THE BEHAVIOUR OF A PLATINIZED-PLATINUM ELECTRODE IN SOLUTIONS OF ALCOHOLS CONTAINING MORE THAN ONE CARBON ATOM, ALDEHYDES AND FORMIC ACID

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The results of the investigation of the processes occurring on a platinized-platinum (Pt/Pt) electrode in methanol solutions at anodic potentials lower than *ca.* 800 mV against the H.E. in the same solution were described in a previous paper[1]. The present communication is concerned with the main results of a similar investigation of the behaviour of saturated alcohols containing more than one carbon atom, aldehydes and formic acid.

The values of the potential, φ_r, are referred to the reversible hydrogen electrode in the same solution at the temperature of the experiment. The measurements, unless otherwise specified, were performed at room temperature ($20 \pm 2°$).

The gaseous products of the processes occurring on the Pt/Pt electrode at open circuit were collected in a special cell, into which a Pt/Pt gauze with 500 cm^2 of apparent surface had been inserted, and analysed by gas chromatography or mass-spectrometry.

1. The processes occurring on a Pt/Pt electrode in contact with solutions of alcohols and aldehydes containing more than one carbon atom

Alcohols and aldehydes containing more than one carbon atom, if introduced into the solution when φ_r is in the "double-layer" region, behave like methanol and cause a sharp shift of the potential of the Pt/Pt electrode in the cathodic direction. At high enough concentrations of the substance considered ($\geqslant 0.1\ M$), however, they differ from methanol in that a minimum value of φ_r is usually reached rather quickly, whereupon φ_r of the electrode either remains almost unchanged or begins to change in the direction of more positive values. The latter effect is especially characteristic of aldehydes, but under certain conditions, it can be sufficiently pronounced in the case of saturated alcohols as well[2]. The values of φ_r^1* established in solutions of C_2H_5OH, C_3H_7OH, C_4H_9OH, CH_3CHO and C_2H_5CHO, although much higher (140–210 mV) than φ_r^1 in methanol solutions, again depend only slightly upon φ_r^0 and the pH of the solution[4,11].

The charging curves of $Pt(X_{ads})$, measured after washing the electrode free of the substance under consideration, show arrests corresponding to the oxidation of the

* The same designations of various quantities are used as in ref. 1.

chemisorbed substances, which are much larger than similar arrests observed in the case of methanol (the coefficient, K, for these substances is 1.1–1.8). Adsorbed hydrogen is found to be present on the electrode surface in small amounts.

On the basis of these data, it can be supposed, just as in the case of methanol, that φ_r[1] values arising in solutions of alcohols and aldehydes containing more than one carbon atom are related to some oxidation–reduction systems. Adsorbed hydrogen should be of major importance in determining these potentials. At the same time, the substances under consideration show a number of specific features from which it can be inferred that the processes determining the establishment of φ_r[1] in solutions of C_2H_5OH, C_3H_7OH, C_4H_9OH and aldehydes, are not only the reactions of dehydrogenation of these substances and the reactions: $H_{ads} \rightleftarrows H^+ + \bar{e}$ (in acid solutions) or $H_{ads} + OH^- \rightleftarrows H_2O + \bar{e}$ (in alkaline solutions).

The difference in the behaviour of these substances and that of methanol becomes most apparent when we compare the curves of the shift of φ_r after the introduction of the substances at φ_r^0 close to zero. Under these conditions, in the case of alcohols and aldehydes containing more than one carbon atom, a shift of φ_r in the direction of more positive values is observed as well as evolution of gas bubbles. A chromatographic analysis of this gas showed that it consists of the hydrogenation products of the original substance.

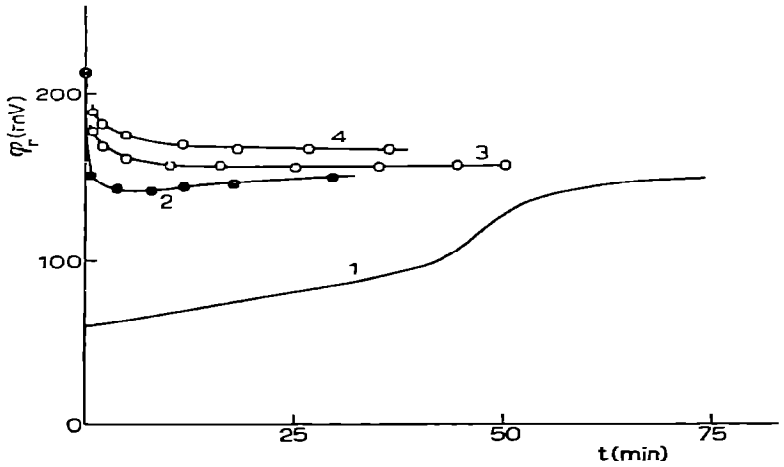


Fig. 1. Dependence of the curves of the potential shift of a Pt/Pt electrode after the introduction of C_2H_5OH on the initial φ_r value: φ_r^0 = (1), 60; (2), 240; (3), 500; (4), 1045 mV Concn. C_2H_5OH, ~ 5 M; supporting electrolyte, 0.1 N H_2SO_4.

The curves of the shift of φ_r after the introduction of ethanol at different potentials, are given in Fig. 1 as an example. It is clear from the figure, that the hydrogenation of ethanol by adsorbed hydrogen starts only after an initial delay, *i.e.*, it is characterized by some induction period. The length of this period is poorly reproducible and in 1 M ethanol solution amounts to 10–45 min. It is not observed with other alcohols[2].

An evolution of gaseous products occurs also when alcohols and aldehydes are brought into contact with the Pt/Pt electrode polarized to φ_r of the "double-layer" region[4]. The results of the analysis of the gases evolved after the introduction of

alcohols and acetaldehyde at φ_r close to zero, and at φ_r in the "double-layer" region, are presented in Table 1*.

