methylammonium salt is 3.26×10^{-5}. The weakest of the substituted salts is choline (hydroxyethyltrimethylammonium) picrate, whose constant is 0.66×10^{-5}, while the strongest salt is methoxymethyltrimethylammonium picrate ($K = 2.54 \times 10^{-5}$), an isomer of the choline salt. The two isomeric ions have the same conductance but one contains the weakly polar methoxy group, the other, the strongly polar hydroxyl group.

Bromomethyltrimethylammonium picrate is a markedly weaker electrolyte than the corresponding bromoethyl salt ($K = 0.78 \times 10^{-5}$ and 1.32×10^{-5}, respectively). Evidently, the effect is the greater, the nearer the substituent lies to the central charge on the nitrogen atom. Larger dissociation constants result with substitution of larger atoms, as, for example, the bromomethyl derivative is weaker than the corresponding iodomethyl compound. The arsenocholine salt is stronger than the choline salt but the corresponding salt of acetylcholine is stronger than that of acetylarsenocholine.

In what manner the electronegative atoms or groups in the onium ions act in order to reduce the values of the dissociation constant of the ion-pair equilibrium is somewhat uncertain as yet. In the case of choline, hydrogen bonding with the negative ion might be suspected through the intermediation of the hydrogen of the hydroxyl group. That such hydrogen bonding occurs in the case of unsubstituted and partially substituted ammonium ions in nitrobenzene is well established.[6] However, the halogens, when introduced into the onium ions, have much the same effect as has the hydroxyl group It seems unlikely that the observed effect may be accounted for on the basis of hydrogen bonding.

The introduction of a negative element or group serves to introduce an electrical dipole into the ion. It is conceivable that interaction occurs between the ions and the dipoles. Perhaps the greatest objection to the dipole interpretation is the fact that the nearer the substituent atom lies to the charge on the nitrogen atom, the greater is its effect. Thus, the constant of the bromoethyl derivative is 1.32×10^{-5}, while that of the bromomethyl derivative is 0.78×10^{-5}. If dipole interaction is a controlling factor, we should expect the effect to be the greater the more exposed the position of the dipole.

On the basis of the available experimental results, it seems more reasonable to ascribe the effect of electronegative elements to a displacement of the center of charge in the ion. This accords with the fact that the effect is the greater, the nearer the negative atom, or group, lies to the nitrogen atom.

V. Summary

1. The conductance of the following picrates has been measured in ethylene chloride at 25°: ethyltrimethylammonium, choline, acetylcholine, arsenocholine, acetylarsenocholine, bromoethyltrimethylammonium, bromomethyltrimethylammonium, iodomethyltrimethylammonium, and methoxymethyltrimethylammonium.

2. Values of Λ_0 and of K (dissociation constant) were obtained for all salts by the method of Fuoss.

3. The dissociation constants of salts containing negative atoms or groups in the cation are markedly lower than those of salts not containing such atoms.

4. Ion conductances have been evaluated.

PROVIDENCE, R. I. RECEIVED NOVEMBER 6, 1946

---

[6] Witschonke. Thesis. Brown University. 1941.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY]

Polarographic Characteristics of Chloro Complexes of +5 Antimony

BY JAMES J. LINGANE AND FUMIO NISHIDA

When present in the +3 state antimony is readily reducible at the dropping mercury electrode from its solutions in hydrochloric, nitric and sulfuric acids,[1-4] and even from sodium hydroxide solutions and in acidic, neutral and basic tartrate media,[4] but +5 antimony is not. Indeed, Page and Robinson[3] observed no reduction wave for +5 antimony (added as sodium antimony (V) gluconate) in 1 N hydrochloric acid, when conditions for reduction ought to be very favorable. Since in various other reactions in strongly acid media, notably the oxidation of iodide ion and sulfurous acid, +5 antimony behaves as a fairly strong but rather slow oxidant the thermodynamic conditions for reduction at the dropping electrode from acid medium are certainly satisfied. The difficulty of obtaining a reduction wave must be attributed to a very small rate of reaction and a very large activation energy (overvoltage).

A similar situation exists in the case of stannic tin, and since in that case the overvoltage can be so greatly diminished by converting the aquo stannic ion to a chloro complex that a very well developed wave is obtained in concentrated chloride solutions,[5] it seemed likely that a similar reduction in overvoltage might be obtained with +5

---

[1] V. Bayerle. *Rec. trav. chim.*, **44**, 514 (1925).

