Veratrylacetophenone (IId).—Veratrylideneacetophenone (Id), m.p. 90–92° (reported 85°,[8] 88°[9]) was hydrogenated with palladium–carbon catalyst in ethyl acetate for four hours to give a 93% yield of solid, m.p. 68–70° (reported[6] 67.5–68.5°) which crystallized from dilute ethanol in colorless scales, with no change in m.p.

Ethyl 5,6-Dimethoxy-3-methylindene-2-carboxylate (IIIa).—A solution of 56 g. of IIa in 45 ml. of 85% phosphoric acid was added slowly with vigorous stirring to a mixture of 90 ml. of concd. sulfuric acid and 45 ml. of 85% phosphoric acid at 0–5°. The reaction mixture became rapidly red, then bluish, and solidified. It was stirred into ice-water almost immediately. The white precipitate was collected, washed with cold water, dissolved in ether, and the solution washed with 10% sodium bicarbonate. Evaporation of the solvent gave 24 g. (46%) of a colorless solid, which after recrystallization from 70% ethanol formed large colorless crystals, m.p. 136–136.5°.

Anal. Calcd. for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92. Found: C, 68.54; H, 6.92.

Acidification of the sodium bicarbonate washings with concd. hydrochloric acid yielded 5 g. (10%) of **5,6-dimethoxy-3-methylindene-2-carboxylic acid** as a heavy white solid, which after recrystallization from acetone melted at 228–230°.

Anal. Calcd. for $C_{13}H_{14}O_4$: C, 66.65; H, 6.02. Found: C, 66.49; H, 5.85.

Ethyl 5,6-Methylenedioxy-3-methylindene-2-carboxylate (IIIb).—A solution of 1 g. of IIb in 3 ml. of sulfuric and 3 ml. of phosphoric acid was prepared and kept at 0° for 40 minutes, at which time the color had changed from yellow to greenish-blue. The pale green crude solid (0.79 g.), obtained as above after treatment with bicarbonate, was recrystallized from dilute ethanol, but the product was still quite impure. It was, therefore, dissolved in ether–ethyl acetate, and the solution shaken exhaustively with 2% aqueous sodium hydroxide, then with water. Drying and evaporating the solvent yielded 0.443 g. (48%) of a solid, m.p. 105–107°, which was recrystallized from 70% ethanol to give tiny colorless needles, m.p. 107–108°.

Anal. Calcd. for $C_{14}H_{14}O_4$: C, 68.28; H, 5.72. Found: C, 68.08; H, 5.71.

From the sodium bicarbonate washings, there was obtained 0.032 g. (3.6%) of **5,6-methylenedioxy-3-methylindene-2-carboxylic acid**, which separated from ethyl acetate–70% ethanol in small colorless crystals, m.p. 280–281° (dec.).

Anal. Calcd. for $C_{12}H_{10}O_4$: C, 66.04; H, 4.62. Found: C, 66.27; H, 4.61.

5,6-Dimethoxy-3-methylindene (IIIc).—This compound was obtained from 21 g. of IIc in 42 ml. of phosphoric acid and 42 ml. of sulfuric acid at 10–15° by the method used for preparing IIIa, except that the crude product (10 g., 52%) was obtained directly by pouring the reaction mixture into 400 ml. of ice-water after 0.5 hour, with omission of the bicarbonate treatment. The product formed small colorless scales (from dilute ethanol), m.p. 132–133°.

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.60; H, 7.63.

5,6-Dimethoxy-3-phenylindene (IIId).—A 91% yield of crude material was obtained similarly from IId, except that the reaction mixture was heated at 60–70° for 30 minutes. Recrystallization from dilute ethanol gave small colorless scales, m.p. 112–113.5°. The yield dropped to 10% when the reaction was carried out below 25°.

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 80.75; H, 6.25.

