and a CCl_4 dry ice (chunks) slush bath (−23 °C) was raised to immerse the horizontal section. The three-way stopcock was set to isolate the system from the no-air line while maintaining connection with the bubble/manometer.

A 100-mL modified Schlenk tube (MST) equipped with a magnetic stir bar was charged with $(CH_3)_4NAsF_6$ (3.5 g, 13.3 mmol). Under positive argon flow, the tube was attached to the SO_2 still, and 75 mL was collected with a dry ice/methanol slush. The Dewar was removed and the MST detached from the still and fitted with a septum. A mercury-filled bubbler was attached via a needle for venting, and the mixture was stirred to produce a clear, colorless solution which was allowed to warm to its boiling point. The bubbler needle was then removed and replaced by a $^1/_{16}$-in. o.d. stainless-steel cannula, which was purged with SO_2 vapors and then used to transfer the solution into the cell, filling each chamber in turn. The current varied positively with voltage, and the Hg pool was polarized at +1.300 V relative to the Ag/AgCl reference electrode. The initial current was 17 mA and dropped to 10 mA over the first 10 min. In $^1/_2$ h, the counterelectrode chamber solution was deep red (SO_2 reduction product) and the working chamber solution was yellow (Hg_3^{2+}) with a 2 mm deep red layer (Hg_4^{2+}) on the Hg surface. After 2 h ($\sim$60 C), the current fluctuated up and down, while golden crystals began to form on the Hg surface and the red color above it began to disappear. The completion of that process required about 20 min and the current steadied at 8 mA with the Hg surface completely covered by golden crystals. After $3^3/_4$ h the electrolysis was stopped (total charge passed 123 C). The counterelectrode chamber was first emptied by means of a cannula and then with a second cannula rinsed with fresh SO_2 (2 × 10 mL) and left empty. Next, the middle chamber was emptied and rinsed (2 × 10 mL). Finally, the working chamber was emptied and rinsed until the rinsings were colorless. The cooling bath was lowered to allow the residual SO_2 to evaporate through the bubbler. The septa were individually replaced by the Teflon stopcocks (argon flush) and the cell briefly and cautiously evacuated before closure for removal to the drybox (Vacuum Atmosphere Corp.). The total yield of bright golden crystals was 0.93 g or 92% on the basis of 1 mol of Hg_3AsF_6/faraday. The presence of Hg in solution was confirmed by precipitation of Hg upon addition of the SO_2 solution to aqueous NH_4OH and ice. Characterization of the product was by direct comparison of Ni-filtered Cu X-ray powder pattern with that of an authentic sample.[11] The powder diffraction data has been submitted to the Powder Diffraction File.

In another experiment, the Hg pool was first seeded with three 10-mg pieces of Hg_3AsF_6. In this case, the current passage remained steady throughout and the production of golden solid was similarly steady. The solution was yellow with some red at the surface in this case as well. The yield, however, dropped to 55%. Electrolyses in $(CH_3)_4NPF_6$ were also performed, with and without seeds, but no solid material was produced. The solution became yellow and deep red at the Hg surface.

Discussion

The electrochemical synthesis of Hg_3AsF_6 is a convenient preparation of this material. Freedom from undesirable byproducts and the on–off control of electrolysis are particular advantages. While we did not attempt to produce large single crystals, it is to be expected that with a suitably constructed Hg electrode such crystals would be produced. The time of reaction is less than that required for previously published methods, which take several days to 1 week. On the other hand, the reaction setup is somewhat more complex and demanding.

Analogous syntheses of Hg_3SbF_6 were also performed, although $(CH_3)_4NSbF_6$ was found to be an unsuitable electrolyte, as the anion (presumably as a fluoride donor) decomposed the intended product and electrolyses with this salt gave small amounts of Hg_3SbF_6 with a large quantity of a flaky gray solid. $(CH_3)_4NSb_2F_{11}$ was effective except that as SbF_5 was released during electrolysis direct chemical reaction ensued and complicated the system. A substantial quantity of Hg_3SbF_6 formed on the frit in the working chamber, and the material in the well was contaminated by an insoluble grayish white material thought to be SbF_3. An alternative system of $(C_6H_5)_3CBF_4{\cdot}SbF_5$ was less complex, but the liberated BF_3 tended to attack O-rings, making it difficult to maintain an air-tight seal. Also in this system and in the $(C_6H_5)_3CAsF_6$ system, unidentified reduction byproducts caused difficulties during workup, frequently destroying the product. We anticipate, then, that with a suitable vessel, $(CH_3)_4NSbF_6{\cdot}BF_3$ would be the best electrolyte for the preparation of Hg_3SbF_6.

