Can the Pre-equilibrium Molecular Complex in a Reactive Mixture of Ethene and Chlorine be Characterised? : An Answer from Rotational Spectroscopy

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The rotational spectrum of a complex of C_{2v} symmetry has been detected in a mixture of ethene and molecular chlorine by using a pulsed nozzle, Fourier-transform microwave spectrometer; the Cl_2 molecule lies along the C_2 axis of ethene that is perpendicular to the molecular plane and interacts only weakly with the π bond.

We report the unambiguous identification of a gas-phase molecular complex formed by the prototype unsaturated aliphatic hydrocarbon ethene with molecular chlorine. The complexes were detected and characterised by means of their rotational spectra, taking advantage of a so-called fast-mixing nozzle which allowed the two component gases to be mixed in the absence of surfaces, thereby inhibiting further progress along the reaction coordinate in this reactive system.

The mechanism for the addition reaction of molecular chlorine to alkenes has been the subject of much investigation and discussion.[1,2] In fairly polar solvents and in the dark, the reaction has been shown to be of first order in both components, indicating that the entity responsible for the electrophilic attack on the alkene is the halogen molecule.[2] It is generally accepted that the mechanism [see eqn. (1)]

$$\mathrm{A} + \mathrm{Cl}_2 = \underset{\textbf{I}}{\mathrm{A}\cdots\mathrm{Cl}_2} \rightarrow \underset{\textbf{II}}{\mathrm{ACl}^+} + \mathrm{Cl}^- \qquad (1)$$

involves a pre-equilibrium molecular association of the alkene A and Cl_2 to give the complex **I**. This complex then ionises in the rate-controlling step to give a cation **II** which reacts rapidly with Cl^-. Not only has there been some controversy about whether intermediate **II** is an open ion or a Dewar-type π-complex in which Cl^+ is covalently linked to the alkene,[3] but also 'the precise nature of the pre-equilibrium complex remains speculative.'[2] Clearly, it is of some interest to establish with certainty and precision the existence of *any* complex formed by alkenes with Cl_2. The simplicity of the prototype unsaturated aliphatic hydrocarbon ethene gives it a special appeal in this context.

Rotational spectroscopy is a precise method for determining the properties (*e.g.* angular geometries, intermolecular force constants, electric charge distributions) of molecular complexes in isolation in the gas phase, *i.e.*, free of lattice or solvent perturbations, but unfortunately the gas mixture is usually in contact with various surfaces.[4] The so-called gas-phase addition of chlorine to ethene, which is actually a reaction on a polar surface,[2] then occurs. The challenge is to find a way of probing the gas mixture spectroscopically in the dark and in the absence of surfaces, for under such circumstances there is experimental evidence that the interaction is then nonreactive.[5] The mechanism in eqn. (1) is consistent with this evidence since the formation of the ionic species **II** from **1** is facilitated by a polar solvent or surface and, in the absence of either, progress beyond **I** does not occur.

The problem of reaction between the premixed gases has been overcome in the work reported here by conducting microwave spectroscopy on pulses of the gas mixture supersonically expanded from a fast-mixing nozzle. In this device,[6] the active component gases remain separate until they expand simultaneously from a pair of co-axial and co-terminal tubes into the evacuated Fabry–Pérot cavity of our Fourier-transform microwave spectrometer. A mixture of *ca.* 2% ethene (Argo International) in argon was pulsed from a stagnation pressure of 3 atm through a solenoid valve into the outer of the two concentric tubes at a rate of 2 Hz while pure chlorine gas (Aldrich) issued continuously from the inner glass tube of 0.3 mm diameter at a rate sufficient to give a nominal pressure of 1×10^{-4} Torr in the vacuum chamber of the spectrometer. Complexes were formed at the cylindrical interface of the two gases but in the absence of any other surface. Under these conditions, collisionless expansion is achieved within a few nozzle diameters downstream so that the complexes which survive this short journey are frozen at a very low effective temperature. No reaction is then possible and the gas pulse can be interrogated by pulses of microwave radiation in the usual way.[7]

The ground-state rotational spectrum attributed to the complex (C_2H_4, Cl_2) was characteristic of a nearly prolate asymmetric-top molecule and consisted of transitions allowed by the *a*-component of the electric dipole moment, which the spectral intensity indicated was of significant magnitude. Each observed transition exhibited the nuclear quadrupole hyperfine structure expected of two $I = 3/2$ chlorine nuclei on or near the *a*-axis. The rotational constants (A_0, B_0, C_0), the centrifugal distortion constants (Δ_J, Δ_{JK}, δ_J; Watson *A*-reduction) and the nuclear quadrupole coupling constants [χ_{gg}(Cl), $g = a,b,c$] for both Cl nuclei in (C_2H_4, $^{35}Cl_2$) were obtained from an analysis of the $J = 4 \leftarrow 3$ and $5 \leftarrow 4$ set of transitions and are recorded in Table 1. Although only the spectroscopic constants of the most abundant isotopomer are presented in this preliminary communication, they allow firm conclusions about the nature of the complex through arguments set out below.

