

# The Reduction Mechanism of a Cyclic $\alpha, \beta$ -Unsaturated Ketone at Mercury in Aqueous Medium; Isophorone

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Received: May 2, 1990, October 9, 1990

Foi investigado o mecanismo de redução da isoforona, uma cetona cíclica  $\alpha, \beta$  insaturada, por polarografia d.c. e a.c., coulometria a potencial controlado e eletrólise. Os produtos da eletrólise foram isolados e identificados por técnicas espectroscópicas. Verificou-se, para todos os pH's analisados, adsorção do substrato e/ou produtos no eletrodo de mercúrio.

Em meio ácido é favorecida a formação do monômero (3,5,5-trimetil ciclohexanona), no entanto, o produto principal da redução na região básica é um dímero. É proposto o mecanismo de redução da isoforona para a região ácida e básica.

The reduction mechanism of isophorone, a cyclic  $\alpha, \beta$  unsaturated ketone, was investigated by dc and ac polarography, controlled potential coulometry and electrolysis. The electrolysis products were isolated and identified by spectroscopic techniques. For all pH values investigated adsorption phenomena were observed.

In acid medium the formation of a monomeric reduction product (3,5,5-trimethyl-cyclohexanone) is favoured, whereas in basic medium the principal reduction product is dimeric. A reduction mechanism for both acid and basic conditions is proposed.

**Key words:** *isophorone; electrochemistry.*

## Introduction

Savéant<sup>1</sup> investigated, by cyclic voltammetry, the reduction mechanism in non-aqueous media of a series of activated olefins, including isophorone. The general mechanism proposed for non-aqueous solvents is characterized by a one electron uptake, followed by the dimerization of the radical formed<sup>1</sup>. On changing the solvent from nonaqueous to aqueous, besides the one-electron transfer (electrohydrodimerization), the uptake of two electrons, resulting in the reduction of the double bond, is also observed<sup>2-4</sup>.

Only two papers dealing with the electrochemistry of isophorone, IS, in aqueous media, were found in the literature. Gabani and Conti<sup>5</sup> investigated by polarography and controlled potential electrolysis the aqueous electrochemistry of IS. These authors isolated the reduction products formed, concluding that three different dimers were formed. No evidence of the original substrate with the double bond reduced was found. Martinet and Simonet<sup>6</sup> investigated the influence of the proton on the reduction of  $\alpha, \beta$  -unsaturated ketones, including IS, in aqueous medium. These authors suggested a general mechanism for the one-electron uptake (electrohydrodimerization) giving proper attention to the influence of the pH on the sequence of proton-electron uptake. They also suggested dimerization as being favoured.

Preliminary results on the reduction in aqueous medium of IS, obtained in our laboratory, pointed to the obtention of the monomer (two-electron uptake). In view of this contradictory result we decided to carry out an investigation of the reduction mechanism, in aqueous medium, of this cyclic  $\alpha, \beta$  -unsaturated ketone. This investigation was

further stimulated by the importance of IS as a starting material, commercially available, in the synthesis of sesquiterpenoids and prostaglandins. In fact the functional transformation of IS results in synthons used in the synthesis of these important chemicals.

## Experimental

Dc<sub>fast</sub> and Ac<sub>fast</sub> polarograms were recorded with a Polarecord E506 polarograph equipped with a model E505 D.M.E. stand (all Metrohm, Swiss). The amplitude of the ac signal used was 10mV p/p while the frequency was 75 Hz. Drop time was controlled mechanically at 2s. All experiments were carried out at (30.0  $\pm$  0.1) $^{\circ}$ C.

Controlled potential electrolysis and coulometric experiments were carried out with a model 173 potentiostat/galvanostat equipped with a digital model 179 coulometer (all P.A.R., U.S.A.). For the coulometric experiments a model 377 synchronous stirring motor equipped with a model 377A cell (all P.A.R., U.S.A.) was used.

