Aqueous Electrochemistry of Quaternary Organoantimony Ions

BY GREGORY L. KOK AND MICHAEL D. MORRIS*

The series of quaternary organoantimony ions, $(CH_3)_m(C_6H_5)_{m-4}Sb^+$ (m = 1–4), has been studied in aqueous solution using dc polarography, cyclic voltammetry, and controlled potential electrolysis. Tetramethylantimony ion undergoes a single two-electron reduction to trimethylantimony and methane. The other three ions in the series are reduced in two one-electron steps. The first electron transfer involves the formation of an antimony(IV) species which rapidly reacts with the electrode metal to form an organomercury radical and a trivalent organoantimony compound. The organomercury radical disproportionates to form a diorganomercury compound. The second electron transfer gives trivalent organoantimony compounds and hydrocarbons. In two of the three possible cases both methyl and phenyl groups are lost by the antimony. The relative losses are different following the first and second electron transfer. Two factors govern the loss of the hydrocarbon group: the stability of the resulting hydrocarbon radical or carbanion and the stability of the resulting antimony compounds.

The electrochemistry of the group V quaternary organometallic ions falls into two groups, that of phosphorus and arsenic and that of antimony and bismuth. A study of these metals as the tetraphenyl derivatives shows that tetraphenylphosphorus and -arsenic ions undergo a single two-electron reduction in aqueous solution,[1] while tetraphenylantimony ions[2] and tetraphenylbismuth ions[3] are reduced in one-electron steps.

In a study of a large number of quaternary phosphorus and arsenic ions, Horner and coworkers[1,4,5] observed that they all undergo single two-electron reductions, represented by reaction 1. The reduction prod-

$$R_4M^+ + 2e^- + H^+ \longrightarrow R_3M + RH \qquad (1)$$
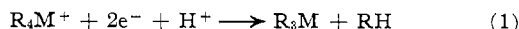
ucts in aqueous solution are the tertiary organometallic compound, R_3M, and the hydrocarbon corresponding to the group lost. For ions containing more than one kind of organic group, loss is governed by the stability of the carbanion that is formed by the leaving group.
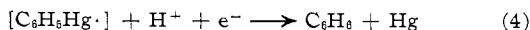
The following mechanism has been proposed by Morris, McKinney, and Woodbury[2] to explain the reduction of tetraphenylantimony ion. The first electron transfer is reduction of a strongly adsorbed tetraphenylantimony ion.

$$(C_6H_5)_4Sb^+ \cdots Hg + e^- \longrightarrow (C_6H_5)_3Sb + [C_6H_5Hg\cdot] \qquad (2)$$
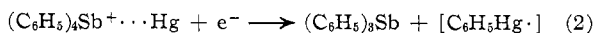
The phenylmercury radical undergoes disproportionation to form diphenylmercury.

$$2[C_6H_5Hg\cdot] \longrightarrow (C_6H_5)_2Hg\cdot + Hg \qquad (3)$$
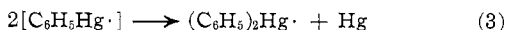
This suggests that the second electron transfer is reduction of the phenylmercury radical to mercury and benzene.

$$[C_6H_5Hg\cdot] + H^+ + e^- \longrightarrow C_6H_6 + Hg \qquad (4)$$

Reaction 4 was postulated on the basis of the coincidence of the second half-wave potential of tetraphenylantimony ion and phenylmercury ion. The same mechanism has been proposed for the tetraphenylbismuth ion. The electrochemistry of other quaternary organoantimony or -bismuth ions has not been reported.

Because of the already observed differences in the electrochemistry of quaternary phosphorus and arsenic ions on the one hand and quaternary antimony and bismuth ions on the other, we have studied the reductions in aqueous solution at a mercury electrode of the series of phenyl–methyl antimony ions of formulas $(CH_3)_m(C_6H_5)_{4-m}Sb^+$, m = 1–4.

