Anal. Found: C, 93.13; H, 6.96.

Fraction 3, 0.40 g., collected at 180°, also was recrystallized from ethanol to give 30 mg. of rhombs, m.p. 168–170°. A pot residue of 0.70 g. was discarded.

(c) Mole Ratio of 2:1.—This reaction was carried out in exactly the same way as the preceding experiment except that the amount of tolane used was reduced to 1.78 g. (0.01 mole). No hexaphenylbenzene was isolated from the ether-insoluble fraction but 1.52 g. of the orange polymer was obtained. The infrared spectrum of this material was the same as that of the insoluble product found above. No crystalline products were found in the ether-soluble fraction.

Reaction of Tolane and Dimesitylchromium (8:1).—A solution of 0.02 mole of mesitylmagnesium bromide in THF was added under nitrogen to 1.23 g. (0.01 mole) of chromium(II) chloride and 14.24 g. (0.08 mole) of tolane suspended in 100 ml. of THF at − 60°. The reaction mixture was gradually raised to room temperature over a period of 8 hr. and then refluxed for 0.5 hr. It was then hydrolyzed with iced water, and the solid reaction product collected on a filter and extracted with ether. The insoluble fraction remaining on the filter consisted of 0.20 g. of hexaphenylbenzene and a green chromium salt. The ether extract contained an organic fraction which on sublimation yielded 0.01 g. of *trans*-stilbene, m.p. 115–120°. The residue from the sublimation was crystallized from ethyl acetate to give 30 mg. of crystalline substance, m.p. 253–255°, identity unknown.

When the above reaction was performed using only 3.56 g. of tolane (0.02 mole) or a mole ratio of 2:1, no hexaphenylbenzene was found on the filter and the ether soluble fraction gave 0.2 g. of stilbene and 0.1 g. of a crystalline hydrocarbon, m.p. 300–302°, unidentified.

Anal. Found: C, 93.45; H, 6.36; mol. wt., 287.

Reaction of 2-Butyne and Dimesitylnickel.—A mixture of 1.08 g. (0.005 mole) of nickel(II) bromide and 7.12 g. (0.15 mole) of 2-butyne in 50 ml. of THF at −20° was treated under nitrogen with 11.0 ml. (0.01 mole) of a 0.92 molar solution of mesitylmagnesium bromide in THF. The mixture was stirred for 4 hr. at − 10°, for 2 hr. at 0° and then allowed to stand for 2 days at room temperature. Since the color of the mixture was still a deep reddish-brown, a large excess of 2-butyne (17.12 g.) was added after the mixture had been cooled to − 20°. It now was allowed to warm to room temperature and then to 60° for 2 hr. Solvent and excess butyne were removed *in vacuo* and the residue covered with 150 ml. of ether before hydrolyzing it with 0.5 N sulfuric acid. An additional 300 ml. of ether and 200 ml. of water was added, the ether layer separated and washed thoroughly with water. An insoluble white amorphous material (2.83 g.) was left which contained nickel but no halogen and which was completely insoluble in organic solvents.

The ether layer contained 6.40 g. of a brown solid after evaporation of solvent. This material yielded 1.66 g. of the picrate of hexamethylbenzene, m.p. 165–170°, which melted undepressed with and gave the same infrared spectrum as an authentic sample, m.p. 166–171°.

Reaction of 2-Butyne and Dimesitylchromium.—A violet solution of 0.01 mole of dimesitylchromium in 100 ml. of THF at − 20° was treated under nitrogen with 5.4 g. (0.1 mole) of 2-butyne. The reaction mixture was gradually brought to room temperature and then put aside to stand overnight. It was freed of THF *in vacuo* at room temperature and the dark brown residue remaining was triturated with water and ether. Elimination of solvent from the ether layer gave 6.24 g. of oily material from which 1.12 g. of the picrate of hexamethylbenzene, m.p. 170–171°, was isolated. No ether-water insoluble residue was observed.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE PENNSYLVANIA STATE UNIVERSITY, UNIVERSITY PARK, PENNSYLVANIA]

Stability Relationships Among the Rare Earth Acetylacetonates

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Step-wise stoichiometric formation constants have been determined for the reaction between acetylacetone and the rare earths including yttrium. The measurements have been made at a temperature of 30° in 0.1 M aqueous perchlorate. A plot of the logarithm of the first formation constant against the ionic potential shows a linear relation from La to Eu with a change of 0.15 in log K_1 between consecutive elements. After Gd the stability remains nearly constant with a total change in log K_1 from Tb to Lu of 0.2. This relation between the ionic potential and log K has been compared with the same relation for other rare-earth complexes.

