centration; hence it would appear preferable to consider the sulfide precipitation reaction to consist of the attack of HS^- ion on the metal ion in aqueous solution.

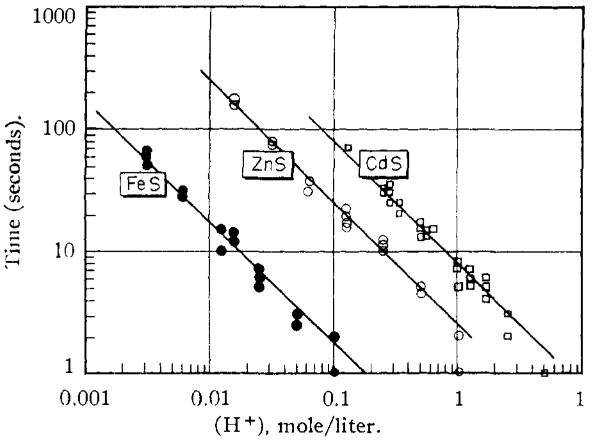

Fig. 1.—The rate of dissolution of precipitated sulfide at 25°.

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The Chelation of Praseodymium by Thenoyltrifluoroacetone[1]

BY T. K. KEENAN AND J. F. SUTTLE

RECEIVED AUGUST 6, 1953

The dependence of chelation of metal ions upon *p*H has been reported by a number of workers[2a,b–6] using the β-diketone, thenoyltrifluoroacetone (referred to as TTA), as the chelating agent in a two-phase system. The over-all equilibrium involved in the distribution of praseodymium between an aqueous phase and an organic phase (TTA in benzene) may be represented by the equation

$$Pr^{+++}(aq) + 3HT(bz) \rightleftarrows PrT_3(bz) + 3H^+(aq)$$

The equilibrium expression for this reaction is

$$K_{eq} = \frac{[PrT_3][H^+]^3}{[Pr^{+++}][HT]^3}$$

The quantity $[PrT_3]/[Pr^{+++}]$ will be defined as the distribution ratio D.R.

The distribution ratio can be evaluated by the use of Pr^{142} as a tracer and counting equal aliquots of each phase. King and Reas[7] have reported the thermodynamic activity coefficients for TTA. The activity coefficient for the metallic chelate in benzene is assumed to be equal to the known coefficient for the unchelated TTA. Kielland[8] lists the activity coefficient for praseodymium. Hydrogen ion activity was determined directly as *p*H using a Model G Beckman *p*H meter. The equilibrium concentration of the unchelated TTA was assumed to be the same as the concentration before equilibration since a large excess was always present.

Experimental

The aqueous phase was initially 0.0071 *f* Pr(III) with ammonium chloride added to give an ionic strength of 0.1. The benzene phase was either 0.2 *f* or 0.5 *f* in TTA. Praseodymium trichloride (Fairmount Chemical Co.) was used to make up the aqueous stock solutions. The authors are indebted to R. P. Hammond (Los Alamos Scientific Laboratory) for a sample of very pure (99.9%) praseodymium oxide. This compound was converted to the chloride and irradiated with neutrons, for use as a tracer. The TTA was obtained from the Dow Chemical Company.

The reaction vessel was made from 45-mm. glass tubing. A section about 20 cm. long was sealed at one end and the open end sealed to a 24/40 ₸ joint. A stirrer, fitted with a 24/40 ₸ bearing, provided constant agitation. The entire apparatus was immersed in a constant temperature bath held at 25.1 ± 0.1°.

Fifty ml. of the TTA–benzene solution and 10 ml. of the praseodymium trichloride solution were used in each run. Since it was desired to measure the extent of chelation as a function of *p*H, either dilute ammonium hydroxide or hydrochloric acid was added. Each mixture was stirred for one hour to ensure thermal and chemical equilibrium.

At the completion of a run, the *p*H of the aqueous phase was then determined immediately. The praseodymium in the aqueous phase was then precipitated by oxalic acid. The oxalate precipitate was filtered with a chimney and spring arrangement on a fritted disc and counted. The counting instrument used a Geiger–Mueller tube with a 3.5 mg./cm.^{2} mica window. The praseodymium was removed from the benzene phase by extraction for one hour with saturated oxalic acid solution. The resulting oxalate precipitate was prepared for counting in the same manner as the sample taken from the aqueous phase

The two samples from one run were always counted within a few minutes of each other. No absorption corrections were made since the Pr^{142} beta has a maximum energy of 2.2 Mev.

