distribution in the local environments of the $FeCl_4^-$ units. The less well-defined structure resulting from increased cationic size may produce the observed line broadening. This line broadening is currently being investigated more thoroughly.

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CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY,
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Formation Constants of the Rare Earth Glyoxylate Complex Species[1]

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The stabilities of the first three complex species formed between tripositive rare earth cations and the glyoxylate anion were measured at an ionic strength of 0.10 at 20° by a method involving potentiometric determination of the pH of glyoxylic acid–sodium glyoxylate buffer solutions containing rare earth perchlorates and sodium perchlorate. It was ascertained that rare earth glyoxylate species are more stable than the corresponding acetate species, but are less stable than the corresponding glycolate species. Yttrium forms glyoxylate species which are slightly less stable than those formed by dysprosium.

Introduction

The isolation of stable crystalline hydrates of various adjacently substituted carbonyl compounds, such as dichloroacetaldehyde, chloral, glyoxal, glyoxylic acid, and mesoxalic acid, coupled with the failure of chloral hydrate to give the Schiff test for aldehydes, has been cited as evidence that hydrates of these compounds exist primarily as *gem*-diols.[2,3] Since glyoxylic acid monohydrate can be prepared readily by hydrolysis of dichloroacetic acid, it is sometimes referred to as dihydroxyacetic acid.

It occurred to us that, if glyoxylic acid does exist substantially as the *gem*-diol in its aqueous solutions, since duplicate α-hydroxyl groups are available, the rare earth chelate species formed with the glyoxylate anion might possibly be more stable than the corresponding glycolate species. On the other hand, it has been observed that the affinities of the anions of the α-hydroxycarboxylate homologous series for rare earth metal ions follow the same trend as the affinities of the respective anions for hydrogen ion, *i.e.*, glycolate < lactate < α-hydroxyisobutyrate; see Table I. On this basis, it appeared that the rare earth glyoxylate species should be considerably less stable than the corresponding glycolate species.

Experimental

Standard solutions were prepared from rare earth oxides supplied by the rare earth separation group of the Ames Laboratory of the U. S. Atomic Energy Commission. All the oxides were of 99.9% or greater purity as determined by emission spectroscopy. Each rare earth oxide (with the exception of cerium oxide) was dissolved in a slight excess of perchloric acid, and the excess acid was removed by evaporation to incipient dryness. The resulting basic perchlorate was then dissolved in water and a portion was titrated with perchloric acid to the pH of the equivalence point. This titrated portion then was mixed with the remaining solution and the entire solution was brought to the desired pH. In the case of cerium, it was found that cerium(III) was partially converted to cerium(IV) oxide before all of the excess perchloric acid could be removed. Consequently, the cerous perchlorate stock was prepared from crystalline cerous perchlorate of 99.9% purity supplied by the Lindsay Chemical Division of the American Potash and Chemical Corporation, West Chicago, Ill. Because this solution was found to be slightly on the acid side of the equivalence point, the excess acid concentration was determined, and a suitable correction was applied when the cerous glyoxylate stability constants were computed.

TABLE I

IONIZATION CONSTANTS FOR THE α-HYDROXY ACIDS

Acid	Ionic strength	Ionization constant	Association constant	Ref.
Glycolic	0.1	2.72×10^{-4}	3.7×10^3	4, 5
Lactic	0.1	2.33×10^{-4}	4.3×10^3	4, 5
α-Hydroxy-isobutyric	0.1	1.76×10^{-4}	5.7×10^3	5, 6
Glyoxylic	0.1	6.64×10^{-4}	1.5×10^3	This work

The rare earth stock solutions were carefully standardized by

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(1) Contribution No. 1412. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

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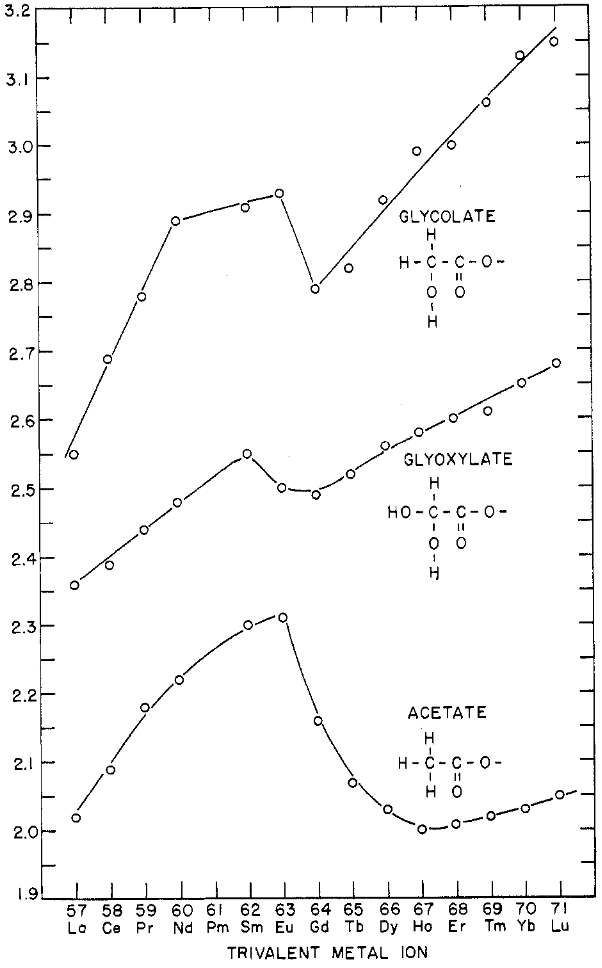

