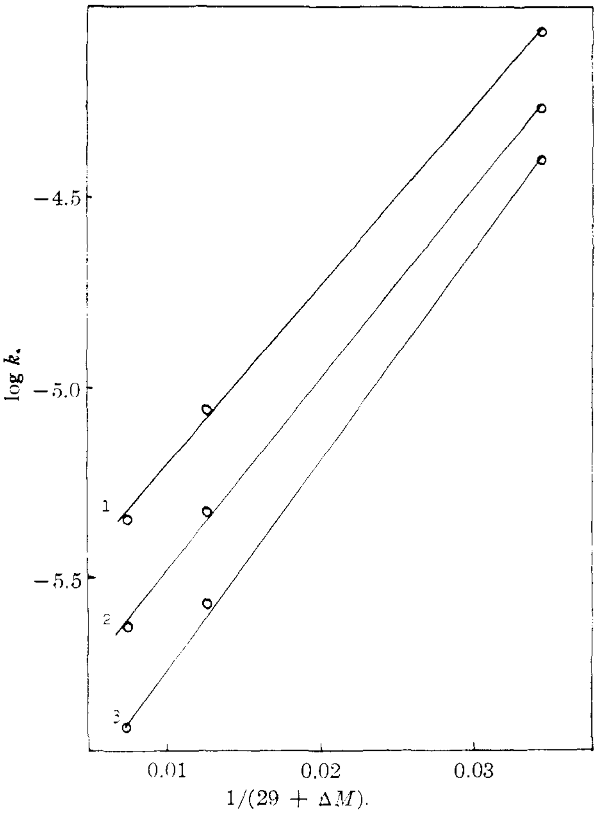

Fig. 2.—(1) $RCO_2C_2H_5$ at 44.9°; (2) $RCO_2C_2H_5$ at 34.9°; (3) $RCO_2C_2H_5$ at 24.9°; (R = CF_3–, C_2F_5– or C_3F_7–).

1. Alkaline hydrolysis[6] of $C_2H_5CO_2R$ where R is CH_3–, C_2H_5–, n-C_3H_7– or n-C_4H_9–.
2. $RI + C_6H_5CH_2O^- \rightarrow C_6H_5CH_2OR + I^-$ where R is CH_3–, C_2H_5–, n-C_3H_7– or n-C_4H_9–.[7]
3. $CH_3CO_2R + HBr \rightarrow RBr - CH_3CO_2H$ where R is CH_3–, C_2H_5–, n-C_3H_7– or n-C_4H_9–.[7]

It was found that increasing the chain length of the perfluorinated acid component of an ester beyond three carbon atoms has only a slight effect upon the rate constants. There is a large decrease in k in going from ethyl trifluoroacetate to ethyl pentafluoropropionate.

Henne and Fox[8] reported that the ionization constants for trifluoroacetic and heptafluorobutyric acids are approximately the same. Thus, the electron withdrawing effects of CF_3– and C_3F_7– groups should be approximately the same. If these two groups have approximately the same electron withdrawing power, then some other explanation must be found for the observed differences in the k's for this series.

According to Newman[9] an ester such as ethyl heptafluorobutyrate (3 atoms in 6-position) should be more sterically hindered than ethyl pentafluoropropionate (zero atoms in 6-position) and ethyl trifluoroacetate (zero atoms in 6-position). Ethyl trifluoroacetate and ethyl pentafluoropropionate should be approximately the same as far as steric hindrance is concerned. Thus, the Newman steric hindrance theory does not explain the large change in k occurring with the pentafluoropropionate.

There is a definite relationship between the k's and the change in molecular weight for the $RCO_2C_2H_5$ series (R = CF_3–, C_2F_5– and C_3F_7–). This relationship (Fig. 2) can be represented by

$$\ln k = a'/(M + \Delta M) + b' \qquad (6)$$

where a' and b' are constants; M is the molecular weight of C_2H_5– and ΔM is the difference between the molecular weight of the ester in question and the molecular weight of $CF_3CO_2C_2H_5$. It is significant that the k's for this ester series can be related quantitatively to molecular weight differences.

LAFAYETTE, INDIANA

---

[6] E. J. Salmi and R. Leimu, *Suomen Kemistilehti*, **20B**, 43 (1947).

