

of doubly bridged compounds.^{1,21} The results in the present work indicate that the same behavior is true for the case of metal-centered autoxidation processes. Doubly bridged dioxygen complexes seem to undergo slower decomposition reactions, probably because the rigidity caused by the double bridge makes dissociative processes more difficult.

The results obtained for the decomposition of BISBAMP in the presence of copper(I) clearly indicate mechanisms that are different from those observed with cobalt(II). Although there is no conclusive evidence that the decomposition of BISBAMP occurs through the formation of copper dioxygen complexes, this seems to be the most plausible route. In general, the synthesis

of copper dioxygen complexes presents many complications, and only recently has their existence been clearly demonstrated.²² Additional work is needed to determine the requirements for formation and decomposition of copper dioxygen complexes with various types of coordinating ligands.

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Registry No. $\text{Co}_2\text{LO}_2(\text{OH})_2^{2+}$, 121574-26-3; $\text{Co}_2\text{LO}_2(\text{OH})_3^+$, 121574-27-4.

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Potentiometry of Mixtures: Metal Chelate Stability Constants of 1-Hydroxy-3-oxapentane-1,2,4,5-tetracarboxylic Acid and 3,6-Dioxaoctane-1,2,4,5,7,8-hexacarboxylic Acid

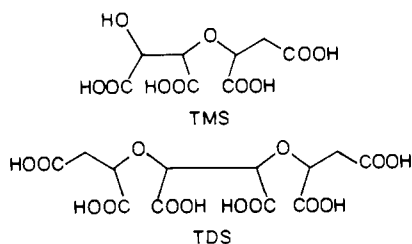
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A novel and unique method is described in which potentiometric p[H] determinations of stability constants are made on two solutions containing mixtures of 1-hydroxy-3-oxapentane-1,2,4,5-tetracarboxylic acid (TMS) and 3,6-dioxaoctane-1,2,4,5,7,8-hexacarboxylic acid (TDS), along with known concentrations of other ligands as minor impurities. This report provides experimental evidence that the method works well because of successful determination of metal ion equilibrium constants for the reaction of TMS and TDS with 11 metal ions— Cu^{2+} , Ni^{2+} , Mn^{2+} , Cd^{2+} , Zn^{2+} , Hg^{2+} , Pb^{2+} , Ca^{2+} , Mg^{2+} , Fe^{3+} , and Al^{3+} . The validity of the method described for the potentiometric determination of equilibrium constants in mixtures is demonstrated by carrying out the same procedures on a pure aqueous solution of TDS.

Introduction

Maleic anhydride reacts with tartaric acid to yield a useful chelating mixture the principal components of which are tartaric monosuccinic acid, TMS (1-hydroxy-3-oxapentane-1,2,4,5-tetracarboxylic acid), and tartaric disuccinic acid, TDS (3,6-dioxaoctane-1,2,4,5,7,8-hexacarboxylic acid). Since the synthesis



creates asymmetric carbon centers at α -succinate positions, several forms of each ligand are possible. Protonation constants and mononuclear metal ion formation constants are not expected to differ greatly for such pairs of stereoisomers.

In practice, the physical separation of pure TMS and TDS from the mixture formed is difficult. However, analytical HPLC has provided complete analyses of the components present. After the removal of extraneous inorganic ions and salts, each solution was found to contain tartaric acid, malic acid, maleic acid, and fumaric acid, in addition to TMS and TDS. The analyses provided not only the qualitative identification of each component but also quantitative determinations of the percentage compositions of the mixtures.

The purpose of this research was to determine the protonation constants and stability constants of TMS and TDS on mixtures where the complete separation of each component had not been accomplished. Since quantitative investigations of such mixtures, as well as of the pure ligands themselves, have not been described

Table I. Compositions of Reaction Mixtures Investigated

species	fractional concn	
	TMS-rich	TDS-rich
TMS	0.738	0.370
TDS	0.053	0.623
tartaric acid	0.134	0.007
malic acid	0.020	
maleic acid	0.031	
fumaric acid	0.024	

in the literature previously, the success and limitations of this study represent a new procedure for stability constant determinations. The development of such a technique for the study of complex mixtures is made possible by the use of iterative methods and the FORTRAN program BEST,¹ which places no constraints on the number and types of components present or the number and types of species formed in complex systems studied by potentiometric measurements of p[H] ($\text{p[H]} = -\log [\text{H}^+]$).

