THE ADSORPTION OF CARBON DIOXIDE ON PLATINIZED PLATINUM IN SULFURIC ACID SOLUTIONS

B. I. Podlovchenko, V. F. Stenin, and A. A. Ekibaeva

UDC 541.138.2:547

Giner [1] was the first to observe that during interaction of CO_2 with hydrogen adsorbed on a platinum surface, a strongly chemisorbed product ("reduced CO_2") is formed. According to [1-4], the species that are chemisorbed on Pt in CH_3OH and HCOOH solutions [1, 2] as well as those remaining on the surface after hydrogenation of chemisorbed hydrocarbons [3, 4], are identical with "reduced CO_2". On the other hand, according to data in [5], the overpotential for electrooxidation of "reduced CO_2" is appreciably higher than that of the chemisorbed products of CH_3OH, HCHO, and HCOOH. It is suggested in [6] that CO_2 only "screens" the H_{ads} without interacting chemically with it. We report here about studies of CO_2 chemisorption on Pt/Pt in 1 N H_2SO_4 using the techniques applied previously to the investigation of adsorption of organic substances [7-9].

For the galvanostatic measurements, a galvanostat with currents from 10 μA to 8 mA was used, while for the potentiostatic i-φ curves a TsLA P-5611 potentiostat was used. The curves were plotted with a one-point-per-second ÉPP-09M3 recorder. The measurements were carried out with an aged Pt/Pt electrode that had a ratio of true to apparent (5.6 cm^2) surface area of 500-600.

In order to free it from possible impurities (O_2, CO, H_2, etc.), technical carbon dioxide was passed through a series of absorbers with solutions of pyrogallol, palladium chloride, sodium bicarbonate, potassium bichromate, and concentrated sulfuric acid [10]. Traces of oxygen were further removed by passing the CO_2 through a nickel-chromium catalyst, and to trap moisture-carrying aerosols, a special filter was put at the exit of the purification system. A series of experiments showed that purified technical CO_2 gives the same results as CO_2 obtained by the thermal decomposition of sodium bicarbonate ("chemically pure") and subsequent removal of water vapor and oxygen traces [10]. Thus we could assume that the purification employed was satisfactory. The cell volume was about 20 ml. Hydrogen adsorption isotherms were obtained from the anodic charging curves [11]. The measurements were carried out at room temperature, 20 ± 2°C. The potential φ_r are given with respect to the rhe in the same solution.

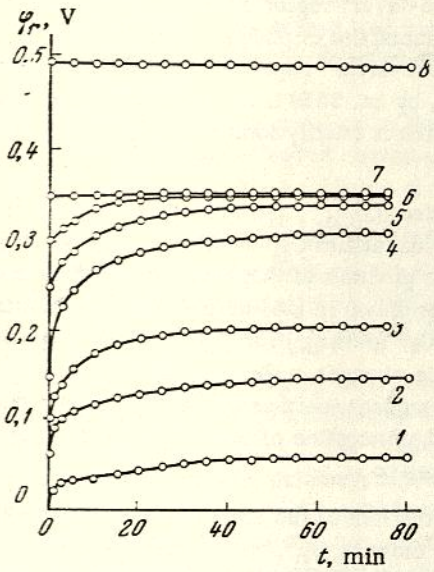


Fig. 1. Curves showing how the potential of a Pt/Pt electrode, upon introduction of CO_2, shifts away from the starting potential φ_r^0: 1) 0; 2) 60; 3) 100; 4) 150; 5) 250; 6) 300; 7) 350; 8) 500 mV. Base electrolyte: 1 N H_2SO_4.

The curves given Fig. 1 show how the potential of a Pt/Pt electrode varies after it has been brought in contact with an H_2SO_4 solution saturated in advance with CO_2*, with subsequent passing of CO_2 into the working compartment of the cell (ca. 1.5 h). The figure shows that presence of CO_2 in the solution causes φ_r to shift to the positive side (as already noted in [5]) so long as the initial potential, φ_r^0, is between 0 and 350 mV. With φ_r in the "double-layer" region, practically no potential shift is observed. The fastest shift and the largest $\Delta\varphi$ ($\varphi_r^1 - \varphi_r^0$)) are observed at $\varphi_r^0 \simeq 150$ mV.

