that an intermediate forms in the reaction. The spectrum of the intermediate, ΔD *vs.* wave length, where ΔD is defined in ref. 2 as the difference in absorbance between the zero time extrapolation of the decreasing portion of the absorbance *vs.* time curve minus the contribution from the initial concentrations of V_{aq}^{2+} and VO_{aq}^{2+}, is identical with the spectrum Newton and Baker find for the intermediate in the reaction between V_{aq}^{2+} and VO_{aq}^{2+}, VOV_{aq}^{4+}.[2] The maximum in the spectrum is at 4250 Å. Measurements at 7600 Å. show that VO_{aq}^{2+} is an initial product in the reaction. No intermediate forms in the reaction between V_{aq}^{2+} and Fe_{aq}^{3+}, a one-electron oxidizing agent. Spectra of the solutions recorded after completion of the reaction between V_{aq}^{2+} and O_2 or H_2O_2 showed only V_{aq}^{2+} and V_{aq}^{3+} to be present. Therefore, it is concluded that one path for the oxidation of excess V_{aq}^{2+} to V_{aq}^{3+} by O_2 or H_2O_2 involves the *rapid* oxidation of V_{aq}^{2+} to VO_{aq}^{2+} followed by the reaction of VO_{aq}^{2+} with V_{aq}^{2+} yielding V_{aq}^{3+}. As stated in ref. 2 about 65% of the V_{aq}^{2+}–VO_{aq}^{2+} reaction goes by the intermediate VOV_{aq}^{4+} while the remainder proceeds by an outer-sphere mechanism. The second path, a one-electron oxidation of V_{aq}^{2+} to V_{aq}^{3+}, must also be rapid.

The question to be answered is what fraction of the V_{aq}^{3+} produced in the reaction of excess V_{aq}^{2+} with O_2 or H_2O_2 proceeds by the V_{aq}^{2+}–VO_{aq}^{2+} path? Newton and Baker have shown that for the reaction between V_{aq}^{2+} and VO_{aq}^{2+} the quantity $\Delta D[H^+]/[V_{aq}^{2+}]\cdot[VO_{aq}^{2+}]$, where $[V_{aq}^{2+}]$ and $[VO_{aq}^{2+}]$ are the initial concentrations of V_{aq}^{2+} and VO_{aq}^{2+}, is a constant at a given temperature.[2] The fraction of the reaction proceeding by a V_{aq}^{2+}–VO_{aq}^{2+} path can be estimated from the discrepancy between the quantity $\Delta D/[V_{aq}^{2+}][VO_{aq}^{2+}]$, at constant $[H^+]$, obtained for the V_{aq}^{2+}–VO_{aq}^{2+} reaction and values obtained for the V_{aq}^{2+}–O_2 and H_2O_2 reactions assuming all of the oxidizing agent reacts rapidly with V_{aq}^{2+} to give VO_{aq}^{2+} ($[VO_{aq}^{2+}]$ equals the concentration of H_2O_2 and twice the concentration of O_2). In all cases $[V_{aq}^{2+}]$ was calculated using $\Delta D/[V_{aq}^{2+}][VO_{aq}^{2+}]$ from the V_{aq}^{2+}–VO_{aq}^{2+} reaction and equations for total vanadium and total oxidizing agent.

Table I presents some typical data collected at 4250 Å. when excess V_{aq}^{2+} was allowed to react with O_2, H_2O_2, and VO_{aq}^{2+}. The quantity $\Delta D/[V_{aq}^{2+}][VO_{aq}^{2+}]$ for the reaction of V_{aq}^{2+} with VO_{aq}^{2+} is approximately $13 \times 10^3\ M^{-2}$ at 20°, $[H^+] \approx 0.3\ M$, and $\mu = 1.0$.[6] The values calculated for the H_2O_2 and O_2 reactions with V_{aq}^{2+} are 4×10^3 and $8 \times 10^3\ M^{-2}$, respectively. This means that in the V_{aq}^{2+}–H_2O_2 and V_{aq}^{2+}–O_2 reactions about 30 and 60%, respectively, of the V_{aq}^{3+} is produced *via* the V_{aq}^{2+}–VO_{aq}^{2+} path.

