ELECTROCHEMICAL BEHAVIOUR OF SOME OLEFINS AND PRODUCTS OF THEIR CHLOROHYDROXYLATION ON PLATINUM AND GRAPHITE ELECTRODES

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The electrochemical behaviour on platinum and graphite electrodes of propylene, 1,3-butadiene and products of their chlorohydroxylation by electrochemically generated chlorine has been studied. It has been demonstrated by two methods: the potential sweep method with the use of a rotating disc electrode and the galvanostatic method. On graphite electrodes (unlike on platinum) redox reactions occur at a very low rate.

At present much attention is being given to the use of electrochemically generated chlorine in production of industrially important compounds: propylene chlorohydrin (PCH) from propylene, glycerol dichlorohydrin (GDCH) from allyl chloride and dichlorobutandiol (DCBD), mainly consisting of 1,4-dichloroisomer from 1,3-butadiene. In the case of propylene, for example, the following reactions take place:

$$2\,Cl^- - 2\,e \rightarrow Cl_2$$

$$Cl_2 + H_2O \rightarrow HCl + HClO$$

$$CH_2{=}CH{-}CH_3 + HClO \rightarrow CH_2Cl{-}CHOH{-}CH_3\,.$$

It is essential to choose the optimum conditions and, especially, the most suitable electrodes for synthesis. With this object in view we studied the electrochemical behaviour of the above-mentioned substances on platinum and graphite electrodes, which are most promising for use in electrochemical chlorohydroxylation.

In addition to chlorine and hydrogen discharge processes, chlorohydroxylation in a diaphragmless cell can be attended by some other reactions, such as oxidation and reduction of starting compounds and reaction products. For this reason it is also important to examine their electrochemical behaviour on the two electrodes mentioned.

The most detailed studies on the electrochemical behaviour of the substances under consideration were made in the case of propylene on a platinum electrode[1-4].

There is less information on the behaviour of 1,3-butadiene[5,6] and allyl chloride and none at all on DCBD, PCH and GDCH. No studies were made on the behaviour of any of these substances on a graphite electrode. We compared their electrochemical behaviour on platinum and graphite electrodes.

EXPERIMENTAL

We studied the electrochemical behaviour of the compounds mentioned by two methods: the potential sweep method with the use of a rotating disc electrode and the galvanostatic method (chronopotentiometry). The chronopotentiometric and potential sweep measurements were performed in a three-electrode cell. The potentiodynamic curves were measured on a rotating disc electrode at the sweep rate 200 and 400 mV/min. The rate of rotation was controlled within 60 – 10 000 r.p.m. The electrodes (platinum and graphite) were in the form of discs, from 1 to 10 mm in diameter, tightly pressed into teflon. A platinized platinum plate served as an auxiliary electrode. Before measurements the working platinum electrode was washed first with alcohol then very thoroughly with water and subjected to alternating cathodic-anodic polarization. In the text and on figures the potentials are referred to the normal hydrogen electrode (N.H.E.), although 0·1M calomel electrode is used as a reference electrode. In the case of the platinum electrode the current density values are given for true surface and in the case of the graphite electrode for geometric surface. All experiments were carried out at 85°C; at lower temperatures the electrochemical oxidation reaction rate is too small. To obtain reproducible data the graphite electrode prepared by us was subjected to treatment for removal of heavy metal admixtures especially iron, by boiling first in concentrated hydrochloric acid during hours, several times substituting fresh portions of acid, then for several hours in boiling bidistillate changing the water many times. Before plotting each set of the curves, the electrode was polished on rough glass, washed with alcohol and boiled in three portions of bidistillate, 10 minutes in each. We have found this treatment to give well reproducible results.

The chronopotentiometric curves were measured according to the three-electrode scheme by means of a chronopotentiometer which allowed keeping the electrode at a fixed potential and applying both positive and negative galvanostatic pulses (up to 3 mA).