Ethyl 1-Ethoxalyl-5,6-dimethoxy-3-methylindene-2-carboxylate (IVa).—To a still warm solution of 1.15 g. of sodium in 50 ml. of absolute ethanol was added rapidly with vigorous swirling 7.5 g. of ethyl oxalate, then a suspension of 18 g. of IIIa in 100 ml. of hot absolute ethanol. The mixture was shaken for another two minutes, the yellowish paste stirred into cold water, and the mixture acidified with dilute hydrochloric acid. The solid was collected, washed with water and purified from 70% ethanol to yield 19 g. (77%) of yellowish crystals, m.p. 143–146°.

Anal. Calcd. for $C_{19}H_{22}O_7$: C, 62.97; H, 6.12. Found: C, 62.92; H, 5.99.

The 2,4-dinitrophenylhydrazone formed small yellow crystals (from ethyl acetate), m.p. 180–182°.

Anal. Calcd. for $C_{25}H_{26}O_{10}N_4$: C, 55.35; H, 4.83. Found: C, 55.20; H, 4.73.

The deep yellow crystalline **enol acetate**, m.p. 132–133°, was prepared by refluxing IVa with acetic anhydride and pyridine, followed by diluting with ice-water and recrystallization from dilute ethanol.

Anal. Calcd. for $C_{21}H_{24}O_8$: C, 62.37; H, 5.98. Found: C, 62.36; H, 6.03.

1-Ethoxalyl-5,6-dimethoxy-3-phenylindene (IVd).—This compound was obtained in 76% yield from 0.46 g. of sodium, 15 ml. of ethanol, 3 g. of ethyl oxalate and 4.2 g. of IIId, and formed deep red needles, m.p. 122–124°.

Anal. Calcd. for $C_{21}H_{20}O_5$: C, 71.50; H, 5.75. Found: C, 71.46; H, 5.57.

The enol acetate crystallized from ethanol in orange-colored cottony needles, m.p. 165–167°.

Anal. Calcd. for $C_{23}H_{22}O_6$: C, 70.03; H, 5.62. Found: C, 69.88; H, 5.86.

Ethyl 5,6-Dimethoxy-3-methylindane-2-carboxylate (VIa).—Hydrogenation of 1 g. of IIIa in 15 ml. of glacial acetic acid with 0.5 g. of 5% palladium–carbon catalyst at 60° and 40 lb. pressure for 2.5 hr. yielded 0.95 g. of oil, which was crystallized from ether–ethyl acetate–pentane to give 0.85 g. (85%) of small colorless crystals, m.p. 48–49°.

Anal. Calcd. for $C_{15}H_{20}O_4$: C, 68.15; H, 7.62. Found: C, 68.03; H, 7.57.

Saponification of VIa provided **5,6-dimethoxy-3-methylindane-2-carboxylic acid** as small colorless crystals (from dilute ethanol), m.p. 176–177°.

Anal. Calcd. for $C_{13}H_{16}O_4$: C, 66.08; H, 6.82. Found: C, 65.85; H, 6.77.

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JOHN HARRISON LABORATORY
UNIVERSITY OF PENNSYLVANIA
PHILADELPHIA, PA., AND
LABORATORY OF CHEMICAL PHARMACOLOGY
NATIONAL CANCER INSTITUTE
BETHESDA 14, MD.

Non-additivity of Polarographic Diffusion Currents with Mixtures of Certain Reducible Species

BY STANLEY L. MILLER[1] AND EDWIN F. ORLEMANN

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Under certain conditions we have found that the polarographic diffusion currents of two species are not additive. This effect has been studied for mixtures of Ce(IV) and O_2 and for mixtures of Fe(III) and Cr(VI) in 1 *M* H_2SO_4 and 1 *M* $HClO_4$. The results show that non-additivity of diffusion currents to give either a larger or smaller current than expected can occur as a result of very fast reactions in the diffusion layer when the species have significantly different diffusion coefficients. The effect is of some theoretical interest and its occurrence must be recognized in connection with a limited number of analytical applications.

Experimental

The polarograms were recorded on a Sargent model XII polarograph. The drop time was about three seconds, and the temperature was 25.00 ± 0.05°. Runs were made with both an internal anode and with an external calomel cell

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(9) R. Dickinson, I. M. Heilbron and F. Irving, *J. Chem. Soc.*, 1888 (1927).