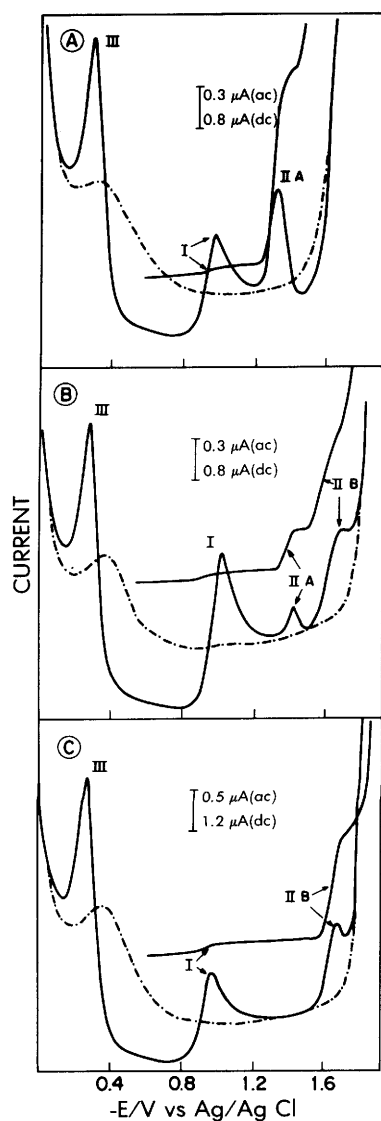
A Metrohm model E500 pH-meter, equipped with a combined glass electrode, was used for the pH measurements. The equipment was standardized, over the pH range investigated, with N.B.S. buffers.

All products, obtained from commercial sources, were of A.R. purity. Isophorone was purified by fractional distillation. Stock solutions of the components used in the preparation of the buffers, as well as the NaCl stock solutions, were prepared at the highest practical concentrations. These solutions were purified by constant potential electrolysis applying to the working electrode (Hg pool) the most negative possible potential. The exact

concentration of the stock solutions was determined using standard volumetric and gravimetric procedures. Working solutions of the appropriate pH and IS concentration were prepared transferring adequate volumes of the stock solutions of the buffer components and of the IS stock solution to a volumetric flask. The ionic strength of the working solutions was kept constant at 1.0 through the addition of NaCl. The concentration of the buffer component, present at the lowest concentration, was always at least twenty times superior to the IS concentration, so as to avoid possible pH changes in the double layer. For the polarographic investigation the IS concentration was maintained constant at  $1.0 \times 10^{-3}$  M. Prepurified nitrogen was used to deaerate the solutions.

### Results and Discussion

DC<sub>last</sub> polarograms were recorded covering the 1.0-14.0 pH range. Some representative polarograms are shown in Figure 1.



**Figure 1.** Dc and ac polarograms as a function of pH. (A) 4.45, (B) 6.31, (C) 10.39. IS = 1 mM,  $\mu = 1.0$ ,  $t = 30^\circ\text{C}$ , (---) supporting electrolyte. Ac polarograms ( $E_i = 0.0$  V).

In the acid pH range ( $\text{pH} < 6.0$ ) the dc polarograms show two polarographic waves, denominated I and IIA. Of these, IIA is the principal wave showing, when compared to wave I, a much higher current intensity. Also, for  $\text{pH} < 4.5$ , wave IIA presents a maximum of the first kind which can be eliminated by the addition of 0.002% Triton X-100 to the solution. The addition of the maximum suppressor not only results in the elimination of the maximum but also suppresses wave I. This behaviour suggests wave I to be an adsorption wave. Starting around pH 6.3 the current intensity of wave IIA decreases on increasing pH. Simultaneously, a new wave, denominated IIB, is observed at more negative potentials. On further increasing the pH the current intensity of wave IIB increases, the total wave height ( $i_{\text{IIA}} + i_{\text{IIB}}$ ) being, however, independent of pH. For pH values superior to 7.5 wave IIA is no longer observed.

The splitting of the polarographic wave on increasing the pH of the solution is a frequently observed phenomenon in the reduction of conjugated ketones<sup>2,4</sup>, being related to the rate of protonation of the ketone group. As the solution becomes more basic, the rate of protonation decreases. As a consequence the two forms,  $\text{RH}^+$  and R, will be present simultaneously in the solution. Both forms being electro-active one observes a first polarographic wave, localized at a less negative potential, due to the reduction of the protonated species  $\text{RH}^+$ , and a second wave, at a more negative potential, due to the unprotonated species, R.

