Isolation and Characterisation of the Transient Complex $H_3N\cdots Cl_2$ in the Gas Phase

A. C. Legon,* D. G. Lister and J. C. Thorn

Department of Chemistry, University of Exeter, Stocker Road, Exeter, UK, EX4 4QD

The ground-state rotational spectra of the isotopomers $H_3^{15}N\cdots{}^{35}Cl_2$, $H_3^{15}N\cdots{}^{37}Cl^{35}Cl$, $H_3^{15}N\cdots{}^{35}Cl^{37}Cl$, $H_3^{14}N\cdots{}^{35}Cl_2$ and $H_2DN\cdots{}^{35}Cl_2$ of a transient complex of ammonia and chlorine have been observed by using a pulsed-nozzle, FT microwave spectrometer incorporating a fast-mixing nozzle; the spectroscopic constants allow the conclusion that the complex has C_{3v} symmetry, with the nuclei in the order shown, and is of the outer type defined by Mulliken.

The reaction between ammonia and chlorine has been known for a long time. When chlorine is in excess the product is the capricious and notorious nitrogen trichloride, a substance discovered by Dulong, at the cost of an eye and three fingers.[1] This compound is also formed as an intermediate when ammonia is the preponderant reactant but is subsequently decomposed[2] to give N_2 and NH_4Cl. In more recent times, molecular complexes formed by the halogens with amines in general, and ammonia in particular, played a central rôle in Mulliken's discussion of donor–acceptor complexes in a classic series of papers in the 1950s and subsequent reviews.[3] The simplest members of the series, namely (NH_3, F_2) and (NH_3, Cl_2) have appeared in theoretical investigations by the *ab initio* SCF method in the last two decades.[4–7] Although the reactions of NH_3 and Cl_2 alluded to above present no barrier to theoretical approaches, they have so far precluded any experimental investigations of the complex (NH_3, Cl_2). Here we present a report of the first identification and characterisation of this (presumably transient) species by means of its rotational spectrum.

Recently, we have isolated a range of thermodynamically stable but short-lived intermediates in chemical reactions. These intermediates include the hydrogen-bonded dimer $(CH_2)_2O\cdots HCl$ formed prior to the ring-opening reaction of oxirane with HCl,[8] the complex $Me\overset{+}{N}\equiv\overset{-}{C}\cdots HCl$ isolated in a mixture of methyl isocyanide and HCl before HCl adds across the $\overset{+}{N}\equiv\overset{-}{C}$ bond,[9] and the ion pair $Me_3NH^+\cdots I^-$ formed before precipitation of solid trimethylammonium iodide.[10] The same method has been adapted to isolate (NH_3, Cl_2) in the reactive mixture of NH_3 and Cl_2 gases.

The ground-state rotational spectrum of (NH_3, Cl_2) was observed by using a pulsed-nozzle, FT microwave spectrometer of the Balle–Flygare type[11,12] fitted with a fast-mixing nozzle. The latter device consisted of a pair of concentric, more or less coterminal tubes of circular cross-section venting into the evacuated Fabry–Pérot cavity of the spectrometer.[13] A continuous jet of chlorine gas (Aldrich) issued from the *ca.* 0.3 mm internal diameter glass capillary that constituted the inner tube at a flow rate sufficient to yield a background pressure of *ca.* 8×10^{-5} Torr within the chamber. A gas mixture composed of 2% ammonia (Argo International) in argon and held at a stagnation pressure of 3 atm. was pulsed through the outer tube at a rate of 1 Hz. Molecules of the complex (NH_3, Cl_2) were formed in the cylindrical sheath generated where the two gases meet at the point of expansion. Since the gas flow has the supersonic speed of *ca.* 5×10^4 cm s^{-1} and collisionless expansion is achieved within *ca.* 10 nozzle diameters, there is a period of only a few microseconds in which the nascent complexes can undergo reactive collisions. Gas pulses containing complexes chemically frozen in this way were then interrogated with microwave pulses and their rotational spectra recorded. Care was taken never to condense mixtures of NH_3 and Cl_2, for fear of forming NCl_3.

A detailed analysis, to be published elsewhere, of the ground-state rotational spectrum of each of the three isotopomers ($^{15}NH_3$, $^{35}Cl_2$), ($^{15}NH_3$, $^{35}Cl^{37}Cl$) and ($^{15}NH_3$, $^{37}Cl^{35}Cl$) showed unambiguously that the chemical species responsible for the observed spectra were symmetric-top molecules carrying a pair of $I = 3/2$ quadrupolar nuclei on the symmetry axis. Only the two C_{3v} geometries I and II shown in Fig. 1 are compatible with this observation. It is possible to discriminate between these cases with the aid of the observed rotational constants B_0 given in Table 1. As well as the three $^{15}NH_3$-containing isotopomers, the species ($^{14}NH_3$, $^{35}Cl_2$) and ($^{14}NH_2D$, $^{35}Cl_2$) were investigated. A detailed analysis was precluded by the extremely complicated hyperfine structure in rotational transitions arising from the presence of three and four quadrupolar nuclei, respectively. The approximate B_0 values recorded in Table 1 were obtained by estimating the unperturbed transition frequencies for two consecutive J transitions.

