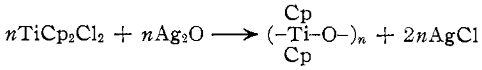
plane, in-phase rock has a strong band at 810 cm.$^{-1}$ with satellites at 845, 831, and 795 cm.$^{-1}$ and possibly 867 and 753 cm.$^{-1}$, caused by crystal effects. A broad strong band at 720 cm.$^{-1}$ was assigned to the Ti–O–Ti stretch.

(C) **Reduction and Oxidation of IV.**—IV (2 g., 0.0045 mole) was dissolved in 100 ml. of tetrahydrofuran in a 250-ml. round bottom, three-necked flask. Argon was swept through the solution to remove the last traces of oxygen in the system. Diborane was then passed into the solution slowly by means of argon and a diborane generator, which was operated by the dropwise addition of boron trifluoride etherate, diluted with diglyme, into a rapidly stirred suspension of sodium borohydride in diglyme. A purple color appeared almost instantaneously, followed by a gradual development of blue-green solution in 3 hr. The reaction was allowed to proceed at room temperature for 16 hr. Dry air was then passed slowly through the reaction mixture causing an exothermic reaction to occur which was accompanied by a color change to bright green and then to yellow with separation of a yellow solid. All of the solvent was removed with the flow of dry air. The solid residue was suspended in 30 ml. of cold de-ionized water, filtered, and washed with a small amount of water and ether, to give 0.54 g. of a yellow solid, m.p. 230° dec. The analysis is shown in Table I. The infrared spectrum showed C–H stretch (3100 cm.$^{-1}$), cyclopentadienyl bands at 1018 cm.$^{-1}$ and a broad band at 855 cm.$^{-1}$; broad bands at 795 and 720 cm.$^{-1}$ were considered to arise from Ti–O–Ti bands. Some evidence for –OH group was seen in the 3050 cm.$^{-1}$ region.

(D) **Simultaneous Oxidation and Reduction of I.**—I (3 g., (0.012 mole) was dissolved in 50 ml. of acetone. Granular zinc (2.00 g., 0.030 g.-atom) was added and the mixture stirred for 4 hr. in dry air. A light yellow precipitate was obtained and removed from the unreacted zinc by decantation and filtering. The precipitate was washed with two 10-ml. and one 5-ml. portions of cold de-ionized water and then dried under vacuum at room temperature to give 1.20 g. of product, m.p. 230° dec. More product was obtained by longer treatment of the acetone solution with the granular zinc followed by a similar work-up (see analysis, Table I). The infrared spectrum was almost identical with that of material obtained in (C).

(E) **Reaction of I and Silver(I) Oxide.**—Equimolar quantities of I and silver oxide were stirred for 16 hr. in acetone in an attempt to obtain the reaction



$$n\text{TiCp}_2\text{Cl}_2 + n\text{Ag}_2\text{O} \longrightarrow (-\overset{\text{Cp}}{\underset{\text{Cp}}{\text{Ti}}}-\text{O}-)_n + 2n\text{AgCl}$$

A yellow precipitate and pale red solution were obtained. The yellow material was insoluble and could not be separated from the silver chloride. Evaporation of the solution gave a gummy material whose infrared spectrum exhibited cyclopentadienyl and Ti–O–Ti bands. It was concluded that this material was mainly the dimer or oligomers.

(F) **Attempted Hydrolysis of I.**—I (1 g.) was refluxed in 50 ml. of de-ionized water for 3 hr. A small amount (0.08 g.) of a pale insoluble material precipitated. Infrared examination of this material shows little or no cyclopentadienyl groups present. The filtrate was reduced in volume and red crystals appeared on cooling (0.23 g.) which were shown by melting point and infrared to be I. A further 0.30 g. of I also was obtained by further reduction in volume. It was also noted in a subsequent experiment that the filtrate obtained after refluxing 3 hr. could be boiled for a further 3 hr. without any signs of decomposition.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CASE INSTITUTE OF TECHNOLOGY, CLEVELAND 6, OHIO

The Reaction Product of Bis(2,4-pentanediono)titanium(IV) Dichloride with Anhydrous Iron(III) Chloride

BY R. J. WOODRUFF, JAMES L. MARINI, AND J. P. FACKLER, JR.