The oxidation of Cr_{aq}^{2+} by O_2 and H_2O_2 has been studied by Ardon and Plane.[7] Oxidation with H_2O_2 yields primarily Cr_{aq}^{3+}. However, a dinuclear chromium(III) species, which is believed to result from a reaction between Cr_{aq}^{2+} and a chromium(IV) species, is the only product when O_2 is used. It is interesting to note that in both cases oxidation with O_2 proceeds primarily by the M(II)–M(IV) path, while the H_2O_2 oxidation proceeds predominantly by a one-electron path.

TABLE I

DATA ON THE OXIDATION OF VANADIUM(II)

Conditions: 20°, $\mu \approx 1.0$ ($HClO_4$, $NaClO_4$, and $Zn(ClO_4)_2$), $[H^+] \approx 0.3\ M$

Run[a]	Oxidizing agent	10^3[oxidizing agent], M	$10^2[V_{aq}^{2+}]$, M	ΔD	$10^{-3}\Delta D/[V_{aq}^{2+}]\cdot[VO_{aq}^{2+}]$,[b] M^{-2}
1	H_2O_2	1.5	2.20	0.15	4.5
2	H_2O_2	3.8	1.81	0.27	3.9
3	H_2O_2	3.9	1.81	0.32	4.5
4	O_2	0.6	2.27	0.20	7.3
5	O_2	0.7	2.18	0.26	8.5
6	O_2	1.2	1.16	0.24	8.6
7	VO_{aq}^{2+}	0.3	2.26	0.09	13.3
8	VO_{aq}^{2+}	1.2	2.26	0.36	13.3
9	VO_{aq}^{2+}	3.3	2.15	0.81	11.5

[a] Each run done in duplicate. [b] $[VO_{aq}^{2+}] = n$[oxidizing agent], where n equals 2 for oxygen and 1 for H_2O_2 and VO_{aq}^{2+}.

Lower limits can be set on the rate constants associated with the oxidation of V_{aq}^{2+} directly to V_{aq}^{3+} and VO_{aq}^{2+}. Assuming pseudo-first-order kinetics ($[V_{aq}^{2+}] = 10^{-2}\ M$ and a half-time less than 1 sec.) the rate constants are greater than $10^2\ M^{-1}$ sec.$^{-1}$ at 20°.

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(6) The quantity $0.693\Delta D/[V_{aq}^{2+}]\ [VO_{aq}^{2+}]t_{1/2}$, where $t_{1/2}$ is defined in ref. 2, is 2900 and 3000 M^{-2} sec.$^{-1}$ for runs 7 and 8, respectively. The value at 20° extrapolated from the data of Newton and Baker is 2900 M^{-2} sec.$^{-1}$.

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Proton Nuclear Magnetic Resonance Studies of the Bismuth(III) and Lead(II) Tartrate Complexes

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Metal tartrate complexes are well known and a number of stability constants have been reported.[2-5]

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(1) To whom correspondence and requests for reprints should be addressed.

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The polarography of these chelates also has been summarized by Meites and co-workers.[6,7] In an optical rotatory study of the thorium(IV) tartrate complex, displacement of the hydroxyl protons of the ligand has been suggested under alkaline conditions.[8] However, most of these studies have been concerned with the species present in neutral, weakly acidic, or weakly basic solutions. Furthermore, the nature of the bonding and the structure of the complexes have been considered only to a limited extent. For these reasons a study of the bismuth(III) and lead(II) tartrate complexes in aqueous solution has been undertaken using proton nuclear magnetic resonance.

Experimental

The proton n.m.r. spectra were recorded with a Varian A-60 high-resolution spectrometer equipped with a 60-Mc. oscillator. Chemical shifts were measured using tetramethylammonium chloride (TMA) as an internal reference. The resonance for this material is 3.177 p.p.m. downfield from 3-(trimethylsilyl)-1-propanesulfonic acid, sodium salt (TMS*), and the reported resonances can be converted to this reference by adding the difference. The TMA reference has the advantage of having a constant chemical shift, independent of solution pH, which is close to the chemical shifts measured for the tartrate complexes. This permitted smaller and more sensitive sweep widths than would have been possible by using TMS*.