Results

The polarographic and coulometric data for the series of quaternary antimony ions studies are shown in Tables I and II. An analysis of the slopes of the plots of log $i/(i_d - i)$ vs. E for the first waves indicates that the first electron transfers are reversible for each of the methyl–phenyl antimony ions. The theoretical slope for a reversible reduction is 0.059 V. For methyltriphenylantimony ion the value is 0.056 V, for dimethylantimony ion the slope is 0.064 V, and for methyltriphenylantimony ion the value is 0.063 V. In each case the second wave does not give a linear plot of log $i/(i_d - i)$ vs. E. Thus the second electron transfers are totally irreversible. The reduction of tetramethylantimony ion is totally irreversible. The limiting currents for all the reduction waves of these ions are diffusion controlled. The various half-wave potentials are independent of concentration of the electroactive species and independent of pH over the accessible range, 4–12.

Controlled-potential electrolysis data are shown in Tables I and II. Tetramethylantimony ion is reduced to trimethylantimony and methane. Following the first electron transfer the mixed ions yield diorganomercury compounds and trivalent organoantimony compounds. After a two-electron reduction the products are benzene and methane along with the trivalent organoantimony compounds. It was impossible to determine if any methylphenylmercury was produced. This compound is quite unstable and will disproportionate rapidly to form the symmetrical diorganomercury compounds.[6] If a small amount were present when the coulometry extracts were assayed, it would have not caused any error in the analysis, as it would be indistinguishable from equivalent amounts of diphenylmercury and dimethylmercury.

Cyclic voltammetry gives very little information

(1) L. Horner and J. Haufe, *J. Electroanal. Chem.*, **20**, 245 (1969).
(2) M. D. Morris, P. S. McKinney, and E. C. Woodbury, *ibid.*, **10**, 85 (1965).
(3) D. Thompson and M. D. Morris, unpublished observations.
(4) L. Horner, F. Rottger, and H. Fuchs, *Chem. Ber.*, **96**, 3141 (1963).
(5) L. Horner and J. Haufe, *ibid.*, **101**, 2903 (1968).
(6) M. M. Koton and A. A. Bolshakova, *Zh. Obshch. Khim.*, **23**, 2037 (1953).

TABLE I
ONE-ELECTRON REDUCTION OF ORGANOANTIMONY IONS

	$E_{1/2}{}^a$	n^b	Found (%)	Trivalent antimony products Calcd from eq 5 (%)		Note
				Ion 3 as ref	Ion 4 as ref	
$(CH_3)_4Sb^+$			One-electron reduction not observed			
$C_6H_5(CH_3)_3Sb^+$	−1.195	0.89	$(CH_3)_3Sb$ (100)	$(CH_3)_3Sb$ (7)	$(CH_3)Sb$ (14)	c
				$C_6H_5(CH_3)_2Sb$ (93)	$C_6H_5(CH_3)_2Sb$ (86)	c
$(C_6H_5)_2(CH_3)_2Sb^+$	−0.900	0.91	$C_6H_5(CH_3)_2Sb$ (81)		$C_6H_5(CH_3)_2Sb$ (68)	c
			$(C_6H_5)_2CH_3Sb$ (19)		$(C_6H_5)_2CH_3Sb$ (32)	
$(C_6H_5)_3CH_3Sb^+$	−0.710	0.92	$(C_6H_5)_2CH_3Sb$ (48)	$(C_6H_5)_2CH_3Sb$ (41)		
			$(C_6H_5)_3Sb$ (52)	$(C_6H_5)_3Sb$ (59)		
$(C_6H_5)_4Sb^+$	−0.635	0.98	$(C_6H_5)_3Sb$ (100)			d

^{a} V *vs.* sce. ^{b} Coulometric n value. ^{c} pH 10.2, carbonate buffer, 2×10^{-3} M. ^{d} pH 6.2, phosphate buffer, ref 2.