Received October 8, 1963

The reaction of anhydrous ferric chloride with bis(2,4-pentanediono)titanium(IV) dichloride in glacial acetic acid is shown to lead to the formation of tris(2,4-pentanediono)titanium(IV) tetrachloroiron(III). This species has been characterized by its ultraviolet spectrum and is shown to be a 1:1 electrolyte in nitrobenzene, nitromethane, and acetonitrile. Mössbauer studies have suggested the presence of the tetrahedral FeCl_4^- species in the solid state. An interesting apparent correlation is observed between the size of the cation in the M[FeCl_4] complexes that have been studied and the Mössbauer half-width for absorption by FeCl_4^-.

The reaction of titanium tetrachloride with acetylacetone (H-acac) in anhydrous solvents[1–5] leads to the formation of $\text{Ti(acac)}_2\text{Cl}_2$. This material originally was formulated[2–4] as $[\text{Ti(acac)}_3]_2\text{TiCl}_6$ by analogy with the formation of cationic species of the type M(acac)_3^+ with other group IV elements.[6] In addition, Dilthey[2] was able to prepare a crystalline material which appeared to be $\text{Ti(acac)}_3\text{FeCl}_4$.

Mehrotra and co-workers[5,7,8] recently re-investigated the reaction of titanium tetrachloride with acetylacetone. Molecular weight and other studies showed quite conclusively that the product is monomeric[7] and corresponds to the simple formula $\text{Ti(acac)}_2\text{Cl}_2$. Based on these results, Pande and Mehrotra[5] suggested the reaction product of $\text{Ti(acac)}_2\text{Cl}_2$ with FeCl_3 in glacial acetic acid[2] could be formulated as a TiCl_4 adduct of iron(III) acetylacetone. Additional studies by Puri and Mehrotra[8] suggested that this material has a low conductivity in nitrobenzene (molar conductance values

---

[1] A. Rosenheim, W. Loewenstamm, and L. Singer, *Ber.*, **36**, 1833 (1903).

[2] W. Dilthey, *ibid.*, **37**, 589 (1904).

[3] R. C. Young and A. J. Van der Weyden, *Inorg. Syn.*, **2**, 119 (1946).

[4] V. Doron, *ibid.*, **7**, 50 (1963).

[5] K. C. Pande and R. C. Mehrotra, *Chem. Ind.* (London), **35**, 1198 (1958).

[6] G. T. Morgan and R. B. Tunstall, *J. Chem. Soc.*, **125**, 1963 (1924).

[7] D. M. Puri and R. C. Mehrotra, *J. Less-Common Metals*, **3**, 247 (1961); *ibid.*, **3**, 253 (1961).

[8] D. M. Puri and R. C. Mehrotra, *ibid.*, **5**, 2 (1963).

