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The Intermediate Chemisorbed Species in Electrocatalysis

Yu.B.Vasil'ev and V.S.Bagotskii

The fundamental data on the adsorption of various organic substances on platinum, obtained by electrochemical methods, are discussed. It is shown that electrochemical pulse methods make it possible to determine the degree of adsorption directly under the steady-state conditions of an electrocatalytic process and also to establish in many instances the nature of the adsorbed complex on the surface of the catalyst electrode.
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I. INTRODUCTION

In many electrochemical oxidation-reduction reactions the electrode behaves simultaneously as a catalyst on the surface of which purely catalytic processes can take place and individual stages of electrochemical processes can be accelerated. The catalytic processes which may precede the electron transfer stage and facilitate it, can follow this stage, or can proceed independently of and simultaneously with the main electrochemical process. The studies in recent years on a large number of electrochemical processes involving organic compounds have shown that the slow stage in such processes is frequently the purely catalytic reaction, while the electrochemical stage merely supplies one of the reactants.

The problem of the direct transformation of the chemical energy of fuel into electrical energy in fuel cells stimulated extensive research on the characteristics of the kinetics of electrode processes, of adsorption on solid electrodes, and of the influence of the nature and structure of the catalyst electrode on its electrochemical activity in relation to various reactions. To embrace the entire range of processes, the term "electrocatalysis" is widely used, showing clearly that these processes are on the border line between two fields of physical chemistry—electrochemistry and catalysis. In the study of the mechanisms of electrocatalytic processes, both the classical methods of heterogeneous catalysis and the electrochemical methods developed in recent years are used.

The considerable advances in electrocatalysis in recent years are due to two main achievements—the development of electrochemical methods for the investigation of the adsorption of reactants (and also of intermediates) and for the preparation of a reproducibly clean electrode surface and the determination of the degree of its purity.

Systematic research on adsorption phenomena by electrochemical methods was begun in 1933–1938 by Frumkin and his coworkers[1-3], who determined with the aid of the so called charging curves (curves relating the potential of a polarisable electrode to the amount of electricity passed through the system) not only qualitative but also quantitative aspects of the adsorption of hydrogen and oxygen on platinum and other platinum group metals. The most important results of these studies were the determination of the distribution of adsorbed species among adsorption sites with different bonding energies and the demonstration that the adsorption isotherm is logarithmic (Temkin's isotherm):

$$\theta = a + \frac{1}{f} \ln c,$$

where θ is the degree of surface coverage by the adsorbed species, c the concentration in solution (the partial pressure for gases), and a and f are constants (the constant f is sometimes called the surface inhomogeneity factor). These experimental observations served as a basis for the development of a theory of adsorption phenomena and of the kinetics of chemical reactions on a surface with uniformly distributed inhomogeneities[4,5], which had been widely used in heterogeneous catalysis. In the above experimental studies the charging curves were recorded very slowly (i.e. small currents were used), thereby ensuring a state close to equilibrium at almost all points.

In recent years electrochemical methods for the investigation of adsorption phenomena have been greatly developed. A number of new experimental procedures have been devised, whereby measurements can be made at a high rate, which admittedly infringes in many cases the equilibrium in the system, but on the other hand such rapid methods permit the determination not only of the overall degree of adsorption but also of its kinetics. Electrochemical methods have been used to study the adsorption of not only hydrogen and oxygen but also of a large group of other substances, particularly various organic compounds[6-8].

Electrochemical pulse methods make it possible to determine the degree of adsorption directly under the steady-state conditions of catalytic and electrocatalytic processes and to establish in many instances the nature of the complex adsorbed on the surface of the catalyst electrode.

II. THE DISSOCIATIVE NATURE OF THE CHEMISORPTION OF ORGANIC SUBSTANCES ON PLATINUM GROUP METALS AND THE NATURE OF THE CHEMISORBED SPECIES

From an analysis of the variation of the kinetics of the decrease of potential in the adsorption of methanol on a platinum electrode with the pH of the solution, Frumkin and Podlovchenko[9] put forward for the first time in 1963 the hypothesis that the adsorption (more correctly chemisorption) of methanol from solution on platinum is accompanied by the abstraction of hydrogen atoms from the adsorbed methanol molecule, i.e. its degradation. The use of various combined electrochemical methods and also the tracer atom method made it possible to show subsequently that, following its adsorption on the platinum electrode, the methanol molecules split off three hydrogen atoms. The resulting COH species is bound directly to three surface platinum atoms, liberating three electrons when it is oxidised to CO_2.[10] The results show that the adsorption of methanol can be represented as follows:

$$CH_3OH \rightarrow \underset{\times\times\times}{COH} + 3H_{ads},$$

where the crosses indicate the number of surface platinum atoms forming strong bonds with the adsorbed species.

