ADSORPTION AND ELECTROOXIDATION OF METHANOL AT A PLATINIZED PLATINUM ELECTRODE USING AN ANALYTICAL METHOD

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To develop further the theory of chemisorption and electrooxidation of methanol at a Pt surface [1-9], we performed electrochemical experiments in which the liquid phase was analyzed chemically for formaldehyde, methanol, and formic acid.

The specific color reaction with chromotropic acid [10] was used to determine H_2CO. This reaction was also used to determine CH_3OH, which was first oxidized to H_2CO with potassium permanganate [11]. The minimum observable concentration was about $2 \cdot 10^{-5}$ M in both cases. With the photoelectric colorimeter FÉK-56M, the accuracy of the quantitative determination of CH_3OH and H_2CO in the concentration range 10^{-4} to 10^{-3} M* was about 6%. Formic acid was determined by iodometric titration as previously described [2], with an accuracy to 10^{-4} M (± 15%). The gas formed during hydrogenation of the chemisorbed species, was analyzed chromatographically at 25°C in a capillary tube filled with the ester of triethylene glycol and n-butyric acid. A flame ionization detector was used.

The adsorption measurements and the determination of the products of the electrochemical reaction of the chemisorbed species were performed at a Pt/Pt-screen having a surface area of about 500 cm^2 and a true area, calculated from H_2 adsorption [12], between 28-40 m^2; these limits correspond to the change of the surface area during the measurements. Under anodic polarization [6] the limiting amount of CH_3OH, considered as HCO_{ads} [4], which was chemisorbed at this electrode, was about $2 \cdot 10^{-4}$ moles. The transfer to the solution (volume = 63 ± 2 cm^3) of this amount of chemisorbed species for any organic substance with one carbon atom in its molecule, would give a final concentration of about $3 \cdot 10^{-3}$ M. The determination of the CH_3OH oxidation products obtained under equilibrium conditions [5, 6] was performed at a rotating Pt/Pt disk electrode at 2.0 mA current. The disk had an apparent surface area of 0.75 cm^2, and a true area of about 1000 cm^2. During the time of polarization (about 13 h) about 2% of the CH_3OH in solution was oxidized. The potentials, φ_r, are given relative to the reversible hydrogen electrode immersed in the same solution.

Formaldehyde and formic acid were not detected at a Pt/Pt electrode immersed in a 1N H_2SO_4 solution containing 0.004-0.5 M CH_3OH and maintained at open circuit up to 24 h at $\varphi_r^0 \simeq 500$ mV. This result agrees well with that previously obtained on the basis of electrochemical measurements which concluded [4] that under these conditions the dehydrogenation process proceeded according to the scheme $CH_3OH \rightarrow HCO_{ads} + 3H_{ads}$. The large true surface area of the electrode used for adsorption, permitted the determination of CH_3OH adsorption at Pt/Pt from the decrease of the alcohol concentration. On the basis of the analytical measurements, the calculated amounts of adsorption, q_{anal}, are given in Table 1 for an initial CH_3OH concentration of $4.5 \cdot 10^{-3}$ M ($\varphi_r^0 \simeq 500$ mV, supporting electrolyte was 1N H_2SO_4); the concentration values of q_{elec} determined from the charging curves after the electrode was washed with the supporting electrolyte [4] are also given. The adsorption quantities are expressed in charge units required for the electrooxidation of CH_3OH_{ads} to CO_2 and related to 1 cm^2 of true surface area ($q_{elec} = q_{HCO} + q_H$ where q_{HCO} and q_H are the adsorption quantities for the chemisorbed radical and for H_{ads}.

As seen from Table 1, the data were sufficiently reproducible to show that under equilibrium conditions the adsorption of CH_3OH, noticeably exceeded the amount calculated from the curves for the oxidation of the chemisorbed species remaining in the electrode of the washing. Also, additional CH_3OH adsorption was confirmed in the following experiments. The Pt/Pt electrode remained in contact for about 2 h with a solution of $3.5 \cdot 10^{-3}$ M CH_3OH;

*In high concentrations of CH_3OH, the optical density deviated from the linearity of the calibration curve.

