

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Polarography of Certain Substances Related to Anthraquinone¹BY K. G. STONE^{1a} AND N. HOWELL FURMAN

Introduction

In a previous communication² a detailed study of the polarography of nineteen anthraquinones has been presented. In connection with studies of the aloins, barbaloin and isobarbaloin, it became evident that the reducible groups are very different from those in the anthraquinones. Even the most highly substituted anthraquinones, such as carminic acid, for example, have a characteristic polarographic wave at -0.6 to -0.7 volt relative to the saturated calomel electrode (S.C.E.). The aloins on the contrary show waves at about -1.34 volts relative to the S.C.E. Since the aloins are related to anthrone a study of the polarographic behavior of anthrones was made.

Experimental

Materials and Apparatus.—The Electrochemograph, capillary electrode, buffers and general technique were as used in the previous investigation.² In examining solutions in 40% dioxane the nitrogen, previously passed through alkaline pyrogallol, was led through dioxane solution before entering the polarographic cell. Half-wave potentials are given relative to the S.C.E. with corrections for *IR* drop based on measured resistances and currents. Polarograms were taken at one twentieth of the full sensitivity of the instrument with solutions at 24–25°. Drop times were measured at the half-wave potential with the current flowing.

Samples of anthraquinone monoxime, 10-hydroxy-10-methylanthrone and 10-vinyl acetate were supplied through the courtesy of Dr. Percy L. Julian who described their preparation.^{3,4} It was found that commercial anthrone obtained from the Paragon Testing Laboratories was partially oxidized and difficult to purify. Anthrone sufficiently pure to give no test with sodium hydro-sulfite was prepared by the reduction of anthraquinone.⁵ Barbaloin and isobarbaloin were prepared from U.S.P. Aloin from Merck & Co., Inc., by the fractional crystallization method of Leger⁶ as modified by Gardner and Joseph.⁷

(1) Abstracted from a thesis submitted by K. G. Stone, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, to the Department of Chemistry, Princeton University, May, 1946.

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(2) N. H. Furman and K. G. Stone, *THIS JOURNAL*, **70**, 3055 (1948).

(3) P. L. Julian, W. Cole and G. Diemer, *ibid.*, **67**, 1721 (1942).

(4) P. L. Julian, W. Cole and E. W. Meyer, *ibid.*, **67**, 1724 (1942).

(5) "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., p. 52.

(6) E. Leger, *Ann. chim.*, [9] **6**, 334 (1916).

(7) J. H. Gardner and L. Joseph, *J. Am. Pharm. Assoc.*, **26**, 794 (1937).

The maximum suppressors that were used contained 0.1% of either methyl cellulose or the sodium salt of methyl red.

The standard solutions that were used and the solvents are shown in Table I.

TABLE I
STANDARD SOLUTIONS

Compound	Solvent	Concn., mg. per ml.
Anthraquinone monoxime	Dioxane	1.00
Anthrone	Dioxane	1.00
10-Methyl-10-hydroxyanthrone	Dioxane	0.500
10-Vinylanthranlyl acetate	Dioxane	0.500
Barbaloin	5% Ethanol	0.500
Isobarbaloin	5% Ethanol	1.00

Results of Experiments.—The polarographic studies of those compounds that were dissolved in dioxane were made in buffered media containing 40% dioxane. The previous studies of anthraquinones both in aqueous media and in dioxane have shown that dioxane does not affect the half-wave potential very considerably unless association occurs in aqueous media.²

The half-wave data that were obtained are shown in Tables II and III, and the general polarographic conclusions regarding the compounds of Table II are presented in Table IV.

TABLE II
HALF-WAVE POTENTIALS IN 40 PER CENT. DIOXANE
Volts negative to the S. C. E.