[7] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p. 154.

[8] A. L. Henne and C. J. Fox, THIS JOURNAL, **73**, 2323 (1951).

[9] M. S. Newman, *ibid.*, **72**, 4783 (1950).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON UNIVERSITY]

The Exchange of Oxygen between Sulfuric Acid and Water[1]

BY THOMAS C. HOERING AND JOSEPH W. KENNEDY

RECEIVED JULY 16, 1956

The kinetics of the exchange of isotopic oxygen between sulfuric acid and water has been studied. The rate of the exchange was found to be first order with respect to hydrogen ion and first order with respect to bisulfate ion concentration. The rate of the exchange was found to vary as the 0.72 power of the sulfuric acid activity in 1.0 to 4.0 f H_2SO_4 at 100° and as the 0.80 power of the activity in 3.0 to 10 f H_2SO_4 at 25°. The activity coefficient of undissociated sulfuric acid in sulfuric acid solutions was approximated by solubility measurements on dimethyl sulfate. From this estimate, the exchange rate appears to vary as the concentration of the undissociated sulfuric acid. The dissociation of sulfuric acid into its anhydride and water is proposed as the rate-determining step.

There exist relatively few quantitative data on the exchange of isotopic oxygen between oxy-anions and water.[2] A reaction of this type is the exchange between sulfuric acid and water.

$$H_2SO_4 + H_2O^* = H_2SO_3O^* + H_2O \qquad (1)$$

This reaction has been studied qualitatively by several workers who found that an exchange occurs only in acid solutions.[3] This paper describes a de-

---

[1] Taken in part from the thesis submitted by T. C. Hoering in partial fulfillment of the requirements of the Ph. D. degree, 1952; supported in part by U. S. A. E. C. contract AT(11-1)-259.

[2] J. O. Edwards, *Chem. Revs.*, **50**, 455 (1952); M. Dole, *ibid.*, **51**, 275 (1952).

[3] S. C. Data, J. N. E. Day and C. K. Ingold, *J. Chem. Soc.*, 1968 (1937); N. F. Hall and O. R. Alexander, THIS JOURNAL, **62**, 3455 (1940); G. A. Mills, *ibid.*, **62**, 2837 (1940); T. Titani and K. Goto, *Bull. Chem. Soc., Japan*, **14**, 77 (1939); J. L. Hyde, THIS JOURNAL, **62**, 873 (1940).

tailed study of the reaction. In the concentration range studied, sulfuric acid is dissociated into hydrogen and bisulfate ions. We have attempted to measure the rate of the exchange as a function of the concentrations of these ions and as a function of the activity of the sulfuric acid.

Experimental

Materials and Apparatus.—The isotopic tracer was received as H_2O^{18} enriched to about 1.5% in oxygen-eighteen from the Stuart Oxygen Company on allocation from the U. S. Atomic Energy Commission. Reagent grade HCl and H_2SO_4 were used without further purification. The $Li_2SO_4 \cdot H_2O$ was recrystallized twice from water to remove an acidic impurity. Powdered carbon was made by grinding spectrographic carbon arc electrodes of 99.99% purity.

Isotopic analyses were made on a Consolidated-Nier Model 21-201 Isotope Ratio Mass Spectrometer. Experiments were performed in insulated water-baths at 10.00 ± 0.05° and 25.00 ± 0.05° as measured by a Bureau of Standards certified thermometer. Experiments at 100.00 ± 0.10° were done in a bath of molten "Carbowax-400," a polyethylene glycol manufactured by the Carbide and Carbon Chemical Corporation.

Separations and Isotopic Analyses.—The separations and isotopic analyses were performed in several ways. The sulfate fraction in solutions less than 10 *f* H_2SO_4 was separated by the precipitation of $BaSO_4$. The precipitate was centrifuged, washed, dried, ground with a threefold excess of powdered carbon, and rolled in a small sheet of 0.001-inch molybdenum foil. The foil was clamped in metal holders on the ends of tungsten rods sealed in a ground glass joint. This assembly was placed in a vacuum line and evacuated. The metal and the sample were outgassed by passing a small current through the foil. The system was then closed off from the pump and the foil heated to about 1100° by a large current. The evolved CO and CO_2 were collected in an evacuated bulb, and the isotopic analyses were made on the CO_2 without further separation.