On open external circuit, both hydrogen and the carbon-containing residues formed during dehydrogenation remain on the electrode surface. However, the hydrogen atoms completely lose their bonds with the carbon-containing species and are linked to the catalyst surface only. They behave as free adsorbed hydrogen atoms in equilibrium with the hydrogen ions in the bulk of the solution and determine the electrode potential. Hydrogen can diffuse to the opposite side of a palladium membrane, where it can be detected[11-14].

Using the large difference between the oxidation potentials of the adsorbed hydrogen and the carbon-containing residues, it is possible to remove the hydrogen atoms from the surface by applying to the electrode a potential $\varphi_r = 0.4$ V (φ_r is the potential relative to that of the reversible hydrogen electrode in the same solution), which is intermediate between the above two potentials; an additional amount of carbon-containing COH residues is then adsorbed on the liberated surface sites. This constitutes the main difference between adsorption under the usual catalytic conditions (on open external circuit) and under electrochemical conditions (when the circuit is closed). When the circuit is closed and the potential is maintained at values more positive than 0.3 V, the maximum degree of adsorption of the species can be almost a factor of two greater than that observed on open circuit.

This mechanism of the adsorption of methanol on platinised platinum was confirmed using methanol labelled with ^{14}C and tritium[15]. Thus in the adsorption of $^{14}CT_3OH$ on a platinised platinum electrode at a potential such that hydrogen should be removed from the electrode surface, only species containing ^{14}C are adsorbed, but the adsorbed species does not contain tritium.

Experiments showed that the nature of the chemisorbed species does not change when the electrode potential, the concentration of methanol, the pH of the solution, and temperature are altered. There is no doubt that the dehydrogenation process does not proceed immediately via the elimination of three hydrogen atoms but involves separate stages:

$$\underset{\times}{CH_3OH} \xrightarrow{k_1} \underset{\times\times}{CH_2OH} + H_{ads};$$

$$\underset{\times\times}{CHOH} \xrightarrow{k_2} \underset{\times\times\times}{COH} + H_{ads},$$

where $k_1 < k_2 < k_3$, so that the elimination of the first hydrogen atom is slowest, the second and third atoms being removed more rapidly.

Similar methods have been used to establish the nature of the chemisorbed species on platinum group metals in the adsorption of various organic substances (hydrocarbons ranging from methane to hexane, alcohols from methanol to octanol, formic acid, formaldehyde, carbon dioxide, ethylene glycol, glycolaldehyde, nitromethane, nitroethane, maleic acid, etc.). It has been shown that the chemisorbed species formed initially in the adsorption of organic molecules can be transformed on the surface as a result of secondary reactions into other species, more stable under the given conditions. For example, formic acid adsorbed on a platinum electrode gives rise to the primary species COOH,[16-18] i.e.

$$HCOOH \rightarrow H_{ads} + \underset{\times}{COOH},$$

which reacts at $\varphi_r < 0.4$ V with adsorbed hydrogen:

$$\underset{\times}{COOH} + 2H \rightarrow \underset{\times\times\times}{COH} + H_2O,$$

yielding the same species as in methanol solutions. Chemisorbed species resulting from the partial oxidation of the initial species can also be present on the surface. For example, in a study of the adsorption of methane on the surface of a platinum electrode it was shown that the chemisorbed species is similar to that derived from methanol, having the composition COH.[19,20]

At room temperature carbon dioxide is not usually adsorbed on the surface of a platinum electrode free from adsorbed gases, but is readily adsorbed on the surfaces of the electrode on which hydrogen has been adsorbed (i.e. as a result of reaction with hydrogen). This leads to the formation of chemisorbed species similar to that obtained in methanol solutions[21-25].

