

COMPETITION REACTIONS BETWEEN ETHANOL AND FORMIC ACID ON PLATINUM IN ACID MEDIA

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Abstract

The electrochemical reactions of 0.01 M CH₃CH₂OH and 0.01 M HCOOH on platinum in 0.1 M HClO₄ were studied by means of Differential Electrochemical Mass Spectrometry (DEMS). Ethanol can be oxidized to CO₂ and ethanal whereas formic acid produces only CO₂. Electroreduction products (ethane and methane) were observed only for ethanol. The competition reactions between ethanol and formic acid were studied when both compounds are present simultaneously in the bulk of the solution (0.01 M CH₃CH₂OH + 0.01 M HCOOH). Using isotope labelled H¹³COOH it was possible to distinguish the contribution of ethanol and formic acid: formic acid oxidizes to ¹³CO₂ (m/z = 45) whereas ethanol produces ¹²CO₂ (m/z = 44). It was observed that the reactivity of ethanol is similar to that found without formic acid in the solution, whereas the production of CO₂ from formic acid was diminished about 50 %.

Key words: ethanol, formic acid, Differential Electrochemical Mass Spectrometry, competition reactions.

Introduction

The reactivity of ethanol and formic acid on platinum in acid media has been the subject of many papers in the past [1-6]. These compounds oxidize through a dual mechanism involving the formation of "reactive intermediates" and "poisons". In the case of formic acid, the final product for both pathways is CO₂ [1]. Ethanol oxidizes to CO₂, ethanal and acetic acid [4]. An important difference in the reactivity of ethanol and formic acid is that the former can be reduced to methane and ethane [5,6] whereas no reduction products can be detected for the latter.

In the present work the electroreactivity of ethanol and formic acid is studied when both species are simultaneously present in the same solution. These results are compared with those obtained individually in the same conditions. In this way, it is possible to establish the competition reactions on platinum between both compounds. For this purpose Differential Electrochemical Mass Spectrometry (DEMS) was applied for, the "on-line" detection of gaseous and volatile species produced on the surface

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during electrochemical reactions [7]. The DEMS technique combined with isotope labelling is an adequate method for these studies: using H^{13}COOH it is possible to distinguish the CO_2 formation of each compound during the electro-oxidation. Thus, the mass signal $m/z = 45$ ($^{13}\text{CO}_2$) is associated to the oxidation of formic acid to CO_2 , and the mass signal $m/z = 44$ ($^{12}\text{CO}_2$) is related to the oxidation of ethanol molecules.

Experimental

The electrochemical cell was a small flow cell containing approximately a 2 cm^3 solution. The working electrode (real area = 12.5 cm^2) was a platinum layer sputtered on a microporous PTFE membrane (Scimat 200/40/60, mean thickness $60\text{ }\mu\text{m}$, porosity 50 %, mean pore size $0.17\text{ }\mu\text{m}$). The electrode was activated by potential cycling at 0.015 V/s in the supporting electrolyte solution between the onset potential for hydrogen and oxygen evolution. A platinum wire was served as counter electrode, and a reversible hydrogen electrode (RHE) in the supporting electrolyte was used as reference.

Solutions were prepared with Millipore-MilliQ[®] water and analytical grade chemicals. 0.01 M HCOOH and $0.01\text{ M CH}_3\text{CH}_2\text{OH}$ in the supporting electrolyte (0.1 M HClO_4) were used. Isotope labelled ^{13}C formic acid (Cambridge Isotope Laboratories, ^{13}C 99 %, chemical purity 94.5 %) was employed. Experiments were made at room temperature under argon atmosphere.

The DEMS cell was directly attached to the vacuum chamber containing the mass spectrometer (Balzers QMG 112) with a Faraday cup detector. More details were described elsewhere [7,8]. After activation of the working electrode, the supporting electrolyte solution was replaced by the organic containing solution. After that, mass spectrometric cyclic voltammograms (MSCVs) and cyclic voltammograms (CVs) were recorded simultaneously during potential cycling at 0.015 V/s . Freshly organic solution was introduced in the cell after each complete cyclic voltammogram in order to maintain constant the concentration of the organic in the DEMS cell.