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TABLE 1

Expt. no.	Final concentration of CH_3OH in solution, M	Equilibrium potential, φ_r, mV	q_{anal} $\mu C/cm^2$	q_{elec} $\mu C/cm^2$	$\frac{(q_{anal}-q_{elec})100\%}{q_{elec}}$
1	$2.16 \cdot 10^{-3}$	165	190	128	49
2	$2.1 \cdot 10^{-3}$	156	191	120	58
3	$2.2 \cdot 10^{-3}$	158	202	135	50

the electrode was washed with the supporting electrolyte (1N H_2SO_4) and $3.5 \cdot 10^{-3}$ M CH_3OH was again put into the cell. In spite of the insignificant change in φ_r of the electrode for 20-30 min after the second addition of CH_3OH (~ 13 mV), only a slight degree of stable chemisorption of the alcohol can be assumed [4]; the decrease in the alcohol concentration in solution corresponded to about 50% of q_{elec} which agrees with results of Table 1. Thus, some of the CH_3OH molecules adsorbed on the surface are not sufficiently stable and are removed during washing. They may be only physically adsorbed or they may be dehydrogenated radical of methanol that is reversibly chemisorbed ($CH_3OH \rightleftharpoons CH_{3-k}OH + kH_{ads}$ where $k < 3$). The first assumption seems more likely, since in the case of reversible chemisorption, a noticeable shift of φ_r in the washing process would be expected; this was not confirmed by experimental data [4]. According to the analytical measurements at a Pt surface saturated with H_{ads} ($\varphi_r = 0$), the adsorption of methanol in any form does not occur. (For stable chemisorption, this was established before by an electrochemical method [4].)

As was noted before [5, 6], comparison of kinetic results of the oxidation of CH_3OH under equilibrium conditions and the stable chemisorption of products also compels the assumption that during washing, some of the particles which are less stably bonded to the surface and more easily oxidized are removed. With the aim of experimentally verifying this assumption, an electrode whose surface was occupied by chemisorbed particles accumulated during the anodic polarization in 0.15 M CH_3OH was introduced into $1.6 \cdot 10^{-3}$ or $3.5 \cdot 10^{-3}$ M solution of CH_3OH. In both cases the change of CH_3OH concentration was within the limits of accuracy of the measurements. Consequently, the additional adsorption of CH_3OH at the Pt surface, limited by the surface coverage of the stable chemisorbed species, was estimated not to exceed ~20 $\mu C/cm^2$. Additional adsorption in the presence of the chemisorbed species already accumulated by anodic polarization, apparently, is small also in the case of a large volume concentration of CH_3OH; this is supported by the adequate agreement of the adsorption values determined by oxidation of the adsorbed layer [6] and by the anodic impulse method [3, 8].

The electrochemical measurements [13, 14] indicated the comparatively small change in the amount and also in the electrochemical character of the chemisorbed methanol during its hydrogenation (passage of hydrogen or cathodic polarization). Analytical measurements showed that the hydrogenation of the chemisorbed species in the course of 1 day (at low cathodic polarization) did not lead to the appearance of CH_3OH in solution in quantities greater than $2 \cdot 10^{-5}$ M, that is desorption with the formation of methanol was practically absent.* At the same time in the gas phase traces of CH_4 were detected.† However, an approximate estimate of the total amount of liberated CH_4 showed that as a result of its formation a change would be expected in the amount of chemisorbed species of less than ~3%, which is within the limits of reproducibility of the electrochemical adsorption measurement. These results showed that the chemisorption of CH_3OH on Pt/Pt is practically irreversible. It should be noted that at sufficiently high temperatures (~80°) when CH_3OH was in contact with the electrode, methane was formed in significant amounts [13]. But in this case also the surface was primarily occupied by particles which were not removed during hydrogenation [13].

According to the analytical measurements made during the electrooxidation of species chemisorbed from methanol solution by anodic polarization HCOOH (or HCOOK) and H_2CO were not formed either in acid (1N H_2SO_4) or in alkaline solution (1N KOH). Therefore, within the limits of accuracy of the analytical method, it may be assumed that substance remaining on the electrode after washing was fully oxidized to CO_2. The results for determinations of the products present in solution of CH_3OH electrooxidation are given in Table 2.

*In these cases particular attention was given to careful washing of the cell in which the adsorption measurements were performed with the electrolyte to remove the solution with methanol (0.15 M).

†We wish to express our sincere gratitude to Yu. V. Fomichev for his help with the gas analysis.

TABLE 2. Products of CH_3OH Electrooxidation

Solution	Rate of rotation, rpm	φ ch, mV	Current efficiency, %		
			H_2CO	HCOOH	CO_2 (by difference)
1 *N* H_2SO_4	710	522—531	2.6	9.0	88.4
+0,5 *M* CH_3OH	2000	519—527	3.2	10.8	86.0
1 *N* KOH	710	453—465	1.0	68.0	31.0
+0,5 *M* CH_3OH		450—468	1.0	71.0	28.0

These data were in good qualitative agreement with previous work [2, 15]; some quantitative deviations are probably due to differences in the potential of CH_3OH oxidation.* According to the measurements in acid, the oxidation of CH_3OH was only slightly dependent on the rotation speed of the disk electrode; as a first approximation this showed the absence of diffusion limitation. From Table 2 it can be seen that unlike the process of the electrooxidation of a stable chemisorbed substance, CO_2 was not the sole product; in the case of alkaline solutions, CO_2 was not even the primary product, of electrooxidation of CH_3OH under equilibrium conditions.