[2] K. Kacirkova, *Collection Czechoslov. Chem. Commun.*, **1**, 477 (1929).

[3] J. E. Page and F. A. Robinson, *J. Soc. Chem. Ind.*, **61**, 93 (1942).

[4] J. J. Lingane. *Ind. Eng. Chem., Anal. Ed.*, **15**, 583 (1943).

[5] J. J. Lingane. THIS JOURNAL, **67**, 919 (1945).

antimony in the presence of a large concentration of chloride ion. This expectation has been realized; the $SbCl_6^-$ ion present in solutions containing very large concentrations of hydrogen and chloride ions is easily reduced at the dropping electrode, first to the +3 state and then to the metal (amalgam). In this investigation the influence of hydrogen and chloride ion concentrations on the characteristics of the +5 antimony wave has been studied, and the optimum conditions for the polarographic determination of +5 antimony have been established.

Experimental Technique

Standard solutions of +5 antimony were prepared from the metal and from potassium antimonyl tartrate hemihydrate. In the former case, a weighed sample of powdered antimony was dissolved in hydrochloric acid with the aid of sufficient nitric acid to effect complete oxidation, the solution was boiled to remove chlorine and oxides of nitrogen, and was finally diluted to a known volume in either 2 or 4 *N* hydrochloric acid. In the latter case, a weighed amount of recrystallized and air-dried potassium antimonyl tartrate hemihydrate was dissolved in 2 *N* hydrochloric acid, a small excess of potassium permanganate solution was added to oxidize the antimony to the +5 state, and after boiling to remove chlorine and complete the reduction of +3 and +4 manganese compounds, the solution was diluted to a known volume in 2 *N* hydrochloric acid. These stock solutions contained from 7 to 14 millimolar +5 antimony, and they were stable indefinitely. Hydrolytic precipitation occurs when the concentration of +5 antimony in 2 *N* hydrochloric acid is greater than about 20 millimolar.

Polarographic measurements were made both with a manual apparatus[6,7] and with a photographically recording polarograph of the Heyrovsky-Shikata type described in a previous paper.[8]

An H-cell[9] with a saturated calomel electrode as anode was used, and all measurements were made at 25.0 ± 0.1°. Dissolved air was removed from the solutions with either nitrogen or hydrogen. The dropping mercury electrode assembly, which included a stop-clock device for automatically measuring the rate of flow of mercury, has been described elsewhere.[10] The *m*-values of the several dropping electrodes used were between 1.4 and 1.6 mg./sec., and the drop times in hydrochloric acid solutions in the neighborhood of −0.6 v. *vs.* the saturated calomel electrode ranged from 3 to 4.5 sec.

Results and Discussion

Figure 1 shows typical polarograms of +5 antimony in various concentrations of hydrochloric acid containing 0.005% gelatin as a maximum suppressor. In 0.2 *N* hydrochloric acid (curve a) no reduction wave is observable. When the concentration of hydrochloric acid is increased above 0.5 *N* a wave appears and becomes better developed as the hydrochloric acid concentration is increased. Finally when the hydrochloric acid concentration is 4 *N* or greater (curves c and d) a double wave results, corresponding to the stepwise reduction of the +5 antimony first to the +3 state and then to the metal. In 4 *N* hydrochloric acid (curve c) the diffusion current of the first reduction stage is not quite completely developed before reduction to the metal begins, the height of the first wave being only 0.30 that of the total double wave instead of the expected 0.40 for successive 2- and 5-electron reductions. In 6 *N* hydrochloric acid (curve d) the first diffusion current does become fully developed, and equal to exactly 0.40 of the total diffusion current (Table I).

The steep slope of the second wave in 4 to 6 *N* hydrochloric acid indicates that the reduction of the chloro-antimonite ion proceeds reversibly, and therefore the half-wave potential (−0.257 v. *vs.* the saturated calomel electrode in 6 *N* hydrochloric acid) is virtually identical with the standard potential of the reaction

$$SbCl_p^{(3-p)+} + 3\,e^- + Hg = Sb(Hg) + p\,Cl^- \quad (1)$$

where the coördination number p is probably either 4 or 6.

The potential at which the first wave in 4 and 6 *N* hydrochloric acid starts does not correspond to the reduction potential of the chloroantimonate ion to the +3 state, but is merely the potential at which anodic dissolution of mercury from the dropping electrode takes place according to $Hg + 4\,Cl^- = HgCl_4^{=} + 2\,e^-$. In 6 *N* hydrochloric acid the true reduction potential of the chloro antimonate ion evidently is more positive than −0.1 v. but its exact value cannot be deduced from the curves in Fig. 1.