TABLE II
TWO-ELECTRON REDUCTION OF ORGANOANTIMONY IONS

Ion	$E_{1/2}{}^a$	n^b	Trivalent organoantimony Products found (%)	Trivalent antimony products calcd from eq 5 (%)		Note
				Ion 3 as ref	Ion 4 as ref	
$(CH_3)_4Sb^+$	−1.490	1.90	$(CH_3)_3Sb$ (100)			d
$C_6H_5(CH_3)_3Sb^+$	−1.515	1.85	$(CH_3)_3Sb$ (100)	$(CH_3)_3Sb$ (11)	$(CH_3)_3Sb$ (15)	c
				$(C_6H_5)(CH_3)_2Sb$ (89)	$C_6H_5(CH_3)_2Sb$ (85)	
$(C_6H_5)_2(CH_3)_2Sb^+$	−1.520	1.85	$C_6H_5(CH_3)_2Sb$ (34)		$C_6H_5(CH_3)_2Sb$ (30)	c
			$(C_6H_5)_2CH_3Sb$ (66)		$(C_6H_5)_2CH_3Sb$ (70)	
$(C_6H_5)_3CH_3Sb^+$	−1.500	1.92	$(C_6H_5)_2CH_3Sb$ (58)	$(C_6H_5)_2CH_3Sb$ (60)		
			$(C_6H_5)_3Sb$ (42)	$(C_6H_5)_3Sb$ (40)		c
$(C_6H_5)_4Sb^+$	−1.200	2.0	$(C_6H_5)_3Sb$ (100)			e

^{a} V *vs.* sce. ^{b} Coulometric n value. ^{c} pH 10.2, carbonate buffer, 2×10^{-3} M. ^{d} Single polarographic wave. ^{e} pH 6.2, phosphate buffer, ref 2.
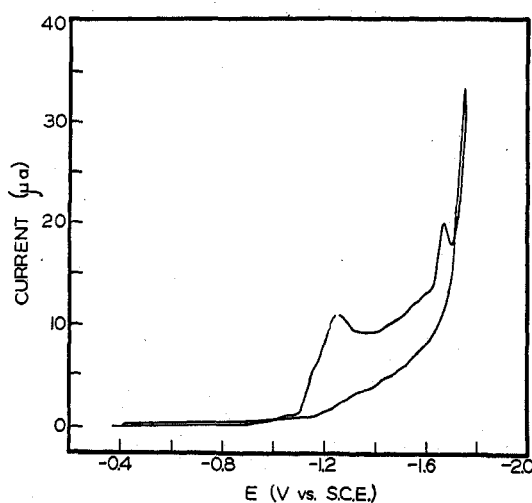

Figure 1.—Cyclic voltammetry of 2×10^{-3} M phenyltrimethylantimony ion: scan rate 0.2 V/sec, pH 7.6, 0.01% Trition X-100.

Figure 2.—Electrocapillary curves of 2×10^{-3} M organoantimony ions: no Trition X-100 present, pH 7.6, 25°. The electrocapillary curve for tetramethylantimony ion is identical with that for the background electrolyte.

about the species produced at the electrode surface. Since a one-electron transfer is observed, one would hope to see evidence for a free radical by cyclic voltammetry. No anodic peaks were observed at scan rates up to 50 Hz (100 V sec), indicating rapid decomposition of intermediates. Figure 1 shows the cyclic voltammetry for trimethylphenylantimony ion. Similar curves were obtained for the other methyl–phenyl ions.