The heat of dilution during the separation procedure made the previously described method unusable in solutions greater than 10 *f* H_2SO_4. It was found that when solutions of sulfuric acid were electrolyzed between platinized platinum electrodes, the oxygen came exclusively from the water. (Erratic results were obtained when bright platinum electrodes were used.) It was determined also that the presence of platinum black during electrolysis had little effect on the rate of the exchange. Thus the oxygen-eighteen content of the water in concentrated solutions was determined by electrolysis followed by introduction of the (dried) oxygen gas into the spectrometer.

An attempt was made to measure continuously the O^{18} content of the water. A small volume of CO_2 was admitted to the reaction mixture at the start of the exchange. If the carbon dioxide reached isotopic equilibrium rapidly with the water, it could be sampled to give values for the changing isotopic composition of the water. However, in the acidic solutions used in these studies, the rate of the carbon dioxide–water exchange becomes too slow for this purpose. A similar method was tried with SO_2 as the exchanging gas. It came to isotopic equilibrium rapidly with water, but we found that SO_2 is not a suitable gas for the routine analysis of samples of widely different O^{18} content. The "memory" effect due to adsorption in the spectrometer made pump-out times too long.

Preparation of Solutions.—The solutions used to determine the hydrogen ion dependence were made by the addition of the proper amounts of $Li_2SO_4 \cdot H_2O$ and 11.05 *f* H_2SO_4 and dilution with enriched water. Correction was made for volume changes upon heating to 100° where necessary. The solutions used to determine the bisulfate ion dependence were made by the addition of the proper amount of 10.01 *f* HCl and 11.05 *f* H_2SO_4 and dilution with enriched water. The induced exchange upon mixing due to the heat of dilution at these concentrations was small.

The more concentrated solutions were made by adding slowly to enriched water the proper amount of standardized concentrated sulfuric acid. The acid was added from the calibrated syringe of a "Micro-Titrator," manufactured by the Micro-Metric Co. The enriched water had been cooled to freezing and was rotated in the holder of this apparatus. Solutions prepared in this manner showed a minimum of zero-time exchange.

Procedures.—Two procedures were developed: one, for solutions less than 10 *f* H_2SO_4 and second, for solutions above this concentration. For the experiments in the lower concentrations, appropriate amounts of sulfuric acid, hydrochloric acid or lithium sulfate were added to a 5-ml. volumetric flask and diluted to the mark with enriched water. Six portions of this solution were placed in Pyrex ampules, sealed off and placed in the thermostat. Five of these samples were removed over a period of two half-lives for exchange and added to a solution of $BaCl_2$. The sixth sample was allowed to remain in the thermostat for a period of greater than ten half-lives for exchange. (In some experiments at 25°, where the half-life was very long, the last sample was brought to isotopic equilibrium by heating at 100° for a period known to be ten half-lives at that temperature.) The barium sulfate was then analyzed for O^{18} as previously described.

The rate of the reaction which leads to isotopic exchange is given by the expression[4]

$$R = \frac{\{H_2O\} \times 4\,\{H_2SO_4\}}{\{H_2O\} + 4\,\{H_2SO_4\}} \times \frac{\ln(1 - F)}{t} \qquad (2)$$

The quantities in braces are formal concentrations, t is the time, and the quantity F is the fraction exchanged as defined by the expression

$$F = \frac{O_t^{18} - O_0^{18}}{O_\infty^{18} - O_0^{18}} \qquad (3)$$

The symbol O^{18} represents the percentage oxygen-eighteen in the barium sulfate at the time indicated by the subscript. The concentration of the water in each sample was calculated from solution density data in the "International Critical Tables."[5] The results of a typical experiment are shown in Fig. 1. The rate has been calculated by the "half-time" method.