All sample solutions were prepared using deuterium oxide (D_2O) because of the close proximity of the tartrate resonance to that for H_2O. For this reason the indicated pH values should be corrected by the expression[9]

$$\text{pD} = \text{“meter reading”} + 0.40$$

However, this has not been done because the n.m.r. sample probe was operated at 40°. Thus, the reported pH values are only approximate, but are meaningful in a relative sense. The metal salts were either the chlorides or the nitrates and tartaric acid or potassium tartrate was used as the source of tartrate. All of these materials were reagent grade and were used without further purification. The sample solutions were prepared by adding 10 mmoles of tartaric acid and 10 mmoles of the metal salt to D_2O and adding KOH pellets to dissolve the complex; the resulting solutions were diluted to a volume of 10 ml. with D_2O. Attempts to prepare 1 F solutions of the 1:1 tartrate complexes of barium(II), aluminum(III), cadmium(II), and zinc(II) were unsuccessful because of lack of solubility.

Results

The C–H protons of tartaric acid exhibit a single sharp resonance line which has a downfield chemical shift of 1.59 p.p.m. for the acid and 1.17 p.p.m. for the divalent anion. The upfield transition occurs between pH 2.5 and 5.0 and coincides with the neutralization of the carboxylic acid protons. The chemical shift for the C–H protons of the anion remains constant even for strongly alkaline solutions (up to 4 F KOH).

Preliminary measurements of metal tartrate solutions containing a large excess of ligand indicated that the chemical shift for the tartrate anion depended on the ratio of metal ion to ligand. Because only a single resonance line is observed, this must represent the weighted average of the chemical shift for the C–H protons of the free ligand and the chelated ligand. Furthermore these two species must be exchanging rapidly. This observation has led to a mole-ratio study for lead(II) and bismuth(III) tartrate using the chemical shift for tartrate as the measured variable. These studies have been made by using two solutions, one containing 1 F potassium tartrate and the other containing 1 F metal tartrate (mole ratio of 1:1), which have both been adjusted to the same pH. By mixing the two solutions in different combinations any mole ratio from 0.0:1 to 1:1 (metal-to-ligand) can be studied. Mole ratios larger than 1:1 are not possible because of precipitation of the excess metal ion.

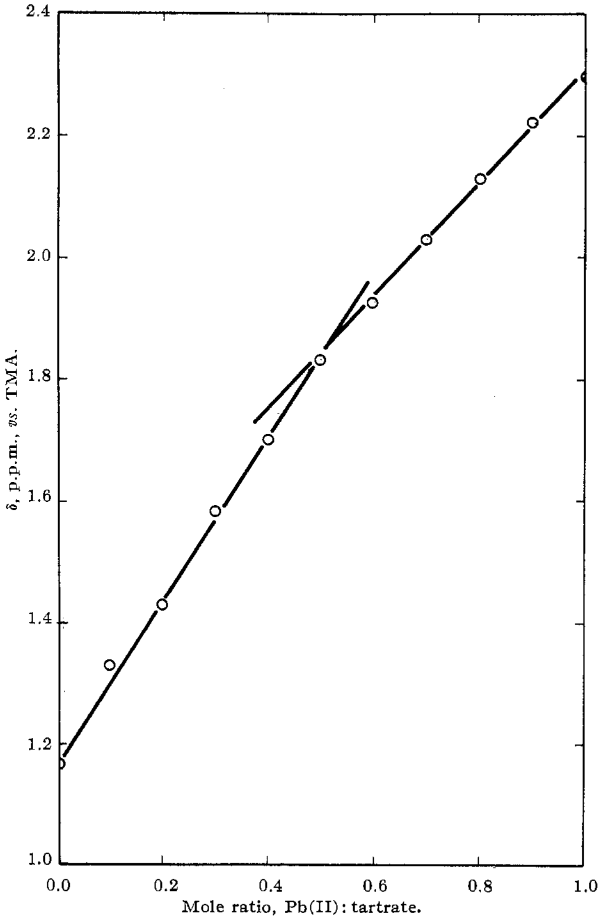

Figure 1.—Chemical shift for the C–H protons of tartrate anion as a function of the mole ratio of added lead(II) ion. The chemical shifts are downfield from the reference. All solutions are 1 F in tartrate ion and have been adjusted to pH 13.