(1) Department of Chemistry, University of Chicago, Chicago, Ill., National Science Foundation Predoctoral Fellow, 1952–1953.

connected by a potassium chloride salt bridge. The vessel for the internal anode had a very small area of mercury exposed to the solution so that no appreciable portion of the species in the solution reacted with the mercury. The results were essentially the same with either anode. Oxygen was eliminated from the solution by tank nitrogen heated over copper at 350°. Freshly prepared gelatin was used as a maximum suppressor.

The ceric solution was prepared by diluting G. F. Smith 0.5 *M* "Perchlorato Ceric Acid" to 0.1 *M* and standardizing with a iodine–thiosulfate titration. The ferric solution was prepared by oxidizing G. F. Smith $Fe(ClO_4)_2 \cdot 6H_2O$ with hydrogen peroxide, adding $HClO_4$ to make 1.0 *M*, boiling off the excess hydrogen peroxide, and standardizing by the usual dichromate procedure. The potassium dichromate solution was prepared by direct weighing, and the oxygen was standardized by letting the solution remain in equilibrium with the air overnight. The concentration of oxygen was taken to be 2.5×10^{-4} *M* although due to the salting out the concentration was probably somewhat lower.

The mixtures were prepared for a run by diluting the appropriate quantity of the stock solution to 100.0 cc. with the 1 *M* acid, adding gelatin and bubbling with nitrogen.

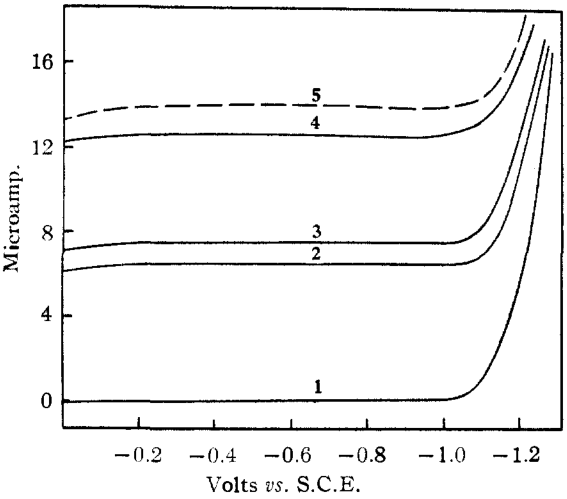

Fig. 1.—Mixtures of ferric and dichromate in 1.0 *M* H_2SO_4: 1, residual current; 2, 2.38×10^{-3} *M* Fe^{+3}; 3, 3.30×10^{-4} *M* $Cr_2O_7^{=}$; 4, 2.38×10^{-3} *M* Fe^{+3} + 3.30×10^{-4} *M* $Cr_2O_7^{=}$; 5, sum of 2 and 3.

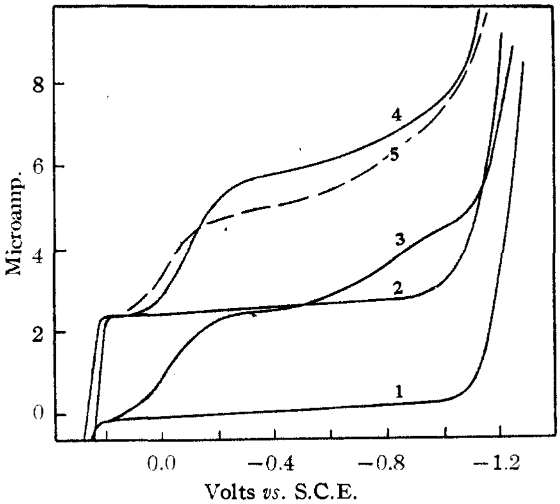

Fig. 2.—Mixtures of ceric and oxygen in 1.0 *M* H_2SO_4: 1, residual current; 2, 0.936×10^{-3} *M* Ce^{+4}; 3, 2.5×10^{-4} *M* O_2; 4, 0.936×10^{-3} *M* Ce^{+4} + 2.5×10^{-4} *M* O_2; 5, sum of 2 and 3.