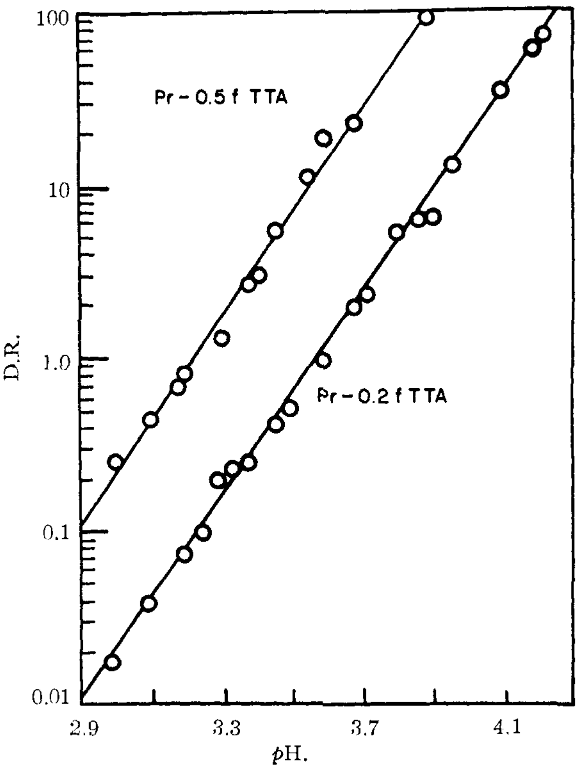

Fig. 1.

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[1] This work was performed at the University of New Mexico in coöperation with the Los Alamos Scientific Laboratory.

[2] (a) R. E. Connick and W. H. McVey, THIS JOURNAL, **71**, 3182 (1949); (b) A. Broido, AECD-2616.

[3] R. Bolomey and L. Wish, THIS JOURNAL, **72**, 4483, 4486 (1950).

[4] E. Huffman and L. Beaufait, *ibid.*, **71**, 3179 (1949).

[5] J. Suttle, AECD-2800.

[6] J. Suttle, AECU-741.

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Discussion of Results

The equilibrium constant is dependent upon the nth power of the hydrogen ion concentration. It was assumed that the metal chelate compound was PrT_3. Rewriting the equilibrium expression in logarithmic form gives

$$\log K_{eq} = \log \text{D.R.} + n \log [H^+] - 3 \log [HT]$$

or

$$\log \text{D.R.} = -n \log [H^+] + 3 \log [HT] + \log K_{eq}$$

A plot of log D.R. *vs.* $-\log[H^+]$ should give a straight line whose slope, n, is both the average charge on the aqueous praseodymium species and the exponent for evaluating H^+ in the equilibrium expression.

The data were plotted (see Fig. 1) and the slope of the line was calculated by the method of least squares, yielding values of 2.96 for the 0.2 *f* and 2.93 for the 0.5 *f* TTA. Since these values are within experimental error of the limiting value, 3, K_{eq} was calculated assuming that $n = 3$. These results are given in Table I. The D.R. values shown in the same table have already been corrected for the activity coefficient of the species involved. No correction for the solubility of TTA in water (2%) was made.

The values marked with an asterisk (*) indicate that this result was approached from the benzene phase. In these runs, all of the praseodymium ions were initially extracted into the benzene phase at a high *p*H, *ca.* 4.4–4.5. Following this, the phases were separated and the aqueous phase discarded. A solution containing the proper amount of ammonium chloride was added to the reaction vessel and the contents were again allowed to approach equilibrium. The results of these runs agree with those obtained by introduction of the praseodymium chloride in the aqueous phase.