A complete set of electrocapillary curves was obtained for the series of ions. These are shown in Figure 2. The strength of ion adsorption on the electrode surface is a function of the number of phenyl groups present. The curves for tetraphenylantimony ion and methyltriphenylantimony ion are almost identical. It was impossible to complete the electrocapillary curve for tetraphenylantimony ion because the capillary be-
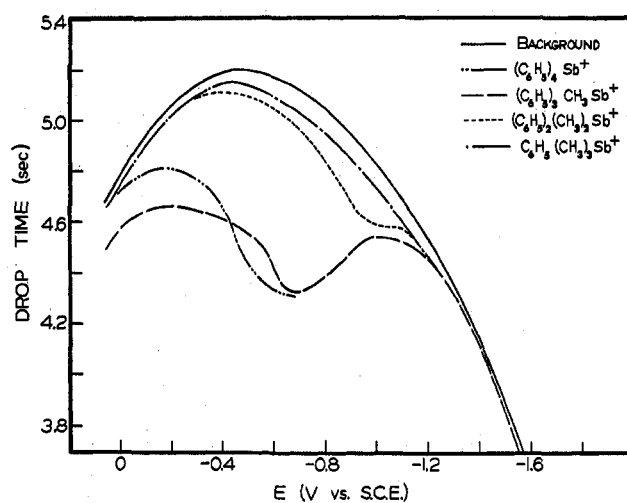
came plugged with triphenylantimony and diphenylmercury at potentials more negative than −0.6 V at the concentration employed for this study.

Discussion

The electrochemical behavior of quaternary organoantimony ions is quite different from that of the corresponding organophosphorus or -arsenic ions, which all undergo only a single two-electron reduction.[1,4,5] In contrast only tetramethylantimony ion undergoes a single two-electron reduction while all the remaining ions in the series give two one-electron reductions. This behavior is a result of the stabilizing influence of phenyl groups on the antimony(IV) products. The ability of phenyl groups to contribute to the ease of reduction can be seen in the systematic positive shift of the first half-

wave potential with an increasing number of phenyl groups on the central metal (Table I).

The group loss data (Tables I and II) obtained by controlled potential electrolysis show that the second reduction step cannot be reduction of an organomercury radical as proposed in eq 4. If organomercury species were formed in the first electron transfer and then reduced, the methyl–phenyl loss ratio observed should be identical for the one- and two-electron reductions of a given ion. This behavior is not observed. The observed product difference is identical for phenyltrimethylantimony ion, but for the other two ions it is quite different.

Reaction 4 was proposed on the basis of the coincidence of the second half-wave potential of tetraphenylantimony ion and phenylmercury ion. However, a polarogram of an equimolar mixture of tetramethylantimony ion ($E_{1/2} = -1.490$ V) and phenylmercury ion ($E_{1/2}(2) = -0.900$ V) shows only two waves. The second reduction step of phenylmercury ion and the reduction of tetramethylantimony ion are superimposed. The first half-wave potential of phenylmercury ion is unaffected. The second half-wave potential of phenylmercury ion, corresponding to reduction of phenylmercury radical to benzene and elemental mercury, is shifted negative to coincide with that of tetramethylantimony ion. The same kind of behavior is observed with a mixture of methyltriphenylantimony ion and phenylmercury ion. In a mixture of trimethyltin ion and phenylmercury ion, the phenylmercury second half-wave potential is shifted negative to the second half-wave potential of the trimethyltin ion. In the reduction of a mixture of zinc ions and phenylmercury ion this shift is not observed. The polarogram is simply the composite of the polarograms of the individual species. The ability of an ion to shift the half-wave potential of phenylmercury ion is related to the adsorption of that ion on the electrode surface. Although the electrocapillary curves do not show adsorption for tetramethylantimony ion at negative potentials, the onset of hydrogen evolution is shifted several hundred millivolts negative. The same behavior is observed with the other organoantimony ions and with trimethyltin ion. Retardation of hydrogen evolution is not observed with zinc ion or with phenylmercury ion alone. In the mixtures of these ions the organoantimony ions or the organotin ions are preferentially adsorbed, and the phenylmercury radical is displaced from the electrode surface. Since zinc ion is not strongly adsorbed at the electrode surface, no displacement of the phenylmercury radical occurs and the normal electrode processes are observed.