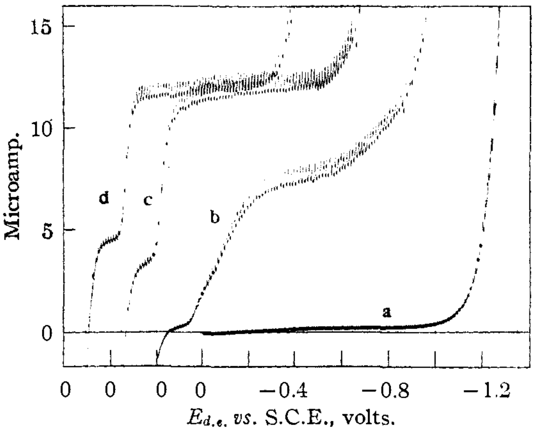

Fig. 1.—Polarograms of 0.975 millimolar +5 antimony in (a) 0.2, (b) 2, (c) 4, and (d) 6 *N* hydrochloric acid, with 0.005% gelatin as a maximum suppressor. The starting voltage of each curve *vs.* the saturated calomel electrode is indicated by 0, and each voltage increment corresponds to 0.2 v. In the absence of gelatin the second wave in 6 *N* hydrochloric acid displayed a sharp maximum.

The polarograms in Fig. 2 demonstrate that a single reduction wave for +5 antimony is obtained when the concentration of hydrogen ion is kept constant at a relatively small value (0.2 *N*) but the chloride ion concentration is increased by

---

(6) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941.

(7) J. J. Lingane and I. M. Kolthoff, THIS JOURNAL, **61**, 825 (1939).

(8) J. J. Lingane, *ibid.*, **68**, 2448 (1946).

(9) J. J. Lingane and H. A. Laitinen, *Ind. Eng. Chem., Anal. Ed.*, **11**, 504 (1939).

(10) J. J. Lingane, *ibid.*, **16**, 329 (1944).

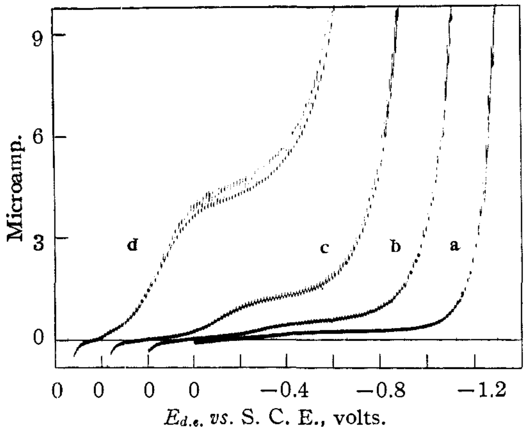

Fig. 2.—Polarograms of 1 millimolar +5 antimony in 0.2 N hydrochloric acid containing (a) 0, (b) 1, (c) 2 and (d) 5 M ammonium chloride.

addition of ammonium chloride. However, even in 5 N ammonium chloride and 0.2 N hydrochloric acid (curve d) the wave is not completely developed, and the limiting current is only about one-half as large as in the same concentration of hydrochloric acid. The single wave in this medium must correspond to the reduction of the +5 antimony directly to the metal, because the potential at which the wave occurs is so much more negative than the reduction potential of +3 antimony that the latter is reduced as rapidly as it is formed.

The effect of increasing concentration of hydrogen ion (as perchloric acid) at a constant concentration of chloride ion (0.2 N) is shown by the polarograms in Fig. 3. Even with a relatively small concentration of chloride ion the characteristic doublet wave is obtained if the concentration of hydrogen ion is made very large (curve d). In 6 N perchloric acid containing 0.2 N hydrochloric acid the half-wave potential of the second stage of reduction is −0.163 v., and thus very close to the half-wave potential (−0.15 v.) of +3 antimony in 1 N hydrochloric acid.[4] The potential at which the first wave in 6 N perchloric acid −0.2 N hydrochloric acid occurs is more positive than in 6 N hydrochloric acid simply because the anodic dissolution potential of mercury is at a more positive potential in the former medium due to the smaller concentration of chloride ion.

