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Gas-Phase Chemisorption and Electroreduction of Oxygen on Phthalocyanines

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The adsorption of oxygen by phthalocyanines has been studied by temperature programmed desorption between −160 and 400°C. A desorption peak is observed at −140°C for copper phthalocyanine and at −115°C for iron phthalocyanine. The associated activation energies of desorption are 7.5 and 9.8 kcal $mole^{-1}$ and these two peaks correspond to a first order kinetics of desorption. These results constitute the first direct evidence on the lack of rupture of the bond between two oxygen atoms in the molecule adsorbed on phthalocyanines. Finally, an attempt is made to examine the mechanistic proposals on the electroreduction of oxygen on phthalocyanines in the light of the present results.

INTRODUCTION

In an attempt to discover suitable catalysts for electroreduction of oxygen in a fuel cell, several phthalocyanines have been examined regarding their electrocatalytic activity towards the oxygen dissolution reaction (o.d.r.). A number of papers have appeared in the literature on the subject. In the present paper, an attempt is made to examine some aspects of electroreduction of oxygen as reported in these studies (*1*, *6*) in relation to the new data on gas-phase chemisorption of oxygen on phthalocyanines reported here. Although there are obvious dangers (7) in this approach, there is ample evidence, e.g., in the literature on hydrogen evolution reactions (*8*) that the general catalytic behavior of various surfaces tends to be roughly the same both in chemical catalysis and electrocatalysis (*9*): for example, metals which do not chemisorb hydrogen appreciably from the gas phase sustain electrolytic hydrogen evolution by a mechanism (i.e., initial discharge step) which does not involve significant steady state coverage by atomic hydrogen (*8*) on the electrode surface.

EXPERIMENTAL METHODS

Materials

The iron (PcFe), copper (PcCu) and metal-free phthalocyanines (PcH_2) investigated in this paper were supplied by Eastman Kodak Co. The specific surface areas of the samples calculated by the BET method are given in Table 1.

Samples were cleaned in the reactor by heating under vacuum (10^{-5} Torr) at 400°C for 1 hr. After cooling under vacuum, oxygen was introduced into the reactor.

Apparatus

The experimental setup is essentially the same as previously described by several authors (*10*, *11*, *12*), but with a modified design of the reactor in order to obtain a continuous linear programmation of the temperature from −195 to 500°C and to record desorption spectra which do not show any discontinuities around room temperature, in contrast to those given by Amenomiya, Tsuchiya, and Cvetanovic (*13*).

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TABLE 1
Specific Surface Area of Phthalocyanine Samples

Sample	Sg ($m^2 g^{-1}$)
PcH_2	6.75
PcCu	1.05
PcFe	23.0

The system is adapted from the microscope stage for low temperature described previously by Hull and Garwood (*14*). The reactor is put in a brass cylinder A, the lower part of which is immersed in liquid nitrogen and cooled till a temperature of −195°C is achieved (Fig. 1). A heating element is placed around the upper part of the brass cylinder for reheating the reactor. Calculation of the power which is necessary to heat the furnace on one hand, and of the thermal losses, on the other, shows that one must have a power of 1500 W for the heating element in order to reach temperatures up to 500°C.

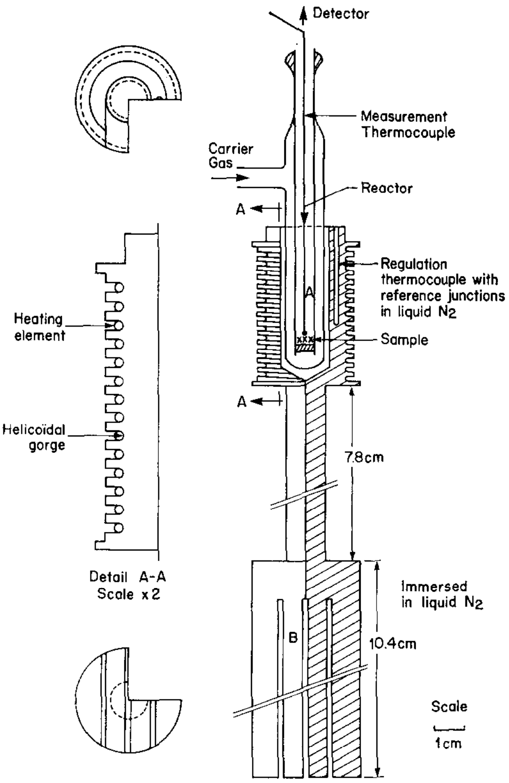

Fig. 1. Design of the reactor used for low temperature programmation.