It can be seen from the table that when alcohols are brought into contact with the electrode saturated with hydrogen, the hydrocarbon containing as many carbon atoms as the initial alcohol predominates in the gas phase, but when an outgassed Pt/Pt electrode is in contact with alcohol solutions a predominant breaking along the C_1—C_2 bond is observed.

TABLE 1

No.	*Substance*	*Concn. (mol/l)*	φ_r^0 *(mV)*	φ_r^1 *(mV)*	*Composition of gases (vol. %)*			
					CH_4	C_2H_6	C_3H_8	C_4H_{10}
1	C_2H_5OH	2	57	159	13.4	86.6	—	—
2	C_2H_5OH	2	499	157	68.2	31.8	—	—
3	C_3H_7OH	1	54	140	—	19.3	76.3	4.4
4	C_4H_9OH	satd.	41	131	<1	<1	23	76
5	C_4H_9OH	satd.	511	138	—	2.8	69.4	27.8
6	CH_3CHO	0.7	38	184	5.4	46	—	—

According to experiment 5, the decomposition of butanol occurs to a small extent also along the C_2—C_3 bond. Consequently, the outgassed surface of the Pt/Pt electrode exerts a stronger destructive action upon the alcohols than a surface covered with adsorbed hydrogen. The data obtained also show that the OH-group lowers the strength of the C—C bond.

The appearance of hydrogenation products when alcohols are introduced at φ_r in the "double-layer" region is an indication of their self-hydrogenation. At the same time, part of the alcohol and of the products of its decomposition, are oxidized. Thus, a reaction of the type of the well-known Canizzaro reaction occurs on the surface of the Pt/Pt electrode. Consideration of thermodynamic data for ethanol, propanol and butanol shows that, from the thermodynamic point of view, the above reaction should be expected[4] to take place. A similar statement is valid also in the case of aldehydes**.

A comparison of the results of the hydrogenation of ethanol and acetaldehyde in the presence of adsorbed hydrogen (expts. 1 and 6 in Table 1) shows that the breaking of the C_1—C_2 bond occurs more readily with aldehydes than with alcohols.

Of special importance is the fact that in the case of the Pt/Pt electrode in contact with propanol solutions, (expt. 3, Table 1), butane appears in the gas phase. This should be considered as the product of a partial recombination of C_2H_5-radicals, formed as the result of the breaking of the C_1—C_2 bond.

Just as in the case of φ_r^0 in the "double-layer" region, when alcohols and

* There is a marked solubility of saturated hydrocarbons in the solutions investigated which increases in the series $CH_4 < C_2H_6 < C_3H_8 < C_4H_{10}$, and the data of the analysis are, therefore, probably somewhat too low in the case of the higher hydrocarbons. This, however, does not introduce any essential error into the evaluation results.

** The self-hydrogenation of aldehydes in the presence of metal catalysts (Pt and Pd) was first established experimentally (for sugars) by WIELAND[5] and BACH[6]. The self-hydrogenation of saturated alcohols on the Pt/Pt electrode at room temperature, however, seems to have been first observed in ref. 2.

aldehydes are introduced at φ_r^0 close to zero, processes of dehydrogenation, self-hydrogenation and decomposition start on the electrode surface as adsorbed hydrogen is removed from it. In fact, the formation of gaseous products continues for a long time after the electrode potential practically ceases to shift, much more of the reaction products being isolated than would be required by the total consumption of all the hydrogen adsorbed on platinum. The results of an analysis of the first 5.5 cm^3 of gas collected after the introduction of alcohol are presented in Table 1 for propanol (expt. 3). The analysis of the gas evolved later (8–10 cm^3) gave the following figures: C_2H_6, 27%; C_3H_8, 69.2%; n-C_4H_{10}, 3.6%. This gas is richer in ethane, as should follow from the fact that it is formed at smaller surface coverages with adsorbed hydrogen, compared to the first portion of the gas.

Apparently there is no reason to expect essential differences in the final states of the Pt/Pt electrode surface when it is brought into contact with alcohols and aldehydes at low and high φ_r^0 values (in the range 50–700 mV). This assumption is confirmed in the case of sufficiently concentrated solutions of alcohols and aldehydes ($>0.1\ M$) by a number of experimental results. Thus, for example, an approximate coincidence of φ_r^1 for different φ_r^0 is observed in ethanol solutions ($\Delta\varphi_r^1 < 10$ mV). The differences are somewhat greater in solutions of propanol and butanol ($\Delta\varphi_r^1 < 30$ mV) and aldehydes ($\Delta\varphi_r^1 < 40$ mV).

