### VAN RYSSELBERGHE ET AL.

# POLAROGRAPHIC OBSERVATIONS ON PERCARBONIC ACIDS AND PERCARBONATES<sup>1</sup>

## PIERRE VAN RYSSELBERGHE, PAUL DELAHAY,<sup>2</sup> ARMIN H. GROPP,<sup>3</sup> JOHN M. McGEE, and ROBERT D. WILLIAMS<sup>4</sup>

### Department of Chemistry, University of Oregon, Eugene, Oregon

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In the course of a program of research dealing with the polarographic study of corrosion phenomena<sup>5</sup> it was noticed that polarograms obtained with solutions containing simultaneously carbon dioxide and oxygen or hydrogen peroxide exhibited, between the two well-known oxygen reduction steps, a new wave which, as far as we were able to ascertain, had not been reported by other workers. This finding led us to the separate investigation reported in the present paper. The initial observations and some of their possible implications from the point of view of corrosion are presented elsewhere (18).

### EXPERIMENTAL METHOD

The polarograms were taken by means of the Sargent photographic polarograph Model XII and by means of a manual polarograph assembled from standard physical-chemical equipment. Various types of cells were used, including the Heyrovský cells and those specially designed for our experiments (18). All supporting electrolytes were "polarographically" pure, i.e., they did not exhibit, in the absence of dissolved oxygen, any reduction wave before their own final reduction currents. In order to achieve this, some electrolytes, in particular tetramethylammonium bromide, had to be carefully and repeatedly recrystallized. Some c.p. electrolytes were satisfactory as obtained. A number of buffers prepared according to Kolthoff and Laitinen (10) were used to study the influence of pH on the newly observed wave. In a number of cases both the oxygen and the carbon dioxide concentrations of the solutions studied were determined analytically by means of the Winkler method for oxygen and by means of a specially designed barium hydroxide titration device for carbon dioxide (18).

In order to suppress the sharp maximum of the first oxygen wave a number of surface-active substances were used, such as methyl red, thymol, etc. (18). In the presence of sodium fluoride used as supporting electrolyte the oxygen peak does not appear and the new wave can be studied in the absence of any maximum

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<sup>2</sup> Present address: Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana.

<sup>8</sup> Present address: Department of Chemistry, University of Florida, Gainesville, Florida.

<sup>4</sup> Present address: Research Laboratories, Aluminum Company of America, New Kensington, Pennsylvania.

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suppressor. This was also the case in some electrolyte mixtures containing certain minimum amounts of magnesium ion. By the simple device of passing the solution through filter paper when introducing it in the polarographic cell, as is done, for instance, by Heyrovský (9) and by Brdička and Wiesner (1), it was possible to study the new wave without any addition of a maximum suppressor. It might be noted in passing that, when the oxygen concentration falls appreciably below the 10 mg./l. corresponding to saturation with air, a maximum suppressor is usually unnecessary.

The capillaries used were such that the  $m^{2/3} t^{1/6}$  product of the Ilkovič equation was always close to 2.5 in the range of potentials corresponding to the new wave, i.e., at a few tenths of a volt negative with respect to the saturated calomel electrode.

The temperature was close to  $25^{\circ}$ C. or to  $20^{\circ}$ C. The electrotitration experiments were run at  $0^{\circ}$ C.

In some crucial experiments designed to identify the nature of the new wave we used two different preparations of Kahlbaum potassium percarbonate and some percarbonate which we prepared electrolytically by the method of Constam and von Hansen (4, 8). Attempts at preparing percarbonates by other methods, in particular that of Wolffenstein and Peltner (19), gave products exhibiting a polarographic behavior different from that of the Kahlbaum compound and from that of our own electrolytic product. Similarly, the sodium carbonate peroxide,  $2Na_2CO_3 \cdot 3H_2O_2$ , of the Buffalo Electrochemical Company gave polarograms different from those obtained with the true percarbonates.