We have used heating element Thermocoax (1 ZEZ I 15/150-150-50) manufactured by Sodern (Société Anonyme d'Etudes et de Réalisations Nucléaires, France). Thermocoax is a sheathed heating microelement, the heating part of which is made from nickel–chromium 80/20 and insulation made of compressed magnesia. The sheath is built with inconel. Insulation of such an element removes possibility of short circuit which can occur from the frost deposited on the reactor at low temperature.

The thermocoax is twisted around the upper part of the brass cylinder in a helicoidal gorge and sparkled with silver in order to give a better thermal exchange. The outer part of the furnace is covered with asbestos to reduce thermal losses. The heating element is connected to a proportional integral and differential temperature programmer (PRT 3000 C-SETARAM, France). This apparatus is controlled by a chromel–alumel thermocouple the reference junctions of which are placed in the Dewar flask, full of liquid nitrogen. The thermocouple is put as near as possible to the heating element and at the same height as the solid sample being studied in the reactor.

Very good linear temperature programs within the range −195 to 500°C for heating rates varying between 2 and 60°C min^{-1} with an accuracy of ±0.5°C were obtained. For rates lower than 1°C min^{-1}, it would be necessary to set a constant level system for liquid nitrogen.

RESULTS: CHEMISORPTION OF OXYGEN ON PHTHALOCYANINES

The oxygen desorption spectra have been recorded in a temperature range varying from −160 to 400°C (Fig. 2). When oxygen is adsorbed at −160°C and evacuated at the same temperature, no desorption peak is observed with metal free phthalocyanine, but one peak is recorded for both copper and iron phthalocyanines. This peak appears at −140 and −115°C, respectively, for a heating rate of 20°C min^{-1} and an initial surface coverage close to unity. The

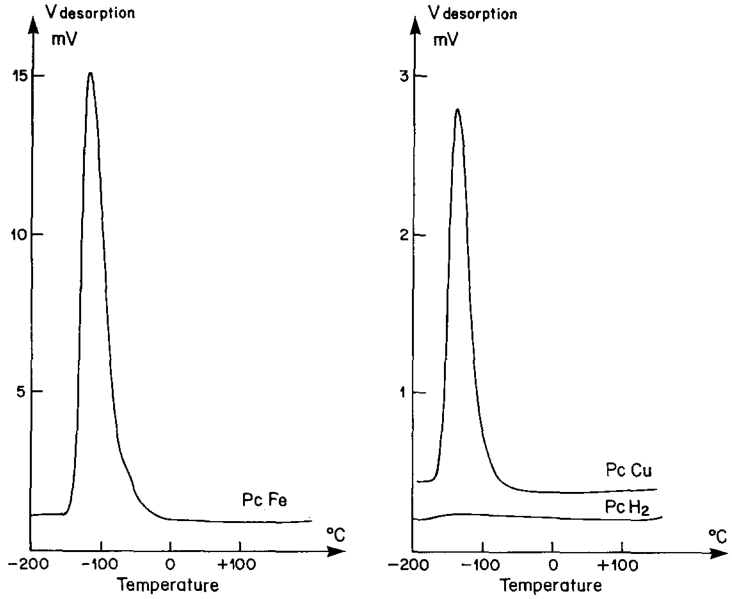

FIG. 2. Desorption spectra of oxygen for metal-free (PcH_2), copper (PcCu) and iron (PcFe) phthalocyanine (adsorption temp, −160°C; heating rate, 20° min^{-1}).

associated energies of desorption are 7.5 and 9.8 kcal $mole^{-1}$ (Table 2).

TABLE 2

	Surface coverage	Temp of max desorption rate (°C)	Activation energy of desorption (kcal $mole^{-1}$)
PcH_2	—	—	—
PcCu	$\simeq 1$	−140	7.5
PcFe	$\simeq 1$	−115	9.8

The theory of thermal desorption indicates that the shape of the desorption peak can give the kinetic order of desorption. It has been demonstrated in previous papers (*15, 16*) that the equations giving the shape of the desorption curves are:

$$\mathrm{Log}\,\frac{V_m}{V} = \frac{E}{R}\left(\frac{1}{T}-\frac{1}{T_m}\right) + \left(\frac{T}{T_m}\right)^2 \exp\left[-\frac{E}{R}\left(\frac{1}{T}-\frac{1}{T_m}\right)_{-1}\right], \qquad (1)$$

for the first order kinetics, and,

$$\frac{V_m}{V} = \cosh^2\left[-\frac{E}{2R}\left(\frac{1}{T}-\frac{1}{T_m}\right)\right], \qquad (2)$$

for the second order kinetics, where E is the activation energy of desorption, T_m the temperature of maximum desorption rate, V_m the maximum desorption rate, V the desorption rate and T the temperature.

