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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DEPARTMENT OF CHEMISTRY   ANTON B. BURG
UNIVERSITY OF SOUTHERN CALIFORNIA
LOS ANGELES 7, CALIFORNIA   WALTER MAHLER
                RECEIVED MARCH 16, 1961

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).
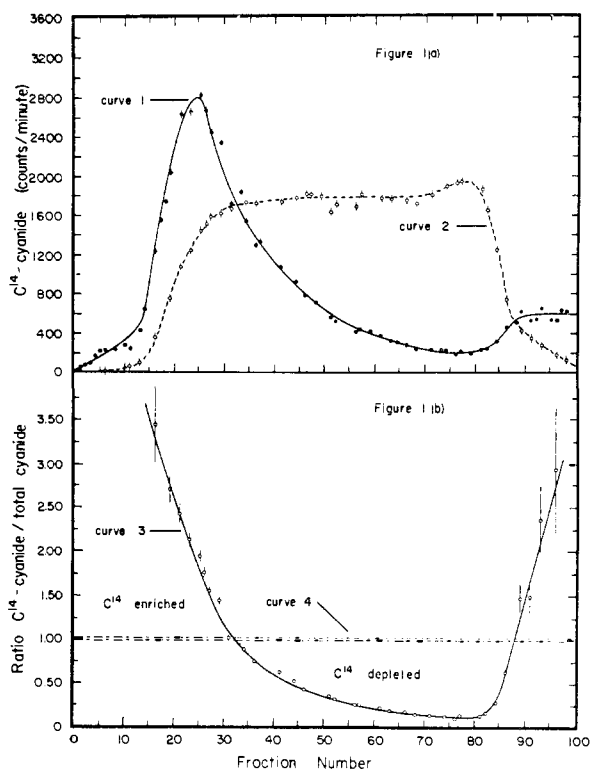
Fig. 1.—Experimental results showing C^{14} enrichment at the band front: curves 1 and 2 in Fig. 1a represent C^{14} after and before the run, respectively. Curve 3 in Fig. 1b illustrates the ratio of C^{14} to total cyanide. The width of curve 4, indicating the pre-run ratio, indicates the experimental 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).

separation had not occurred. It is the specific activity originally in the HCN solution multiplied by the amount of total cyanide in each fraction after the run and is therefore identical in shape with the total cyanide band contour. The constant errors shown are those involved in fraction collection. Figure 1b illustrates the ratio of C^{14} to total cyanide in each fraction with the pie-run ratio normalized to 1.00.

As can be seen from the figure, C^{14}-enriched cyanide appeared at the front of the band, the enrichment factor being of the order of 3.5. Toward the rear of the band, C^{14} was depleted by a factor of about 10. There was slight tailing of total cyanide at the band rear. It is evident that areas under curves 1 and 2 in Fig. 1a are not equal. This definitely indicates that the ratio of C^{14}/C^{12} in the cyanide lost in the run is greater than in the cyanide originally utilized in the run. It further indicates that the successful solution of the problem of cyanide depletion in the band will lead to an even more successful isotope separation.

The degree of C^{14} enrichment as a result of this relatively short experiment demonstrates the practicality of this approach to carbon isotope fractionation. We are presently investigating the $C^{12}-C^{13}$ separation which must have occurred in this experiment and the cyanide and resin decomposition described above and expect to make a detailed report at a later date.

We wish to thank the University of Florida and Dr. William Dunavant for the use of the Tri-Carb Liquid Scintillation Spectrometer in determining C^{14}-cyanide.

DEPARTMENT OF CHEMISTRY   CHARLES N. DAVIDSON
FLORIDA STATE UNIVERSITY   CHARLES K. MANN
TALLAHASSEE, FLORIDA   RAYMOND K. SHELINE

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RUTHENIUM HEXAFLUORIDE[1]

Sir:

The preparation of ruthenium hexafluoride, which we now report, brings to three the number of volatile hexafluorides known for the second transition group elements. Molybdenum hexafluoride has been known for some time and technetium hexafluoride recently has been prepared.[2] In contrast, hexafluorides are known for all the third transition group elements that might be expected to form them, namely, tungsten through platinum.[3] Prior to the present work the only known binary compounds of ruthenium and fluorine were the trifluoride[4] and the pentafluoride.[5,6]