The processes occurring in the adsorption of compounds containing two and more carbon atoms in the molecule are much more complex, so that it is now difficult to determine their nature, particularly when the adsorption proceeds on open circuit and the adsorbed hydrogen remains on the surface. Cracking, hydrogenation, and polymerisation can then occur[26,27]. The mechanism of cracking, i.e. of the dissociation of the C–C bond, has been studied in detail[29-32] in the adsorption and oxidation of ethylene, ethane, and other hydrocarbons on a platinum electrode. In the adsorption of ethylene and ethane two types of chemisorbed carbon-containing species are formed—species which are oxidised readily and with difficulty. The species which are difficult to oxidise contain two carbon atoms and are readily removed from the surface by hydrogenation, forming ethane. The readily oxidised species contain one carbon atom and are hardly hydrogenated.

The mechanism of the adsorption of ethylene and ethane on platinum can be represented as follows:

$$\begin{array}{l} CH_2{=}CH_2 \\ \quad\downarrow k_{ads} \\ CH_3{-}CH_3 \underset{+2H_{ads}}{\overset{-2H_{ads}}{\rightleftharpoons}} \underset{\times\quad\times}{CH_2{-}CH_2} \xrightarrow{k_{decomp}} \end{array}$$

[species (II)]

$$\begin{array}{l} \quad\quad CO_2 \\ \quad\quad\uparrow \\ \rightarrow \underset{\times\times}{CH_2} \rightarrow \underset{\times\times\times\times\times\times}{CH} \rightarrow \underset{\times\times\times\times\times\times}{COH} \end{array}$$

[species (I)]

The principal constants for the adsorption of various organic substances on a platinum electrode.

Substance	Electrode, solution*	φ_r, e	t, °C	Nature of chemisorbed species	$\theta'_{R}{}^{max}$	a	f'	k_{ads}, cm s^{-1}	E_a^0, kcal $mole^{-1}$	Cc	References
1	2	3	4	5	6	7	8	9	10		11
H_2	A	0	20	H ×	1	—	14	$2.7\cdot10^{-3}$	—		33–35
	B	0	20	H ×	1	—	14	—	—		
	A, alk	0	20	H ×	1	—	14	$3.4\cdot10^{-3}$	—		
CH_4	B	0.2	80	COH ×××	—	—	—	—	—		19, 20
CH_3OH	A	0.4	25	COH ×××	0.78	0.82	14	$1.4\cdot10^{-5}$	9.5		
	B	0.4	25	COH ×××	0.75	0.82	7.4	$2\cdot10^{-6}$	9.5		8, 10, 26, 36–43
	A, alk	0.4	25	COH, CO^- ××× ×××	0.7	0.65	14.4	$2.1\cdot10^{-6}$	—		
HCHO	A	0.4	25	C=O ××	0.85	1.6	—	$2.4\cdot10^{-3}$	—		
	B	<0.4	25	COH ×××	—	—	—	—	—		44, 45
HCOOH	A	0.4	41	COOH ×	0.83	0.96	15	$4.3\cdot10^{-5}$	5.2		
	A	0.2	41	COH ×××	0.83	1.22	15	$1.7\cdot10^{-3}$	—		8, 16, 17, 26, 37, 38
	B	<0.4	20	COH ×××	—	—	—	—	—		
CO_2	A	0 02	20	COH ×××	0.75	—	15	$1–2\cdot10^{-4}$	7.4		21–25
	B	<0.4	20	COH ×××	—	—	—	—	—		
CH_3NO_2	A	0.4	20		0.6	0.69	14	$7.4\cdot10^{-6}$	—		46, 47
	A	0.2	20		—	0.8	21	$4.2\cdot10^{-4}$	—		
C_2H_4	B	0.2	90	H_2CCH_2, CH_2, CH, COH ×× ×× ××× ×××	—	—	14	$7.9\cdot10^{-4}$	—		28–32
C_2H_6	B	0.2	90	H_2CCH_2, CH_2, CH, COH ×× ×× ××× ×××	—	—	14	$5.1\cdot10^{-4}$	—		28–32
C_2H_5OH	AB	0.4	25	COH, CH_3COH etc. ××× ××	0.79	0.95	14	$3.5\cdot10^{-5}$	—		26, 48, 49
$(CH_2OH)_2$	A	0.4	25	HOC——COH ××××	0.65	1.05	14	$8.7\cdot10^{-4}$	16.4		27
	A	0.4	>50	COH ×××	—	—	—	—	—		
OCH—CH_2OH	A	0.4	20	OCH—COH, OC—COH ×× × ××	0.84	1.2	13,5	$1\cdot10^{-3}$	12.8		50
HOOCCH= =CHCOOH	A	0.4	20	HOOCCH—CHCOOH × ×	0.43	1.3	14	$1.1\cdot10^{-3}$	2.3		51–42
cis-	A	0.05	20	HOOCCH—CHCOOH × ×	0.3	0.6	16	$2.5\cdot10^{-4}$	—		
trans-											
C_3H_8	B	0.2	90	C_3, CH, CH_2, COH ××× ×× ×××	—	—	14–19	$2\cdot10^{-5}$	—		53
C_3H_7OH	A	0.4	25	C_3, COH etc. ×××	0.62	0.95	14	$8\cdot10^{-6}$	—		48, 49
n-$C_5H_{11}OH$	A	0.4	25	C_5, COH etc.	0.44	0.95	14	$1\cdot10^{-5}$	—		
i-$C_5H_{11}OH$	A	0.4	25	C_5, COH etc.	0.62	0.92	14	$4.7\cdot10^{-7}$	—		48, 49
	A	0.4	25	—	0.88	1.5	11.5	$1\cdot10^{-3}$	—		54
Urea	A	2.1	25	—	0.5	0.39	13	$3.5\cdot10^{-5}$	—		55