* Prior saturation is necessary so that the reaction on the electrode during the initial period will not be limited by CO_2

M. V. Lomonosov Moscow State University. Translated from Élektrokhimiya, Vol. 4, No. 8, pp. 1004-1008, August, 1968. Original article submitted January 25, 1968.

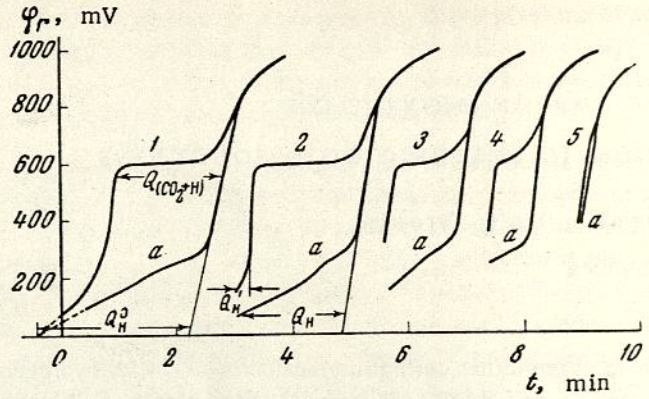


Fig. 2. Curves for th electrooxidation of "reduced CO_2" corresponding to different φ_r^0: 1) 0; 2) 60; 3) 150; 4) 250; 5) 350 mV. The charging curve in the base electrolyte, 1 N H_2SO_4, are indicated by α. Current density: i = 0.36 mA/cm^2.

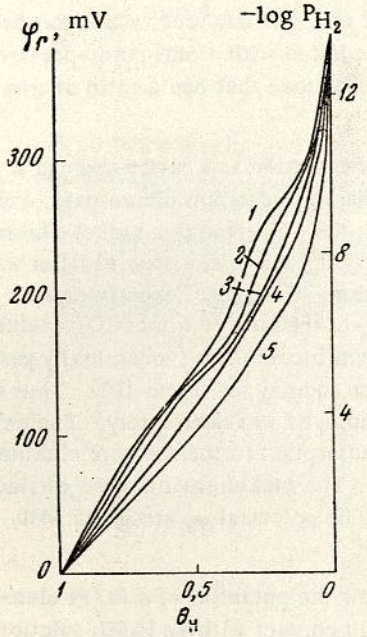


Fig. 3. Hydrogen adsorption isotherms in 1 N H_2SO_4 at various surface coverages of "reduced CO_2". Values of the coefficient k: 1) 0; 2) 0.1; 3) 0.31; 4) 0.54; 5) 0.85.

The plateaus on the charging curves (Fig. 2) at φ_r values of the "double-layer" region correspond to the electrooxidation of "reduced CO_2". The dependence of the adsorption coefficient k ($Q_{(CO_2 + H)}/Q_H^0$) on φ_r^0 is characterized by the following values: 0 mV, 0.74; 60 mV, 0.85; 100 mV, 0.73; 150 mV, 0.54; 250 mV, 0.31; 300 mV, 0.10; 350 mV, 0.05. As expected, the amount of $(Co_2 + H)_{ads}$ increases with increasing initial coverage of the surface with H_{ads}, however, the maximum surface coverage with "reduced CO_2" occurs for φ_r^0 values somewhat more positive than the reversible hydrogen electrode potential.

According to [12-14], one must assume that adsorbed oxygen or hydrogen are present at φ_r values of the "double-layer" region in sulfuric acid solutions. The fact that the formation of small quantities of $(CO_2 + H)_{ads}$ in the case φ_r^0 = 350 mV leads to a drop in the "double-layer" capacity* of the Pt/Pt electrode from about 70 to 50-55 μF/cm^2 (i.e., by ca. 25%) is most probably due to (at least partial) bonding of the H_{ads}, which is usually ionized at φ_r of the "double-layer" region by the carbon dioxide.

