentration.

The presence of a substituent in the equatorial homoallylic position neither alters the geometry of the double bond nor shields the π system; therefore, taking into account the nature of the substituents (X) they are probably able to modify the dispersion forces of the cage through electronic effects and thereby affect the direction of the bromine approach, which in turn affects the stability of all the involved intermediates. This interpretation is supported by ab initio calculations carried out by using Gaussian 98 at the DFT and ONIOM levels, with the inclusion of the solvent effect. In agreement with the experimental data, calculations show a larger stabilization energy for the 1:1 π complex between adamantylideneadamantane and Br_2 with respect to the simple case of ethylene. Two hypothesis have been advanced for this difference: 1) in the π complex of adamantylideneadamantane, the halogen is hosted in a "molecular pocket" in which there are stabilizing interactions between the Br_2 molecule and the adamantyl groups; 2) the pyramidalization of the double bond, present only in the adamantylideneadamantane complex, favors the complexation of the halogen molecule. Furthermore, the comparison of the free energy changes ($\Delta\Delta G$) on going from adamatylideneadamantane to the F, Cl, Br, OH, and OEt-derivatives, arising from the experimentally determined K_f values, show a trend that is reproduced quite correctly by the calculated relative energies, though the stability of the OH derivative is overestimated. The larger stability of the π complex of this derivative may be explained by looking at the difference between the Mulliken charges on the C1 and C2 carbon atoms; this reveals the existence of an important inductive effect of the OH group, which has a large dipole. Bromine and chlorine substituents have an inductive effect that is about a quarter of that of the hydroxy group. Although the OEt group is chemically the most similar to OH, the inductive effect on the π complex is very similar to that of the halogen substituent. This has been explained by considering the different geometries of the π complexes of the OEt and OH derivatives; these are affected by the different steric requirements of the two groups.[30]

π Complexes formed from Alkynes and Allenes and Bromine

Recently electrophilic bromine addition to the triple bond in the series of arylacetylenes in DCE has been studied kinetically yielding (*E*)- and (*Z*)-vinyldibromides.[31] For reactions with positive activation energies the *E* isomer is obtained exclusively, and bridged bromirenium ions have been suggested. Some deactivated acetylene derivatives show apparent negative activation energy yielding *E*/*Z* mixtures. For 1-phenylpropyne, we could measure the 1:1 π complex by the UV band situated at 294 nm using a diode-array stopped-flow technique. The formation enthalpy, $\Delta H = -2.95\,\text{kcal mol}^{-1}$, and entropy, $\Delta S = -15.4$ eu is in the same range to those of charge-transfer complexes observed between bromine and alkenes. However, the equilibrium constant, $K_f = 0.065\,\text{M}^{-1}$[28] measured at 25 °C is much smaller relative to normal alkenes, see Table 1; this is in agreement with recent calculations. A detailed theoretical analysis of the 1:1 and 1:2 complex has been given[31] and is further discussed below.

The electrophilic bromine addition to a series of five cyclic allenes from cyclonona-1,2-diene to cyclotridodeca-1,2-diene was studied kinetically in DCE and methanol.[32] Depending on ring size 1,2-dibromoadducts are formed as well as intramolecular H-rearranged products. For the smallest cyclic allene a stable 1:1 complex with $K_f = 7.4\,\text{M}^{-1}$ was measured in DCE; this is in good agreement with ab initio calculations, see below.

π Complexes Formed from Benzenes and Bromine

Several π complexes have prepared in situ by Kochi et al. by the reaction of benzene and toluene with bromine at low temperature (−150 °C).[33] X-ray crystallography of the complexes (a master piece of experimental art) revealed a structure in which bromine is oriented perpendicular to the aromatic planes, but residing on a formal double bond of the aromatic system in a slightly disymmetric way (over bond coordination). This result is in striking contrast to the benzene ring symmetric structure (over ring coordination) derived by Hassel about 40 years ago[34] and resembles more our calculated T-shaped structure of ethene and bromine, see below. Our text books should be corrected.