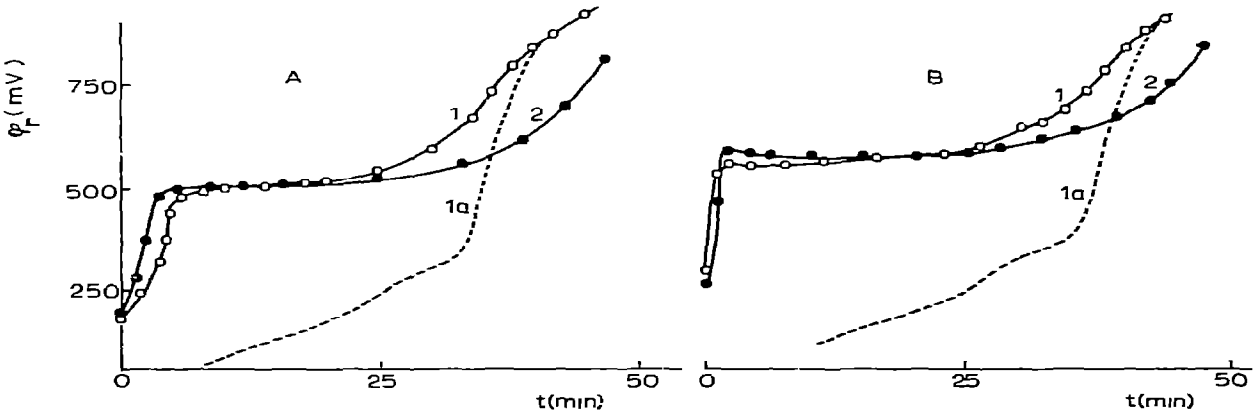


Fig. 2. Charging curves of Pt(X_{ads}), corresponding to the introduction of the substance at: (1), ~ 500; (2), 60 mV. Concn. X, 0.5 M; (1a), charging curve in 0.1 N H_2SO_4; supporting electrolyte soln.: (A), $X = C_2H_5OH$; (B), $X = CH_3CHO$.

It can be seen in Figs. 2A and 2B, that the charging curves of $Pt(C_2H_5OH)_{ads}$ and $Pt(CH_3CHO)_{ads}$, corresponding to the washing of the electrode after the establishment of the steady potential for low and high φ_r^0, are basically similar for each substance. However, when φ_r^0 is close to zero, appreciably larger values of the adsorption coefficient, K, are observed. This seems to indicate that the particles chemisorbed at φ_r^0 in the "double-layer" region are somewhat less rich in hydrogen than the products of chemisorption at φ_r^0 close to zero. The greatest difference in the values of φ_r^1 corresponding to different φ_r^0 was observed in the solution 0.01 N HCl + 0.09 N KBr + 0.5 M CH_3CHO ($\Delta\varphi_r^1 \approx 70$ mV). The comparison of the charging curves of $Pt(CH_3CHO)_{ads}$ shows that the surface states of the Pt/Pt electrode at φ_r^1 correspond-

ing to $\varphi_r^0 \sim 500$ mV and $\varphi_r^0 \sim 60$ mV in this solution, actually differ appreciably.

Thus, when a steady potential is established in solutions of alcohols and aldehydes containing more than one carbon atom, processes of dehydrogenation, hydrogenation and self-hydrogenation of the original substances and of their decomposition products (mainly along the C_1—C_2 bond), occur. A steady concentration of H_{ads} on the electrode surface, established and maintained by these processes, determines the final potential, as it can be hardly supposed that the rates of any processes could be commensurable with those involving H_{ads}[7], even when the latter is present in a small concentration. At a given φ_r[1], the amount of H_{ads} is determined by the coverage of the surface with the chemisorbed substance and, hence, the supporting electrolyte being kept unchanged, it can vary with the nature of the substance being investigated, its concentration and other factors. Thus, for example, it was experimentally established[4] that in ethanol solutions, at φ_r[1] the amount of adsorbed hydrogen decreases with increasing alcohol concentration and the amount of the chemisorbed substance considerably increases. At small ethanol concentrations, the balance between the processes of hydrogenation and dehydrogenation of alcohol is practically established at much larger coverages of the Pt/Pt electrode surface with hydrogen than at high concentrations. However, the values of φ_r[1], themselves, depend only slightly on the concentration of ethanol within the concentration range 10^{-3}–3 M. As a result, at practically the same potentials the amount of hydrogen on the electrode is proved to change 4–5 times. A similar situation presents itself when the Pt/Pt electrode surface is poisoned with inorganic substances[8]. As the degree of poisoning increases, the amount of hydrogen corresponding to a given φ_r decreases, but until very high degrees of poisoning are reached, the electrode continues to behave as a reversible hydrogen electrode.

As in the case of the Pt/Pt electrode in contact with the solutions of the substances under consideration, where processes of dehydrogenation and of destructive hydrogenation of initial molecules and their transformation products occur, we may expect the particles of the type HCO, RCHOH, C_nH_{2n+1}, C_nH_{2n}, etc. to be chemisorbed on the surface. The problem of a sufficiently accurate determination of the composition of the chemisorbed substance is therefore complicated and the experimental data so far obtained permit only some assumptions regarding its nature.

No appreciable amounts of methane are formed during the hydrogenation of propanol and butanol in the presence of adsorbed hydrogen (expts. 3 and 4 in Table 1) in spite of the breaking of the C_1—C_2 bond. We can suppose that either methanol is formed in the solution, or that a particle containing a C_1 atom, *e.g.* HC_1O, is chemisorbed on the electrode surface, the latter hypothesis being more probable.

The fact that the beginning of oxidation of chemisorbed substances is always characterized by an approximately identical φ_r, which, for example, in 0.1 N H_2SO_4 at $i = 10^{-4}$ A/cm², is equal to 500 ($\pm$20) mV (the values of φ_r past the maximum on the φ_r—t curve being considered in the case of aldehydes) points in favour of chemisorption of particles of an identical composition (*e.g.* HCO) in solutions of various alcohols (including methanol) and aldehydes. On the other hand, the analysis of the experimental data points to the inhomogeneity of adsorbed particles. Thus, with an increasing number of carbon atoms in the alcohol molecule, oxidation of the chemisorbed substance ends at higher φ_r, as follows from galvanostatic and potentiostatic measurements. According to the charging curves of Pt(X_{ads}) measured at $i = 1 \cdot 10^{-4}$

A/cm², a practically complete oxidation of chemisorbed methanol is over at ~700 mV[1], of ethanol—at ~850 mV (Fig. 2A) and of propanol — at ~1100 mV. It is clear from Figs. 3a and 3b that oxidation of chemisorbed ethanol and acetaldehyde in the case of a potentiostatic sweep is not over at the potentials of the "double-layer" region and occurs in the range of φ_r corresponding to the coverage with oxygen. Under similar conditions, the substance chemisorbed on the Pt/Pt electrode in methanol solutions is completely oxidized before ~800 mV[1]. The fact that the oxidation of the same chemisorbed substance with potentiostatic sweeps is over at more anodic potentials than in the case of galvanostatic measurements at the current densities used by us, is due to a higher rate of potential change in the case of potentiostatic measurements. The oxidation of chemisorbed aldehyde is over at about the same φ_r as the oxidation of the corresponding chemisorbed alcohols (Figs. 2A and 2B, 3a and 3b).

