uct of the reaction of *p*-methoxyphenacyl bromide with 8-chloroquinoline and recrystallized, this is a white, water-soluble salt, m.p. 222–223° (dec.).

Anal. Calcd. for C_9H_9BrCl: Br, 32.94. Found: Br, 32.89, 32.99.

Since quaternary salts of 2-halopyridines have been shown to have a reactive halogen atom and to be converted into N-substituted 2-pyridones in alkaline solution,[3] it seems likely that this change occurs in the blood stream of animals after the compound has been injected. A pyridone was prepared for comparison of its effect with those of the parent compound.

1-*p*-Fluorophenacyl-2-pyridone.—Two grams of 1-*p*-fluorophenacyl-2-chloropyridinium bromide and 1.64 g. of Na_2CO_3 in 140 ml. of H_2O was allowed to stand overnight at room temperature. Upon cooling and filtering, 3.4 g. (79%) of crude product was obtained. After recrystallization from hot acetone, by chilling, the white crystals melted at 126°.

Anal. Calcd. for $C_{13}H_{10}FNO_2$: C, 67.55; H, 4.37. Found: C, 67.73; H, 4.25.[4]

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[3] F. Krohnke and W. Heffe, *Ber.*, **70B**, 864 (1937).

[4] We wish to thank Dr. J. L. Hartwell of the National Cancer Institute for obtaining these analyses.

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The Polarizing Effect of Trace Amounts of Antimony(III) on the Electrolytic Oxidation of Arsenic in Acid Solution

BY BERTSIL B. BAKER AND WILLIAM M. MACNEVIN

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In a previous investigation[1] the electrolytic oxidation of arsenic has been shown to proceed with 100% current efficiency in strong acid solution and, more recently, use has been made of this reaction in a coulometric determination of arsenic.[2] During this latter work it was found that the magnitude of the current during the electrolysis did not diminish in a regular fashion as was expected, but instead exhibited the unusual minimum shown in Fig. 1. This paper is concerned with the explanation of this behavior.

It has been shown[3,4] that the current in a 100% current efficient electrolysis conducted at constant electrode potential may be expected to follow the equation $i_t = i_0e^{-tk}$, where i_t is the current at any time t, i_0 the initial current, and k a constant. Integration of this equation[2] gives the area under the curve as equal to $i_0/2.303\ kt$, where i_0 is the intercept and k the slope of the straight line obtained by plotting $\log_{10}$ current *vs.* time. That the current in ordinary primary coulometric determinations does follow such an equation has been demonstrated in the case of the controlled potential reduction of lead,[3] copper,[4] picric acid,[3] and the oxidation of iron.[2] In this latter case agreement with the equation was sufficiently close to allow calculation of the results of a coulometric determination of iron from the integrated equation by determining only the slope and intercept of the log current *vs.* time curve. It was expected that this same technique could be applied to the coulometric determination of arsenic, and it was in attempting to do so that the unusual shape of the electrolysis curve was observed.

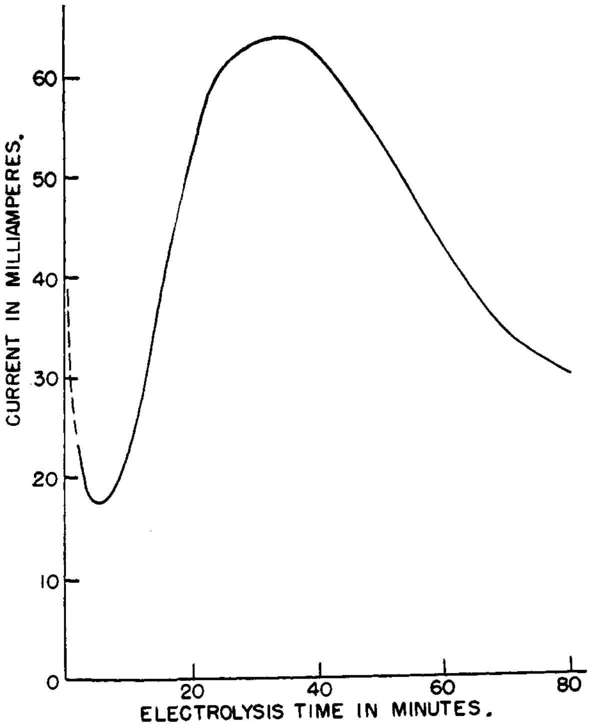

Fig. 1.—A typical minimum in the current–time curve for the electrolytic oxidation of "Analytical Reagent" quality As_2O_3.