Thus the apparent coincidence of phenylmercury waves and those of other phenylmetal ions is not convincing evidence of reaction sequence 1–3.

In a complete study of several mixed alkyl–aryl phosphorus and arsenic ions, Horner and Haufe[5] proposed an expression, eq 5, which allowed calculation of the proportions in which each group would be lost. In eq

$$X = \frac{100a(4-n)m}{a(4-n)m + b(4-m)n} \tag{5}$$

5, X is the calculated amount of RH lost from ion $[R_mR'_{4-m}M]^+$, a (b) is the observed loss in per cent of

RH (R'H) from ion $[R_nR'_{4-n}M]$, n is the number of groups, R, on the reference ion $[R_nR'_{4-n}M]^+$, and m is the number of groups R on ion $[R_mR'_{4-m}M]^+$. Equation 5 combines a statistical factor for the number of groups present with weighting factors for the relative acidities of the carbanions generated. The fact that mixed alkyl–aryl phosphorus and arsenic ions obey eq 5 demonstrates that for these ions organic group loss is governed by the stabilities of the leaving carbanions.

Tables I and II shows application of eq 5 to the series of antimony ions under study. No agreement is noted for the first or second wave. This lack of agreement shows that the group loss for the organometallic antimony ions is governed by factors other than just the stability of the leaving group.

It is often observed that unsymmetrical organometallic compounds are very unstable or undergo redistribution to form the symmetrical species. In the case of tertiary antimony compounds it appears that the monophenyl derivatives are the most prone to undergo redistribution. Both phenylantimony dichloride and phenylantimony oxide undergo redistribution to form the corresponding diphenylantimony compounds and inorganic antimony salts.[7] Diphenylantimony compounds show no tendency to undergo redistribution. Unfortunately no data are available on the stability of the mixed methyl–phenyl antimony compounds.

The stabilities of the groups lost are important in determining the behavior of this series of organoantimony compounds. The equal C–H bond dissociation energies show that the phenyl and methyl radicals have equal stabilities.[8] In the case of the carbanions there is a large difference in stability. The pK_a of benzene is 37 on the MSAD scale while the pK_a of methane is 40.[9] In reactions involving carbanions the formation of a phenyl carbanion will be favored over formation of methyl because of the increased stability of the former.

Both the stability of the leaving group and that of the tertiary antimony compounds formed determine the product distribution after the electrochemical reduction. Phenyltrimethylantimony ion undergoes quantitive loss of the phenyl group after both reduction steps. Trimethylantimony is the sole organoantimony compound formed. Phenyl loss is favored by the stability of the leaving group and of the product formed. Trimethylantimony is the symmetrical antimony product and its generation is favored over the production of the rather unstable dimethylphenylantimony. After the second reduction the phenyl group will form the most stable leaving group and its loss is doubly favored.

In the reduction of dimethyldiphenylantimony ion 19% phenyl group loss is observed following the first electron transfer, with 34% phenyl group loss occurring after two-electron reduction. The antimony products will be either dimethylphenylantimony or diphenylmethylantimony. The production of diphenylmethylantimony would be favored as it is the more stable product. The loss of the phenyl group would be favored by the stability of the leaving group after the second

(7) H. H. Jaffé and G. O. Doak, *J. Amer. Chem. Soc.*, **72**, 3027 (1950).

(8) C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957, p 50.

(9) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, p 19.

step. Since these two factors oppose each other the observed product ratios reflect a balance between these stabilities.

Following the first electron transfer a hydrocarbon radical is lost. Since there is little difference in stabilities between methyl and phenyl radicals, the leaving group will not affect the product distribution. The factor influencing the product distribution is the formation of the more stable antimony compound. Following the two-electron transfer the relative stabilities of the antimony products will remain the same, but the differences in stabilities between the phenyl anion and the methyl anion will be reflected in the product distribution. This difference is shown in the increase of phenyl group loss from 19% to 34%.