The chemical shifts for lead tartrate solutions at pH 13.0 as a function of metal-to-ligand mole ratio are shown in Figure 1. This same study has been repeated for solutions which are 2 F in hydroxide ion, and the results are virtually identical with those shown in Figure 1 for pH 13 solutions. This implies that between pH 13 and 2 F OH^- the nature of the bonding between the lead ion and the tartrate ion is independent of pH. Because of the limited solubility below pH 13 for this complex, studies have not been made at lower pH values.

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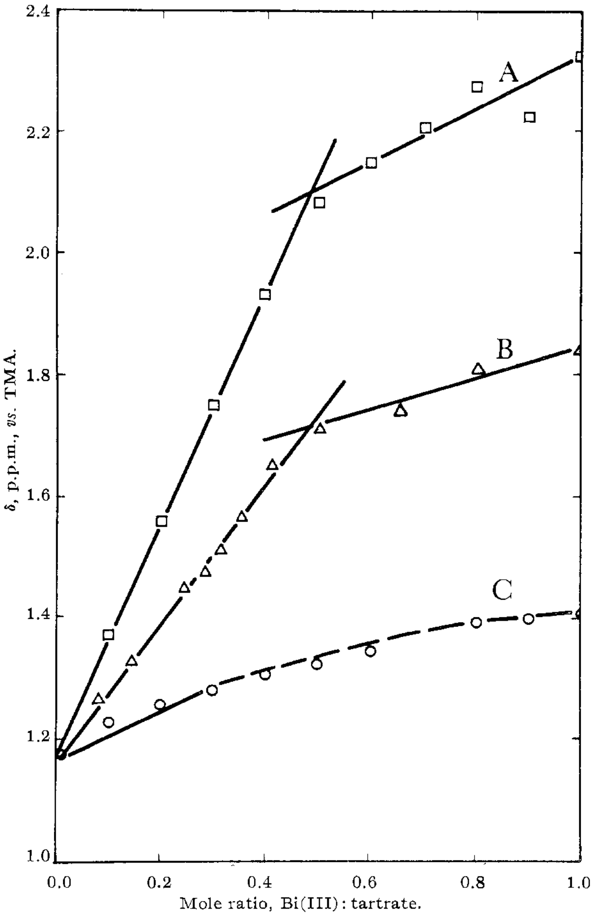

Figure 2.—Chemical shift for the C–H protons of 1 *F* tartrate anion as a function of the mole ratio of added bismuth(III) ion. pH of the solutions: curve A, pH 14.3; curve B, pH 13.5; curve C, pH 13.3.

The significant increase of chemical shift with increase in metal-to-ligand mole ratio as shown in Figure 1 indicates that there is strong interaction between the lead(II) ion and the ligand. Furthermore, the discontinuity at a ratio of 0.5 gives an indication that two stable chelate species are formed, one containing one metal ion per two ligands and a second containing one metal ion per ligand. The inability to keep mole ratios higher than one in solution implies that other stable tartrate chelates of lead(II) are not formed in strongly alkaline solutions.

A similar set of mole-ratio studies for the bismuth(III) tartrate system in strongly alkaline solutions has been made and the results are shown in Figure 2. In contrast to the lead(II) tartrate complex, increasing alkalinity causes the chemical shift for the bismuth(III) tartrate complex to increase significantly as illustrated by the three curves. The discontinuity at a mole ratio of 0.5 indicates a stable bismuth tartrate containing one metal per two ligands in addition to a 1:1 complex; mole ratios larger than 1:1 are insoluble.