These equations are second order approximations and are valid only when $[|T/T_m - 1|]$ has the same magnitude as $[RT_m/E]$, i.e., *only in the upper ca. 20% of the peak shown in Fig. 3.*

Thus one can see (Fig. 3) that for first order kinetics of desorption (nondissociative adsorption), the shape of the peak is asymmetrical with respect to the maximum of the desorption rate and for a second order reaction (dissociative adsorption), the peak is symmetrical.

The experimental desorption peak of oxygen is asymmetrical with respect to its maximum (Fig. 3), which indicates a first order kinetics of desorption and thereby a nondissociative oxygen adsorption. Figure 3 also shows that Eq. [1] is only verified in a narrow temperature range.

Figure 4 shows that the desorption spectrum is not significantly affected by adsorption times longer than 3 min. Such a short time of oxygen adsorption lets us suppose that the oxygen uptake is restricted

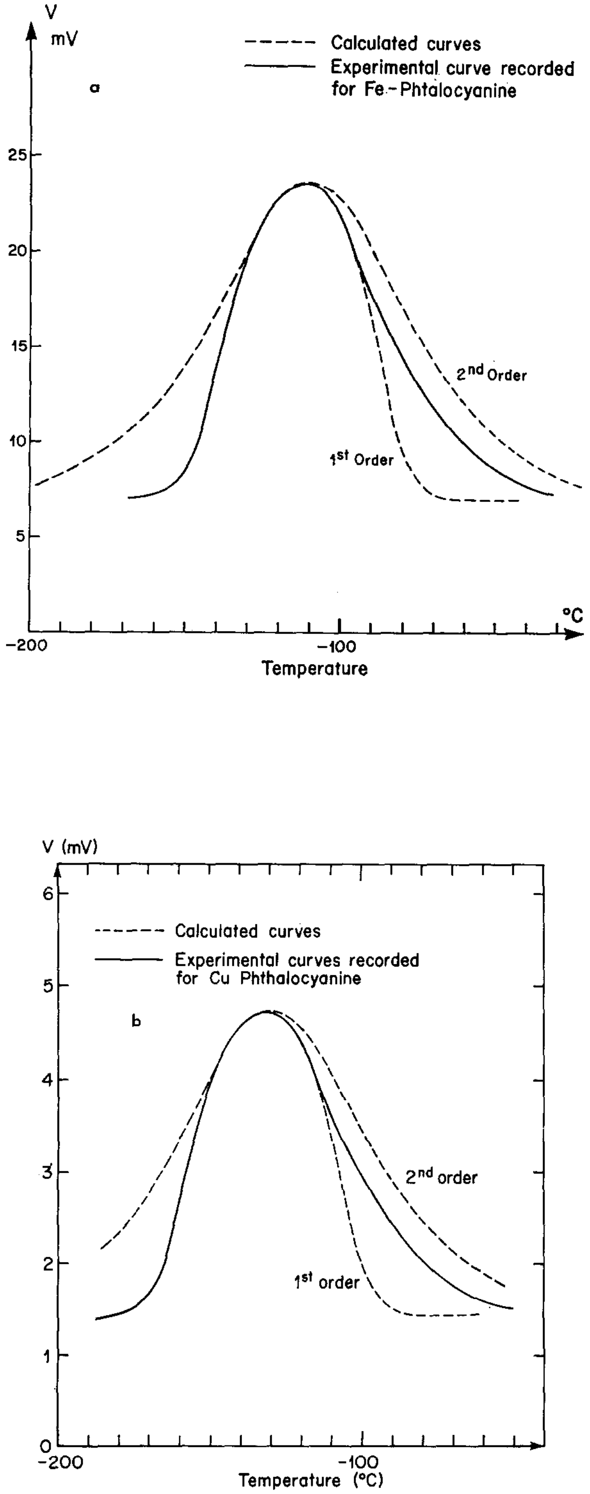

FIG. 3. Determination of order of reaction by examination of the shape of the desorption peak for metal phthalocyanine: (a) iron phthalocyanine; (b) copper phthalocyanine.

