The Rate as a Function of Undissociated Sulfuric Acid Concentration.—The considerations already presented led us to attempt a test of the hypothesis that the exchange rate at a given temperature was simply proportional to the concentration of undissociated sulfuric acid molecules;

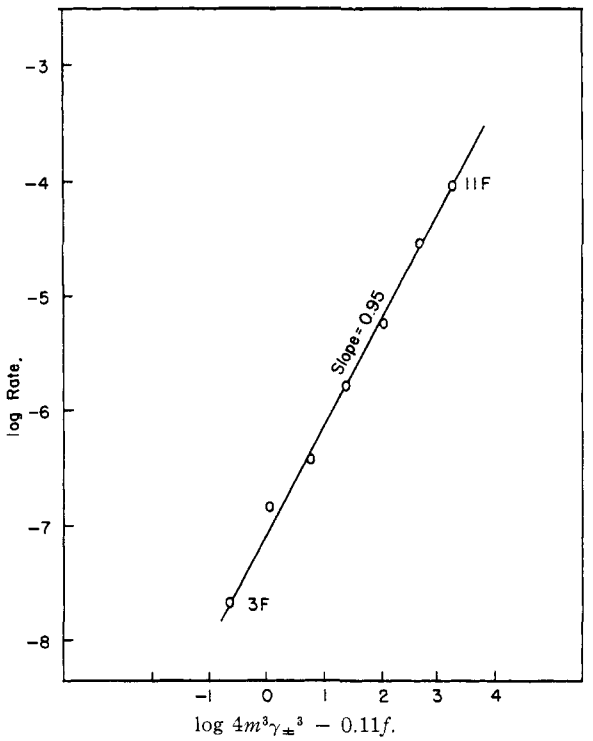

Fig. 5.—Rate of exchange as a function of concentration of undissociated sulfuric acid molecules at 25°

this concentration we presume to be proportional to the concentration of activated H_2SO_4 molecules which then constitutes the Brönsted transition state. The thermodynamic expression for this concentration is proportional to $4m^3\gamma_\pm^3/y_0$, where y_0 is the activity coefficient of undissociated acid. For lack of better information we make the assumption[12] that y_0 is proportional to the activity coefficients of dimethyl sulfate as measured by its solubility in sulfuric acid solutions, where we found $\log y_0 = 0.11 f$. Figure 5 is a plot of log rate *versus* $\log 4m^3\gamma_\pm^3$ minus $0.11 f$. Rate data in 3 to 11 f H_2SO_4 at 25° are used. The slope of the line, 0.95, is close to unity and seems to verify the hypothesis stated, namely

$$R = k(H_2SO_4) = k\frac{(a_{H^+})(y_{HSO_4^-})}{y_0} \times \frac{(HSO_4^-)}{K_1} \quad (7)$$

It may be noted that the negative logarithm of the term $(a_{H^+})(y_{HSO_4^-})/y_0$ in eq. 7 is the Hammett acidity function[13] $H_{(-)}$. Although there are no published measurements of $H_{(-)}$ in sulfuric acid solutions, unpublished work of Coryell and Shepherd[14] indicate that above about 4 f sulfuric acid, $H_{(-)}$ and $H_{(0)}$ become parallel, separated by 0.8 log unit. A plot (not shown) of log rate *versus* log (HSO_4^-) minus $H_{(0)}$ for all data at 25° over the entire range from 3 to 15 f is linear with slope 0.95.

T. F. Young and co-workers have used the Raman spectra of aqueous solutions of sulfuric acid to measure the concentrations of the actual species present.[15] Their data show that the concentration of undissociated acid increases rapidly with concentration above 14 f where it becomes measurable by their method. It is at this concentration that the rate of isotopic exchange becomes very fast.

On the basis of the data presented, the best hypothesis is that the exchange of oxygen-eighteen proceeds through the following reactions, where the first represents a rapid equilibrium and the second the rate-determining step.

$$H^+ + HSO_4^- = H_2SO_4 \quad (8)$$

$$H_2SO_4 \longrightarrow H_2O + SO_3 \quad (9)$$

(12) H. S. Harned and B. B. Owen, ref. 8a, p. 400.

(13) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p. 268-269.

(14) Cited by C. D. Coryell and R. C. Fix, *J. Inorg. Nuclear Chem.*, **1**, 119 (1955).

(15) T. F. Young, *Rec. Chem. Prog.*, **12**, 81 (1951).

ST. LOUIS, MO.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, KANSAS STATE COLLEGE]

Chemical Species Produced by Neutron Irradiation of Phosphorus Trichloride

BY P. K. CONN[1] AND R. E. HEIN

RECEIVED AUGUST 6, 1956

The labeled chemical species produced by neutron irradiation of phosphorus trichloride were separated after addition of carriers by distillation techniques. Analyses of PCl_3 samples, which had been irradiated both in the gaseous and liquid phase for time intervals varying from 3 weeks to 19 hours and at reactor temperatures varying from 140 to 30°, indicated 88% of the P^{32} was present in the mother molecule. The remaining P^{32} present in higher boiling fractions may have distilled over in part with the added carriers, $POCl_3$ and $PSCl_3$. About 30% of the S^{35} was found in $PSCl_3$ and a large percentage of the remainder was present as elemental sulfur. No visual decomposition of the compound was noted for any of the irradiation exposures.

Introduction

To elucidate further the nature of bond rupture processes by which newly formed radioactive phosphorus and sulfur atoms lose their energy and form stable chemical combinations, a more comprehensive study of the effect of neutron irradiation of phosphorus trichloride was undertaken. A part of the "hot-atom" chemistry of this compound has been reported by Hein and McFarland.[2]

(1) Based on a dissertation submitted by Paul K. Conn in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) (a) R. E. Hein and R. H. McFarland, THIS JOURNAL, **74**, 1856 (1952); (b) part of this work was presented at the 128th National ACS Meeting, Minneapolis, Minn., September, 1955.