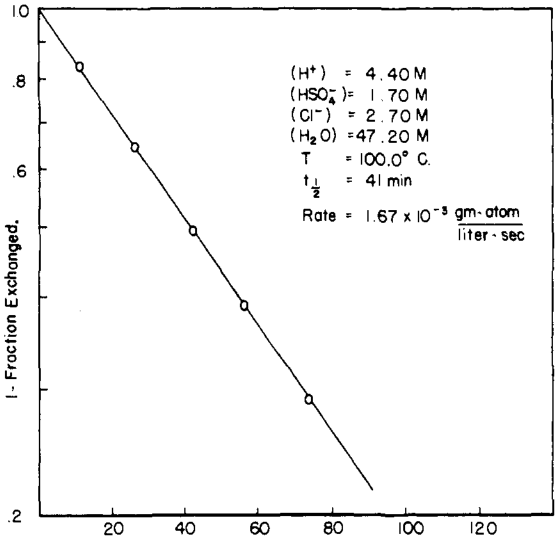

Fig. 1.—A typical exchange run.

For experiments in the more concentrated region, appropriate amounts of concentrated sulfuric acid were diluted in the manner described. Each solution was placed in a flask with a ground glass joint and with two platinized platinum electrodes sealed in. The flask was attached to a manifold and placed in a thermostat and evacuated. The water in the mixture was sampled for oxygen-eighteen analysis by the electrolysis procedure previously described. The amount of heating or chemical reaction produced by this sampling was negligible. The exchange curves were linear and reproducible.

---

(4) A. C. Wahl and N. A. Bonner, "Radioactivity Applied to Chemistry," John Wiley and Sons, New York, N. Y., 1951.

(5) "International Critical Tables," McGraw-Hill Book Co., New York, N. Y., 1928.

Solubility of Dimethyl Sulfate in Sulfuric Acid Solutions.—To obtain a rough estimate of the activity coefficient of undissociated sulfuric acid molecules in sulfuric acid solutions, we measured the solubility of dimethyl sulfate in sulfuric acid solutions. Liquid dimethyl sulfate was shaken with solutions of 1 to 5 *f* H_2SO_4 for 30 minutes at room temperature. The layers were separated and the aqueous layer was centrifuged to remove droplets of dimethy sulfate. The solution was chilled and titrated rapidly with standard base. It was then analyzed for dimethyl sulfate by two methods: first, by methoxyl determination,[6] and second, by combustion to CO_2. In this concentration range and for this time and temperature, the amount of hydrolysis of dimethyl sulfate was small.[7]

Experimental Results

Hydrogen Ion Dependence at 100°.—The results of experiments at three fixed bisulfate ion concentrations in which the hydrogen ion concentration has been varied by replacement with lithium ions are shown in Fig. 2. The slope of each of the lines drawn on this log-log plot is unity.

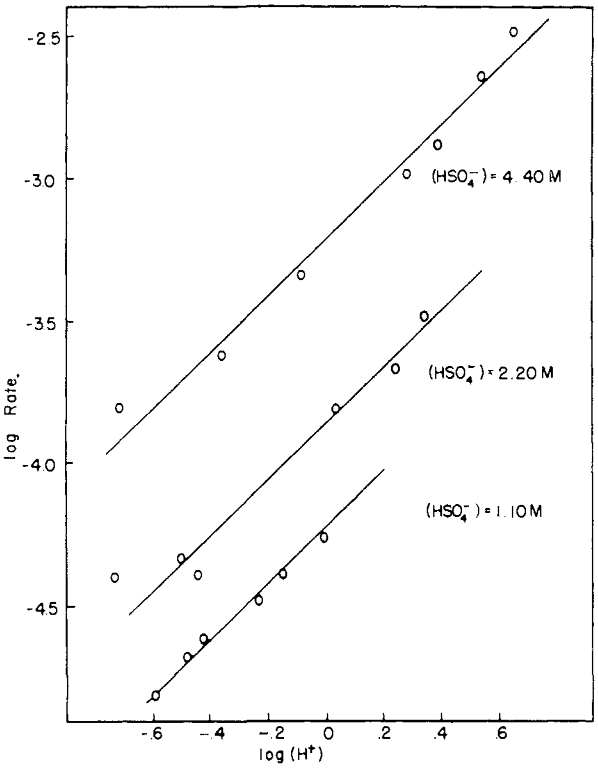

Fig. 2.—Hydrogen ion dependence at 100°.