The hydrogen peroxide used in this work was obtained by diluting C.P. acidfree 30 and 90 per cent hydrogen peroxide obtained from the Buffalo Electrochemical Company. All pH measurements and the electrotitration experiments on percarbonic acid were carried out by means of a Beckman pH meter.

The carbon dioxide used was obtained from cylinders supplied by Pure Carbonic, Inc.

### RESULTS

# 1. Air-saturated solutions with various additions of carbon dioxide

As previously reported (18) many air-saturated 0.1 N solutions of unbuffered electrolytes such as potassium chloride, potassium nitrate, tetramethylammonium bromide, etc. containing approximately 0.4 mg. carbon dioxide per liter gave polarograms exhibiting a small intermediate wave between the two reduction steps of oxygen. When methyl red is used as a maximum suppressor this new reduction step is almost always present and its height increases when additional amounts of carbon dioxide are dissolved. With thymol the step appears only in the alkaline range with air-saturated solutions but with sufficient addition of carbon dioxide it appears also in unbuffered neutral solutions. In both cases these waves, including the initial ones, are not waves of the maximum suppressors. With solutions which do not require a maximum suppressor the step may not be immediately apparent, but it always develops upon addition of carbon dioxide. As this wave increases in height the second oxygen wave decreases and the sum of the two waves remains equal to the original height of the second oxygen wave. The first oxygen wave remains unaltered except when the pH becomes smaller than 5.5, at which point the new intermediate wave becomes an extension of the first oxygen wave on account of a shift of half-wave potential towards less cathodic values (see below). Several typical polarograms obtained by the manual method have been presented previously (18) for qualitative discussion. In table 1 we give the ratios of the heights of the new wave to the original height of the second oxygen wave for different concentrations of oxygen and carbon dioxide analytically determined, the supporting electrolyte being 0.1 N

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Apparent number of electrons per molecule of carbon dioxide in the new reduction wave 0.1 N tetramethylammonium bromide

CO1	O2	$i_{O_2}/i_{CO_2}$	*	CO2	O2	i <sub>02</sub> /i <sub>CO2</sub>	n
mg./l.	mg./l.				mg./l.		
0.4	9.5	6.01	10.6	5.8	9.2	5.37	0.88
0.4	9.3	7.34	9.4	9.7	9.8	5.23	0.56
0.8	10.0	6.85	5.3	17.4	9.4	5.00	0.3
1.3	9.2	6.54	3.2	23.7	9.4	1.32	0.9
3.4	9.2	6.92	1.2	23.7	8.8	1.24	0.90
4.1	9.5	8.59	0.78	47.8	9.0	1.26	0.44
4.3	10.0	6.89	0.98	67.5	9.4	1.18	0.34

TABLE 2

Apparent number of electrons per molecule of carbon dioxide in new reduction wave 0.1 N potassium chloride

CO2	O2	i02/iCO2	n	CO2	O2	i <sub>02</sub> /i <sub>CO2</sub>	73
mg./l.	mg./l.			mg./l.		1	
0.4	9.8	6.80	8.4	2.2	10.5	5.69	2.4
1.0	10.1	6.60	4.7	2.9	9.6	6.81	1.4
1.1	10.5	7.31	3.5	17.5	9.6	10.2	0.16
1.6	9.3	6.63	2.6	50.0	9.7	4.54	0.12
2.0	9.7	5.73	2.5				

tetramethylammonium bromide. In table 2 similar data are given for 0.1 N potassium chloride. Since it was immediately noticed that, at very small carbon dioxide concentrations, the height of the new wave was much larger than could be expected for a two-electron reduction of some compound derived from the carbon dioxide present, we computed an apparent number of electrons n per molecule of carbon dioxide by taking the ratio of the two limiting currents (that of the new wave,  $i_{\rm Co_2}$ , and the one corresponding to the total second oxygen wave,  $i_{\rm O_2}$ ) derived from the Ilkovič equation:

$$\frac{i_{CO_2}}{i_{O_2}} = \frac{n}{2} \cdot \frac{C_{CO_2}}{C_{O_2}} \cdot \frac{D_{CO_2}^{1/2}}{D_{O_2}^{1/2}} \tag{1}$$

in which  $C_{Co_2}$  and  $C_{o_2}$  are the molar concentrations of carbon dioxide and oxygen and  $D_{Co_2}$  and  $D_{o_2}$  are their diffusion coefficients; the ratio of their square roots was taken constant and such that

$$n = 2.16 \frac{C_{O_2}}{C_{CO_2}} \cdot \frac{i_{CO_2}}{i_{O_2}}$$
(2)

Values of n much larger than 2 would tend to indicate that each molecule of carbon dioxide is involved several times in the reduction process and very small values of n would indicate that only a small fraction of the carbon dioxide present is involved in the process. The flattening of the wave with the establishment of an apparent diffusion current would be due to the disappearance, by reduction to water, of the other compound essential to the occurrence of the new wave: namely, the hydrogen peroxide resulting from the first reduction step of oxygen.

Other experiments, with appreciably higher carbon dioxide concentrations, showed that, in tetramethylammonium bromide solutions, the second oxygen wave can be nearly entirely replaced by this new wave while, in potassium chloride solutions, it is much more difficult to reach these high carbon dioxide concentrations and the replacement of the second oxygen wave by the new wave is always far from complete. Our experience with solutions of electrolytes containing carbon dioxide shows that quaternary ammonium salts are able to keep carbon dioxide at supersaturation much more easily than all other salts.

The foregoing results will be discussed below but it is already apparent that the new wave results from the formation and the subsequent reduction of a compound involving carbon dioxide and the hydrogen peroxide resulting from the reduction of oxygen along the first oxygen wave.

A typical polarogram showing the phenomena described above is given in figure 1. In figure 2 the previously observed reduction of carbon dioxide (15, 16, 17) at a half-wave potential of 2.16 v. with respect to the saturated calomel electrode appears in addition to the new wave observed at low potentials.

### 2. Solutions of hydrogen peroxide with various additions of carbon dioxide

When dilute solutions of hydrogen peroxide in 0.1 N unbuffered electrolytes are treated with pure nitrogen to remove all or most of the oxygen, polarographic reduction waves of the type of the first curve on the left of figure 3 are obtained. No maximum suppressor is needed in this case. When carbon dioxide is gradually added to such solutions the hydrogen peroxide wave is split into two fragments and, with sufficient addition of carbon dioxide, it is finally entirely replaced by the new wave already observed on polarograms of mixtures of oxygen and carbon dioxide.

In mixtures of hydrogen peroxide and carbon dioxide the reducible compound is present in bulk concentration, while in mixtures of oxygen and carbon dioxide the compound is formed at the dropping cathode through reaction between carbon dioxide and hydrogen peroxide. In mixtures of hydrogen peroxide and carbon dioxide the simplest compound one could expect is the percarbonic acid  $(H_2CO_4)$  formed by direct addition of carbon dioxide to hydrogen peroxide.



FIG. 1. Gradual addition of carbon dioxide to a 0.1 N solution of tetramethylammonium bromide saturated with air. First curve on left has no added carbon dioxide. Last curve on right shows maximum transformation of second oxygen wave to intermediate wave with slight decrease of first oxygen wave due to displacement by carbon dioxide. Drop of methyl red used. Recording by Sargent Polarograph Model XII. Picture is tracing of original polarogram with minute galvanometer oscillations left out.



FIG. 2. Curve I is similar to curve on the left of figure 1. Curve II is the result of the addition of a large amount of carbon dioxide to an air-saturated solution of 0.1 N tetramethylammonium bromide with both the low and high potential waves due to carbon dioxide observable. Recording by Sargent Polarograph Model XII. Picture is tracing of original polarogram with minute galvanometer oscillations left out.



