Experimental

The Preparations of O,O-Diethyl Hydrogen Dithiophosphate, Bis-(diethoxythiophosphoryl) Disulfide, and Bis-(diethoxythiophosphoryl) Trisulfide.—These compounds were prepared by reported procedures.[3,7]

The Oxidation of O,O-Diethyl Hydrogen Dithiophosphate by Concentrated Sulfuric Acid.—$(C_2H_5O)_2P(S)SH$ (30 g.) was added slowly to concentrated H_2SO_4 (25 g.) with vigorous stirring and cooling in an ice bath. The addition took approximately 1 hr., then an additional 10-g. sample of H_2SO_4 was added to the reaction mixture. The ice bath was removed and the reaction mixture was stirred overnight. The mixture was diluted with 120 ml. of H_2O and then was extracted with three 66-ml. aliquots of aqueous NaOH (4%). The ether extract was dried over Na_2SO_4 and then blown free of solvent with N_2 gas on the steam bath. Cooling the residual oil resulted in the crystallization of a 3.82-g. sample of bis-(diethoxythiophosphoryl) trisulfide which was isolated by filtration (27% yield based on P), m.p. 72°. *Anal.* Calcd. for $C_8H_{20}O_4P_2S_5$: C, 23.9; H, 5.0; P, 15.4; S, 39.8. Found: C, 23.3; H, 4.9; P, 15.5; S, 40.0. The filtrate, weighing 14.6 g., had an infrared spectrum identical with that of an authentically prepared sample of bis-(diethylthiophosphoryl) disulfide (49% yield based on P). *Anal.* Calcd. for $C_8H_{20}O_4P_2S_4$: C, 25.9; H, 5.4; P, 16.7; S, 34.6. Found: C, 25.1; H, 5.2; P, 16.3; S, 34.2. This material was readily converted into the trisulfide (identified by mixed melting point determination) upon being heated with excess sulfur. The conversion was catalyzed by a few per cent of added P_2S_5.

The combined aqueous NaOH extracts were acidified with concentrated HCl. An additional 5-ml. sample of HCl was added and the resultant solution extracted with three 50-ml. aliquots of ethyl ether. The ether extracts were dried over Na_2SO_4 and blown free of solvent with N_2 gas on a steam bath. A 3-g. sample of $(C_2H_5O)_2P(S)OH$ was obtained (11% yield based on P). *Anal.* Calcd. for $C_4H_{11}O_3PS$: C, 28.2; H, 6.5; P, 18.2; S, 18.8; neut. equiv., 170. Found: C, 28.5; H, 6.8; P, 18.3; S, 19.0; neut. equiv., 169. The melting point of the potassium salt, 195–197°, was in excellent agreement with the literature value of 196–197°.[7]

The Modified Oxidation of O,O-Diethyl Hydrogen Dithiophosphate with Iodine.—To a mixture of $(C_2H_5O)_2P(S)SH$ (9.3 g.), H_2O (100 ml.), and 3 *N* KOH (17 ml.) were added simultaneously and with vigorous stirring 0.5 *N* Na_2S (100 ml.) and 0.1 *N* KI–I_2 solution (1000 ml.). The addition took approximately 20 min. and the resultant mixture was stirred for an additional 1 hr. At the end of this time, the reaction mixture was extracted with five 200-ml. portions of benzene. The combined benzene extracts were washed with two 100-ml. portions of 3 *N* KOH and with 100 ml. of H_2O. The benzene solution was dried over Na_2SO_4 and then blown free of solvent on a steam bath under a stream of N_2 gas; 1.8 g. of bis-(diethoxythiophosphoryl) trisulfide (18% yield) and 7.7 g. of the disulfide (83% yield) remained.

The Hydrogen Peroxide Oxidation of O,O-Diethyl Hydrogen Dithiophosphate in Concentrated Acid Medium.—To 180 ml. of concentrated HCl were added successively 18.6 g. of $(C_2H_5O)_2P(S)SH$ and 11.5 cc. of 30% H_2O_2 solution. The latter was added dropwise with vigorous stirring over a period of 2 hr. at a temperature of 25–30°. The reaction mixture was extracted with three 50-ml. aliquots of benzene. The extracts were washed with dilute sodium hydroxide followed by distilled water and the solvent was removed as before. Bis-(diethoxythiophosphoryl) trisulfide (2.5 g., 12% yield) and 11.5 g. of the disulfide (62% yield) remained.

---

[7] H. Rudel and J. M. Boyle, U. S. Patent No. 2,523,146.

CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC
RESEARCH AND DEPARTMENT OF CHEMISTRY,
IOWA STATE UNIVERSITY, AMES, IOWA

Formation Constants of the Complex Species Formed by Interaction of Rare Earth N'-Hydroxyethylethylenediamine-N,N,N'-triacetate Complexes with an Equivalent Amount of Base[1]

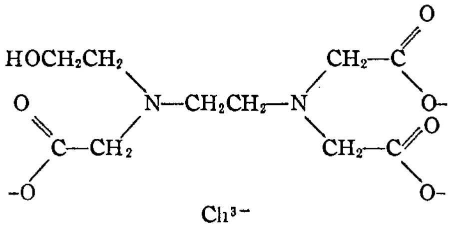
BY ASIM K. GUPTA AND JACK E. POWELL

Received March 5, 1962

From the pH buffering properties and solubility of rare earth N'-hydroxyethylethylenediamine-N,N,N'-triacetate (HEDTA) complexes in base, it has been assumed tentatively that sparingly soluble, neutral, RCh species combine with an equivalent amount of base to form new complex species of the type $RChOH^-$. That is, at constant ionic strength

$$K'_{RChOH} = \frac{[RChOH^-]}{[RCh][OH^-]} \qquad (1)$$

is a constant. Whether the reaction mechanism is regarded as the substitution of a hydroxyl ion for a molecule of coördinated water, as the displacement of the coördinated hydroxyethyl donor group of HEDTA by OH^-, or merely as the loss of a proton by a coördinated entity (either a coördinated water molecule or the hydroxyethyl group) is immaterial.



