

## Intermediates in the Gas-phase Reactions of Acetylene and Halogens: the Identification of the Acetylene–BrCl Complex by Rotational Spectroscopy

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A T-shaped complex formed between acetylene and bromine monochloride is identified and characterised through its rotational spectrum, as detected in a mixture of the two components by using a fast-mixing nozzle incorporated into a pulsed-nozzle, F–T microwave spectrometer.

The reaction of acetylene with a halogen such as chlorine or bromine in the gas phase occurs vigorously, often accompanied by a temperature rise and explosion.<sup>1</sup> Under conditions that do not favour the formation of halogen atoms, the addition reaction appears to involve a mechanism analogous to that for electrophilic substitution in aromatic compounds, with intermediates of the type **I** and **II** shown in Fig. 1 invoked when XY is the halogen.<sup>2</sup> The intermediates **I** and **II** are of the 'outer' and 'inner' type of  $\pi$ -donor charge-transfer complex, respectively, in the language of Mulliken.<sup>3</sup>

It is of some interest to establish the existence of a complex of either type in mixtures of acetylene and halogens under the appropriate conditions, *i.e.* those for which radical chain reactions are precluded. Ideally, these conditions should allow the complex to be characterised in isolation so that the determined properties are free from perturbations due to lattice or solvent molecules. Rotational spectroscopy has proved a powerful way to investigate weakly bound complexes in isolation<sup>4</sup> but when acetylene and a halogen are involved there are obvious difficulties and dangers involved with handling the gas mixtures.

We report here the first identification of a  $\pi$ -donor complex involving acetylene with a halogen or interhalogen in the gas phase. We have chosen the interhalogen bromine monochloride for convenience to give the complex a substantial electric dipole moment and therefore a reasonably intense rotational spectrum. We used a fast-mixing nozzle in our pulsed-nozzle, Fourier-transform microwave spectrometer as the means of first forming and then freezing by supersonic expansion complexes of the normally reactive components. In this device,<sup>5</sup> the two gases are kept separate until the point of expansion into the vacuum chamber of the spectrometer. The gases then mix in a concentric, coaxial flow in the absence of surfaces and the complexes formed achieve collisionless expansion in *ca.* 10  $\mu$ s, so precluding further progress along the reaction coordinate. The isolated complexes can then be investigated through their rotational spectrum in the usual way.<sup>6</sup>

An equilibrium mixture containing approximately equal amounts of bromine and chlorine gases (Aldrich) held at a stagnation pressure of *ca.* 30 kPa was flowed continuously through the 0.3 mm diameter glass capillary that constituted the inner of the two concentric tubes of the fast-mixing nozzle to give a background pressure of *ca.* 0.013 Pa in the spectrometer vacuum chamber. A mixture of *ca.* 1% acetylene (BOC) in argon (stagnation pressure 300 kPa) was pulsed down the outer tube of the nozzle by means of a Series 9 solenoid valve (General Valve Corp.) at a rate of 2 Hz. The complexes (HCCH, BrCl) formed at the interface of the concentric jets were probed by microwave pulses when in collisionless expansion and their rotational spectra recorded.

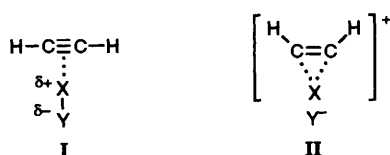


Fig. 1 Possible complexes of halogens XY with acetylene. **I** is described as an 'outer' complex and **II** as an 'inner' complex.

The ground-state spectrum attributed to (HCCH, BrCl) was that of a nearly prolate asymmetric rotor carrying two quadrupolar nuclei having spins  $I$  3/2. A detailed spectral analysis, using the Watson A reduction and to be described elsewhere, yielded the set of spectroscopic constants given in Table 1 for the two isotopomers (HCCH, <sup>79</sup>Br<sup>35</sup>Cl) and (HCCH, <sup>81</sup>Br<sup>35</sup>Cl). These constants allow a detailed characterisation of the complex, as described below.

First, the values 0.68(7) and 0.69(9)  $\text{u}\text{\AA}^2$  for the inertia defects  $\Delta = I_c^0 - I_b^0 - I_a^0$  of (HCCH, <sup>79</sup>Br<sup>35</sup>Cl) and (HCCH, <sup>81</sup>Br<sup>35</sup>Cl), respectively, are of the magnitude expected for a planar weakly bound complex.<sup>7</sup> Secondly, the rotational constant  $A_0$  of the complex is almost unchanged from  $B_0 = 35273.3(4)$  MHz of free acetylene<sup>8</sup> and is independent of <sup>79</sup>Br/<sup>81</sup>Br substitution. This indicates that the complex is T-shaped, with the principal inertial plane *ab* as the molecular plane, the acetylene subunit forming the bar of the T and the BrCl subunit lying on the  $C_2$  axis. Such a T-shaped structure should be associated with a 3:1 nuclear-spin statistical weight ratio for  $K_{-1} = 1$  relative to  $K_{-1} = 0$  transitions. Qualitatively, we observe an enhanced intensity for  $K_{-1} = 1$  transitions but intensity measurements are too unreliable to establish the effect quantitatively. The fact that  $\chi_{aa}(\text{Br})$  and  $\chi_{aa}(\text{Cl})$  are almost unchanged from the coupling constants  $\chi_0(^{79}\text{Br}) = 875.309(1)$  MHz,  $\chi_0(^{81}\text{Br}) = 731.223(1)$  MHz and  $\chi_0(^{35}\text{Cl}) = -102.450(2)$  MHz of the free BrCl molecule<sup>9</sup> confirms that the BrCl subunit lies along the *a* axis of the complex. The final piece of evidence characterising (HCCH, BrCl) is the very small change in the rotational constants that accompanies <sup>79</sup>Br/<sup>81</sup>Br isotopic substitution. This means that the Br atom lies very close to the dimer centre of mass and establishes that the Br atom rather than Cl is involved in the weak bond to the centre of the acetylene  $\pi$ -bond.

