SovietRxiv

Soviet-era science, translated into English

A. I. FEDOROVA, I. V. SHELEPIN and N. B. MOISEEVA

1961

SovietRxiv

View the original and related papers at https://sovietrxiv.org/items/ru-196101.35151

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

A. I. FEDOROVA, I. V. SHELEPIN and N. B. MOISEEVA

POLYMERIZATION OF METHYL METHACRYLATE DURING THE ELECTROREDUCTION OF OXYGEN

(Presented by Academician A. N. Frumkin, December 29, 1960)

There are several works in the literature on the cathodic initiation of the polymerization of unsaturated organic compounds ([1–6]). A substantial shortcoming of these works is the absence of measurements of the electrode potential and the absence of indications that the medium in which the experiments were carried out was controlled for removal of oxygen. As will be shown in the present work, the electrode potential and the presence of oxygen play a major role in electrochemical initiation. Control of the degree of removal of oxygen from the electrolyte is especially necessary also because, in the opinion of the authors of a number of works, atomic hydrogen serves as the main initiator of polymerization in electroreduction reactions.

The aim of the present investigation is to determine the conditions for polymerization of the methyl ester of methacrylic acid (MMA) in acidic solutions at a mercury cathode. As electrochemical reactions initiating the polymerization of MMA in solution, the reduction reactions of molecular oxygen, hydrogen peroxide, and hydrogen ions were studied ([7]). The present communication gives results obtained in the electrolytic reduction of oxygen.

The experiments were carried out at 20° in acidic aqueous and aqueous-alcoholic solutions of MMA in electrochemical thermostated cells in which the cathode compartment was separated from the anode compartment by a closed ground-glass stopcock. All connections between the individual parts of the cells, as well as the devices for distilling the reagents, were made by ground joints. The design of the cells and of the devices for distilling the reagents ensured their tightness. The anode was a platinum palladized electrode, saturated with hydrogen so that during the experiment no oxygen was evolved in the anode compartment. The monomer was introduced without the latter coming into contact with air. Ampoules with MMA were broken inside the cell in a hydrogen atmosphere with the aid of a striker and an electromagnet. The purity of the mercury cathode and of the electrolyte was monitored by the value of the overvoltage for reduction of hydrogen ions measured before each experiment.

The reagents and gases were subjected to thorough purification. Commercial

SovietRxiv

Fig. 1. Dependence of the shape of the polarograms of oxygen reduction in a solution of 1 N H2SO4 in the presence of MMA on time. Division value along the abscissa 0.2 V; the beginning of each curve is shifted by 0.4 V. MMA concentration 0.02 M. 1 —without addition of MMA. 2, 3, 4, 5 —respectively after 1, 16, 31, 90 min after introduction of MMA

Figure 1: Fig. 1. Dependence of the shape of the polarograms of oxygen reduction in a solution of 1 N H2SO4 in the presence of MMA on time. Division value along the abscissa 0.2 V; the beginning of each curve is shifted by 0.4 V. MMA concentration 0.02 M. 1 —without addition of MMA. 2, 3, 4, 5 — respectively after 1, 16, 31, 90 min after introduction of MMA

chemically pure MMA was distilled in an atmosphere of nitrogen freed from traces of oxygen, in a glass column for precise rectification with a packing height of 400 mm. The second fraction, boiling at 43—43.5°/90 mm, was distilled further directly from the receiver in a nitrogen atmosphere at a pressure of 40 mm into ampoules, which were sealed in the frozen state and stored in a refrigerator at −20°. The monomer purified in this way should contain no traces of peroxides ([8]). Analysis for traces of polymer gave a negative result; n_D^{25} 1.4148, d_4^{20} 0.946. For preparation of the electrolyte, twice-distilled water, sulfuric acid, and methyl alcohol twice distilled in nitrogen were used. The mercury was subjected to chemical purification and double distillation in vacuum.

In order to select the electrode potential for experiments on initiating the polymerization of MMA during the electroreduction of oxygen, the effect of MMA on the process of reduction of O_2 at a mercury dropping electrode in acidic solutions was first studied with an automatic polarograph.

The polarograms obtained with MMA solutions show a distinctive character of the action of the latter on the process of oxygen reduction at a mercury electrode in acidic solutions. If freshly distilled MMA is rapidly introduced into the reaction medium to a concentration of $2.0 \cdot 10^{-2}$ M and the polarogram is measured, strong current oscillations are observed in the interval from $\varphi =$ +0.3 V* to the potential of hydrogen-ion reduction (Fig. 1).

