3. Mechanisms have been proposed for the electrode reactions.

1. A.N.Frumkin, V.S.Bagotskii, Z.A.Iofa, and B.N.Kabanov, "Kinetika Elektrodnykh Protsessov" (Kinetics of Electrode Processes), Izd.Moskov.Gos.Univ., 1952.
2. H.Gerischer, Z.phys.Chem.(Leipzig), 202, 292, 302(1953); Z.Elektrochem., 57, 604 (1953).
3. A.G.Stromberg, "Trudy IV Soveshchaniya po Elektrokhimii" (Proceedings of the Fourth Electrochemical Conference), Izd.Akad.Nauk SSSR, 1959, p.213.
4. N.V.Gudin, "Materialy Elektrokhimicheskoi Konferentsii" (Proceedings of the Electrochemical Conference), Kazan, 1959, p.67.
5. A.A.Galkin, Ya.L.Shamfarov, and A.V.Stefanishina, Zhur. Eksper.Teor.Fiz., 32, 1581 (1957).
6. O.H.Geske and A.H.Maki, J.Amer.Chem.Soc., 82, 2671 (1960).
7. A.H.Maki and O.H.Geske, J.Amer.Chem.Soc., 83, 1852 (1961).
8. L.H.Piette, P.Ludvig, and R.N.Adams, Analyt.Chem., 34, 916 (1962).
9. N.V.Gudin and M.S.Shapnik, Symposium, "Teoriya i Praktika Blestyashchikh Gal'vanopokrytii" (Theory and Practice of the Production of Bright Electrodeposits), Izd. Akad.Nauk Lit.SSR, Vilna, 1963, p.217.
10. L.A.Belyakova and N.V.Gudin, *ibid.*, p.227.
11. B.M.Kozyrev, Doctoral Thesis(D.Sc.Equivalent), Physical Institute of the USSR Academy of Sciences, Moscow, 1957.
12. N.N.Tikhomirova and K.I.Zamaraev, Zhur.Strukt.Khim., 4, 224 (1963).

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INITIATION OF THE POLYMERISATION OF METHYL METHACRYLATE AT A LEAD ELECTRODE

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In the cathodic polarisation of a lead electrode in aqueous acid solutions of methyl methacrylate some workers[1-4] observed polymerisation, which in their view was initiated by the hydrogen atoms formed on the lead cathode. This view contradicts the electrochemical theory of hydrogen overvoltage and the results of numerous investigations of the hydrogen overvoltage of the lead cathode[5-7], and in any case lacks adequate experimental justification, since the above workers did not measure the electrode potential and introduced the monomer into the reaction medium in contact with air.

In the present study an attempt was made to obtain the polymer by electrolysis of saturated acid solutions of methyl methacrylate over a period of several hours at cathode potentials φ = -1.20, -1.15, -1.07, and -0.9 V†. The potentials were selected on the basis of the hydrogen overvoltage–current density curves which were obtained from preliminary experiments on the lead electrode in the same solutions. The surface area of the cathode S = 2.0 cm² and the volume of the electrolyte V = 20 ml. The electrolysis and the experiments designed to investigate the effect of methyl methacrylate on the hydrogen overvoltage were carried out at 20.0° in solutions freed from traces of oxygen; the absence of oxygen was checked by preliminary measurements of the hydrogen overvoltage in 1 N sulphuric acid without the monomer. Particular attention was paid to the cleaning of the lead electrode, and the purification of the reagents and the monomer; after preliminary purification and double distillation at a reduced pressure in a current of nitrogen, the monomer was introduced into the reaction medium out of contact with air[8].

The results of the electrolysis, which were found to be reproducible in numerous experiments, showed that there was no visible formation of the polymer over a period of 6–20 h at a lead electrode in 1 N sulphuric acid saturated with methyl methacrylate and also in the presence of an excess of the monomer as a second phase.

At cathode potentials φ = -1.20, 1.15, and -1.07 V polymerisation always took place when, other conditions being the same, the monomer came into contact with atmospheric oxygen before being introduced into the reaction mixture or when small amounts of hydrogen peroxide were added to the latter. However, under these conditions it cannot be assumed that hydrogen atoms initiate the reaction, since the reduction of hydrogen ions might be accompanied by the simultaneous cathodic reduction of peroxy-compounds of the monomer, formed when the latter came into contact with atmospheric oxygen, or the products of their decomposition (carbonyl compounds).