*Electrode: A—smooth platinum; B—platinised platinum; solution: alk—alkaline (1 *N* KOH); no symbol acid (0.5–1 *N* H_2SO_4).

The relative amounts of species (II) and (I) depend on the ratio of the rate constants for adsorption and decomposition.

The experimental data available at present show that, in the adsorption of organic compounds on platinum, triple and double bonds are dissociated most readily, dehydrogenation at the α-carbon atom is more difficult, and the hydrocarbon group is dehydrogenated and C–C bonds are ruptured only under more severe conditions. With increase of temperature, the degrees of dehydrogenation and degradation of the initial molecule also increase.

The Table presents the main constants characterising the adsorption processes of certain organic substances on smooth and platinised platinum electrodes.

III. THE FUNDAMENTAL CHARACTERISTICS OF THE ADSORPTION OF ORGANIC SUBSTANCES ON PLATINUM

It has been shown in numerous investigations [8,16,27,38,56,57] that the dependence of the surface coverage of the platinum electrode θ'_R on the bulk-phase concentration of the organic substance at different potentials, temperatures, and pH values is described by Temkin's logarithmic isotherm at moderate coverages (Figs. 1 and 2):

$$\theta'_R = a + \frac{1}{f'}\ln c$$

(the degree of coverage θ'_R is defined as the ratio of the occupied sites to the number of surface sites available for

the adsorption of hydrogen; since f depends on the definition of θ, it is designated in this case by f'). The quantity a (characterising adsorbability) depends on the electrode potential, the pH of the solution, and the nature of the organic substance, while the values of f' are almost the same ($f' = 14 \pm 2$) for the adsorption of a wide variety of organic substances on platinum electrodes. The dimensions of the adsorbed species have a marked influence on the limiting surface coverage $\theta_R'^{max}$ and on the fraction of the surface blocked owing to steric hindrance.

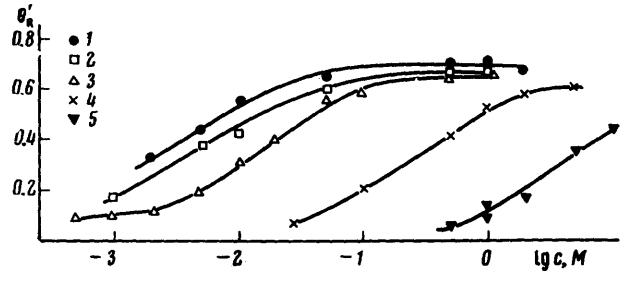


Figure 1. Steady-state methanol adsorption isotherms on a platinised platinum electrode in 1 N H_2SO_4 at various potentials φ_r (V): 1) 0.5; 2) 0.55; 3) 0.6; 4) 0.7; 5) 0.8.