Examination of Fig. 1 shows that  $\Delta E_{1/2}$  between waves IIA and IIB is very small. A further complication is represented by the fact that the polarographic wave IIA (in the acid region) or wave IIB (in the intermediate and basic region) are localized very close to the discharge of the supporting electrolyte. In order to obtain the values of the electrochemical parameters with the required precision under these adverse experimental conditions, the polarograms were analysed using the Gauss-Newton algorithm, as recently proposed by one of us<sup>7</sup>. The results of the analysis are shown in Table 1.

The values of the dc slopes obtained are superior to the theoretical value of 29.6 mV for a reversible two electron

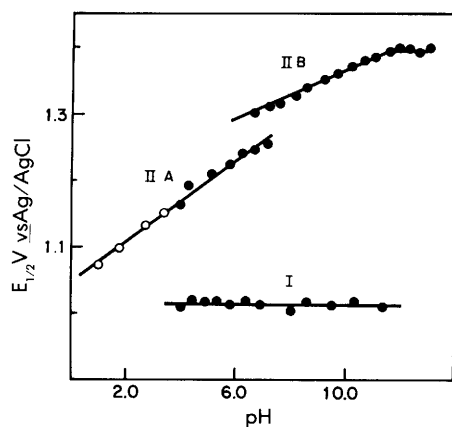
**Table 1.** Dc slopes and width at half-height of the ac peak. (SF) = 1 mM.

pH	Dc Wave IIA slope/mV	Dc wave IIB slope/mV	IIA $E_{p/2}$ /mV	IIB $E_{p/2}$ /mV
1.0	68*	-	96	-
2.7	68*	-	112	-
3.4	64*	-	110	-
4.0	37*	-	104	-
4.8	38	-	100	-
5.9	38	-	72	-
6.2	39	58	68	112
6.7	36	71	68	128
7.2	47	71	-	-
7.8	-	65	-	136
8.4	-	67	-	136
9.0	-	57	-	136
9.7	-	55	-	120
10.5	-	51	-	96
11.6	-	40	-	96
12.0	-	46	-	96
12.7	-	40	-	-

\*Solutions containing Triton X-100 (0.002%)

transfer without kinetic complications<sup>8</sup>. A possible reason for the deviation observed could be found in: (a) a certain degree of irreversibility of the charge transfer process; (b) a kinetic complication coupled to a reversible charge transfer; or (c) a combination of (a) and (b).

Figure 2 shows the dependence of the half-wave potentials on pH. The half-wave potential of wave I is independent of pH, while the half-wave potential of wave IIA is displaced, to more negative potentials, by 61.5 mV for each pH unit increase. Since the reduction of IS involves two electrons (see coulometric results) one can conclude that in this pH region the number of protons involved in the reduction mechanism is also equal to two. The  $E^{IIA}$  vs pH graph shows two linear parts. For pH < 11.5 the straight line presents a slope of 36.5 mV suggesting only one proton is involved in the reduction mechanism. For pH > 11.5 the half-wave potential of wave IIB is independent of pH suggesting that there is no proton participation in the reduction mechanism.



**Figure 2.** Half-wave potential as a function of pH. IS = 1 mM,  $\mu = 1.0$ ,  $t = 30^\circ\text{C}$ . (•) values obtained without Triton X-100, (◊) in the presence of 0.002% Triton X-100.

The influence of the IS concentration was investigated over the 0.05-7.0 mM interval for the pH values of 4.6, 10.0 and 13.0.

For the first two pH values a linear relationship between the IS concentration and the limiting current was observed until approximately 1 mM. Above this concentration the maximum disturbs the polarographic d.c. wave. Until  $10^{-3}$  M the half wave potential is independent of the IS concentration. For the ac polarograms, however, a linear relationship between  $i^{IIA}$  ( $i^{IIB}$ ) and the IS concentration was observed until approximately 3 mM. Above this concentration the faradaic peaks are deformed probably due to the polarographic maxima observed in the dc waves. For pH 13.0, over the complete concentration interval examined, a linear relationship was obtained between the IS concentration and the limiting current, suggesting the electrode process to be diffusion controlled at this pH.