TABLE I

0.2 *f* TTA			0.5 *f* TTA		
*p*H	D.R.	$K_{eq} \times 10^9$	*p*H	D.R.	$K_{eq} \times 10^9$
3.00	0.0183	3.3	2.85	0.0934	3.8
3.10	.0406	3.8	2.90	.139	4.0
3.20	.0771	3.4	3.00	.226	3.9
3.25	.100	3.2	3.10	.464	3.4
3.30	.204	4.6	3.18	.720	3.1
3.34	.235	4.0	3.20	.856	3.1
3.35	.259	3.8	3.30	1.34	2.5
3.46	.436	3.2	3.38	2.79	3.0
3.50	.529	3.0	3.41	3.11	2.7
3.60	1.01	2.8	3.46*	5.71	3.5
3.69*	2.04	3.3	3.55	11.5	3.7
3.71	2.48	3.3	3.59	19.8	4.9
3.80	5.37	3.8	3.68	23.3	3.1
3.86	6.46	3.0	3.89	96.1	3.0
3.90	6.70	3.4	3.92	134	3.4
3.96*	13.2	3.1		Average	3.4 ± 0.5
4.09*	36.6	3.5			
4.18	61.1	3.1			
4.21	72.9	3.0			
	Average	3.3 ± 0.5			

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The Kinetics of the Oxidation of Phenyl Sulfoxide[1]

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RECEIVED DECEMBER 11, 1953

The comprehensive study of the reactions of ketones with peracids[2] and the recent publications of Overberger and Cummins[3,4] concerning the kinetics of the oxidation of *p*-chlorobenzyl sulfide, make it desirable to record the results obtained in the investigation of the kinetics of the peracid oxidation of phenyl sulfoxide. We wish to publish these results at this time since this work has been temporarily discontinued.

Experimental

The experimental work consists of two groups of experiments. The first group of kinetic experiments was carried out using perbenzoic acid in an acetone medium. The perbenzoic acid (PBA) was prepared according to Swern, *et al.*,[5] by the photochemical oxidation of benzaldehyde in an acetone solution. Phenyl sulfoxide purified by crystallization from methanol (m.p. 70–71°),[6] was dissolved in 80–90 ml. of acetone in a volumetric flask and on addition of PBA the resulting solution was diluted with additional acetone to the 100 ml. mark. The flask was placed in a constant temperature bath at 30.4°, and at desired intervals aliquots were removed and titrated iodometrically.[7] The strength of the PBA stock solution was determined before each experiment. The rate of decomposition of PBA in acetone under identical conditions with those employed in the kinetic runs (except for the absence of the sulfoxide) was found to be insignificant when compored with the reaction rates of the sulfoxide oxidation. Thus, it was found that in a two-hour period less than 10% of the PBA was lost, and the same period of time was sufficient for the completion of about 80% of the sulfoxide oxidation.

The second group of experiments involved the oxidation of the phenyl sulfoxide with peracetic acid (PAA) in a glacial acetic acid medium. Stabilized 40% peracetic acid (Buffalo Electro-Chemical Co.)[8] was diluted with glacial acetic acid and the resulting stock solution was kept in a refrigerator at −5°. This series of kinetic runs was carried out at 29.0° and the reaction rate was followed by iodometric titration of aliquots. The PAA solution contains according to the manufacturer's specifications a minimum of 40% PAA and approximately 5% hydrogen peroxide. In order to determine the total residual active oxygen, an ammonium molybdate-catalyzed iodometric titration was employed.[9]

The experimental results are summarized in Tables I and II. The bimolecular rate law, first order with respect to sulfoxide and to the peracid, was assumed to calculate the rate constant since a linear relationship was obtained when the log $(C_{\text{peracid}})/(C_{\text{PH}_2\text{SO}})$ was plotted against time.

Discussion

Overberger and Cummins[3] concluded that the perbenzoic acid (PBA) oxidation of a sulfide involves a nucleophilic attack of the sulfur atom upon

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(1) From the M.S. thesis of F. K., Duquesne University, August, 1950. Presented in part at the 118th Meeting of the Am. Chem. Soc., 1950.

(2) S. L. Friess and P. E. Frankenburg, THIS JOURNAL, **74**, 2679 (1952), and earlier papers.

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(4) C. G. Overberger and R. W. Cummins, *ibid.*, **75**, 4783 (1953).

(5) D. Swern, T. W. Findley and J. T. Scanlan, *ibid.*, **66**, 1925 (1944).

(6) W. J. Hickenbottom, "Reactions of Organic Compounds," Longmans, Green and Co., New York, N. Y., 1948.

(7) A. Baeyer and V. Villiger, *Ber.*, **33**, 2481 (1900).

(8) We gratefully acknowledge the gift from the Buffalo Electrochemical Co. for the stabilized peracetic acid which was used in this study. We also wish to thank Dr. Greenspan for his interest in this work.

(9) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1947.