FIG. 3. Gradual addition of carbon dioxide to 0.1 N solution of tetramethylammonium bromide containing one drop of 3 per cent hydrogen peroxide per 10 ml. of solution. First curve on left has no added carbon dioxide. Last curve on right shows maximum transformation of hydrogen peroxide wave to new wave. No methyl red used. Recording by Sargent Polarograph Model XII. Picture is tracing of original polarogram with minute galvanometer oscillations left out.

Other percarbonic acids could also be expected, such as  $H_2CO_5$  and  $H_2C_2O_6$ . Our previous polarographic studies on carbon dioxide (15, 16, 17) have shown that, in the absence of oxygen or hydrogen peroxide, the new wave now being discussed is not observed. We are definitely dealing with the reduction of a compound formed by reaction of carbon dioxide with hydrogen peroxide.

## 3. Buffered solutions

In eight different buffers prepared according to Kolthoff and Laitinen (10)and saturated with air at 20°C. the new wave was registered and its half-wave potential was determined for each pH. Mixtures of carbon dioxide and hydrogen peroxide were added to samples of the same buffers. At the pH's which were studied these solutions exhibited percarbonic waves of about the same height as in air-saturated solutions. In all cases very satisfactory percarbonic waves were registered by using the higher sensitivities of the Sargent polarograph. It was immediately noticed that an increase of acidity shifts the half-wave potential to lower cathodic values. When the pH becomes smaller than 5.5 the new wave is no more distinguishable from the first oxygen wave of which it becomes an extension with a short inflection connecting the two segments of curves. The



FIG. 4. Variation of the half-wave potential of the percarbonic wave with pH at 20°C. Zero of potential scale corresponds to standard hydrogen electrode.

half-wave potentials observed at 20°C. are plotted on figure 4. By interpolation one finds that at pH = 7 the half-wave potential is 0.37 v. negative with respect to the saturated calomel electrode. In the range pH = 5.50 to pH = 9.71 the following relation holds:

$$E_{1/2} = 0.06 - 0.061 \text{ pH}$$
(3)

If the extrapolation shown on figure 4 to pH = 0 is assumed to have at least theoretical meaning one may conclude that at activity 1 of hydrogen ion the half-wave potential is  $\pm 0.06$  v. against the saturated calomel electrode or  $\pm 0.31$ v. against the standard hydrogen electrode. It will be remembered that the halfwave potentials of both the first and the second oxygen waves do not vary with pH but are slightly affected by the nature of the buffers (11, 12), while the half-wave potential of the intermediate wave observed by us in the case of the buffered solutions and due to the presence of carbon dioxide does depend linearly on pH. The slope  $\Delta E/i_d$  at the half-wave is  $0.055 \pm 0.003$  in the case of the waves obtained in buffers. This would be in agreement with a two-electron reduction per molecule (15). The potential interval  $\Delta E$  and the diffusion current  $i_d$  are the horizontal and vertical sides of a rectangular triangle whose hypotenuse is the tangent at the half-wave. These properties of the waves make it possible that we are dealing with a reversible reduction. However, with percarbonic waves obtained with mixtures of carbon dioxide and hydrogen peroxide and with unbuffered solutions the slope is often quite different from that required for a two-electron reversible reduction.

## 4. Solutions of potassium percarbonate

The interpretation of the nature of this intermediate reduction step between the two oxygen waves was greatly helped by crucial observations on solutions containing the potassium percarbonate,  $K_2C_2O_6$ . A Kahlbaum bottle of this product, which had never been opened, was available in our laboratory. Although no formula was given on the label it seems certain that this product was



FIG. 5. Polarographic waves of potassium percarbonate taken at 10-min. intervals. On each curve the intermediate wave is that of percarbonate. The first wave is that of oxygen; the third wave includes oxygen and hydrogen peroxide. Supporting electrolyte is 0.1 Npotassium nitrate. Each curve begins at zero applied potential. Recording by Sargent Polarograph Model XII. Picture is tracing of original polarogram, with minute galvanometer oscillations left out.