To gain a better idea of the formulas and possible structures for the lead and bismuth tartrate complexes, pH titrations have been made for the 1:1 complexes. Blank titrations have been run on equal volumes of water, titrating to pH 13.1, and have been subtracted from the amount of titrant required to reach this pH for the chelate titration. The titrations indicate that in going from pH 7 to 13.1 two hydroxide ions are added per lead tartrate molecule and four hydroxide ions are added per bismuth tartrate molecule. Thus, at pH 13.1 the two chelates have molecular charges of −2 and −3, respectively. This assumes that at pH 7 the 1:1 complexes have the formulas $Pb(C_4H_4O_6)$ and $Bi(C_4H_4O_6)^+$. These conclusions are in general agreement with previously proposed formulas for the 1:1 complexes under alkaline conditions.[10,11]

Discussion and Conclusions

In alkaline solutions the chemical shift for the tartrate anion is 1.17 p.p.m. and is independent of pH. Conversely, the chemical shift for the 1:1 lead tartrate chelate is 2.30 p.p.m., but also is independent of pH from pH 13 to 14.3. In the case of the 1:1 bismuth tartrate complex the chemical shift up to pH 13 is only 1.34 p.p.m., but this rises rapidly to 2.34 p.p.m. at pH 14.3 as shown in Figure 2. Previous n.m.r. studies of aqueous metal chelate systems have shown that the coordination of the metal ion by the carboxylate group does not produce a significant change in chemical shift for the protons on the α carbon.[12] However, metal ion coordination by the alcoholic oxygens of the tartrate molecule and the resultant displacement of the alcohol proton would be expected to cause a large chemical shift for the C–H proton.[13] At pH 13.1 the stoichiometric formulas for the 1:1 lead and bismuth tartrate complexes, based on pH titrations, are $Pb(C_4H_2O_6)^{2-}$ and $Bi(OH)_2(C_4H_2O_6)^{3-}$, respectively, where $(C_4H_2O_6)^{4-}$ represents the tartrate tetraanion (with the hydroxyl protons displaced).

From these considerations, the conclusion is made that for solutions more alkaline than pH 13 the 1:1 lead tartrate complex involves direct bonding by the alcoholic oxygens as well as the carboxylate groups. If this were not so, the chemical shift for the complexes should be much closer to that for the free ligand anion. Thus, a plausible and consistent structure for the complex would involve coordination by the two carboxylate groups and the two alcoholic oxygens with the lead acting as a four-coordinate metal ion. In the case of the bismuth tartrate complex at pH 13, the small chemical shift (not greatly different from that for the free anion) indicates that the alcoholic oxygen atoms of the ligand are not involved in coordination of the bismuth ion. A reasonable structure for the complex at pH 13 would be a dimeric or polymeric form with each bismuth ion coordinated by two carboxylate groups and four hydroxide ions and thereby acting as a six-coordinate metal ion.

The sharp increase in chemical shift for the 1:1 bismuth tartrate complex at pH values above 13 indicates

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that the alcoholic protons of the ligand are being displaced by the bismuth ion. Assuming this occurs and that the stoichiometry of the number of hydroxide ions added per chelate molecule does not change significantly, a reasonable structure for the 1:1 bismuth tartrate complex at pH 14.5 would involve coordination by the two carboxylate groups and the two alcoholic oxygens with an additional two hydroxy groups attached to the bismuth ion to maintain it as a six-coordinate metal ion.

Reference to Figures 1 and 2 indicates that the chemical shifts due to chelation are approximately half as great for the 1:2 complexes as for the 1:1 complexes of lead ion and bismuth ion. This would imply for the 1:2 complexes either that the interaction between metal ion and the alcoholic oxygens is much weaker than for the 1:1 complex or that on the average only one alcoholic oxygen per tartrate is coordinated to the metal ion. The latter seems more reasonable and is consistent with the expected coordination for the two metal ions under alkaline conditions.