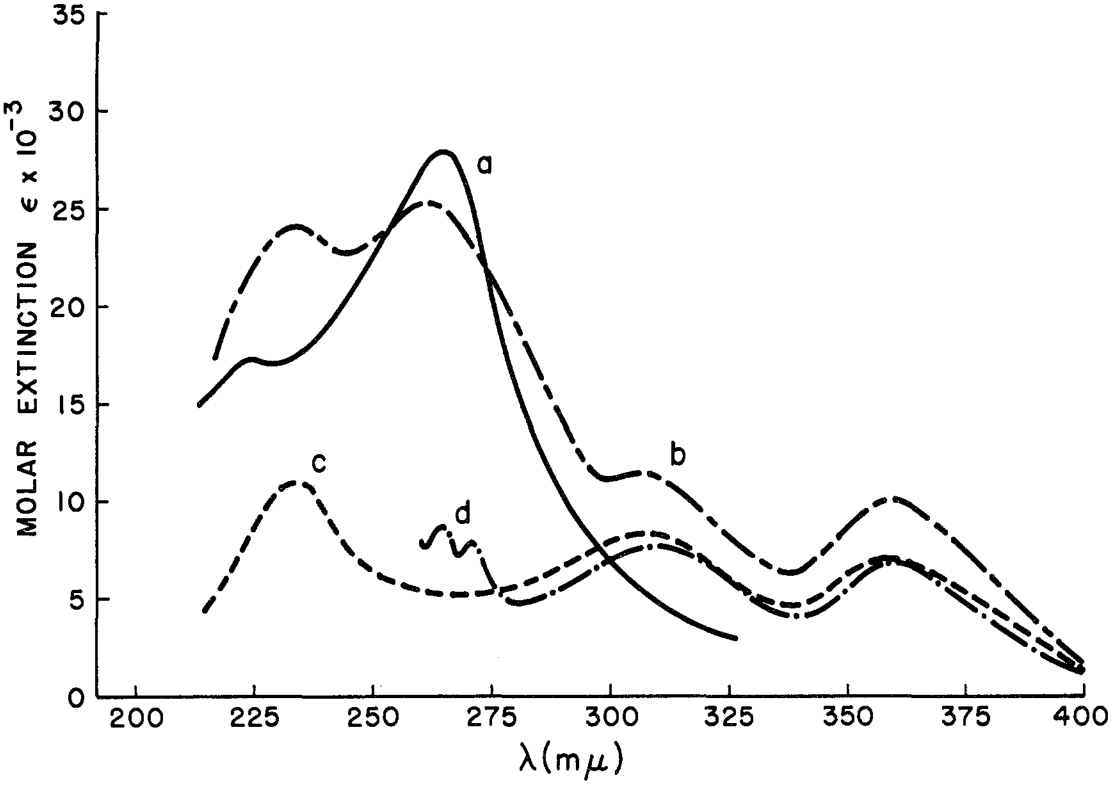
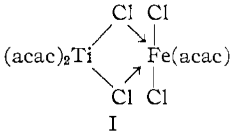
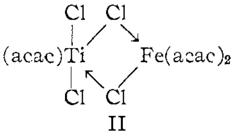


Fig. 1.—The ultraviolet spectra of complexes in acetonitrile: a, Ti(acac)$_3$FeCl$_4$ (4.64 × 10^{-4} *M*); b, Fe(acac)$_3$; c, KFeCl$_4$; d, (C$_6$H$_5$)$_4$AsFeCl$_4$ (1.27 × 10^{-3} *M*).

of 8.6–15.3 at 21° are reported for 1.4–3.4 × 10^{-3} *M* solutions), and since it can be formed starting with Fe(acac)$_3$ they formulated it as either I or II. Since the ultraviolet spectrum of tetrahedral FeCl$_4^-$ is quite characteristic of the species[9-11] and since the original formulation by Mehrotra, Fe(acac)$_3$·TiCl$_4$, left much to be understood, we[12] began an investigation of this material.



I



II

Experimental

Materials.—Tris(2,4-pentanediono)titanium(IV) tetrachloroferrate(III) was prepared by the method of Dilthey,[2] m.p. 173–175° (uncor.). *Anal.* Calcd. for C$_{15}$H$_{21}$O$_6$TiFeCl$_4$: C, 33.1; H, 3.9; Fe, 10.2; Ti, 9.2. Found: C, 33.3; H, 4.0; Fe, 10.5; Ti, 8.9.

Solvents used were distilled through a 3-ft. glass helix column and stored over Linde Molecular Sieves.

Potassium tetrachloroferrate(III) for spectral measurements was prepared according to the method of Kurnakov.[13]

Tetraphenylarsonium(III) tetrachloroferrate(III) was prepared by mixing stoichiometric amounts of anhydrous FeCl$_3$ with (C$_6$H$_5$)$_4$AsCl in a minimum amount of nitromethane and adding ethyl ether. The yellow needles were removed and recrystallized from nitromethane with ether,[14] m.p. 183–185°.