Fig. 1. Dependence of the shape of the polarograms of oxygen reduction in a solution of 1 N H_2SO_4 in the presence of MMA on time. Division value along the abscissa: 0.2 V; the beginning of each curve is shifted by 0.4 V. MMA concentration 0.02 M. 1 —without addition of MMA. 2, 3, 4, 5 —respectively after 1, 16, 31, 90 min after introduction of MMA.

These oscillations decrease with time and, finally, the curve assumes the form of the initial one, with the difference that the second oxygen wave is found to be somewhat shifted toward more negative potential values.

This action of MMA is apparently connected with the fact that MMA, having been introduced into the solution, polymerizes in the adsorption layer and forms a film that causes changes in the dropping period. The damping of the current

SovietRxiv

Fig. 2. Effect of MMA concentration on the oxygen-reduction wave at a mercury dropping electrode in a solution of 1 N H_2SO_4: 1—without MMA; 2—0.033 M MMA; 3—0.066 M MMA; 4—0.1 M MMA; 5—0.4 M MMA with addition of methyl alcohol; the scale division along the abscissa axis is 0.2 V; the beginning of each curve is shifted by 0.4 V

Figure 2: Fig. 2. Effect of MMA concentration on the oxygen-reduction wave at a mercury dropping electrode in a solution of 1 N H_2SO_4: 1—without MMA; 2—0.033 M MMA; 3—0.066 M MMA; 4—0.1 M MMA; 5—0.4 M MMA with addition of methyl alcohol; the scale division along the abscissa axis is 0.2 V; the beginning of each curve is shifted by 0.4 V

oscillations with time can be explained by the fact that the introduced MMA during this time interacts with the oxygen dissolved in the bulk of the electrolyte, and, as a result of the chemical processes taking place, polymerization on the freshly forming surface of the dropping electrode ceases.

In accordance with the above, polarograms of MMA solutions prepared in air several hours before the measurements do not show current oscillations (Fig. 2). However, the shift of the hydrogen peroxide reduction wave toward more negative potential values is retained. The inhibiting effect on the reaction of hydrogen peroxide reduction depends on the monomer concentration; with an increase in the latter it becomes stronger. At a monomer concentration in solution of approximately 0.1 M, the hydrogen peroxide reduction wave is not observed at all on the polarogram, since

---

* The potential values of the electrode under study are in all cases given relative to the normal hydrogen electrode.

since the reduction of the latter already occurs at the reduction potential of hydrogen ions. Higher concentrations of monomer in the aqueous-alcoholic sulfuric acid solution also shift the oxygen-reduction wave toward negative potential values (Figs. 2, 5).

The initiation of MMA polymerization with accumulation of polymer was carried out on a stationary mercury cathode ($S = 10$ cm^2) in the reduction reaction

Fig. 2. Effect of MMA concentration on the oxygen-reduction wave at a mercury dropping electrode in a solution of 1 N H_2SO_4: 1—without MMA; 2—0.033 M MMA; 3—0.066 M MMA; 4—0.1 M MMA; 5—0.4 M MMA with addition of methyl alcohol; the scale division along the abscissa axis is 0.2 V; the beginning of each curve is shifted by 0.4 V.

of O_2, proceeding, as is known, in an acidic medium through the following stages:

SovietRxiv

Fig. 3. Polarization curve at 18°. 1–1 N H_2SO_4; 2–50% 1 N H_2SO_4 + 50% CH_3OH; 3–monomer solution in 50% 1 N H_2SO_4 + 50% CH_3OH after 3 hours of standing in air. MMA concentration 0.4 M

Figure 3: Fig. 3. Polarization curve at 18°. 1–1 N H_2SO_4; 2–50% 1 N H_2SO_4 + 50% CH_3OH; 3–monomer solution in 50% 1 N H_2SO_4 + 50% CH_3OH after 3 hours of standing in air. MMA concentration 0.4 M

$$O_2 + \bar{e} + H^+ \rightarrow HO_2, \tag{a}$$

$$HO_2 + \bar{e} + H^+ \rightarrow H_2O_2. \tag{b}$$

The electrode potential had a value equal to −0.2 V, i.e., approximately 0.1 V more negative than the potential of the oxygen-reduction half-wave in the presence of MMA. The potential was established upon introduction of the monomer and then maintained constant for 3 h; measurements were made of the dependence of current strength on time, and visual observations of the solution were carried out, on the basis of which the time of appearance of solid polymer was recorded. After completion of the experiment, the resulting polymer was separated from the solution, washed with water and alcohol, dried in a vacuum desiccator at room temperature, and weighed.