Typical results for the dichromate–ferric system and the ceric–oxygen system are shown in Figs. 1 and 2, respectively. At concentrations of 2.38×10^{-3} *M* ferric and 3.30×10^{-4} *M* dichromate the current is 9% lower than would be expected if the currents were additive. The percentage reduction in current becomes less at lower concentrations of reducible species and is about 6% at concentrations of 3.80×10^{-4} *M* ferric and 0.678×10^{-4} *M* dichromate. In the ceric–oxygen case with respective concentrations of 0.936×10^{-3} *M* ceric and 2.5×10^{-4} *M* oxygen the observed current is 14% high at 0.3 v. and 7% high at 0.8 v. (S.C.E.). The percentage reduction or enhancement of current is the same in both 1 *M* H_2SO_4 and 1 *M* $HClO_4$.

This effect was also observed in the cases of chromic–oxygen and chromic–iodine in 1 *M* $HClO_4$. With concentrations of 1.23×10^{-3} *M* chromic and 2.5×10^{-4} *M* oxygen the observed current is 8% lower than expected in the diffusion current region of chromic (1.0 v.). In the chromic–iodine case the concentrations were 2.26×10^{-3} *M* chromic, 1.03 *M* I_3^- and 4×10^{-2} *M* NaI. The current was 9% lower than expected at 1.0 v.

Discussion

The decrease in total current in the ferric–dichromate solutions can be understood in the following terms. The ferrous ion formed from the reduction of the ferric diffuses into the body of the solution and encounters the dichromate ions that are diffusing to the electrode. In this diffusion layer the following reaction takes place very rapidly

$$6Fe^{+2} + Cr_2O_7^{--} + 14H^+ = 6Fe^{+3} + 2Cr^{+3} + 7H_2O$$

To the extent that this reaction occurs one equivalent of dichromate having a diffusion coefficient of about 13×10^{-6} cm.^{2} sec.$^{-1}$ is replaced by one equivalent of ferric having a diffusion coefficient of about 7×10^{-6} cm.^{2} sec.$^{-1}$. The same number of equivalents of reducible material is diffusing to the electrode, but is diffusing at a reduced rate. The current is therefore decreased. The decrease in percentage reduction of current at lower concentrations is consistent with this picture because at lower concentrations the fraction of dichromate replaced by the ferric is decreased.

The increase in current in the ceric–oxygen solution can be readily understood in an analogous manner. The hydrogen peroxide formed from the reduction of the oxygen diffuses into the body of the solution and encounters ceric ions that are diffusing to the electrode. The reaction that takes place very rapidly in the diffusion layer is

$$2Ce^{+4} + H_2O_2 = O_2 + 2Ce^{+3} + 2H^+ \qquad (1)$$

The ceric ion having a diffusion coefficient of about 6×10^{-6} is thus replaced by an equivalent of oxygen having a diffusion coefficient of about 26×10^{-6}. The same number of equivalents is being transported to the mercury drop, but at an increased rate. The current is therefore increased. Between the potentials of 0.5 and 1.0 v. where a significant portion of the oxygen is being reduced directly to water, less of the hydrogen peroxide can diffuse back into the body of the solution and react with the ceric. As is seen in Fig. 2, the difference between the expected and observed current is correspondingly reduced.

The above interpretation would not be correct if the number of equivalents of reducible material could be increased by a catalytic reduction of the hydrogen peroxide to water. It has been shown by Cahill and Taube[2] in tracer experiments that when

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(2) A. E. Cahill and H. Taube, This Journal, **74**, 2312 (1952).

hydrogen peroxide is oxidized by Ce^{+4} the O–O bond is not severed. Thus a possible reaction mechanism for eq. 1 would be

$$Ce^{+4} + H_2O_2 = Ce^{+3} + H^+ + HO_2 \qquad (2)$$

followed by

$$HO_2 + Ce^{+4} = Ce^{+3} + O_2 + H^+ \qquad (3)$$

or at the electrode

$$e^- + HO_2 + H^+ = H_2O_2 \qquad (4)$$

If HO_2 is produced at the electrode by the reduction of O_2 and diffuses into the solution, it will react with the Ce^{+4} as in eq. 3. In any of the cases, eq. 3 or 4 or the production of HO_2 at the electrode, the same number of equivalents of material is being reduced. Because the O–O bond is not severed, the reaction