Experimental Section

Mixtures of two considerably different ratios of TMS and TDS concentrations were investigated. HPLC analyses (accuracy <1%) of the mixtures were performed by Procter and Gamble Co., Inc. The complete results of the analysis for the components present in these TMS-rich and TDS-rich solutions are displayed in Table I.

The basic experimental plan is to make parallel measurements in TMS-rich and TDS-rich solutions followed by data analysis accomplished in the following steps: (1) refinement of the TMS constants by using TMS-rich data; (2) refinement of the TDS constants by using TDS-rich data; (3) iteration of the calculations between steps 1 and 2 until the calculated equilibrium constants become constant.

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Table II. Overall Equilibrium Constants Used To Correct for the Presence of Tartaric Acid, Malic Acid, Maleic Acid, Fumaric Acid, and Chloride Complexes

central ion	overall equil ^b const	log β				Cl ⁻
		tartaric acid	malic acid	maleic acid	fumaric acid	
H ⁺	β_{HL}	3.95	4.71	5.82	4.10	
Cu ²⁺	β_{H_2L}	6.77	7.95	7.57	6.95	
	β_{ML}	3.42	3.42	3.4	2.0 ^c	
	β_{MHL}		6.71			
	$\beta_{MH_{-1}L}$	-1.45	-1.12			
Ni ²⁺	$\beta_{M_2H_{-3}L_3}$		-5.17			
	β_{ML}	2.20	3.17	2.0	1.5 ^a	
	β_{MHL}	4.96	6.54			
Cd ²⁺	β_{ML}	1.70	2.36	2.4 ^c	1.9 ^c	
	β_{MHL}	4.92	6.05			
Zn ²⁺	β_{ML}	2.68	2.93	2.0	1.5 ^c	
	β_{MHL}		6.37			
Hg ²⁺	β_{ML}	7.0	7 ^c	6 ^c	3 ^c	6.74
	β_{ML_2}					13.22
	β_{ML_3}					14.20
	β_{ML_4}					15.30
	$\beta_{MH_{-1}L}$					3.51
Pb ²⁺	β_{ML}	3.12	2.45	3.2	2 ^a	
	β_{MHL}	5.71				
Mn ²⁺	β_{ML}	2.49	2.24	1.68	0.99	
	β_{MHL}	5.16				
Ca ²⁺	β_{ML}	1.94	1.96	1.1 ^c	0.48	
	β_{MHL}	5.06	5.77			
Mg ²⁺	β_{ML}	1.36	1.70	1.4 ^c	0.5 ^c	
	β_{MHL}	4.87	5.61			
Al ³⁺	β_{ML}			3.0 ^c	2.5 ^c	
	$\beta_{MH_{-1}L}$	1.18	1.2 ^c			
Fe ³⁺	$\beta_{MH_{-2}L}$	-3.97				
	β_{ML}	6.49	7.13	6 ^c	2 ^c	
	$\beta_{M_2H_{-2}L_2}$	11.87	12.85			
	$\beta_{M_2H_{-3}L_2}$	9.05				
	$\beta_{M_3H_{-4}L_3}$	9.48				
	$\beta_{M_3H_{-2}L_2}$		17.85			
	$\beta_{M_3H_{-4}L_3}$		25.97			

^a $t = 25.0$ °C; $\mu = 0.20$ M. ^b $\beta_{HL} = [HL]/[H^+][L]$; $\beta_{H_2L} = [H_2L]/[H^+]^2[L]$; $\beta_{ML} = [ML]/[M][L]$; $\beta_{MHL} = [MHL]/[M][H^+][L]$; $\beta_{MH_{-1}L} = [MH_{-1}L][H^+]/[M][L]$; $\beta_{MH_{-2}L} = [MH_{-2}L][H^+]^2/[M][L]$; $\beta_{M_2H_{-3}L_2} = [M_2H_{-3}L_2][H^+]^3/[M]^2[L]^2$; $\beta_{M_2H_{-2}L_2} = [M_2H_{-2}L_2][H^+]^2/[M]^2[L]^2$; $\beta_{M_3H_{-4}L_3} = [M_3H_{-4}L_3][H^+]^4/[M]^3[L]^3$; $\beta_{M_3H_{-2}L_2} = [M_3H_{-2}L_2][H^+]^2/[M]^3[L]^2$; $\beta_{M_3H_{-4}L_3} = [M_3H_{-4}L_3][H^+]^4/[M]^3[L]^3$. ^c Estimated values.