The geometry of the complex is unambiguously established as follows. The value of A_0 is only slightly larger than the rotational constant $C_0 = 24924.17(5)$ MHz of free ethene. This proves that in the complex the Cl_2 subunit lies along the *c*-axis of free ethene.[8] Since the *c*-axis of ethene coincides with the C_2 axis perpendicular to the molecular plane, the geometry of the complex must be of the type shown in Fig. 1. The fact that A_0 (complex) > C_0 (ethene) is readily understood by allowing for zero-point motion.[9] Moreover, the near identity of $P_b = \frac{1}{2}(I_a^0 + I_c^0 - I_b^0) = \sum_i m_i b_i^2 = 16.91(3)$ u Å^2 and $P_c = \frac{1}{2}(I_a^0 + I_b^0 - I_c^0) = \sum_i m_i c_i^2 = 2.89(4)$ u Å^2 of (C_2H_4, $^{35}Cl_2$) with $P_a = 16.8665(1)$ u Å^2 and $P_b = 3.49188(2)$ u Å^2, of free ethene,[8] respectively, also indicates that the geometry of C_2H_4 is only weakly perturbed in the complex. When the unperturbed monomer geometries are assumed[10,11] and the distance r between the centre of the ethene C=C bond and the inner Cl atom is adjusted to fit B_0 and C_0 the result is $r = 3.128(2)$ Å.

The conclusion that the intermolecular interaction in (C_2H_4, $^{35}Cl_2$) is weak is also available from the nuclear quadrupole coupling constants and Δ_J given in Table 1. First,

Table 1 Ground-state spectroscopic constants of (C_2H_4, Cl_2)

Spectroscopic constant	(C_2H_4, $^{35}Cl_2$)
A_0/MHz	25520(90)
B_0/MHz	1224.3817(4)
C_0/MHz	1184.1446(4)
Δ_J/kHz	1.242(5)
Δ_{JK}/kHz	54.5(2)
δ_J/kHz	0.038(4)
$\chi_{aa}(Cl_o)$/MHz	−107.24(2)
$\chi_{aa}(Cl_i)$/MHz	−111.99(2)
$\{\chi_{bb}(Cl_o) - \chi_{cc}(Cl_o)\}$/MHz	−0.07(5)
$\{\chi_{bb}(Cl_i) - \chi_{cc}(Cl_i)\}$/MHz	−0.55(6)

we note that $\chi_{bb}(\mathrm{Cl}) - \chi_{cc}(\mathrm{Cl})$ is small for both nuclei. This demonstrates that the cylindrical symmetry of the electric charge distribution of Cl_2 is only slightly perturbed when the Cl_2 molecule is incorporated into the complex, a result consistent with a weak interaction in an arrangement of the type depicted in Fig. 1. The larger anisotropy must clearly be associated with the Cl nucleus that lies nearest to the ethene subunit, hence the assignments of $\chi_{gg}(\mathrm{Cl_i})$ and $\chi_{gg}(\mathrm{Cl_o})$ to the inner (i) and outer (o) chlorine atoms given in Table 1. The fact that $\chi_{aa}(\mathrm{Cl})$ for each atom has the same sign as and is of very similar magnitude to $\chi_0(\mathrm{Cl}) = -111.790(4)$ MHz of the free Cl_2 molecule[12] is also consistent with a weak complex in which the Cl_2 axis coincides with the a-axis and in which there is little electric charge redistribution relative to the component molecules. The value $k_\sigma = 7.05(5)$ N m^{-1} for the intermolecular quadratic stretching force constant can be determined from Δ_J by using the expression derived by Millen[13] in the approximation of rigid subunits for a molecule having the symmetry shown in Fig. 1. This value is typical of a weakly bound complex and is indeed almost identical with $k_\sigma = 6.4$ N m^{-1} for the isostructural hydrogen bonded complex[14] of ethene and HCl. Thus, not only does (C_2H_4, Cl_2) have a very similar angular geometry to (C_2H_4, HCl) but the interaction between the subunits seems to be of a similar type. Since various qualitative[15] and quantitative[16] electrostatic models successfully predict the angular geometry of the hydrogen-bonded dimer, it is likely that similar models will account for the Cl_2 analogue.

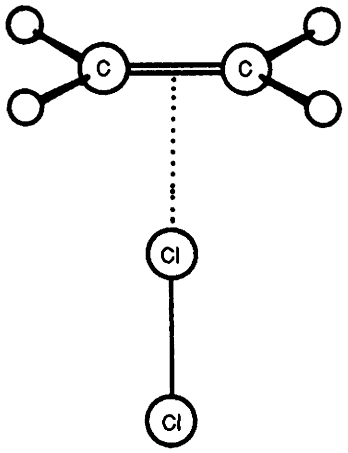

Fig. 1 The geometry of the ethene-molecular chlorine complex

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