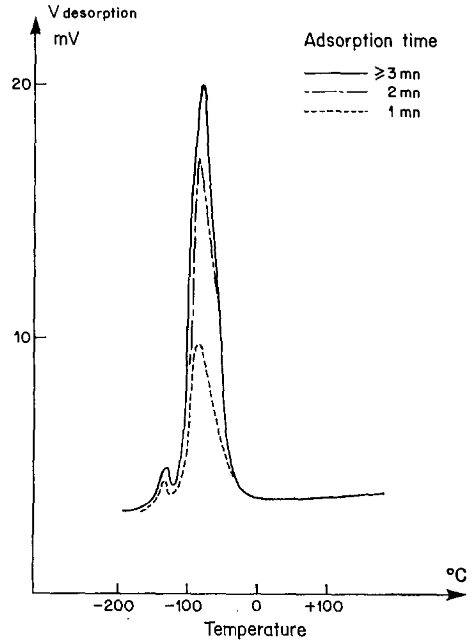

FIG. 4. Influence of adsorption time on oxygen desorption spectrum for iron phthalocyanine (adsorption temp, $-160°C$, heating rate, $20°C\ min^{-1}$).

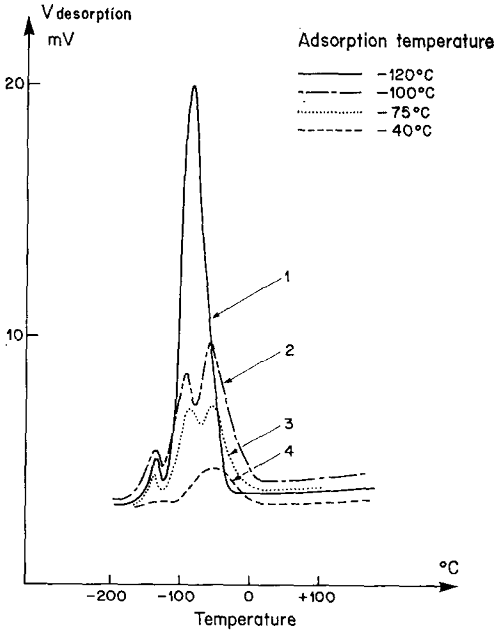

FIG. 5. Effect of adsorption temperature on the oxygen desorption spectrum for iron phthalocyanine.

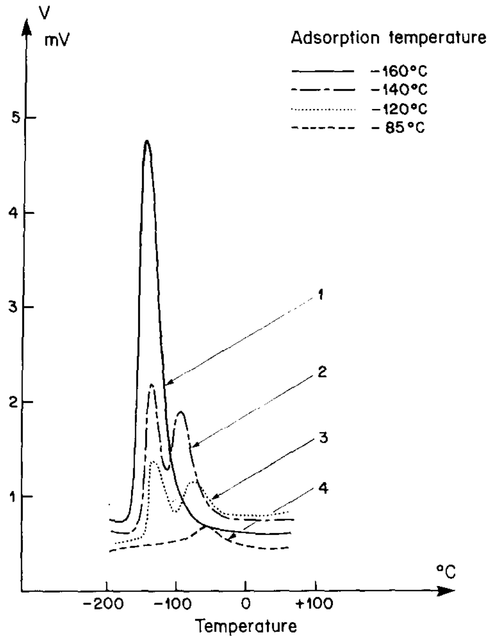

FIG. 6. Effect of adsorption temperature on the oxygen desorption spectrum for copper phthalocyanine.

to the surface, thus excluding the interaction of oxygen with the bulk of phthalocyanines.

The spectra reported in Figs. 5 and 6 show how the shape of the peak and T_m vary with the temperature of oxygen adsorption for iron and copper phthalocyanines. When the adsorption temperature is raised from $-160°C$ to room temperature, the amount of adsorbed oxygen decreases with increasing temperature. Simultaneously T_m increases, showing desorption occurs from adsorption sites having higher and higher energies of adsorption.

Finally, it may be observed that from $-140°C$ for PcCu and from $-100°C$ for PcFe a splitting of the desorption peak was recorded, which indicates the existence of two types of adsorption sites or adsorbed species.

SIGNIFICANCE OF PRESENT RESULTS IN RELATION TO LITERATURE INFORMATION ON ELECTROREDUCTION OF OXYGEN

The first order kinetics of desorption of oxygen from Fe and Cu phthalocyanines reported here constitutes the first direct evidence on the lack of rupture of the bond between two oxygen atoms in the oxygen molecule adsorbed on these phthalocyanines. This would tend to explain why electroreduction of oxygen on phthalocyanine leads principally to the peroxide formation (*1*, *6*), instead of complete four electron reduction to the hydroxyl ions or water molecules. In order for the latter process to occur, it is necessary that the oxygen molecule chemisorbs dissociatively on the phthalocyanine surface, a requirement not fulfilled on the basis of our gas-phase data.

The adsorption time was found to have no effect on the desorption spectra, showing thereby that the bulk of material does not participate in the chemisorption process. In term of electrocatalysis, this would tend to favor the preparation of suitable fuel cell electrodes by deposition of thin film of phthalocyanines (on suitable support, of course), in addition to having some mechanistic consequences to be discussed below.