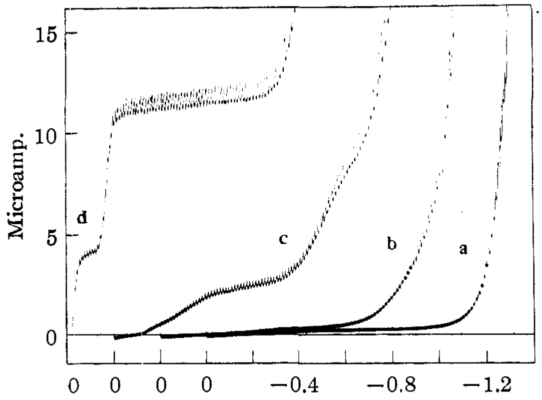

Fig. 3.—Polarograms of 1 millimolar +5 antimony in 0.2 N hydrochloric acid containing (a) 0, (b) 1, (c) 3 and (d) 6 N perchloric acid, with 0.005% gelatin as a maximum suppressor.

The following experiment proved that +5 antimony does not produce a reduction wave from a strongly acid solution when no chloride is present. A filtered saturated solution of pure potassium pyroantimonate in 6 N perchloric acid was transferred to a polarographic cell with a mercury pool anode. The polarogram of this solution showed no reduction wave before the reduction of hydrogen ion, but when 0.25 N hydrochloric acid was added the characteristic double wave of the +5 antimony appeared.

It is clear from these results that both hydrogen and chloride ions are essential in the formation of the reducible species of +5 antimony, which very probably is the hexachloro antimonate ion, $SbCl_6^-$. It seems likely that in acid solutions containing only a relatively small concentration of chloride ion the predominant species is an ion containing both oxygen and chloride ion, such as $SbO_2Cl_2^-$, which evidently is not easily reduced. With increasing concentration of hydrogen and chloride ions more of the oxygen in the complex is replaced by chloride ion until finally the reducible $SbCl_6^-$ predominates.

$$SbO_2Cl_2^- + 2H^+ + 2Cl^- = SbOCl_4^- + H_2O \quad (2)$$

$$SbOCl_4^- + 2H^+ + 2Cl^- = SbCl_6^- + H_2O \quad (3)$$

The fact that a very large concentration of either hydrogen or chloride ion is required to produce the reducible species indicates that the equilibrium constants of these reactions must be quite small.

The data in Table I demonstrate that both the diffusion current of the first wave and that of the total wave in 6 N hydrochloric acid containing

TABLE I

DIFFUSION CURRENT CONSTANTS OF +5 ANTIMONY

Supporting electrolyte consisted of 6 N hydrochloric acid containing 0.005% gelatin. The diffusion current of the first wave was measured at about −0.2 v. *vs.* S. C. E. ($m^{2/3}t^{1/6}$ = 1.602 mg.$^{2/3}$ sec.$^{-1/2}$), and the total diffusion current was measured at −0.4 v. ($m^{2/3}t^{1/6}$ = 1.620 mg.$^{2/3}$ sec.$^{-1/2}$). Correction was applied for the residual current. Temp. = 25.00°.

Sb^{+5} millimolar	i_d, microamp. First wave	i_d, microamp. Total	$i_d/(Cm^{2/3}t^{1/6})$ First wave	$i_d/(Cm^{2/3}t^{1/6})$ Total
0.0731	0.34	0.87	2.91	7.35
.1434	0.68	1.72	2.97	7.43
.2685	1.30	3.27	3.02	7.50
.3389	1.62	4.12	2.99	7.50
.6346	3.10	7.81	3.04	7.57
1.065	5.18	13.00	3.04	7.55
1.995	9.70	24.49	3.03	7.56
2.620	12.67	31.83	3.03	7.53
			Av. 3.00 ± 0.04	7.50 ± 0.05

0.005% gelatin are accurately proportional to the concentration of +5 antimony.

The ratio of the average observed diffusion current constants, 7.50/3.00, agrees exactly with the theoretical value 2.50 for successive 2- and 5-electron reduction reactions. The observed diffusion current constants correspond to a value of 0.61 × 10^{-5} cm.^{2}/sec. for the diffusion coefficient of the hexachloroantimonate ion under these conditions. By means of relations that have been described elsewhere (ref. 6, p. 45), it follows from these data that the equivalent conductance of the $SbCl_6^-$ ion at infinite dilution at 25° is in the neighborhood of 23 ohm^{-1} cm.^{2}.