The sum of the amounts of bonded ($Q_{(Co_2 + H)}$) and nonbonded (Q_H^1) adsorbed hydrogen is close to the initial quantities Q_H at all φ_r^0 (Fig. 2). From this we may conclude that none of the products of CO_2 reduction passes into the solution. An analogous conclusion was drawn in [15] from analytical measurements. Hydrogenation of "reduced CO_2" (passing hydrogen or cathodic polarization of Pt/Pt) does not cause notable changes in the behavior of the electrooxidation curves for the chemisorbed product, neither qualitatively nor quantitatively, which is proof for the strong chemisorption of the latter. According to Giner [1], CO_2 chemisorbs also at negative φ_r.

Since for different $\theta_{(CO_2 + H)}$ the sum of the amounts of "reduced CO_2" and of hydrogen adsorbed at $\varphi_r = 0$ is close to Q_H^0, one must suppose that the species $(CO_2 + H)_{ads}$, like "chemisorbed methanol" [8, 11], occupies as many hydrogen sites as the number of electrons it gives off upon oxidation.

Hydrogen adsorption isotherms in presence of $(CO_2 + H)_{ads}$ show (Fig. 3) that with increasing coverage of the surface with "reduced CO_2", the work of removal of one mole H_{ads} decreases from ca. 3.4 kcal in 1 N H_2SO_4 to ca. 2.2 kcal at the maximum $\theta_{(CO_2 + H)}$.

Practically the same values were obtained in [11] for CH_3OH chemisorption at anodic polarization. The "effect of preferential chemisorption" on sites with high H_{ads} bond energy [11] can, in fact, also be due to the decrease in hydrogen bond energy at sites neighboring those occupied by "reduced CO_2". One must probably assume that

*As calculated from the slope of the linear portions of the corresponding anodic charging curves at φ_r values in the "double-layer" region.