The order of the nuclei is readily established as that shown in structure **I** of Fig. 1. Assuming the NH_3 and Cl_2 geometries[14,15] to be unchanged on formation of the complex, the distance $r(N\cdots Cl_i)$ (i = inner) was varied until B_0 for the isotopomer ($^{15}NH_3$, $^{35}Cl_2$) was reproduced. The resulting value $r = 2.724$ Å was then used to predict the change ΔB_{calc} in B that accompanies isotopic substitution in the parent species to give each of the isotopomers ($^{15}NH_3$, $^{37}Cl^{35}Cl$), ($^{15}NH_3$, $^{35}Cl^{37}Cl$), ($^{14}NH_3$, $^{35}Cl_2$) and ($^{14}NH_2D$, $^{35}Cl_2$). The values $\Delta B^{I}_{calc.}$ and $\Delta B^{II}_{calc.}$ generated when this procedure is applied to the C_{3v} geometries **I** and **II** are given in Table 2. It is clear that only structure **I** leads to complete agreement between ΔB_{obs} and ΔB_{calc}.

Evidence about the nature of the interaction between NH_3 and Cl_2 in $H_3N\cdots Cl_2$ can be deduced from the spectroscopic constants of the isotopomer $H_3{}^{15}N\cdots{}^{35}Cl_2$. The centrifugal distortion constants D_J and D_{JK} of this species are included in Table 1. The ^{35}Cl-nuclear quadrupole coupling constants are $\chi(Cl_i) = -115.784(6)$ MHz and $\chi(Cl_o) = -101.798(6)$ MHz (i = inner, o = outer).

Fig. 1

Table 1 Observed spectroscopic constants for five isotopomers of (NH_3, Cl_2)

Spectroscopic constant	($^{15}NH_3$, $^{35}Cl_2$)	($^{15}NH_3$, $^{37}Cl^{35}Cl$)	($^{15}NH_3$, $^{35}Cl^{37}Cl$)	($^{14}NH_3$, $^{35}Cl_2$)	($^{14}NH_2D$, $^{35}Cl_2$)
B_0/MHz	1830.3551(1)	1829.7798(1)	1790.3262(7)	1889.6(3)	1813.9(5)[a]
D_J/kHz	1.347(3)	1.336(4)	1.258(3)	—	—
D_{JK}/kHz	101.11(5)	101.12(7)	96.72(4)	—	—

[a] This species is an asymmetric-top and hence the determined qualitity is $(B_0 + C_0)/2$

First, the centrifugal distortion constant D_J leads, *via* a model for the complex in which the subunits are assumed rigid,[16] to the intermolecular quadratic stretching force constant k_σ = 12.71(3) N m^{-1}. This value suggests that the complex is about as strongly bound as $H_2O\cdots HCl$ (k_σ = 12.5 N m^{-1})[17] but somewhat weaker than $H_3N\cdots HCl$ (k_σ = 18.2 N m^{-1}).[18]

Secondly, the ^{35}Cl-nuclear quadrupole coupling constants $\chi(Cl_i)$ and $\chi(Cl_o)$ reveal that the inter- and intra-molecular charge transfer on complex formation is small. A detailed theoretical analysis of $^{14}N_2\cdots HC^{15}N$ has examined [19] the effect of the electric charge distribution of $HC^{15}N$ on the electric field gradients q_i and q_o at $^{14}N_i$ and $^{14}N_o$, and hence, through $\chi(^{14}N) = eqQ$, on the ^{14}N-nuclear quadrupole coupling constants $\chi(^{14}N_i)$ and $\chi(^{14}N_o)$. It was found that the *mean* value, $\frac{1}{2}\{\chi(^{14}N_i) + \chi(^{14}N_o)\}$, is negligibly different from the free molecule coupling constant $\chi_0(^{14}N)$ because the efgs at $^{14}N_i$ and $^{14}N_o$ change by almost equal and opposite amounts. We note that in $H_3{}^{15}N\cdots{}^{35}Cl_2$ the mean value $\frac{1}{2}\{\chi(^{35}Cl_i) + \chi(^{35}Cl_o)\} = -108.769(5)$ MHz is only slightly smaller in magnitude than $\chi_0(^{35}Cl) = -111.790(4)$ MHz of the free $^{35}Cl_2$ molecule.[20] The reduction in magnitude almost certainly arises from the angular oscillation of the Cl_2 subunit in the complex and therefore we conclude that, as in the very weakly bound molecule $^{14}N_2\cdots HC^{15}N$, the difference $\Delta\chi(^{35}Cl) = \chi(^{35}Cl_o) - \chi(^{35}Cl_i) = 13.99(1)$ MHz results mainly from electron redistribution *within* Cl_2 rather than from charge transfer between the subunits. Indeed, the fractional change $\Delta\chi(^{35}Cl)/\chi_0(^{35}Cl)$ relative to the free $^{35}Cl_2$ molecule is only 0.125. According to the Townes–Dailey model for interpreting nuclear quadrupole coupling constants[21] we predict $\Delta\chi(^{35}Cl) = 0$ for the valence bond structure $^{35}Cl{-}^{35}Cl$ but $\Delta\chi(^{35}Cl) \approx 223$ MHz for $^{35}Cl^{+35}Cl^{-}$. The observed value of $\Delta\chi(^{35}Cl)$ for the complex would then correspond to a transfer of 0.06 e from Cl_i to Cl_o. $H_3N\cdots Cl$ therfore appears to be an outer complex, in the nomeuclature of Mulliken.[3]

