The Infrared Spectrum of P_2I_4

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THE existence of a *gauche* conformer of P_2I_4 was originally postulated on the basis of dipole moment[1] and infrared spectroscopic[2,3] studies of CS_2 solutions of this compound. However, in a more recent and extensive infrared and Raman study,[4] it was concluded that the *trans* conformation of solid P_2I_4 persists in a variety of solvents which includes CS_2. Accepting this conclusion there still remains the question as to why CS_2 solutions of P_2I_4 exhibit more than two infrared frequencies in P–I stretching region[2,3] [only 2 infrared-active P–I stretching modes (A_u + B_u) are predicted for *trans*-P_2I_4]. Specifically we refer to frequencies at 303vw, 313m, 328s, 332s, and 355w. We believe that this apparent anomaly can be explained in terms of the equilibrium

$$3P_2I_4 \rightleftharpoons 4PI_3 + \tfrac{1}{2}P_4$$

Thus, the 303 and 328 cm.$^{-1}$ absorptions can be assigned to PI_3,* and the 313 and 332 cm.$^{-1}$ absorptions to *trans*-P_2I_4. The 355 cm.$^{-1}$ band can be assigned to a combination, overtone, or impurity as pointed out previously.[2] The existence of the above equilibrium is strongly supported by the behaviour of ^{31}P n.m.r. spectra of CS_2 solutions of freshly recrystallized P_2I_4. Within five minutes of dissolving the P_2I_4, the ^{31}P n.m.r. spectrum showed the presence of small amounts of PI_3 (−170 p.p.m.) and P_4 (460 p.p.m.) in the predicted phosphorus atom ratio of 2 : 1. Moreover, when twice-recrystallized P_2I_4 was dissolved in CS_2, cyclohexane, or carbon tetrachloride, which were rigorously protected from moisture and oxygen, the characteristic u.v. absorption spectrum of PI_3 was evident upon complete dissolution. Also, solutions of P_2I_4 and PI_3 are unstable with respect to formation of colloidal material. This probably results from the catalytic conversion[5] of the white phosphorus by iodine into red phosphorus and/or phosphorus–iodine polymers, which could account for the absence of a strong band[6] for P_4 at 461 cm.$^{-1}$ This band is rather broad and, if present, could be masked by the strong broad CS_2 band at 400 cm.$^{-1}$. Additional evidence illustrating lability and complexity of the phosphorus–iodine system will be presented separately.[7]

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* Previous values for the i.r.-active P–I stretching modes of PI_3 in CS_2 solution are 305w and 327s (ref. 2).

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