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POLAROGRAPHIC BEHAVIOUR OF CITRACONIC AND MESACONIC ACID DIBROMIDES IN PHOSPHATE BUFFER

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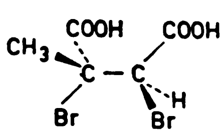
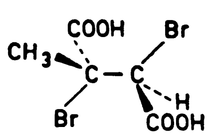
The examination of the polarographic behaviour of citraconic and mesaconic acid dibromides have shown that the pH value of the solution has a great influence on the number of waves, their heights and values of the half-wave potential. By the reduction of citraconic acid dibromide three waves are produced. The first wave corresponds to the reduction of citraconic acid dibromide to citrocanic acid (at pH 3.4) and to mesaconic acid (at pH 6.1). The third wave results from the reduction of the corresponding unsaturated acid to methylsuccinic acid. The second wave results perhaps from the reduction of a product obtained during the hydrolysis of citraconic acid dibromide. By the reduction of mesaconic acid dibromide two waves appear, the more positive one results from the reduction of mesaconic acid dibromide to mesaconic acid and the more negative one corresponds to the reduction of mesaconic acid to methylsuccinic acid.

The aim of this study was to examine the polarographic behaviour of the bromination products of citraconic and mesaconic acids. The trans-addition of bromine to the double bond takes place, according to the lliterature[1–4], by the action of bromine on citraconic and mesaconic acids. In the first case citraconic acid dibromide (DL-*threo*-α,β-dibromomethylsuccinic acid) is produced:



and in the second case mesaconic acid dibromide (DL-*erythro*-α,β-dibromomethylsuccinic acid) is obtained:



While the polarographic behaviour of meso or racemic 2,3-dibromosuccinic acids, which are prepared by the action of bromine on maleic and fumaric acids, has been reported in literature[5,6], there exists no information about citraconic and mesaconic acid dibromides.

EXPERIMENTAL

The citraconic and mesaconic acid dibromides were prepared according to the procedures of Vaughan and Milton[2]. The purity of the products was chacked by recording IR spectra.

The polarographic curves were recorded on a polarograph Radiometer Polariter PO4. Capillary characteristics were determined in distilled water at a potential of 0 V (with respect to the saturated calomel electrode) and with a height of mercury column of 35 cm. Mercury drop time was 4.0 s, while the rate of flow was 2.29 mg s^{-1}. The oxygen was being removed from the investigated solution by bubbling purified nitrogen for 8 to 10 min. An inert atmosphere above the solutions during the measurments was maintained by flushing with nitrogen. All the measurements were done at 25 $\pm$ 0.5°.

Phosphate buffers of the desired pH-values were obtained by neutralization of phosphoric acid of a corresponding concentration by means of concentrated solution of potassium hydroxide[8]. For maximum suppression freshly prepared 1% gelatine solution was used. Its concentration in the investigated solution was 0.005%.

RESULTS

a. *Citraconic acid dibromide*

Citraconic acid dibromide gives in 0.1 mol dm^{-3} phosphate buffer in the presence of 1 mol dm^{-3} KCl in the pH-range from 4 to 7, three waves (Fig. 1),

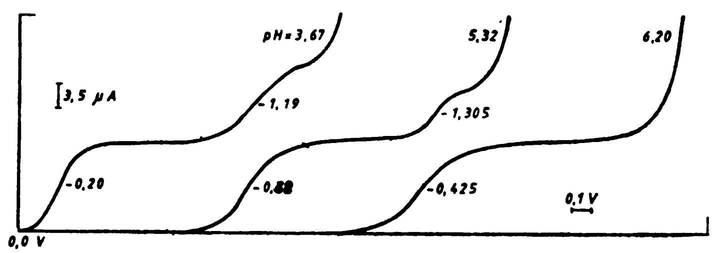


Fig. 1. Polarographic waves of mesaconic acid dibromide (2 mmol.dm^{-3}) in phosphate buffer (0.1 mol dm^{-3} H_3PO_4 + KOH, 1 mol dm^{-3} KCl) at different pH values

whose heights and values of half-wave potentials change by altering the acidity of the solution. The heights of the first and the third waves reduce with the increase of pH and the height of the second wave increases. The total height of the first and the second waves is constant. The half-wave potentials of the first and the third waves changes considerably between pH 3.4 and 6.95 (for the first wave from -0.07 V to -0.30 V, and for the third from -1.08 V to 1.31 V). The half--wave potential of the second wave is constant in the mentioned range of pH values (-0.52 V)