A similar electrolysis was performed in $(CH_3)_4NMoF_6{\cdot}BF_3$ solution. This reaction produced a substantial quanity of red and yellow solid in the working chamber and spongy red solid in the counterelectrode chamber as well. No golden or other metallic solid was evident and the products that did form were not isolated.

Comparison of the results for syntheses of Hg_3AsF_6 with and without added crystals of the product suggests that initial formation of the chain compound is a critical aspect. Apparently in the absence of the chain compound, the concentration of Hg_4^{2+} at the mercury surface must build to a considerable level before synproportionation occurs to form the chain compound. Evidence for the equilibrium

$$3Hg^0 + Hg_3^{2+} + 2AsF_6^- \rightleftharpoons 2Hg^0 + Hg_4^{2+} + 2AsF_6^- \rightleftharpoons 2Hg_3AsF_6$$

has been obtained in previous chemical syntheses; both Hg_3^{2+} and Hg_3AsF_6 were necessary for the isolation of $Hg_4(AsF_6)_2$,[23] and also the reaction of Hg and $Hg_3(AsF_6)_2$ to form Hg_3AsF_6[11] was incomplete. The equilibrium is manifested in our system in the transient red color in solution. The delayed formation of Hg_3AsF_6 is unusual for an electrochemical reaction, as the final oxidation state is apparently skipped at first and only reached by subsequent chemical reaction.

The failure to form a chain compound with PF_6^- is probably associated with the smaller size of the anion.[10] Thus MoF_6^- (which falls between AsF_6^- and SbF_6^- in size)[10] was chosen for the subsequent experiment. This system was complicated with byproduct precipitation, with the reactions taking a course other than the desired one. Direct reaction of MoF_6 with Hg produces only $Hg_2(MoF_6)_2$.[24]

Sulfur dioxide has not received much attention as a solvent for inorganic electrosynthesis although it has been employed for electrochemical organic preparations.[17] Our experience indicates that it should be useful in other systems requiring a nonreactive, aprotic solvent offering high solubility to a large range of compounds.

Acknowledgment. Financial support of this work by the Cornell University Materials Science Center is gratefully acknowledged.

Registry No. Hg_3AsF_6, 59539-90-1; Hg_3SbF_6, 59539-91-2; SO_2, 7446-09-5.

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(24) Prescott, A.; Sharp, D. W. A.; Winfield, J. M. *J. Chem. Soc., Dalton Trans.* **1975**, 936.

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Reduction of Nitric Oxide by Tin(II)[1]

Dan E. Hendriksen* and Richard E. Powell[2]

Received August 17, 1981

We have reported earlier from this laboratory[3a] the kinetics of the very fast copper(I)-catalyzed reduction of nitric oxide

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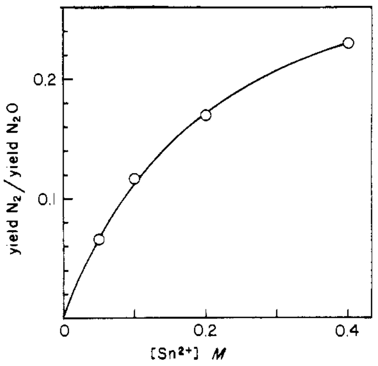

Figure 1. Relative yield of N_2 produced with changing [Sn^{2+}]. Initial pressure of NO is 305 torr, [H^+] = 1.00 M, and T = 0 °C. The form of the curve is discussed in the text.

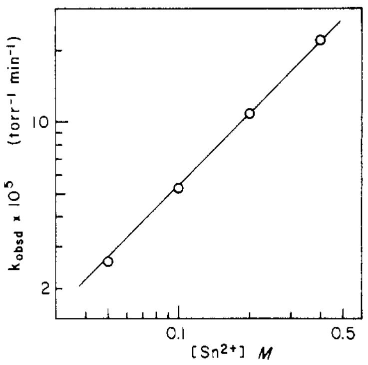

Figure 2. Kinetic dependence on [Sn^{2+}]. Initial pressure of NO is 305 torr, [H^+] = 1.00 M, and T = 0 °C. The line is drawn with a slope of 1.

by aqueous tin(II). We report here the kinetics of the much slower uncatalyzed reaction.

Since preliminary experiments showed that chloride ion had a considerable effect on the rate, it was avoided except when its effect was specifically under study. Thus most of the data reported here were obtained with use of the noncomplexing anions fluoborate or perchlorate.