Spectral Measurements.—Ultraviolet spectra were recorded for acetonitrile solutions of TiCl$_4$, KFeCl$_4$, Fe(acac)$_3$, Ti(acac)$_3$-FeCl$_4$, and (C$_6$H$_5$)$_4$AsFeCl$_4$ using Cary Model 11 and Beckman DK spectrophotometers. Solutions of Ti(acac)$_3$FeCl$_4$ and Fe(acac)$_3$ were prepared accurately by weight to ~10^{-3} *M* and subsequently diluted. The most concentrated solution observed with a 0.1-cm. cell is that recorded in Fig. 1 for Ti(acac)$_3$-FeCl$_4$.

Conductance Measurements.—A Fisher vertical-plate cell, fitted with a thermometer and platinized by usual methods, was

Table I

Molar Conductances of Ti(acac)$_3$FeCl$_4$ in Various Solvents at 30°

Solvent	Concn., l.$^{-1}$ mole × 10^3	Λ^b
CH$_3$CN^a	0.240	177
	0.979	184
	10.0	156
	23.2	116
	40.1	100
C$_6$H$_5$NO$_2$^{a}	0.540	37.5
	0.800	37.8
	3.10	35.5
	8.65	30.8
CH$_3$NO$_2$^{a}	4.72	107
	10.8	93.5
	21.5	82

[a] Specific conductance of pure solvents (ohm^{-1} cm.$^{-1}$): CH$_3$CN, 1.048 × 10^{-6}; CH$_3$NH$_2$, 8.00 × 10^{-6}; C$_6$H$_5$NO$_2$, <1.0 × 10^{-7}. [b] Molar conductance, ohm^{-1} mole^{-1} cm.^{2}.

---

(9) P. A. McCusker and S. M. S. Kennard, *J. Am. Chem. Soc.*, **81**, 2976 (1959).

(10) R. S. Drago, 145th National Meeting, American Chemical Society, New York, N. Y., Sept., 1963.

(11) H. L. Friedman, *J. Am. Chem. Soc.*, **74**, 5 (1952).

(12) In addition to R. Woodruff, M. Nelson, and M. Burleigh contributed to this study as members of the Chemistry 106 class at the University of California, Berkeley, during 1962.

(13) N. S. Kurnakov, *Akad. Inst. Obshch. Neorgan. Khim.* (*Sekt. Fiz. i Anal. Khim. Izv.*), May 16, 1961.

(14) B. Zastow and R. E. Rundle, *J. Phys. Chem.*, **61**, 490 (1957), determined the X-ray crystal structure of a sample of (C$_6$H$_5$)$_4$AsFeCl$_4$ supplied to them by H. Friedman.[11] No characterization data other than X-ray analysis are reported.

TABLE II

MÖSSBAUER ABSORPTION SPECTRA OF SPECIES CONTAINING $FeCl_4^-$

Complex	Isomeric shift, cm./sec.[a]	Line width,[a] cm./sec.
$(C_5H_5N)_3Fe_2Cl_9$[b]	0.047	0.045
$(CH_3)_4NFeCl_4$[b]	0.045	0.054
$Ti(acac)_3FeCl_4$	0.045	0.095
$(C_6H_5)_4AsFeCl_4$	0.045	0.110
$Fe(acac)_3$ (octahedral)	0.075	0.20
$FeCl_3$ (octahedral)[b]	0.069	0.041

[a] Uncertainty appears to be approximately ±0.002 cm./sec. All spectra were determined at 78°K. The shifts reported are with respect to the resonance observed in a dilute solution of iron in chromium. [b] Reference 21.

used. The cell constant using 0.10 *M* KCl at 30° was determined to be 2.022 cm.$^{-1}$. A Leeds and Northrup No. 4866 galvanometer was used or the measurements, which are presented in Table I.

Mössbauer Spectra.—Isomeric shifts and line widths for Mössbauer absorbance by Fe^{57}, at 78°K., were kindly supplied by G. K. Wertheim. These data are presented in Table II.

