Dimethylnitrosamine—Monomer or Dimer in Solution?

SHERRIL D. CHRISTIAN* and PETER KLÆBOE

Department of Chemistry, University of Oslo, Oslo 3, Norway

The structure and physical properties of dimethylnitrosamine (DMNA) have been studied by various workers. Haszeldine et al.[1] recorded the infrared and the ultraviolet spectra, and Tarte[2] made an infrared study of DMNA. These authors noted a significant variation in the infrared spectra with the state of aggregation. In particular large differences were observed between the gas and the liquid spectra in the 1500—1100 cm^{-1} region. These features were explained as an equilibrium between predominantly monomer molecules in the gas phase and dimer molecules in the liquid. This interpretation could explain many of the infrared spectral features. Later Looney et al.[3] supported the assumption of dimers in DMNA from NMR and IR measurements and they assigned many of the infrared bands on this basis. Thus, the N-nitroso compounds should show a parallel behaviour to the C-nitroso compounds, many of which exist as dimers in the condensed phases.[4] The high boiling point of DMNA (151°) compared to related molecules of similar molecular weight were also interpreted in favour of association.

On the other hand the infrared spectrum of liquid DMNA is not very different from the spectra obtained in dilute solution of carbon tetrachloride or carbon tetrabromide. Nor does the spectrum of the liquid vary from room temperature to 130°.[3]

These data do not seem compatible with the hypothesis of a monomer-dimer equilibrium since the constancy of the IR-spectrum in the dilution experiment would indicate either: (1) mostly monomeric species or (2) predominantly dimers with a very high dimerization constant. However, a large dimerization constant should be

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* On sabbatical leave from Dept. of Chemistry, University of Oklahoma, Norman, Okla., U.S.A.

accompanied by large negative values for $\Delta H°$ and $\Delta S°$ and the spectrum should change considerably with temperature. Finally, infrared studies of the solvent shifts[5] and the ultraviolet spectra obtained in various non-polar and polar solvents[6] have been interpreted on the basis of monomer species in solution.

We have recently studied the infrared and the Raman spectra of DMNA under various conditions.[7] In order to interpret these data the question of monomer-dimer equilibrium in liquid and dissolved DMNA should be settled. We decided, therefore, to employ a classical thermodynamic method, since the spectroscopic data alone do not appear to be conclusive. In the present communication we report a study of the partial vapour pressure of DMNA in water and heptane.

Experimental and results. DMNA, from Aldrich, was purified by two times distillation under reduced pressure in a rotaband column. No impurity peaks were detected in a gas chromatogram. Stock solutions of DMNA in Merck Uvasol heptane and distilled water were prepared by weight and diluted volumetrically to give solutions of the required concentration.

Relative concentrations of DMNA in the vapour phase in equilibrium with liquid solutions of the compound were determined by measuring the absorbance of the strong band in the ultraviolet spectrum at 227 mμ. A Beckman model DK-1 spectrometer, equipped with a thermostatted cellholder, was employed for all spectral measurements. Vapour absorbances of aqueous solutions were obtained by placing approximately 0.2 ml of each sample directly on the bottom of an 8 cm cylindrical cell, tightly stoppering the cell and thermostatting it for approximately 10 min before recording the spectra. Vapour concentrations appeared to reach equilibrium values within about 5 min, and remained constant for at least one hour. Fogging of the windows was avoided by maintaining the cell several degrees below ambient temperature.

Because of the greater escaping tendency of DMNA from heptane, it was necessary to employ a cell of shorter path-length to obtain vapour spectra of the heptane solutions. Rectangular 1 cm cells were equipped with shallow, cylindrical glass cups which rested on the bottom. Approximately 0.1 ml of each solution was placed in the cup, and the cell
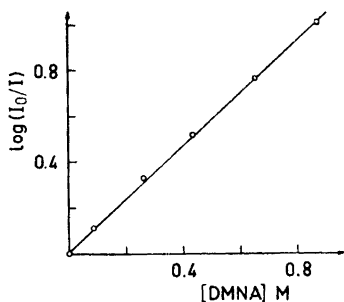
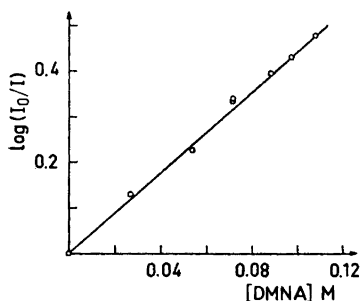*Fig. 1.* Absorbance at 227 mμ of vapours in equilibrium with solutions of DMNA in water at 21.2°, 8 cm cell.

Fig. 2. Absorbance at 227 mμ of vapours in equilibrium with solutions of DMNA in heptane at 25.0°, 1 cm cell.

tightly stoppered and inserted in the thermostatted holder.*

Figs. 1 and 2 show the dependence of vapour absorbance at 227 mμ, on liquid concentration for solutions of DMNA in water at 21.2 ± 0.1° and heptane at 25.0 ± 0.1°, respectively. The vapour absorbance of pure liquid DMNA at 25.0°, in a 1 cm cell, was observed to be 1.01 ± 0.01.

Discussion. The near linearity of the plots of A *versus* the DMNA concentration may be interpreted as evidence that the

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* It was found that if heptane solutions were added directly to the bottom of the 1 cm cell, the cell windows frequently became covered with a layer of liquid; use of the cylindrical cups eliminated this wetting problem.

compound is not highly associated in dilute solution in water or in heptane. If the compound exists as the monomer in the vapour (as is generally assumed [1-3]) but as the dimer in liquid solution, the partial pressure or vapour concentration of DMNA above dilute solutions should vary linearly with the square root of the liquid concentration.[8] On the other hand, if DMNA is monomeric in both phases, the vapour concentration should vary linearly with solution concentration in the limit of infinite dilution. The slight tendency of the curve in Fig. 1 to decrease in slope as the concentration of DMNA increases might be regarded as an indication of the presence of small concentrations of associated species (possibly dipole-dipole complexes) in the more concentrated solutions. However, in view of the observation that ten-fold dilution of DMNA in CCl_4 and CBr_4 does not change the relative intensities of the infrared absorption bands of the compound,[5] it is unlikely that molecular aggregation of DMNA is responsible for any of the spectral features previously reported for the compound in water and organic solvents.

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