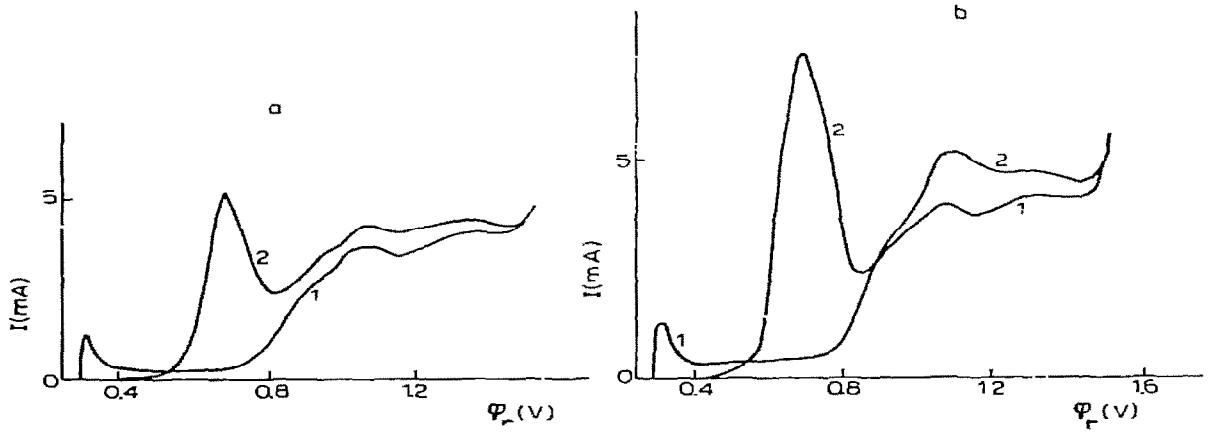


Fig. 3. Potentiostatic curves of the Pt/Pt electrode in: (1), 0.1 N H_2SO_4; (2), in the presence of the substance X chemisorbed at open circuit: (a), $X = C_2H_5OH$; (b), $X = CH_3CHO$. $\varphi_r^0 \sim 500$ mV; concn. X, 0.5 M; rate of potential change, 5 mV/sec; apparent electrode surface, 1.78 cm².

When hydrogen is bubbled through the ethanol solution, only about 50% of the chemisorbed substance is removed from the electrode surface[12]. This seems to be the result of the presence, in the chemisorbed substance, both of particles reacting relatively readily with hydrogen and those which practically do not interact with it. The particles chemisorbed in methanol solutions can be removed by this method to a considerably lesser degree (*ca.* 15%)[3]. The difference in the behaviour of ethanol and methanol chemisorbed at open circuit is, possibly, due to the presence on the surface in the former case of considerable amounts of hydrocarbon radicals, which, as follows from the study of chemisorption of hydrocarbons from the gas phase[9] react relatively readily with hydrogen.

2. Some peculiarities in the behaviour of the Pt/Pt electrode in solutions of formaldehyde and formic acid

The behaviour of formaldehyde differs, in some respects, from that of higher aldehydes. Values of φ_r[1] (Fig. 4a) are established in its presence which are almost as

low as in methanol solutions (70–90 mV), although formaldehyde is hydrogenated by hydrogen adsorbed on platinum (curve 1, Fig. 4a)*. Evidently, as no gaseous products are evolved during the hydrogenation of formaldehyde in sulfuric acid solutions, this process proceeds only until methanol is formed.

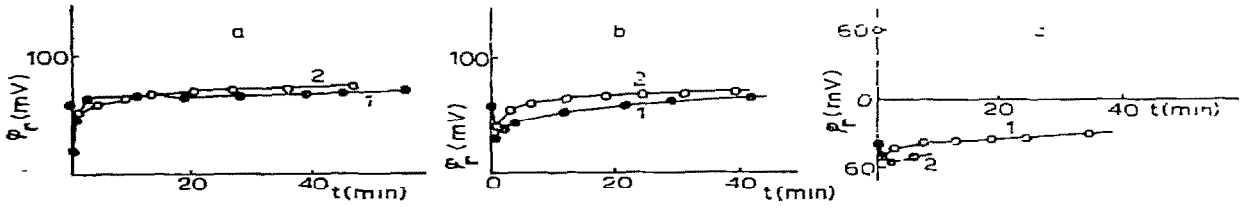


Fig. 4. Curves of the potential shift of the Pt/Pt electrode after the introduction of HCHO at: (1), 60; (2), 500 mV: (a), $t = 20°$; concn. HCHO = 0.1 M (1) and 0.6 M (2), supporting electrolyte, 0.1 N H_2SO_4; (b), $t = 80°$; concn. HCHO = 0.1 M (1) and 0.6 M (2); supporting electrolyte, 0.1 N H_2SO_4; (c), $t = 80°$; concn. HCHO = 0.2 M (1) and (2); supporting electrolyte, 7 N KOH.

