

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 Hoekstra² that, in the pH 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,
(CF₃)₂PH¹

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 P₂(CF₃)₄ is produced by shaking (CF₃)₂PI with mercury³ becomes a good source of (CF₃)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 (CF₃)₂PI to (CF₃)₂PH. Even small proportions of water give minor yields of (CF₃)₂PH, probably through hydrolytic formation of hydrogen iodide. When hydrogen chloride is used, some (CF₃)₂PCl is formed (but can be removed easily by treatment with water), and the remainder of the starting material is accounted for as P₂(CF₃)₄. When phosphoric acid is used the by-products include CF₃-P-O compounds, one of which has properties corresponding to the unstable (CF₃)₂PHO.

In each of these experiments, the (CF₃)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 (CF₃)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 F¹⁹ 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 P³¹ and one H¹ 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 (CF₃)₂PI-Hg-

(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.*, 1585 (1952).

acid reaction was obtained from an experiment in which 0.50 mmole of (CF₃)₂PI was first shaken with mercury alone to give a 95% yield of P₂(CF₃)₄. Then the non-volatile residue was treated with dry hydrogen chloride, producing an amount of (CF₃)₂PH which would account for the missing 5% of the original (CF₃)₂P groups. Thus it would appear that a phosphorus-mercury bond had been established, possibly as (CF₃)₂PHg₂I, from which one could get either (CF₃)₂PH by the action of acid or P₂(CF₃)₄ by further action of (CF₃)₂PI. It is proposed that a wide variety of new materials containing the (CF₃)₂P group might be made by shaking (CF₃)₂PI with mercury in the presence of halides of polyvalent metals or non-metals.

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RECEIVED JULY 1, 1957

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.

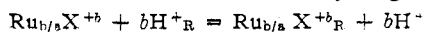
Two experiments are performed: the first measures the ionic charge per ruthenium atom, *a*, while the second gives the net ionic charge of the species, *b*. The ratio *b/a* equals the number of ruthenium atoms per species, *i.e.*, the degree of polymerization. Using the oxidation number, the number of 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 technique¹ 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 elutant, minus the molarity of hydrogen ion in the eluted

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

ruthenium solution, all divided by the gram atoms of ruthenium per liter in the eluted solution.

The charge per species is found from the concentration dependence of the exchange of ruthenium with a known ion—in our case hydrogen ion



$$Q = \frac{[\text{Ru}_{b/a}\text{X}^{+b}]_{\text{R}} [\text{H}^+]^b}{[\text{Ru}_{b/a}\text{X}^{+b}] [\text{H}^+]^b_{\text{R}}}$$

where X denotes anions in the ruthenium species, R designates the resin phase and concentrations are indicated by brackets. The ratio of ruthenium concentrations is proportional to the ratio of hydrogen ion concentrations to the $-b$ power. From two equilibrations at different hydrogen ion concentrations b may be calculated. Conditions were chosen such that the great majority of the resin was in the hydrogen ion form and most of the ruthenium was present in the resin phase. There is an unpredictable change in activity coefficients in the aqueous phase but the method is believed to be sufficiently accurate in most cases because b must be an integer as well as a multiple of a .

It can be shown that any changes in hydrolysis on exchange do not affect the results.

This method has been used to establish the formulas of the species Ru^{+3} and RuCl^{+2} .

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SEMI-QUANTITATIVE GAS CHROMATOGRAPHY

Sir:

We have found relationship (1) reasonably accurate in relating the fraction by weight of a component in a mixture to the corresponding area in a liquid-vapor chromatogram obtained using helium as the carrier gas and a tungsten wire thermal conductivity gage as detector

$$\left(\frac{m_i}{W}\right) = \frac{A_i \sqrt{M_i}}{\sum_i A_i \sqrt{M_i}} \quad (1)$$

where (m_i/W) is the fraction by weight of the i th component, A_i the planimeter-determined area under the peak on the chromatogram corresponding to the i th component and M_i the molecular weight of the i th component.

Clearly the equation may be applied only to mixtures which are completely resolved and such that all components appear in the chromatogram.

Component	Known mole %	Known wt. %	Found area %	Calcd. wt. %
Ethanol	43.4	45.4	47.3	44.6
Water	46.6	19.1	31.1	18.3
1,8-Cineole	10.0	35.5	21.5	37.1

The equation has been applied with comparable results to chromatograms of several mixtures: α and β -pinene plus ethanol; α and β -pinene plus benzene; methyl ethyl ketone, n -propyl alcohol and p -xylene.

Although the expression was arrived at empirically, the appearance of the square root function is not unreasonable on the basis of kinetic theory.

Further, it is apparent that the expression may be utilized to determine the molecular weight of a component from the chromatogram of a mixture of known weight composition of the material of unknown molecular weight with a known substance. Although the square root function through its leverage places a premium on accurate determination of the areas on the chromatogram, we have had some success in this utilization of the relationship.

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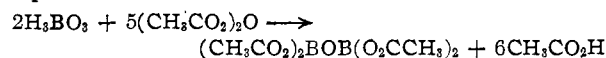
TETRAACETYL DIBORATE AND SO-CALLED "BORON ACETATE"

Sir:

There has been considerable confusion in the literature over the constitution of the product obtained by the reaction between orthoboric acid and acetic anhydride. Two types of compounds have been reported at various times. One, said to melt around 121° , has been called boron triacetate, $(\text{CH}_3\text{CO}_2)_3\text{B}$,^{1,2,3} and the other, m.p. 150 – 152° , pyroboron acetate, $(\text{CH}_3\text{CO}_2)_2\text{BOB}(\text{O}_2\text{CCH}_3)$.^{4,5,6} Both have been supported by analytical data but, in several cases, the authors used identical procedures only to obtain different products.

We have repeated some of the previous preparations, our results agreeing with those of Gerrard and Wheelans⁶; no evidence was obtained for boron triacetate, although the methods described for its preparation^{1,2} were carefully followed. The analytical data for $(\text{CH}_3\text{CO}_2)_2\text{BOB}(\text{O}_2\text{CCH}_3)_2$ were improved and extended and the name *tetraacetyl diborate* is proposed.

The reaction between orthoboric acid and acetic anhydride was found to occur according to the equation



Orthoboric acid (0.534 mole) and acetic anhydride (1.96 mole) were heated together at 50 – 100° with vigorous stirring in a nitrogen atmosphere until all the solid had dissolved. On cooling, the product crystallized as colorless needles. One sample was purified by recrystallization from a benzene-chloroform mixture, another by precipitation from solution in dry acetic acid by the addition of ether. Both melted at 147 – 148° .

All filtrations were carried out using a pressure of dry nitrogen and the products were dried in vacuum at room temperature before being transferred to a dry box for subsequent handling.

The acetate content was determined by titration with standard base, the end-point (around $p\text{H}$ 6.7)

- (1) A. Pictet and A. Geleznoff, *Ber.*, **36**, 2219 (1903).
- (2) H. Cook, L. Ilett, B. Saunders and G. Stacey, *J. Chem. Soc.*, 3125 (1950).
- (3) T. Ahmad and M. Khundkar, *Chem. and Ind.*, 248 (1954).
- (4) O. Dimroth, *Ann.*, **446**, 97 (1925).
- (5) H. Meerwein and H. Maier-Hüser, *J. prakt. Chem.*, **184**, 51 (1932).
- (6) W. Gerrard and M. Wheelans, *Chem. and Ind.*, 758 (1954).