To elucidate the effect of methyl methacrylate on the reduction of hydrogen ions, we obtained overvoltage–current density curves in a pure hydrogen atmosphere and also after introduction of the monomer which had been in contact with atmospheric oxygen. The overvoltage–current density curves obtained in a pure hydrogen atmosphere in 0.5 M H_2SO_4 solutions containing the monomer at varying concentrations showed that the overvoltage is reduced over the entire potential range investigated (Fig. 1). The effect depends on the concentration of the monomer and the electrode potential. As the concentration of methyl methacrylate is increased, the overvoltage falls further, the lowering extending to higher current densities. In saturated acid solutions of the monomer at a current density i = $= 1 \times 10^{-3}$ A cm^{-2} the hydrogen overvoltage for a negatively charged electrode surface is reduced by 0.150 V. At certain current densities, which are higher the greater the concentration of methyl methacrylate, the hydrogen overvoltage becomes equal to that in 1 N sulphuric acid without the monomer.

The lowering of the overvoltage appears to be related to catalytic evolution of hydrogen[9], for the first time observed on a solid electrode. As an ester, methyl methacrylate possesses weakly basic porperties and interacts with sulphuric acid to form a protonated species[10] which by virtue

† The potentials of the test electrode are in all cases given relative to the normal hydrogen electrode.

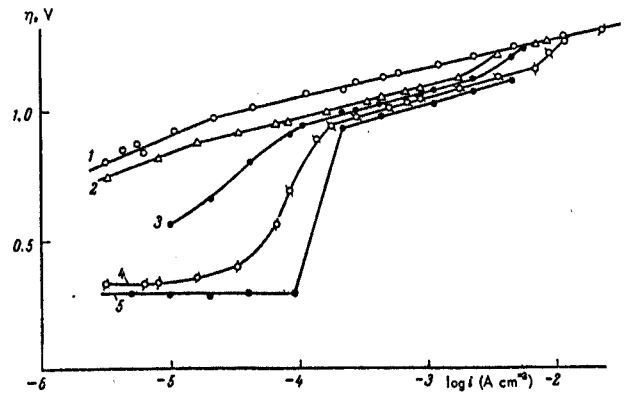

Fig.1. Variation of hydrogen overvoltage with the polarising current density at the lead electrode:
1) 1 N H_2SO_4; 2) 1 N H_2SO_4, 10% saturation of methyl methacrylate; 3) 1 N H_2SO_4, 20% saturation of methyl methacrylate; 4) 1 N H_2SO_4, 50% saturation of methyl methacrylate; 5) 1 N H_2SO_4 saturated with methyl methacrylate.

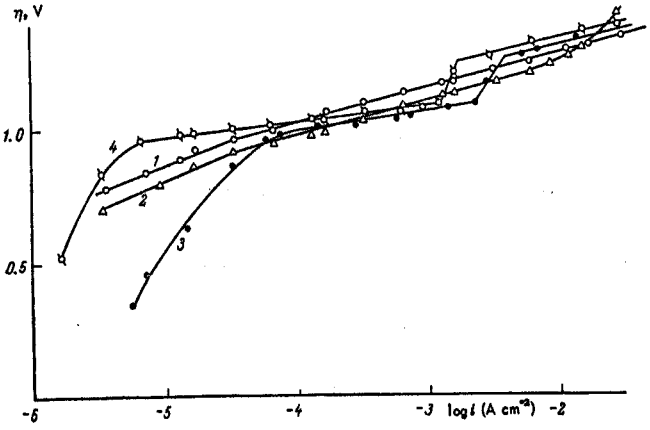

Fig.2. Variation of hydrogen overvoltage with the polarising current density at the lead electrode:
1) 1 N H_2SO_4; 2) 1 N H_2SO_4, $^1/_6$ saturation with methyl methacrylate; 3) 1 N H_2SO_4, $\frac{1}{3}$ saturation with methyl methacrylate; 4) 1 N H_2SO_4 saturated with methyl methacrylate.

of its surface-active properties is strongly adsorbed on the electrode, thereby accelerating the evolution of hydrogen.

The differential capacitance curve for the electrode measured during the reduction of hydrogen ions in the presence of methyl methacrylate shows that a surface-active substance is adsorbed on the electrode over the potential range from 0.25 to -1.15 V. The accelerating effect of the monomer on the evolution of hydrogen occurs in the same potential range.