Upon reduction of methyltriphenylantimony ion the two possible products are triphenylantimony and diphenylmethylantimony. Since triphenylantimony is a symmetrical product its production would probably be favored slightly. This is reflected in the methylphenyl loss ratios. Following the first electron transfer a 48% phenyl group loss is observed, while after the second electron transfer 58% of the phenyl groups are lost. This increase of phenyl group loss with the second electron transfer shows that the stability of the leaving group is affecting the product loss ratio.

The data obtained by coulometry are useful in formulating a reduction mechanism for these ions. Since a one-electron transfer is observed, antimony(IV) species must be at least transient products. One-electron reduction is aided by two factors, the presence of an aromatic ring on the ions and an energetically favorable decay mechanism. The necessity of an aromatic ring is demonstrated by the difference in reduction mechanism between tetramethylantimony ion and the phenyl-containing ions. The need for a favorable decay mechanism has been demonstrated by Williams and McKinney.[10] They reduced tetraphenylantimony ion at a pyrolytic graphite electrode under different conditions. Reduction at a clean graphite electrode occurred in a single two-electron step to triphenylantimony and benzene. Reduction at a graphite electrode plated with a monolayer or more of mercury occurred in two one-electron steps. The products of the first step were triphenylantimony and diphenylmercury. These experiments show that mercury not only acts as a trap for the free radical formed, but that its presence is required to promote a one-electron transfer.

We propose a mechanism differing significantly from that suggested earlier for the reduction of the tetraphenylantimony ion.[2] The first reduction step is a one-electron transfer, eq 6. The organoanti-

$$(CH_3)_m(C_6H_5)_{4-m}Sb^+ + e^- \longrightarrow (CH_3)_m(C_6H_5)_{4-m}Sb \cdot \quad (6)$$

mony(IV) radical generated by the first electron transfer rapidly reacts with the electrode mercury to form an organomercury radical and a triorganoantimony. Equation 7 demonstrates the stoichiometry for phenyl group loss. The phenylmercury radical so

$$(CH_3)_m(C_6H_5)_{4-m}Sb \cdot + Hg \longrightarrow$$
$$(CH_3)_m(C_6H_5)_{3-m}Sb + C_6H_5Hg \cdot \quad (7)$$
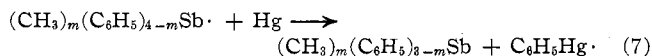
formed undergoes rapid disproportionation to diphenylmercury, eq 3. An analogous pair of reactions can

be written for formation and disproportionation of methylmercury radical. The formation of methylphenylmercury cannot be ruled out on the basis of our data, but formation of this species does not change the argument about the behavior of the organoantimony ions and radicals.

We propose that the second electron transfer is direct reduction of an organoantimony radical. Equation 8 describes the stoichiometry for phenyl loss.

$$(CH_3)_m(C_6H_5)_{4-m}Sb \cdot + H^+ + e^- \longrightarrow$$
$$(CH_3)_m(C_6H_5)_{3-m}Sb + C_6H_6 \quad (8)$$
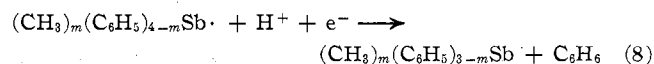
The half-wave potential for this reduction step is pH independent because the electron transfer occurs prior to the protonation step.

We propose that reaction sequence 6–8 applies to tetraphenylantimony ion as well as to the mixed phenyl–methyl antimony ions. The proposal of phenylmercury radical as the species reduced in the second step of the reduction of tetraphenylantimony ion was made on the basis of evidence now known to be misleading.