Experimental Section

Apparatus. The apparatus, consisting of a Virtis freeze-drying flask fitted with a Vibromixer, has been described.[3a] Our only modification was to fit it with a thermostated buret so that reagent solutions could be added. Temperature was maintained at 0 °C by an ice bath, or at higher temperatures to ±0.05 °C by a thermistor-sensor proportional controller. The reaction was slow enough to be followed manometrically with a cathetometer.

Reagents. Tank nitric oxide (Matheson) was pumped on once from liquid nitrogen, distilled twice from isopentane slush, and then passed through silica gel at dry ice temperature;[3b] no contaminants were detectable by gas chromatography. Tin(II) fluoborate solution (Apache Chemical) upon analysis proved to be 99% pure. All other reagents were reagent grade and were used as received: solutions were acidified with perchloric acid, tin(IV) was added as sodium stannate, and the ionic strength was adjusted to 1.2 M with sodium perchlorate (except that in the series of runs involving variable Sn(II) or Sn(IV) it was 2.2 M). All reagents were handled in a nitrogen-filled glovebox, and each reaction mixture was degassed by four cycles of freeze–pump–thaw.

Analyses. $Sn(BF_4)_2$ solutions were indirectly titrated against ceric sulfate standardized against high-purity metallic tin.[4] Stock perchloric acid was titrated against sodium carbonate with use of methyl orange indicator. The gaseous products were measured for every run, being first Toepler-pumped from liquid nitrogen, then from isopentane slush, and then from dry ice. The composition of each fraction was established with an Aerograph gas chromatograph using a 20-ft column of 30/60 mesh molecular sieve 13X at 25 or 100 °C; mass spectrometry was also used. Whenever a reagent had been added from the argon-pressurized buret, there was a significant pressure of argon in the nitrogen fraction, and this has been subtracted in the data reported here.

Results

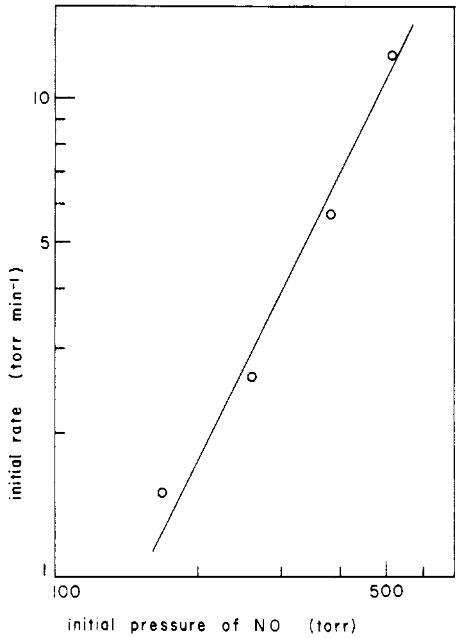

Figure 3. Dependence of the initial rate on the initial pressure of NO at 0 °C, [Sn(II)]$_0$ = 0.0368 M, [H^+] = 1.00 M, and [Cl^-] = 0.110 M. The line is drawn with a slope of 2.

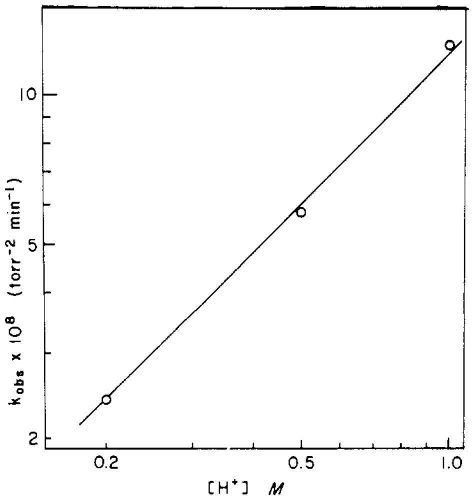

Figure 4. Kinetic dependence on [H^+] with stoichiometric amounts of Sn(II) and NO. [Sn^{2+}]$_0$ = 0.0368 M, and the initial pressure of NO is 520 torr at 0 °C. The line is drawn with a slope of 1.

Stoichiometry. The principal product is always N_2O, with N_2 as a minor product. Together they account entirely for the NO consumed, so that there is no water-soluble product such as hydroxylamine. The relative yield of N_2 increases with increasing Sn(II) concentration, as shown in Figure 1. The data in Figure 1 were taken at 0 °C. The relative yield of N_2

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(1) Based on the dissertation of Dan E. Hendriksen, submitted in partial fulfillment of the requirements for the Ph.D. degree, Berkeley, CA, Aug 1975.