Sulphuric acid solutions with or without additions of potassium chloride (twice recrystallized from bidistillate and heated at 600°C) were used as electrolyte. For preparation of sulphuric acid solutions twice distilled concentrated sulphuric acid was used.

Before starting experiments purified argon was bubbled through solution (during 1 hour) and the curve for the supporting electrolyte was measured. Then the solution was saturated with the required gaseous organic substance. The DCBD, PCH and GDCH solutions were of definite concentration.

RESULTS AND DISCUSSION

The experimental device and the cell as well as the procedure of calculating the adsorption from the chronopotentiometric data are described in[7].

The potentiodynamic curve obtained with the use of a rotating platinum disc electrode in the presence of 1,3-butadiene is given on Fig. 1 (curve *b*). The wave height at the peak potential does not depend on the rate of rotation, which points to practically complete absence of diffusion hindrances. As can be seen from Fig. 1 (curve e), the presence of chlorine ions in solution shifts the oxidation wave of 1,3-butadiene in the direction of positive potentials. Similar dependences were obtained for propylene and allyl chloride.

The slow step limiting the peak height is either olefin adsorption or slow charge transfer to fragments formed as the result of destructive adsorption of the organic substance. In the latter case the current decrease can be due to passivation of electrode surface by adsorbed oxygen.

In order to find the reason of the current decrease observed on Fig. 1 (curves *b*,e) we subjected the platinum electrode to polarization under potentiodynamic conditions on 0·05M-H_2SO_4 solution at the potentials 0·7, 0·8 and 0·9 V, so that the amount of electricity passed through the electrode should be the same at all potentials. In the case of slow adsorption of olefin, or passivation by reaction products, the amount of electricity necessary for decreasing the current to a certain value should be the same. In actual fact, the picture was quite different: at the potential 0·7 V the current was practically independent of the amount of electricity passed through the

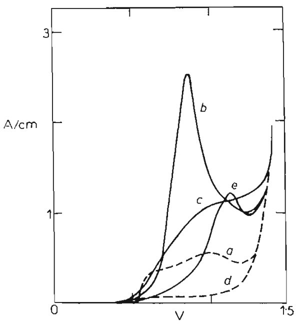

FIG. 1

Anodic potentiodynamic curves for a platinum electrode obtained passing through 0·05M-H_2SO_4: *a* argon, *b* 1,3-butadiene; through 0·05M-H_2SO_4 + 0·1M-KCl solution: *d* argon, e 1,3-butadiene; *c*: 0·05M-H_2SO_4 + + 0·1M-DCBD. The sweep rate (v) 400 mV/min, m = 3 000 r.p.m.

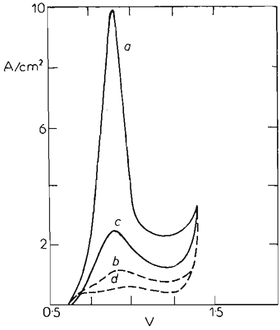

FIG. 2

Potentiodynamic curves for a graphite electrode obtained passing through 0·05M-H_2SO_4: *a* 1,3-butadiene, *b* argon. The same for a platinum electrode: *c* 1,3-butadiene, *d* argon; v = 400 mV/min; m = 3 000 r.p.m.

electrode, at 0·8 V it decreased markedly and at 0·9 V it dropped practically instantly 5 – 10 times as compared to initial value. This result could be interpreted as testifying in favour of the suggestion of an inactivation process by adsorbed oxygen layers. Below we will show that the chronopotentiometric studies support this conclusion.

On platinum, under potentiodynamic conditions GDCH, PCH, and DCBD undergo oxidation at a much lower rate than olefins. This is clearly evident in the case of 1,4-dichlorobutandiol (Fig. 1, curve *c*). In spite of its very high concentration the oxidation current of DCBD is small. As would be expected, it does not depend on the rate of rotation.

