

Fig. 1.—The high field conductance of an aqueous solution of cadmium chloride, 1.697×10^{-4} molar, relative to potassium chloride at 25° .

approximation the increase in equivalent conductance has been found³ to be proportional to $(z_+z_-)^2$; thus, $(z_+z_-)^2 = 4$, and 4×0.4 (for potassium chloride) = 1.6%. The curve has a shape something like that of a strong electrolyte, but fails to bend over at so low a field or in so pronounced a manner as does magnesium sulfate, for example.

Determinations on similar valence-type, but stronger, electrolytes, *e.g.*, calcium chloride, are now under way. When completed, these will offer more information on the influence on the high field behavior of the weak ionization referred to in equation 1, above.

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Quaternary Salts of Halogenated Heterocyclic Nitrogen Compounds¹

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A previous article² has reported the preparation of quaternary salts of halogenated pyridines and

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(2) C. T. Bahner, W. K. Easley, M. D. Pickens, H. D. Lyons, L. L. Norton, B. G. Walden and G. E. Biggerstaff, *THIS JOURNAL*, **73**, 3499 (1951).

quinolines for screening against tumors in mice. The series have been extended by synthesis of the salts of 2-chloropyridine and 3-bromopyridine listed in Table I and the salts of 3-bromoquinoline, 6-chloroquinoline and 4,7-dichloroquinoline listed in Table II. Results of screening tests at the National Cancer Institute are to be published elsewhere.

4,7-Dichloroquinoline was particularly unreactive and was recovered unchanged from mixtures with several halogen compounds although a small quantity of quaternary salt was obtained in a few cases. Attempts to prepare quaternary salts of 8-chloroquinoline by reaction of the base with substituted phenacyl bromides at 45° produced the hydrobromide as the chief crystalline product instead of the expected quaternary salt.

TABLE I
SALTS OF SUBSTITUTED PYRIDINES

Salt from 2-Chloropyridine and:	Empirical formula	M.p., $^\circ\text{C}$.	Ionic halogen, % Calcd. Found ^a	
<i>p</i> -Methoxyphenacyl bromide	$\text{C}_{14}\text{H}_{13}\text{BrClNO}_2$	171	23.32	23.04
β -Naphthacyl bromide	$\text{C}_{17}\text{H}_{13}\text{BrClNO}$	175	22.04	22.00
5,6,7,8-Tetrahydro- β -naphthacyl bromide	$\text{C}_{17}\text{H}_{17}\text{BrClNO}$	190	21.79	21.69
4,4'-Bis-(bromoacetyl)-phenyl ether	$\text{C}_{26}\text{H}_{26}\text{Br}_2\text{Cl}_2\text{N}_2\text{O}_3$	210	25.01	24.79
3-Bromopyridine and:				
β -Phenylethyl iodide	$\text{C}_{12}\text{H}_{14}\text{BrIN}$	152–154	32.45	32.29
Iodoacetone	$\text{C}_8\text{H}_9\text{BrINO}$	180	37.10	37.29
Glycerol- α -monochlorohydrin	$\text{C}_8\text{H}_{11}\text{BrClNO}_2$	216	13.20	13.07
Iodoacetoneitrile	$\text{C}_7\text{H}_5\text{BrIN}$	177–178	39.06	38.83
4,4'-Bis-(bromoacetyl)-phenyl ether	$\text{C}_{26}\text{H}_{26}\text{Br}_4\text{N}_2\text{O}_4$	220	21.95	21.52

^a Average of two analyses.