On the basis of our work, and also of earlier data [5, 6], oxidation of CH_3OH under equilibrium conditions (the degree of oxidation of the original substance being small), may be represented by several parallel reactions:

$$CH_3OH_{p\text{-}p} \rightarrow CH_3OH_{ads} \begin{cases} \rightarrow CS \xrightarrow{i_1} CO_2 \\ \rightarrow A_1 \xrightarrow{i_2} CO_2 \\ \rightarrow A_2 \xrightarrow{i_3} HCOOH\ (HCOO^-) \\ \rightarrow A_3 \xrightarrow{i_4} H_2CO, \end{cases}$$

where CS is the stably chemisorbed species observed at the electrode after washing (the presumed composition being HCO [8, 9, 13], COOH or CO_2 [16], $H_2C_2O_3$ [17]); A_1, A_2, and A_3 are relatively weakly adsorbed (or chemisorbed) particles present on the electrode in small quantity and removed during washing. Considering the composition of the final product and also the fact that the overpotential of the oxidation of CS is higher than the overpotential of methanol oxidation under equilibrium conditions [5, 6], for acid solutions the following relative rates of parallel reactions can be assumed: $i_2 > i_3$, i_4, and i_1; for alkaline solution: $i_3 > i_2 > i_1$ and i_4. Consequently, it can be assumed that the composition, properties and also the mechanism of the oxidation of species CS and A for acid and alkaline solutions are definitely different [6]. However, in alkaline and also acid media, species CS, even though it is one of the intermediate products of the current-determining reaction, cover the surface and simultaneously passivate the electrooxidation of CH_3OH. In an analogous manner, the explanation of the role of CS in the general process of methanol oxidation was discussed recently by Breiter [17]. The passivating action of stably chemisorbed substances appears in storage form in the oxidation of HCOOH on Pt [18-20].

The previously noted similarity [6, 13] in the rate dependence of the oxidation of CH_3OH and CS under equilibrium conditions on φ_r, pH, and temperature, apparently, is due to the similarity in the mechanism of oxidation of CS and species A_1, taking part in the rate-determining step of, at least, the most rapid reactions. In connection with this, species A_1 and A_2 (but not species A_3) may be identical to CS, differing only in the rates of reaction and the final products of the reaction may be determined only by a difference in the bonding energy with the surface.† Schemes of the possible rate-determining steps were considered before [6]. When the parallel reactions are taken into account, some additional conditions must be stipulated for the explanations offered in [6] for the observed dependence of i on φ_r and pH [6]. Thus, in the interval of where the Tafel dependence was maintained, the relative rates of the separate parallel reactions do not undergo a large change with changing φ_r and pH. This may be expected if at that φ_r, an approximately constant surface coverage by CS (determined experimentally [5, 6]) corre-

*Previously [2, 15] the electrooxidation of CH_3OH was performed at higher φ_r ($\geq$ 0.6 V) where there is a deviation of the φ_r-i relation from the Tefel equation.

†In this case the views developed in our work and by others [9] are fairly close; but the dependence of the oxidation rate of CS on θ_{CS} [19, 22] leads one to expect a discrete change in the bond energy in going from CS to species A_1 or A_2.

sponds to $\theta_{A_1} \simeq$ constant. Apparently, these conditions are satisfied only approximately, which may be one of the primary reasons for the difficulties in quantitative interpretation of the experimental data for electrochemical oxidation of CH_3OH under equilibrium conditions, particularly in alkaline solutions [6].

In our work as well as in others [5, 6] the mechanism of CH_3OH oxidation at constant and complete surface coverage by species CS is considered, whereas the Temkin mechanism, established for methanol oxidation on smooth Pt, is related to the range of intermediate values of θ_{CS} [8, 9]. Apparently, definite discrepancies are to be expected in the analysis of the role of CS in the methanol oxidation on smooth and platinized Pt, owing to the different states of CS caused by different experimental conditions. Activation of the smooth Pt electrode before plotting each point and a short time span (2-8 min) for establishment "stationary" i-φ_r points make it possible to consider these points as "quasi-stationary" in relation to Pt/Pt [5, 6].

After introduction of methanol (0.5 M) into contact with a Pt/Pt electrode with oxides present on its surface with oxides,* HCOOH appears in solution in $\sim 2 \cdot 10^{-4}$ M concentration in 1 N H_2SO_4 and $\sim 7.7 \cdot 10^{-4}$ M in 1 N KOH. No H_2CO was detected. Evolution of CO_2 was observed visually. There is a similarity in the obtained results with the data of analysis of the products of CH_3OH oxidation under equilibrium conditions. The interaction of surface oxides with CH_3OH can be assumed to be at least partially determined by the two mixed reactions: methanol oxidation and the reduction of O_{ads}, each proceeding on different parts of the surface (analogous to the interaction of Pt oxides with H_2 [21]).

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