Quantum Chemical Calculations of the Structures and Nature of the π Complexes: Synergy of Experiment with Theory

The existence of CT complexes formed from alkenes, alkynes, and allenes with bromine in various solvents were derived from measuring their typical CT bands centered at 280 and 310 nm in the UV spectra. Determination of thermodynamic parameters such as enthalpies of formation and entropies have been obtained mainly in DCE as solvent, see above. However, no direct determination of the structures of the complexes has been obtained due to their instability. Structures of related complexes from ethene and ethyne with halogens in the gas phase have been obtained by use of rotational spectroscopy (Fabry–Perot–technique).[19] For a detailed understanding of structures and nature of these species we have performed extensive theoretical calculations by state-of-the-art ab intio (MP2/-311 + G**) and DFT (B3LYP/6-311 + G**) methods.[35] The results are in reasonable agreement with those obtained from former calculations by Herges using MP2/6-31G* as basis set.[7, 36] However, in our recent calculations entropy contributions have also been considered.

1:1 complexes: The enthalpies calculated with lower basis sets are fairly consistent with the experimental values in DCE as solvent and with derivatives of ethylene[7] and acetylene.[31]. For alkene **9**, discussed above, exothermic enthalpy values of $-3.5 \pm 2\,\mathrm{kcal\,mol^{-1}}$ have been measured, while a value of $-4.85\,\mathrm{kcal\,mol^{-1}}$ (B3LYP) and $-5.07\,\mathrm{kcal\,mol^{-1}}$ (MP) has been calculated for most stable structure of ethene and bromine.[7] For other alkenes shown in Table 1 similar small values for their enthalpies have been measured. The more recent results including the allene–bromine complex are summarized in Figure 5.[32]

All three bromine complexes formed either from ethene, ethyne, or allene exhibit T-shaped structures with C_{2v} symmetry for ethene and ethyne, and C_s symmetry for allene. All complexations of the unsaturated moiety with bromine are exothermic in the order allene ~ ethylene < ethyne, reflecting the lower nucleophilitiy of alkynes. MP2 energies can be considered to be more reliable than those at DFT level, because the dispersion interaction is handled quite well by the former method.[33]. Calculations with Gaussian 98 that include ZPE (corrected complexation energy) and E_{ZPE} (entropy change on complexation), see Table 2, show that these complexes are not stable in the gas phase at room temperature, as a result of the calculated large entropic terms leading to positive (endergonic) values of their Gibb's energies (ΔG). However, under conditions in the liquid phase, the entropy change would be less negative. Typical reductions in entropy on going from the gaseous to the liquid phase are around 40%, for example, $\Delta(\Delta S)$ is 22.29 cal mol^{-1}K^{-1} for Br_2 and 24.27 cal mol^{-1}K^{-1} for ethylene,[34] due to the more restricted translational and rotational motion. Similar corrections if applied to the entropies of the other complexes would reduce the value of entropy term and the free energy should be favorable in solution. Computation of

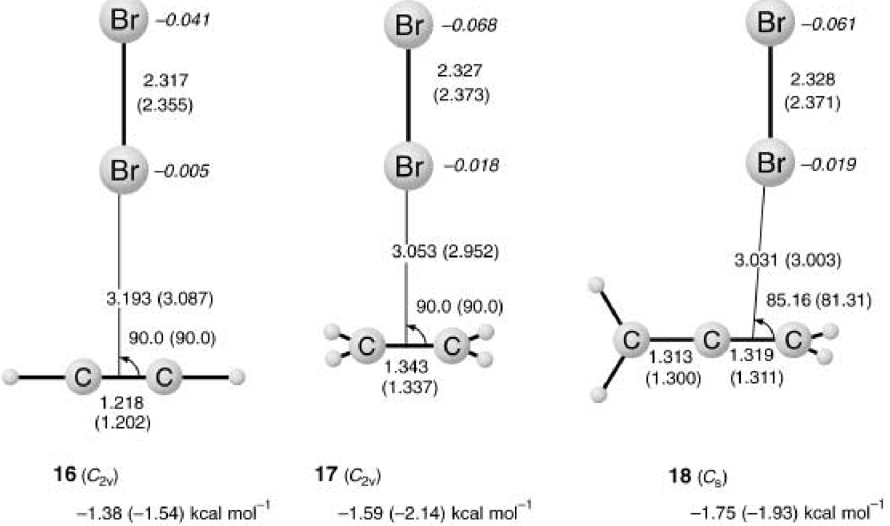


Figure 5. Geometries (at MP2/6–311 + G**) and complexation energies (at MP2/6–311 + G**), corrected for ZPE and BSSE of 1:1 bromine complexes of acetylene, ethylene, and allene, from ref. [32]. Data in parentheses are the corresponding values from B3LYP16-311+G**.