(2) Deceased.

(3) (a) T. L. Nunes and R. E. Powell, *Inorg. Chem.*, **9**, 1912 (1970). (b) E. E. Hughes, *J. Chem. Phys.*, **35**, 1531 (1961).

(4) J. D. Donaldson and W. Moser, *Analyst (London)*, **84**, 10 (1959).

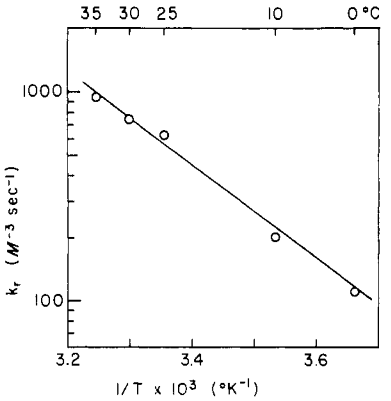


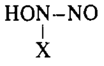
Figure 5. Arrhenius plot from runs with stoichiometric amounts of Sn(II) and NO. $[Sn^{2+}]_0 = 0.0368$ M, and $[H^+] = 1.00$ M. The rate constant k_r is calculated from the observed rate constant and the solubility of NO in water at that temperature. The derived activation parameters are $\Delta H^{*} = 10.0$ kcal and $\Delta S^{*} = -12$ cal deg^{-1}.

is independent of $[H^+]$, at least within the range 0.2–1.0 M. The smooth curve in Figure 1 is drawn to the equation

$$\frac{\text{yield of } N_2}{\text{yield of } N_2O} = 1.65\frac{[Sn^{2+}]}{1 + 4.63[Sn^{2+}]}$$

which for the moment may be regarded as empirical, although we shall show in the discussion how it can be rationalized.

Kinetics of the Principal Reaction. The reaction leading to N_2O, which is the only one of significance under most conditions, is kinetically first order with respect to $[Sn^{2+}]$ (Figure 2), second order with respect to [NO] (Figure 3), and first order with respect to $[H^+]$ (Figure 4). The transition state therefore has the composition $[Sn(NO)_2H]^{3+}$. Although many reactions of nitric oxide in solution may be inferred to require transition states (or intermediates) of the type



$$\mathrm{HO}\underset{\mathrm{X}}{\underset{|}{\mathrm{N}}}\mathrm{-NO}$$

this is to our knowledge the first instance of one that is kinetically second order with respect to [NO].

Temperature Dependence. The Arrhenius plot for data taken between 0 and 35 °C is shown as Figure 5. The activation parameters are $\Delta H^{*} = 10.0$ kcal and $\Delta S^{*} = -12$ cal deg^{-1}. The rate constants and the entropies of activation are referred to the concentration of dissolved NO, as calculated from the literature values of the Henry's law constants for distilled water, which may, to be sure, introduce a small systematic error in the numerical values since a salt solution of ionic strength 1.2 M is hardly distilled water.

Dependence on Tin(IV). The observation that the rate coefficient decreases if the measurements are pursued much beyond the first half-life led us to suspect that the product tin(IV) was inhibiting the rate. We therefore made a series of runs in which known concentrations of Sn(IV) were present initially (Figure 6). The rate does indeed fall off linearly with added Sn(IV), extrapolating to zero rate with 0.100 M Sn(II) plus 0.100 M Sn(IV). The obvious inference is that Sn(II) and Sn(IV) form a 1:1 binuclear complex, which is comparatively unreactive in these experiments.

Mixed-valence complexes of Sn(II)–Sn(IV) have been reported twice before, but perhaps not with such a dramatic result. In 1951 Davidson and co-workers[5] noted spectroscopic evidence for a 1:1 Sn(II)–Sn(IV) species in a high-chloride medium. In 1961 Tobias and Hugus[6] noted "a strong absorption in the blue region of the spectrum" for what they, surely correctly, regarded as some Sn(II)–Sn(IV) species. We also have observed a yellow color in our reaction mixtures at the late stages, or whenever Sn(IV) was added initially. However, a Job's-method plot with various mixtures indicated that at 200 nm the most intensely colored species is more nearly 4:1 Sn(IV):Sn(II) than 1:1. The general question of mixed-valence tin species clearly invites attention.