Results and Discussion

Cyclic voltammograms for 0.01 M HCOOH , $0.01\text{ M CH}_3\text{CH}_2\text{OH}$ and $0.01\text{ M H}^{13}\text{COOH} + 0.01\text{ M CH}_3\text{CH}_2\text{OH}$ solutions in 0.1 M HClO_4 are shown in Figures 1a, 1b and 1c, respectively. Two anodic peaks at 0.70 V and 0.80 V are apparent for formic acid during the positive-going potential scan (Fig. 1a), whereas for ethanol the contributions are located at 0.87 V and 1.23 V (Fig. 1b). For the ethanol + formic acid solution (Fig. 1c), the CV is similar to that of ethanol. However, the current involved in the peak around 0.82 V in Fig. 1c is increased in respect to the contribution in the same potential region for the ethanol solution. During the negative-going potential scan, the oxidation of the organics occurs as soon as the reduction of platinum oxide takes place, specially for the case of formic acid.

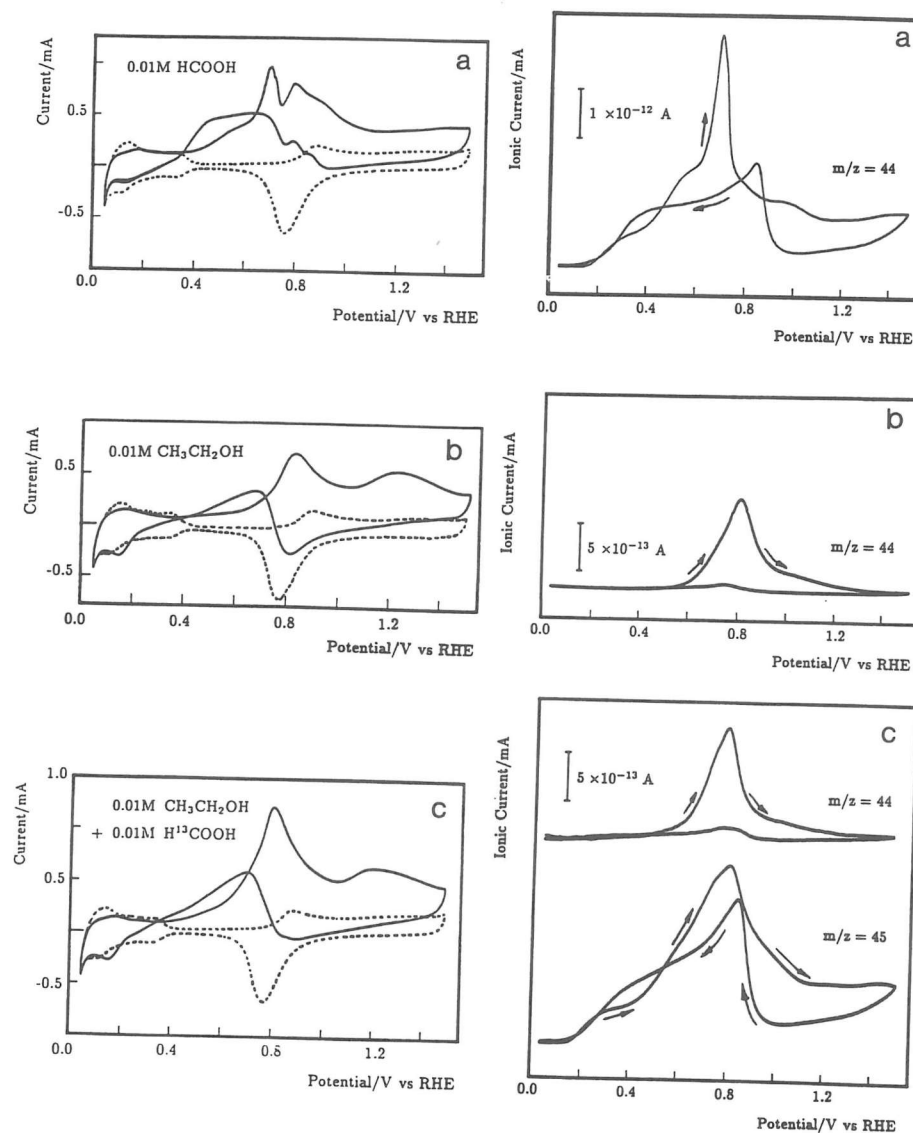


Figure 1.

Figure 2.