Summary

From its solutions in 4 to 6 N hydrochloric acid, or in 6 N perchloric acid containing 0.2 N hydrochloric acid, +5 antimony undergoes stepwise reduction at the dropping electrode, first to the +3 state and then to the metal. The reducible species is the $SbCl_6^-$ ion. Both diffusion currents of the resulting double wave are very well developed.

In 6 N hydrochloric acid containing 0.005% gelatin the first wave starts at zero applied e.m.f., and the half-wave potential of the second wave is −0.257 v. *vs.* the saturated calomel electrode. Both diffusion currents are directly proportional to the concentration of +5 antimony, and the diffusion current constants $i_d/(C\,m^{2/3}t^{1/6})$ are equal to 3.00 and 7.50 microamp./millimole/liter/mg.$^{2/3}$/sec.$^{1/2}$ at 25°.

Solutions of +5 antimony in 6 N perchloric acid in the absence of chloride ion show no indication of a reduction wave before reduction of hydrogen ion.

CAMBRIDGE, MASS. RECEIVED OCTOBER 26, 1946

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KENTUCKY]

The Effect of the Hydrogen Ion Concentration upon the "Salt Error" of the Quinhydrone Electrode

BY JAMES L. GABBARD[1]

Introduction

In a previous investigation data were obtained indicating that the "salt error" of the quinhydrone electrode, which has been investigated by a number of workers,[2-8] is a function of the hydrogen ion concentration as well as the concentration of the salt present. In all previous investigations the solvent for the salt solutions was 0.01 N hydrochloric acid. This means that the *p*H of the solutions were low, and varied only slightly. Therefore, it was felt that a study of the "salt error" as a function of the hydrogen-ion concentration would be valuable.

Apparatus and Materials

The electrode vessel, shown in Fig. 1, consisted of three 2.5 × 6 cm. Pyrex tubes connected by a three-way stopcock and fitted, respectively, with a pair of hydrogen electrodes, a pair of quinhydrone electrodes, and the connecting arm of a calomel cell. A rubber stopper was fitted over the lower portion of the stopcock and sealed with picene.

The salt solutions of the various concentrations were made by diluting in volumetric flask concentrated stock solutions which were made by weighing and diluting commercial C.P. chemicals. Those of magnesium salts were quantitatively analyzed for their magnesium content. The solvent for the salt solutions was approximately 0.01 N acetic acid. However, to avoid fermentation the calculated amount of glacial acetic acid was added at the time of dilution and the exact acid strength determined by titration. The quinhydrone was obtained from the Eastman Kodak Company. The platinizing solution made by dissolving C.P. platinum in aqua regia, repeatedly evaporating to near dryness in hydrochloric acid, diluting to a strength of 2% and adding a trace of lead acetate. The hydrogen electrodes were made from thin sheet platinum in the usual manner while the quinhydrone electrodes were the regular L. and N. gold electrodes. Before each series of measurements the platinum black was removed from the hydrogen electrodes by dipping in hot aqua regia and with the gold electrodes placed in hot chromic acid cleaning solution (110–125°) and allowed to stand overnight. A series of experiments included all the measurements on any particular salt concentration at the various *p*H values. The electrolytic hydrogen was purified by passing it through bottles containing concentrated potassium hydroxide, water and cotton, and then over hot metallic copper (450–500°).

Experimental

A pair of clean, well-rinsed hydrogen electrodes were platinized for exactly one minute by use of a three-volt heavy duty dry cell, washed under the

---

[1] Senior Research Chemist, Carbide and Carbon Chemicals Corporation, Oak Ridge, Tennessee.

[2] E. S. Amis and J. L. Gabbard, THIS JOURNAL, **59**, 557 (1937).

[3] F. Hovorka and W. C. Dearing, *ibid.*, **57**, 446 (1935).

[4] A. V. Kiss and A. Urmanczy, *Z. Physik. Chem.*, **A169**, 31 (1934).

[5] Sörensen, Sörensen and Linderstrøm-Lang, *Ann. chim.*, **16**, 283–320 (1921).

[6] Einar Biilmann, *Bull. soc. chim.*, **41**, 213–286 (1927).

[7] Von G. Tammann and E. Jenekel, *Z. anorg. allgem. Chem.*, **173**, 337 (1928).

[8] Antal Urmanczy, *Magyar Chem. Falyoiat*, **39**, 125–137 (1933); *C. A.*, **28**, 3971 (1934).