

**THERMODYNAMIC INVESTIGATION OF THE
RARE EARTH CHELATES OF
o-(α -2-OXOPROPYLBENZYLIDENEIMINO)
ETHANESULPHONIC ACID**

A SURVEY^{1,2} of the literature has indicated that no work has been done on the La(III), Ce(III), Pr(III), Nd(III), Sm(III) and Gd(III)-chelates of o-(α -2-oxopropylbenzylideneimino) ethanesulphonic acid (H₂OE) derived from benzoylacetone and taurine. Hence the work on the thermodynamic studies of these chelates was undertaken. The measurements were carried out by Calvin-Bjerrum pH-titration technique as used by Irving and Rossotti³ at 25°, 30° and 35° C in aqueous-media having low ionic strengths ($\mu = 0.1, 0.5$ and $0.01M NaClO_4$).

The apparatus and the reagents employed were the same as reported earlier⁴. H₂OE was synthesized by the usual procedure⁵ and its aqueous solution was used.

The following mixtures (total Vol. 25.0 ml.) were titrated against standard carbonate-free sodium hydroxide (0.1 M), and the titration curves had the usual shapes (i) 5.0 ml 0.01 M HClO₄ + 2.5 ml 1.0 M NaClO₄ + 17.5 ml water, (ii) 5.0 ml 0.01 M HClO₄ + 2.5 ml 1.0 M NaClO₄ + 10.0 ml 0.01 M H₂OE + 7.5 ml water, (iii) 5.0 ml 0.01 M HClO₄ + 2.5 ml 1.0 M NaClO₄ + 10.0 ml 0.01 M H₂OE + 2.0 ml 0.01 M(III) + 5.5 ml water.

The dissociation constants of H₂OE and the stability constants of its rare earth chelates were obtained at different ionic strengths and temperatures. The formation curves of the metal chelates suggest the formation of 1:2 complexes. The stabilities of the metal chelates follow the order L(III) < Ce(III) < Pr(III) < Nd(III) < Sm(III) < Gd(III) in agreement with lanthanide contraction.

The thermodynamic stability constants were obtained by the extrapolation of the experimentally obtained constants to zero ionic strength in the plots between log of stability constants against $\sqrt{\mu}$, where μ is the ionic strength. The values of thermodynamic stability constants thus obtained for La(III), Ce(III), Pr(III), Nd(III), Sm(III) and Gd(III)-chelates are respectively: 14.10, 15.70, 17.05, 17.75, 18.45 and 18.70 at 25° C; 14.30, 15.80, 17.20, 17.80, 18.55 and 18.85 at 30° C and 14.45, 15.95, 17.30, 17.95, 18.70 and 18.90 at 35° C. The values of ΔG° (in K. Cal/mole) for these chelates at 25°, 30° and 35° C respectively are: La(III) (19.23, 19.83, 20.37); Ce(III) (21.41, 21.91, 22.49); Pr(III) (23.25, 23.84, 24.39); Nd(III) (24.20, 24.68, 25.30); Sm(III) (25.16, 25.71, 26.36) and Gd(III) (25.50, 26.13, 26.65). The more negative

values of ΔG° at 35° than at 25° or 30° C indicate endothermic nature of reactions.

Harned *et al*⁶ gave the relation between log K₁^H and temperature as $(pK_m^H - ct^2) = -2c\theta t + (pK_m^H - ct^2)$. A plot of $(pK_m^H - ct^2)$ Vs t must be linear and this was found to be true in the present case. The values of θ and pK_m^H for H₂OE were found 254.6° C and 16.36 respectively. ΔH values evaluated from Harned's equation were found by calculation as 9.33, 9.44 and 9.54 at 25°, 30° and 35° C, respectively. These values are found in agreement with those obtained from Gibb's-Helmholtz equation.