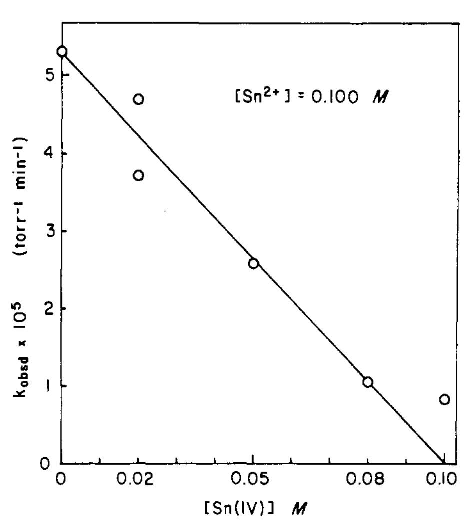


Figure 6. Rate dependence on Sn(IV), added as sodium stannate. [Sn(II)] = 0.100 M, the initial pressure of NO is 305 torr, $[H^+] = 1.00$ M, and $T = 0$ °C.

Dependence on Chloride. Runs were made at 0 °C, $[H^+] = 1.00$ M, and [Sn(II)] = 0.0368 M, with a stoichiometric amount of NO, at ionic strength 1.20 M, with added chloride as follows:

$[Cl]_{tot}$, M	obsd rate coeff, 10^{-8} min^{-1} torr^{-2} M^{-1}
0	12.6
0.042	13.4
0.110	16.0
0.193	19.6

From these observations and the literature equilibrium constants for the several Sn(II) chloro complexes,[7] it is possible to compute rate coefficients for all the species separately:

rate coefficient for $Sn^{2+} = 12.6 \times 10^{-8}$
for $SnCl^+ = 12.5 \times 10^{-8}$
for $SnCl_2 = 39.2 \times 10^{-8}$

The value calculated for $SnCl_3^-$, 34.2×10^{-8}, is inconsistent with the much faster reaction observed in more concentrated chloride solution and lends credence to the assumption that the $SnCl_3^-$-induced mechanism is not operating in these tabulated runs. A marked increase in reactivity for the $SnCl_3^-$ complex is consistent with the observations by Haight and co-workers[8] on the molybdenum-catalyzed reduction of hydroxylamine by tin(II) chloride, and also with the observation by Duke and Peterson[9] that $SnCl_3^-$ is the only tin(II) chloride species that will reduce methyl orange.

Discussion

The rate law for the N_2O-producing reaction suggests that the transition state is a protonated (nitrosohydroxylamine-*N*)tin(3+)

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(5) C. I. Browne, R. P. Craig, and N. Davidson, *J. Am. Chem. Soc.*, **73**, 1946 (1951).

(6) R. S. Tobias and Z. Z. Hugus, *J. Phys. Chem.*, **65**, 2165 (1961).

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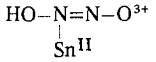
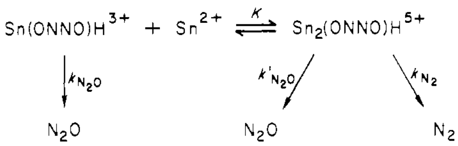


$$\mathrm{HO{-}\underset{\underset{\displaystyle Sn^{II}}{|}}{N}{=}N{-}O^{3+}}$$

by analogy with nitrosohydroxylamine-*N*-sulfonate, which also decomposes to yield N_2O and the two-electron oxidized form of the substituent.[10]

If it is assumed that this species is stable enough to be present in traces, to which a second stannous ion can add reversibly, the production of N_2 is accounted for. The observed form of the stoichiometric law is recovered if it is assumed that either the one-Sn(II) or two-Sn(II) species can yield N_2O, but only the two-Sn(II) species can yield N_2:



The stoichiometry predicted by this scheme is

$$\frac{\text{yield of N}_2}{\text{yield of N}_2\text{O}} = (Kk_{N_2}/k_{N_2O})\frac{[Sn^{2+}]}{1 + (Kk'_{N_2O}/k_{N_2O})[Sn^{2+}]}$$

and the experimental data indicate that $k_{N_2}/k'_{N_2O} = 0.36$.

Registry No. NO, 10102-43-9; Sn, 7440-31-5.

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[10] T. L. Nunes and R. E. Powell, *Inorg. Chem.*, **9**, 1916 (1970).