Introduction

Previous investigators[1] have studied complex formation between the acetylacetonate ion and the lighter rare-earth ions from La to Eu. The purpose of the present investigation was to extend these measurements to include all the rare earths. Since the earlier measurements were made in a medium of low but varying ionic strength, they were repeated at a constant ionic strength 0.1 M in order to find out the magnitude of the medium effect.

Experimental

Perchlorates of the rare earths and yttrium were obtained by repeated digestion of the corresponding nitrates with perchloric acid. The nitrates (Lindsay Light and Chemical Company, West Chicago, Illinois) were all of analytical grade. Stock solutions of the different metal perchlorates were prepared by dissolving the corresponding perchlorates in water. Their stoichiometric concentrations in the case of La, Ce, Pr, Nd and Sm were determined by precipitation of the oxalates and subsequent ignition of these to the corresponding oxides. The remaining rare earths were analyzed by running a fixed volume of the perchlorate solutions through a hydrogen-saturated ion-exchanger and then titrating the released hydrogen ions with standard sodium hydroxide. The analysis of the first five elements was also checked using this method; the agreement between the two methods was better than 0.5%. Excess perchloric acid in the stock solutions was determined by measuring the hydrogen ion concentration electrometrically. The hydrogen ion concentration in all cases except Ce was found to be less than 1% of the total metal-ion concentration; that is, the hydrogen ion concentration was negligible. Acetylacetone (Eastman Kodak Company) was purified by distillation. The boiling point (136°) and density (0.975 g./ml.) of the distillate agreed with the values reported in the literature for acetylacetone.

Standard sodium hydroxide solution was prepared by dissolving a concentrated carbonate-free sodium hydroxide solution in boiled distilled water. The solution was standardized against potassium hydrogen phthalate. Experimentally, *p*H measurements were made using a Beckman Model G *p*H meter equipped with calomel and glass electrodes. The general procedure in the titration was as follows: 100 ml. of a solution with a metal ion concentration, C_M, of about 2 mM, an acetylacetone concentration of 9.65 mM, a perchloric acid concentration of 3.40 mM

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(1) R. M. Izatt, *et al.*, *J. Phys. Chem.*, **59**, 170 (1955).

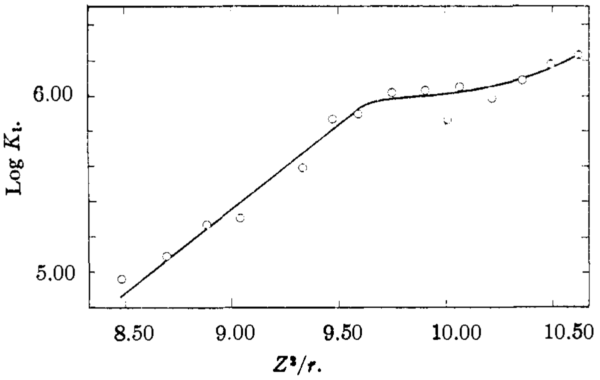

Fig. 1.—Log K_1 as a function of ionic potential, Z^2/r, for the rare earth acetylacetonates.

and sodium perchlorate in an amount sufficient to give an ionic strength of 0.1 *M* was titrated with a standard sodium hydroxide solution.

The *p*H of the solution was read after each addition of base and the lapse of sufficient time for the attainment of equilibrium. All titrations were repeated at least two times and agreement between the *p*H-readings of the different titrations was usually within ±0.02. The solutions were stirred continuously by bubbling nitrogen through them. The temperature was kept constant at 30.0 ±0.1°. Before and after each titration the *p*H-meter was checked against standard buffers of known *p*H. The titrations were continued until precipitation of the neutral complexes occurred. This usually happened at about *p*H 8.0.

Calculations and Results

The formation constants (Table I) were calculated by solving simultaneous equations as described by Block and McIntyre.[2] The uncertainties in the numerical values of the constants are obtained as the maximum deviations from the different mean values obtained by using different sets of *n* values in the simultaneous equations. For comparison, the results of Izatt *et al.*,[1] have also been included in Table I. The solubility product for the neutral complex seems to be increasing with increasing atomic number. This means that higher *n* values can be obtained before precipitation occurs for the later rare earths. Consequently, the accuracy of the second and third constants is greater for these elements. For lanthanum, precipitation occurred at $\bar{n} = 2.1$ while for lutetium not until $\bar{n} = 2.4$.