The potentiometric equilibrium measurements of the ligand solutions in the absence and presence of metal ions were carried out with a Corning Model 130 pH meter fitted with blue-glass and calomel reference electrodes and were calibrated to read $-\log [H^+]$ directly. The temperature was maintained at 25.00 ± 0.02 °C, and the ionic strength was adjusted to 0.100 M by the addition of the appropriate amount of KCl. Typical concentrations of experimental solutions are on the order of 0.002 M in total ligand and molar equivalent or 2 times the molar equivalent concentrations of metal ion. Carbon dioxide was excluded from the reaction mixture by maintaining a slight positive pressure of purified nitrogen in the reaction cell. A solution of carbonate-free 0.1009 M NaOH was used as titrant and $-\log K_w$ was measured as -13.78 .² The p[H] profiles obtained consisted of approximately 40–50 p[H] measurements vs mole of standard base per moles of chelating ligand present in the experimental solution.

All proton association constants were calculated with the program BEST¹ with the aid of a Digital PDP/11 computer. Formation constants of the 1:1 and 2:1 metal-ligand complexes were obtained through least-squares refinement of 1:1 and 2:1 p[H] profiles. Throughout this investigation the function minimized is the weighted average of the sums of the squares of deviations between calculated and observed p[H⁺] values, σ_{fit} .

The species considered present in the experimental solutions are those that one would expect to be formed according to established principles of coordination chemistry, while taking into account types of donor groups, their numbers and arrangement in the given ligand, the nature

Table III. Logarithms of the Protonation Constants^a Resulting from Refinement of Data from Mixtures of TMS and TDS

n	log $K_n^{H^+}$ ^b	
	TMS	TDS
1	5.73	5.97
2	4.38	5.40
3	3.34	4.40
4	2.41	3.69
5		2.99
6		2.28
σ_{fit}	0.0015	0.0007

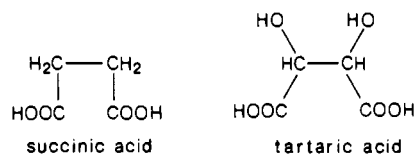
^a $\log K_n^{H^+} = [H_nL]/[H^+][H_{n-1}L]$. ^b $t = 25.0$ °C; $\mu = 0.100$ M (KCl).

of the metal ion, the shapes of the p[H] profiles, and analogous known metal complex systems. Because the two main components TMS and TDS have not been reported previously, initial estimates of protonation constants and metal complex formation constants were made by selecting values based on analogous ligands with carboxylate and aliphatic α -hydroxyl groups and adjusting these values to take into account differences in ligand structure. This procedure was employed for both protonation constants and metal ion stability constants. The relevant values of the protonation constants of the minor constituents listed in Table I, and their metal ion stability constants were taken from ref 2. When data were not available, they were estimated by analogy to similar dicarboxylic acid data. These stability and protonation constants, including the estimated values, are listed in Table II. It is noted that in most cases the estimated values are assigned one less significant figure than the measured constants.

Results and Discussion

Protonation Constants. The protonation constants, four for TMS and six for TDS, were determined from TMS-rich and TDS-rich solutions in the absence of metal ions. The presence of tartaric acid in the TDS-rich test solutions and the presence of tartaric, malic, maleic, and fumaric acids in the TMS-rich solutions was taken into account through the use of the data listed in Table II. The final results of these calculations are presented in Table III.

In order to appreciate the magnitudes and trends of the protonation constants shown in Table III, it is important to consider the moieties from which the TDS and TMS molecules are composed. In TMS only one succinic acid residue is present while two are present in TDS. The log (protonation constants) of succinic acid are 5.24 and 4.00 while those of the tartaric acid are considerably lower at 3.95 and 2.82.



The first protonation constant of TMS is somewhat higher than that of succinic acid. This seems reasonable because of the higher charge in the TMS anion. This protonation reaction probably involves the only carboxylate in TMS that does not have an α -electron-withdrawing substituent. The next protonation constant is 1.35 log units lower and is comparable to the first protonation constant of tartaric acid. The diprotonated ligand could consist of a combination of four microspecies having protons between the four carboxylate groups of the ligand. The successively lower values of the two remaining protonation constants are expected because of the decreasing negative charge on the ligand. They are about of the expected magnitude, given the differences in charge and statistical factors.