Fig. 1.—A comparison of the first formation constants of rare earth acetates, glyoxylates, and glycolates.

the usual gravimetric procedure and 0.100 *M* stock solutions were prepared by dilution.

Reagent grade glyoxylic acid was dissolved in distilled water to form a concentrated solution which was passed through a hydrogen-form Dowex 50W cation-exchange column, and the effluent solution was standardized by potentiometric titration with standard carbonate-free sodium hydroxide solution.

Glyoxylic acid–sodium glyoxylate buffer solutions were prepared by half-neutralizing aliquots of the stock solution with standard carbonate-free sodium hydroxide solution. It was necessary to use these buffer solutions promptly, due to the fact that the reagent was subject to attack by microorganisms.

The carbonate-free sodium hydroxide solution was prepared by the method of Powell and Hiller.[7] The base was standardized against both potassium acid phthalate and cadmium hydrogen N-hydroxyethyl(ethylenedinitrilo)N,N′,N′-triacetate.[8]

Aliquot portions of standard rare earth perchlorate, glyoxylic acid–sodium glyoxylate buffer, and sodium perchlorate were combined in 100-ml. volumetric flasks to provide a series of solutions for each rare earth which were 4.00×10^{-3} *M* in rare earth and had a final ionic strength of 0.10. These solutions contained varying amounts of glyoxylic acid and sodium glyoxylate. Each solution was then stored for 24 hr. in a constant temperature bath at 20 ± 0.02° before the pH of the equilibrated mixture was read on the expanded scale of a Beckman Model GS pH meter with a reproducibility of ±0.003 pH unit.

The dissociation constant of glyoxylic acid at an ionic strength of 0.10 at 20° was determined from pH values observed in a series of glyoxylic acid–sodium glyoxylate buffer solutions in which the supporting electrolyte was also sodium perchlorate. The constant computed was $(6.64 \pm 0.04) \times 10^{-4}$. This compares favorably with the value of 4.7×10^{-4} determined by Ostwald from electrical conductivity measurements at zero ionic strength.[9]

Titration of glyoxylic acid with base failed to yield any indication that a metal ion might displace more than one proton per ligand molecule, at least not at pH values below 5. Glycolic, lactic, and α-hydroxyisobutyric acids, likewise, combine with metal ions as monobasic bidentate ligands,[4-6] and neutral 1:3 rare earth glycolate, lactate, and α-hydroxybutyrate species have been isolated.[5] As with glycolate, lactate, and α-hydroxyisobutyrate, rare earth cations form 1:1, 1:2, and 1:3 species with the mononegative glyoxylate anion. In our experiments, the average ligand number, $\bar{n}$, never exceeded 3; consequently, it was assumed that only the following equilibria need be considered.

$$R^{3+} + Ch^- \rightleftarrows RCh^{2+};\quad k_1 = [RCh^{2+}]/[R^{3+}][Ch^-]$$

$$RCh^{2+} + Ch^- \rightleftarrows RCh_2^{+};\quad k_2 = [RCh_2^{+}]/[RCh^{2+}][Ch^-]$$

$$RCh_2^{+} + Ch^- \rightleftarrows RCh_3;\quad k_3 = [RCh_3]/[RCh_2^{+}][Ch^-]$$

The stepwise formation constants (k_1, k_2, and k_3) of the individual rare earth glyoxylate species were calculated from the solution compositions, the hydrogen ion concentration (determined from the pH measurements), and the ionization constant of glyoxylic acid, using the method developed by Fronaeus[10] from the earlier method of Bjerrum[11,12] and Leden.[13-15] The

TABLE II

STEPWISE FORMATION CONSTANTS[a] OF THE RARE EARTH GLYOXYLATE SPECIES (20°, $\mu = 0.10$ ($NaClO_4$))

