Spectroscopic Detection and Theoretical Studies of a 2:1 Bromine–Olefin π Complex**

Roberto Bianchini,* Cinzia Chiappe, Dieter Lenoir,* Peter Lemmen, Rainer Herges,* and Jörg Grunenberg

Dedicated to the memory of Giuseppe Bellucci

Bromine–alkene 1:1 π complexes are the first (and usually short-lived) intermediates in electrophilic bromination.1,2 Thermodynamic and spectroscopic properties of these complexes have been investigated in a variety of cases in which the very rapid subsequent reactions (formation of a bromonium ion and the backside attack of Br⁻) are hampered, as in sterically hindered,3 cage4 and strained5 olefins. In the reaction of bromine with cyclohexene6 and with (E)-2,3,4,5,5-hexamethylichex-3-ene6 in 1,2-dichloroethane (DCE), however, the intermediacy of a second bromine–alkene π complex with a 2:1 stoichiometry was inferred on the basis of thermodynamic evidence. There are indications that the 2:1 complex has to be interposed between the 1:1 complex and the bromonium ion as an additional intermediate in electrophilic bromination reactions7 (Scheme 1).

Recently G. Maier and S. Senger found evidence that such a 2:1 complex is also formed by cocondensation of ethylene with an excess of bromine in an argon matrix at 10–20 K.8

We now report the first direct UV-spectroscopic detection of a 2:1 bromine–olefin complex. Theoretical investigations reveal the structure of the so far elusive species. Suitable candidates for our studies are highly hindered olefins, which prevent a close approach of bromine and thus formation of the bromonium ion, such as tetraneopentylethene (TNPE). TNPE was first synthesized and studied by Olah et al. and indeed was claimed not to react with bromine.9

We recorded first the UV spectra of a series of solutions containing low concentrations of TNPE and 1.5 × 10⁻³ M TNPE and 2.35–0.4 M Br₂ in DCE. At these massive bromine concentrations, deviations from Beer's law are apparent starting between 340 and 260 nm, probably at least partly due to dimerization of the halogen itself.10 In order to avoid interferences from this process, we recorded the difference of the absorbance of TNPE–Br₂ mixtures and pure Br₂ solutions each at the same Br₂ concentration.11 Fitting of this second set of spectrophotometric data proved that in addition to the 1:1 complex a 2:1 complex was formed. The new absorption band (εmax = 2535 M⁻¹ cm⁻¹ at 310 nm, Figure 1) does not overlap with that of the well-known 2:1 ionic species, the bromonium–tribromide ion pair (εmax = 48000 M⁻¹ cm⁻¹ at 272 nm)12 and provides the first direct demonstration of the existence of a 2:1 π complex.

The thermodynamic data reported in Table 1 account well for the elusiveness of the weak complex. While the charge transfer (CT) band of the 1:1 complex can be easily detected even in dilute solutions of bromine and TNPE, molar concentrations of bromine are needed to form the 2:1 complex in measurable concentrations. The thermodynamic values of the 1:1 complex are in good agreement with results of similar systems that were recently reported.14–16 The enthalpy of formation ΔH of the 2:1 complex of -1.6 kcal mol⁻¹ (Table 1, note [a]) almost exactly matches that inferred from the kinetic approach to the fast

\[ \text{Br}_2 + 2 \text{Br}_2 \rightarrow 2 \text{Br}^- \]

\[ \text{Br}_2 + \text{Br}_2 \rightarrow \text{Br}^- \]

\[ \text{Br}^- + \text{Br}_2 \rightarrow \text{Br}^- \text{Br}_2 \]

Scheme 1.

Figure 1. UV spectra of the 1:1 (▲) and 2:1 complex (▲) of bromine with tetraneopentyl ethene in dichloroethane as compared with free bromine (●). A_m = molar absorption.
Table 1. Thermodynamic parameters for the 1:1 and 2:1 bromine–TNPE π complexes.

<table>
<thead>
<tr>
<th>Br₂–TNPE Complex</th>
<th>$\Delta_{r}H$ [kcal mol⁻¹]</th>
<th>$\Delta_{s}S$ [cal mol⁻¹ K⁻¹]</th>
<th>$K_r$ (25°C)</th>
<th>$K_r$ (10°C)</th>
<th>% at equilibrium (10°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.4 M TNPE</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2 x $10^{-1}$ M TNPE</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.5 x $10^{-3}$ M TNPE</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Br₂, 2.0 M Br₂</td>
</tr>
</tbody>
</table>

1:1
-3.5 (1.1) -11.1 (3) 1.6 (0.4) 2.2 (0.5) 46 37
2:1[a]
-5.1 (2.1) -17.2 (12) 1.0 (0.5) 1.6 (0.7) 46 37

[a] These values refer to the equilibrium TNPE$^+$Br₂$^-$ + TNPE$^-$(Br₂)$^+$Br₂$^-$.