The electrocapillary curves (Figure 2) show that strong adsorption at the electrode surface is not necessary for transmetalation to take place. Previous studies[2,11] have shown that transmetalation is often accompanied by strong adsorption. In the case of trimethylphenylantimony ion the curve is slightly depressed from the background, and no inflections are noted at the first half-wave potential. Dimethyldiphenylantimony ion shows slightly more adsorption and there is a small inflection at the first half-wave potential. The adsorption of triphenylmethylantimony ion is very close to that observed for tetraphenylantimony ion. It is difficult to draw any conclusions about the geometry of the molecules at the electrode surface from these data. Because of the strong adsorption of tetraphenylantimony ion at the electrode surface, Morris, McKinney, and Woodbury[2] suggested that it may be distorted to form a trigonal-pyramidal molecule at the electrode surface. Studies of the vibrational spectroscopy of tetraphenylantimony ion in aqueous solution indicate that it may possess this geometry in solution.[12] This may also be the case with triphenylmethylantimony ion. Far-infrared and Raman pulsed nmr studies are underway on this series of organoantimony ions to determine their geometries in aqueous solution.

Experimental Section

Tetramethylantimony iodide[13] was prepared by addition of trimethylantimony to methyl iodide. Phenyltrimethylantimony iodide[14] was prepared by the addition of dimethylphenylantimony to methyl iodide. Methyltriphenylantimony tetrafluoroborate[15] was prepared by reaction of triphenylantimony with trimethyloxonium tetrafluoroborate[16] in anhydrous liquid sulfur dioxide.

Dimethyldiphenylantimony compounds have not been previously reported. The fluoroborate was prepared by reacting diphenylmethylantimony with trimethyloxonium tetrafluoroborate, mp 131–132°. *Anal.* Calcd: Sb, 31.02. Found:

(10) T. R. Williams and P. S. McKinney, *J. Electroanal. Chem.*, **30**, 131 (1971).

(11) J. S. Di Gregorio and M. D. Morris, *Anal. Chem.*, **40**, 1286 (1968).

(12) J. B. Orenberg, M. D. Morris, and T. V. Long, *Inorg. Chem.*, **10**, 933 (1971).

(13) W. von E. Doering and D. K. Hoffman, *J. Amer. Chem. Soc.*, **77**, 52, (1955).

(14) G. Guttner and M. Wiernik, *Ber.*, **48**, 1760 (1915).

(15) M. C. Henry and G. Wittig, *J. Amer. Chem. Soc.*, **82**, 563 (1960).

(16) H. Meerwein, *Org. Syn.*, **46**, 120 (1966).

Sb, 31.07, 31.04. In contrast to the salts of the other ions of the series, dimethyldiphenylantimony salts are quite unstable. The tetrafluoroborate salt must be recrystallized from water immediately before use. The tetrafluoroborate salt loses boron trifluoride and methyl fluoride to form diphenylmethylantimony.

Polarographic data were taken on a locally constructed operational amplifier polarograph. A three-electrode system was used with a saturated calomel reference electrode. The cell was maintained at 25° and the solution blanketed with prepurified nitrogen during each run. The solutions were deaerated for 15 min with prepurified nitrogen before each polarographic run. All background solutions were prepared from distilled water and reagent grade chemicals. Potassium nitrate was used as the supporting electrotype. The solutions were buffered at pH 10.2 using carbonate buffer. It was necessary to work at this pH to obtain sufficient separation of the second wave from hydrogen reduction. All polarograms and coulometric runs were made at this pH unless otherwise noted. Concentration of the electroactive species was generally 2×10^{-3} M. All polarographic and coulometric solutions contained 0.01% Trition X-100.

Cyclic voltammetry was done at a hanging mercury drop on a Kemula electrode (Brinkman Instruments). Low-frequency scans were recorded on an X–Y recorder while high-frequency measurements were photographed from an oscilloscope trace. A Wavetek Model 112 signal generator was used to generate the triangular wave.