The significant increase in chemical shift for the ligand protons of the lead complex and the bismuth complex at pH 14.5 gives strong support to the conclusion that the alcoholic groups are involved in direct coordination of the metal ions. This conclusion is in agreement with an earlier proposal for such coordination for the thorium(IV) tartrate complex.[8]

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Chloro Complexes of Lead(II)

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The finding that $BiCl_4^-$ and $BiCl_6^{-3}$ are prominent in solutions of Bi(III) in hydrochloric acid[1] prompted us to investigate halide complexes of lead of high ligand number. Kivalo[2] deduces from polarographic measurements at $\mu = 1.0$ that no higher complex than $PbCl_3^-$ is observed, but his calculations involved no measurements in which the average ligand number ($\bar{n}$) exceeded 2.2. We had hoped to measure the solubility of $[(CH_3)_4N^+][PbCl_3^-]$ as a function of $[Cl^-]$ but were unable to prepare it owing to the great insolubility of $PbCl_2$. Therefore, the solubility of the latter salt has been determined at ionic strength 4.0 as a function of $[Cl^-]$, and the results have been interpreted with the help of spectrophotometric observations on solutions of Pb(II) in the same media.

Experimental

Reagent grade HCl and $HClO_4$ were diluted with de-ionized distilled water. The dilute acids were standardized using anhydrous sodium carbonate. Lead chloride was recrystallized from hot dilute hydrochloric acid.

Solutions were saturated with $PbCl_2$ by means of a Brønsted saturator[3] thermostated at 25.0 ± 0.1°. Usually one pass was found sufficient for saturation, but more than one pass was used in practice. At least two determinations of the solubility were made at each chloride ion concentration.

Analysis of Pb(II) was done spectrophotometrically by measuring the absorbance of Pb(II) in 6 *M* HCl at 271 mμ, according to the method of Merritt, Hershenson, and Rogers.[4] All spectrophotometric measurements were made using a Beckman DU spectrophotometer with the cell compartment thermostated at 25 ± 0.5°. $PbCl_2$ was the only solid phase present at all times.

Theoretical

No test for polynuclear complexes could be made since no ions not involved in the equilibrium are present in the salt. None was found[1] in the study of $BiCl_n^{3-n}$ at Bi(III) concentrations higher than Pb(II) concentrations encountered in this study. It is assumed therefore that none is present here, although this has by no means been proved. The working equations for deriving equilibrium constants are

$$S = \frac{[\mathrm{PbCl_2}]}{\beta_2[\mathrm{Cl^-}]^2}\sum_{1}^{N}\beta_n[\mathrm{Cl^-}]^n \tag{1}$$

$$[\mathrm{Cl^-}] = \frac{[\mathrm{Cl^-}]_0}{1 + \mathrm{d}S/\mathrm{d}[\mathrm{Cl^-}]} \tag{2}$$

$$\frac{\mathrm{d}\ln S}{\mathrm{d}\ln [\mathrm{Cl^-}]} = \bar{n} - 2 \tag{3}$$

where S is the solubility (M) of $PbCl_2$, $\beta_n = [PbCl_n^{2-n}]/[Pb^{+2}][Cl^-]^n$, $\bar{n}$ is the average ligand number, and $[Cl^-]_0$ is the concentration of Cl^- in the solvent before saturation. Chemical reactions assumed are

$$\mathrm{PbCl_2(s)} \rightleftharpoons \mathrm{PbCl_2(aq)}$$

$$\mathrm{PbCl_2} + (n-2)\mathrm{Cl^-} \rightleftharpoons \mathrm{PbCl}_n^{\,2-n}$$

Equation 2 is used to estimate free $[Cl^-]$ and then eq. 1 is applied to the data using the graphical method of Leden as follows. The slope of the solubility curve in Figure 1 gives $\bar{n} \approx 4$ in 4.0 *M* $[Cl^-]$. An initial plot of S *vs.* $[Cl^-]^2$ for the points at higher $[Cl^-]$ gives a straight line. The slope and intercept give $[PbCl_2]$ and β_4/β_2 to a first approximation. Similarly, approximate values of β_3/β_2, β_1/β_2, and $1/\beta_2$ are obtained. The approximate values are used to obtain improved values until plots of $S - F_n$ *vs.* $[Cl^-]^{n-2}$ give straight lines all with the same intercept, $[PbCl_2]$. (F_n includes all terms on the right-hand side of eq. 1 except that used in the plot and $[PbCl_2]$.)

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