The only geometry for the dimer consistent with all of the above observations is that of  $C_{2v}$  symmetry shown in Fig. 2. If

Table 1 Ground-state spectroscopic constants of two isotopomers of (HCCH, BrCl)

Spectroscopic constant	(HCCH, <sup>79</sup> Br <sup>35</sup> Cl)	(HCCH, <sup>81</sup> Br <sup>35</sup> Cl)
$A_0/\text{MHz}$	35590(175)	35625(225)
$B_0/\text{MHz}$	1254.2594(3)	1254.2898(3)
$C_0/\text{MHz}$	1209.5996(3)	1209.6285(3)
$\Delta_J/\text{kHz}$	0.761(5)	0.773(7)
$\Delta_{JK}/\text{kHz}$	47.0(3)	46.9(4)
$\chi_{aa}(\text{Br})/\text{MHz}$	883.34(3)	738.01(4)
$\chi_{aa}(\text{Cl})/\text{MHz}$	-96.58(1)	-96.52(2)
$\{\chi_{bb}(\text{Br}) - \chi_{cc}(\text{Br})\}/\text{MHz}$	16.99(5)	14.21(6)
$\{\chi_{bb}(\text{Cl}) - \chi_{cc}(\text{Cl})\}/\text{MHz}$	-0.36(4)	-0.20(5)
$M_{bb}(\text{Br})/\text{kHz}$	-3.4(3)	-4.2(4)

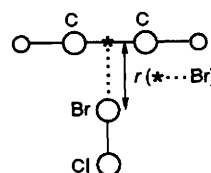


Fig. 2 The geometry of the acetylene–BrCl complex

the monomer geometries are assumed unperturbed<sup>8,10</sup> on dimer formation (an assumption justified below), the geometry of the (HCCH, BrCl) complex is then completely defined by the distance from the centre \* of the  $\pi$ -bond to Br. The value of  $r(*\cdots\text{Br}) = 3.059(1)$  Å results from a least-squares fit of the observed quantities  $I_b^0$  and  $I_c^0$  for both isotopomers investigated. The standard deviation of the fit is equivalent to only 1 MHz in the rotational constants. This completes the geometrical characterisation of (HCCH, BrCl).

It remains to consider the extent of any electric or geometrical perturbation of the subunits on dimer formation. The near agreement of  $A_0$  for both isotopomers (HCCH, <sup>79</sup>Br<sup>35</sup>Cl) and (HCCH, <sup>81</sup>Br<sup>35</sup>Cl) and  $B_0$  of free acetylene is evidence that the acetylene geometry is not significantly changed. The relatively small difference between  $\chi_{aa}(X)$  of the complex and  $\chi_0(X)$  of free BrCl for both X = Br and Cl (0.9 and 5.7%, respectively, of the free molecule values) indicates only a very weak perturbation of the BrCl subunit in the complex. This conclusion is reinforced by the very small differences  $\chi_{bb}(X) - \chi_{cc}(X)$ , which indicate that the cylindrical symmetry of BrCl is barely perturbed. Changes of such magnitude can be readily understood by taking into account only the small zero-point angular oscillations of the subunits and the small additional electric field gradients at the nuclei due to the presence of the HCCH subunit nearby, a detailed discussion of which will be given elsewhere. It seems unnecessary to invoke significant charge transfer from HCCH to BrCl and we conclude that the observed complex is of the 'outer' type I in Fig. 1. It is likely that the interaction between the subunits is predominantly electrostatic in nature.

Finally, we note that (HCCH, BrCl) is very similar in its properties to (HCCH, HCl).<sup>11</sup> Both are T-shaped; in the first there is an intermolecular interaction involving the centre of the acetylene  $\pi$ -bond and  $\delta^+$  of Br while in the second  $\delta^+$  of H in HCl is the electrophile. In both complexes the binding is weak, the values of the intermolecular stretching force constant  $k_\sigma$  determined<sup>12</sup> from the centrifugal distortion constant  $\Delta_J$  being 9.4 and 6.4 Nm<sup>-1</sup>, respectively. Such parallelism of the properties of the complexes B $\cdots$ BrCl and B $\cdots$ HCl also holds for B = CO<sup>13</sup> and NH<sub>3</sub>,<sup>14</sup> as well as for several complexes B $\cdots$ Cl<sub>2</sub>.<sup>15</sup> This suggests that the simple rules governing geometry<sup>16</sup> and binding strength<sup>17</sup> in complexes B $\cdots$ HX also apply to complexes B $\cdots$ XY where XY is a halogen. The rules for angular geometry are electrostatic in

character<sup>18</sup> and require that the HX molecule in B $\cdots$ HX lies at equilibrium along the axis of a nonbonding electron pair carried by the acceptor atom of B or the symmetry axis of a  $\pi$ -orbital in complexes where a  $\pi$ -type hydrogen bond occurs. The modified rules would merely replace HX by XY, where XY is a halogen or an interhalogen molecule.

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