Buffer	Apparent ϕH	Anthraquinone monoxime	Anthrone	10- Methyl- 10- hydroxy anthrone
Acetate	5.6	0.57	0.87 1.01	1.11
Acetate	6.7	0.64	0.88 0.98	1.19
Acetate	7.4	0.64	0.85	1.10
Acetate	8.2	0.70	.91	1.20
Citrate	7.0	0.79	.98	1.18
Phosphate	6.8	0.76 0.91	.99	1.30
Phosphate	7.9	0.74	.92	1.27
Phosphate	8.9	0.72	..	1.27
Borate	10.0	0.74 0.99	..	1.30
Borax	11.2	0.90 1.13	..	1.35
Tartrate	11.5	1.06 1.21	..	1.35
Ammonia	9.0	0.66	.99	1.17
Ammonia	9.7	0.70	..	1.20
0.1 N KCl	7.1	1.29

In general the waves had maxima that could be suppressed either by methyl red or by methyl cellulose. The maxima for the aloins were only fairly well suppressed in the acetate buffers of ϕH 4 and 5, and not in the alkaline buffers. In some cases half-wave potentials varied slightly with concentration and quantitative work was possible

TABLE III

HALF-WAVE POTENTIALS IN 1 PER CENT. ETHANOL				
Buffer	pH	Volts negative to S. C. E.		
		Barbaloin	Isobarbaloin	
Acetate	4	1.29	1.32	
Acetate	5	1.28	1.30	
Acetate	7	1.20	1.23	
Acetate	8	1.24	1.20	
Citrate	6	1.22	1.25	
Phosphate	6	1.37	1.38	
Phosphate	7	1.26	1.28	
Phosphate	8	1.33	1.29	
Phosphate	11	1.37	..	
Phosphate	12	1.46	..	
Borate	8	1.31	1.32	
Ammonia	9	1.28	1.25	
Ammonia	10	1.34	..	
Tartrate	11	1.48	..	
0.1 N KCl	..	1.36	..	

TABLE IV

REDUCTION DATA IN 40% DIOXANE

Substance	Concn., milli- molar	Diff. coeff. $D \times 10^4$ sq. cm./ sec. ^a	n	i_d ma./milli- mol. ^a	$i_d/$ $m^2/s^2/e_0$ ^b
Anthraquinone monoxime	0.895	2.7	4	5.36 ^c	4.36
Anthrone	1.03	3.6	2	2.60	2.12
10-CH ₃ -10-OH-anthrone	0.446	3.3	2	2.69	2.19

^a Based on the most frequent current in various buffers. ^b $m^2/s^2/e_0$ was 1.23 in all buffers. ^c Total current for reduction to 9-OH-10-NH₂-anthracene.

only with empirical calibration. The interesting details about the individual compounds were as follows:

Anthraquinone Monoxime.—As one would expect from the structure, this compound shows typical waves in the anthraquinone region. The hydroxylamino group that is formed in the first stage of the reduction is reduced later to an amino group so that the sum of the waves corresponds to $n = 4$. At pH 6.8 a separation of the wave into two parts becomes evident and the waves are well separated at pH 10 or higher. The first wave decreases and the second increases with pH until at pH 11.5 the waves are approximately equal. It is believed that the ionization of the phenolic hydroxyl in alkaline media of pH greater than pK_a makes the further reduction of the hydroxylamino group to $-NH_2$ more difficult. On this basis, from the shift of the ease of reduction with pH, the K_a for the hydroxyl group was calculated to be from 2 to 3×10^{-11} which is in agreement with values for similar molecules.^{2,8}

At pH 6.7 (acetate) i_d vs. concentration was approximately linear from 0.18 to 1.8 millimolar, but an empirical calibration curve is necessary in quantitative work.

(8) J. B. Conant, H. M. Kahn, L. F. Fieser and S. S. Kurtz, THIS JOURNAL, **44**, 1382 (1922).

Anthrone.—This compound is oxidized extremely readily and anthraquinone waves are then evident. The dioxane solution was prepared and kept under air-free nitrogen and the buffer mixtures were thoroughly deaerated before adding the standard solution. Two waves appeared in acetate buffers. The wave form was poor in all cases and maxima, that could not be suppressed, occurred in the alkaline buffers. No quantitative work was attempted. A single wave of fair form, with maximum suppressed by methyl red, was obtained in pH 6.8 phosphate buffer. It is believed that 9,10-dihydroanthranol is the product of the reduction of anthrone.