Experimental

Apparatus.—The electrolysis cell consisted of two 180-ml. electrolytic beakers sealed together at the bottom by a tube *ca.* 40 mm. long and 20 mm. in diameter containing a medium porosity fritted-glass disk. The anode compartment was stirred with a plastic-coated magnetic stirring bar.

A potentiostat of the design of Lingane[5] was used to provide control of the anode potential to *ca* 0.01 volt.

Current values were recorded automatically by a Leeds and Northrup Model S 40000 Series Micromax Multiple Point Recorder which measured the voltage drop across a resistance in series with the electrolysis cell. The instrument was designed to record about once a minute but during the latter part of this work was modified to record about every 10 seconds.

The electrodes used were "Slomin" platinum gauze electrodes. The cathode area was 75 sq. cm. and the anode 40 sq. cm. by approximate geometric measurement. The actual area was undoubtedly much larger, since the surface was sand-blasted.

Procedure.—When it was found[6] that an oxide film on the anode affects the magnitude of the current in the electrolytic oxidation of arsenic, the anode was pre-polarized at hydrogen evolution to remove any oxide layer. This was done by electrolyzing 1 *M* sulfuric acid between two platinum electrodes for two minutes with a total of four volts applied potential, supplied from two cells of a six-volt storage battery. The cathode in this electrolysis was then used as anode in the oxidation of arsenic.

The catholyte was 100 ml. of 1 *M* sulfuric acid and the anolyte 100 ml. of *ca.* 0.025 *N* arsenic(III) in 1 *M* sulfuric acid, except during the concentration studies. The electrolyses were conducted with a controlled anode potential of either −1.0 or −1.2 volts *vs.* satd. calomel electrode. Slightly higher initial currents were obtained with the higher potential, but the general shape of the curves remained the same.

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[1] W. M. MacNevin and G. L. Martin, THIS JOURNAL, **71**, 204 (1949).

[2] W. M. MacNevin and B. B. Baker, *Anal. Chem.*, **24**, 986 (1950).

[3] J. J. Lingane, THIS JOURNAL, **67**, 1916 (1945).

[4] J. J. Lingane, *Anal. Chim. Acta*, **2**, 584 (1948).

[5] J. J. Lingane, *Ind. Eng. Chem.*, *Anal. Ed.*, **17**, 332 (1945).

[6] B. B. Baker and W. M. MacNevin, THIS JOURNAL, **75**, 1476 (1953).

Results and Discussion

It has been shown previously from coulometric studies[2] that the over-all electrolytic process occurring at −1.0 to −1.2 volts in 1 *M* sulfuric acid solution is the oxidation of arsenic(III) to arsenic(V) with 100% current efficiency. This means that the area under the curve shown in Fig. 1 is correct; it is only the shape of the curve that is anomalous.

The effect of concentration of the arsenic(III) solution on the shape of the electrolysis curve was the first study which gave any hint as to what might be happening. Figure 2 shows this effect. Here it is seen that an extremely dilute solution (0.0009 *N*) gives a normal curve, (the log plot is nearly a straight line), a somewhat more concentrated solution (0.0044 *N*) exhibits a plateau, a still more concentrated solution (0.027 *N*) a minimum, while the most concentrated solution (0.09 *N*) has such a pronounced minimum that it is very difficult to oxidize at all.