$$HO_2 + H_2O_2 = H_2O + O_2 + HO\cdot \qquad (5)$$

cannot take place at an appreciable rate in the body of the solution. However, since the reduction of O_2 takes place at a metal surface, it may be that there is still some mechanism by which H_2O_2 can be reduced to H_2O. Additional experiments would be necessary to determine if the non-additivity in the case of ceric and oxygen is due to reduction of the H_2O_2 to H_2O or by the replacement of the ceric by a faster diffusing O_2.

The reduction in current for mixtures of chromic and oxygen and for chromic and iodine can be explained in the same manner as the ferric–dichromate mixture. The reactions in the diffusion layer are, respectively

$$4H^+ + 4Cr^{+2} + O_2 = 4Cr^{+3} + 2H_2O$$
$$2H^+ + 2Cr^{+2} + H_2O_2 = 2Cr^{+3} + 2H_2O$$
$$2Cr^{+2} + I_3^- = 2Cr^{+3} + 3I^-$$

In these last two cases, although the current reduction is significant, it is somewhat difficult to make a residual current correction because of the rapidly rising hydrogen wave.

The hydrogen ion concentration of 1 *M* is high enough so that there will be very little change in its concentration at the surface of the electrode. Therefore these results cannot be due to precipitation of hydroxides or other compounds such as have been reported previously.[3]

A quantitative treatment of the decrease or increase in current cannot be made on the basis of a simple replacement of the oxidized form of one species by the oxidized form of another species. Thus in the dichromate–ferric case the difference in the observed current from the sum is not the fraction of the replaced ions (which cannot be determined) times the fractional difference in diffusion coefficients. An exact treatment must take into account the combined factors of diffusion and reaction kinetics. The equations describing these combined factors can be formulated readily as a system of four non-linear partial differential equations with appropriate boundary conditions. The difficulty of solving these equations is too great to permit a quantitative treatment at this time.

DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA

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The Preparation and Properties of Brown Phosphorus

BY FRANCIS OWEN RICE, RITA POTOCKI AND KENNETH GOSSELIN

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Of the various allotropic forms of phosphorus, the common white form has been most thoroughly studied. Both vapor density[1] and cryoscopic measurements,[2] as well as X-ray[3] and electron diffraction studies,[4] all indicate that the molecule is P_4. Vapor density measurements[1] show that P_4 is an extremely stable molecule that dissociates appreciably to P_2 only near 1000° even at 1 mm. pressure. A spectroscopic study[5] of the P_2 molecule indicates that the strength of the bond in P_2 is 115.5 kcal. and that any thermal dissociation at 1000° even at very low pressures, would be negligible.

Although the other common form, red phosphorous, has been studied extensively, its structure has not as yet been settled conclusively. Pauling[6] has suggested that red phosphorus is formed from from white phosphorus by rupture of one bond and formation of long chains of P_4 units, each unit consisting of two equilateral triangles with a common base. This view is consistent with the results of X-ray studies,[3] which indicate that each atom in red phosphorus has three nearest neighbors and is also consistent with the results of kinetic studies[7] on the rate of reaction of white to red phosphorus. If, however, red phosphorus actually consists of long chains of P_4 units, the results of two studies of Melville and Gray[8] are rather unexpected. They concluded that the abnormally high vapor pressure of red phosphorus in a closed system could be understood on the basis that only P_2 molecules evaporate from red phosphorus *in vacuo* and these immediately dimerize to P_4 since the equilibrium, $2P_2 \rightleftarrows P_4$, even at red heat is almost entirely on the P_4 side. Our own work helps confirm this conclusion.

Our preliminary experiments were performed with white phosphorus in an apparatus described in previous work.[9] The phosphorus was kept at a temperature of about 45° where its vapor pressure is about 0.2 mm. According to vapor density measurements, the dissociation of phosphorus vapor at 1000° is

Pressure	P_4 at equilibrium, %
1.0	3.36
0.5	1.73
0.1	0.35
0.04	0.25

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