Pre-reactive Intermediates in Mixtures of Hydrocarbons with Chlorine Monofluoride: Characterisation of Ethyne···ClF and Ethene···ClF by Rotational Spectroscopy

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Pre-reactive complexes B···ClF, where B is ethyne or ethene, of C_{2v} symmetry have been isolated in mixtures of B and ClF by using a fast-mixing nozzle in a pulsed-nozzle, Fourier-transform microwave spectrometer and characterised by their rotational spectra.

The reactions of simple Lewis bases, such as CO, H_2S, C_2H_2 and C_2H_4, with the interhalogen ClF are of interest not only because of their vigour but also by virtue of the fundamental nature of the molecules involved. However, such reactions have a sparse literature, no doubt because of their violence. Although the CO/ClF system has been used in the preparation of carbonyl chloride fluoride,[1] even this reaction must be conducted in the gas phase at reduced temperature and with CO in excess to achieve the simple stoichiometry. The reactions of ClF with hydrogen-containing organic compounds owe their violence to the large amounts of energy released when C–H bonds are broken on the one hand and C–X and H–X bonds (X is Cl or F) are formed on the other. According to Musgrave,[2] 'The earlier workers carried out the usual uncontrolled tests to show that most organic compounds, especially those containing hydrogen, will take fire spontaneously in it [ClF]...'. A significant challenge to the experimentalist is therefore to investigate the interaction of ClF with hydrocarbons, particularly the unsaturated prototypes ethyne and ethene, under controlled conditions. Questions of interest to be answered include: Does the violent reaction occur in the gas phase when surfaces are rigorously excluded? What is the nature of the initial interaction of the hydrocarbon with ClF when the reactants are mixed in the absence of a surface?

In this preliminary communication, we describe the first isolation and characterisation of gas-phase complexes B···ClF, where B is ethyne or ethene. The use of a fast-mixing nozzle[3] incorporated into a pulsed-nozzle, Fourier-transform microwave spectrometer[4] not only precludes chemical reaction but also allows the pre-reactive complexes to be investigated with all the power and precision available via rotational spectroscopy. The same technique has also been applied to the complexes OC···ClF and H_2S···ClF, with results as reported elsewhere.[5,6]

The utility of the fast-mixing nozzle in the present context results from its ability to allow gases to mix in the effective absence of surfaces. The device[3] consists of a pair of small-diameter, concentric, almost coterminal tubes attached to the outlet of a solenoid valve (Series 9, General Valve Corp.). Pure hydrocarbon (either ethyne or ethene) was flowed continuously through the inner (0.3 mm diameter) capillary into the vacuum chamber of the spectrometer to produce there a steady state nominal pressure of $ca.$ 10^{-4} mbar. A mixture containing 1% of ClF in argon was pulsed from a stagnation pressure of 3 bar, via the solenoid valve, into the outer of the tubes. The concentric jets of gas so produced met only as they emerged from the coterminal exits, by which time, presumably, they were travelling at near-supersonic speed ($ca.$ 5×10^4 cm s^{-1}) in a hydrodynamic flow in a direction away from any surface. Moreover, the complexes formed in the initial encounter of the gases are predicted[7] to have achieved collisionless expansion and low rotational/vibrational temperatures within $ca.$ 10 nozzle diameters (i.e. after $ca.$ 10 μs) downstream of the exits. Once in collisionless expansion, the gas pulses were probed by microwave pulses and their rotational spectra recorded as described elsewhere.[4]

The ground-state rotational spectra ascribed to C_2H_2···ClF and C_2H_4···ClF were characteristic of nearly prolate asymmetric

rotor molecules with only the component μ_a of the electric dipole moment nonzero and carrying a single Cl nucleus ($I = 3/2$) on the a axis. Detailed spectral analyses of the Cl nuclear quadrupole hyperfine structure in the $J = 2 \leftarrow 1$ and $3 \leftarrow 2$ transitions for each of C_2H_2···^{35}ClF and C_2H_4···^{35}ClF, to be described elsewhere, generated the rotational constants A_0, B_0 and C_0, the quartic centrifugal distortion constants Δ_J, Δ_{JK} and δ_J, and the Cl nuclear quadrupole coupling constants $\chi_{aa}(Cl)$ and $\chi_{bb}(Cl)$-$\chi_{cc}(Cl)$ recorded in Table 1. These constants allow the nature of the species responsible for the observed spectra to be diagnosed unambiguously.