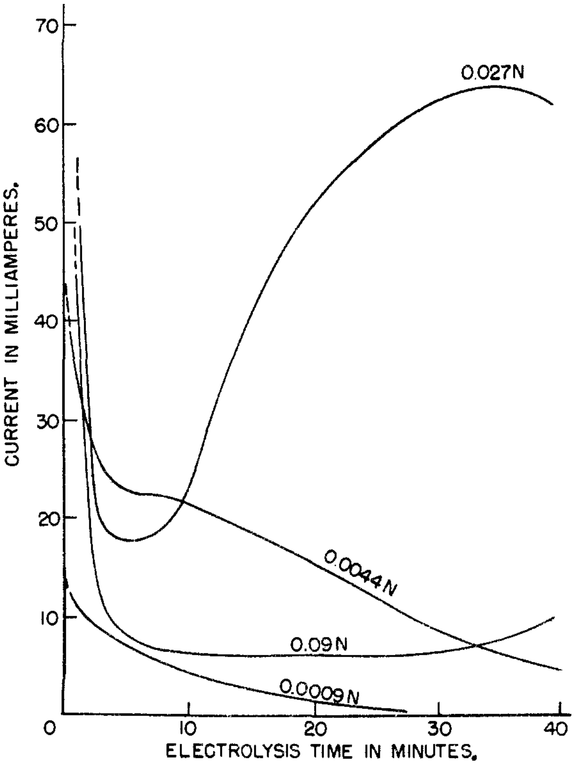

Fig. 2.—Time-current electrolysis curves for the oxidation of solutions of "Analytical Reagent" quality As_2O_3 of various concentrations.

This suggested the presence of an interfering impurity. The arsenic solution had been prepared in the usual way by dissolving As_2O_3 in excess potassium hydroxide and then acidifying with sulfuric acid. The potassium hydroxide as a source of impurity was eliminated by preparing a solution by shaking As_2O_3 in water for several days. This solution gave a curve very similar to those prepared with hydroxide, indicating that the impurity must be in the As_2O_3 itself. The As_2O_3 that had been used was Mallinckrodt "Analytical Reagent" quality. Mallinckrodt "Primary Standard" quality is of a higher degree of purity so solutions were prepared using this material. Figure 3 shows current-time curves for the oxidation of two solutions of As_2O_3 identical in every respect except that one was prepared from "Analytical Reagent" As_2O_3 and the other from "Primary Standard" As_2O_3. These results established that an impurity in the As_2O_3 was the cause of the minimum. Lead(II), bismuth(III) and sulfide were added to the "Primary Standard" As_2O_3 solution, but when present in amounts corresponding to the probable amount of impurity (*i.e.*, less than 0.02%) their effect on the curve was negligible. Antimony(III) and tin(II), however, were found to produce the minimum quite readily. Of the two, antimony had a much greater effect. Electrolysis curves resulting after the addition of antimony(III) to the arsenic solution prepared from "Primary Standard" As_2O_3 are shown in Fig. 4.

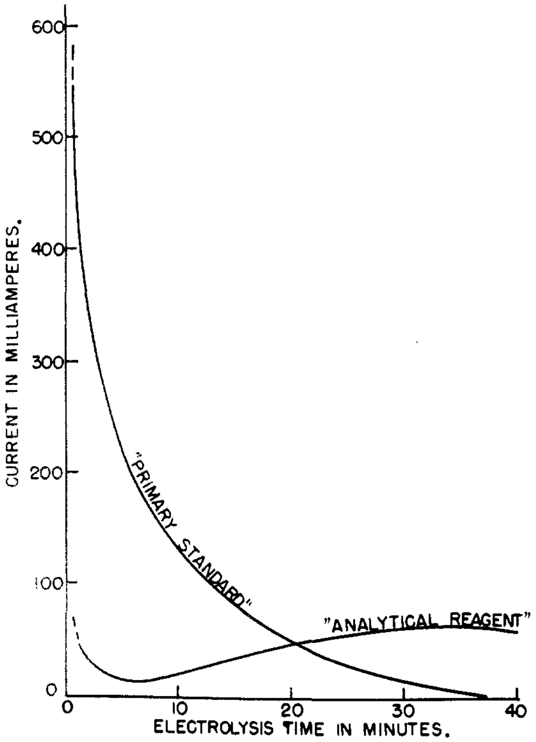

Fig. 3.—Time-current electrolysis curves for the oxidation of solutions of "Analytical Reagent" and "Primary Standard" quality As_2O_3.