Bisulfate Ion Dependence at 100°.—The results of experiments at two fixed hydrogen ion concentrations in which the bisulfate ion concentration has been varied by replacement with chloride ions are shown in Fig. 3. The slope of each of the lines is unity.

The Rate of Exchange in Sulfuric Acid Solutions.—The results of experiments at three temperatures, 100, 25 and 10° in solutions of sulfuric acid are listed in Table I.

TABLE I

THE RATE OF EXCHANGE IN SULFURIC ACID SOLUTIONS AT 100, 25 AND 10°

H_2SO_4, *f*	H_2O, *f*	$T_{1/2}$ (sec.)	Rate (g. atom/l. sec.)
	(a) Temperature: 100.00 ± 0.10°		
1.04	51.2	5.04×10^4	5.28×10^{-5}
1.10	51.1	4.20×10^4	6.68×10^{-5}
1.72	49.6	2.47×10^4	2.25×10^{-4}
2.25	48.3	1.25×10^4	3.50×10^{-4}
2.85	46.9	8.46×10^3	7.49×10^{-3}
3.52	45.3	5.22×10^3	1.43×10^{-3}
4.40	43.2	1.80×10^3	3.30×10^{-3}
	(b) Temperature: 25.00 ± 0.05°		
3.00	49.1	3.10×10^8	2.16×10^{-8}
4.00	46.7	5.97×10^7	1.40×10^{-7}
5.00	44.4	2.66×10^7	3.58×10^{-7}
6.00	41.9	6.53×10^6	1.62×10^{-6}
7.00	39.2	1.98×10^6	5.72×10^{-6}
8.00	36.5	4.39×10^5	2.70×10^{-5}
9.00	33.9	1.42×10^5	8.53×10^{-5}
10.00	31.0	5.83×10^4	2.08×10^{-4}
11.00	28.2	1.91×10^4	6.25×10^{-4}
11.8	26.0	4.50×10^3	2.42×10^{-3}
12.5	24.0	3.36×10^3	3.33×10^{-3}
12.6	23.7	1.77×10^3	6.31×10^{-3}
13.0	22.5	1.67×10^3	6.53×10^{-3}
13.7	20.2	4.50×10^2	2.27×10^{-2}
13.8	19.8	7.20×10^2	1.41×10^{-2}
14.4	18.0	3.12×10^2	3.05×10^{-2}
14.9	16.4	2.10×10^2	4.25×10^{-2}
15.0	16.0	1.92×10^2	4.56×10^{-2}
	(c) Temperature: 10.00 ± 0.05°		
14.0	19.8	4.20×10^3	2.41×10^{-3}
14.5	18.2	2.67×10^3	3.60×10^{-3}
15.0	16.6	1.16×10^3	7.77×10^{-3}
15.5	15.0	6.00×10^2	1.40×10^{-2}
16.0	13.1	3.66×10^2	2.06×10^{-2}

Activation Energies.—In addition to the rates tabulated above, an average of four determinations were made at each of three concentrations over selected temperature ranges. Activation energies as measured by the slopes of plots of log *R* *vs.* 1/*T* are given in Table II.

TABLE II

SUMMARY OF ACTIVATION ENERGIES

H_2SO_4,	Temp. range (°C.)	Activation energy (cal./mole)
3.59	60 to 100	31,300
8.00	25 to 35	24,600
13.00	10 to 25	20,400

The Activity Coefficient of Dimethyl Sulfate in Sulfuric Acid Solutions.—The activity coefficient of a non-electrolyte in aqueous solutions of electrolytes often may be expressed by the simple relationship[8]

$$\ln \gamma_0 = \ln \frac{S_0}{S} = k\mu \qquad (4)$$

where S_0 is the solubility of the non-electrolyte in pure water, S is the solubility in the solution of electrolyte, γ_0 is the activity coefficient of the non-electrolyte and μ is the ionic strength. The results

---

(6) D. O. Hoffman and M. L. Wolfrom, *Ind. Eng. Chem., Anal. Ed.*, **19**, 225 (1947).

(7) C. Boulin and L. J. Simon, *Compt. rend.*, **170**, 392 (1920).

(8) (a) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 2nd edition, 1950; F. A. Long and W. F. McDevitt, *Chem. Revs.*, **51**, 119 (1952).