Table 2 Changes ΔB in the rotational constant B of ($^{15}NH_3$, $^{35}Cl_2$) on isotopic substitution[a]

Isotopomer	ΔB_{obs}/MHz	$\Delta B^{I}_{calc.}$/MHz	$\Delta B^{II}_{calc.}$/MHz
($^{15}NH_3$, $^{35}Cl_2$)	0.00	0.00	0.00
($^{15}NH_3$, $^{37}Cl^{35}Cl$)	0.575	0.40	0.63
($^{15}NH_3$, $^{35}Cl^{37}Cl$)	40.029	39.71	39.72
($^{14}NH_3$, $^{35}Cl_2$)	−59.2	−59.9	−65.3
($^{14}NH_2D$, $^{35}Cl_2$)[b]	16.5	19.0	−10.8

[a] $\Delta B^{I}_{calc.}$ and $\Delta B^{II}_{calc.}$ refer to the changes calculated when models **I** and **II**, respectively, of Fig. 1 are assumed. See text. [b] For this species the appropriate quantity is $\Delta\{(B + C)/2\}$.

We thank the SERC and MURST (60% funds) for research grants in support of this work. The Ruth King Trust of the University of Exeter generously supported J. C. T. through a studentship. The permanant address of D. G. L. is Dipartimento di Chimica Industriale, Salita Sperone 31, Casella Postale 29, 98166 Sant'Agata di Messina, Italy.

Received, 23rd December 1993; Com. 3/07583D

References

1 See, for example, H. E. Roscoe and C. Schorlemmer, *A Treatise on Chemistry*, MacMillan and Co. Ltd, London, 1920, vol. 1, p. 528.
2 W. A. Noyes and A. C. Lyon, *J. Am. Chem. Soc.*, 1901, **23**, 460.
3 R. S. Mulliken and W. B. Person, *Molecular Complexes*, Wiley-Interscience, New York 1969. This book reprints many of Mulliken's important series of papers and provides a commentary on them.
4 R. R. Lucchese and H. F. Schaefer III, *J. Am. Chem. Soc.*, 1975, **97**, 7205.
5 H. Umeyana, K. Morokuma and S. Yamabe, *J. Am. Chem. Soc.*, 1977, **99**, 330.
6 A. E. Reed, F. Weinhold, L. A. Curtiss and D. J. Pochatko, *J. Chem. Phys.*, 1986, **84**, 5687.
7 I. Røeggen and T. Dahl, *J. Am. Chem. Soc.*, 1992, **114**, 511.
8 A. C. Legon, C. A. Rego and A. L. Wallwork, *J. Chem. Phys.*, 1992, **97**, 3050.
9 A. C. Legon, D. G. Lister and H. E. Warner, *J. Am. Chem. Soc.*, 1992, **114**, 8177.
10 A. C. Legon and C. A. Rego, *J. Chem. Phys.*, 1993, **99**, 1463.
11 T. J. Balle and W. H. Flygare, *Rev. Sci. Instrum.*, 1981, **52**, 33.
12 A. C. Legon, *Annu. Rev. Phys. Chem.*, 1983, **34**, 275.
13 A. C. Legon and C. A. Rego, *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 1915.
14 P. Helminger, F. C. DeLucia and W. Gordy, *J. Mol. Spectrosc.*, 1971, **39**, 94.
15 H. G. M. Edwards, D. A. Long and H. R. Mansour, *J. Chem. Soc., Faraday Trans. 2*, 1978, **74**, 120.
16 D. J. Millen, *Can. J. Chem.*, 1983, **63**, 1477.
17 A. C. Legon and D. J. Millen, *J. Am. Chem. Soc.*, 1987, **109**, 356.
18 N. W. Howard and A. C. Legon, *J. Chem. Phys.*, 1988, **88**, 4694.
19 A. C. Legon and P. W. Fowler, *Z. Naturforsch., Teil A*, 1992, **47**, 367.
20 Y. Xu, W. Jäger, I. Ozier and M. C. L. Gerry, *J. Chem. Phys.*, 1993, **98**, 3726.
21 See C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy*, McGraw-Hill, New York, 1955, ch. 9.