An inquiry was made of the Mallinckrodt Chemical Works about the differences between these two grades of As_2O_3. They furnished spectrographic analyses of each, indicating that the principal difference was the presence of a detectable amount of antimony (estimated 0.1 to 0.01%) in the "Analytical Reagent" quality.

The current-time curve for the oxidation of the "Primary Standard" As_2O_3 nearly follows the $i_{t0} = i_0e^{-kt}$ relation. Figure 5 is a log current *vs.* time plot. It was not established whether the deviation during the first five minutes was due to a trace of antimony(III) remaining in the "Primary Standard" As_2O_3 or to another cause.

One possible explanation for the effect of antimony is that a layer of higher oxide, perhaps Sb_2O_4, may form on the surface of the electrode rendering it passive to the oxidation of arsenic. Some evi-

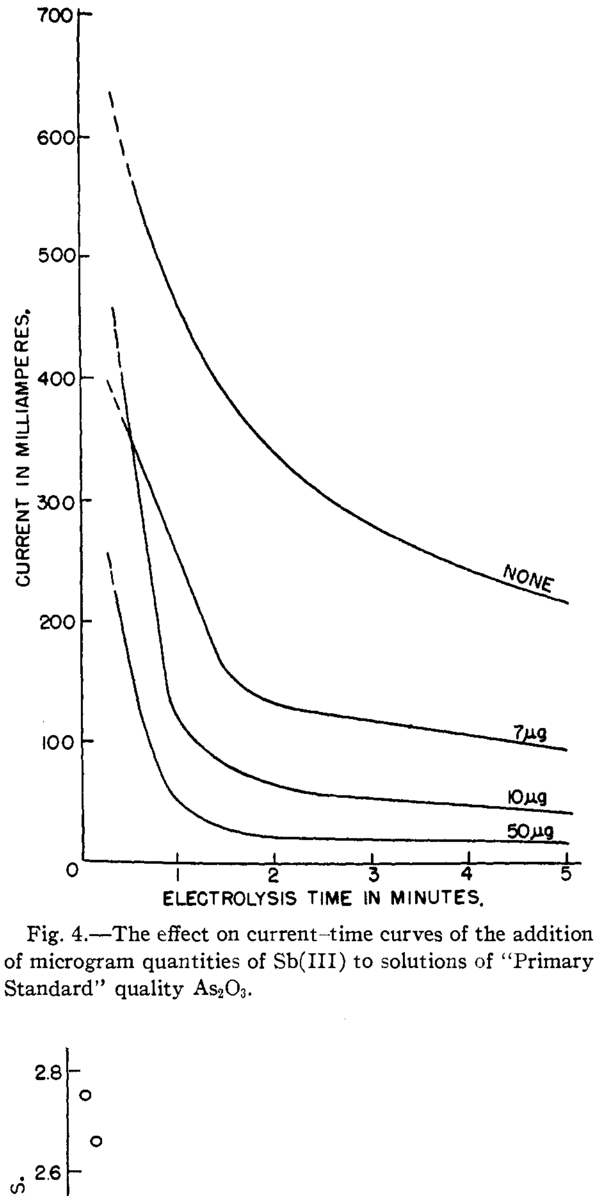

Fig. 4.—The effect on current-time curves of the addition of microgram quantities of Sb(III) to solutions of "Primary Standard" quality As_2O_3.