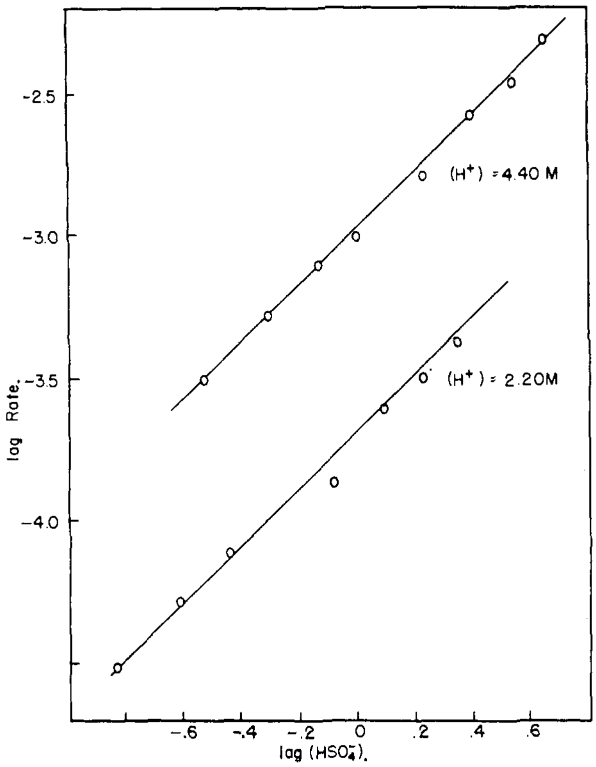

Fig. 3.—Bisulfate ion dependence at 100°.

of the solubility measurements are consistent with this relation and may be expressed

$$\log_{10} y_0 = 0.11f \qquad (5)$$

where f is the concentration of sulfuric acid in formula weights per liter. We have replaced γ_0 by y_0 the activity coefficient of dimethyl sulfate on a volume molar basis, since the solubility is small.

Discussion

If a single exchange path is operative, then by varying the concentrations of the reactants in separate experiments one can evaluate the order of the reaction. At a given temperature the rate of the exchange will be given by

$$R = k(\mathrm{H}^+)^m (\mathrm{HSO_4}^-)^n (\mathrm{H_2O})^p \,\Gamma \qquad (6)$$

where parentheses are used to indicate actual species concentrations in moles per liter and Γ is a function of the activity coefficients of the reactants and transition state raised to the proper powers.

The experiments at constant ionic strength with added Li_2SO_4 or HCl show the rate of oxygen exchange between sulfuric acid and water to be first order with respect to the hydrogen ion concentration and first order with respect to the bisulfate ion concentration. We were not able to determine directly the dependence upon the water concentration because we found no suitable inert solvent with which the water could be diluted. (Dioxane, di-N-methylformamide and dimethyltetraethylene glycol were tried. Dioxane was found to be an effective catalyst for the reaction.)

The Rate as a Function of Sulfuric Acid Activity. —Explicit values for the activity of sulfuric acid at 100° are not available in the literature. Relative values may be computed by standard methods from the vapor pressure data of Collins,[9] or values may be extrapolated from the e.m.f. data of Harned and Hamer[10] at 0, 25, 40 and 60°. The averages of the values so obtained were converted to formula-weights-per-liter concentrations and are listed in Table III. These activity values are all relative and have been normalized to unity at 1.00 f sulfuric acid.

TABLE III

AVERAGE RELATIVE ACTIVITY OF H_2SO_4 IN SULFURIC ACID SOLUTIONS AT 100° (CALCD. FROM LIT. DATA[9,10])

Concn. (formula wt./l.)	Log $a_{H_2SO_4}$ + log constant	Concn. (formula wt./l.)	Log $a_{H_2SO_4}$ + log constant
1.00	0.000[a]	3.29	1.800
1.36	0.365	3.57	1.994
1.78	0.720	3.98	2.280
2.20	1.050	4.30	2.476
2.55	1.260	4.62	2.630
2.87	1.536		

[a] The values of log $a_{H_2SO_4}$ have been normalized to zero at 1.00 f sulfuric acid.