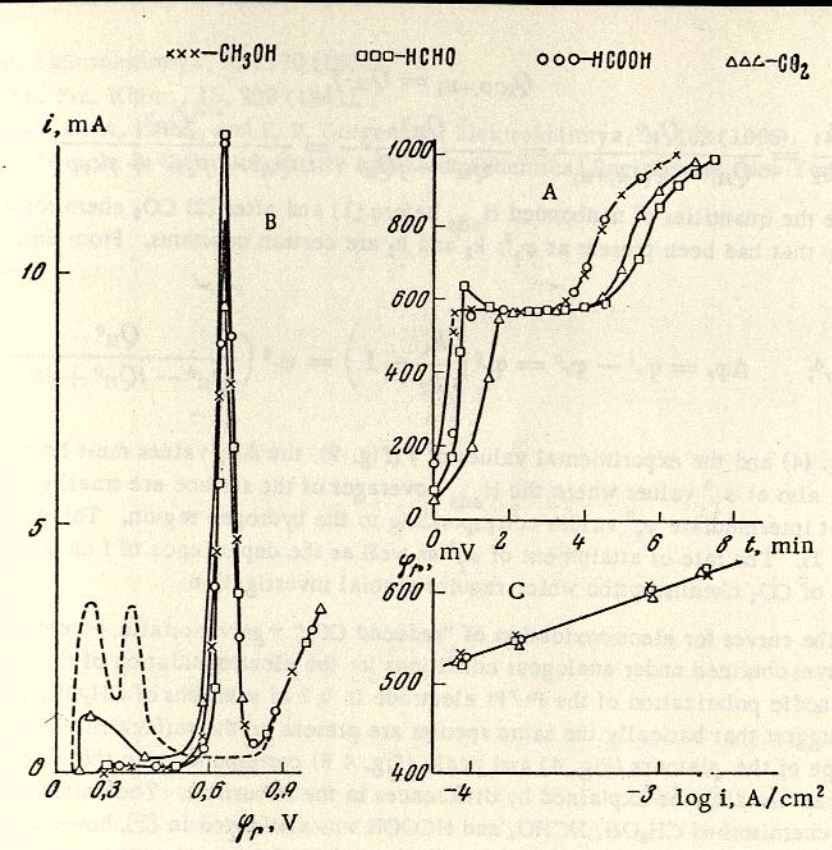


Fig. 4. Curves for the electrooxidation of "reduced CO_2" and of CH_3OH, HCHO, and HCOOH chemisorbed during anodic polarization. A) galvanostatic curves, i = 0.36 mA/cm², B) potentiostatic curves, i = 0.36 mA/cm², the dashed line being the potentiostatic curve in the base electrolyte, 1 N H_2SO_4, C) polarization curves for the oxidation of chemisorbed products.

$(CO_2 + H)_{ads}$ changes the structure of the electric double layer on platinum, shifting in particular the potential of zero charge. A strong effect of chemisorbed organic species on the adsorption of anions and cations on platinum has been demonstrated in [16] by the use of labeled atoms.

Notwithstanding a certain preferential chemisorption of "reduced CO_2" on sites with high $Pt-H_{ads}$ bond energy, as mentioned above, one finds always that after the introduction of CO_2 at φ_r^0 values of the hydrogen region, hydrogen sites corresponding to $\varphi_r < \varphi_r^0$ are occupied to a considerable extent. This effect is difficult to explain assuming [6] that CO_2 only screens H_{ads} without undergoing any chemical interaction with it*.

Since with increasing surface coverage with $(CO_2 + H)_{ads}$ the amount of potential-determining nonbonded H_{ads} diminishes, we find it insufficient to explain the shift of φ_r upon introduction of CO_2 only with a lowering of the surface concentration of H_{ads} [5]. The character of the distribution of chemisorbed species over the surface is of great importance for this problem, especially chemisorption of $(CO_2 + H)_{ads}$ also on those sites corresponding to $\varphi < \varphi_r^0$. In fact, one can find a relationship between the potentials φ_r^0 and φ_r^1 for the case where any preferential chemisorption of CO_2 on sites with larger H_{ads} bond energy is completely absent, assuming to a first approximation Temkin conditions for the adsorption of hydrogen [17], and starting from the following relations:

$$Q_H = Q_H^0 - k_1\varphi_r^0 \quad (1)$$

$$Q_H^1 = (Q_H^0 - Q_{(CO_2+H)}) - k_2\varphi_r^1, \quad (1')$$

$$Q_{(CO_2+H)} = Q_H \cdot j, \quad (2)$$

*Breiter [5] made certain critical remarks concerning the concepts developed in [6].

$$Q_{(CO_2+H)} = Q_H \cdot j, \tag{2'}$$

$$\frac{k_1}{k_2} = \frac{Q_H^0}{Q_H^0 - Q_{(CO_2+H)}} = \frac{Q_H^0}{Q_H^0 - jQ_H} = \frac{Q_H^0}{Q_H^0 - jQ_H^0 + jk_1\varphi_r^0}, \tag{3}$$

where Q_H and Q_H^1 are the quantities of nonbonded H_{ads} before (1) and after (2) CO_2 chemisorption; j is the degree of bonding of hydrogen that had been present at φ_r^0; k_1 and k_2 are certain constants. From Eqs. (1-3) we obtain by simple substitutions

$$\varphi_r^1 = \frac{k_1}{k_2}\varphi_r^0; \qquad \Delta\varphi_r = \varphi_r^1 - \varphi_r^0 = \varphi_r^0\left(\frac{k_1}{k_2} - 1\right) = \varphi_r^0\left(\frac{Q_H^0}{Q_H^0 - jQ_H^0 + jk_1\varphi_r^0} - 1\right). \tag{4}$$

According to Eq. (4) and the experimental values of j (Fig. 2), the $\Delta\varphi_r$ values must be small at φ_r^0 values close to 0 ($j < 1$), and also at φ_r^0 values where the H_{ads} coverages of the surface are small ($j \simeq 1$, $jk_1\varphi_r^0 \simeq Q_H^0$), and they must be largest at intermediate φ_r^0 values corresponding to the hydrogen region. This agrees qualitatively* with experiment (Fig. 1). The rate of attainment of φ_r^1 as well as the dependence of f on φ_r^0 are obviously determined by the kinetics of CO_2 chemisorption which require special investigation.