In addition to the main experiments on accumulation of polymer, control experiments were carried out under the same conditions, but with the electrochemical reduction reaction of O_2 excluded, namely in the absence of O_2, or without application of polarization. In both cases no polymer formation was observed. Polarization curves measured under the experimental conditions did not show the presence of impurities reducible at the controlled potential (Fig. 3).

The results of the experiments showed that in saturated aqueous sulfuric-acid solutions of MMA of approximately $0.1\,M$, no polymer precipitate is formed during 3 h after introduction of the monomer. When the concentration of monomer was raised to $0.4\,M$ using aqueous-alcoholic (sulfuric-acid) solutions of the monomer, it was found that in solutions containing O_2 at a concentration of $1.25 \cdot 10^{-4}\,M$ and higher, and also in the complete absence of oxygen, polymerization is not observed over the same period of time. With a decrease in con-

concentration of O_2 by factors of 20 and 100, i.e., at its concentrations equal, respectively, to $6.25 \cdot 10^{-6}$ M and $1.25 \cdot 10^{-6}$ M, under the same experimental conditions polymer formation is observed; in the first case polymerization proceeds faster than in the second. The current strength over the course of 3 hours, exhibiting oscillations, gradually falls to zero, which is associated with a decrease in the oxygen concentration.

SovietRxiv

Fig. 3. Polarization curve at 18°. 1–1 N H_2SO_4; 2–50% 1 N H_2SO_4 + 50% CH_3OH; 3–monomer solution in 50% 1 N H_2SO_4 + 50% CH_3OH after 3-hour standing in air. MMA concentration 0.4 M

We carried out long-duration experiments, the purpose of which was to obtain large amounts of polymer (0.035–0.05 g) for further investigation. In this case, along with the potential, an approximately constant oxygen concentration was also maintained; the current strength did not decrease, and polymer accumulation could be carried out over a prolonged period.

From repeated determinations by the method of measuring the viscosity of the polymer solution in benzene, the average molecular weight of the polymer obtained was calculated; it proved to be $2.5\text{–}3 \cdot 10^6$.

The results obtained on the initiation of MMA polymerization by electroreduction of oxygen indicate the dual character of the action of the latter on MMA polymerization. Oxygen, on the one hand, inhibits the process and, on the other, participates in its initiation, probably through HO_2 radicals, formed at the electrode during the reduction of O_2 in the first stage (a). Polymerization of MMA under the given experimental conditions may also be regarded as experimental confirmation of the formation of radicals as intermediate products in the electroreduction of oxygen.

The effect of stirring the electrolyte at 700 rpm on the process of initiating MMA polymerization by electroreduction of oxygen under the described conditions was also studied. These experiments were carried out both in the diffusion region and in the kinetic region with respect to this reaction; the oxygen concentration was maintained the same as in experiments with an unstirred electrolyte. It turned out that, with stirring of the electrolyte, polymerization is not observed. Possibly this is connected with disruption of the conditions for initiation of the polymer chain, which occurs at the electrode surface, or of its growth, if the latter proceeds from the electrode. This question, however, requires further study.

We express our deep gratitude to Academician A. N. Frumkin for his interest in the work and for valuable suggestions.

Moscow State University
named after M. V. Lomonosov

Received
13 XII 1960

CITED LITERATURE

1. E. Dineen, T. Schwan, C. Wilson, Trans. Electrochem. Soc., **96**, 226 (1949).

SovietRxiv

2. C. Walling, *Free Radicals in Solutions*, 1957, p. 591.

3. G. Parravano, J. Am. Chem. Soc., **73**, 628 (1951).

4. J. Kolthoff, L. Ferstandig, J. Polym. Sci., **6**, 563 (1951).

5. W. Kern, H. Qast, Makromolek. Chem., **10**, 202 (1953).

6. J. W. Breitenbach, H. Gabler, Monatsh. Chem., **91**, 202 (1960).

7. A. I. Fedorova, I. V. Shelepin, N. B. Monseeva, Abstracts of reports at the II Conference on the Electrochemistry of Organic Compounds, Moscow, 1959, p. 8.

8. J. C. Schoonover, G. M. Brauer, W. T. Sweeney, J. Res. Nat. Bur. Stand., **49**, No. 6, 359 (1952); C. E. Barnes, J. Am. Chem. Soc., **67**, 217 (1945); W. Kern, Makromolek. Chem., **1**, 199 (1948).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.