The influence of the temperature on the limiting current of the dc wave, (IIA and IIB) was investigated over the 5-50°C temperature range for the pH values of 4.6, 10.0 and 13.0. For all cases a linear relationship between the temperature and the limiting current was observed. The temperature coefficients obtained, calculated using the following equation<sup>9</sup>:  $(2.303/\Delta t \log (i_2/i_1))$ , were 1.22, 1.53 and 1.00% /deg for the pH values of 4.6, 10.0 and 13.0, respectively. These values are representative of

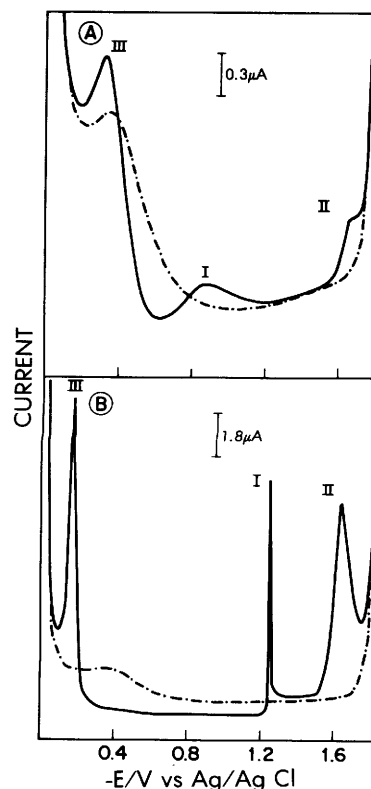
diffusion controlled currents.

The dependence of the limiting current on the height of the mercury column and the drop time was also examined. A linear relationship between the limiting current and  $h_{\text{Hg}}^{1/2} (t^{1/6})$  was observed, confirming the results of the other diagnostic criteria applied.

The ac polarographic spectrum is quite complex showing, over the complete pH region, at least three peaks (see Figure 1). Of these, peak III, localized at -0.34 V and having no counterpart in the dc polarogram, is of high current intensity. Its peak potential is independent of pH. Furthermore the current at the foot of peak III is inferior to the pure background current for the potential region comprised between peaks I and III (see e.g. Fig. 1A). This behaviour suggests peak III to be a non-faradaic adsorption peak<sup>10</sup>.

Over the complete pH region peak I, localized at -0.98 V and having wave I as counterpart in the dc polarogram, is observed. Its peak potential is independent of pH while the addition of small quantities of Triton X-100 results in its complete elimination in a way similar to that observed in dc polarography. Since Triton X-100 is strongly adsorbed on mercury<sup>11</sup> it is able to displace the adsorbed electroactive species from the electrode surface explaining the disappearance of peak I from the ac polarographic spectrum in the presence of Triton X-100. This behaviour of peak I suggests it is a faradaic adsorption peak.

Further evidence that adsorption is involved in peaks I and III arises from its behaviour as a function of IS concentration. For the higher concentrations both peaks are of the needle type presenting a very low half-width and high current intensity (see Fig. 3). Besides, at pH 13 and low IS concentration ( $[\text{IS}] = 1 \times 10^{-4}$  M), only peaks I and III



**Figure 3.** Ac polarograms as function of IS concentration. (A) 0.4 mM, (B) 7.0 mM, pH = 10.0,  $\mu = 1.0$ ,  $t = 30^\circ\text{C}$ , (---) supporting electrolyte.

are observed, there being no evidence of peak II (A or B) in the ac polarographic spectrum. On increasing the IS concentration above 0.1 mM the drop area becomes a limiting factor for the adsorption and peak II (A or B) shows up.

So the difference between peaks I and III, both involving adsorption, is that, while peak III is nonfaradaic in nature, peak I is the result of charge transfer between adsorbed IS species.

Peaks IIA and IIB (see Fig. 1A,C) coincide perfectly with the principal dc polarographic waves for identical pH values. We are thus dealing with faradaic reduction peaks. For the acid pH region one can verify (see Fig. 1A) that at the foot of peak IIA, and on both sides of it, the current is lower than the pure background current suggesting one (or more) species involved in the reduction mechanism are still adsorbed at these negative potentials. This behaviour is different from that observed in the almost neutral and basic region (see Fig. 1B,C) where a perfect coincidence is observed between the current and the pure background current on both sides at the foot of peak IIA (IIB). This behaviour suggests that for the almost neutral and basic pH region the reduction process occurs without the participation of adsorption.