Propylene is known to be readily reduced on platinum. So are 1,3-butadiene and allyl chloride, whereas PCH, GDCH and DCBD are not reduced, though they increase hydrogen overvoltage. This proves that the chloro alcohols mentioned are adsorbed on platinum.

On graphite, under potentiodynamic conditions propylene, 1,3-butadiene and allyl chloride are as easily oxidized as on platinum (Fig. 2), in the case of 1,3-butadien (curve *a*) the peak current on graphite being much higher than on platinum (curve *c*). Just as for platinum, the peak currents do not depend on the rate of rotation of the electrode.

On the contrary, GDCH, PCH and DCBD are not oxidized on graphite, but decrease the supporting electrolyte current, the more, the higher is the chloro alcohol concentration. 1,3-butadiene, propylene, allyl chloride, PCH, GDCH, DCBD are not reduced on a graphite electrode. This points to complete inactivity of these chloro alcohols on graphite.

Since the scan rates of sweeping potential were not high, the method under consideration proved unsatisfactory in quantitative investigation of the adsorption of the above-mentioned substances. Much more information was obtained by chronopotentiometry.

Fig. 3 (curve *c*) shows the total charging curve in $0{\cdot}1\text{N-H}_2\text{SO}_4$ solution. This curve consists of three sections: I – desorption of adsorbed hydrogen. II – double layer, III – oxygen adsorption. In the presence of olefins the curve is markedly distorted (Fig. 3, curves *a*, *b*): section I disappears, so that the double layer section becomes steeper, which, undoubtedly,indicates that the hydrogen surface concentration is decreased by fragments formed as the result of destructive adsorption of olefin on platinum. In the presence of propylene, 1,3-butadiene, GDCH, DCBD and PCH, section III – oyxgen adsorption is substituted by a potential arrest (Fig. 3) which ends in the region of more positive potentials.

Comparison of the curves on Fig. 3 shows that the arrests on the charging curves in the presence of propylene are as clearly defined as in the case of 1,3-butadiene oxidation, where the potentials of the arrests are somewhat less positive than in the case of propylene. From these arrests we plotted for all substances investigated the curves of the dependence of the amount of electricity corresponding to the arrest of the pre-exposure potential.

In determining the extent of adsorption on the basis of the obtained charging curves, it is necessary to take into consideration the possibility that its value thus calculated will be too high for the following reasons: *a*) due to additional oxidation of an electrochemically active substance as the result of diffusion; *b*) because part of the electricity was expended in additional oxygen adsorption on the sites freed due to oxidation of adsorbed substance during the anodic pulse. The amount of electricity corresponding to the arrest does not depend on the current density in a wide range of its values. This means that the contribution of diffusion to the arrest on the curves of Fig. 3 is insignificant.

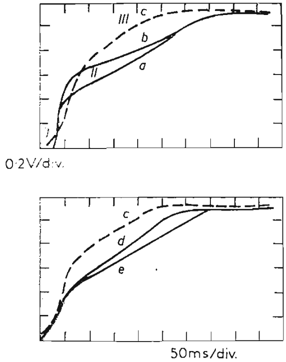

FIG. 3

Charging curves for a platinum electrode ($i = 3 . 10^{-3}$ A/cm^2, $E_\circ = 0{\cdot}1$ V) obtained passing through 0·05M-H_2SO_4: *a* 1,3-butadiene, *b* propylene, *c* argon; Cerovex obtained in the presence of: *c* 10^{-3}M-PCH and *d* DCBD in the same supporting electrolyte