Comparison of the curves for electrooxidation of "reduced CO_2" – galvanostatic, potentiostatic, and polarization curves† – with curves obtained under analogous conditions for the electrooxidation of the chemisorbed species accumulated during anodic polarization of the Pt/Pt electrode in 0.1 M solutions of CH_3OH, HCHO, and HCOOH (Fig. 4) allows us to suggest that basically the same species are present on the surface in all cases. Certain differences in magnitude and shape of the plateaus (Fig. 4) and peaks (Fig. 4 B) corresponding to the electrooxidation of the chemisorbed species can certainly be explained by differences in the Pt surface. The uniformity in the electrochemical characteristics of chemisorbed CH_3OH, HCHO, and HCOOH was also noted in [5], however, the higher overpotential for electrooxidation of $(CO_2 + H)_{ads}$ found in [5] was not confirmed in our experiments.

We express our deep gratidude to Academician A. N. Frumkin for participation in the discussion of the experimental results.

LITERATURE CITED

1. J. Giner, Electrochim. Acta, 8, 857 (1963); 9, 63 (1964).
2. W. Vielstich and U. Vogel, Ber. Bunsenges. Physik. Chem., 68, 688 (1964).
3. S. Gilman, Trans. Faraday Soc., 61, 2561 (1965).
4. L. W. Niedrach, J. Electrochem. Soc., 111, 1309 (1964).
5. M. Breiter, Electrochim. Acta, 12, 1313 (1967); Z. Physik. Chem. (1957).
6. B. Piersma, T. Warner, and S. Schuldiner, J. Electrochem. Soc., 113, 841 (1966).
7. A. N. Frumkin and B. I. Podlovchenko, Dokl. Akad. Nauk SSSR, 150, 349 (1963).
8. B. I. Podlovchenko and E. P. Gorgonova, Dokl. Akad. Nauk SSSR, 156, 673 (1964).
9. O. A. Petrii (Petry), B. I. Podlovchenko, A. N. Frumkin, and Hira Lal, J. Electroanal. Chem., 10, 253 (1965).
10. F. M. Rapoport and A. A. Il'inskaya, Laboratory Methods for Obtaining Pure Gases [in Russian], Goskhimizdat, Moscow (1963).
11. B. I. Podlovchenko and V. F. Stenin, Élektrokhimiya, 3, 649 (1967).
12. A. Frumkin and A. Shlygin, Izv. Akad. Nauk SSSR, Ser. Khim., 773 (1936).
13. V. E. Kazarinov and N. A. Balashova, Dokl. Akad. Nauk SSSR, 157, 1174 (1964).
14. R. V. Marvet and O. A. Petrii, Élektrokhimiya, 3, 901 (1967).
15. P. R. Johnson and A. T. Kuhn, J. Electrochem. Soc., 112, 599 (1965).

*Quantitative agreement can hardly be expected for a number of reasons, among which we must mention: a) the Temkin isotherm is highly approximate in H_2SO_4 solutions [19]; b) Eqs. (1-4) do not account for variations in the surface charge; c) the presence of a certain preferential chemisorption of CO_2 on the sites of most strongly bound H_{ads}, which must cause a decrease in $\Delta\varphi_r$.

† The polarization curves (Fig. 4 C) were obtained during one experiment by changing the current after reaching the plateau (Fig. 4 A) from large to small densities [7]. In the case of HCHO, the i-φ curve corresponds to the potentials of the plateau following the maximum.

16. V. E. Kazarinov, Élektrokhimiya, 2, 1170 (1966).
17. M. I. Temkin, Zh. Fiz. Khim., 15, 296 (1941).
18. B. I. Podlovchenko, O. A. Petrii, and E. P. Gorgonova, Élektrokhimiya, 1, 182 (1965).
19. A. N. Frumkin, Advances in Electrochemistry and Electrochemical Engineering, New York-London (1963).