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**REDUCTION OF THIOPHOSPHORYL FLUORIDE
AND THIOPHOSPHORYL CHLORIDE WITH
HYDRAZINE HYDRATE**

HYDRAZINE HYDRATE is a powerful reducing agent¹. Recently it has been shown that elemental sulphur undergoes reduction to hydrogen sulphide quantitatively². It is of interest to see whether bound sulphur also would undergo such reductions. Preliminary experiments indicated that thiophosphoryl fluoride and thiophosphoryl chloride would undergo reduction quantitatively giving rise to hydrogen sulphide and phosphorus trihalides. These reactions are found to be highly exothermic. It is therefore necessary to allow the reactants to mix at lower temperature and gradually warm upto room temperature (25° C). The phosphorus trihalides formed undergo further hydrolysis forming phosphorus acid and hydrofluoric/hydrochloric acid. These acids react further with hydrazine hydrate to give respective salts.

Experimental

Reduction of thiophosphoryl fluoride: Pure thiophosphoryl fluoride (PSF₃) is prepared³ and stored in glass globes fitted with suitable ground glass joints and stopcocks. A known amount of the

gas is frozen with liquid nitrogen and the reaction vessel is evacuated. 2 ml of hydrazine hydrate is sucked into the reaction vessel. The reactants are allowed to attain room temperature slowly. A brown solution is formed. The contents are left aside for two hours for completion of the reaction. At the end of this period, two bubblers one containing sodium hydroxide (2N) holding cadmium hydroxide suspension (for the absorption of hydrogen sulphide) and the other containing mercuric chloride solution (5%) (for the absorption of phosphine) are attached. Reaction mixture is then warmed and the gases liberated are swept in a current of nitrogen through the bubblers. The rate of evolution of hydrogen sulphide is enhanced by the addition of 2N hydrochloric acid (20 ml). The flushing is continued for about an

spectrophotometrically using ceric sulphate⁶. The analytical results obtained are presented in Table I.

Reduction of thiophosphoryl chloride: Pure thiophosphoryl chloride is prepared by the addition of sulphur to phosphorus trichloride in the presence of anhydrous aluminium chloride⁷. A known amount (about 200 mg) of thiophosphoryl chloride is treated with 2 ml of hydrazine hydrate. As in the earlier case, a vigorous exothermic reaction sets in. The reaction is controlled by cooling. Hydrogen sulphide formed and traces of phosphine produced are estimated as in the earlier case. The chloride is determined by Volhard's method⁸ in the same aliquot used for phosphorus estimation after filtering off the ammonium phosphomolybdate. The analytical results are presented in Table I.

TABLE I

Reduction of thiophosphoryl fluoride and thiophosphoryl chloride by hydrazine hydrate

Compound	Trial No.	Amount of compound taken in mg	Total sulphur in mg		Total phosphorus in mg.		Total fluoride (a)/chloride (b) in mg	
			Experimental	Calculated	Experimental	Calculated	Experimental	Calculated
a. PSF ₃	1	75.50	20.26	20.17	19.38	19.48	35.50	35.86
	2	101.20	26.90	27.03	26.04	26.11	48.00	48.06
	3	150.00	39.75	40.06	38.69	38.71	71.00	71.25
b. PSCl ₃	1	203.00	38.70	38.62	37.07	37.30	126.70	128.00
	2	298.20	56.02	56.26	54.34	54.64	186.82	188.50
	3	335.70	63.62	63.66	61.41	61.50	209.30	211.30

hour. The bubblers are disconnected. The cadmium sulphide is estimated iodometrically² for the sulphur content. The phosphorus content of the evolved phosphine is estimated iodometrically⁴. It is observed that only traces of phosphine is liberated (less than 0.5% of the total phosphorus).

After removing the gaseous products, the contents of the reaction vessel are made upto a known volume (100 ml) and aliquots are taken for the estimation of phosphorus and fluoride. Hydrazine present in the aliquot is oxidised by refluxing with hydrogen peroxide. This treatment will oxidise phosphite partially to phosphate. For complete oxidation, the solution is refluxed with concentrated nitric acid when all the phosphite gets oxidised quantitatively to phosphate. The phosphate formed is estimated by phosphomolybdate method⁵. In another aliquot, fluoride is estimated

From the analytical results in Table I, it is evident that hydrazine hydrate reduces thiophosphoryl fluoride/chloride quantitatively. The pentavalent phosphorus getting reduced to trivalent state. This reaction can be used as a method for the estimation of thiophosphoryl fluoride/chloride.

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