data for pyrophosphate buffer. This would indicate that the rate of hydrolysis is influenced by the presence of different anions, which is contrary to the conclusion of Hoekstra[2] that, in the *p*H range below 9, the hydrolysis is independent of the type of buffer system used.

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A NEW SYNTHESIS OF BIS-TRIFLUOROMETHYL-PHOSPHINE, $(CF_3)_2PH$[1]

Sir:

Compounds of the type $(R_F)_2PH$ are important enough to the development of fluorocarbon–phosphorus chemistry to warrant a search for new synthetic methods offering greater convenience than the previously-reported catalytic hydrogenation processes.[2] We have found that the method whereby $P_2(CF_3)_4$ is produced by shaking $(CF_3)_2PI$ with mercury[3] becomes a good source of $(CF_3)_2PH$ if it is performed in the presence of a protic acid. Dry hydrogen chloride, technical phosphoric acid, and trifluoroacetic acid serve equally well as sources of protons, leading to 35% conversion of the $(CF_3)_2PI$ to $(CF_3)_2PH$. Even small proportions of water give minor yields of $(CF_3)_2PH$, probably through hydrolytic formation of hydrogen iodide. When hydrogen chloride is used, some $(CF_3)_2PCl$ is formed (but can be removed easily by treatment with water), and the remainder of the starting material is accounted for as $P_2(CF_3)_4$. When phosphoric acid is used the by-products include CF_3–P–O compounds, one of which has properties corresponding to the unstable $(CF_3)_2PHO$.

In each of these experiments, the $(CF_3)_2PI$ was distilled from the high-vacuum system into a flask containing a large proportion of acid and mercury. The flask was closed by a stopcock, disconnected from the vacuum system, and shaken while warming to room temperature, and for 15 minutes thereafter. The volatile products were brought into the vacuum system and separated by distillation methods. The $(CF_3)_2PH$ was identified by observation of a 760 mm. vapor tension at 2° (literature b.p. 1°) and a molecular-weight value of 170 (calcd., 170.00). The F^{19} nuclear magnetic resonance spectrum (obtained with the aid of Dr. Harden McConnell and Philip Bromberg at the California Institute of Technology) showed spin–spin interactions with one P^{31} and one H^1 nucleus to give a pair of doublets. The proton magnetic spectrum consisted of two groups of seven lines due to spin–spin splitting of one phosphorus nucleus and six equivalent fluorine nuclei. Quantitative data on the splittings and chemical shifts will be published elsewhere.

An insight into the course of the $(CF_3)_2PI$–Hg–acid reaction was obtained from an experiment in which 0.50 mmole of $(CF_3)_2PI$ was first shaken with mercury alone to give a 95% yield of $P_2(CF_3)_4$. Then the non-volatile residue was treated with dry hydrogen chloride, producing an amount of $(CF_3)_2PH$ which would account for the missing 5% of the original $(CF_3)_2P$ groups. Thus it would appear that a phosphorus–mercury bond had been established, possibly as $(CF_3)_2PHg_2I$, from which one could get either $(CF_3)_2PH$ by the action of acid or $P_2(CF_3)_4$ by further action of $(CF_3)_2PI$. It is proposed that a wide variety of new materials containing the $(CF_3)_2P$ group might be made by shaking $(CF_3)_2PI$ with mercury in the presence of halides of polyvalent metals or non-metals.

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RECEIVED JULY 1, 1957

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[1] This research was supported by the United States Air Force under Contract AF 33(616)-2743, monitored by the Materials Laboratory, Wright Air Development Center, Wright–Patterson Air Force Base, Ohio.

[2] F. W. Bennett, H. J. Emeléus and R. N. Haszeldine, *J. Chem. Soc.*, 3896 (1954).

[3] F. W. Bennett, H. J. Emeléus and R. N. Haszeldine, *ibid.*, 1565 (1953).

IDENTIFICATION OF RUTHENIUM SPECIES IN AQUEOUS SOLUTION

Sir:

We have used an ion-exchange technique for identifying aqueous ruthenium species. The method promises to be very useful in studies of this element where solutions usually contain a mixture of complex ions and polymers which do not equilibrate rapidly. The method will be applicable to other systems with similar characteristics.

Two experiments are performed: the first measures the ionic charge per ruthenium atom, *a*, while the second gives the net ionic charge of the species, *b*. The ratio *b*/*a* equals the number of ruthenium atoms per species, *i.e.*, the degree of polymerization. Using the oxidation number, the number of negatively charged groups in the complex can be inferred. If only one complexing anion is present, the stoichiometric formula of the species is fixed.

The charge per ruthenium atom is determined from the equivalents of charge with an ion-exchange resin per gram atom of ruthenium. It was convenient to use a column technique[1] because separation and concentration of the ruthenium species could be achieved simultaneously. A dilute solution of ruthenium species, primarily in the +3 oxidation state, was stirred with Dowex 50, 200–400 mesh resin in the hydrogen ion form until most of the ruthenium was taken up by the resin. This resin was added to the top of a tapered column already containing approximately one tenth as much resin in the hydrogen ion form. The column was eluted slowly with a dilute cerous perchlorate–perchloric acid solution. The cerous ion displaced most of the ruthenium species, which formed nearly pure bands as they descended. Several samples of a particular band were collected, analyzed for total ruthenium and hydrogen ion, and the spectra checked as an indication of purity. The value of *a* is equal to the molarity of hydrogen ion plus 3 times that of cerous ion in the elutriant, minus the molarity of hydrogen ion in the eluted

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[1] Similar in principle to that of D. A. Everest and J. E. Salmon, *J. Chem. Soc.*, 1444 (1955).