Here $E_{1/2}$ is E when $t = \tau/2$. A plot of E vs. log $t/(\tau - t)$ for a chronopotentiogram such as those in Fig. 1 gave a straight line with a slope of 0.063 volt. This compares favorably with the theoretical value of 0.059 volt.

The analysis of chronopotentiograms for adsorbed reactants by means of plots of E vs. log $t/(\tau - t)$ is of particular value in cases where more than one form of the adsorbed reactant is possible. For example, cathodic chronopotentiograms for iodine adsorbed on a platinum electrode would obey the equation (3) if the iodine were present on the electrode as iodine molecules

$$E = E' - \frac{0.059}{2} \log \frac{t^2}{\tau - t} \qquad (3)$$

But the chronopotentiograms would obey equation 2 if the adsorbed iodine were present as iodine atoms. Experimentally, chronopotentiograms for adsorbed iodine give straight lines with slopes near the theoretical value for plots according to equation 2 but not with equation 3. Thus it may be concluded tentatively that iodine adsorbed on platinum electrodes is present as atomic iodine.

The extension of this technique should provide much useful information on the nature of reactants adsorbed on electrodes. It may even be possible to determine directly the contribution of adsorbed reactants to exchange currents measured in solutions of the reactants by performing rapid galvanostatic experiments with electrodes containing adsorbed reactants in separate, reactant-free solutions.

Further studies of this technique and its application to the examination of adsorbed Fe(II), Fe(III), I_2 and I^- are in progress and will be reported later.

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BICOÖRDINATE PHOSPHORUS: BASE-PCF₃ ADDUCTS[1]

Sir:

The cyclopolyphosphines $(PCF_3)_4$ and $(PCF_3)_5$[2] react easily and reversibly with trimethylphosphine or trimethylamine to form $(CH_3)_3PPCF_3$ or $(CH)_3NPCF_3$. These evidently employ the PCF_3 unit in the same role as the $=O$, $=NH$, and $=CH_2$ units in the system of analogous R_3P and R_3N compounds discussed by Wittig and Rieber,[3] with the interesting difference that the PCF_3 complexes at room temperature easily dissociate to the tertiary base and $(PCF_3)_{4 \text{ and } 5}$, thus offering a way to improve the chemical availability of the PCF_3 unit.

(1) This research was supported by the United States Air Force under successive subcontracts of Prime Contracts AF 33(616)-5435 and 6913, monitored by the Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.
(2) W. Mahler and A. B. Burg, *J. Am. Chem. Soc.*, **80**, 6161 (1958).
(3) G. Wittig and M. Rieber, *Ann.*, **562**, 181 (1949).

It is also interesting that the R_3PPCF_3 compounds are isomers of the diphosphines R_2PPR_2, and represent the first authentic examples of bicoördinate phosphorus in neutral molecules.

Formation of the Trimethylphosphine Complex. —When 0.990 mmole of pure $(PCF_3)_4$ and 4.22 mmoles of $(CH_3)_3P$ in a closed tube were warmed slowly from $-196°$, combination occurred with transient appearance of a yellow liquid but ending with a white solid. Removal of the excess $(CH_3)_3P$ in high vacuum at $-45°$ left a residue containing $0.98(CH_3)_3P$ per PCF_3 unit. With the absorption of small measured portions of $(CH_3)_3P$ by $(PCF_3)_4$ (weighed sample) at constant temperature, constant pressure was observed except for a distinct rise as the combining ratio approached 1:1. With 114 mm. pressure of $(CH_3)_3P$ at $21°$ (1 hr.) the ratio in the solid phase reached $0.985(CH_3)_3P$ per PCF_3 unit, but decreased as a small side reaction fouled the mercury manometer.

The quickly reproducible dissociation pressures in the mid-range of composition were 12.0 mm. at $23°$ and 53 mm. at $43°$, determining the equation $\log P_{\text{mm}} = 11.276 - 3020/T$ (calcd. at $0°$, 1.69 mm.; obsd., 1.65). Defining K_{eq} as pressure in atm., this gives $\Delta F^0 = 13.82 - 0.0384 \ T$ for the dissociation of the solid complex to gaseous $(CH_3)_3P$ and the slightly volatile mixture of $(PCF_3)_4$ and $(PCF_3)_5$. Complete dissociation could be accomplished by high-vacuum fractional condensation, with all of the $(CH_3)_3P$ passing a trap at $-78°$. The trapped-out $(PCF_3)_n$ compounds showed an average vapor-phase mol. wt. of 414, indicating six $(PCF_3)_4$ (solid) to one $(PCF_3)_5$ (liquid) in the equilibrium mixture.