According to curve 1, Fig. 4a, after the introduction of formaldehyde at 60 mV in 0.1 N H_2SO_4, a sharp drop of the potential to ~20 mV is observed during the first 30 sec, followed by a rise to ~65 mV after 2 min. Subsequently, the potential changes very slowly. Although the potential changes under the above conditions are slight, after the electrode is washed free of formaldehyde, its surface proves to be practically completely covered with the chemisorbed substance ($K \approx 1.0$). It is most likely that, in this case, the hydrogenation and dehydrogenation processes occur at high and commensurable rates.

The curves of the shift of φ_r in acid solutions of formaldehyde at 80° (Fig. 4b) are similar to the corresponding curves at room temperature both in their shape and in the values of φ_r^1 established. The increase in the rates of the hydrogenation and dehydrogenation processes of formaldehyde with rising temperatures seems to occur in acid solutions in approximately the same ratio. In alkaline solutions of formaldehyde at high temperatures potentials below the reversible hydrogen potential are established and violent hydrogen evolution is observed (Fig. 4c)**. Thus, on transition from acid to alkaline solutions, the ratio of the rate of oxidation of formaldehyde to that of its hydrogenation, under the conditions of the measurements of the curves of the shift of φ_r, changes in favour of the former process. This can be due both to the increasing rate of oxidation of formaldehyde in an alkaline medium and to a decrease in the hydrogenation rate. It should be noted that a decrease in the hydrogenation rate on platinized platinum in alkaline solutions at pH $\gtrsim$ 12 is observed with many substances[15].

As shown in ref. 2, the minimum on the curves of the potential shift, occurring after the substance is brought into contact with the Pt/Pt electrode, is characteristic of compounds which can be both oxidized and reduced on the electrode surface; it is due to the competition of the above-mentioned processes and shows that the hydrogenation process is initially somewhat inhibited. Evidently, this explanation is true both

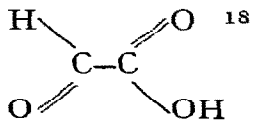
* We did not observe the high final φ_r^1 values (~ 450 mV) in formaldehyde solutions, which were noted in ref. 13.

** Hydrogen evolution at a Pt/Pt electrode in alkaline solutions of formaldehyde and methanol at 80° was pointed out also in ref. 14.

in cases when the effect being considered is observed at $\varphi_r > 0$ (*e.g.*, Fig. 4a, b) and when it occurs at $\varphi_r < 0$ (Fig. 4c) But in the latter case it should also be taken into account that one of the possible reasons for the $\varphi_r - t$ curve passing through a minimum, may be the increased poisoning of the electrode surface with time, which exerts a stronger inhibitive action upon the process of oxidation of the organic substance than upon the reaction of hydrogen evolution.

In formic acid solutions, just as in methanol solutions[1], regardless of φ_r^0, the shift of the potential occurs only in the direction of more negative values*; but in formic acid solutions, about twice as much adsorbed product is accumulated at $\varphi_r^0 \sim 500$ mV ($K \simeq 0.90$) than in methanol solutions, and in contrast to the latter, appreciable amounts of the adsorbed product ($K \simeq 0.45$) are observed at $\varphi_r^0 = 60$ mV. The ratio k/m' is not constant and can assume values much larger than $1 (\leqslant 7)$. These results are similar to those obtained for ethanol[4] and therefore we can suppose that hydrogenation of formic acid occurs on the Pt/Pt electrode at $\varphi_r > 0$.

According to the adsorption measurements, the sum $k + m$ for different φ_r^0 and formic acid concentrations, remains approximately constant and close to 1, as with methanol[3]. This means that the chemisorbed particle occupies as many adsorption sites as it gives off electrons during oxidation. A similar conclusion regarding the adsorption of formic acid on smooth platinum was drawn by BRUMMER AND MAKRIDES[18]. As already pointed out in ref. 18, these results are at variance with the assumption that it is mainly the COOH particles which are chemisorbed in formic acid solutions[19]. Apparently, it is either the HCO particle formed as the result of hydrogenation of formic acid which is chemisorbed, or both the HCO and COOH particles are chemisorbed together. Stoichiometrically, the latter assumption is similar to that concerning the chemisorption of the molecule



After the introduction of formic acid at $\varphi_r^0 < 100$ mV, the potential of the electrode in 0.1 *N* and 1 *N* H_2SO_4 reaches values close to 0 ($\sim$4–20 mV). In these cases, at $\varphi_r \leqslant 30$ mV, gas bubbles were evolved from the electrode. The analysis of the gas showed it to consist only of hydrogen and the inert gas (nitrogen or argon) used to remove oxygen from the solutions. Without contradicting the assumption that φ_r^1 established in the solutions of organic substances are determined by H_{ads}, we can explain hydrogen evolution at low but still positive φ_r values in formic acid solutions by the supposition that molecular hydrogen results from the interaction of the products formed upon contact of formic acid with the Pt/Pt electrode. Evidently, we should also assume in this case the process of hydrogen adsorption: $H_2 \rightarrow 2H_{ads}$, to be a slow one. A similar assumption was made earlier[20] to explain the evolution of gaseous hydrogen at considerable anodic polarizations on a number of metals (Cu, Ag, Au, etc.) in alkaline solutions of formaldehyde. It is of interest, also, to note that there are some non-electrochemical oxidation reactions which are known to be accompanied by hydrogen evolution[21].

* The complex dependence of φ_r upon t in the case of formic acid, described in refs. 16 and 17, was not observed by us.

A more detailed elucidation of the nature of the phenomenon observed by us, *i.e.*, the evolution of hydrogen in formic acid solutions at $\varphi_r > 0$, necessitates further experimental investigation.

