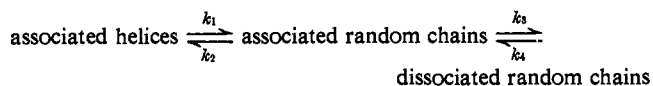


original value also with no further change with time. These viscometric experiments suggest that, once the polymer has undergone the change associated with this loss in viscosity, this conversion cannot be reversed. The optical rotation experiments, on the other hand, suggest that the change in structure associated with them is essentially reversible. Thus there appear to be two transitions, the first responsible for a reversible change in conformation, the second for a further and irreversible change in hydrodynamic shape.

This mechanism is similar to that suggested for collagen denaturation. As a result of an interesting series of light scattering studies on collagen, Engel suggested<sup>25</sup> that collagen first unfolds to associated random chains and then dissociates (in the random chain form)



Applying such an interpretation to our work with poly(-Gly-Pro-Gly-),  $k_2$  would be obtained from the optical rotation kinetics described above. The absence of viscosity increase after quenching suggests that  $k_4$  is very small.  $k_3$ , associated with the hydrodynamic change, must be highly temperature dependent. None of the measurements reported here gives the value of  $k_1$  or  $k_3$ . Added support for this suggestion is given by the slow and incomplete refolding of poly(-Gly-Pro-Gly-) in acetic acid after complete dissociation and unfolding in concentrated formic acid.

### Conclusions

As a result of these studies, it appears that the repeating sequence Gly-Pro-Gly polymer serves as a useful, but not complete, model for collagen structure and association. The chain interaction revealed by the physical-chemical measurements suggests that the

(25) J. Engel, *Arch. Biochem. Biophys.*, **97**, 150 (1962).

parallel is perhaps closest between this polymer and the  $\alpha$  strands of collagen which renature into a more randomly associated structure containing approximately 60% of the initial helical character of collagen.<sup>24</sup> It has been suggested by Piez and Carrillo<sup>24</sup> that in the case of  $\alpha$  strands, re-formation is initially between two strands with pyrrolidine-rich sections of one chain acting as a guide for pyrrolidine-poor sections of the adjacent chain. From the work reported here it appears that adjacent proline residues are not required for helix formation in structures stabilized by interchain interaction, but may be important in the more specific ordering of collagen. Further studies of interactions of pyrrolidine-rich with pyrrolidine-poor organized sequence polymers may increase understanding in this area.

The interesting lack of ordered structure in the Gly-Pro-Ala polymer, assuming little or no racemization has occurred,<sup>2</sup> can be attributed either to an increased stability of the random chain alanyl residue compared to the glycyl residue in water or to a decreased stability of the alanyl residue in the corresponding polyproline II type helix. In view of the lack of knowledge of solvation effects of this kind, it is difficult to make a definite choice between the two possibilities. However, with the knowledge that model studies show that alanyl residues can fit into the polyproline II or collagen helix with little hindrance and that alanine shows little hydrophobic character,<sup>26</sup> it appears that solvation of the random chain may be a critical factor in determining the resultant structures of the polymers.

**Acknowledgments.** We thank Dr. L. Bethune for help and advice in the ultracentrifugation work, Dr. C. Cohen for valuable assistance in the X-ray studies, and Dr. E. R. Simons for critical and helpful comments during the writing of this manuscript.

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## Communications to the Editor

### Tetraphosphorus Hexaoxide-Diborane

Sir:

In a recent communication, Riess and Van Wazer<sup>1</sup> reported that  $P_4O_6$  will replace one CO from  $Ni(CO)_4$  to give  $Ni(CO)_3P_4O_6$ ; they also indicated that  $P_4O_6$  can behave as a polydentate ligand. In order to determine how diborane is cleaved by  $P_4O_6$ , we have recently examined the reaction of  $P_4O_6$  and  $B_2H_6$  and have isolated the solid  $P_4O_6 \cdot B_2H_6$ . Two possible structures for this solid might be suggested. The first one, arising from nonsymmetrical cleavage of the diborane molecule<sup>2</sup> and utilizing the polydentate characteristics of

(1) J. G. Riess and J. R. Van Wazer, *J. Am. Chem. Soc.*, **87**, 5506 (1965).