Catalytic Reorganization of the Polyphosphines. —The reversible formation of the PCF_3 complex implied that $(CH_3)_3P$ would catalyze the interconversion of $(PCF_3)_4$ and $(PCF_3)_5$. In fact, a one mole-per cent. addition of $(CH_3)_3P$ to pure $(PCF_3)_5$ caused a 50% conversion to $(PCF_3)_4$ during 48 hr. at $25°$. Such a conversion previously had required heating to $260°$.[2] In solution in ether or hexane, the catalyst converts the tetramer mostly to the pentamer, but without solvent, the tetramer (m.p. $66°$) is strongly favored by its solid-state energy. Higher $(PCF_3)_n$ polymers[2] are not found in the equilibrium mixtures.

A possibly similar catalysis occurred during a very fast 90% conversion of the triphosphine $H_2(PCF_3)_3$[2] to $(HPCF_3)_2$ and $(PCF_3)_n$ by a trace of $(CH_3)_3P$ at $25°$.

Solution Behavior of the Complex.—The nearly colorless solutions of $(PCF_3)_4$ in liquid $(CH_3)_3P$ show average mol. wt. values (by vapor-tension lowering at $0°$) at least 25% higher than expected for pure $(CH_3)_3PPCF_3$, even at PCF_3 concentrations as low as 0.7 mole per cent. Also, when the solutions are chilled suddenly to $-78°$ and the free $(CH_3)_3P$ is distilled off, the residues never contain more than $0.88 \ (CH_3)_3P$ per PCF_3 unit. Thus in solution with much excess $(CH_3)_3P$ the complex $(CH_3)_3PPCF_3$ is less completely formed than in the solid with little excess $(CH_3)_3P$. Apparently the conversion of solid tetramer (or liquid pentamer) to solid $(CH_3)_3PPCF_3$ is favored by the greater

solid-state energy of the relatively polar complex, but this advantage is lacking in solution, wherein some $(PCF_3)_4$ and $(PCF_3)_5$ can remain.

The actual presence of $(PCF_3)_4$ and $(PCF_3)_5$ in the $(CH_3)_3P$ solutions (or in CH_3CN or ether solutions containing excess trimethylphosphine) is confirmed by small peaks in the F^{19} n.m.r. spectra. The main pattern, demonstrating the $(CH_3)_3P$-PCF_3 structure in solution, is four equally intense peaks showing F^{19} interacting with the near and far P^{31} nuclei. The chemical shift (to low field relative to CF_3COOH) is -51.5 p.p.m., with coupling constants $J_{F-P} = 35$ cps. and $J_{F-P'} = 22$ cps. For $(n\text{-}C_4H_9)_3PPCF_3$ in excess $(n\text{-}C_4H_9)_3P$ the corresponding values are -53 ppm. with 39.5 and 20.5 cps. There is no evidence for $R_3P(PCF_3)_n$ chains even when a deficiency of base is used.

Other Adducts.—The liquid product empirically formulated as $(CH_3)_3NPCF_3$ is made in the same manner as $(CH_3)_3PPCF_3$ but has not been studied so fully. With excess trimethylamine it forms two liquid phases, the denser of which has the more intense orange color. Its role in the effective amine-catalysis of $(PCF_3)_n$ conversion doubtless is the same as that of the corresponding $(CH_3)_3P$ complex.

Of similar interest is a reaction between P_2-$(CF_3)_4$ and $(CH_3)_3P$, producing a brown oily adduct which reacts with HCl to form $(CF_3)_2PH$, as P_2-$(CF_3)_4$ itself does not. The implied P–P bond scission to form $P(CF_3)_2$ ionic units is being studied further.