Results

In Fig. 1 the spectra of $Fe(acac)_3$, $Ti(acac)_3FeCl_4$, $(C_6H_5)_4FeCl_4$, and $KFeCl_4$ are presented as they occur in anhydrous acetonitrile. Due to some solubility problems, the spectrum of $KFeCl_4$ is presented with an arbitrary absorbance scale. However, the spectra of $FeCl_4^-$ in various solvents[10] suggest that the molar extinction values will be near those found in HCl-dioxane[9] solutions. The spectrum of $Fe(acac)_3$ is essentially identical with those of Holm and Cotton[15] and Barnum.[16]

The spectrum of $Ti(acac)_3FeCl_4$ recorded in Fig. 1 is that of a solution $\sim 4.6 \times 10^{-4}$ *M*. Reducing the concentration to $\sim 3.7 \times 10^{-5}$ *M* in acetonitrile causes the 310 and 370 mμ bands, characteristic[9,10] of $FeCl_4^-$, to decrease considerably in intensity. $(C_6H_5)_4FeCl_4$ also has been noticed to display spectral changes at concentrations less than 10^{-3} *M* in CH_3CN.

The conductivity data of Puri and Mehrotra[8] could not be duplicated by us.

In nitrobenzene at 30°, molar conductances from two to three times the values reported by Mehrotra were obtained. Qualitative measurements in both nitrobenzene and nitromethane suggest that small amounts of water in these solvents lower the molar conductances of the solutions of $Ti(acac)_3FeCl_4$. In each of the solvents used, acetonitrile, nitrobenzene, and nitromethane, molar conductances observed agree reasonably well with data reported by others[17-19] for 1:1 electrolytes in these media.

The Mössbauer isomeric shift[20] for $Ti(acac)_3FeCl_4$ (Table II) in the solid state compares favorably with that of $(C_6H_5)_4AsFeCl_4$ which is known to contain slightly distorted tetrahedra[14] of $FeCl_4^-$. In fact, the isomeric shift for the tetrahedral $FeCl_4^-$ species in all cases measured to date appears very near 0.045 cm./sec. A significant shift occurs when the iron is octahedrally bound.[21]

Discussion

The spectral and conductivity data presented here suggest strongly that $[Ti(acac)_3]^+$ and $FeCl_4^-$ are the predominant species when $Ti(acac)_3FeCl_4$ is dissolved in acetonitrile and other weakly interacting solvents.[22] In addition, Mössbauer spectra support the structure proposed for $Ti(acac)_3FeCl_4$ by suggesting this structure is present in the solid state. The data indicate that the environment of the Fe^{57} in $Ti(acac)_3FeCl_4$ (see below) is similar[23] to the environment of Fe^{57} in $(C_6H_5)_4AsFeCl_4$. X-Ray powder patterns show[24] that the compounds are not isostructural, however.

The unusually large line width observed for the Mössbauer spectrum of $Ti(acac)_3FeCl_4$ initially was surprising in view of the natural line width of 0.020 cm./sec. for the equipment and the observed line width of ~0.050 cm./sec. in other tetrahedral $FeCl_4^-$ complexes. Since the large width in $Fe(acac)_3$ still remains unexplained, some doubt was raised concerning the structure of $Ti(acac)_3FeCl_4$. For this purpose the Mössbauer spectrum of $(C_6H_5)_4AsFeCl_4$ was observed.

The line width for $(C_6H_5)_4AsFeCl_4$ was found to be similar to that in $Ti(acac)_3FeCl_4$. This indicated that the size of the cation M may strongly influence the line width of the Fe^{57} in $M[FeCl_4]$. In fact, using Pauling[25] radii to estimate effective cationic sizes,[26] a correlation between cationic size and line width can be made. Assuming cationic radii of 1.6 Å. for $C_6H_5N^+$, 2.8 Å. for $(CH_3)_4N^+$, 6.0 Å. for $Ti(acac)_3^+$, and 6.5 Å. for $(C_6H_5)_4As^+$, a plot of line width *vs.* cationic radii suggests a linear relationship,[26] intersecting the natural line width of 0.020 cm./sec.