Table 2. Total energies E [au], association energies ΔE [kcal mol^{-1}], ZPE corrected association energies E_{ZPE} [kcal mol^{-1}], entropy changes on complexation $\Delta(\Delta S)$ [cal mol^{-1}K^{-1}], and free energy changes $\Delta(\Delta G)$ [kcal mol^{-1}] of acetylene:Br_2 (**16**), ethylene:Br_2 (**17**), allene:Br_2 (**18**), and different allene:2Br_2 complexes (**19**–**22**) computed by using ab initio and density functional theory.

		Symmetry	E[a]	ΔE[a]	ΔE_{ZPE}[b]	$\Delta(\Delta S)$[c]	$\Delta(\Delta G)$[c]
16	MP2	C_{2v}	– 5222.09006	– 2.80	– 2.49	– 18.72	1.78
	B3LYP	C_{2v}	– 5225.64494	– 2.16	– 1.68	– 21.56	2.39
17	MP2	C_{2v}	– 5223.32436	– 3.57	– 2.92	– 22.48	2.39
	B3LYP	C_{2v}	– 5226.90543	– 3.18	– 2.35	– 24.65	2.94
18	MP2	C_S	– 5261.28689	– 3.97	– 3.37	– 23.38	2.04
	B3LYP	C_S	– 5264.98477	– 2.87	– 2.16	– 23.75	2.79
19	MP2	C_2	– 10406.26608	– 8.25	– 7.18	– 52.46	4.67
	B3LYP	C_2	– 10413.27229	– 4.70	– 3.53	– 46.78	7.41
20	MP2	C_S	– 10406.26393	– 6.90	– 5.79	– 51.81	3.48
	B3LYP	C_S	– 10413.27212	– 4.44	– 3.24	– 51.77	5.52
21	MP2	C_1	– 10406.26278	– 6.18	– 5.31	– 41.48	2.34
	B3LYP	C_1	– 10413.27212	– 4.44	– 3.39	– 46.32	4.79
22	MP2	C_{2v}	– 10406.26543	– 7.85	– 6.90	– 49.85	5.29
	B3LYP	C_{2v}	– 10413.27253	– 4.55	– 3.54	– 51.20	6.67

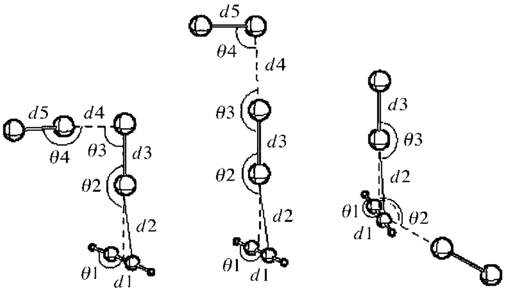
[a] MP2/6–311 + G** and B3LYP/6–311 + G**. [b] MP2/6–311 + G** + ZPE (at MP2/6–31G*, 0.97 scaling factor) and B3LYP/6–311 + G** + ZPE (B3LYP/6–31G*, unscaled). [c] MP2/6–31G* and B3LYP/6–31G* at 298.15 K.

Gibbs′ energy in solution is still beyond the scope of the theoretical methods.

The multiple C–C bonds and the Br–Br bonds are slightly elongated in the complexes relative to the calculated ones for the reacting molecules.[7, 31, 32]. For example, by using BLYP for ethyne bromine complex the C–C bond is stretched by 0.004 Å, while the Br–Br bond is elongated by 0.038 Å. The distance of the midpoint of the C–C bond to the first bromine atom is quite long; it is calculated to be in the order of 3.00 Å for all three types of complexes. The calculated geometry of complex **17** (Figure 5) is in close agreement with Legan's experimental results.[19d] Only little charge is transferred from the carbon fragment to bromine in all three types of complexes. For example, in ethyne–bromine complex with use of BLYP calculation method only 0.08 electrons are transferred from the carbon fragment to the two bromine atoms; this charge is spread over the two atoms so that a charge of 0.01 resides on the central bromine atom and a charge of 0.07 goes to the terminal bromine atom.[31] The same behavior is observed in the complexes of ethene[7]and allene[31] with bromine.