The reaction of (E)-2,2,3,4,5,5-hexamethyl-3-ene[6] with Br₂ in DCE ($\Delta_r H = -1.5$ kcal mol⁻¹). The small contribution to the entropic factor ($\Delta S = -6.1$ cal mol⁻¹ K⁻¹) can be attributed to a large degree of conformational freedom of the second bromine molecule (see Figure 2).

$^1$H and $^{13}$C NMR spectra recorded at bromine concentrations of a similar range as used in the UV experiments did not exhibit measurable changes in the chemical shifts of either the vinyl carbons or the allylic protons. Raman spectra of pure TNPE and TNPE/Br₂ solutions (in CCl₄) are identical [13]. This indicates that the reaction of the title olefin with bromine indeed stops at the stage of the 2:1 complex. In agreement with Olah's report, no bromonium ion or even olefin dibromide is formed. The second complex therefore is of the Mulliken outer type [4].

The structure of 1:1 olefin–bromine complexes is known to be of "T-type" [14]. However, a number of different spatial arrangements of an olefin with two bromine molecules is conceivable. Since the experimental data do not provide direct information on the structure of the new 2:1 complex, we performed an exhaustive search on the energy hypersurface of the parent system: ethene + 2 Br₂ to find the energetically most favorable arrangement. Two different theoretical methods were applied to secure the reliability of our computational results. Density functional theory (DFT) [15] at the B3LYP/6-31 +G* level [16, 17] and ab initio MP2/6-31 +G* calculations [18] were used to optimize three different structures of 1:1, ten conceivable structures of 2:1 complexes, and five different structures for bromine dimers. Two minima for each system were found [19]. Energies and geometries of the six structures are given in Table 2 and Figure 2.

The most stable 1:1 complex is of the well-known T-type (1). [13] Surprisingly we found a second minimum. Structure 2, however, is a very weak complex ($\Delta_{r} H \approx 1-2$ kcal mol⁻¹). Among the 2:1 complexes, structures 3 and 4 are the only minima on the energy hypersurface. In structure 4 both sides of the π system of ethene interact with bromine (Br₂$^-$(olefin•Br₂) complex). In structure 3 the second bromine is bound to the first bromine (olefin•Br₂$^-$(Br₂) complex). The midpoint of the C=C bond, the two Br atoms of the first bromine molecule, and one Br atom of the second bromine almost lie in line. The remaining Br atom approximately forms a 90° angle with respect to this line. According to a frequency analysis of 3 there is almost free rotation of the second bromine atom around this axis and a very small force constant for bending of the 90° angle (Figure 2, structure 3).

In principle both structures 3 and 4 have to be considered as candidates for a 2:1 complex in the parent system. The energy difference between them, even though in favor of 3, is too small for an unequivocal assignment within the accuracy of our calculations ($\Delta_{r} H = 0.37$ kcal mol⁻¹ at B3LYP/6-31 +G* + ZPE and 0.17 kcal mol⁻¹ at MP2/6-31 +G* + ZPE; see Table 2). The situation in the tetraenepentyl-substituted system, however, is less ambiguous. Even though the TNPE system is too large to be calculated with ab initio methods or DFT, the effect of the bulky substituents can be reliably estimated. Steric hindrance low-

![Figure 2](structure-of-1-1-complexes-1-and-2-and-the-2-1-complexes-3-and-4-between-bromine-and-ethene-as-well-as-the-bromine-dimers-5-and-6-optimized-by-density-functional-theory-(b3lyp/6-31-g)*-and-ab-initio-methods-(mp2/6-31-g*-in-parentheses)-bond-lengths-are-given-in-Å-and-angles-in°)
ers the enthalpy of complexation of the first bromine with the π system of the olefin by about 1 kcal mol⁻¹ (relative to unhindered cyclohexene). Such interactions are operative in complexes of the type of structure 1 (olefin•Br₂•olefin complex) and 4 (Br₂•olefin•Br₂ complex). However, the neopentyl substituents hardly affect the bromine–olefin interaction of the type of structure 3 (olefin•Br₂•Br₂ complex), because the second bromine molecule and the olefinic carbons are more than 8 Å apart (see PM3-calculated structure[20] in Figure 3).

Based on our ab initio and DFT calculations on the parent system and assuming a steric effect of the neopentyl substituents of 1 kcal mol⁻¹ for the olefin•Br₂•olefin complex, the 2:1 complex should be about 1.4 kcal mol⁻¹ more stable than the Br₂•olefin•Br₂ complex (which is inherently less stable by about 0.4 kcal mol⁻¹ and which suffers twice from steric hindrance). The theoretically estimated absolute value for the formation enthalpy of olefin•Br₂•Br₂ including steric effects (9–11 kcal mol⁻¹), however, is still about 5 kcal mol⁻¹ larger than the experimental value (5.1 ± 2.1 kcal mol⁻¹, Table 1), whereas ΔH of olefin•Br₂ after correction for steric factors almost exactly matches the experiment. A deviation of 5 kcal mol⁻¹ is beyond the error limit of our theoretical calculations. The reason for the discrepancy between theory and experiment is probably due to the fact that at the large Br₂ concentrations (0.4–2.35 M) used in the experiment, bromine dimerizes to a considerable extent[11].