The geometries of C_2H_2···ClF and C_2H_4···ClF are as shown in Fig. 1. Each has C_{2v} symmetry at equilibrium, with the ClF subunit lying along a C_2 axis of the free hydrocarbon molecule. For C_2H_4···ClF, the C_2 axis is that perpendicular to the plane of the nuclei of the parent C_2H_4 molecule. As established below, the Cl nucleus lies closer to the π-bond of the hydrocarbon than does F. The intermolecular interaction is weak and, although formally classified as the bπ.aσ type described by Mulliken,[8] seems to be mainly electrostatic in origin. The arguments leading to these conclusions are as follows.

If the angular geometries of C_2H_2···ClF and C_2H_4···ClF are as shown in Fig. 1 and the hydrocarbons are essentially unperturbed by complex formation, the rotational constants A_0 of these two species should be almost unchanged from the rotational constants $B_0 = 35273.8(4)$ MHz of ethyne[9] and $C_0 = 24924.17(5)$ MHz of ethene,[10] respectively. The values in Table 1 show that this is clearly so. The slight increase of the quantity in the complex relative to the free molecule can be attributed to the effects of the zero-point angular oscillations of the subunits.[11] The planarity of C_2H_2···ClF is confirmed by the small positive inertia defect $\Delta_0 = I_c^0 - I_b^0 - I_a^0 = 0.65(4)$ u Å^2. Values of this magnitude and sign are typical of weakly bound complexes that are known to be planar.[12] The T-shaped

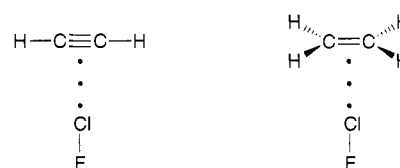| Spectroscopic constant	C_2H_2···^{35}ClF	C_2H_4···^{35}ClF
A_0/MHz	35690(102)	24958(51)
B_0/MHz	2099.7094(7)	2090.3338(6)
C_0/MHz	1977.9629(7)	1977.4378(6)
Δ_J/kHz	3.17(3)	2.95(2)
Δ_{JK}/kHz	89.6(5)	37.0(5)
δ_J/kHz	0.19(2)	0.16(2)
$\chi_{aa}(Cl)$/MHz	−144.857(3)	−144.028(3)
{$\chi_{bb}(Cl)$ − $\chi_{cc}(Cl)$}/MHz	−2.631(6)	−2.338(5)

Fig. 1 The angular geometries of the ethyne and ethene complexes of chlorine monofluoride

geometry of $C_2H_2\cdots ClF$ (Fig. 1) requires that within a given set of a-type, $J + 1 \leftarrow J$ transitions, those having $K_{-1} = 1$ should enjoy a nuclear spin statistical weight of 3 relative to the corresponding $K_{-1} = 0$ component. This effect was qualitatively evident but could not be established quantitatively because the rotational temperature was unknown. The corresponding ratio of 6:10 for $K_{-1} = 1:K_{-1} = 0$ implied by the geometry of $C_2H_4\cdots ClF$ in Fig. 1 was more difficult to establish even qualitatively, for the nuclear spin statistics and rotational cooling both operate to weaken $K_{-1} = 1$ transitions.