3. The kinetics of electro-oxidation. Some specific features of the charging curves of Pt(X_{ads})

The investigation of the behaviour of the Pt/Pt electrode in solutions of alcohols containing more than one carbon atom and in solutions of aldehydes leads to the conclusion that in these cases, just as in the case of methanol[1], it is necessary to distinguish between the processes on a bare surface (immediately after the introduction of organic substances) and those occurring under steady-state conditions. Thus, the evolution of gases, which at first proceeds very actively, slows down and, for instance after one day at a steady potential becomes extremely slow. No evolution of gaseous products is observed during the measurements of the steady-state polarization curves in solutions of alcohols and aldehydes*.

Just as in the case of methanol[10], a high rate of ethanol dehydrogenation on the surface of the Pt/Pt electrode, from which adsorbed hydrogen is gradually removed, can be observed during the first potentiostatic sweep after the introduction of alcohol at ~0.05 V (Fig. 5). The decrease in the current during the subsequent pulses,

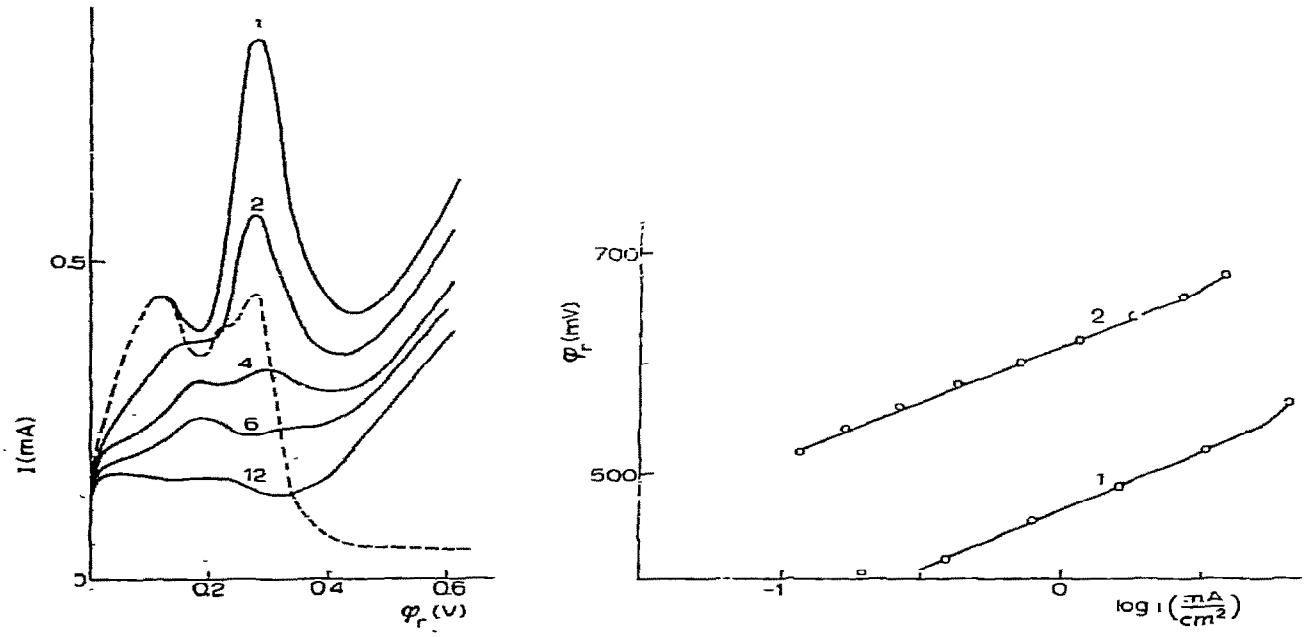


Fig. 5. Potentiostatic curves during the first and subsequent anodic sweeps (numbers of sweeps are indicated on figure) in 0.5 *M* C_2H_5OH + 0.1 *N* H_2SO_4 soln. Rate of potential change, 124 mV/sec; apparent electrode surface, 0.02 cm²; — —, supporting electrolyte.

Fig. 6. Polarization curves of the Pt/Pt electrode in the presence of C_2H_5OH in the soln. (1) and after washing of the electrode free of C_2H_5OH (2), measured by the potentiostatic method at a rate of potential change of 5 mV/sec. Concn: C_2H_5OH, 0.5 *M*; supporting electrolyte, 0.1 *N* H_2SO_4.

* According to ref. 25 practically the only products of electro-oxidation of ethanol at low φ_r are acetaldehyde and acetic acid.

with the final potential of the pulses corresponding to the double layer region, proceeds slowly and the steady-state curve is obtained only after a great many pulses. Similar phenomena are observed in the case of slow potentiostatic pulses in solutions of formic acid in sulfuric acid and of sodium formate in alkali. They cannot be observed in the case of acetaldehyde and formaldehyde, which are hydrogenated and dehydrogenated at appreciable rates on platinum at φ_r close to zero. Because of this, large amounts of chemisorbed substances accumulate on the electrode prior to the measurements. However, rapid rates of processes can be observed on the platinum surface free of the chemisorbed substances, also in the case of aldehydes, which can be seen from the measurements of the current–time dependence after their introduction at constant φ_r.

In accordance with the results of potentiostatic measurements in the φ_r range 300–450 mV, the steady-state $\log i - \varphi_r$ curves in acid solutions of ethanol are characterized by poor reproducibility, a considerable dependence on the direction of the change in the current values, and by a decrease in the slope at low φ_r. The absence of the latter effects in methanol solutions leads us to suppose that they are to some extent associated with the ability of ethanol not only to be oxidized, but also to be reduced on the Pt/Pt electrode. In alkaline solutions of ethanol, the steady state is readily established. When the polarization curves are measured in formic acid solutions, the steady-state potentials, as has already been noted in ref. 22, become established very slowly (at $i < 10^{-4}$ mA/cm^2, $d\varphi_r/dt$ exceeds 0.1 mV/min after time intervals of several hours*). In Table 2 are listed the values of the slopes of the steady-state Tafel lines for 0.5 M solutions of ethanol, formaldehyde and formic acid.