Our calculations predict two minima 5 and 6 as conceivable bromine dimer structures (Table 2, Figure 2). DFT and ab initio methods do not concur on which would be more stable. Structure 5 is favored by orbital interactions and 6 on dispersion energy grounds. However, since the bromine dimer is known to be polar, structure 6 can be excluded. The enthalpy of dimerization according to the equation: 2 Br₂ → Br₂•Br₂ was calculated to be 4.9 kcal mol⁻¹ (B3LYP/6-31 +G*+ZPE) and 5.3 kcal mol⁻¹ (MP2/6-31 +G*+ZPE). For the reaction olefin + Br₂→ Br₂•olefin•Br₂, theory (ΔH = 3.9 kcal mol⁻¹ at B3LYP/6-31 +G*+ZPE and 5.3 kcal mol⁻¹ at MP2/6-31 +G*+ZPE) and experiment (ΔH = 5.1 ± 2.1 kcal mol⁻¹) are in excellent agreement.

Further evidence favoring olefin•Br₂•Br₂ over Br₂•olefin•Br₂ is provided by the small entropy of formation of the 2:1 complex. This is probably due to the large degree of conformational freedom of the second bromine molecule in olefin•Br₂•Br₂ as opposed to that in Br₂•olefin•Br₂ and olefin•Br₂ where the bromine is directly bound to the olefinic π bond.

Bromine not only forms a 1:1 but also a 2:1 complex with TNPE in DCE. The thermodynamic data of both species were determined by UV-spectroscopy. According to our theoretical calculations the 2:1 complex has an olefin•Br₂•Br₂ type structure as shown in Figure 3. The intermediacy of such a 2:1 complex well accounts for the second-order dependence on [Br₂] in the kinetics of electrophilic bromination reactions.[5] Moreover, charge separation and hence formation of the bromonium–tribromide ion pair (olefin•Br₂•Br₂ → olefin•Br₂ + Br₂⁺) is favored by the assistance of the second bromine. In the TNPE system this process is inhibited by the steric hindrance of the neopentyl substituents and therefore the 2:1 species can be detected in the equilibrium. Such 2:1 complexes most probably are of general importance as intermediates in electrophilic bromination reactions.

### Experimental Section

TNPE was prepared as described[9] and purified by flash chromatography on silica gel with hexane as eluent (yield 53%). Recrystallization from ethanol at ~20 °C yielded colorless crystals (m.p. 64–65.5 °C; ref. [9] 59 °C).

All the spectrophotometric measurements were carried out on a Cary 2200 UV/VIS spectrophotometer fitted with a Haake D8 thermostat. Freshly prepared prethermostated solutions of TNPE and Br₂ at the appropriate concentrations were rapidly mixed, and their spectra measured after 5 minutes of further thermal equilibration inside the cell holder. In the first set of experiments (170 spectrophotometric data), the concentrations after mixing were: Br₂ 5 × 10⁻⁶ M; TNPE 0.4, 0.31, 0.29, 0.18, 0.1, and 0.05 M. In the second set of experiments (170 data) the spectra of 1.5 × 10⁻⁴ M TNPE and 2.35, 2.13, 1.64, 1.25, 1.0, 0.74, 0.5, and 0.4 M Br₂ were recorded in a thermostated cell (0.01 cm path length). Measurements were taken every 5 nm in the 260–400 nm range. Wavelengths shorter than 260 nm could not be used, because of considerable absorption by the excess of either TNPE or Br₂.

Unlike with other tetrasubstituted, hindered, or strained ethenes (see refs [2–4, 6]) no side reaction occurred. Solutions started to exhibit some change after only 30 minutes in the worst case. An already described[21] nonlinear least-squares procedure was applied to fit the spectrophotometric data. The first set of data (high excesses of TNPE) was processed to obtain data for the 1:1 complex. The results of this fitting (formation enthalpy and entropy, molar absorptivities at each examined wavelength) were taken as fixed values in the second fitting (large excess of Br₂). In both fittings about 30 fitting parameters, including the molar absorptivities of the complexes at each examined wavelength, were used besides the formation enthalpies and entropies. The root mean-square deviation of the fitting was 0.05 in absolute units. The highest correlation coefficient between ΔH and ΔS of 0.98 is acceptable considering the small temperature interval used (10–35 °C).

