Halogen and Interhalogen Compounds of Pyridazine

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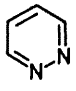
Summary Iodine, iodine monochloride, and bromine react with pyridazine to form compounds of different stoicheiometries: the iodine compound shows remarkable stability.

IT has recently been reported that pyridazine (I) and iodine react in several different solvents to form a compound of variable composition (empirical formula $C_4H_4N_2$, 1—1·4 I_2).[1] In view of the interesting electrical properties of this material we report here our somewhat different findings, made during a general investigation of the interaction of (I) with halogens and interhalogens.



(I)

$3(C_4H_4N_2),2I_2$ (II)
$C_4H_4N_2, 2ICl$ (III)
$2(C_4H_4N_2),Br_2$ (IV)

When solutions of (I) and iodine in carbon tetrachloride were mixed at room temperature, a sticky black precipitate formed immediately.† On being triturated with methanol, this material formed a sharp-melting (240—242°) black powder, which gave analytical figures (C, H, N, I) consistent with the empirical formula (II). The same compound was obtained using a range of mole ratios for the reactants. We suggest that the reported[1] variable composition stems from the incomplete removal of free iodine. (II) is remarkably stable, although some decomposition was reflected in the m.p. and in the elemental analysis after three months storage. The freshly prepared material is insoluble in benzene and carbon tetrachloride but dissolves with dissociation in dimethylformamide and tetrahydrofuran.

Iodine monochloride reacted directly with (I) in CCl_4 to give an orange solid (m.p. 54—55°) for which analysis (ICl) indicates the stoicheiometry (III).‡ (Pyrimidine forms an analogous 1:2 adduct which on the basis of i.r. data is not ionic).[3] The contrasting stability of the pyridazine–iodine compound (II) is strikingly demonstrated by the fact that (III), on standing at room temperature, decomposes quite rapidly to form (II).

The reaction of (I) with bromine in CCl_4 gave a dark brown solid from which an excess of bromine was extracted by washing with methanol: analysis (Br) of the orange-brown residue (m.p. 75—77°) indicates the stoicheiometry (IV).

This compound is less stable than (III) and, as in the case of 1,3,5-triazine perbromide,[4] the decomposition appears to involve nuclear bromination: this is being further investigated.

The stoicheiometric composition of (II) is difficult to reconcile with the simple polymeric structure suggested by Hoare and Pratt,[1] but could be accounted for by, for example, a 1:1 mixture of the closely related species $[(C_4H_4N_2)_2I]^+ I^-$ and *catena*-$[C_4H_4N_2I]^+ I^-$.§

(*Received, December 8th,* 1969; *Com.* 1858.)

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† The rapid appearance of turbidity when dilute solutions of iodine and (I) in cyclohexane are mixed has been reported previously (ref. 2).

‡ The instability of (III) and (IV) necessitated oxygen-flask combustion immediately after isolation. We thank Mr. I. Blackwell (Shell Research Ltd., Sittingbourne) for carrying out these analyses.

§ We thank Dr. J. M. Pratt for this suggestion.

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[3] H. Bredereck, R. Gompper, and H. Herlinger, *Chem. Ber.*, 1958, **91**, 2832.
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