obtained by the electrolytic process (4, 8), which is known to give percarbonates of the  $K_2C_2O_6$  type. Solutions containing small amounts of this salt in 0.1 Mpotassium nitrate gave the waves shown in figure 5. We note that, with polarograms taken at intervals of 10 min., the height of the percarbonic acid step increases with time. In the alkaline solutions resulting from the dissolution of the percarbonate the reduction must be that of the negative ion  $CO_4^{-}$  formed by the relatively slow hydrolysis reaction (13):

$$K_2C_2O_6 + H_2O \rightarrow K_2CO_4 + H_2CO_3$$
(4)

In later experiments it was found that the percarbonate had quickly deteriorated after the bottle had been opened for the first time. A second bottle of Kahlbaum percarbonate was located and similar observations were made with its contents. Attempts at preparing percarbonates resulted in compounds which gave only hydrogen peroxide waves or at most negligible intermediate waves, unless some acid was added, in which case what must have been a percarbonic acid was formed between carbon dioxide and hydrogen peroxide. In particular the methods of Wolffenstein and Peltner (19) for the preparation of both  $Na_2CO_4$  and  $Na_2C_2O_6$  were used but resulted in compounds which gave only hydrogen peroxide waves. This leads us to the opinion that these percarbonates were actually addition products of carbonate and hydrogen peroxide. The same situation holds for the sodium carbonate peroxide,  $2Na_2CO_3 \cdot 3H_2O_2$ , of the Buffalo Electrochemical Company. It must be concluded from these and many other similar attempts that only the Kahlbaum product was a true percarbonate.

On the other hand, some potassium percarbonate which we prepared ourselves by the electrolytic method of Constam and von Hansen (4, 8) and which, in accordance with the description given by these authors, was of a light sky-blue color, gave the intermediate waves shown on the three polarograms of figure 6.

## 5. Percarbonic acids and their titration

It can be deduced from these observations that the new wave is due to one or several of the possible forms of percarbonic acid:  $H_2CO_4$ ,  $H_2CO_5$ ,  $H_2C_2O_6$ , or their ions. In the case of air-saturated solutions percarbonic acid would be formed between carbon dioxide and the hydrogen peroxide accumulating near the dropping mercury cathode during the first oxygen wave. The resulting per-



FIG. 6. Identification of the intermediate wave as percarbonic wave with solution of potassium carbonate containing some percarbonate formed by electrolysis. Middle curve obtained with solution as removed from electrolysis cell. Curve on right obtained with same solution after removal of some oxygen by nitrogen. Curve on left is repeat run at higher sensitivity. Recording by Sargent Polarograph Model XII. Picture is tracing of original polarogram with minute galvanometer oscillations left out.

carbonic acid would then be reducible at potentials smaller than those required for the reduction of hydrogen peroxide and for the complete reduction of oxygen to water. In the case of mixtures of hydrogen peroxide and carbon dioxide percarbonic acid is present before polarographic reduction. This has been confirmed by the electrotitration of solutions of percarbonic acid obtained by mixing carbon dioxide with an excess of acid-free hydrogen peroxide. After 24 hr. at  $0^{\circ}$ C. these solutions have reached equilibrium and constant acid strength. They also have lost most of the unreacted carbon dioxide. The mathematical analysis of the titration curves according to the treatment of Britton (2), assuming that only one dibasic acid is present, was attempted. Further work will be needed to obtain accurate ionization constants. The only statement we shall make at present is that percarbonic acid is stronger than carbonic acid, in agreement with the statement of Charlot (3).