NMR experiments: TNPE (0.1 M): 1H NMR (400 MHz, CDCl₃, 15°C); δ = 0.94 (s, (CH₃)₂CO), 1.80 and 2.53 (d, CH₃), 1.24 (t, CH₂), 1.17 (t, CH₂), 1.05 (CH₂CO); ΔC NMR (100.6 MHz, CDCl₃, 15°C): δ = 31.13 (CH₂CO), 34.23 (quat. C), 40.32 (CH₃), 135.40 (C=O). Both 1H and 13C spectra remained unchanged upon addition on an excess of Br₂ (up to 2.5 M).

**Keywords**: ab initio calculations • alkenes • bromine • density functional calculations • reaction mechanisms

Received: November 14, 1996 [Z97671E]

German version: Angew. Chem. 1997, 109, 1340–1343

© VCH Verlagsgesellschaft mbH, D-69451 Weinheim, 1997 0570-0833/97/0412-1286 $ 17.50 + 50/0
Enantioselective Formation of Double and Triple Helicates of Silver(i): The Role of Stacking Interactions**

Christophe Provent, Sujatha Hewage, Guy Brand, Gérard Bernardinelli, Loïc J. Charbonnière, and Alan F. Williams*

Dedicated to Professor Werner Haedri on the occasion of his 70th birthday

The formation of helical complexes or helicates by simple mixing of ligands and metal ions has attracted considerable attention in recent years as a prototypical self-assembly reaction.\(^1\)\(^2\) Although these complexes are chiral, the combination of achiral ligands and metal cations leads generally to racemic mixtures. Enantiospecific synthesis of helicates has been achieved by incorporation of a chiral element in the bridge between the two metal centers,\(^3\) into the template of a tripod,\(^4\) or bipodal\(^5\) ligand system, or by the introduction of a chiral substituent at the extremity of a biscatechol ligand.\(^6\) In this communication we show how enantiospecificity may also be achieved by the use of the readily accessible chiral oxazoline (dihydrooxazole) unit as a ligand, and how the nature of the group introducing the chirality can dramatically influence the structure.

Some years ago we reported that ligand \(1\) forms a double helical complex \([\text{Cu}_2(1)_2]^+\) with copper(\(\text{II}\))\(^7\) in which each copper center is approximately linearly coordinated by two benzimidazole moieties, one from each ligand. Ligands such as \(2\) were originally developed by Nishiyama and others\(^8\)\(^-\)\(^10\) for enantioselective catalysis, and are closely related to \(1\); they should therefore form double helicates with ions such as Cu\(^{\text{II}}\) and Ag\(^{\text{II}}\) that are subject to linear coordination. Models showed that the configuration of the oxazoline group determines the configuration of the helix: an S,S ligand such as \(2\) will form the \(P\) or \(A\) helix (Scheme 1), since in the alternative \(M\) helix the oxazoline substituents would prevent the binding of the second ligand strand.

\(^1\) H NMR titration of a solution of (S,S)-2,6-bis(4'-benzyl-oxazolin-2'-yl)pyridine (2) in [D\(_5\)]acetone with AgBF\(_4\) showed initial formation of a complex of stoichiometry [Ag(2)]\(^+\), on addition of more Ag\(^{\text{II}}\) ions the peaks broadened, narrowing again for a 1:1 metal-to-ligand ratio, after which the spectrum remained sharp even in excess of silver. This is consistent with formation of a complex [Ag(2)]\(^+\). Electrospray (ES) mass spectrometry of solutions of [Ag(2)]\(^+\) in acetone showed peaks at \(m/z\) 505.3 ([Ag(2)]\(^+\), base peak), 901.4 ([Ag(2)],\(^+\)), and 1097.3 ([Ag(2)][BF\(_4\)]\(^-\)). Examination of the isotopic abundances of the peak at \(m/z\) 505.3 showed the peak separation of 0.5 units typical of a doubly charged species, confirming the presence of the complex [Ag(2)]\(^+\). However, the isotopic distribution pattern suggested that a small amount of [Ag(2)]\(^+\) was present, which we attribute to fragmentation in the mass spec.

---

\(\text{[S]}\) This work was supported by the Swiss National Science Foundation (Program Chiral2). We thank Werner Kloeti and Dr. Gérard Hopfgartner for recording ES mass spectra.

---

\(\text{[\*]}\) Prof. A. F. Williams, Dr. C. Provent, Dr. S. Hewage, Dr. G. Brand, Dr. L. J. Charbonnière

Department of Inorganic, Analytical and Applied Chemistry
University of Geneva
30 quai Ernest Ansermet, CH 1211 Genève 4 (Switzerland)
Fax: Int. code + (22) 702 6069
e-mail: alan.williams@chiam.unige.ch
Dr. G. Bernardinelli
Laboratory for X-ray Crystallography, University of Geneva (Switzerland)