Molecular Structure of the Electron Donor–Acceptor Complex of Trimethylamine–Dibromine in the Gas Phase as determined by Electron Diffraction

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A gas-phase electron diffraction study of trimethylamine–bromine complex indicates that principal bond lengths (r_a) are N–Br 1.98(3), Br–Br 2.29(1), C–N 1.67(2) Å, and the Br–Br bond is out of the C_{3v} axis of trimethylamine with the NBrBr angle 112(3)°. Thus the structure of gaseous $(CH_3)_3N$–Br_2 is considerably different from the C_{2v} configuration found for $(CH_3)_3N$–I_2 in the solid phase.

It is well known that alkylamines and halogens react to yield a 1:1 electron donor–acceptor complex classified as n–σ type by Mulliken.[1] Until now many studies on such complexes have been carried out by electronic and vibrational spectra, and n.m.r. spectra in the gas and/or solid phases.[2] However, structural studies have been carried out only in the solid phase, for example, X-ray crystallography on $(CH_3)_3N$–I_2[3] and $(CH_3)_3N$–ICl,[4] but have not been carried out in the gas phase which is free from crystal-field effects. The molecular structure observed in the solid phase could be markedly different from that in the vapour because of the complicated mechanism of the formation of the charge-transfer bond. A recent study by photoelectron spectra for alkylamine–bromine complexes in the gas phase[5] supports the charge-transfer mechanism upon structure change by complex formation. This paper reports the structure of the gaseous $(CH_3)_3N$–Br_2 complex determined by electron diffraction.

Experimental

The sample was prepared by mixing equimolar amounts of the component molecules in a vacuum line. Trimethylamine was obtained from the commercial hydrogen chloride salt. Bromine was of special grade commercially obtained. The gas was stored in a flask (3 l) at a pressure of *ca.* 75 Torr at room temperature and let into the diffraction chamber through a nozzle. The 40 kV electron diffraction experiment[6] was performed at camera distances of 144 and 294 mm by using an r^3 sector. The exposure time for the short camera distance was 40—60 s and that for the long camera distance was 20—30 s with a beam current of 0.6 μA. The optical densities of three photographic plates for the short camera distance and two plates for the long camera distance were measured by means of a digital microphotometer.[6]

Methods

The experimental total intensities were estimated with the help of theoretical factors obtained from elastic and inelastic scattering data from Schäfer *et al.*[7] and Cromer and Mann,[8] respectively, and were averaged for the range q 8.0—97.0 after combining the long and short camera distance data at q 32.0 ($q = 10/\pi$ s). The molecular intensities are shown in Figure 1. The radial distribution functions are shown in Figure 2. The peaks appearing at *ca.* 3 and 4 Å suggest the existence of trimethylamine–bromine complex in the gaseous phase.

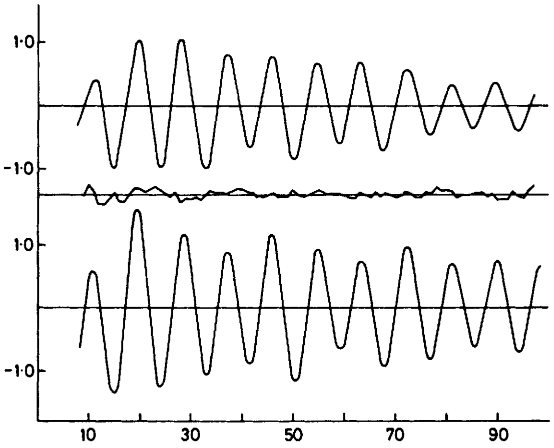

Figure 1. Molecular intensities of $(CH_3)_3N$–Br_2. The upper curve is the calculated molecular intensity for the best-fit model (Table), the middle one the difference between observation and calculation, the lower the calculated one for the completely dissociated model

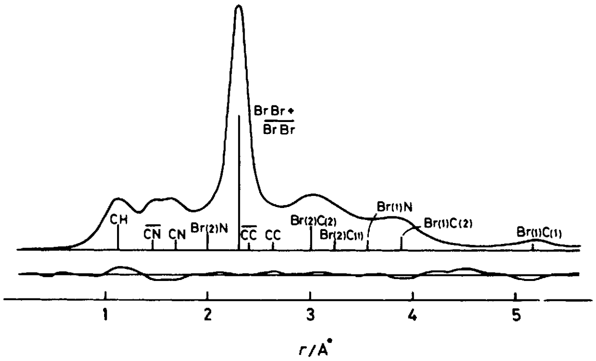

Figure 2. Radial distribution functions for $(CH_3)_3N$–Br_2. The upper curve is the experimental radial distribution. The vertical bars represent interatomic distances, the bars belong to the component molecules from dissociation. The lower curve shows the residuals.