On increasing pH the peak potentials of peaks IIA and IIB are displaced to more negative values in a way analogous to that observed in the dc polarographic study. In the pH region around 7 peaks IIA and IIB exist simultaneously (Fig. 1B). The half-widths,  $E_{p/2}$ , of these faradaic peaks (shown in Table 1) are superior to the theoretical value<sup>8</sup> of 67.5 mV for a reversible two electron transfer without kinetic complications coupled to it. The half-width of wave II is a function of pH, the value deviating more from the theoretical value of 67.5 mV the more acid the solution becomes, suggesting that for acid conditions the reaction mechanism deviates more from a reversible behaviour than for basic conditions.

The fact that at all pH values investigated peak II is observed excludes the possibility that the electron transfer is irreversible; otherwise, for the IS concentration ( $10^{-3}$ M) used, no faradaic current would be observed in the ac polarograms<sup>12</sup>.

Several controlled potential coulometric experiments, CPC, were carried out at the pH values 4.8 and 10.4, using 20 ml of  $5 \times 10^{-5}$  M IS solutions. When the potential applied to the mercury pool working electrode corresponds to a value at the plateau of the dc polarographic wave (pH 4.8,  $E_{ap} = -1.40$  V; pH 10.4,  $E_{ap} = -1.65$  V vs ECS) a value of two is obtained for the number of electrons transferred. In the case of pH 4.8, on applying  $-1.30$  V (SCE) to the working electrode a value of  $n_{ap}$  equal to 1.9 is obtained. This slightly lower value can be explained accepting that a chemical process, e.g. dimerization of the radical, is coupled to the electron transfer<sup>13</sup>.

Controlled potential electrolysis experiments, CPE, of 100 ml IS solutions of  $1.5 \times 10^{-2}$  M concentration were carried out at several pH values. In view of the higher IS concentration used, the buffer concentration was increased so that the component, present at the lowest concentration, was at least 20 times the IS concentration. The ionic strength was, however, kept at 1, the value used in all experiments. For all the CPE experiments the potential of the mercury pool working electrode ( $A = 23\text{cm}^2$ ) was fixed at a potential corresponding to the plateau of the dc polarographic wave. For pH 4.8 a more detailed investigation was conducted examining also working electrode potentials corresponding to the ascending part of the polarographic wave. The CPE experiments were

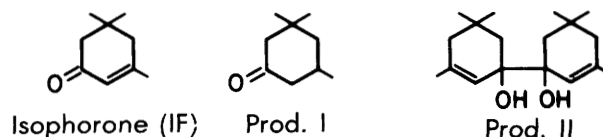
considered to be ended when the current fell to a value close to the residual current. After extraction of the products with ethyl ether they were separated by thin layer chromatography on silica and identified by i.r. and n.m.r. spectroscopy. The CPE experimental conditions used, as well as the distribution as a function of pH of the products formed, are shown in Table 2.

**Table 2.** Distribution of the reduction products of IS, obtained under controlled potential electrolysis conditions, as a function of pH and potential, (IS) = 15 mM.

pH	$E_{ap}/V$ vs SCE	Prod.I (%)*	Prod.II (%)
1.0	-1.12	100	-
4.8	-1.29	61	39
4.8	-1.35	82	18
4.8	-1.42	100	-
7.5	-1.65	47	53
10.0	-1.74	45	55

(\*) % of the mass of isolated products which, in all cases, was at least 80% of the mass of starting material used.

Basically two products are obtained. A product I which is 3,5,5-trimethyl-cyclohexanone, i.e. the starting material with the double bond reduced (Fig. 4), and a product II (see Fig. 4) which is the dimer (pinacol).



**Figure 4.** Structural formula of the substrate and electrolysis products.

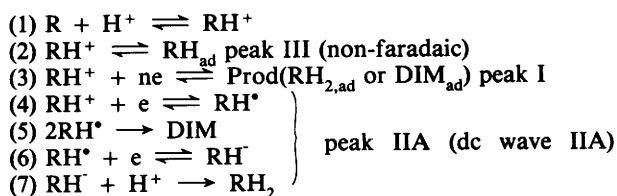
Two interesting conclusions emerge from the data of Table 2.