Hydrolysis of the central atom would seriously affect the accuracy of the formation constants. No problem of this kind arises in the present investigation because the hydrolysis is strongly suppressed by the strong complexing with acetylacetone (HCh). This is shown easily by an estimate of the relative amounts of $MeOH^{+2}$ and $MeCh^{+2}$ in a titration solution of *p*H 7.5: the most strongly hydrolyzed of the rare earths is Lu^{+3} with a hydrolysis constant of about 10^7; we thus have

$$\frac{[MeOH^{+2}]}{[Me^{+3}][OH^-]} = 10^7$$

$$\frac{[MeCh^{+2}]}{[Me^{+3}][acac^-]} = 10^6$$

$$\frac{[MeOH^{+2}]}{[MeCh^{+2}]} = 0.02$$

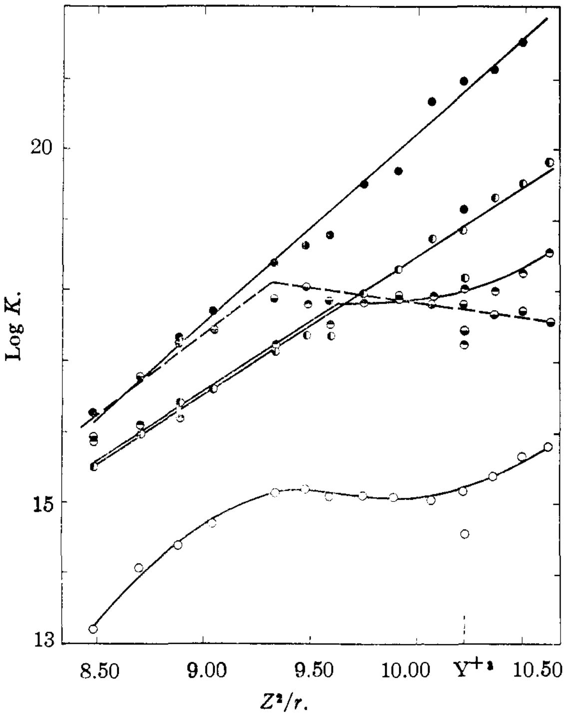

Fig. 2.—Log K_1 as a function of ionic potential, Z^2/r, for various rare earth complexes: O, N-hydroxyethylethylenediaminetetraacetic acid; ◓, ethyleneglycolbis-(aminoethylether)-tetraacetic acid; ◒, bis-(2-aminoethyl)-ether tetraacetic acid; ◐, EDTA; ●, DCTA.

where the last expression has been obtained by dividing the first by the second and inserting known values of $[OH^-]$ and $[Ch^-]$.

Discussion

The tervalent rare-earth ions, all having the same configuration $5s^25p^6$ of the outer electron shells form a unique series for a study of the influence of the size of the central ion on the properties of the coördination compounds. If the metal–ligand bond is considered to be purely electrostatic in nature, the strength of the bond should increase linearly with increasing ionic potential Z^2/r, where Z is the charge and r is the radius of the ion. A measure of this bond strength is ΔH for the reaction

$$Me + A \rightleftarrows MeA \qquad (1)$$

Because of the experimental difficulties in the determination of ΔH, ΔF for the same reaction is often used as an alternative. $\Delta F = -RT \ln K$ where K is the equilibrium constant for the reaction 1. This is a reasonable approximation because the entropy changes ΔS for reactions of the type 1 are often very small and are constant through the series.

In Fig. 1 the logarithms for the first formation constants, log K_1, between the rare earths and acetylacetone have been plotted as a function of the ionic potential. Instead of the expected linearly increasing course, a curve is obtained where only the first part, lanthanum to europium, increases linearly while the second part, gadolinium to lutetium, is nearly constant. The difference in log K_1 between consecutive elements in the first

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[2] B. P. Block and J. H. McIntyre, Jr., THIS JOURNAL, 75, 5667 (1953).

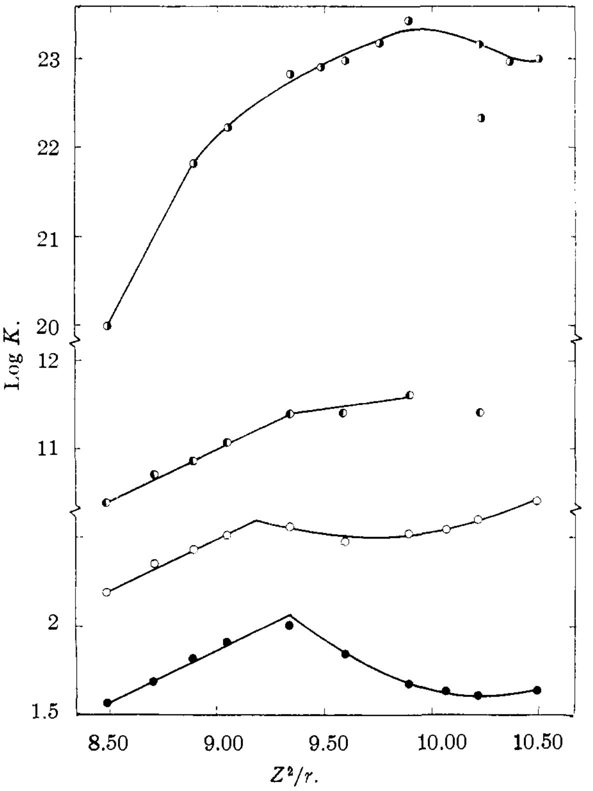

Fig. 3.—Log K_1 as a function of ionic potential, Z^2/r, for rare earth complexes: ●, acetic acid; ○, glycolic acid; ◐, nitrilotriacetic acid; ◑, diethylenetriaminepentaacetic acid; isolated ◑'s, Y^{+3}.

part is about 0.15 and the total variation from Tb to Lu is only 0.2. There is evidently a sharp decrease in the rate of change in stability for the Gd–Lu group as compared with the La–Eu group, a behavior which cannot be explained by the electrostatic bond theory.