Figure 1. CVs in 0.1 M HClO_4 on Pt at 0.015 V/s ; area = 12.5 cm^2 . a) 0.01 M HCOOH ; b) $0.01\text{ M CH}_3\text{CH}_2\text{OH}$; c) $0.01\text{ M HCOOH} + 0.01\text{ M CH}_3\text{CH}_2\text{OH}$.
Figure 2. MSCVs in 0.1 M HClO_4 on Pt at 0.015 V/s for $m/z = 44$ ($^{12}\text{CO}_2$) and $m/z = 45$ ($^{13}\text{CO}_2$); area = 12.5 cm^2 . a) 0.01 M HCOOH ; b) $0.01\text{ M CH}_3\text{CH}_2\text{OH}$; c) $0.01\text{ M H}^{13}\text{COOH} + 0.01\text{ M CH}_3\text{CH}_2\text{OH}$.

The MSCVs related to the CO₂ formation can be seen in Figures 2a-c. These MSCVs were obtained simultaneously with the CVs in Figures 1a-c. The ion current for m/z = 44 from HCOOH in Fig. 2a shows an onset potential of 0.15 V, attaining a peak at 0.70 V during the positive-going scan and at 0.85 V during the negative-going one. In the case of ethanol the shape of the curve for m/z = 44 is rather different: the onset potential is displaced 0.41 V to more positive potentials, and a peak centered at 0.80 V is observed during the anodic scan. The ion current for the CO₂ signal diminishes at higher potentials being approximately 0 at 1.50 V. The MSCV for m/z = 44 is also very small during the cathodic scan.

The competition reactions related to the formation of CO₂ can be followed in the system 0.01 M H¹³COOH + 0.01 M CH₃CH₂OH (Fig. 2c). The mass signal for m/z = 44 represents the oxidation of ethanol. The shape of this MSCV is similar to the ion current in Fig. 2b. However, the integrated ion current related to the oxidation of HCOOH (m/z = 45), is significantly smaller than in Fig. 2a, and the sharp peak at 0.70 V is suppressed.

The integrated ion current for the CO₂ signals in Figures 2a-c are summarized in Table 1.

Table 1. Integrated ion current related to the production of CO₂

m/z	Integrated mass signal (C)			
	CH ₃ CH ₂ OH	HCOOH	CH ₃ CH ₂ OH + HCOOH	CH ₃ CH ₂ OH + H ¹³ COOH
44	1.8x10 ⁻¹¹	2.2x10 ⁻¹⁰	1.4x10 ⁻¹⁰	1.9x10 ⁻¹¹
45	---	---	---	1.2x10 ⁻¹⁰

From these values it can be established a diminution in the reactivity of HCOOH of about a 50 % (from 2.2 x 10⁻¹⁰ C to 1.2 x 10⁻¹⁰ C) by the presence of CH₃CH₂OH, whereas ethanol seems to react as in the absence of formic acid.

The contribution of the species acting as poisons can be separated from bulk reactions of the organics by means of flow cell experiments. These investigations will be discussed in a forthcoming publication.

From the mass signals related to the formation of ethanal (m/z = 29, [COH]⁺), methane (m/z = 15, [CH₃]⁺) and ethane (m/z = 30 [C₂H₆]⁺), the same values for the integrated ion currents were obtained in 0.01 M CH₃CH₂OH and 0.01 M HCOOH + 0.01 M CH₃CH₂OH solutions, thus providing new evidence for the lack of interference of formic acid in the ethanol reactivity on platinum in acids (the MSCVs for these mass

signals are not shown in the present paper).

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References

1. A. Capon and R. Parsons, *J. Electroanal. Chem.*, **44** (1973) 1; **44** (1973) 239; **45** (1973) 205.
2. T. Iwasita, F. C. Nart, B. López and W. Vielstich, *Electrochim. Acta*, **37** (1992) 2361.
3. O. Wolter, J. Willsau and J. Heitbaum, *J. Electrochem. Soc.*, **132** (1985) 1635.
4. T. Iwasita, B. Rasch, E. Cattaneo and W. Vielstich, *Electrochim. Acta*, **34** (1989) 1073.
5. B. Bittins-Cattaneo, S. Wilhelm, E. Cattaneo, H. W. Buschmann and W. Vielstich, *Ber. Bunsenges. Phys. Chem.*, **92** (1988) 1210.
6. T. Iwasita and E. Pastor, *Electrochim. Acta*, **39** (1994) 531; **39** (1994) 547.
7. B. Bittins-Cattaneo, E. Cattaneo, P. Königshoven and W. Vielstich in A. Bard (Ed.): *"Electroanalytical Chemistry: A Series of Advances"*, Vol. 17, Marcel Dekker, New York, 1991, p. 181.
8. E. Pastor, C. M. Castro, J. L. Rodríguez and S. González, *J. Electroanal. Chem.*, in press.