Ch^{3-}

---

[1] Contribution No. 1111. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

Experimental

Preparation of Reagents.—Rare earth oxides of 99.99% purity were obtained from the rare earth separation group of the Ames Laboratory of the United States Atomic Energy Commission and were converted to rare earth HEDTA chelates either by direct dissolution of the oxide in HEDTA acid or by ion exchange. The complex compounds then were recrystallized several times from water to eliminate possible impurities, and weighed specimens of each were assayed for rare earth content by ashing to R_2O_3 at 900° and weighing.

A 0.002 *M* stock solution of each rare earth chelate was prepared by dissolving the required amount of solid rare earth chelate in conductivity water. Each solution subsequently was standardized by determining its rare earth content by the usual gravimetric procedure, *i.e.*, precipitation as the oxalate followed by thermal decomposition to the oxide at 900°.

A 0.01 *M* solution of carbonate-free KOH was prepared by the method of Powell and Hiller[2] and was standardized against HCdCh by the method of Powell, Fritz, and James.[3]

Experimental Procedure.—Fifty ml. of a RCh stock solution and 10 ml. of 1 *M* KNO_3 solution were introduced into each of ten calibrated 100-ml. volumetric flasks. Varying known amounts (from 1 to 10 ml.) of 0.10 *M* KOH were added to each flask. The solutions next were diluted to 100 ml. so that they were 0.1 *M* with respect to KNO_3 and 0.001 *M* with respect to total rare earth species, and were allowed to equilibrate in a 25° water bath for 100 hr. Then, the pH of each solution was read by means of a Beckman Zeromatic pH meter, standardized against Beckman pH 7 buffer. From the pH values of the various solutions, the hydroxyl ion concentration was computed and substituted in the expression

$$K'_{\mathrm{RChOH}} = \frac{\{[\mathrm{OH_t}] - [\mathrm{OH^-}]\}}{\{1.00 \times 10^{-3} - [\mathrm{OH_t}] + [\mathrm{OH^-}]\}[\mathrm{OH^-}]} \quad (2)$$

where $[\mathrm{OH_t}]$ represents the concentration of hydroxyl ion that would have resulted from the amount of base added had no association occurred.

Results

The log K'_{RChOH} values for individual rare earths given in Table I are average values computed from five to seven random points taken from a plot of pH *vs.* ml. of base added between the limits $a = 0.35$ and $a = 0.85$ (a is the ratio of moles of base added to moles of RCh originally present). The data were treated statistically so that the limits given in Table I define the interval of 90% confidence.

TABLE I

FORMATION CONSTANTS OF THE MONOHYDROXO RARE EARTH HEDTA CHELATES

Rare earth	Atomic no.	Log K'_{RChOH}
Y	39	4.76 ± 0.05
La	57	3.46 ± .03
Ce[a]	58	. . .
Pr	59	3.69 ± .07
Nd	60	3.59 ± .06
Pm	61	. . .
Sm	62	3.70 ± .06
Eu	63	4.03 ± .03
Gd	64	3.98 ± .07
Tb	65	4.52 ± .07
Dy	66	4.88 ± .04
Ho	67	5.12 ± .04
Er	68	5.14 ± .05
Tm	69	5.11 ± .04
Yb	70	5.21 ± .06
Lu	71	5.13 ± .09

[a] The cerium HEDTA solutions became colored when base was added, indicating that the cerium was being oxidized to the tetravalent state.

A real difference is apparent in the stabilities of the hydroxo complexes formed by the light and heavy rare earth HEDTA chelates. For the rare earths lanthanum through samarium the increase in the formation constant is less than twofold (0.24 ± 0.09 log unit) and from holmium through lutetium the increase is less than the experimental error. The difference in log K'_{RChOH} values of the light and heavy groups, however, corresponds to nearly 1.5 log units. This is extremely interesting, since the values of

$$K'_{\mathrm{RCh}} = \frac{[\mathrm{RCh}]}{[\mathrm{R^{3+}}]\,[\mathrm{Ch^{3-}}]} \quad (3)$$

are virtually constant for the middle rare earths, samarium through holmium.[4,5] The value of K'_{YChOH} falls between the values of K'_{TbChOH} and K'_{DyChOH}.

---

[2] J. E. Powell and M. A. Hiller, *J. Chem. Educ.*, **34**, 330 (1957).

[3] J. E. Powell, J. S. Fritz, and D. B. James, *Anal. Chem.*, **32**, 954 (1960).

[4] J. E. Powell and J. L. Mackey, *Inorg. Chem.*, **1**, 418 (1962).

[5] T. Moeller, L. C. Thompson, and R. Ferrús, "Some Aspects of the Stabilities of Amine Polycarboxylic Acid Chelates of Tripositive Rare Earth Metal Ions," in "Rare Earth Research," E. V. Kleber, ed., The Macmillan Co., New York, N. Y., 1961.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MICHIGAN STATE UNIVERSITY,
EAST LANSING, MICHIGAN

The Preparation and Properties of Some Lanthanum(III) Monotelluroöxides

BY RICHARD A. KENT AND HARRY A. EICK

Received March 24, 1962

Since isostructural monothio- and monoselenooxides of all the lanthanum elements have been