This first preparation of ruthenium hexafluoride was made by heating ruthenium metal powder in a fluorine atmosphere at 300 mm. pressure. The

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.
(2) H. Selig, C. L. Chernick and J. G. Malm, J. Inorg. & Nuclear Chem., in press.
(3) M. Stacey, J. C. Tatlow and A. G. Sharpe, eds.. "Advances in Fluorine Chemistry," Vol. I, Chap. 2, Academic Press, Inc., New York, N. Y., 1960.
(4) E. E. Aynsley, R. D. Peacock and P. I. Robinson, Chem. & Ind., 1002 (1952).
(5) O. Ruff and E. Vidic, Z. anorg. Chem.. 72, 329 (1911).
(6) M. A. Hepworth, R. D. Peacock and P. L. Robinson, J. Chem. Soc., 1197 (1954).

reaction was carried out in a cylindrical quartz reactor (2.9 cm. o.d.) provided with an internal, cold finger that ended about 3 mm. above a shallow, annular, nickel trough which contained the ruthenium. This crucible was supported on three nickel legs and was heated with an induction coil until the ruthenium began to react. The burning metal sustained a reddish incandescence without further heating. The volatile reaction products were condensed rapidly by keeping the walls of the reactor and the cold finger at liquid nitrogen temperature. The main product was a dark-brown solid that collected on the cold finger and distilled under vacuum at room temperature. A light-green material, possibly RuF_5, that was not volatile at room temperature was obtained in lesser yield. The volatile product was handled and purified by techniques described elsewhere.[7] Ruthenium metal (1.0 g.) was converted into RuF_6 in 49% yield.

Vapor density determinations indicate a molecular formula RuF_6 (mol. wt. found, 214.3; calcd. for RuF_6, 215.1). Chemical analyses give the calculated value for fluoride, based on the formula RuF_6, but give results light in ruthenium possibly owing to volatilization of RuO_4 during analysis (Found: Ru, 39.3; F, 48.1. Calcd. for RuF_6: Ru, 43.0; F, 48.4). The solid is dark brown in color, has a transformation at 2.5°, and a fusion point at 54°. X-Ray powder patterns show each solid form to be isostructural with the corresponding form of the other transition metal hexafluorides.[8] The vapor is brownish-red in color, resembling bromine. Preliminary vapor pressure measurements with the solid give the results:

t, (°C.)	0.0	4.6	8.6	11.1	14.4	17.6
p, (mm.)	23	32	40	46	56	67

Ruthenium hexafluoride is the least volatile of the three known 4d transition series hexafluorides. Although the volatility of these hexafluorides decreases with increasing atomic number within each transition group, the 4d hexafluorides are less volatile than their 5d counterparts despite being 90 units lighter in molecular weight.

The infrared spectrum has characteristics similar to the other hexafluoride spectra. However, the band $\sigma_3 + \sigma_2$ is even more diffuse than that observed for osmium hexafluoride,[9] probably because of a stronger Jahn–Teller vibronic coupling in this transition series. The infrared active fundamental, σ_3, has been observed at 735 cm.$^{-1}$, compared with 745 cm.$^{-1}$ for TcF_6 and 742 cm.$^{-1}$ for MoF_6.

Although ruthenium hexafluoride is unstable, it can be stored for weeks at room temperature in a nickel can with only slight decomposition. Ruthenium hexafluoride attacks Pyrex glass rapidly at room temperature but is less reactive in quartz. At 200° RuF_6 is decomposed rapidly and completely into a non-volatile fluoride and fluorine. Measurement of the amount of fluorine produced per mole of RuF_6 decomposed indicates that the decomposition proceeds according to the reaction

$$RuF_6 \longrightarrow RuF_5 + \tfrac{1}{2}F_2$$
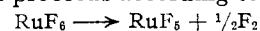
(7) B. Weinstock and J. G. Malm, J. Inorg. Nuclear Chem.. 2, 380 (1956).
(8) S. Siegel and D. Northrup, ANL Memorandum, March 24, 1961.
(9) B. Weinstock, H. H. Claassen and J. G. Malm, J. Chem. Phys., 32, 181 (1960).