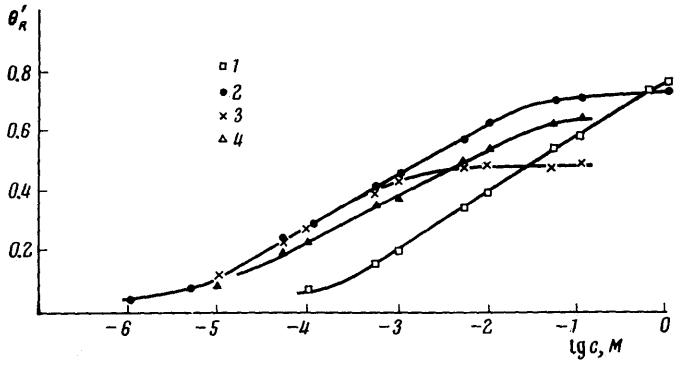


Figure 2. Steady-state isotherms for the adsorption of various aliphatic alcohols on a smooth platinum electrode in 1 N H_2SO_4 at an adsorption potential $\varphi_r = 0.4$ V: 1) CH_3OH; 2) C_2H_5OH; 3) n-$C_5H_{11}OH$; 4) t-$C_5H_{11}OH$.

The rates of adsorption on platinum of all the organic substances investigated are described under different conditions by the Roginskii–Zel'dovich equation (Figs. 3 and 4): [8,16,27,38,56–59]

$$v_{ads} = k_{ads} c \exp(-\alpha f' \theta_R'),$$

where α is the transfer coefficient (usually $\alpha \simeq 0.5$). On passing from one organic substance to another, the adsorption rate constants vary approximately in the same sequence as the adsorbabilities. The results of studies of the variation of k_{ads} with potential have shown that it is influenced mainly by the adsorption of hydrogen and oxygen which is related to the potential, and not by the electrode potential itself [8,16,26,27]. Therefore the equation for the rate of adsorption of an organic substance can be written as follows:

$$v_{ads} = (1 - \Sigma\theta_i) k_{ads} c \exp(-\alpha f' \Sigma\theta_i'),$$

where the summation is carried out over all the chemisorbed species: organic species, oxygen, hydrogen, etc.

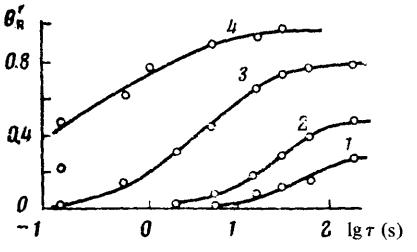


Figure 3. Kinetics of the adsorption of methanol on a smooth platinum electrode in 1 N H_2SO_4 at an adsorption potential $\varphi_r = 0.4$ V and various methanol concentrations (M): 1) 0.001; 2) 0.01; 3) 0.1; 4) 1.

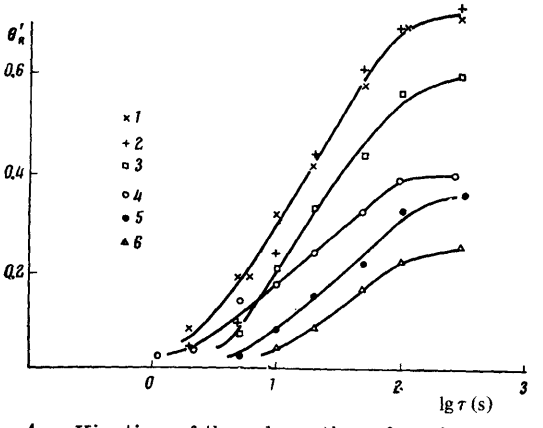


Figure 4. Kinetics of the adsorption of various organic substances on a platinum electrode at a potential $\varphi_r = 0.4$ V: 1) saturated ethylene solution in 1 N KOH; 2) saturated ethylene solution; 3) 10^{-4} M allyl alcohol; 4) 10^{-4} M maleic acid; 5) saturated styrene solution diluted 100 times; 6) 10^{-4} M furmaric acid; 2) 1 N H_2SO_4.

The activation energies E_a for the adsorption of various organic substances on platinum increase linearly with surface coverage (Fig. 5): [16,27,50,57]

$$E_a = E_a^0 + \alpha f' RT\theta_R'.$$

The observed kinetic and adsorption characteristics permitted a quantitative interpretation of the nature of the curves describing the decrease of the electrode potential on open circuit when an organic substance is introduced into the solution [60,61].

The kinetics of the elimination of chemisorbed species from the surface of platinum (Fig. 6) are described by the equation

$$v_{sp.} = k_{sp.} \exp(\beta f' \theta'_R),$$

where β is the transfer coefficient (usually $\beta \simeq 0.5$). Chemisorbed nitromethane, nitrobenzene, acetic acid, and maleic acid species are removed as a result of their hydrogenation [47,51] and methanol species are removed as a result of oxidation.

