Since the breaking of the Ar—X bond is very fast (the order of a molecular vibration, $\sim 10^{-13}$ sec) it would occur before the back reaction of the equilibrium (4). The observed deviation of the halobenzenes from the linear $\Delta G(H_3)$ versus EA_{PhCl} plot would indicate that the dissociation process (reaction 6) is more important in the liquid phase than under the gas-phase conditions[8] where the EA_{PhCl} values were obtained.

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Ultra-violet Absorption Spectrum of Thymine in Ice

WANG[1-3] has found that the production of photodimers is much greater when frozen aqueous solutions of thymine are irradiated with ultra-violet light than when liquid solutions of thymine are similarly irradiated. Adding alcohol to the solution before freezing or using thymidine, thymidylic acid, or uracil compounds instead of thymine all markedly reduce the formation of photodimer. He believes that the dimer formation in ice is facilitated by aggregation of the molecules. We have measured the absorption spectrum of various frozen solutions and have thus been able to obtain direct evidence of aggregation.

Samples were frozen on to a quartz plate to give a specimen about 1 mm thick and then immersed in liquid nitrogen in a quartz Dewar flask. The samples used were either pure water or an aqueous solution at a concentration of about 1 mg/ml. The apparent absorption of the pure ice was subtracted from that of each frozen solution. The absorption spectrum was measured with a Cary 14 spectrophotometer and a 2-in. diameter photo-multiplier placed 2 in. from the sample (model 1462 light scattering attachment). This apparatus detects a large fraction of the forward scattered light in addition to the transmitted light and thus more nearly gives an accurate absorption spectrum.

The absorption of thymine in ice is shown as the solid line in Fig. 1. A room temperature aqueous spectrum of

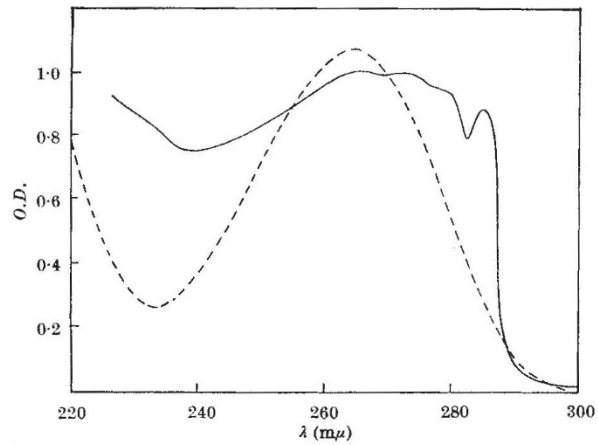

Fig. 1. Ultra-violet absorption spectrum of thymine frozen in ice at liquid nitrogen temperature (solid line) compared with a sample in liquid aqueous solution (dashed line)

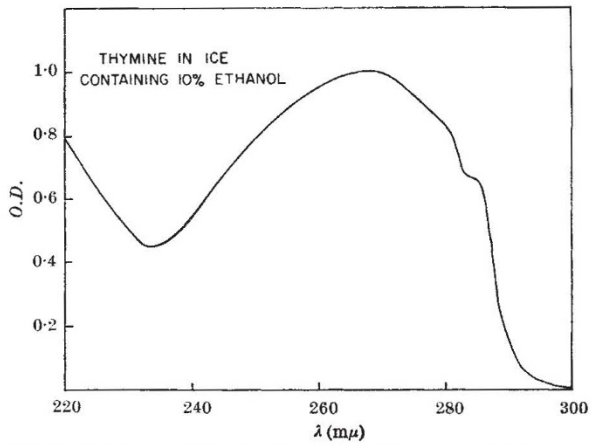

Fig. 2. Spectrum of thymine frozen in a 10 per cent (v/v) aqueous ethanol solution

thymine is also shown for comparison. The change in absorption is quite pronounced. In a frozen 10 per cent (v/v) solution of ethanol (Fig. 2) the thymine spectrum is more nearly like that in the liquid solution. The spectra of frozen solutions of thymidylic acid (5′), uracil, uridine and uridylic acid (5′) were also measured. Although they all gave broadened spectra in the frozen solutions relative to their liquid solution spectra, none showed the striking differences found in thymine.

The spectrum of the thymine in ice at liquid nitrogen temperature is essentially identical to that found by Sinsheimer *et al.*[4] for dry, sublimed films of thymine at this temperature. The four maxima seen in the ice spectrum agree with those in the dry film to ± 1 mμ. This is strong evidence that aggregates of thymine occur in the ice similar to those present in the sublimed film. Furthermore, the fact that alcohol partially restores the liquid solution spectrum strengthens the conclusion that the frozen solution spectrum indicates interaction between thymine molecules. Apparently, for thymine in ethanol or for thymidylic acid, uracil, uridine and uridylic acid, the solute–solute attraction is less (or the solute–solvent repulsion is less) than for thymine in water.

These conclusions are in accordance with Wang's photochemical experiments and his interpretation of them in terms of aggregation. However, the spectral evidence is a more direct measure of this aggregation.

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PHYSIOLOGY

Heparin-induced Hypocalcaemia in Rabbits

IT has been reported[1] that heparin contains certain mineral substances of the alkaline earth series, among them calcium. The amounts of these minerals vary with the batch of heparin and the quantities of these impurities are sufficient to cause error in the analysis of plasma calcium, barium and strontium if heparin is added *in vitro* to blood samples. We have found a much more serious