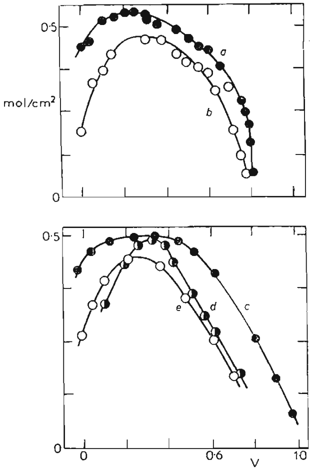

FIG. 4

Curves of the dependence of adsorption on a platinum electrode on potential obtained passing through 0·05M-H_2SO_4: *a* 1,3-butadiene, *b* propylene and in the presence of: *c* DCBD, *d* PCH and *e* GDCH in 0·05M-H_2SO_4 + 10^{-3}M chlorohydrin solution

It was estimated by means of the cathodic charging curves measured in solutions of the supporting electrolyte and the substance being examined that about 40% of the amount of electricity corresponding to the total arrest on the charging curve is accounted for by oxygen.

Fig. 4 shows the curves of the dependence of propylene (*b*) and 1,3-butadiene (*a*) adsorption on potential and those for GDCH (*e*), DCBD (*c*) and PCH (*d*) plotted from chronopotentiometric data taking into consideration what has been said above.

It can be readily seen that the curves are all bell-shaped with a peak in the potential range from +0·1 to +0·4 V. In the potential range more positive than 0·9 V, or close to the reversible hydrogen electrode potential, adsorption of olefins is practically nonexistent. Comparison of curves *a* and *b* on Fig. 4 shows that the amount of electricity consumed in adsorbed 1,3-butadiene oxidation is somewhat greater than for propylene. The region of 1,3-butadiene adsorption is also somewhat broader.* A similar calculation of the number of electrons was also performed for benzene[8]. As propylene oxidation requires 18 electrons the charges necessary for desorption of monolayers of these substances should differ in the ratio 1 to 1·2. Fig. 4 shows that this is the actual ratio.

It follows from Fig. 4 that the adsorption region of DCBD is much broader than that for PCH, GDCH and allyl chloride. Evidently it is not the presence of two chlorine atoms in a DCBD molecule which is responsible for this fact, because a GDCH molecule contains the same number of chlorine atoms. Most likely, the sharp increase of adsorbability is due to a larger number of hydroxyl groups in a DCBD molecule.

The chronopotentiograms obtained in the presence of chlorine ions show that the charging curves of platinum have some specific features. In particular, the section corresponding to oxygen adsorption (Section III, Fig. 3) is absent. Instead here appears a section corresponding to chlorine adsorption. These specific features of the charging curves in the presence of chlorine ions are well known and are explained by the antagonism between chlorine and oxygen during the adsorption process: in the presence of chlorine ions in solution formation of adsorbed oxygen layers is hindered. On the other hand, oxygen adsorption on platinum surface hinders chlorine adsorption.

The presence of chlorine ions alters insignificantly the length of the arrest corresponding to oxidation of all the substances studied but affects markedly the shape of the charging curve. The presence of olefins and product of their chlorohydroxylation in Cl^--ions containing solutions decreases sharply the capacity of the platinum electrode in the double layer region. Here, however, the double layer region is much broader than in the absence of chlorine ions, and the arrests due to desorption

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* 1,3-butadiene oxidation to CO_2 requires 22 electrons per molecule.

of hydrocarbons as the result of electrochemical reaction are located at much more positive potentials than in the absence of chlorine ions. Undoubtedly, this points to a connection between the kinetics of electrochemical oxidation of olefine and the existence on the electrode surface of adsorbed oxygen atoms. Evidently, the presence of adsorbed oxygen atoms favours oxidation of the fragments formed as the result of destructive adsorption of hydrocarbons. Let it be recalled that the same adsorbed oxygen atoms forming part of oxide layers hinder the oxidation process. The charging curves in the presence of Cl^--ions have an important distinctive feature, namely the arrest corresponding to desorption of the adsorbed organic substance layer begins at more negative potentials than the potential at which chlorine adsorption on platinum starts. This fact can have only one meaning, *viz.* that desorption of organic substance, from the surface is associated not with its chlorination but with its oxidation.