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Determination of the Stability Constant for MHL Formation by a Tracer Method

S. M. Shanbhag and G. R. Choppin*

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Many polybasic acid ligands form protonated metal complexes in solutions of appropriate acid pH values. Since the deprotonated complex is usually formed also, evaluation of the stability constants from the usual potentiometric titration technique is relatively complicated. In this note we describe a tracer method that allows direct measurement of β_{101} (for the formation of ML) and of β_{111} (for that of MHL) when both ML and MHL form. In principle, the method can be extended to obtain the constants for any pair of complexes ML_i and MHL_i. Although this technique is an extension of the standard method for measuring stability constants by solvent extraction, it provides a convenient and straightforward means to study relatively complicated equilibrium systems.

For a solvent extraction system we define a distribution coefficient as

$$D = \Sigma[M]_o/\Sigma[M]_a \qquad (1)$$

With the assumption of a constant organic-phase composition—e.g., MS_n where S is the extracting agent—and the presence of various species in the aqueous phase, eq 1 can be expanded

$$D = [MS_n]_o/([M]_a + [ML]_a + [MHL]_a + [ML_2]_a + [MHL_2]_a + ...) \qquad (2)$$

where L is a complexing anion. This equation can be rewritten with the conventional symbols for stability constants[1] as

$$D = [MS_n]_o/([M]_a(1 + [\beta_{101} + \beta_{111}[H]_a] \times [L]_a + [\beta_{102} + \beta_{112}[H]_a][L]_a^2 + ...)) \qquad (3)$$

At constant pH

$$\beta_1 \equiv \beta_{101} + \beta_{111}[H] \qquad \beta_2 \equiv \beta_{102} + \beta_{112}[H]$$

and

$$D = \frac{[MS_n]_o}{[M]_a(1 + \beta_1[L]_a + \beta_2[L]_a^2 + ...)}$$

In the absence of the complexing ligand

$$D_o = [MS_n]_o/[M]_a$$

and

$$D = \frac{D_o}{1 + \beta_1[L]_a + \beta_2[L]_a^2 + ...}$$

This is the usual equation for determination of stability constants by solvent extraction.

If the extraction experiments are conducted over limited ranges of [L], to minimize formation of ML_2 and MHL_2, β_1 can be determined at various values of [H]. Then a plot of β_1 vs. [H] gives an intercept equal to β_{101} and a slope of β_{111}.

To show the validity of this approach, we studied the Eu(III)–malonic acid system. The relatively few values of β_{111} reported in the literature for lanthanide complexes have been obtained by computer analysis of systems containing LnL, LnHL, LnL_2, etc., and hence, no reliable "standard" values are available for comparison. The malonate system is possibly the one most studied.

Experimental Section

Bis(2-ethylhexyl)phosphoric acid, HDEHP, was obtained from Pfaltz and Bauer Inc. and purified by a modification[3] of a method of Peppard et al.[4] Analytical grade malonic acid and sodium perchlorate were used without further purification. ^{152}Eu, ^{154}Eu tracer in HCl solution was obtained from Oak Ridge National Laboratory. A portion was evaporated to dryness and redissolved in 1 M $HClO_4$ prior to use.

A 10-mL quantity of an aqueous solution of constant pH and total ionic strength of 0.1 M ($NaClO_4$) with varying total concentrations of malonic acid up to 10^{-3} M and europium tracer were equilibrated with an equal volume of toluene solution of HDEHP of concentration 1×10^{-3} to 6×10^{-3} appropriate for the pH. After overnight equilibration at 25.0 °C in a water bath, the phases were separated and aliquots counted in a NaI(Tl) well type scintillation counter.

Results and Discussion

These distribution studies were conducted at pH 2.50, 2.80, 3.02 and 3.20. The values of β_1 from these experiments are shown in Figure 1 as a function of the $[H]_a$. From this figure, we calculate

$$\beta_{101} = (1.92 \pm 0.06) \times 10^4$$

$$\beta_{111} = (9.22 \pm 0.26) \times 10^6$$

The errors in β_{101} and β_{111} are calculated according to Student's *t* test, 95% significance level.

Ke et al.[5] have reported $\beta_{111} = 1.5 \times 10^7$ at $\mu = 0.15$ M ($NaClO_4$) but Dellien and Grenthe[6] questioned this value. At $\mu = 1.0$ M ($NaClO_4$) these authors reported $\beta_{101} = 5.25 \times$

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[4] D. P. Peppard, G. W. Mason, J. L. Vaier and W. F. Driscoll, *J. Inorg. Nucl. Chem.*, **4**, 334 (1957).

[5] C. H. Ke, P. C. Kong, H. S. Cheng, and N. C. Li, *J. Inorg. Nucl. Chem.*, **30**, 961 (1968).

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