Rare earth	$k_1 \times 10^{-2}$	$k_2 \times 10^{-2}$	$k_3 \times 10^{-1}$	$\log k_1$	k_1/k_2
La	2.29	0.4	0.7	2.36	5.5
Ce	2.45	0.6	0.8	2.39	4.3
Pr	2.72	0.8	1	2.44	3.4
Nd	3.02	1.0	2	2.48	2.9
Sm	3.55	1.1	3	2.55	3.2
Eu	3.17	1.2	3	2.50	2.6
Gd	3.12	1.1	3	2.49	2.8
Tb	3.33	0.8	5	2.52	4.2
Dy	3.64	0.8	5	2.56	4.6
Ho	3.78	0.8	5	2.58	4.8
Er	3.95	1.0	4	2.60	4.0
Tm	4.10	1.0	5	2.61	3.9
Yb	4.45	1.2	5	2.65	3.7
Lu	4.77	1.4	5	2.68	3.4
Y	3.59	0.7	3	2.56	4.9

[a] We are in accord with previous investigators who have used this method[4-6,16] regarding the magnitudes of the possible errors introduced by the inability to determine the hydrogen concentration of the solutions accurately. The values given in this table are subject to absolute errors as great as ±10% in the case of k_1, ±20% in the case of k_2, and ±50% in the case of k_3. In a relative sense, however, values of k_1 can be compared to values of k_1 for adjacent rare earths with somewhat greater confidence. That is to say, a change in k_1 from one element to the next in excess of 2% is probably a real one. In order to allow a close comparison of the experimentally determined k_1 values, we have reported them to three figures. Only the first two digits should be considered significant.

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method has been reviewed recently by Sonesson[16] and has been used so frequently in recent years that no further discussion should be necessary. The constants are listed in Table II.

Discussion

In Fig. 1, log k_1 for the rare earth glyoxylates has been compared to log k_1 for the acetates[17] and the glycolates.[4,5] It is readily apparent that the affinity of the glyoxylate anion for a given rare earth cation is greater than the affinity of the acetate anion, but is less than the affinity of the glycolate anion. One must conclude, therefore, that either the hydrated glyoxylate ion is not really a *gem*-diol, or that the effect of adding a second hydroxyl ion to the α-carbon is to weaken the affinity of the carboxyl group for the rare earth. The latter alternative appears to be the most logical in view of the fact, previously mentioned, that the glyoxylate anion has less affinity for the hydrogen ion than the glycolate anion does.

The stability trend in the rare earth glyoxylate series is more like the trend observed in the glycolate series than that observed in the acetate series. The ratio of k_1 to k_2, however, indicates that the glyoxylate ligand is probably less bidentate in character than the glycolate or lactate ligands. It does not appear that glyoxylate buffer solutions would be of any great value in the ion-exchange separation of rare earths.

The position of yttrium in the rare earth glyoxylate stability sequence is about the same as in the glycolate and lactate sequences, *i.e.*, yttrium tends to resemble terbium and dysprosium.

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Properties and Infrared Spectra in the Potassium Bromide Region of 8-Quinolinol and Its Metal Chelates

BY JAMES E. TACKETT AND DONALD T. SAWYER

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The infrared absorption spectra in the 11–25 μ region of 8-quinolinol and the 8-quinolinol chelates of the alkaline earth ions, manganese(II), cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), lead(II), aluminum(III), iron(III), thorium(IV), and uranium(VI) have been recorded and band assignments have been made. A consideration of the spectral shifts has been used to study the structures of the divalent metal chelates in the solid phase. The spectral data indicate that the divalent ions which have available d-orbitals bond differently with 8-quinolinol from those without available d-orbitals. The "solvate" oxine in the thorium(IV) and uranium(VI) chelates is not distinguishable from the "ligand" oxines on the basis of the infrared data. Structures for the α and β forms of copper oxinate are proposed.

Although the infrared absorption spectra of 8-quinolinol (8-hydroxyquinoline; oxine) and its chelates have not been examined in the potassium bromide region (11 to 25 μ), several groups have considered the spectra of these compounds in other regions; both as saturated solutions in carbon tetrachloride[1] and as crystals.[2–5] In addition there has been much interest in the structures of the various metal oxinates. X-Ray studies have been made of the dihydrates of zinc oxinate[6,7] and copper oxinate[8] as well as of anhydrous copper oxinate.[9] Bis(8-quinolinol-5-sulfonic acid)zinc(II) has been shown to be tetrahederal by resolving its optical isomers.[10] The reaction of copper(II) ion with oxine under various solution conditions results in two forms of anhydrous copper oxinate[11] which have distinctive color, density, infrared spectra, and magnetic moments. Several groups have discussed the nature of the bonding of the "extra" oxine molecule in thorium pentaoxinate ($Th(Ox)_4 \cdot HOx$) and uranium trioxinate ($UO_2(Ox)_2 \cdot HOx$).[12–14]

The present discussion is concerned with the infrared absorption spectra of these compounds in the potassium bromide region and the interpretation of the spectra in terms of bonding and structures. The oxinates of the alkaline earths, the divalent transition metals, lead(II), aluminum(III), iron(III), thorium(IV), and uranium(VI) have been studied as well as the two forms of copper oxinate.

Experimental

Equipment.—The infrared spectra were recorded with a Perkin-Elmer Model 421 recording spectrophotometer equipped with a potassium bromide, linear wave length interchange. The

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