The $\eta-\log i$ curves, obtained under the same conditions but in the presence of methyl methacrylate which had been in contact with atmospheric oxygen before being added to the reaction medium, have a different shape (Fig. 2). At low current densities the hydrogen overvoltage falls and then rises as the current density is increased to values

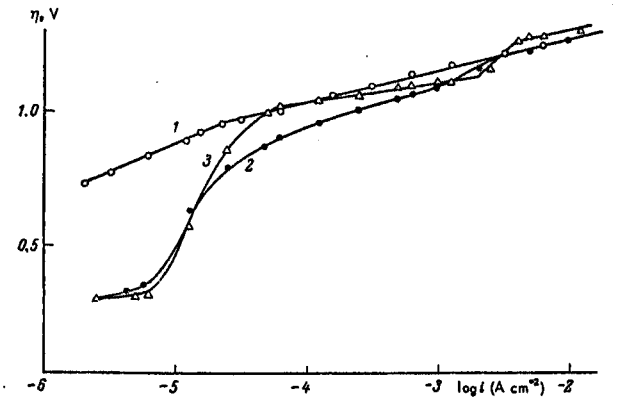

Fig.3. Variation of hydrogen overvoltage with the current density at the lead electrode:
1) 1 N H_2SO_4; 2) 1 N H_2SO_4 + 2 × 10^{-3} N H_2O_2;
3) 1 N H_2SO_4 + 2 × 10^{-3} N H_2O_2 saturated with methyl methacrylate.

which are higher than in the absence of the monomer (Fig. 2, curve *2*), to an extent which depends on the concentration of the monomer. Unlike the case described above (Fig. 1), the rise above the value in the absence of monomer occurs at a higher concentration of the monomer the lower the polarisation, this being due not to desorption of the monomer but to its polymerisation, which is initiated primarily by the electrochemical reduction of the peroxy-compounds of the monomer, formed when the latter was in contact with atmospheric oxygen, or the products of their decomposition (carbonyl compounds).

The $\eta-\log i$ curve obtained in the solution containing hydrogen peroxide and the monomer which had not been in contact with air has a similar shape (Fig. 3). Methyl methacrylate introduced into 1 N sulphuric acid containing H_2O_2 inhibits the reduction of the latter which occurs at more positive electrode potentials than the reduction of hydrogen ions. This is reflected on the $\eta-\log i$ curve by an increase in the overvoltage (*cf.* curves *2* and *3* in Fig. 3). At more negative potentials the shape of the curve is determined by the catalytic evolution of hydrogen, and finally at even more negative potentials the hydrogen overvoltage increases as a result of adsorption on the electrode of the polymerisation product.

SUMMARY

Visible formation of the polymer in an acid saturated aqueous solution of methyl methacrylate at the reduction potentials of hydrogen ions occurs only in the presence of peroxy-compounds in the monomer. The reduction of hydrogen peroxide added to the methyl methacrylate solution accelerates the formation of the polymer.

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1. E.Dinen, T.Schwan, and C.Wilson, Trans.Electrochem. Soc., 96, 226 (1949).
2. G.Parravano, J.Amer.Chem.Soc., 73, 628 (1951).
3. W.Kern and H.Quast, Makromol.Chem., 10, 202 (1953).
4. N.S.Tsvetkov, Vysokomol.Soed., 4, 549 (1961).

5. A.N.Frumkin, V.S.Bagotskii, Z.A.Iofa, and B.N.Kabanov, "Kinetika Elektrodnykh Protsessov" (Kinetics of Electrode Processes), Izd.Moskov.Gos.Univ., Moscow, 1952.
6. Ya.M.Kolotyrkin and A.N.Frumkin, Zhur.Fiz.Khim., 15, 346 (1941); Ya.M.Kolotyrkin and N.Ya.Bune, *ibid.*, 21, 581 (1947).
7. B.N.Kabanov, S.T.Filippov, L.I.Banyukov, and Z.A.Iofa, Zhur.Fiz.Khim., 13, 341 (1939).
8. A.I.Fedorova, I.V.Shelepin, and N.B.Moiseeva, Dokl. Akad.Nauk SSSR, 138, 165 (1961).
9. A.N.Frumkin and E.P.Andreeva, Dokl.Akad.Nauk SSSR, 90, 417 (1953).
10. O.A.Reutov, "Teoreticheskie Problemy Organicheskoi Khimii" (Theoretical Problems of Organic Chemistry), Izd. Moskov.Gos.Univ., 1956.

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TABLE.

