

Structure of Gaseous Ammonium Chloride

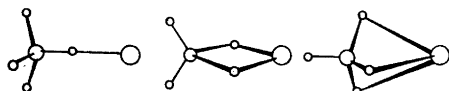
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The extent of dissociation of ammonium chloride vapour has been discussed for a long time. According to earlier investigations,¹ partial dissociation takes place. However, later investigations,² including a recent mass spectroscopic experiment,³ indicates complete dissociation of the equilibrium vapour into ammonia and hydrogen chloride. The present study by electron diffraction was intended to identify the ammonium chloride molecule if present and to obtain information concerning its molecular structure. The purpose of this note is to report some preliminary results.

A sample of ammonium chloride was stored in a vacuum overnight before the experiment. It was heated to 250° in a furnace made of Monel metal and its vapour was led into vacuum through a fine-tipped nozzle. Electron-diffraction photographs⁴ were taken with 40 kV electrons at a camera distance of 127 mm using an r^3 sector. The densities of the photographic plates were measured by a microphotometer and were converted to intensities in the usual way. The average intensity of several plates, after careful correction for the imperfection of the sector shape, was leveled by use of a theoretical background function over the range $16 \leq q \leq 75$. The leveled intensity curve exhibited only small fluctuations; therefore it was not feasible to draw in an artificial background curve. Analysis was performed by use of the "smooth background method".⁵

For the structure of ammonium chloride, the monomeric forms of single, double, and triple approach models, shown in Fig. 1, as well as a diamond shaped dimeric



single approach double approach triple approach

Fig. 1. Monomeric forms of single, double and triple approach models.

form were individually tested. In addition, the partial dissociation of each monomer was considered taking the structure parameters of NH_3 and HCl from other measurements.^{6,7} Thus, in the least-squares procedure, the inter-atomic distances r_g and amplitudes l for $\text{N}\cdots\text{Cl}$, $\text{N}-\text{H}$ (four distances were assumed to be equal), $\text{H}\cdots\text{Cl}$, and $\text{H}-\text{Cl}$ in each monomeric model were refined. In the dimeric model, the distances and amplitudes for six atomic pairs were refined. Computations based on various assumed degrees of dissociation led to the smallest variance for the 60% dissociated single approach model.* For this model the most probable values for the parameters of an NH_4Cl molecule are given in Table 1.

Table 1.

$r_g = 2.54 \pm 0.02 \text{ \AA}$	$l = 0.17 \pm 0.01 \text{ \AA}$	for $\text{N}\cdots\text{Cl}$
$1.22 \pm 0.01 \text{ \AA}$	$0.08 \pm 0.01 \text{ \AA}$	for $\text{N}-\text{H}$
$2.90 \pm 0.02 \text{ \AA}$	$0.12 \pm 0.02 \text{ \AA}$	for $\text{H}\cdots\text{Cl}$
$1.54 \pm 0.03 \text{ \AA}$	$0.10 \pm 0.03 \text{ \AA}$	for $\text{H}-\text{Cl}$

Since the variance for each monomeric model less than 60% dissociated was not much different from that for the above model, it was difficult to determine definitely the degree of dissociation and the form of the monomer. However, the assumption of complete dissociation of the vapour should evidently be ruled out because the variance for this system was much larger than that for any model incorporating partial dissociation. A dimeric model was also rejected.

To check further the impossibility of complete dissociation the following experiment was carried out. Electron-diffraction photographs of NH_3 and HCl were taken in turn on a single plate at the same pressure of each of the gases and with the same exposure time. The intensity curve thus obtained could be distinguished from that of NH_4Cl . As expected, the molecular intensity was in good agreement with the intensity calculated for complete dissociation, shown in Fig. 2.

As can be seen from the above values of the structural parameters, if the single approach model is taken, the $\text{N}\cdots\text{Cl}$ distance of 2.54 Å is much shorter than

* Our recent electron diffraction study of gaseous ammonium fluoride has confirmed that this molecule also has this form.

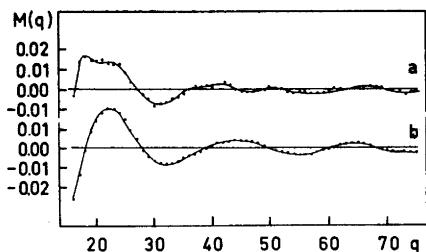


Fig. 2. Comparison of the experimental and calculated molecular intensity curves $M(q)$. The experimental data are shown in dots, a: NH_4Cl , b: NH_3 and HCl .

the distance 3.26 Å found in crystals of the NaCl type⁸ and is also shorter than ordinary $\text{NH}\cdots\text{Cl}$ hydrogen-bonded distances which range from 2.91 to 3.41 Å.⁹ This shortening seems to be due to the covalent character occurring from the change of phase as seen in the cases of alkali halides,¹⁰ and also due to the presence of a strong hydrogen bond in the gaseous NH_4Cl molecule. With respect to this point, it is of interest to note that the bond length obtained for $\text{H}-\text{Cl}$ in an NH_4Cl molecule is longer than that in HCl molecule, 1.29 Å, by about 0.2 Å. The amplitude of vibration for $\text{N}\cdots\text{Cl}$ was found to be 0.17 Å. A simple calculation gives 0.26 md/Å for the force constant of the $\text{NH}\cdots\text{Cl}$ hydrogen bond.

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A Reinvestigation of the General Acid Catalysis Reported for the Hydrolysis of Ethyl Orthoformate in Dioxane-Water Solvents

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In recent papers¹⁻³ we showed that the hydrolysis of ethyl orthoformate proceeds in water and in 65/35 w/w dioxane-water by the A-1 mechanism. First, the structural effects in the hydrolysis of a series of orthoformates in water and in 65 wt. % dioxane-water were in accordance with this mechanism. Second, the solvent deuterium isotope effect, $k_{\text{D}_2\text{O}^+}/k_{\text{H}_2\text{O}^+} = 2.98$, in water point to a proton transfer pre-equilibrium. The ratio was of the same magnitude in 65/35 w/w dioxane-water. Third, the lack of general acid catalysis in water excluded the alternative mechanism, a rate-determining proton transfer reaction. Thus it is surprising that DeWolfe and coworkers^{4,5} have presented experimental evidence for general acid catalysis in the hydrolysis of ethyl orthoformate in 50–70 % dioxane-water solutions although the reaction is subject to specific hydronium ion catalysis in water. On the basis of the