In the case of TDS, the two higher protonation constants are separated by a log value of 0.57 log units, which is close to the statistical value of 4 ($\Delta \log 0.60$). This statistical constant is based on two proton acceptors, which is quite reasonable because the TDS anion, with six negative carboxylates, has only two that do not have adjacent electron-withdrawing substituents. The fully dissociated ligand has an appreciably higher protonation constant than does succinate, which is due in part to the higher charge and

(2) Smith, R. M.; Martell, A. E. *Critical Stability Constants* Plenum Press: New York, 1977, 1982, 1989; Vols. 3, 5, 6.

Table IV. Logarithms of the Stability Constants^a of Metal Ion TDS and TMS Complexes Obtained from Refinement of Data from TDS-Rich and TMS-Rich Solutions

	Cu ²⁺	Ni ²⁺	Mn ²⁺	Cd ²⁺	Zn ²⁺	Pb ²⁺	Hg ²⁺	Ca ²⁺	Mg ²⁺	Al ³⁺	Fe ³⁺
TDS Quotient											
[ML]/[M][L] = K_{ML}	9.38	8.28	7.00	6.80	8.07	8.66	15.49	6.82	4.53	8.56	20.96
[MHL]/[ML][H ⁺] = K^H_{MHL}	4.27	4.24	4.67	4.93	4.53	4.80	5.48	5.39	5.44	5.73	
[MH ₂ L]/[MHL][H ⁺] = $K^H_{MH_2L}$			4.03	4.09	3.54	4.05	5.20	4.37		3.23	7.78 ^b
[MH ₃ L]/[MH ₂ L][H ⁺] = $K^H_{MH_3L}$	6.38 ^c	6.65	3.54	3.18	2.94	3.18	4.04	2.83			
[MH ₄ L]/[MH ₃ L][H ⁺] = $K^H_{MH_4L}$								2.72			
[M ₂ L]/[ML][M] = $K^M_{M_2L}$	4.10	2.66	2.57	2.69	2.92	5.93	8.9 ^d	3.19	0.1 ^d	1.2 ^d	
[MLH ₋₁][H ⁺]/[ML] = $K^{-H}_{MLH_{-1}}$							-8.26			-4.95	-7.01
[M ₂ LH ₋₁][H ⁺]/[M] ² [L] = $\beta_{M_2LH_{-1}}$							22.33			10.96	22.98
[M ₂ LH ₋₂][H ⁺] ² /[M] ² [L] = $\beta_{M_2LH_{-2}}$											20.26
[M ₂ LH ₋₃][H ⁺] ³ /[M] ² [L] = $\beta_{M_2LH_{-3}}$							5.16				16.22
[M ₂ LH ₋₄][H ⁺] ⁴ /[M] ² [L] = $\beta_{M_2LH_{-4}}$											11.02
[M ₂ LH ₋₅][H ⁺] ⁵ /[M] ² [L] = $\beta_{M_2LH_{-5}}$							-13.18				5.06
σ_{fit} for TDS ^e	0.006	0.007	0.008	0.002	0.004	0.016	0.035	0.001	0.013	0.006	0.093
TMS Quotient											
[ML]/[M][L] = K_{ML}	6.63	6.06	5.69	4.63	6.31	7.01	14.18	5.20	3.91	7.63	10.70
[MHL]/[ML][H ⁺] = K^H_{MHL}	3.70	3.75		3.98	3.47	3.98	5.57	4.43	4.27	2.98	2.11
[MH ₂ L]/[MHL][H ⁺] = $K^H_{MH_2L}$	2.90	3.03	7.25 ^b	3.53	2.85	2.67	4.33	2.94			
[MLH ₋₁][H ⁺]/[ML] = $K^{-H}_{MLH_{-1}}$	-7.00						-8.66			-5.05	-3.67
[MLH ₋₂][H ⁺]/[MLH ₋₁ L] = $K^{-H}_{MLH_{-2}}$							-8.86				-5.36
[MLH ₋₃][H ⁺]/[MLH ₋₂ L] = $K^{-H}_{MLH_{-3}}$							-9.88				
σ_{fit} for TMS ^e	0.006	0.007	0.010	0.007	0.002	0.002	0.0160	0.002	0.013	0.003	0.004

^a $t = 25.0$ °C; $\mu = 0.100$ M (KCl). ^b $[MH_2L]/[ML][H^+] = K^{2H}_{MH_2L}$. ^c $[MH_3L]/[MHL][H^+]^2 = K^{2H}_{MH_3L}$. ^d Values obtained during refinement, but negligible species concentration results in low accuracy. ^e Average values.

in part to the larger statistical factor.