The molecular model is shown in Figure 3. Here C_{2v} symmetry of $(CH_3)_3N$–Br_2 and C_{2v} symmetry of trimethylamine were assumed. The parameters of bond distances, bond angles, and mean amplitudes of vibration: r(N–Br), r(Br–Br), r(C–N), C$\hat{N}$C, l(N–Br), l(Br–Br), and l(C–N), and two parameters related to the orientation of the acceptor; the angles α and β, shown in Figure 3, were refined by a least-squares treatment. Here r(C–H) 1.111 Å and H$\hat{C}$H 109.7° were assumed with a staggered form of the CH_3 group relative to the C–N axis. The mean amplitudes of vibration for other distances were calculated by the use of force constants obtained from the i.r. spectra of $(CH_3)_3N$–Br_2 in the solid phase.[9] In the analysis the

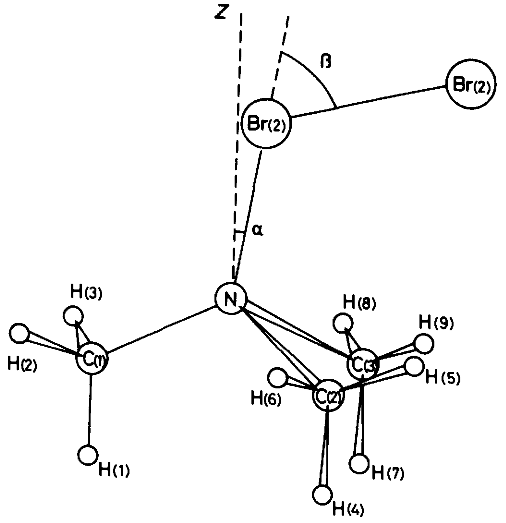

Figure 3. Molecular model of $(CH_3)_3N–Br_2$

Table. Molecular parameters (distances in Å, angles in degrees) of $(CH_3)_3N–Br_2$ and the components molecules.

	$(CH_3)_3N–Br_2$		$(CH_3)_3N$ and Br_2	
	r_a	l	r_a	l
N–Br	1.98(3)	0.07(4)		
Br–Br	2.29(1)	0.08(1)	2.286	0.045
C–N	1.67(2)	0.051	1.459	0.049
∠CNC	104(2)		110.9	
∠NBrBr	112(3)			
tilt (α)	9(2)			
bend(β)	68(3)			
dissociation/%	48(7)			

degree of dissociation of the complex was taken into consideration and the structures of the component molecules were taken from the literature.[10,11] The parameters obtained are given in the Table in comparison with those for the component molecules. The values in parentheses are 99% confidence errors including a systematic error.

Results and Discussion

According to X-ray analysis complexes such as $(CH_3)_3N–I_2$[3] or $(CH_3)_3N–ICl$[4] have been found to have C_{3v} symmetry about the linear N–I–I or N–I–Cl axes in the solid phases. The present study indicated that in the gaseous $(CH_3)_3N–Br_2$ complex N–Br–Br is not linear. This bending cannot be explained by a shrinkage effect because the calculated shrinkage was very small, about one-tenth of the expected value (0.53 Å) if the above force constants were used.[9] Thus it is interesting that such a bent structure was suggested by Reid and Mulliken for the 1:1 pyridine–I_2 complex.[12]

The observed N–Br distance (1.98 Å) is nearly equal to the sum of the covalent radii (1.88 Å) with an increase of *ca.* 5%. The observed Br–Br distance of 2.29 Å is the same as that in a free bromine molecule.[12] On the other hand the C–N distance increases and the CNC angle decreases in comparison with those in a free molecule. As expected,[13] it was predicted that the structural changes for the donor molecule are larger than those for the acceptor molecule. The former may be due to the decrease of charge densities in the C–N bonds, which is caused by the charge transfer, from the viewpoint of VSEPR.[14]

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