More detailed mechanistic proposals on the electroreduction of oxygen on phthalocyanines may now be examined in the light of present results on gas-phase chemisorption of oxygen on phthalocyanines.

Andro, Bernard, and Savy (*6*) have proposed the following mechanism of reaction for the electroreduction of oxygen on phthalocyanines:

$T \rightarrow T^+ + e^-$	Ionization of the adsorption site,	(3)
$O_2 \text{ (surface)} \rightarrow O_2 \text{ (solid)}$	Oxygen diffusion,	(4)
$T^+ + O_2 \text{ (solid)} \rightarrow T^+\overset{\pi}{-}O_2$	A π bond is established between the oxygen molecule and the adsorption site,	(5)
$T^+\overset{\pi}{-}O_2 + e^- \rightarrow O_2^- + T^+$	Formation of molecular ion O_2^-,	(6)
$T^+ + e^- \rightarrow T$	Regeneration of the adsorption site,	(7)
$O_2^- \text{ (solid)} \rightarrow O_2^- \text{ (surface)}$	Migration of the molecular ion,	(8)
$O_2^- \text{ (surface)} + H_2O + e^- \rightarrow HO_2^- + OH^-$	Reduction of the molecular ion.	(9)

This mechanism, however, involves steps which are not sustained by the present experimental results, for example, step [8] in which migration of an oxygen ion O_2^- from the bulk of the phthalocyanine to the surface was postulated. This step is in contradiction with our data which indicates that the adsorption of oxygen and thence the existence of O_2^-, is restricted only to the *surface* of the phthalocyanine. In the light of the new data on the chemisorption behavior of oxygen on Fe and Cu phthalocyanines reported in the present work, a modification of the above mechanism may be proposed as follows:

$$T \rightarrow T^+ + e^-, \tag{10}$$

$$O_2(g) + T^+ + e^- \rightarrow T^+\overset{\pi}{-}O_2^- \text{ (surface)}, \tag{11}$$

$$T^+\overset{\pi}{-}O_2^- + H_2O + e^- \rightarrow HO_2^- + OH^- + T^+, \tag{12}$$

$$T^+ + e^- \rightarrow T. \tag{13}$$

Since electroactivity is observed on all phthalocyanines one must conclude the presence of adsorbed oxygen on all of them. However, since the chemisorption of oxygen appears to be associated with the central metal atom of phthalocyanines, one must conclude that for the metal-free phthalocyanine oxygen adsorbs on the organic groups, presumably in a reversible way. Previous work (*17*) also supports the contention that chemisorption of oxygen takes place on the metal atom. This is postulated to occur by formation of π bond at the central metal atom in an axial position.

Comments on Desorption Spectra

The splitting of the peak in the desorption spectrum observed when the temperature is increased is rather difficult to interpret. It is possible that at low temperature, at which the surface is highly covered, the interaction between adsorbed molecules leads to multilayer adsorption. Only the second peak of desorption, i.e., the one appearing at −140°C on PcCu and at −155°C on PcFe, corresponds to the saturation coverage by oxygen. The amount of oxygen adsorbed is 0.035 cm^3 g^{-1} for copper phthalocyanine and 0.25 cm^3 g^{-1} for iron phthalocyanine. Surface density of metallic atoms which constitute the sixth free axis of coordination on the principal faces (001, 010 and 100) were calculated using crystallographic data (*18, 19*) and found to be:

$$\left\{\begin{array}{l}[001] = 0\\ [010] \simeq 1\ \text{atom}/123\ \text{A}^2\\ [100] \simeq 0.\end{array}\right.$$

If one assumes an equal distribution of these three crystal faces on the reacting surfaces of a given sample of phthalocyanine, one can estimate that about 360 Å^2 of area correspond to one site for the adsorption of oxygen. This would then lead to a specific surface area of 27.5 m^2 g^{-1} for PcFe and 3.6 m^2 g^{-1} for PcCu. The experimental value of surface area for iron phthalocyanine agrees with the one thus calculated but for copper phthalocyanine the calculated value is too high by a factor of about 3 (Table 1). This result would tend to indicate that there is preferential orientation of 010 face on the reacting surface of copper phthalocyanine. In the extreme case of such preferential orientation the theoretically estimated effective area of adsorption would be 1.2 m^2 g^{-1}, a value in good agreement with the one experimentally observed. This hypothesis of preferential orientation is somewhat supported by the electron microscopic examination of the samples in which the copper phthalocyanine shows well-crystallized structure, whereas the iron phthalocyanine has an amorphous appearance.

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