TABLE II
QUATERNARY SALTS OF HALOGENATED QUINOLINES

Salt from	Empirical formula	M.p., $^\circ\text{C}$.	Ionic halogen, % Calcd. Found ^a	
3-Bromoquinoline and:				
Glycerol- α , γ -dibromohydrin	$\text{C}_{12}\text{H}_{12}\text{Br}_2\text{NO}$	251	18.76	18.91
3,4-Dihydroxyphenacyl chloride	$\text{C}_{17}\text{H}_{13}\text{BrClNO}_2$	245	^b	
<i>p</i> -Methoxyphenacyl bromide	$\text{C}_{16}\text{H}_{15}\text{Br}_2\text{NO}_2$	241	18.28	18.30
<i>p</i> -Chlorophenacyl bromide	$\text{C}_{17}\text{H}_{12}\text{Br}_2\text{ClNO}_2$	240	18.10	18.15
<i>p</i> -Bromophenacyl bromide	$\text{C}_{17}\text{H}_{12}\text{Br}_3\text{NO}$	237	16.45	16.63
6-Bromoquinoline and:				
Glycerol- α , γ -dibromohydrin	$\text{C}_{12}\text{H}_{12}\text{Br}_2\text{NO}$	241	18.76	19.05
Allyl bromide	$\text{C}_{12}\text{H}_{11}\text{Br}_2\text{N}$	171	24.29	24.07
6-Chloroquinoline and:				
Iodoacetone	$\text{C}_{12}\text{H}_{11}\text{ClINO}$	186–187	36.50	36.54
<i>p</i> -Iodophenacyl bromide	$\text{C}_{17}\text{H}_{12}\text{BrClINO}$	230	16.36	16.32
4,7-Dichloroquinoline and:				
Phenacyl bromide	$\text{C}_{16}\text{H}_{12}\text{BrCl}_2\text{NO}$	163	20.12	19.93
<i>p</i> - <i>t</i> -Butylphenacyl bromide	$\text{C}_{19}\text{H}_{20}\text{BrCl}_2\text{NO}$	185–186	17.68	17.50

^a Average of two analyses. ^b Calcd.: C, 51.73; H, 3.32. Found: C, 51.58; H, 3.49.

8-Chloroquinoline Hydrobromide.—Prepared by direct reaction of equimolecular quantities of the base and concentrated hydrobromic acid or as the principal crystalline prod-

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

(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 Arsenic(III) on the Electrolytic Oxidation of Arsenic in Acid Solution

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In a previous investigation¹ 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 $i_t = i_0 e^{-kt}$, where i_t is the current at any time t , i_0 the initial current, and k a constant. Integration of this equation² 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 ar-

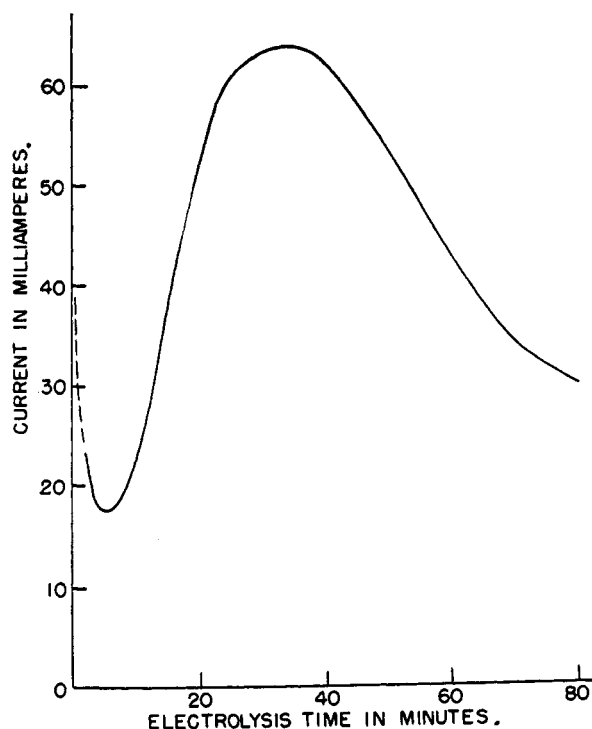


Fig. 1.—A typical minimum in the current-time curve for the electrolytic oxidation of "Analytical Reagent" quality As_2O_3 .

senic, and it was in attempting to do so that the unusual shape of the electrolysis curve was observed.

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 Lingane⁵ 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 found⁶ 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.

(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).