For persistent complexes like those from bromine and di-*tert*-butylstilbene[23] or tetraneopentylethylene[7] no changes in the ^{1}H and ^{13}C spectra were found compared to the reacting molecules due to the weakness of charge transfer. IGLO calculations have been used to explain this result. The calculations predict a downfield shift of 1.7 ppm for the vinylic signal in the complex. However, the change in chemical shift is due almost exclusively to the geometry change that is induced by steric effects of the bromine molecule. Charge transfer, which is very weak, accounts only for 0.17 of the total change of 1.7 ppm. Therefore, in sterically extremely congested alkenes only a very small change in chemical shift should be observed. However, shifts in frequency were observed in IR and Raman spectra of the complexes.[20]

1:2 complexes: The structures of the trimolecular complexes for the system of ethyne and bromine are shown in Figure 6. These complexes are formed from the 1:1 complex by addition of a second molecule of bromine. For ethylene[7] two main structures with C_s (Br-C_2H_4-Br) and D_{2h} (($Br_2)_2$-C_2H_4) symmetry were found. For acetylene[31] similar structures were calculated, while allene[32] yields four different structures. Besides of the reported C_s structures for ethylene,[7] a second structurally closely related minimum with C_s symmetry was found with the second bromine at the same height as the first one and with a very low conversion barrier.[35]. The C_s and D_{2h} configurations are close in energy. The addition of a second bromine atom leads to additional stabilization. For the C_s structure of the ethylene and bromine system,[7] the extra stabilization is calculated to be 4.98 kcal mol^{-1} (B3LYP) or 6.29 kcal mol^{-1} (MP2). Thus the energetic effect of two bromine molecules is nearly additive. An analogous energetic behavior is found for acetylene[31] and allene.[32]



23 (C_s) **24** (C_s) **25** (C_{2v})

Figure 6. Calculated structures of 1:2 acetylene bromine complexes, taken from ref. [31], for values of geometrical parameters, see also ref. [31].

The trimolecular complex can be regarded as a combination of the T-shaped 1:1 complex with an additional bromine molecule perpendicular to the first one. The fragment of the monomolecular T-shaped complex donates electron density into the empty σ orbital of the second bromine molecule through the π and π* orbitals.[31] Similar arguments can be used for alkene and allene 1:2 bromine complexes.

Conclusion

The relevance of CT complexes on the reaction coordinate of electrophilic brominations can now be understood. It has been shown that these CT complexes are essential intermediates in the overall reaction; this means the reaction must proceed via these species. Although the complexes do not contribute much in thermodynamics, the 1:2 complex plays a significant role in the kinetic behavior of the overall reaction. In discussion to Figure 3 (see above), it was pointed out that a 1:2 alkene–bromine complex may resemble a bromonium ion with Br_3^- as anion. Heterolytic bond cleavage is extremely unlikely to be observed in the gas phase. Only in ionizing solvents will the formation of an ionic species occur giving a bromonium ion. For example, for the transformation of the 1:1 bromine complex of acetylene into the bromirenium ion and bromide, a value of 161.4 kcal mol^{-1} has been calculated.[31]. However, the enthalpy of formation of Br_3^- from Br^- and Br_2 lies around 40 kcal mol^{-1}; this significantly reduces the energy required for heterolytic dissociation. Thus, the formation of the hypervalent trihalide anions like Br_3^- via such trimolecular complexes lowers the barrier for the ionic pathways in electrophilic halogenation reaction to a great extent. This is a special effect of electrophilic catalysis performed by the halogen as the reacting species. In ionizing solvents the formation of bromonium or bromirenium ions from the trimolecular complexes will additionally be strongly favored energetically. Geometry and "the preorganization can lead to a determined viable transition state structure, which hitherto may be discounted owing to the high endergonic driving force".[38].

The nature of these weak intermolecular complexes can be described as donor–acceptor complexes, with the carbon fragment as donor and the halogen as acceptor. However, only a little charge is transferred from the donor to the acceptor. The system may be regarded as the interaction of two induced dipoles. In Mulliken's classification scheme[39] these types of complexes are generally termed outer complexes, since the interactions do not involve a significant amount of charge transfer, in agreement with our state-of-art MO calculations. These kinds of complexes have also been recognized recently as essential in biological systems.[40]

Note added in proof:
After submission of the manuscript a related work has been published by J. K. Kochi et al., *J. Org. Chem.* **2002**, *67*, 5106, describing the bromination of adamantylideneadamantane and sequihomoadamantane.

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