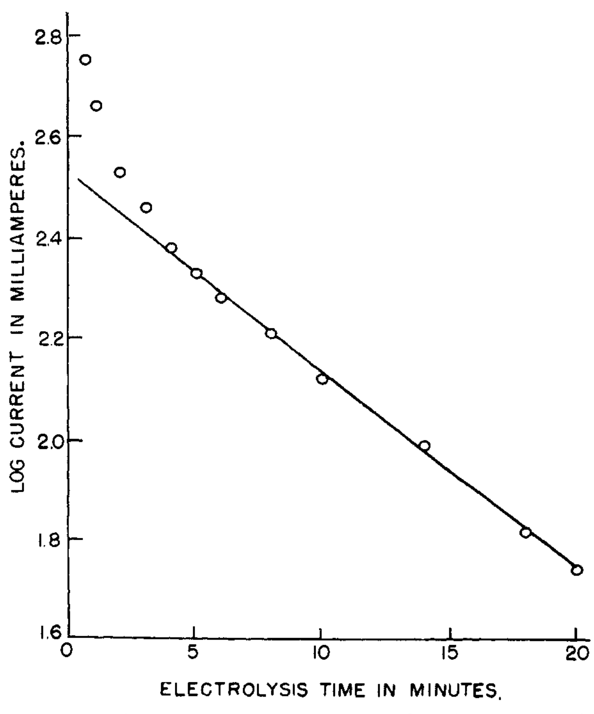

Fig. 5.—A log current *vs.* time curve for the electrolytic oxidation of "Primary Standard" quality As_2O_3.

dence to support this may be drawn from Fig. 4 which shows the current lowering to be very great for amounts of antimony up to about ten micrograms, and that then additional amounts cause relatively less change. Ten micrograms is of the order of magnitude needed for the formation of a monomolecular layer of oxide over the surface of the electrode. Two other experimental observations are in general accord with this theory. These are, that the addition of antimony(V) to the solution has no effect on the electrolysis curve, and that the antimony(III) minimum does not appear at all when the electrolysis is carried out in molar sodium hydroxide. The absence of the minimum in alkaline solution could be the result of the disproportionation of Sb_2O_4 which Latimer[7] reports to be slow in acid but rapid in alkaline solution.

It was further observed that if, after the acid solution electrolysis had run several minutes, the current were turned off and the electrode allowed to stand in the solution a much higher current was observed on resumption of electrolysis. This could be the result of the slow disproportionation and dissolution of the Sb_2O_4 layer from the surface of the electrode. The effect is represented in Fig. 6.

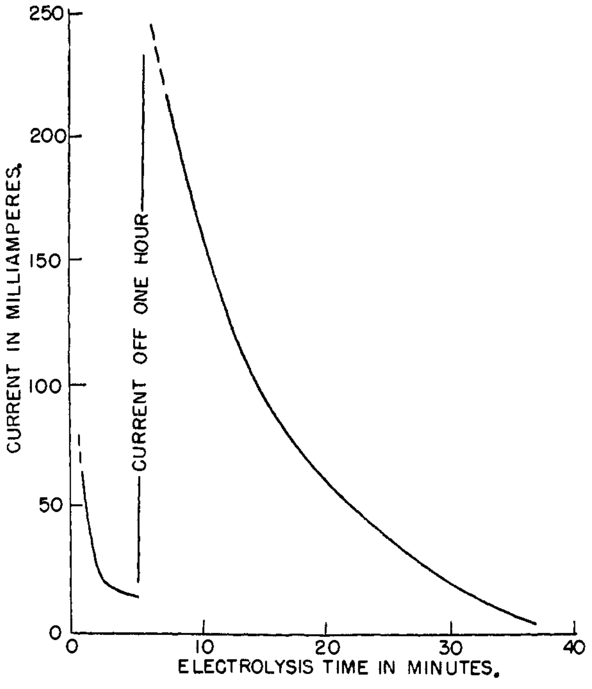

Fig. 6.—Effect of current interruption on the time-current curve for the oxidation of "Analytical Reagent" quality As_2O_3.

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[7] W. M. Latimer, "Oxidation Potentials," 2nd edition, Prentice-Hall, Inc., New York, N. Y., 1952, p. 119.