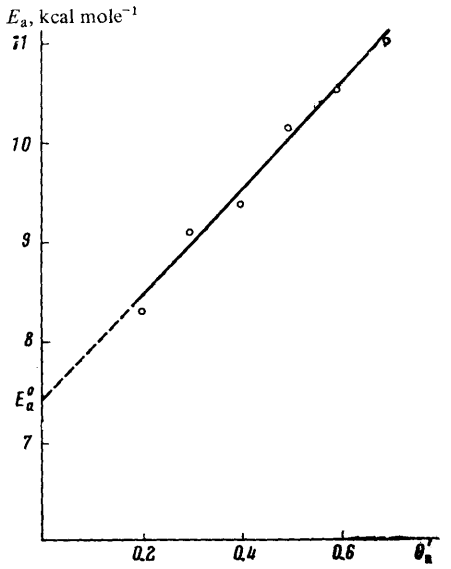


Figure 5. Variation of the activation energy E_a with θ'_R in the adsorption of CO_2 in 1 N H_2SO_4 at a potential φ_r = 0.1 V and p_{CO_2} = 1 atm.

Determination of the variation of the heat of adsorption of methanol on a platinum electrode with surface coverage showed that the applicability of Temkin's logarithmic isotherm to adsorption is a result of a linear relation between the heat of adsorption Q_{ads} of methanol and surface coverage [57]:

$$Q_{ads} = Q^0_{ads} - f' R T \theta'_R.$$

IV. DEPENDENCE OF THE ADSORPTION OF ORGANIC SUBSTANCES ON THE POTENTIAL

The dependence of the adsorption of neutral organic substances on the potential for mercury and many other metallic electrodes is determined primarily by the position of the zero-charge point and the electrostatic effect of the charges of the electrical double layer [62,63]. Frumkin showed by a thermodynamic procedure [64,65] that a different situation should obtain for platinum and certain other electrodes capable of adsorbing large amounts of hydrogen and oxygen. When the adsorption process is reversible, the degree of adsorption of the organic substance should decrease even for low degrees of surface coverage by hydrogen or oxygen; the maximum degree of adsorption of the organic substance may be expected in the range of potentials between the regions corresponding to the adsorption of hydrogen and oxygen.

Experiment has shown that the variation of the degrees of adsorption of many organic substances on platinum with the potential is normally described by a dome-shaped curve with a broad maximum in the potential range 0.3 to 0.6 V, where the degree of adsorption of hydrogen and oxygen are minimal (Figs. 7 and 8). [5,8,17,38,66] The constancy of surface coverage in this range of potentials shows that the potential itself on the charge of the double layer hardly affects the adsorption of methanol, since the specific adsorption forces are much greater than the electrostatic influence of the surface charge.

When the potential shifts towards more negative ($\varphi_r <$ 0.3 V) or more positive ($\varphi_r \geq$ 0.5–0.6 V) values, the

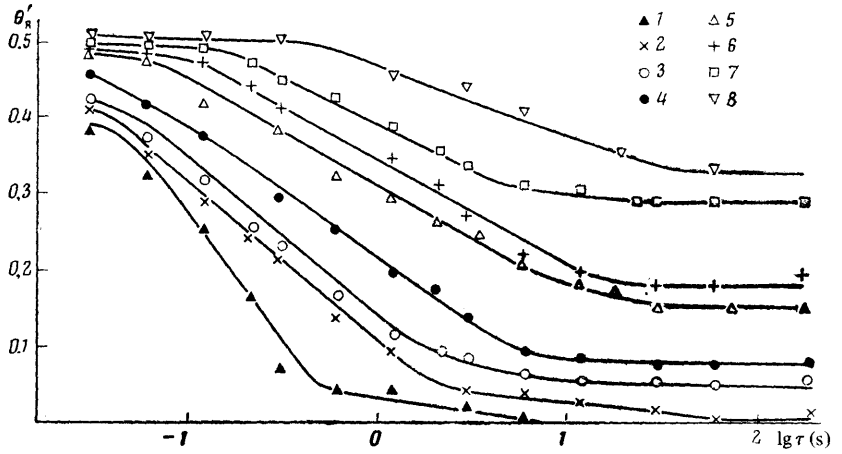


Figure 6. Kinetics of the hydrogenation of species chemisorbed at φ_r = 0.2 V from 10^{-4} M $C_4H_4O_4$ + 1 M H_2SO_4 solutions at various hydrogenation potentials (V): 1) −0.025; 2) 0.0; 3) 0.0125; 4) 0.025; 5) 0.05; 6) 0.075; 7) 0.1; 8) 0.125.

degree of adsorption falls (to a first approximation linearly as the potential is altered). The decrease of the degree of adsorption at negative potentials is due to the influence of the adsorption of hydrogen on the adsorption of the organic residue or to the hydrogenation of the species.