(a) As a function of pH and considering only those experiments where the working potential applied was fixed at the plateau of the dc polarographic wave, the results suggest that in acid media the reduction of the double bond is favoured over the dimerization reaction (e.g., pH = 1.0 and pH 4.8 with  $E_{ap} = -1.42$  V). This behaviour is confirmed by the results obtained in the basic pH region where a mixture of products is obtained, the dimer concentration found being slightly higher than the monomer concentration.

(b) The influence of the applied working potential on the distribution of the products formed at pH 4.8 clearly shows that the dimerization of the radical, formed after the first electron is transferred, is an important step in the total reduction mechanism. The fact that at the more negative potential only the monomer is formed is easily understood considering that  $k_{sh}$  is an exponential function of the potential while the dimerization constant is independent of potential. So, on using a more negative working potential one creates experimental conditions where less time is allowed for the radical to dimerize.

## Conclusions

The reduction mechanism which best explains the experimental results in acid solution is:



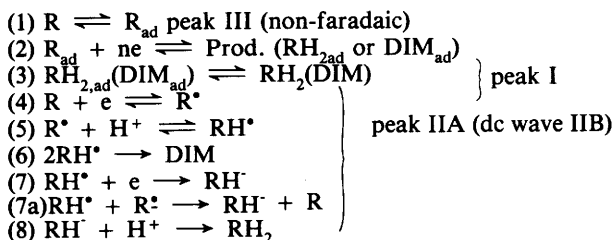
It is well known that in acid medium the protonation of unsaturated ketones occurs before the transfer of the first electron<sup>6</sup>. Thus it can be assumed that protonation of IS is quite fast and the specie reduced is the protonated form (RH<sup>+</sup>).

The E<sup>IIA</sup> vs pH graph shows that under acid conditions two protons participate in the electrode mechanism. This experimental result suggest that the uptake of the second proton occurs after the carbanion formation (step 6) and is reversible; otherwise, only the participation of one proton in the electrode mechanism would be observed polarographically<sup>14</sup>.

The reduction of unsaturated ketones normally takes place with chemical reactions (e.g. protonation, dimerization) coupled to the electron transfer<sup>2</sup>. In the case of IS it was verified that besides chemical reaction adsorption on mercury also occurs.

Under controlled potential electrolysis conditions, especially when the working potential applied corresponds to a value on the ascending branch of the *i* vs *E* curve, analysis of the isolated products demonstrates dimerization of the radical to occur after the first electron is transferred. Examination of the results of Table 2 (e.g. pH 4.8) suggests that using a macro-electrode and acid conditions the reduction of the double bond is favoured over dimer formation. In fact even with the working potential fixed in the lower region of the *i* vs *E* curve (*E*<sub>ap</sub> = -1.29 V, pH 4.8), the dimer is still the minor product formed. The polarographic study does not furnish clear evidence for the dimerization; on the contrary, all criteria point to a diffusion controlled limiting current, whereby one must conclude that step 5 (dimerization) occurs only marginally on a small electrode surface (Hg drop). The fact that dimer formation is observed under C.P.E. conditions and basic pH, or when *E*<sub>ap</sub> is not localized in the potential region of the limiting current, is not an unreasonable result because, whenever hydrodimerization competes with saturated monomer formation, a progressive increase in the bulk reactant concentration (IS is ten times higher under C.P.E. conditions) tends to gradually favour hydrodimerization on account of its second-order kinetics as compared with the first-order kinetics of saturated monomer formation.

The mechanism which best represents the experimental results under neutral and basic conditions is:



In a similar way as observed for the acid pH region, in the neutral and alkaline pH region, adsorption of the Ox form occurs, giving rise to the non-faradaic peak III. For the basic pH region, however, desorption occurs before the potential of the principal reduction peak (IIB) is reached.

In the neutral and basic pH regions the protonation occurs after the first electron has been transferred, so the initial electroactive species is the unprotonated IS molecule. The protonated radical formed accepts a second electron, resulting in a carbanion, which is easily protonated<sup>15</sup>. For strongly basic conditions (pH > 11.5) the participation of protons in the total reduction mechanism is not detected polarographically. This result suggests that two electrons are transferred before protonation occurs resulting in a dianion, R<sup>2-</sup>, which afterwards abstracts protons from the medium giving rise to the final products.