There is other evidence, apart from the magnitudes of the A_0 values, that the hydrocarbon geometries are not significantly perturbed on complex formation. The geometry of $C_2H_4\cdots ClF$ in Fig. 1 is consistent with the observed values of the planar moments $P_\alpha = \frac{1}{2}<I_\beta + I_\gamma - I_\alpha) = \Sigma_i m_i \alpha_i^2$ (α, β and γ to be permuted over a, b and c). In particular, the values $P_b = 17.03(4)$ u Å^2 and $P_c = 3.22(4)$ u Å^2 are almost unchanged from $P_a = 16.8665(1)$ u Å^2 and $P_b = 3.49188(2)$ u Å^2, respectively, of free ethene.[10] When the ethyne,[9] ethene[13] and ClF[14] geometries are taken unchanged from the free molecules, the ground-state rotational constants of $C_2H_2\cdots{}^{35}ClF$ and $C_2H_4\cdots{}^{35}ClF$ can be fitted to give $r = 2.869(2)$ and $2.765(2)$ Å, respectively, where r is the distance from the centre of the C–C bond to Cl.

A minor electrical perturbation of the subunits is implied by the magnitudes of the Cl nuclear quadrupole coupling constants. For both $C_2H_2\cdots{}^{35}ClF$ and $C_2H_4\cdots{}^{35}ClF$, $\chi_{aa}(Cl)$ (see Table 1) is almost identical to $\chi_0(Cl) = -145.8718$ MHz of the free ^{35}ClF molecule.[15] Therefore, the ClF subunit must lie along (or very nearly so) the a-axis in each complex and the electric field gradient at Cl must be very little changed from that for free ClF. Since the zero-point angular oscillations of the ClF subunit will operate to reduce the magnitude of the equilibrium value $\chi_{aa}^e(Cl)$ of this coupling constant by a few percent, $\chi_{aa}^e(Cl)$ must indeed by larger in magnitude than $\chi_0(Cl)$. Experience with $C_2H_2\cdots Cl_2$ and $C_2H_4\cdots Cl_2$ reveals[16,17] such an increase to be associated with the inner Cl nucleus while the outer nucleus suffers an equal decrease. Thus, in the ClF complexes the Cl nucleus must lie on the a axis but closer to the π-donor than does the F nucleus. The anisotropy $\chi_{bb}(Cl) - \chi_{cc}(Cl)$, necessarily zero in the cylindrically symmetric free ClF, is only a few percent of $-\frac{1}{2}\chi_0(Cl)$. This again testifies to the weakness of the interaction and indicates only a slight perturbation of cylindrical symmetry of the ClF charge distribution.

The weakness of the interaction is also demonstrated by the values of the intermolecular stretching force constant k_σ. These quantities have been determined from the centrifugal distortion constants Δ_J by using the appropriate expressions derived for rigid subunits in the quadratic approximation by Millen.[18] The results are $k_\sigma = 9.98(9)$ N m^{-1} and $10.97(7)$ N m^{-1} for $C_2H_2\cdots{}^{35}ClF$ and $C_2H_4\cdots{}^{35}ClF$, respectively. Such values are typical of weakly bound complexes[19] but considerably smaller than expected for an ion pair [BCl]$^+\cdots$F$^-$ resulting from a significant charge transfer between B and ClF. For example, $k_\sigma = 9.2$ N m^{-1} in HCN$\cdots$HCl[19] but 176.1 N m^{-1} in, e.g. Na$^+\cdots$F$^-$.[20]

This preliminary investigation demonstrates that pre-reactive complexes of the type $C_2H_2\cdots ClF$ and $C_2H_4\cdots ClF$ can indeed be isolated and characterised in gas-phase mixtures when prepared by coaxial supersonic expansion in the effective absence of surfaces. The intermolecular interactions are relatively weak, with little evidence of significant perturbation (electric or geometric) of the subunits. This result is consistent with earlier observations[21,22] in the series B$\cdots$XY (where XY is Cl$_2$ or BrCl), for which observed angular geometries, k_σ values and coupling constants $\chi_{gg}(X)$ ($g = a$, b, c) could be understood using a simple electrostatic interpretation of the interaction. There is parallel behaviour in the series B$\cdots$ClF for the members B = CO, H$_2$S, C$_2$H$_2$ and C$_2$H$_4$ so far investigated and a similar model seems appropriate.

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