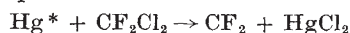


Fig. 3. Ratio of secondary to primary products against time. ▲,  $\text{CF}_2\text{Cl}_2$  photolysis; □,  $\text{C}_2\text{F}_4\text{Cl}_2$  photolysis

amounts must be added before any effect is perceptible, and these amounts are more than three times the concentration of 1,2-dichlorotetrafluoro ethane usually observed in the mercury photosensitized decomposition of  $\text{CF}_2\text{Cl}_2$ . In Fig. 2B, it is shown that the ratio of 1,3-dichlorohexafluoro propane to 1,2-dichlorotetrafluoro ethane actually decreases when extra amounts of 1,2-dichlorotetrafluoro ethane are added.

Finally, in Fig. 3, the ratios  $[\text{C}_3\text{F}_6\text{Cl}_2]/[\text{C}_2\text{F}_4\text{Cl}_2]$  and  $[\text{C}_6\text{F}_{12}\text{Cl}_2]/[\text{C}_4\text{F}_8\text{Cl}_2]$  are plotted against irradiation time, and it can be seen that the induction period, clearly visible for  $\text{C}_6\text{F}_{12}\text{Cl}_2$  formation, is absent for  $\text{C}_3\text{F}_6\text{Cl}_2$  formation.

It therefore appears probable that 1,3-dichlorohexafluoro propane, formed in the mercury photosensitized decomposition of  $\text{CF}_2\text{Cl}_2$ , arises by the interaction of primary radicals and does not involve a second excited mercury atom colliding with initially formed products. This does not rule out the possibility that  $\text{CF}_2$  is formed in a single step:



but this appears unlikely in view of the appearance of 1,3-dichlorohexafluoro propane in the photolysis products of 1,3-dichlorotetrafluoro acetone, where such a process cannot occur. Further, the ratio  $[\text{C}_3\text{F}_6\text{Cl}_2]/[\text{C}_2\text{F}_4\text{Cl}_2]$  has the same value (0.04) in both systems.

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<sup>1</sup> Bowles, R., Derbyshire, H., Majer, J. R., and Robb, J. C., *Nature*, **185**, 683 (1960).

<sup>2</sup> Bowles, R., Majer, J. R., and Robb, J. C., *Trans. Faraday Soc.*, **58**, 1541 (1962).

<sup>3</sup> Gunning, H. E. (private communication).

<sup>4</sup> Mastrangelo, S. V. R., *J. Amer. Chem. Soc.*, **84**, 1122 (1962).

### Reaction of Tetrafluoroethylene with Pentacyanocobaltate Ions and with Reduced Vitamin B<sub>12</sub>

We have previously shown<sup>1</sup> that a cobalt-carbon bond can be formed in aqueous solution by the interaction of acetylene with the pentacyanocobaltate(II) anion, while recently<sup>2</sup> benzyl and alkyl halides have been similarly shown to give a Co-C bond.

We have found that tetrafluoroethylene is readily absorbed at atmospheric pressure by aqueous solutions of the hydridopentacyano-cobaltate(III) ion,  $[\text{HCo}(\text{CN})_5]^{3-}$ , as well as by the pentacyano-cobalt(II) ion. The well-crystallized salts analyse correctly for  $\text{K}_3[(\text{CN})_5\text{CoCF}_2\text{CF}_2\text{H}]$  (A) [for example, Found: C, 20.8; N, 17.4; F, 18.0; Co, 14.2; K, 29.1. Required: C, 20.6; N, 17.2; F, 18.7; Co,

14.5; K, 28.8 per cent] and  $\text{K}_6[(\text{CN})_5\text{Co}(\text{CF}_2)_2\text{Co}(\text{CN})_5] \cdot 2\text{H}_2\text{O}$  (B); the salts are stable in air and thermally up to about 300° C.

The nuclear magnetic resonance spectra support these formulations. Thus the  $\text{H}^1$  spectrum for (A) is a triple triplet while the fluorine-19 resonance of the  $\beta$ - $\text{CF}_2$  is split into a doublet by the proton and further into a triplet by the  $\alpha$ - $\text{CF}_2$  group; all these lines are sharp and well resolved. In contrast the  $\alpha$ - $\text{CF}_2$  resonance is a broad single line; the broadening is presumably due to incomplete averaging of the spin coupling with the cobalt-59 nucleus produced by quadrupole relaxation of this nucleus. For the same reason, the fluorine-19 spectrum of (B) is only a broad single line.

The interaction of  $\text{C}_2\text{F}_4$  with the hydrido-species is interesting in that it can provide a probe for the detection of transition metal to hydrogen bonds in aqueous media where detection by the high-field proton resonance line is difficult. Thus we have failed to observe such a high-field line in saturated aqueous solutions of the grey-green reduction product of cyanocobalamin. A search was made at 40 Mc/s several years ago<sup>3</sup>, at the time of our first investigations of the hydridic nature of lower oxidation states, and, more recently, at 56.45 Mc/s. However, the reduced species immediately absorbs tetrafluoroethylene, and the resulting red product—dissolved in chloroform-phenol, in which it is much more soluble than in water—shows a  $^{19}\text{F}$  resonance spectrum in which there is a doublet of splitting similar to that observed for the  $-\text{CF}_2\text{H}$  group of (A). While this suggests that reduced cyanocobalamin ( $B_{12a}$ ) is a hydrido-species, we cannot rigorously exclude the possibility that it is a cobalt(I) species as recently suggested<sup>4</sup>, since such a cobalt(I) species could react with  $\text{C}_2\text{F}_4$  with subsequent hydrogen transfer from the solvent.

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<sup>1</sup> Griffith, W. P., and Wilkinson, G., *J. Chem. Soc.*, 1629 (1959).

<sup>2</sup> Halpern, J., and Maher, J. P., *J. Amer. Chem. Soc.*, **86**, 2311 (1964).

<sup>3</sup> Griffith, W. P., Pratt, L., and Wilkinson, G., *Nature*, **182**, 466 (1958); we thank Dr. E. Lester Smith of the Glaxo Laboratories for a gift of the cyanocobalamin used at that time.

<sup>4</sup> Collat, J. W., and Abbot, J. C., *J. Amer. Chem. Soc.*, **86**, 2308 (1964).

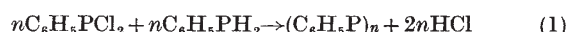
### Molecular Structure of Phosphobenzene

THE following polyphosphines of formula  $(\text{C}_6\text{H}_5\text{P})_n$  have been reported in the literature: (A) m.p. 149°–150° (refs. 1–9); (B) m.p. 190° (refs. 2 and 3); (C) m.p. 252°–256° (ref. 3); (D) m.p. 260°–285° (ref. 8). Compounds C and D are insoluble in organic solvents and have, presumably, a polymeric structure. The molecular weights of A and B in solution have not been established definitely. Several isopiestic, ebullioscopic and cryoscopic methods have been used by various workers and the following identities have been proposed.  $A = B = \text{I}^2$ ;  $A = \text{I}$ ,  $B = \text{II}^2$ ;  $A = B = \text{II}^2$ ;  $A = \text{II}^{4,5,9}$ . Recently it has also



been shown<sup>8</sup> that compounds A and B are tetraphenyl-cyclo-tetraphosphines (II) which differ in both the dissolved and solid states and are stereoconformers.

We have prepared compound A by the reaction of phenylphosphonous dichloride and phenyl phosphine<sup>1,3-5</sup> (equation 1):



and by a new method which involves the heating of phenylphosphine and a stoichiometric amount of phenyl-