A Gas-phase Donor–Acceptor Complex

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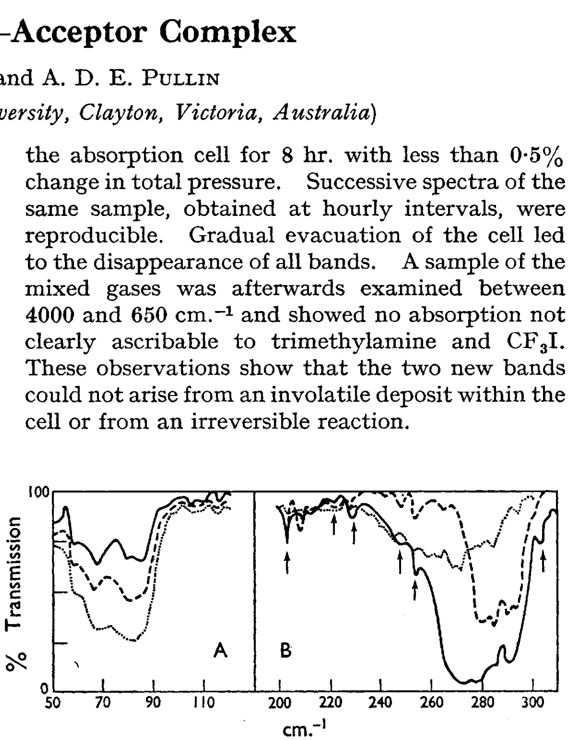
PREVIOUSLY we reported[1] the formation of solid adducts between tertiary amines and perfluoro-organic halides at reduced temperatures. In solution the related association of 2,4,6-collidine and CF_3I has been investigated by Larsen and Allred.[2] We now report evidence for association between trimethylamine and CF_3I in the gas phase. Gaseous mixtures of these, at room temperature, show an infrared absorption band at 77 cm.$^{-1}$ (Figure). This occurs in a spectral region in which the separate components do not absorb at the pressures used. In addition a strong band can be observed in gaseous mixtures which is partly overlapped by the C–I stretching fundamental of CF_3I at 286 cm.$^{-1}$ and also by a strong band of trimethylamine at 266 cm.$^{-1}$. This is clear from the Figure and is confirmed by an examination of the corresponding optical density spectra which indicates a frequency of 272 cm.$^{-1}$ for this new band. We interpret these new bands at 77 and 272 cm.$^{-1}$ as the N ··· I (intermolecular) and C–I stretching fundamentals of a gas-phase donor–acceptor complex $CF_3I{\cdot}NMe_3$ in equilibrium with the free components

$$CF_3I + NMe_3 \rightleftharpoons CF_3I{\cdot}NMe_3 \qquad (1)$$

It is known that under certain conditions trimethylamine and CF_3I react irreversibly to form a white solid, involatile at room temperature.[1] In the present work the mixed gases could be kept in the absorption cell for 8 hr. with less than 0·5% change in total pressure. Successive spectra of the same sample, obtained at hourly intervals, were reproducible. Gradual evacuation of the cell led to the disappearance of all bands. A sample of the mixed gases was afterwards examined between 4000 and 650 cm.$^{-1}$ and showed no absorption not clearly ascribable to trimethylamine and CF_3I. These observations show that the two new bands could not arise from an involatile deposit within the cell or from an irreversible reaction.



FIGURE

Infrared spectra at 100 *cm. path length, the arrows indicating traces of water vapour.* A: 1 : 1 *molar trimethylamine and* CF_3I *at* 320, 240, *and* 180 *mm.* B: 1 : 8 *molar trimethylamine and* CF_3I *at* 427 *mm.* (———), *trimethylamine at* 50 *mm.* (. . . . . .), *and* CF_3I *at* 400 *mm.* (- - - - -).

TABLE 1

P (mm.)	430	240	180
O.D. (320)/O.D. (P)	0·52 ± 0·03	1·8 ± 0·1	3·1 ± 0·3
$320^2/P^2$	0·55	1·77	3·17

TABLE 2

C–I *str. and* N–I *str. fundamentals in cm.*$^{-1}$

	CF_3I	$CF_3I\cdot NMe_3$		CF_3I·Quinuclidine	$CF_3I\cdot SMe_2$
	C–I	C–I	N–I	C–I	C–I
Solid (−185°)	280 ± 1	256 ± 1	126 ± 1	256 ± 1	270 ± 1
Gas (22 ± 2°)	286 ± 1	272 ± 1	77 ± 1		

We deduce the stoicheiometry of the gas-phase complex as $CF_3I\cdot NMe_3$ with nitrogen to iodine bonding on general chemical grounds, by analogy with the corresponding low-temperature adduct,[1] and from the pressure dependence of the measured optical densities (O.D.) of the band at 77 cm.$^{-1}$. Total pressures, P, used included 430, 320, 240, and 180 mm., all below the saturation vapour-pressure (470 ± 5 mm.)[3] of an equimolar liquid mixture at this temperature, at which composition the vapour pressure has a sharp minimum. For an equimolar ideal-gas mixture lying well to the left in equilibrium (1), P_1^2/P_2^2 = O.D. (P_1)/O.D. (P_2). Mean values of O.D. (P_1)/O.D. (P_2) were determined from its value at 1 cm.$^{-1}$ intervals over the range 66—90 cm.$^{-1}$, choosing P_1 as 320 mm. (see Table 1).

The attribution of the 272 cm.$^{-1}$ band to a C–I stretching mode is supported by a comparison with the frequencies observed[3] for the solid adduct at low temperatures (see Table 2). The band at 256 cm.$^{-1}$ in the solid adduct is assigned to the C–I stretching fundamental, although trimethylamine has a band in this region, because several other donor–CF_3I solid adducts exhibit a similar band at lower frequency than that of the C–I fundamental in solid CF_3I.

To an approximation the N · · · I force constants of the solid and gaseous complexes are (see Table 2) in the ratio $126^2/77^2 = 2{\cdot}7$. It is probable that the ratio of the corresponding intermolecular bond strengths will be similar. This dependance of donor–acceptor adduct bond parameters on phase is perhaps indicative of the need for caution in the theoretical interpretation of existing data on donor–acceptor complexes obtained from solution data.

All spectra below 320 cm.$^{-1}$ were obtained with an R.I.I.C. FS 520 Fourier spectrophotometer. The reproduced spectra were obtained using 312 input points, providing a theoretical resolution of 4 cm.$^{-1}$ (A), or with 625 input points giving a theoretical resolution of 2 cm.$^{-1}$ (B).

(*Received, January 23rd,* 1967; *Com.* 064.)

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[1] N. F. Cheetham and A. D. E. Pullin, *Chem. Comm.*, 1965, 418.

[2] D. W. Larsen and A. L. Allred, *J. Phys. Chem.*, 1965, **69**, 2400.

[3] N. F. Cheetham and A. D. E. Pullin, unpublished data.