(2) R. W. Parry, D. R. Schultz, S. G. Shore, and P. R. Girardot, *ibid.*, **80**, 1 (1958); G. E. McAchran and S. G. Shore, *Inorg. Chem.*, **4**, 125 (1965); S. G. Shore, C. W. Hickam, Jr., and D. Cowles, *J. Am. Chem. Soc.*, **87**, 2755 (1965); O. T. Beachley, *Inorg. Chem.*, **4**, 1823 (1965).

$P_4O_6$ , would be represented as  $[H_2BP_4O_6^+][BH_4^-]$ . The second structure, arising from symmetrical cleavage of diborane, would involve direct coordination of  $BH_3$  groups to two of the four phosphorus atoms in  $P_4O_6$ . The latter structure is somewhat analogous to the structure of  $P_4O_{10}$  and suggests the analogy between  $BH_3$  and O used earlier to interpret the reaction of  $F_3PBH_3$  with ammonia.<sup>3</sup> The  $^1H$  nmr spectrum of the compound offers strong support for the second formulation,  $H_3BP_4O_6BH_3$ , indicating symmetrical cleavage of the diborane molecule by  $P_4O_6$ .

All reactions were carried out in a standard high-vacuum system. Liquid  $P_4O_6$ , contained in an evacuated tube attached to the vacuum line, was exposed for several hours at room temperature to gaseous diborane

(3) G. Kodama and R. W. Parry, *J. Inorg. Nucl. Chem.*, **17**, 125 (1961).

at an initial pressure of about 250 mm. White, well-defined crystals of  $P_4O_6 \cdot B_2H_6$  formed slowly. Fractionation of volatiles gave unreacted  $P_4O_6$  and/or  $B_2H_6$  but no other materials. In eight runs the initial ratio of  $B_2H_6/P_4O_6$  was varied from 0.35 to 5.0, but the ratio of  $B_2H_6$  reacting with  $P_4O_6$  was  $1.00 \pm 0.03$ . The X-ray powder pattern using Fe  $K\alpha$  radiation was recorded with a camera 114.6 mm in diameter. The  $d$  values (uncorrected for film shrinkage) are given in Angstrom units: 8.8 (m), 8.2 (m), 7.1 (vs), 6.55 (vw), 6.19 (w), 5.34 (m, diffuse), 4.79 (s), 4.36 (w), 3.94 (w), 3.65 (m), 3.37 (w), 3.11 (m), 2.94 (w), 2.81 (vw), 2.70 (vw), 2.59 (vw), 2.50 (vw), 2.426 (vw), 2.362 (w). The compound is very hygroscopic and hydrolyzes readily, usually catching fire when brought in contact with a drop of water.

The  $^1H$  nmr spectrum of a methylene chloride solution of the compound was obtained at  $29^\circ$ . Four equally spaced broad peaks due to three protons attached to boron were observed. The value of  $J_{B-H}$  of 100 cps is clearly inconsistent with a  $BH_4^-$  ion (78 cps),<sup>4a</sup> but is close to the values for  $BH_3$  groups bound to phosphorus ligands.<sup>4b</sup> Our observation that treatment of the methylene chloride solution of the compound with anhydrous HCl did not yield  $B_2H_6$  and  $H_2$  gas also confirms the absence of  $BH_4^-$  in the compound.

(4) (a) T. P. Onak, H. Landesman, R. E. Williams, and J. Shapiro, *J. Phys. Chem.*, **63**, 1533 (1959); (b) C. W. Heitsch, *Inorg. Chem.*, **4**, 1019 (1965); J. G. Verkade, R. W. King, and C. W. Heitsch, *ibid.*, **3**, 884 (1964).