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THE ISOTOPIC SEPARATION OF CARBON BY ION EXCHANGE[1]

Sir:

An efficient and rapid process for the fractionation of the isotopes of carbon offers promise of benefits to several areas of research. An increase in the C^{14}/C^{12} ratio would permit extension of the presently available range of carbon dating experiments. High purity C^{12} targets have a variety of uses in nuclear physics, among them being, *e.g.*, the accurate determination of (p,n) thresholds in nuclear reactions using the C^{12} as a backing. Synthesis of compounds highly enriched in C^{13} would permit increased utilization of nuclear magnetic resonance measurements.

The feasibility of using ion exchange displacement chromatography to effect resolution of C^{12}–C^{14} mixtures has been investigated. Experiments concerned with isotope separations using ion exchange techniques have been reported previously for several other elements (see *e.g.*, references 2 and 3).
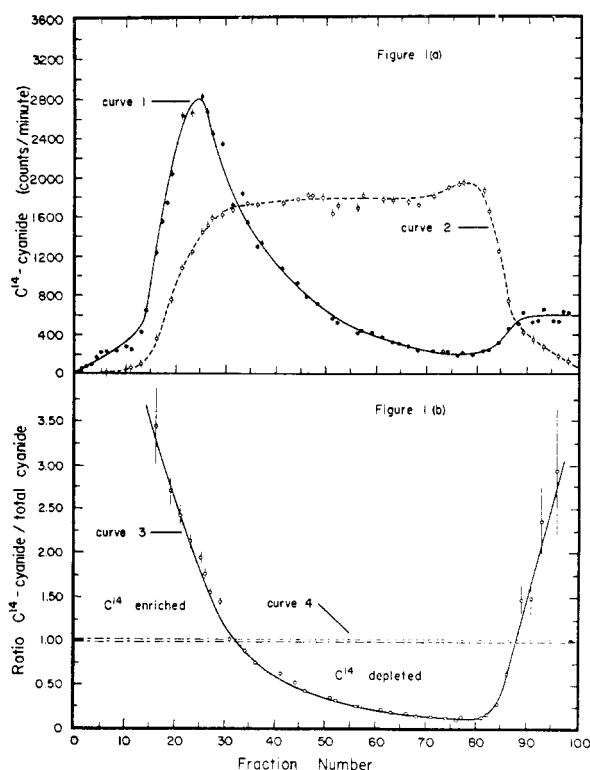
Fig. 1.—Experimental results showing C^{14} enrichment at the band front: curves 1 and 2 in Fig. 1a represent C^{14} after and before the run, respectively. Curve 3 in Fig. 1b illustrates the ratio of C^{14} to total cyanide. The width of curve 4, indicating the pre-run ratio, indicates the experimental error.

The present work involves the use of the system hydroxide–hydrogen cyanide–hydrogen chloride on the strongly basic resin, Dowex 2. Preliminary investigation indicated that self-sharpening boundaries are obtained at both ends of the cyanide band, permitting it to be passed through an extended length of resin bed without appreciable dispersion. It was found that a reaction, resulting in evolution of an insoluble gas, takes place at the rear (HCN–HCl) boundary. Gas evolution is minimized by decrease in solute concentrations and by operation under pressures of 12 to 15 p.s.i. in excess of atmospheric. In spite of these precautions, however, an appreciable loss of cyanide occurs during an extended run.

The cyanide form of Dowex 2 apparently is less stable than the chloride or hydroxide forms. This is indicated by discoloration which becomes progressively greater as the resin remains in the cyanide form. Although decomposition occurs, loss in resin capacity under the conditions of these experiments is negligible.

Figure 1 shows the results of the run. Curve 1 in Fig. 1a represents C^{14}-cyanide after the run. The error bars indicate standard deviation. Curve 2 represents C^{14}-cyanide to be expected if isotope

(2) S. Forberg, W. Barnevik, I. Fogelstrom-Fineman, T. Westermark and H. v. Ubisch, "Proceedings of the International Symposium on Isotope Separation," North-Holland Publishing Co., Amsterdam, Netherlands, 1958, p. 243.

(3) F. H. Spedding, J. E. Powell and H. J. Svec, *J. Am. Chem. Soc.*, **77**, 6125 (1955).