10-Hydroxy-10-methyl-anthrone.—In marked contrast with anthrone, the waves for the 10-hydroxy-10-methyl derivative were of good form and easily measurable. In the range up to 0.89 millimolar i_d was strictly proportional to concentration in buffers of pH 5.6 (acetate), 7.9 (phosphate), 9.7 (ammonia), 11.2 (borax) and in 0.1 N potassium chloride. In all cases i_d for a millimolar solution was constant (Table II) and the half-wave potential was constant with change in concentration.

10-Vinylnthranyl Acetate.—It was not expected that this compound could be reduced in buffered solutions.⁹ However a wave was formed in buffers in which -1.80 volt vs. S.C.E. could be reached before hydrogen evolution. In none of the buffers that were used was the terminal wave far enough out for good wave formation, although that in tartrate of pH 11.5 was fairly well formed at certain concentrations. The site of the reduction is not certain, but the half-wave potential is not far from that found for the reduction of the anthracene nucleus in 75% dioxane solution.¹⁰

The Aloins, Barbaloin and Isobarbaloin.—The aloins are believed to be isomeric substances of structure still unknown in full detail. An early empirical formula, C₁₆H₁₈O₇,¹¹ was displaced by the fairly widely accepted formula, C₂₀H₁₈O₉, of Leger,¹² who postulated the aloins as aloe-emodin-*d*-arabinosides. Rosenthaler¹³ found no evidence for an aldehyde group but obtained a positive test for an anthranol after hydrolysis. Gardner and associates^{14,15} concluded from hydrolytic studies of the aloins and of true glucosides of aloe emodin that the aloins are not arabinosides of aloe emodin because their rates of hydrolysis are thousands of times smaller than those of the true glucosides. They also demonstrated that aloe-emodin-9-anthrone is readily obtained from both aloins and

(9) See H. A. Laitinen and S. Wawzonek, *ibid.*, **64**, 1765 (1942).

(10) S. Wawzonek and H. A. Laitinen, *ibid.*, **64**, 2365 (1942).

(11) J. L. Simonsen and R. Robinson, *J. Chem. Soc.*, **95**, 1085 (1909).

(12) E. Leger, *Ann. chim.*, **6**, 318 (1916); **8**, 265 (1918).

(13) L. Rosenthaler, *Pharm. Acta Helv.*, **4**, 128 (1929).

(14) J. H. Gardner and T. F. McDonnell, THIS JOURNAL, **56**, 1246 (1934).

(15) J. H. Gardner and H. Foster, *ibid.*, **58**, 597 (1936).

hence concluded that the two aloins are not derivatives of isomeric anthrones.^{7,16}

The most recent empirical formula, $C_{21}H_{24}O_9$, has been proposed by Owen and Simonsen¹⁷ on the basis of analyses and X-ray studies of the methyl ether derivative, $C_{21}H_{17}O_2(OCH_3)_7$. This recent formula is also supported by Gardner¹⁸ on the basis of analyses made in his laboratory by Joseph. He stated that the present evidence is compatible with a structure for the aloins of a β -methylanthracene nucleus with side chain, but it is not certain whether the side chain has six or five carbon atoms with corresponding uncertainty as to the location of one of the carbon atoms.

In our polarographic work it was noted that the aloins are very readily oxidized in alkaline buffers which introduces waves not typical of the aloins. In acetate buffers of pH 4 or 5 the waves are of satisfactory form and suitable for quantitative measurement. The maxima that occur in alkaline media are not suppressed by methyl red and methyl cellulose. The half-wave potentials, Table III, show that the reduction resembles that of a substituted anthrone (Table II). The close similarity of the half-wave potentials of the two compounds suggests that they are position isomers, that have the same structural groups.