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### Isomorphous Complex Fluorides of Tri-, Tetra-, and Pentavalent Uranium<sup>1</sup>

Sir:

We wish to report the first preparation of complex fluorides formed between  $UF_3$  and the alkali fluorides KF, RbF, and CsF. The  $3KF \cdot UF_3$  crystalline phases are of face-centered cubic symmetry and isomorphous with the  $3KF \cdot UF_4$  and  $3KF \cdot UF_5$  analogs with nearly identical cell parameters. The significance of this finding is that the oxidation state of uranium in some cases can be varied for oxidation numbers III to V (and perhaps VI) within pure single-phase, crystalline compounds without affecting the crystal symmetry.

Recently many new compounds were found to be formed between the alkali fluorides and the fluorides of pentavalent actinides, protactinium,<sup>2-5</sup> uranium,<sup>6-8</sup>

neptunium,<sup>9</sup> and plutonium.<sup>10</sup> The crystalline compounds formed between alkali fluorides and  $UF_4$  have also been studied extensively.<sup>11,12</sup> However, except for  $NaF \cdot UF_3$ ,<sup>13a</sup> no compounds between  $UF_3$  and alkali fluoride were known.

Ruedorff and Leutner<sup>6</sup> reported that the X-ray powder diffraction photographs of  $3NaF \cdot UF_4$  and  $3NaF \cdot UF_5$  were almost identical and that the unit cell of  $3NaF \cdot UF_5$  is but slightly larger than  $3NaF \cdot UF_4$ . On comparing our crystallographic data for U(IV) and U(V) analogs, we noted that the pentavalent uranium phases,  $3KF \cdot UF_5$ ,  $3RbF \cdot UF_5$ , and  $3CsF \cdot UF_5$ , were apparently isostructural with their tetravalent analogs,  $3KF \cdot UF_4$ ,  $3RbF \cdot UF_4$ , and  $3CsF \cdot UF_4$ , and were of nearly identical unit cell size. To see whether this was a general phenomenon, we synthesized the previously unknown U(III) analogs.

The several  $UF_3$ -alkali fluoride compounds were synthesized under anhydrous conditions by the reaction of uranium metal, alkali fluoride, and  $UF_4$  at temperatures of approximately  $1000^\circ$ . A double-chambered reactor was used with one chamber mounted over the other and separated by a ball valve. Each chamber could be evacuated independently and refilled with inert gas. The upper chamber held uranium metal. Melting, purification, and reduction of the uranium(IV) fluoride took place in the bottom nickel chamber. Stoichiometric amounts of  $UF_4$  and the alkali fluoride were first loaded into the lower chamber and melted with  $NH_4F \cdot HF$  in a dry helium atmosphere. After volatile phases were removed by distillation, the ball valve separating the two chambers was opened and the uranium metal suspended in the melt. The melted reaction mixture was stirred continuously with helium gas. Freshly prepared specimens of the complex fluorides of  $UF_3$  were examined immediately after preparation, using polarizing microscopic methods, X-ray diffraction, and absorption spectrum (400 to  $1500 \mu\mu$ ) measurements. The results of the optical analyses indicated that tetravalent uranium was either absent or of lower concentration than can be detected by this method. The U(III) compounds are readily oxidized to U(IV) compounds and must be protected from moist air.

The current investigation has demonstrated that reaction of  $UF_3$  with the alkali fluorides yields many complex compounds of U(III). Those found have  $MF:UF_3$  ratios of 1:1 for  $M = Na^+$ ,  $K^+$ ,  $Rb^+$ , or  $Cs^+$ ; 2:1 (except for  $Na^+$ ); and 3:1 (except for  $Na^+$ ). No complex compounds of  $UF_3$  are formed with  $LiF$ .<sup>13b</sup> Results obtained with  $3KF \cdot UF_3$ ,  $3KF \cdot UF_4$ , and  $3KF \cdot UF_5$  are listed in Table I; other results will be reported when the investigation is completed. On the basis of these findings, isomorphous complex fluorides may therefore be anticipated in the 4+ and 5+ states of Pa, in the 3+, 4+, and 5+ oxidation states of Pu and Np, as well as for the heavier actinides.

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