This behavior is not peculiar for the acetylacetonates; on the contrary, it seems to be common for most of the rare-earth complexes. Complexes of different substituted ethylenediamine acetic acids have been investigated thoroughly.[3-8] Log K *vs.* ionic potential data for these compounds obtained from the literature have been plotted in Fig. 2 and 3. From the figures it can be seen that all the ligands investigated, except ethylenediaminetetraacetic (EDTA) and cyclohexanediaminetetraacetic (DCTA) acids, show deviation from the expected linear relation. In all cases the first part, La to Eu, shows a fairly good linearity. Because of the many possible coördination sites in these types of ligands, there is a possibility of a change in the number of points of attachment before and after gadolinium. This will result in a change both in ΔH and ΔS and the approximation $\Delta H \approx \Delta F$ is thus no longer valid. That such a configuration change really can occur has been shown by infrared studies of Moeller, *et al.*,[9] and by the thermodynamic work by Betts and Dahlinger.[10] In both cases complexes with EDTA were studied, and the exceptional stability of the heavier rare earths was found to result from an entropy contribution of ΔF. Formation constants are also available for the rare-earth acetates, glycolates and oxalates. A steric effect for the addition of the first ligand is very improbable both for these ligands and for acetylacetone, $\Delta F \approx \Delta H$ should thus be a good approximation for the bond strength.

Sonesson's data[11] for acetates and glycolates are reproduced in Fig. 3. Crouthamel and Martin[12] found log K_1 for the oxalates of Ce, Nd and Yb to be 6.52, 7.21 and 7.30; that is, Yb is much less stable than expected.

The inadequacy of the electrostatic description is also seen if we look at the position of yttrium in the above diagrams. Yttrium with an ionic radius between Ho and Er should have a formation constant between log K_1 for these two ions. However, it is seen from the figures that yttrium actually falls in the Nd-Sm-Eu region for complexes of acetylacetone, bis-(2-aminoethyl)-ether tetraacetic acid, ethyleneglycolbis-(aminoethyl ether)-tetraacetic acid. N-hydroxyethylethylenediaminetriacetic acid and cyclohexanediaminetetraacetic acid.

TABLE I

LOG K_n VALUES FOR THE REACTION OF TERVALENT RARE EARTH IONS WITH ACETYLACETONE (pK = 8.88 ± 0.02) AT T = 30° AND THE IONIC STRENGTH μ = 0.1 AND 0 M

Metal ion	μ = 0.1 M			μ = 0.0 M		
	log K_1	log K_2	log K_3	log K_1	log K_2	log K_3
La^{+3}	4.96 ± 0.03	3.45 ± 0.05	2.5 ± 0.1	5.1	3.8	3.0
Ce^{+3}	5.09 ± .04	3.3 ± .1	2.9 ± .1	5.3	4.0	
Pr^{+3}	5.27 ± .03	3.93 ± .05	3.2 ± .05	5.4	4.1	3.0
Nd^{+3}	5.30 ± .04	4.10 ± .03	3.20 ± .05	5.6	4.3	3.2
Sm^{+3}	5.59 ± .02	4.46 ± .01	2.90 ± .01	5.9	4.5	3.2
Eu^{+3}	5.87 ± .03	4.48 ± .03	3.29 ± .02	6.0	4.5	3.5
Gd^{+3}	5.90 ± .03	4.48 ± .05	3.41 ± .01			
Tb^{+3}	6.02 ± .01	4.61 ± .04	3.41 ± .01			
Dy^{+3}	6.03 ± .01	4.67 ± .02	3.34 ± .04			
Ho^{+3}	6.05 ± .01	4.68 ± .01	3.40 ± .10			
Er^{+3}	5.99 ± .01	4.68 ± .03	3.38 ± .01			
Tm^{+3}	6.09 ± .01	4.76 ± .02	3.48 ± .02			
Yb^{+3}	6.18 ± .01	4.86 ± .02	3.60 ± .02			
Lu^{+3}	6.23 ± .04	4.77 ± .07	3.63 ± .07			
Y^{+3}	5.87 ± .02	4.98 ± .06	3.25 ± .02			

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