The extraordinarily good σ_{fit} (0.0015 for TMS-rich and 0.0007 for TDS-rich solutions) provides assurance that the experimental refinement is as complete as can be expected and is comparable to the results achieved in much simpler, monocomponent systems. It also shows that the technique employed achieved a good least-squares minimum for each solution by the use of a common set of equilibrium constants with mixtures of species at widely different concentrations.

Metal Ion Formation Constants. Equimolar (moles of TDS + moles of TMS = moles of metal ion) solutions of the metal ions investigated were equilibrated with TMS-rich and TDS-rich solutions and were studied as a function of $p[H^+]$. By the use of a process similar to the "ligand-alone" procedure described above, a final set of log stability constants was obtained and is presented in Table IV.

TMS-Metal Ion Formation Constants. The high 3+ charge on the small Al³⁺ cation contributes considerably to the magnitudes of its stability constants. For the divalent transition-metal ions, the stability constant of Cu(II) (β_{ML}) is the highest, as usual. The trend of the relative stability constants of Ca²⁺ and Cd²⁺ seem to be the reverse of the trend usually found for these metal ions. The explanation must lie in the stereochemistry of the octahedral complexes formed, with a better fit for Ca²⁺ than for Cd²⁺. Of the 11 metal ions studied, only Mg²⁺, Fe³⁺, and Al³⁺ do not form diprotonated (MH₂L type) complexes. The Mg²⁺ complex has such a low stability that when the pH is raised to the value necessary to form a complex, the ligand readily loses the second proton. The polarizing effect of Al³⁺ and Fe³⁺ are so high that the first chelate protonation constants occur at least one log unit lower than that of most other divalent ions. Cu²⁺, Al³⁺, Fe³⁺, and Hg²⁺ have sufficiently high coordination tendencies to ionize the aliphatic hydroxyl group present on the monosubstituted tartaric acid (i.e., TMS). Further hydrolysis of the Fe³⁺ and Hg²⁺ complexes obviously involves hydroxo complex formation.

It is perhaps surprising that stability constants of the divalent ion Hg²⁺ are higher than those of the trivalent ion Fe³⁺, but in general Hg²⁺ possesses high stability constants due to the high covalent bond character of its coordination compounds. It is noted that the TMS iron(III) chelate has a low protonation constant whereas the corresponding first and second protonation constants of Hg-TMS are quite high. The geometric requirements of the coordination sphere characteristic of Hg(II) complexes probably result in lower utilization of the donor groups of TMS, thus making

them available for protonation. The above rationalization notwithstanding, the higher stability constant of the 1:1 complex of Hg(II) over Fe(III) is surprising. The stability constants of the remaining metal ions seem normal with the exception of those of Mn²⁺, which seems to undergo deprotonation in one step, with formation of very little of the monoprotonated intermediate species, probably indicating a concomitant change in coordination geometry.

TDS-Metal Ion Formation Constants. The relative order of the magnitude of the stability constants of divalent metal complexes for TDS is quite different from that for TMS: Hg²⁺ > Cu²⁺ > Pb²⁺ > Ni²⁺ > Zn²⁺ > Mn²⁺ > Cd²⁺ > Ca²⁺ > Mg²⁺. In each case, TDS constants are larger in magnitude than the corresponding TMS constants. The Cu²⁺-Al³⁺ transposition is interesting and is probably related to the participation of the aliphatic hydroxyl group in TMS and the lack of such a donor group in TDS. The ability of Al³⁺ to displace protons from hydroxyl groups α to coordinated carboxyls is now well documented,³ and the complex represented in Table IV for TMS as ML may very well be the monoprotonated form of the very stable species AlH₋₁L (i.e., AlH₋₁L·H⁺) with the proton on a carboxyl group and the deprotonated α -hydroxy group coordinated to the Al(III) ion. Since these two species differing in the position of a proton are indistinguishable thermodynamically, the high stability assigned to ALL for TMS may be due to the high stability contribution of the coordinated α -alkoxy group. The deprotonated Al(III) chelates of TDS must involve coordination of the hydroxide ion, because of the lack of a hydroxyl group on the ligand. In the case of Cu(II) the formation of a deprotonated chelate MLH₋₁ with TMS, but not with TDS, suggests the involvement of the deprotonated α -hydroxyl group of the former ligand.