Figure 4 is a plot of the logarithm of the rate *versus* the logarithm of the relative activity at 100° from Table III. In the range 1.0 to 4.4 f sulfuric acid, the points fall about a line of slope 0.73. A similar plot (not shown) for the rate data at 25° is likewise linear with slope 0.80. For the relative activity of sulfuric acid at the lower temperature, we used the quantity $4m^3 \gamma_\pm^3$, where m is the weight-molar concentration and $\gamma_\pm$ is from the data collected by Yost and Russell.[11]

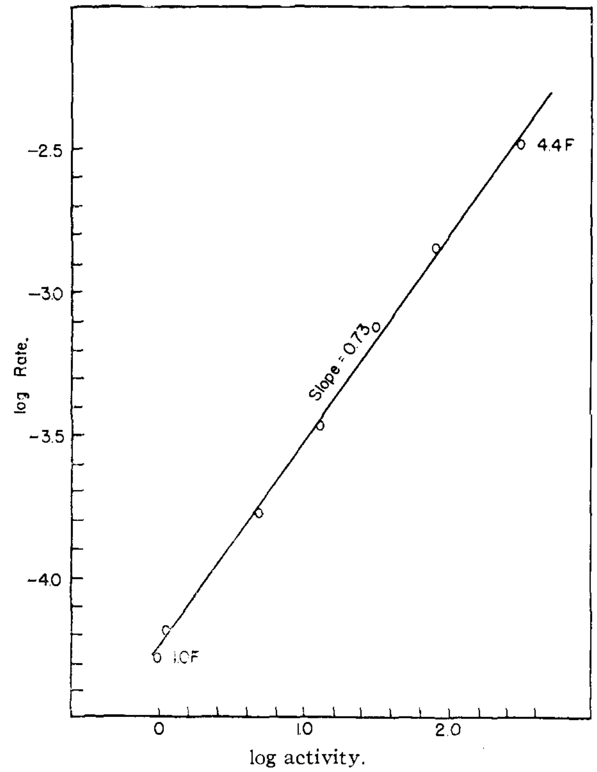

Fig. 4.—The exchange rate as a function of the sulfuric acid activity at 100°.

---

[9] E. M. Collins, *J. Phys. Chem.*, **37**, 1191 (1933).

[10] W. J. Hamer, THIS JOURNAL, **57**, 9 (1935); H. S. Harned and W. J. Hamer, *ibid.*, **57**, 27 (1935).

[11] D. M. Yost and H. Russell, "Systematic Inorganic Chemistry," Prentice-Hall Co., New York, N. Y., 1944.

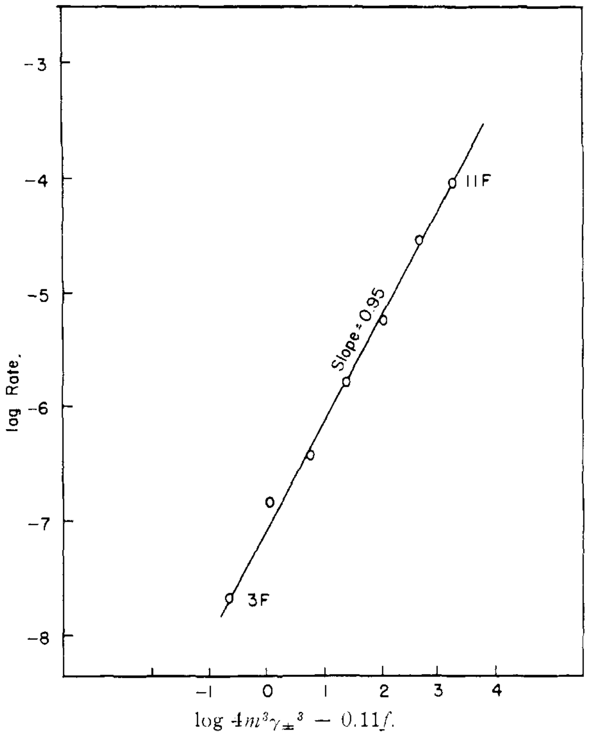

Fig. 5.—Rate of exchange as a function of concentration of undissociated sulfuric acid molecules at 25°.

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; 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 $4f$ 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. 409.

(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.