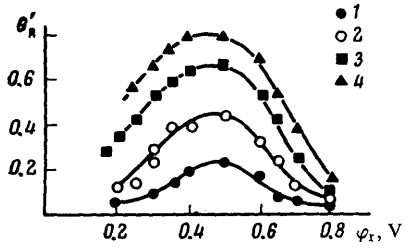


Figure 7. Variation of θ'_R with the potential φ_r in the adsorption of methanol on a smooth platinum electrode in 1 *N* H_2SO_4 solutions for different methanol concentrations (M): 1) 0.001; 2) 0.01; 3) 0.1; 4) 1.

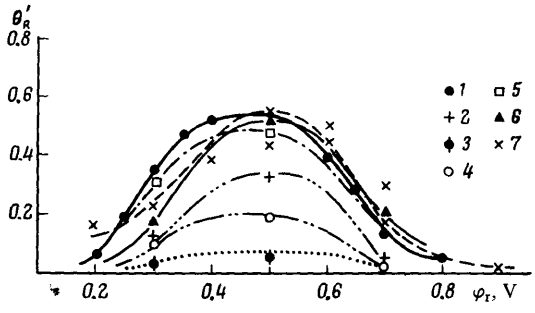


Figure 8. Variation of θ'_R with the potential φ_r on a smooth platinum electrode for 0.01 M methanol in 1 M phosphate buffer solutions at different pH: 1) 0.32; 2) 1.4; 3) 2.8; 4) 6.2; 5) 10.1; 6) 12.2; 7) 13.1.

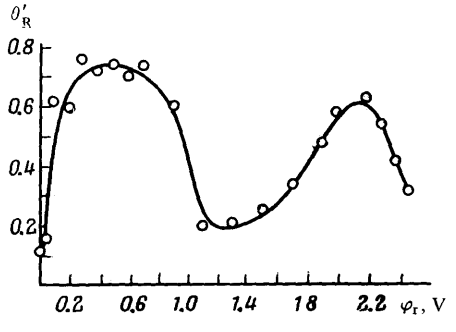


Figure 9. Variation of θ'_R with the potential φ_r in 1 *N* H_2SO_4 + 10^{-3} M C_4H_6 solution.

The decrease of surface coverage at positive potentials is associated with the oxidation of the chemisorbed species, since the rates of adsorption and electrochemical oxidation become comparable. The width and position of the dome-shaped curve for different organic substances may vary somewhat owing to the changes in the relative rates of individual processes (adsorption, oxidation, hydrogenation, etc.).

Experiment shows that, to a first approximation, the curve relating the degree of adsorption of the organic substance to the potential shifts with pH in the same way as the hydrogen and oxygen adsorption regions [8,47,51]. The shift of the adsorption regions of the organic substances as the pH of the solution is varied constitutes a characteristic property of the platinum electrode and of other electrodes adsorbing considerable amounts of hydrogen.

It has been shown for the adsorption of butadiene [54] and urea [55] on platinum that at high anodic potentials the organic substance can be adsorbed on an oxide layer, which leads to the appearance of a second adsorption maximum at $\varphi_r = 2.2$ V (Fig. 9).

V. THE INTERMEDIATE CHEMISORBED SPECIES AND THE MECHANISMS OF ELECTROCATALYTIC PROCESSES

The influence of pH and electrode potential on the rates of electrochemical oxidation [67-70] and electrochemical reduction [46-51] of various organic substances on platinum group metals shows that, apart from the adsorbed organic species, another species, formed in the preceding rapid electrochemical stage is involved in the slow stage. In an oxidation reaction the adsorbed species is OH_{ads}, formed as a result of the electrochemical oxidation of water:

$$H_2O \rightleftarrows OH_{ads} + H^+ + e.$$

The slow stage in the oxidation of methanol is the non-electrochemical interaction of carbon-containing chemisorbed species with OH_{ads} radicals. In acid solutions the slow stage is

$$\underset{\times\times\times}{C} - OH + OH_{ads} \rightarrow \underset{\times\times}{C}{=}O + H_2O;$$

the subsequent oxidation stages being faster. Similarly the slow stages in the oxidation of formaldehyde and formic acid are the reactions

$$\underset{\times\times}{C}{=}O + OH_{ads} \rightarrow \underset{\times}{C}\begin{matrix}{=}O\\ \diagdown OH\end{matrix};$$

$$\underset{\times}{C}\begin{matrix}{=}O\\ \diagdown OH\end{matrix} + OH_{ads} \rightarrow CO_2 + H_2O.$$