Since several things contribute to line broadening, such as dislocations, impurities, etc., a linear variation with cationic size may be fortuitous. Due to the molecular complexity accompanying the increased cationic size, it is possible that the larger cations allow a greater

---

(15) R. H. Holm and F. A. Cotton, *J. Am. Chem. Soc.*, **80**, 5658 (1958).

(16) D. W. Barnum, *J. Inorg. Nucl. Chem.*, **21**, 221 (1961).

(17) D. J. Phillips and S. Y. Tyree, Jr., *J. Am. Chem. Soc.*, **83**, 1806 (1961).

(18) J. Lewis, R. S. Nyholm, and D. J. Phillips, *J. Chem. Soc.*, 2177 (1962).

(19) H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Co., New York, N. Y., 1958, p. 705.

(20) "The Mössbauer Effect," H. Frauenfelder, Ed., W. A. Benjamin Company, New York, N. Y., 1962.

(21) A. P. Ginsberg and M. B. Robin, *Inorg. Chem.*, **2**, 817 (1963). The visible spectrum of $Ti(acac)_3FeCl_4$, as obtained by melting the material between glass plates, shows no detail due to a strong ultraviolet tail extending to about 600 mμ.

(22) It is known that hydrolysis of the material leads to the formation[5] of $Fe(acac)_3$. The spectral changes which occur at low concentrations of $Ti(acac)_3FeCl_4$ and $(C_6H_5)_4AsFeCl_4$ may be due to hydrolysis with residual water present in the solvent or, more reasonably, solvolysis of the $FeCl_4^-$ (*e.g.*, $FeCl_4^- \rightleftharpoons FeCl_3(\text{solvent}) + Cl^-$) may take place.[10]

(23) M. Cox indicates that in work done with J. Lewis and R. S. Nyholm, several solid complexes containing $M(acac)_3^+$ cations have been obtained with group IV elements including titanium(IV). We wish to thank these people for informing us of their study prior to publication of these results.

(24) The authors wish to thank Joyce Hashagen for these results.

(25) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948, p. 164.

(26) These radii admittedly are rather subjective but should display expected trends in cationic sizes. The cationic size calculated for $(C_6H_5)_4As^+$ appears to be somewhat larger than observed[14] in $(C_6H_5)_4AsFeCl_4$. Recent data from A. P. Ginsberg suggest β-$Cs_3Fe_2Cl_9$ does not follow this correlation, however the crystal structure of this latter material probably is considerably different from that of the other complexes studied.

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.

Acknowledgments.—We wish to thank Dr. G. K. Wertheim for supplying Mössbauer results to us and Dr. A. P. Ginsberg for furnishing some data on line widths in other $M[FeCl_4]$ complexes. Discussions with K. Knox and D. Whitman were particularly beneficial. Acknowledgment is made to the donors of the Petroleum Research Fund administered by the American Chemical Society and the Case Research Fund for partial support of this work.

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

Formation Constants of the Rare Earth Glyoxylate Complex Species[1]

BY J. E. POWELL AND Y. SUZUKI

Received December 16, 1963

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.

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

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.

The rare earth stock solutions were carefully standardized by

---

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

(2) L. F. Fieser and M. Fieser, "Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1944, p. 222.

(3) D. J. Cram and G. S. Hammond, "Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1959, p. 272.

(4) R. H. Karraker, "Stability Constants of Some Rare Earth Metal Chelates," unpublished doctoral dissertation, Iowa State University of Science and Technology, Ames, Iowa, 1961.

(5) J. E. Powell, R. H. Karraker, R. S. Kolat, and J. L. Farrell, "Complex Systems of the Rare-Earth Metals with Glycolate, Lactate and α-Hydroxyisobutyrate Ligands," paper presented to the 3rd Rare Earth Conference held at Clearwater, Fla., April 21–24, 1963, to be published in "Rare-Earth Research," K. S. Vorres, Ed., 1964.

(6) R. S. Kolat, "A Study of the Rare-Earth Metal Complexes," unpublished doctoral dissertation, Iowa State University of Science and Technology, Ames, Iowa, 1961.