All metal chelates of TMS are characterized by protonation reactions, and with the exception of Fe(III), the same is true of TDS. The metal ions Cd²⁺, Zn²⁺, and Ca²⁺ readily form both di- and triprotonated chelates. In the case of Ca²⁺ a tetraprotonated TDS chelate corresponding to a complex with an overall zero charge, as well as species with lower degrees of protonation, is formed. Apparently, for reasons similar to those cited for TMS, MgTDSH₂²⁻ could not be detected. The protonated species detected in the case of Cu(II) are unique in that the triprotonated chelate forms easily, but as the pH was raised

(3) Motekaitis, R. J.; Martell, A. E. *Inorg. Chem.* 1984, 23, 18.

Table V. Protonation Constants^a of TMS and Pure TDS^b

<i>n</i>	log K_m^H	
	TMS	TDS
1	5.73	5.98
2	4.40	5.38
3	3.30	4.40
4	2.44	3.70
5		3.00
6		2.20
σ_{fit}	0.001	0.0005

$$^a t = 25.0\text{ }^\circ\text{C}; \mu = 0.100\text{ M. } ^b K_m^H = [H_nL]/[H^+][H_{n-1}L].$$

two protons were found to dissociate in a concerted manner, probably with a change in geometry of the complex, to give a monoprotated species directly.

The order of the magnitude of the stability constants (log K_{ML}) for TDS is what would be expected by comparison with the stability constants for other multidentate ligands, with $K_{FeL} > K_{HgL}$ (compare with EDTA). Perhaps a more favorable geometry is operating with TDS, relative to the TMS complex. A comparison of the normal stability constants (K_{ML}) and their protonation constants reveals a concerted two-proton reaction in going from FeTDS to FeTDSH₂. Such behavior has now been observed in several examples and seems to involve change in the coordination geometry and/or the coordination number in the complexes involved. The reactions of Hg(II) are interesting with respect to the binuclear complexes that seem to be formed at higher pH values. Three of these chelates, each two protons apart—M₂H₁L, M₂H₃L, and M₂H₅L—are indicated by analysis of the p[H] data. This result may be interpreted in terms of stepwise coordination of oxo donors or by pairwise coordination of hydroxide ions, probably in bridging positions. Also, it seems that the original M₂H₁L complex is probably hydroxide ion bridged. In contrast, Fe(III) undergoes each hydrolysis step sequentially.

Of special interest is the unusually large value of the formation constant of TDS and Fe³⁺. The carboxylate groups of this ligand would be completely dissociated at physiological pH (7.4) and at environmental pH (~8.2 for sea water), whereas the donor groups of other ligands such as ethylenediaminetetraacetic acid (EDTA) and *N,N'*-bis(*o*-hydroxybenzyl)ethylenediamine-*N,N'*-diacetic acid (HBED) would be strongly protonated under these conditions. Thus the constants (log $\beta = 20.96$) for TDS may make it competitive with ligands having much larger Fe(III) stability constants.

Pure TDS. When the initial work on mixtures (TMS-rich and TDS-rich) had nearly been completed, a small sample of pure TDS in solution was obtained. With this pure ligand, protonation constants were determined and potentiometric measurements of 1:1 and 2:1 metal ion to ligand solutions were carried out, thus providing a comparison with the determinations that had been

carried out on mixtures. The new values with pure TDS were then employed for determination of the TMS-rich mixture, with corrections based on the minor constituents present (listed in Table I).

Table V lists the protonation constants of pure TDS and those of TMS obtained from the TMS-rich solution. Comparison of the TDS column of Table V with that of Table III shows that the constants obtained for the major species are within 0.01 log unit. The second protonation constant differs by 0.02 log unit, while the value which deviates the most differs by 0.08 log unit. This remarkable agreement demonstrates the validity of this new method of working with mixtures. Inspection of the TMS data shows that the first protonation constant is the same by either method, the second differs by 0.02 log unit, the third differs by 0.04 log unit, and the last differs by 0.03 log unit. The slightly larger scatter for TMS may be due to the inclusion of literature data (Table II) for the four additional impurities present in the TMS solution. It is suggested that even more accurate results could be achieved if the protonation constants of tartaric, malic, maleic, and fumaric acids were determined as part of this investigation under conditions identical with those employed for the TMS and TDS determinations.

