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## The Gaseous Equilibrium of 1,3,5-Trimethylhexahydro-1,3,5-triazine and N-Methylenemethylamine

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The equilibrium constant,  $K_p$ , for the reversible system containing N-methylenemethylamine (MeN:CH<sub>2</sub>) and its cyclic trimer, 1,3,5-trimethylhexahydro-1,3,5-triazine, has been measured over the temperature range 98-164 °c

It is known that 1,3,5-trimethylhexahydro-1,3,5-triazine is produced from reaction of dimethylamino radicals, 1-3 presumably by disproportionation followed by ring trimerisation of the N-methylenemethylamine.

$$2Me_2N \longrightarrow Me_2NH + MeN:CH_2$$

The trimerisation reaction has been shown to be reversible,<sup>4</sup> and the infrared <sup>4,5</sup> and microwave <sup>6</sup> spectra of the monomeric N-methylenemethylamine have been studied. It seemed feasible to investigate the gaseous equilibrium between the ring trimer and the monomer.

## EXPERIMENTAL

1,3,5-Trimethylhexahydro-1,3,5-triazine was made by the reaction of methylamine with formaldehyde in aqueous solution followed by addition of solid potassium hydroxide.7 The triazine was separated from the water, dried, fractionally distilled, bulb-to-bulb distilled in vacuo, and the purity checked by gas chromatography. Cylinder boron trifluoride was vacuum-distilled.

The apparatus consisted of a reaction vessel with thermocouple inlet tube, having a capillary greaseless tap at one end and a glass spiral gauge fitted with a small concave mirror at the opposite end. The reaction vessel and spiral gauge fitted into a heated furnace (temperature variation  $<1^{\circ}$  over the reaction vessel length), and the portion of the gauge which carried the mirror projected beyond the furnace. By means of the usual optical lever method, the spiral gauge was used as a null instrument for measuring reactionvessel pressure, the balancing pressure being measured on a mercury manometer read by a cathetometer. The triazine was placed in a detachable glass reservoir and weighed. The reservoir was then attached to the apparatus, evacuated, and some triazine was allowed to enter the reaction vessel through the greaseless tap. The tap was then closed, the

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reservoir detached and weighed; the exact amount of material within the reaction vessel was then known. The reaction vessel was then heated, and the pressure-temperature variation studied for both ascending and descending temperatures. The procedure was modified by adding about 3 mm. of boron trifluoride to the reaction vessel after introduction of the triazine, and before starting the pressuretemperature cycle.

## **RESULTS AND DISCUSSION**

From the known amount of triazine contained within the reaction vessel, the pressure-temperature graphs corresponding to (a) no dissociation, and (b) complete dissociation can be drawn. These two graphs, in conjunction with the observed variation, make possible an immediate qualitative estimate of the extent of dissociation. As the experimental curve approaches that for (b), the reaction-vessel temperature is lowered and the cycle of readings repeated at  $4-5^{\circ}$  intervals. When a run was carried out under these conditions, the pressure-temperature values obtained during cooling were higher than those for the heating process, and the pressure slowly dropped with time towards the curve obtained for the heating cycle. It was therefore assumed that the equilibrium was established too slowly for the measurements to be made, and recourse was made to the addition of boron trifluoride as a possible catalyst. When a run was carried out in the presence of 3-5 mm.



FIGURE 1 Pressure-temperature graph when 3-5 mm. of boron trifluoride was present. [], Heating; (), cooling. (The lines A and B are for trimer and monomer pressure-temperature variation, respectively)

of boron trifluoride, the pressure-temperature graphs were coincident for heating and cooling (Figure 1), and no other products were formed. Repetition of the runs gave the same behaviour, but after a few runs the coincidence of the heating-cooling cycle values gradually worsened. These later discrepancies were shown to be due to decomposition of either the monomer or the trimer, or both, and the reaction-vessel surface, which had previously remained clean throughout, was coated with



FIGURE 2 Temperature variation of the equilibrium constant.  $\bigcirc$ , Run 1;  $\times$ , run 2

a carbonaceous film, and small quantities of an involatile brown oil were present in the reaction vessel. We shall make the assumption that the coincident heatingcooling cycles represent a genuine gaseous equilibrium, and on this basis we can represent the temperature variation of the equilibrium constant,  $K_p$  (Figure 2). More points, all of which fall on or very close to the line, could have been included but are omitted for the sake of clarity. The best straight line gives  $\Delta H$  as 35 kcal. mole<sup>-1</sup>.

The enthalpy change for the equilibrium can be given as

 $\Delta H = 3[D(C-N) - \pi$ -bonding energy (C-N)]

If we estimate D(C-N) as 75 kcal. mole<sup>-1</sup> (*i.e.*,  $\sim D[Me_2N-Me])$ ,<sup>8</sup> then we obtain a value of 63 kcal. mole<sup>-1</sup> for the  $\pi$ -bonding energy in MeN:CH<sub>2</sub>, *i.e.*, approximately the same as for the  $\pi$ -bonding energy in a simple alkene.

This work on nitrogen ring systems has been discontinued. These results, which are the only ones known to us in this field, are presented with the hope that further studies in such systems will be encouraged.

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