

Synthetic and Mechanistic Aspects of the Electrochemical Behavior on Mercury of 4-Keto-Isophorone in Aqueous Medium: Selectivity of the Reduction Process

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Received: July 7, 1993; December 29, 1993

Estudos polarográficos dc e ac foram realizados com a 4-ceto-isoforona, 4KIS, no intervalo de pH 1-13. Experimentos de coulometria e eletrólise a potencial controlado em vários pH's e E_{ap} mostram boa seletividade sendo o monômero (produto original com redução da dupla ligação etilênica) o produto principal da eletrólise para pH's ácidos (pH < 5). Em pH básico forma-se além do monômero uma pequena proporção de dímero (20%). Um mecanismo de redução é proposto para a região ácida e básica.

A dc and ac polarographic investigation of 4-keto-isophorone, 4KIS, a conjugated diketone, was executed covering the complete pH interval. Controlled-potential coulometric and electrolysis experiments as a function of pH and applied potential, E_{ap} , showed good selectivity, with the monomer (original material with the double bond reduced) the only product obtained for pH \leq 5 and E_{ap} localized as cathodic as possible on the plateau of the reduction wave. In the basic pH region, the monomer remains the principal product although a small amount (~20%) of dimer is also obtained. A reduction mechanism is proposed for the complete pH region.

Key words: electrochemistry; α,β unsaturated ketones; 4-keto-isophorone.

Introduction

There are several papers in the literature dealing with the aqueous electrochemical reduction of α,β unsaturated ketones.^{1,5} Reduction executed under controlled-potential electrolytic conditions results in a variety of products showing a strong dependency on the media, pH, applied potential and other experimental variables.³ We therefore decided to re-evaluate the electrochemical behaviour of this class of compounds giving special attention to the problem of selectivity with respect to the products formed. In an earlier paper⁶ investigating isophorone, a simple, conjugated ketone, it was shown that selective reduction of the double bond (monomer) is possible if the applied potential, E_{ap} , is controlled at the plateau of the reduction wave and a strongly acid medium (pH~1) is used. This result differs from the literature^{1,7,8} where large-scale electrolysis experiments report the hydrodimer as the principal product of reduction. For isophorone⁶ the dimer was obtained, with a ~ 40% yield when basic pH conditions and E_{ap} at the lower part of the reduction wave were used.

According to Zuman³ selectivity of the products formed is very sensitive to structural modifications. In order to inves-

tigate if the selectivity observed with isophorone is retained with a structurally slightly more complicated, conjugated ketone, we decided to investigate the diketone 4-keto-isophorone, 4KIS. Since no electrochemical results with respect to 4KIS were found in the literature, the electrode mechanism was also investigated. We now report the results of our investigations.

Experimental

Apparatus. D_{ctast} and ac_{tast} polarograms were recorded on a Polarecord E506 polarograph equipped with a model E505 DME stand (all Metrohm, Swisse). The amplitude of the ac signal used was 10 mV p/p and the frequency was 75 Hz. Drop time was controlled mechanically at 2s. All experiments were done at 30 ± 0.1 °C.

Controlled-potential electrolysis and coulometric experiments were done with a model 173 potentiostat/galvanostat equipped with a model 179 digital coulometer (all P.A.R., U.S.A.). Coulometric experiments were done with a model 377 synchronous stirring motor, equipped with a model 377A cell (all P.A.R., U.S.A.).

A Metrohm model E500 pH-meter, equipped with a com-

vanostat + universal programmer (PARC). The area of the hanging mercury drop electrode (Metrohm E 410A) used was 0.02 cm^2 .

Controlled potential electrolysis and coulometric experiments were done with a model 173 potentiostat/galvanostat equipped with a model 179 digital coulometer (all PARC, U.S.A.). Coulometric experiments were done with a model 377 synchronous stirring motor, equipped with a model 377A cell (all PARC, U.S.A.).

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

Products and Solutions. All products, obtained from common commercial sources, were of A.R. purity. The ketal of 4-keto-Isophorone, 4-KKIS, was synthesized according to a procedure described in the literature^{8,9} and purified by fractional distillation. Stock solutions of the components used in the preparation of the buffers, as well as the NaCl stock solution, were prepared at the highest practical concentration. These solutions were purified by constant potential electrolysis applying to the Hg working electrode the most negative potential possible. The exact concentration of the stock solutions was determined using standard volumetric and gravimetric procedures. Working solutions of adequate pH and 4-KKIS concentration were prepared transferring appropriate volumes of the buffer components and 4-KKIS stock solutions to a volumetric flask. The ionic strength, μ , of the working solutions was kept constant at 1.0 M through addition of NaCl. During the polarographic and cyclic voltammetric investigations the 4-KKIS concentration was maintained constant at 1.0 mM. Pre-purified nitrogen was used to deaerate all solutions.

Results and Discussion

D.C. Polarography. A representative dc_t polarogram is shown in figure 1. A single dc wave is observed over the pH region investigated ($6.5 < \text{pH} < 13$). The logarithmic treatment of the waves resulted in straight lines.