Pure TDS and Metal Ions. Because of the large number of donor groups in TDS, the potentiometric studies of this ligand were carried out with both 2:1 and 1:1 molar ratios of metal ion to ligand. Table VI presents all of the metal ion stability constants obtained with pure TDS. With these more accurate TDS constants, the data obtained from the TMS-rich system were recalculated to get the best stability constants for TMS. Because the TDS constants employed as corrections of the calculations of the TMS constants of the TMS-rich mixture were more accurate in this case, the data in Table VI are considered the best available under the circumstances.

A comparison of the TMS constants in Tables IV and VI shows that the agreement is excellent with only minor variations in the second decimal place. The pure TDS values also agree quite well in most cases with the constants obtained from mixtures only, within 0.1 or 0.2 log unit. The M₂L constants disagree somewhat more, but this is expected because, for the TDS-rich mixture, no effort was made to measure solutions with 2:1 M:L ratios of components, so that the stability constants for the binuclear complexes calculated from the 1:1 stoichiometry would be expected to be less accurate.

Given so many competing equilibria and the presence of so many buffer reactions, it is remarkable that a precise set of equilibrium constants was obtained from mixtures of the two compounds, in the presence of minor impurities. With such good results from such complex systems, it seems that this new analytical technique could also be applied with even more confidence to simpler mixtures to determine individual protonation constants and metal chelate stability constants. It should be pointed out,

Table VI. Logarithms of the Stability Constants^a Obtained from Pure TDS Solution and a Mixed-Composition TMS Solution

	Cu ²⁺	Cd ²⁺	Zn ²⁺	Ca ²⁺	Mg ²⁺	Al ³⁺
TMS Quotient						
[ML]/[M][L] = K_{ML}	6.65	4.62	6.30	5.20	3.94	7.63
[MHL]/[ML][H ⁺] = K_{MHL}^H	3.69	3.99	3.46	4.42	4.21	2.99
[MH ₂ L]/[MHL][H ⁺] = $K_{MH_2L}^H$	2.89	3.48	2.89	2.96		
[MLH ₋₁][H ⁺]/[ML] = $K_{MLH_{-1}}^{-H}$	-7.0					-5.03
σ_{fit} for TMS	0.005	0.007	0.002	0.003	0.011	0.006
Pure TDS Quotient						
[ML]/[M][L] = K_{ML}	9.24	7.02	8.09	6.86	4.40	9.04
[MHL]/[ML][H ⁺] = K_{MHL}^H	4.40	4.79	4.45	5.33	5.41	5.34
[MH ₂ L]/[MHL][H ⁺] = $K_{MH_2L}^H$	2.52	4.11	3.60	4.31		3.04
[MH ₃ L]/[MH ₂ L][H ⁺] = $K_{MH_3L}^H$	3.78	3.17	2.81	2.91		
[MH ₄ L]/[MH ₃ L][H ⁺] = $K_{MH_4L}^H$				2.36		
[M ₂ L]/[ML][M] = $K_{M_2L}^M$	3.57	2.52	3.22	2.63	1.59	<.2
[MLH ₋₁][H ⁺]/[ML] = $K_{MLH_{-1}}^{-H}$						-6.72
[M ₂ LH ₋₁][H ⁺]/[M] ² [L] = $\beta_{M_2LH_{-1}}$						9.36
σ_{fit} for TDS ^b	0.007	0.009	0.008	0.004	0.026	0.012

^a *t* = 25.0 °C; μ = 0.100 M (KCl). ^b The σ_{fit} listed is the larger of the two values found for the 1:1 and 2:1 titrations.

however, that the high accuracy of these determinations could not have been accomplished if the ligands present in the mixtures had not been pure and if their precise concentrations had not been known.

Conclusions

It has been shown that potentiometry may be applied successfully to the determination of protonation constants and stability constants when the experimental solutions consist of mixtures of

ligands. It was found that all metal ions studied form normal 1:1 complexes with TMS and TDS. In addition mono, di-, and triprotonated metal complexes form with TDS, while only mono- and diprotonated metal complex species form with TMS. At slightly alkaline pH, the Fe^{3+} and Hg^{2+} chelates have a strong tendency toward hydroxo complex formation.