The first wave results from the two-electron, irreversible ($\alpha = 0.36$ at pH 4.07) reduction of citraconic acid dibromide. The values of half-wave potentials, especially at lower pH, are near to the values of the half-wave potential of anodic dissolution of mercury in the presence of chloride ions and the wave is not often properly developed. The better formed waves can be obtained in 1 mol dm^{-3} phosphate buffer, in which case the presence of KCl is unnecessary.

The second wave at pH of solution under 4.0 does not appear at all, if the recording is made immediately after the preparation of the solution. After 24 hours of standing of the solution, the height of the first wave decreases and the second increases. This shows that at higher pH-values, especially after standing, the hydrolysis of citraconic acid dibromide takes place. This phenomenon has been noticed by Kingsbury[7] who has found the values of hydrolysis constant in strong basic medium being of the order of magnitude of 10^{-4}. Among the products of hydrolysis he discovered as the major products *cis* and *trans* forms of bromomethacrylic acid, 2.3-hydroxy-2-methylsuccinic acid, 2-hydroxy-2-methyl-3--bromosuccinic acid, 3-oxybutane acid and acetone. Therefore the second wave is produced by the reduction of the product obtained by hydrolysis of citraconic acid dibromide.

The identity of the third wave is shown by comparing the wave of citraconic acid dibromide with the wave of citraconic acid (Fig .2, curve 3), or mesaconic acid (Fig. 2, curve 2).

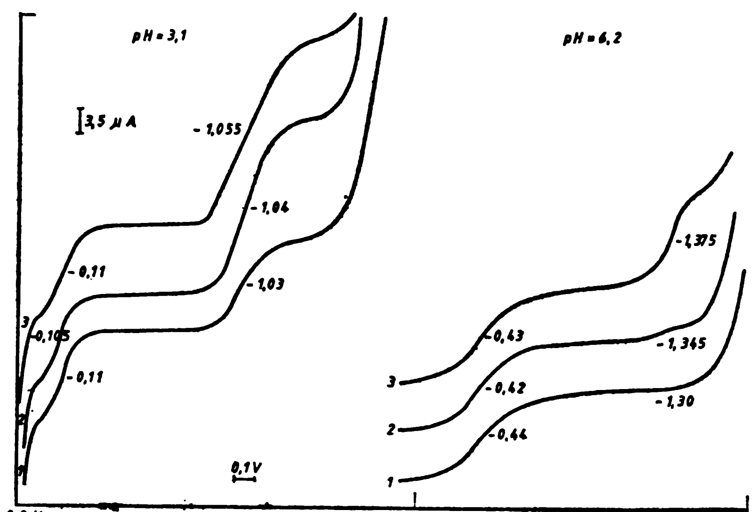


Fig. 2. Polarographic waves of 2 mmol mesaconic acid dibromide (1), in the presence of 2 mmol dm^{-3} mesaconic acid (2)and in the presence of 2 mmol dm^{-3} citraconic acid (3) in 0,1 mol dm^{-3} phosphate buffer, 1 mol dm^{-3} KCl, pH 6.2 and 3.1

The mentioned examinations were performed in phosphate buffer at pH 3.4 and 6.1. It can be observed from the curves 1 and 2 that the wave at pH 6.1 is scarcely visible. This is in accordance with the polarographic behaviour of mesaconic acid at this pH-value and we can assert that the third wave is a result of a reduction of mesaconic acid. In the solutions of pH 3.4, the half-wave potentials of the third waves from curves 1 (citraconic acid dibromide alone) and 2 (citraconic acid dibromide and citraconic acid) are very close -1.08 V and -1.10 V.