Nevertheless, it is known that in solutions containing chlorine ions anodic polarization of platinum leads to formation of the products of chlorination or chlorohydroxylation of unsaturated hydrocarbons. These results and the kinetic data can only be reconciled by assuming that chlorination and chlorohydroxylation are chemical processes occurring in solution bulk upon transition into it of ion radicals formed as the result of oxidation of unsaturated hydrocarbons adsorbed on platinum. The scheme of the reactions which may occur *e.g.* in the case of propylene, is given by equations (*1*)–(*4*):

$$C_3H_6 - e \rightarrow C_3\dot{H}_6^+ \qquad (1)$$

$$C_3\dot{H}_6^+ + Cl^- \rightarrow C_3H_6Cl^{\bullet} \qquad (2)$$

$$C_3H_6Cl^{\bullet} - e \rightarrow C_3H_6Cl^+ \qquad (3)$$

$$C_3H_6Cl^+ + H_2O \rightarrow C_3H_6ClOH + H^+ . \qquad (4)$$

It should be pointed out, however, that at high current densities an ordinary chemical reaction is more likely to occur in accordance with the equation:

$$C_3H_6 - 2e + Cl^- + H_2O \rightarrow C_3H_6ClOH + H^+ . \qquad (5)$$

When polarizing platinum by a cathodic galvanostatic pulse, it was found that in the presence of PCH, allyl chloride and DCBD, there is no arrest on the chronopotentiogram, the charging curves lie at more negative potentials than that of the supporting electrolyte: upon cathodic polarization the above-mentioned substances adsorbed on the electrode are electrochemically inactive.

In the case of solutions through which divinyl or propylene have been bubbled the cathodic chronopotentiogram shows a clearly defined arrest, which disappears at the pre-exposure potentials more positive than 0·4 V. The length of these arrests is almost by an order of magnitude less than on anodic chronopotentiograms. As would be expected, it is clear from the cathodic potentiodynamic curves that 1,3-butadiene is somewhat more readily reduced than propylene.

The charging curves obtained for a graphite electrode have nothing in common with those for a platinum electrode at the same current densities.

Neither in sulfuric acid solutions nor in solutions containing chlorides are there any arrests on the charging curves corresponding to oxidation of olefins or their chlorohydroxylation products. In the case of graphite the charging curves obtained in the presence of the above mentioned organic substances lie higher than those obtained in the supporting electrolyte. This result unambiguously indicates, first, that divinyl, propylene and their chlorohydroxylation products are adsorbed on graphite and, second, that the oxidation rate of these substances on graphite is much lower than on platinum: only at very small current densities ($i \leqq 10^{-4}$ A/cm^2) the curve obtained in the presence of 1,3-butadiene and propylene lies lower than that measured in the supporting electrolyte. On platinum, however, even at the highest current densities ($i = 6 . 10^{-3}$ A/cm^2) the arrest is quite pronounced. Hene its follows that the true oxidation rate of these substances onplatinum is at least by there orders higher than on graphite.

Thus, on graphite, 1,3-butadiene and propylene undergo oxidation to an appreciable degree only under polarization by negligible current densities ($i \leqq 10^{-4}$ A/cm^2), which are at least by two orders of magnitude less than those used in synthesis of DCBD and GDCH[9,10] so that the oxidation process may be ignored.

Summing up, it should be pointed out that the measurements carried out demonstrate that graphite electrodes have unquestionable advantages in the case of electrochemical chlorohydroxylation of olefins in a diaphragmless cell in spite of the fact that platinum has a higher stability in diluted hydrochloric acid. In the case of graphite electrodes no electrochemical side transformations of substances and reaction products are possible which would lead to a decrease of the target product yield. It is also evident from our studies that the appropriate electrode material and electrolysis conditions can be chosen by studying the kinetics of electrochemical reactions at electrodes from different materials.

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