#### DISCUSSION

If the experiments carried out with percarbonates can be regarded as definitely proving that the new wave is due to one or several percarbonic acids or their ions, it becomes of interest to inquire into the nature of the reduction reaction. If one assumes that the equilibrium constant for the formation of  $H_2CO_4$  from hydrogen peroxide and carbon dioxide is of the same order of magnitude as those observed by d'Ans and Frey (5, 6) for peracids such as performic and peracetic, i.e., of the order of unity, one could estimate the free energy of formation of  $H_2CO_4$  as being -124 kcal. (-31.5 for  $H_2O_2$  aq.; -92.3 for  $CO_2$  aq.). The reduction

$$H_2CO_4 + 2H^+ + 2e^- \rightarrow CO_2 + 2H_2O \tag{5}$$

involves a free energy decrease of -82 kcal. at pH = 0, while the energy corresponding to the polarographic potential is -14 kcal. One may conclude either that reaction 6 occurs irreversibly with an overvoltage of the order of 1.5 v. or that it occurs reversibly with respect to the formation of orthocarbonic acid,  $C(OH)_4$ , which would decompose spontaneously into  $CO_2$  and  $2H_2O$ . Starting with the free energy of formation of methanol, -40 kcal., and using the value -34 kcal. for each substitution of H to OH (Parks and Huffman (14)) one arrives at -142 kcal. for the free energy of formation of  $C(OH)_4$ . The difference -142 - (-124) is -18 kcal, which is similar to the -14 kcal, derived from the polarographic potential. It is possible that this polarographic potential corresponds to the activation energy of a complex having the gross formula  $C(OH)_4$ but properties quite different from those of the hypothetical orthocarbonic acid. An explanation based upon a reduction to perform c acid was examined but not retained. We found experimentally that performic acid is itself reducible at potentials corresponding to the reduction of percarbonic acid. Performic acid has been reported as unstable by d'Ans and Frey (5, 6) and quite recently by Greenspan (7). Since carbon dioxide is apparently formed again by reduction of percarbonic acid, one may expect in the experiments with air-saturated solutions, where the acid is formed at the dropping electrode, that the carbon dioxide will react again with hydrogen peroxide and possibly go through several successive cycles of reaction and reduction, leading to a wave height much greater than would be expected from the concentration of carbon dioxide. That this is indeed the case is shown by the fact that, in air-saturated solutions containing about 0.4 mg. of carbon dioxide and 10 mg. of oxygen per liter, the ratio of the height of the percarbonic wave to that of the first oxygen wave was found to vary, in one series of runs, from 0.242 to 0.214 as the drop time of the mercury cathode was changed from 3.05 to 0.54 sec. If the carbon dioxide present were involved in only one cycle of reaction with hydrogen peroxide and reduction back to  $CO_2$  through  $C(OH)_4$ , the ratio of these wave heights should be of the order of 0.05. It is evident that the amount of hydrogen peroxide available determines the maximum height of the percarbonic wave which can never be larger than the original hydrogen peroxide wave in the absence of carbon dioxide. We hope to obtain more precise information concerning these cycles of formation and reduction by means of an oscillographic method being developed by one of us (P.D.).

An interesting observation for which we have no complete explanation is the following: basic air-saturated solutions give percarbonic waves of about the same height as neutral solutions, in spite of the fact that the carbon dioxide concentration is then greatly decreased. Apparently reducible percarbonate ions are readily formed with the hydrogen peroxide formed at the dropping cathode, while the mixing of hydrogen peroxide with a carbonate or a bicarbonate solution does not lead to any detectable formation of percarbonates. Addition of acid to such mixtures immediately results in the formation of percarbonic acid. One might assume that the hydrogen peroxide formed at the dropping cathode is in some sort of activated state with greater reactivity. The possibility of the formation of other reduction products, such as OH or  $O_2^-$ , which would react readily with carbonate and bicarbonate ions might be considered, but there are thermodynamic difficulties involved in the postulation of such mechanisms.

### SUMMARY

A new polarographic wave is observed between the two oxygen waves whenever carbon dioxide is present with oxygen or hydrogen peroxide in solution. Percarbonates exhibit the same wave, which is thus ascribed to one or several of the possible percarbonic acids or their ions.

The characteristics of the new wave, i.e., variation of half-wave potential with pH, slope, height, and possible reversibility or irreversibility, are discussed.

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