Reaction product	^{18}O content (at. %) in excess of the natural level in various compounds: in initial H_2O	in initial H_2O_2	in initial $^{18}O_2$	in product	Uptake of $^{18}O_2$, %	Experimental conditions
			$H_2O_2 + Fe^{2+}$			
Phenol	0.81	—	—	0.16	20%	0.13 mole of 2% H_2O_2, 1–2 drops of $HClO_4$, 0.26 mole of benzene, and 0.008 mole of $FeSO_4.7H_2O$ were shaken for 15–20 min in a vacuum, until the mixture blackened and became spontaneously heated to 60°
	0.77	—	—	0.18	23%	
	—	0.59	—	0.42	71%	
	—	0.59	—	0.42	71%	
Catechol	0.81	—	—	0.09	11%	
	0.77	—	—	0.08	10%	
	—	0.59	—	0.54	92%	
	—	0.59	—	0.55	93%	
			$H_2O_2 + Cu^{2+}$			
Phenol	1.09	—	—	0.16	15%	0.23 mole of 8% H_2O_2, 1.7 mole of benzene, and 0.012 mole of $CuSO_4$ were shaken in a vacuum for 45–50 h at room temperature
	1.09	—	—	0.18	18%	
			$H_2O_2 + Fe^{2+} + {}^{18}O_2$			
Phenol	—	—	2.22	0.11	5%	the same conditions as in the preceeding experiment without O_2; flow rate of $^{18}O_2$ 0.006–0.007 litre × × s^{-1}
	—	—	2.22	0.12	5%	

OXYGEN TRANSFER IN THE HYDROXYLATION OF BENZENE WITH HYDROGEN PEROXIDE IN THE PRESENCE OF FERROUS AND CUPRIC IONS

N.A.Vysotskaya

Using oxygen-18, it was shown earlier[1-2] that in the oxidation of phenol and salicylaldehyde with Fenton's reagent ($H_2O_2 + Fe^{2+}$) the oxygen of the hydroxy-group introduced into the compound being oxidised originates from the peroxide. Thus the rapid exchange of free OH radicals with water[3,4] or their generally accepted participation in the reaction became doubtful.

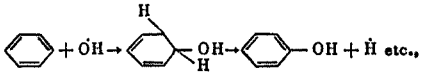
In the present work a study was made of the oxidation of benzene with Fenton's reagent and its analogue $H_2O_2 + Cu^{2+}$, and it has been established that between 15 and 23% of the oxygen from water passes into the phenol. The data obtained are given in the Table below.

The isotopic analysis of $H_2{}^{18}O_2$ [5] and $H_2{}^{18}O$ [6] was carried out by standard methods. To facilitate analysis, phenol was first converted into tribromophenol or phenyl benzoate. The latter and catechol were analysed mass-spectrometrically as CO_2, obtained by decomposition in a silent discharge[7] or by heating with $HgCl_2$ in a vacuum[8]. Both methods gave concordant results. Allowing for the errors in the preparation of the samples, the accuracy of the analysis was 5%†. H_2O_2, O_2,[5,9] and the reaction products[10] do no exchange oxygen with water under the conditions of the experiment. The reaction products were identified from their melting points, which in all cases agreed with literature values.

The smaller extent of incorporation of oxygen from water into catechol (by a factor of two) compared with phenol can be explained by the initial formation of phenol with 20–23% of ^{18}O from water followed by its oxidation to catechol without the participation of water. The light oxygen isotope of the second hydroxy-group of catechol diminishes the concentration of ^{18}O by a factor of two. This is consistent with the author's previous data[1] on the oxidation of phenol with Fenton's reagent to catechol, the newly introduced hydroxy-group of which contained oxygen from the peroxide only.

The Table shows that more than 70% of the oxygen in the oxidised compounds comes from the oxidising agent. This excludes the mechanism of Baxendale and Maggee[11] in which the formation of the phenol hydroxy-group from water is postulated. The preferential incorporation of oxygen from peroxide cannot at present be explained unambiguously. The data obtained are consistent with another mechanism of Baxendale and Maggee:

$$H_2O_2 + Fe^{2+} \longrightarrow \dot{O}H + Fe(OH)^{2+}$$



if it is assumed that the OH radicals add on to benzene more rapidly than they undergo exchange with water, or that these rates are commensurate. Such a hypothesis is supported by the very high rate of addition of hydroxyl radicals to benzene in water at 23°, which is $(4.3 \pm 0.9) \times \times 10^9$ litre $mole^{-1}$ s^{-1}.[12]

The rate of oxidation of benzene by $H_2O_2 + Cu^{2+}$ is much lower than with Fenton's reagent, but the amount of oxygen passing from water into phenol differs only slightly in the two cases. This is probably because the rate-limiting stage is the formation of OH radicals and not their addition to benzene or exchange with water.

The present author's data also do not exclude a mechanism involving the oxidation of benzene by HO_2 radicals[13], which do not exchange oxygen with water, or a mechanism with intermediate formation of H_2O_2 complexes with iron ions and the reaction products[14]. Oxygen exchange in such complexes may be difficult. In this case the incorporation of oxygen from water would occur in some subsidiary stage.

The results obtained in experiments in the presence of gaseous $^{18}O_2$ are at the limit of the accuracy of the measurements. They show that the extent of incorporation of oxygen into phenol is only slight.

† The reason for the 6–9% systematic deficiency in the overall balance of ^{18}O remained obscure.