TABLE 2

Substance	*Supporting electrolyte*	$d\varphi_r/d \log i$ (mV)	*Potential range* (mV)
C_2H_5OH	1 N H_2SO_4	95–115	400–550
C_2H_5OH	0.1 N KOH	70–80	300–450
H_2CO	0.1 N H_2SO_4	55–65	420–550
H_2CO	0.1 N KOH	80–90	180–320
HCOOH	0.1 N H_2SO_4	50–60	300–450
HCOONa	0.1 N KOH	60–70	280–360

At potentials exceeding those given in the last column of Table 2, passivation of the electro-oxidation process is observed. This phenomenon has not been studied by us in detail (*cf.* ref. 26 and 27).

Figure 6 shows the polarization curves of the electro-oxidation of chemisorbed ethanol and of the dissolved alcohol obtained by means of slow potentiostatic potential pulses. The slopes of curves 1 and 2 are similar and equal to 100–120 mV (for electro-oxidation of ethanol chemisorbed at open circuit, see also ref. 11). According to the data obtained, the rate of oxidation of the chemisorbed substance is about one-tenth of the rate of electro-oxidation of ethanol when it is present in the solution. Thus, the effect of the removal, in the process of washing, of the particles less strongly bound

* In this connection, the conclusion regarding the change in the mechanism of HCOOH anodic oxidation with changing temperature, made in ref. 22, does not seem to be sufficiently convincing, as it was obtained from measurements performed at states removed to varying degrees from the steady state.

with the surface and more readily oxidized, is more pronounced in the case of ethanol than methanol. In the case of formic acid, the above effect is even more marked, $\Delta\eta$ reaching ~200 mV (Fig. 7). In all cases, however, the polarization curves of oxidation of the chemisorbed particles and those obtained in the presence of the substance in the solution have practically the same slope.

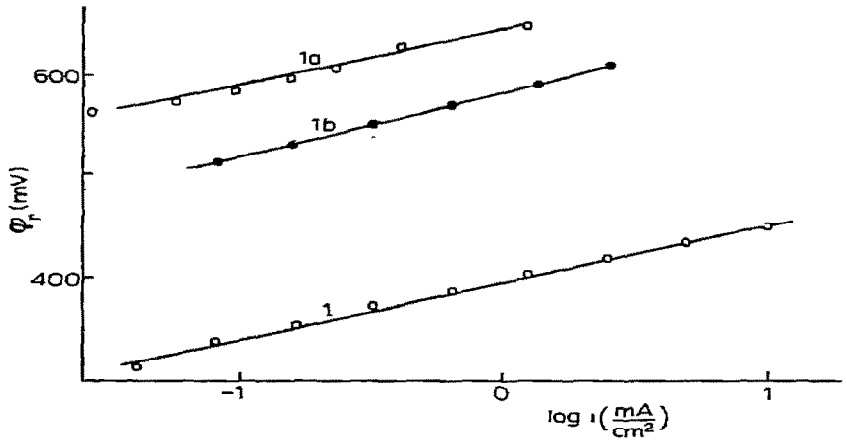


Fig. 7. Steady-state polarization curve of electro-oxidation of 0.5 M HCOOH (1) and curves of electro-oxidation of the chemisorbed substance during the first (1a) and the second (1b) anodic sweeps at a rate of 5.4 mV/sec. Supporting electrolyte, 0.1 N H_2SO_4.

The difficulties in explaining the kinetic data for methanol electro-oxidation were pointed out in ref. 1. The experimental data given above show that the process of electro-oxidation of the substances considered in the present paper seems to be even more complicated. Thus, for example, it is not possible to explain at the present time the peculiarities in the establishment of the steady state, the reasons for the difference in the slopes of the Tafel lines for the substances investigated, as well as the values of these slopes. Further experimental data are needed for the solution of these problems.

A characteristic feature of the charging curves of Pt(X_{ads}) in acid solutions for all the substances studied, is either the appearance of an approximately horizontal section on the φ_r–t curves during electro-oxidation (Fig. 2A), or even the presence of a maximum on these curves (Fig. 2B). The maximum is especially pronounced in the case of substances chemisorbed at open circuit in aldehyde solutions, and after the polarization in acid solutions of all the substances investigated. Accordingly, under the conditions of the potentiostatic sweeps, the curve measured by the first anodic pulse lies higher than that measured by subsequent pulses (the final potential in the first sweep being chosen in such a way as to have only a small amount of the substance oxidized, less than one-tenth of the total quantity adsorbed) (Fig. 7). Apparently, these features are due to the oxidation process of the chemisorbed substance being determined not only by its quantity, but also by the proportion of the uncovered surface*. The latter may be associated with the participation in the oxidation process of the particles adsorbed on the sites not covered by the chemisorbed substance, *e.g.*,

* A similar concept was advanced by GILMAN[23].

the OH-radicals, as suggested above. Evidently, the effect under consideration should, to a great extent, depend both on the absolute value of the bare surface and on the character of distribution of the chemisorbed particles over the electrode surface, or the interaction between the particles and other factors. This seems to account for the complex dependence of the shape of the charging curves of $Pt(X_{ads})$ upon the nature