Large-scale controlled-potential electrolyses were carried out on a mercury pool using a potentiostat constructed in these laboratories. The coulometric cell had a nominal working electrode area of 30 cm². The mercury was agitated with a magnetic stirrer. The anode was isolated in a separate chamber behind a fritted glass disk. The reference electrode was positioned directly above the working electrode to minimize the effect of solution resistance. The solution compositions were the same as those used for polarography. Prepurified nitrogen was bubbled through the solution for about 15 min before each electrolysis, and the cell was sealed to eliminate the possibility of loss of the various products. All connections to the cell were made through ground-glass joints.

Product analysis was done by nuclear magnetic resonance spectroscopy on a Varian T-60 spectrometer. After electrolysis 2 ml of CDCl₃ was injected into the electrolysis cell under an argon atmosphere. The electrolysis solution and the CDCl₃ were then stirred for 30 min. The mixture of aqueous electrolysis solution, CDCl₃, and mercury was transferred to a modified separatory funnel and the CDCl₃ removed through a septum. Evaporation of the CDCl₃ from a known volume of the extract showed recovery of the products was 95–100% complete. The product distributions could be obtained by taking the ratios of the areas of the phenyl and methyl peaks obtained by nmr. The mixtures gave very well-defined spectra, and no interferences from the Trition X-100 were noted.

Control experiments were carried out to verify that no exchange of groups occurs between the antimony and mercury compounds. Equimolar amounts of diphenylmercury and tetramethylantimony iodide were introduced into electrolysis. The tetramethylantimony ion was then reduced under the conditions of the other electrolyses. The products were extracted into CDCl₃ and analyzed by nmr as previously described. No exchange of groups between the antimony and mercury was noted. Methylmercury chloride was reduced to dimethylmercury in the presence of triphenylantimony to check another possible redistribution. Assay by nmr showed no redistribution in this case either. As a check on the stability of the unsymmetrical products, dimethylphenylantimony was prepared and placed in the electrolysis cell along with phenylmercury acetate. The phenylmercury acetate was reduced to diphenylmercury and the electrolysis solution analyzed as before. Careful examination of the nmr spectra showed that no decomposition of the dimethylphenylantimony had taken place. This control was repeated using methylmercury chloride in place of the phenylmercury acetate. Following the electrolysis an assay of the solution showed no decomposition of the dimethylphenylantimony.

Synergistic Effect of Tri-*n*-octylamine on the Solvent Extraction of Cerium(III) by Thenoyltrifluoroacetone[1]

BY L. NEWMAN* AND P. KLOTZ

The synergistic effect of tri-*n*-octylamine (R_3N) on the solvent extraction of cerium by thenoyltrifluoroacetone (HT) is shown to arise from the organic-phase reactions $CeT_3 + R_3NHCl = CeT_3R_3NHCl$, $CeT_3 + R_3NHT = CeT_3R_3NHT$, and $CeT_3 + R_3NHClHT = CeT_3R_3NHClHT$, where T^- represents the enolate ion of HT. It was ascertained that the formation constants for each of these reactions as measured in benzene are the same, and a value was found for $\log K_s = 4.83 \pm 0.15$. The synergistic effect in this system was found to be identical in kind and almost in magnitude with that observed in a previous investigation involving americium.

Introduction

The synergistic effect of tri-*n*-octylamine (TNOA or R_3N) on the thenoyltrifluoroacetone (TTA or HT) extractions of thorium(IV),[2] americium(III),[3] cobalt(II), and zinc(II)[4] have been previously examined. In the first two studies, the aqueous phase contained hydrochloric acid and lithium chloride. Under the conditions used in these studies, three amine species were known to exist: R_3NHCl, R_3NHT, and $R_3NHClHT$.[5,6]

The enhancement in the extraction of thorium was attributed to the attachment of R_3NHCl to one of the TTA molecules in the $Th(TTA)_4$ complex. In the americium(III) study, the enhancement was found to be 400 times greater than the effect exhibited in the thorium study. The three amine species were found to contribute equally to this effect and it was believed that they were bonded directly to the metal.

(1) This research performed under the auspices of the United States Atomic Energy Commission.

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