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Reaction Dynamics of Photosubstitution Intermediates of the Triruthenium Cluster $\text{Ru}_3(\text{CO})_{12}$ As Studied by Flash Photolysis with Infrared Detection¹

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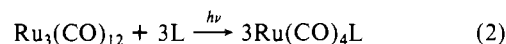
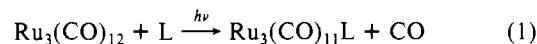
The reaction dynamics of intermediates formed by 308-nm XeCl excimer-laser excitation of the triruthenium cluster $\text{Ru}_3(\text{CO})_{12}$ in room-temperature isooctane solution were studied by using a flash-photolysis apparatus with a tunable infrared laser probe source and Hg/Cd/Te fast-risetime IR detector. The primary photoreaction is the dissociation of CO to give $\text{Ru}_3(\text{CO})_{11}$, which is rapidly trapped in second-order reactions by CO or by an added nucleophile such as tetrahydrofuran. The rate constants for such trapping are shown to be 2.4×10^9 and $6.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for CO and THF, respectively. The intermediate $\text{Ru}_3(\text{CO})_{11}(\text{THF})$ reacts with CO to re-form $\text{Ru}_3(\text{CO})_{12}$ via an apparent first-order dissociation of the THF with a rate constant about $2 \times 10^6 \text{ s}^{-1}$. The flash-photolysis apparatus with the IR detection system is described in detail.

Introduction

Flash-photolysis techniques have proved especially valuable in probing the reaction dynamics of reactive organometallic intermediates of the type often proposed in thermal catalysis mechanisms but rarely directly observable in thermal reactions.² Optical (UV/visible spectral region) detection techniques, which have the advantage of good sensitivity and reliability, are the most commonly used with flash-photolysis experiments. In contrast, detection procedures using infrared frequencies have much greater diagnostic potential with regard to specific species or structural types being formed as transients.³ This is especially true for metal carbonyl and other organometallic compounds, which often have sharp, characteristic transitions in vibrational spectra but rather broad and featureless absorptions in the electronic spectra. For this reason we have constructed a nanosecond flash-photolysis apparatus that uses an IR detection technique based on a lead salt diode laser as the probe source and a Hg/Cd/Te fast-risetime detector and have used this apparatus to study the photosubstitution mechanism of the triruthenium cluster $\text{Ru}_3(\text{CO})_{12}$ ⁴ in ambient-temperature solutions.

The photoreactions of $\text{Ru}_3(\text{CO})_{12}$ in solution have been extensively investigated.⁴⁻¹⁰ Early studies⁵ reported the photo-

fragmentation of the trinuclear cluster in the presence of various donor ligands; however, it was later demonstrated⁸ that the photochemical pathways display a dependence on excitation wavelength now recognized to be common to di- and polynuclear metal carbonyls.¹¹ Photolysis at short wavelengths (<366 nm) leads predominantly to ligand substitution on the cluster (eq 1),



while longer wavelength excitation (>400 nm) leads exclusively to fragmentation of the cluster framework (eq 2) under otherwise identical conditions. The photosubstitution pathway has previously been investigated by conventional flash-photolysis techniques at ambient temperature.⁴ While this study, which used xenon lamp flash excitation and UV/vis detection methodology, provided kinetic information regarding transients as short-lived as 30 μs , it was clear that other key species with shorter lifetimes must also be involved. Subsequently, Wrighton and Bentsen⁹ demonstrated the presence of possible such intermediates by using FTIR techniques to probe the spectra of low-temperature (90 K), glassy solutions of $\text{Ru}_3(\text{CO})_{12}$ that had been subjected to photoexcitation at 313 nm. Described here are the reaction dynamics of such transients formed by laser flash photolysis of $\text{Ru}_3(\text{CO})_{12}$ in ambient-temperature solutions as measured with a new apparatus using a XeCl excimer laser (308 nm) as the excitation source and the IR detection technique.

Experimental Section

Materials and Solutions. Triruthenium dodecacarbonyl was prepared as reported¹² and purified by sublimation in vacuo. Isooctane (Burdick and Jackson Spectrograde) was dried over CaH_2 and then distilled under N_2 immediately before use. Tetrahydrofuran (THF) was freshly distilled under N_2 from a sodium benzophenone ketyl solution.

Solutions for photolysis studies were prepared under N_2 with freshly distilled isooctane by using Schlenk techniques. Concentrations for transient bleaching experiments were chosen to give infrared absorbances 0.2-0.5 at the absorbance bands used as monitoring frequencies for a

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