So it was concluded that by the reduction of citraconic acid dibromide, citraconic acid has been produced. This conclusion, however, does not exclude the possibility of formation of some mesaconic acid at this pH which might be similar to the phenomenon that Rosenthal and Elving[5] discovered with racemic dibromosuccinic acid. These conclusions give the answer to the question which are the products of the reduction of citraconic acid dibromide on the dropping mercury electrode.

With regard to the polarographic determination of citraconic acid dibromide it is preferable to use the first wave, which is the more characteristic one. Besides, it is better to perform the recording in the presence ot 1 mol dm^{-3} phosphate buffer, and at is the best at pH about 2, where the height oi the wave slightly changes by changing pH.

b. *Mesaconic acid dibromide*

Mesaconic acid dibromide gives in 1.0 mol dm^{-3} phosphate buffer in the presence ot 1 mol dm^{-3} KCl at lower pH, two well-defined polarographic waves. The height of the first wave, the more positive one, is almost unchangeable by pH 5.32. Above this value appears a hardly visible doubling of the wave.

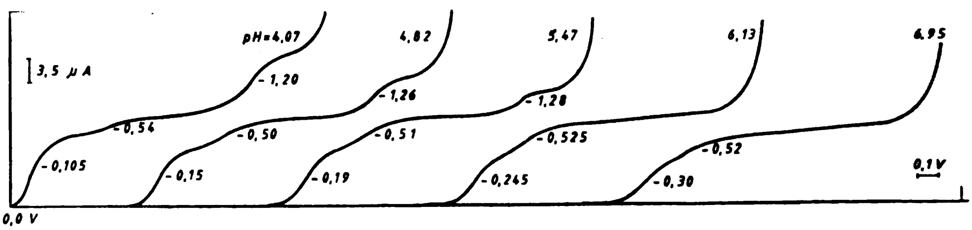


Fig. 3. Polarographic waves of citraconic acid dibromide (2 mmol dm^{-3}) in phosphate buffer (0.1 mol dm^{-3} H_3PO_4 + KOH, 1 mol dm^{-3} KCl) at different pH values

The height ot the second wave is constant by pH 4. Above this pH value, the wave height begins to decrease, and at pH 6.97 the wave completely disappears The half-wave potentials are shifted to the more negative values with the decrease ot the solution acidity. By changing pH trom 2.0 to 6.20 the half-wave potential ot the more positive wave changes from −0.04 V to −0.43 V, and of the more negative one from −0.92 V to 1.35 V.

The first wave results from the two-electron, irreversible ($\alpha = 0.21$ at pH 3.67) reduction of mesaconic acid dibromide and is controlled by the diffusion current. The values of half-wave potentials, especially at lower pH, are close to the values oi the half-wave potential ot anodic dissolution ot mecrury, in the presence of chloride ions and both waves are joined, as with citraconic acid dibromide. The better developed waves can be obtained in 1 mol dm^{-3} phosphate buffer, because in this case the presence of potassium chloride is unnecessary.

With regards to the second wave, the values of the half-wave potentials of this wave and the height at different pH-values are close to thevalues of mesaconic acid, obtained in the same conditionis With the intention to find out whether mesaconic of citraconic acids are formed by the reduction of mesaconic acid dibromide, we added mesaconic acid (Fig. 4, curves 2) and citraconic acid (Fig.