Under steady-state electrochemical oxidation conditions, methanol is dehydrogenated and OH_{ads} radicals are formed simultaneously. Bearing in mind that the dehydrogenation of methanol does not proceed in a single stage via the abstraction of three hydrogen atoms but involves a series of stages, presumably the OH radicals formed react with methanol at any stage in its dehydrogenation, giving rise to various oxidation products. Therefore the entire oxidation process can be represented schematically as shown in Fig. 10.

Detailed studies of the mechanism of the adsorption and electrochemical oxidation of simple organic substances ranging from methane to carbon dioxide on platinum group metals have shown that, despite the great complexity and wide variety of these reactions, they can be described by a single multistage mechanism. The nature of the chemisorbed species on the surface is determined by the relative

rates of the individual stages in the processes, illustrated in the scheme, and also by the simultaneous electrochemical formation of the chemisorbed species OH_{ads} or H_{ads}. In its turn it determines the nature of the oxidation products under steady-state conditions. For example, at low pressures, where the conversion of species (II) into species (I) is fairly rapid, ethane and ethylene are oxidised fairly rapidly and completely to CO_2. On the other hand, at fairly high ethylene pressures, where the main chemisorbed species is H_2C-CH_2, ethylene undergoes mild oxidation to ethylene glycol.

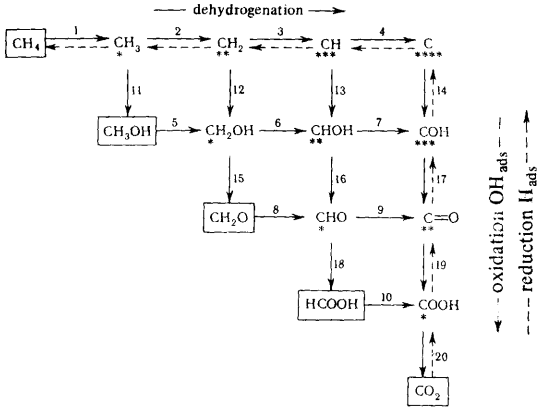
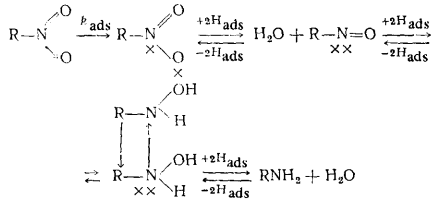


Figure 10. General scheme for the adsorption, electrochemical oxidation, and electrochemical reduction of simple organic substances.

The mechanism of the reduction of compounds with a C=C double bond has been studied in the electrochemical hydrogenation of maleic acid on a platinum catalyst electrode[51]. It has been shown that the slow stage in this process involves the interaction of the chemisorbed organic species with the adsorbed hydrogen formed in the preceding rapid electrochemical stage:

$$\underset{\times\quad\times}{HOOCCH{-}CHCOOH} + 2H_{ads} \rightarrow HOOCCH_2{-}CH_2COOH.$$

In contrast to this, in the electrochemical reduction of aliphatic nitro-compounds on platinum group metal catalyst electrodes the addition of the first hydrogen atoms is fast and the slow stage involves the addition of subsequent hydrogen atoms, which leads to the desorption of the chemisorbed organic species from the electrode surface[47]. Under these conditions, in the electrochemical reduction of nitro-compounds the surface is covered by partly reduced chemisorbed species. The overall process mechanism can be represented as follows:



Similarly, as can be seen from Fig. 10, the reduction of CO_2 by adsorbed hydrogen to the COH species is rapid and the slow stage is the subsequent interaction of this species with adsorbed hydrogen to form methane.

Thus chemisorbed species play a very important role in electrocatalytic processes, determining the direction of the process, its rate, and the yields of various products.

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Institute of Electrochemistry,
USSR Academy of Sciences,
Moscow