(16) J. H. Gardner and J. A. Campbell, *THIS JOURNAL*, **64**, 1378 (1942).

(17) L. N. Owen and J. L. Simonsen, *ibid.*, **64**, 2516 (1942).

(18) J. H. Gardner, *ibid.*, **67**, 2111 (1945).

It is of practical interest that the wave due to the aloins is shown in extracts of crude aloes or in pharmaceutical products made from aloes. The practical details of the polarographic estimation of the aloins have been published.¹⁹ For both compounds a current of 0.43 microamp. per mg. in 25 ml. was found up to concentration of 10 mg. per 25 ml. with a capillary of $m^{2/3}t^{1/6} = 1.23$.

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Summary

The polarography of the aloins has been compared with that of simple and substituted anthrone. Anthraquinone monoxime and 10-vinyl-anthranyl acetate have also been examined polarographically.

The close similarity of the polarographic behavior of the aloins to 10-hydroxy-10-methyl anthrone suggests that they are anthrones; the close similarity of the polarograms of the isomeric aloins suggests that they are position isomers with the same structural groups.

(19) K. G. Stone and N. H. Furman, *Anal. Chem.*, **19**, 105 (1947).

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The Crystal Structure of Ammonium Pentachloroindate Monohydrate¹

BY HAROLD P. KLUG, ELIZABETH KUMMER AND LEROY ALEXANDER

Introduction

The stereochemistry associated with a 1:5 stoichiometric ratio in crystalline inorganic compounds is of special theoretical interest. Compounds with such a ratio occur rather infrequently, and to date only a few of them have been studied structurally. Already, however, five different structural methods for achieving the 1:5 ratio have been demonstrated, and none of them involves five-fold coordination. Phosphorus pentachloride, PCl_5 , has a CsCl-type packing of ionic tetrahedral PCl_4^+ and octahedral PCl_6^- groups.² Phosphorus pentabromide, PBr_5 , has a different structure consisting of a packing of tetrahedral PBr_4^+ and spherical Br^- ions.³ Brosset⁴ demon-

strated the AlF_6^- ratio in Tl_2AlF_6 and $K_2AlF_6 \cdot H_2O$ to be achieved through infinite chains of AlF_6^- octahedra extending through the crystal. Cs_3CoCl_5 and Rb_3CoCl_5 were investigated by Powell and Wells,⁵ and more recently $(NH_4)_3ZnCl_5$ was completely studied by Klug and Alexander.⁶ These compounds are packings of the spherical metallic cations, tetrahedral $CoCl_4^-$ or $ZnCl_4^-$ anions, and extra Cl^- ions. Their formulas might be more accurately written in the form $Cs_2CoCl_4 \cdot CsCl$ and $(NH_4)_2ZnCl_4 \cdot NH_4Cl$.

Lindqvist⁷ recently determined the structure of $(NH_4)_2FeCl_5 \cdot H_2O$ and found it to contain discrete octahedral $[FeCl_5H_2O]^-$ groups. The water molecule is not distributed randomly among the six corners of the octahedra, but occupies a particular corner of the octahedra that lie on the symmetry planes in the cell. This investigation of $(NH_4)_2InCl_5 \cdot H_2O$ has established it as another ex-

(1) Presented before the Division of Physical and Inorganic Chemistry, Chicago meeting of the American Chemical Society, April 20, 1948.

(2) Powell, Clark and Wells, *J. Chem. Soc.*, 642 (1942).

(3) Powell and Clark, *Nature*, **145**, 971 (1940).

(4) Brosset, *Z. anorg. allgem. Chem.*, **235**, 139 (1937); "Electrochemical and X-Ray Crystallographic Investigation of Complex Aluminum Fluorides," separate, Stockholm, 1942.

(5) Powell and Wells, *J. Chem. Soc.*, 359 (1935).

(6) Klug and Alexander, *THIS JOURNAL*, **66**, 1056 (1944).

(7) Lindqvist, *Arkiv Kemi Mineral. Geol.*, **24A**, 1 (1946).