4, curves 3) to the solutions of mesaconic acid dibromide (Fig. 4, curves 1) in phosphate buffer at pH 3.1 and 6.2. At pH 3.1 the half-wave potentials of the second waves from the curves 1 (mesaconic acid dibromide alone) and 2 (mesaconic acid dibromide and mesaconic acid) are almost the same (−1.03 V and −1.04 V) so we have concluded that the second wave is a result of the reduction of mes-

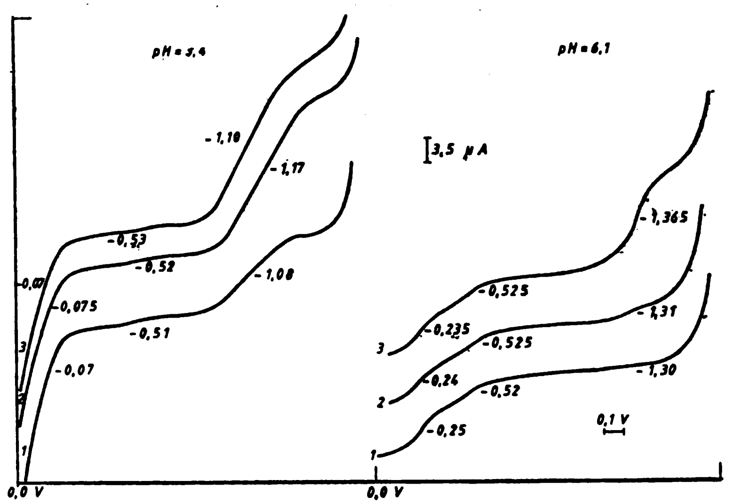


Fig. 4. Polarographic waves of 2 mmol dm^{-3} citraconic acid dibromide (1), in the presence of 2 mmol dm^{-3} mesaconic acid (2) and in the presence of 2 mmol dm^{-3} citraconic acid (3) in 0.1 mol dm^{-3} phosphate buffer, 1 mol dm^{-3} KCl, pH 3.4 and 6.1

aconic acid. At pH 6.2 the second wave is hardly visible on the curves 1 and 2, that is in accordance with polarographic behaviour of mesaconic acid at this pH value[8]. We have therefore concluded that in this case too occurs the reduction of mesaconic acid. These conclusions give the answer to the question which are the reduction products of mesaconic acid dibromide, as in the case of citraconic acid dibromide.

The schemes of the electrode processes of reduction of citraconic and mesaconic acid dibromides can be expressed by the following equations:

$$\underset{\text{mesa- or citradibromosuccinic acids}}{HOOC-CHBr-\underset{\displaystyle CH_3}{\underset{|}{C}}Br-COOH} \xrightarrow{+2e} \underset{\text{mesaconic or citraconic acids}}{HOOC-CH=\underset{\displaystyle CH_3}{\underset{|}{C}}-COOH} + 2Br^-$$

$$HOOC-CH=\underset{\displaystyle CH_3}{\underset{|}{C}}\ COOH \xrightarrow{+2e,\ 2H^+} \underset{\text{methylsuccinic acid}}{HOOC-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-COOH}$$

With regard to the polarographic determination of mesaconic acid dibromide it is better to use the first wave which is a more characteristic one. The recording should be performed in the presence of 1 mol dm^{-3} phosphate buffer at pH about 2.

ИЗВОД

ПОЛАРОГРАФСКО ПОНАШАЊЕ ЦИТРА И МЕЗАДИБРОМ ЋИЛИБАРНИХ КИСЕЛИНА У ФОСФАТНОМ ПУФЕРУ

ИЛИНКА СПИРЕВСКА

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ВЛАДИМИР Ј. РЕКАЛИЋ

Технолошко-металуршки факултет Универзитета у Београду

Испитивања поларографског понашања цитра- и мезадибромћилибарне киселине показују да на број таласа, њихову висину и вредност полуталасног потенцијала има значајан утицај pH-вредност раствора. При редукцији цитрадибромћилибарне киселине јављају се три таласа. Први талас одговара редукцији цитрадибромћилибарне киселине до цитраконске (при pH 3,4) и мезаконске киселине (при pH 6,1). Трећи талас се јавља услед редукције одговарајуће незасићене киселине до метил ћилибарне киселине. Други талас вероватно настаје редукцијом производа добивеног хидролизом цитрадибромћилибарне киселине. Редукцијом мезадибромћилибарне киселине јављају се два таласа, позитивнији који настаје редукцијом мезадибромћилибарне киселине до мезаконске и негативнији који потиче од редукције мезаконске до метил ћилибарне киселине.

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