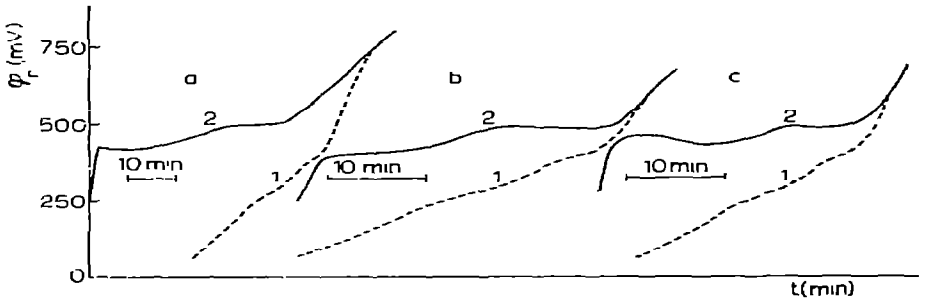


Fig. 8. Galvanostatic curves of oxidation of the substance chemisorbed after the polarization of the Pt/Pt electrode in 0.1 N KOH + 0.1 M X soln. (2); (1), charging curve in 0.1 N KOH: (a), $X = C_2H_5OH$; (b), $X =$ HCOOH, (c), $X =$ HCOH.

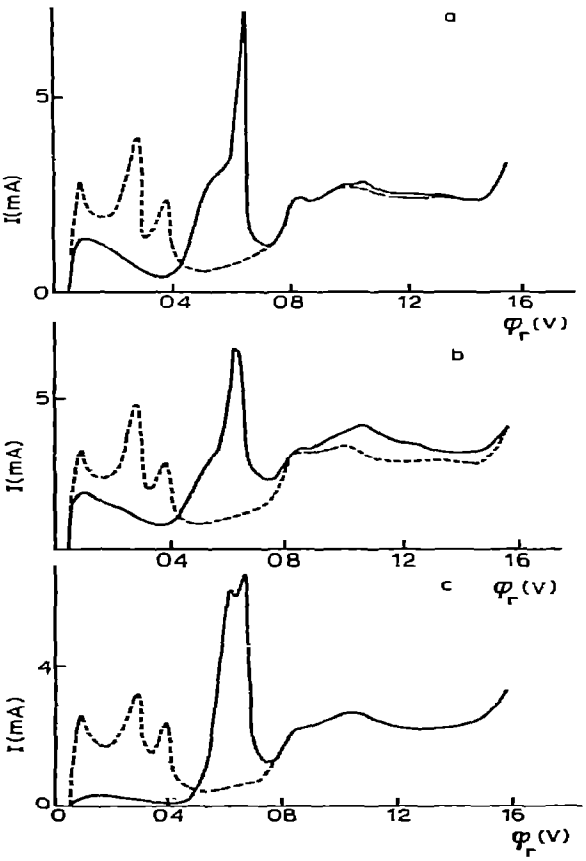


Fig. 9. Potentiostatic curves of oxidation of substances chemisorbed after polarization of the Pt/Pt electrode in solns.: (a), 0.1 M HCOONa + 0.1 N KOH, (b), 0.1 M C_2H_5OH + 0.1 N KOH; (c), 0.1 M HCOH + 0.1 N KOH; — —, curve in 0.1 N KOH; rate of potential change, 5.4 mV/sec; apparent electrode surface, 1.78 cm².

of the organic substance and the conditions of the experiment. Of essential importance in this case are the pH of the solution and, especially, the presence of specifically adsorbed anions in the electrolyte.

As shown in ref. 1 in the case of oxidation of methanol chemisorbed during polarization in alkaline solutions, two arrests are observed. According to Fig. 8, the same effect is observed in the electro-oxidation of substances chemisorbed after the polarization of the Pt/Pt electrode in alkaline solutions of ethanol, formaldehyde and formate-ion. The potentiostatic curves (Fig. 9) show pre-waves in the case of ethanol, formic acid and formate and one wide wave with two maxima in the case of formaldehyde.

Two steps are observed also on the charging curve of $Pt(HCOONa)_{ads}$ corresponding to adsorption of the substance in an alkaline solution at open circuit.

Apparently in all the cases considered, two forms of the chemisorbed substance are present on the surface. It is possible, as already pointed out in ref. 1, that the second form results from the interaction of the chemisorbed particles with the OH^- anions. It should be noted that the maximum on the charging curves of $Pt(X_{ads})$ is observed also in alkaline solutions; it may occur both on the first and on the second arrests (Fig. 8).

According to refs. 12, 2 and 24, in the presence of halogen anions in acid solutions, the rate of the shift of φ_r after the introduction of alcohols and aldehydes slows down, the amount of the chemisorbed substance decreases, and the overvoltage of its electro-oxidation increases. The effect of the anions increases in the series: $SO_4^{2-} < Cl^- < Br^-$. The phenomena under consideration point to the inhibition of the processes occurring on the electrode as the result of the specific adsorption of anions.

SUMMARY

According to electrochemical measurements and the analysis of gases evolved when a Pt/Pt electrode is immersed in solutions of saturated alcohols and aldehydes containing more than one carbon atom, processes of dehydrogenation, hydrogenation and self-hydrogenation of the original substances and their decomposition products (mainly along the C_1—C_2 bond) occur on the electrode surface. A steady concentration of H_{ads} on the electrode surface, which determines the final potential, is established and maintained due to the above processes. The outgassed Pt/Pt surface exerts a stronger destructive action upon these substances than the surface covered with H_{ads}.

Some specific features of the establishment of the potential in the formaldehyde and formic acid solutions are considered. A hypothesis is advanced that the complex character of the dependence of the oxidation rate of the chemisorbed substance upon the coverage (in particular, the presence of a maximum on the galvanostatic curves corresponding to oxidation of the chemisorbed products) is due to the participation in the process of particles formed on the sites free of the chemisorbed substance, *e.g.*, the OH^- radicals.

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