Analysis of the products obtained with C.P.E. (mercury pool W.E. and higher IS conc.) suggests that for almost neutral and basic conditions dimer formation is favoured over monomer formation (see Table 2). So, from a synthetic point of view, if one is interested in obtaining the monomer it is best to choose as experimental conditions an acid medium and fix the working potential as negative as possible. In contrast, if one is interested in obtaining as much dimer as possible it is better to use a basic medium and a less negative potential. In our opinion it is worthwhile to investigate if at still higher IS concentrations the electrolysis still favours the monomer formation. This could be a possible alternative to a selective reduction of the double bond through catalytic reduction with hydrogen<sup>16</sup>. This latter procedure, however, is more elaborate, frequently requiring the use of a pressure of several atmospheres.

Gabani and Conti<sup>5</sup>, using similar experimental conditions, identified three different dimers without identifying the monomer. From their coulometric measurements at buffered pH 4.6 (9.5) they found *n*<sub>ap</sub> values of 0.97 (1.4) for the apparent number of electrons transferred. A *n*<sub>ap</sub> value of 0.97 suggests the dimerization reaction at pH 4.6 to be much faster than the electron transfer contrary to our findings which indicate monomer formation is highly favoured under acid conditions. A possible explanation for this discrepancy can be found in the potential applied to the working electrode. In fact, as shown by our CPE results at pH 4.8 (see Table 2) a certain amount of dimer is formed at less negative potentials, which, for a coulometric experiment signifies a *n*<sub>ap</sub> value less than two. The fact that for pH 9.5 Gabani and Conti<sup>5</sup> found a value of 1.4 *n*<sub>ap</sub> indicates monomer (*n*=2) and the dimer (*n*=1) formation occurs simultaneously, explaining the fractional value of *n*<sub>ap</sub> (1 < *n*<sub>ap</sub> < 2).

## Acknowledgements

The authors wish to acknowledge financial support received from FAPESP (Fundação de Amparo à Pesquisa do Estado de São Paulo) and CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico).

## References

1. E.Lamy, L.Nadjo e J.M.Saveant, *J. Electroanal. Chem.* **42**, 189 (1973).
2. P.Zuman, D.Barnes and A.Ryvolaka-Kejharova, *Discuss. Faraday Soc.* **45**, 202 (1968).
3. P.Zuman and L.Spritzer, *J. Electroanal. Chem* **69**, 433 (1976).

4. L.Spritzer and P.Zuman, *J. Electroanal. Chem.* **126**, 21 (1981).
5. S.Gabani and G.Conti, *Ann. Chim. (Rome)* **52**, 409 (1962).
6. P.Martinet and J.Simonet, *Bull.Soc.Chim.France* 3533 (1967).
7. O.L.Bottecchia, L.Degreve and J.F.C.Boodts, *J. Electroanal. Chem.* **285**, 37 (1990).
8. A.J.Fry, *Synthetic Organic Electrochemistry*, Harper and Row Publ., (1972).
9. L.Meites, *Polarographic Techniques*, Interscience Publ., N.Y. (1967), Ch. 3.
10. B.Breyer and H.H.Bauer, *Alternating Current Polarography and Tensammetry*, Interscience Publ. (1965)
11. R.G.Barradas and F.M.Kimmerle, *J. Electroanal. Chem.*, **11**, (1966) 128.
12. B.Timmer, M.Sluyters-Rebbach and J.H.Sluyters, *J. Electroanal. Chem.* **14**, 169 (1967).
13. A.J.Bard and K.S.V.Santhanan, *Electroanal. Chemistry*, vol. 4, Marcel Dekker, N.Y., (1970), 215.
14. P.Zuman and C.L.Perrin, *Organic Polarography*, Interscience Publ., N.Y., (1969) 95.
15. D.Bethell in J.F.Stoddarts (Ed.), *Comprehensive Organic Chem.*, vol. 1, Pergamin Press, Oxford, (1979), 44.
16. H.O. House, *Modern Synthetic Reactions*, vol. 2, W.A. Benjamin, (1972), 1.