The slopes are summarized in Table 1. Reduction of

Table 1. Polarographic parameters of 4-KKIS. $[4\text{-KKIS}] = 1 \text{ mM}$, $\mu = 1.0$, $t = 25^\circ\text{C}$.

pH	Dc_t slope (mV)	Ac_t slope (mV)	$E_{p/2}$ (mV)	$E_p - E_{1/2}$ (mV)
6.42	86	229	128	-62
7.05	84	208	132	-62
7.82	73	188	128	-56
8.67	72	195	134	-48
9.20	66	188	132	-40
9.50	62	185	120	-38
10.07	65	190	128	-43
10.39	64	180	124	-48
10.79	60	188	120	-54
11.60	64	180	124	-49
12.35	60	186	128	-50
12.71	54	181	128	-46

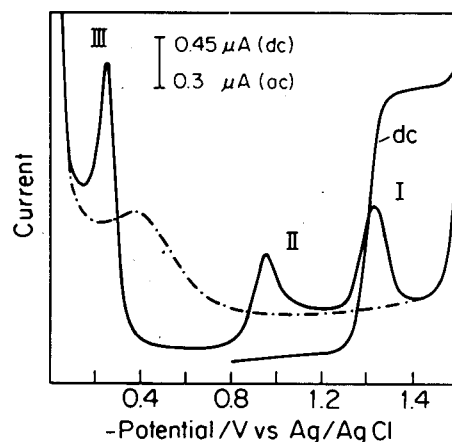


Figure 1. Dc_t and ac_t polarogram of 4-KKIS. $[4\text{-KKIS}] = 1 \text{ mM}$, $\text{pH} = 9.20$, $t = 25^\circ\text{C}$, $\mu = 1.0 \text{ M}$, (---) supporting electrolyte.

4-KKIS occurs with the uptake of two electrons (see coulometric results), so the values for the dc polarographic slopes are much higher than the theoretically predicted value of 29.6 mV for a reversible two electron transfer.

The influence of pH on the half-wave potential, $E_{1/2}$, is shown in Figure 2. Two straight segments, designated I and II, can be seen in the $E_{1/2}$ vs pH graph. For the strongly basic region ($\text{pH} > 9.6$) $E_{1/2}$ is independent of pH, so proton participation in the electrode mechanism is not "seen" polarographically. Under almost neutral and weakly basic conditions, (region I, $6.5 < \text{pH} < 9.6$), the half-wave potential is displaced to more negative values by 31.3 mVpH^{-1} on increasing the pH of the solution. Since the number of electrons transferred, n , is equal to 2 this result suggests the participation of one proton in the electrode mechanism¹⁰. It is well established that the reduction of unsaturated ketones occurs with the participation of protons, being the proton/electron uptake sequence a function of the acidity of the solution². From the intersection of segments I and II in the $E_{1/2}$ vs pH graph (Fig. 2) a value of 9.6 was obtained for $\text{pK}_{a,2}$.

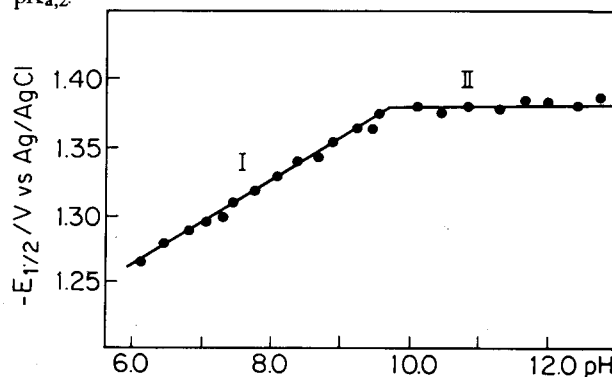
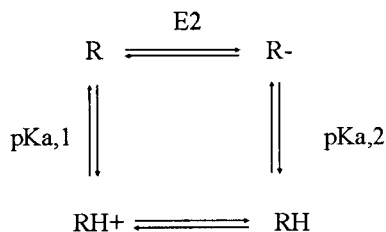


Figure 2. Half-wave potentials as a function of pH. $[4\text{-KKIS}] = 1 \text{ mM}$, $t = 25^\circ\text{C}$, $\mu = 1.0 \text{ M}$.

To confirm that the specimen accepting the first electron is the unprotonated molecule, R, we applied the square scheme of four members proposed by Laviron¹¹. In this model the possibilities of the first electron and proton uptake are represented as shown below:



To calculate the relative concentration of each specimen as a function of pH next values were used for the dissociation constants: $\text{pK}_{a,1} = -4$; $\text{pK}_{a,2} = 9.6$. Since the $\text{pK}_{a,1}$ value for 4-KKIS cannot be determined directly because of the hydrolysis of the ketal group, we used the value of isophorone (-4), determined by u.v. spectroscopy¹². This approximation is reasonable in view of the similarity between the 4-KKIS and isophorone structures; so the $\text{pK}_{a,1}$ value of -4 must be very close to reality. The relative percentages of each specimen present in the solution, calculated for the pH region investigated, are shown in table II. Examination of the values of Table 2 clearly shows the specimen accepting the first electron to be the unprotonated molecule.

Table 2. Percentage distribution of specimen and current calculated according to the four members square scheme¹². $\text{pK}_{a,1} = -4$; $\text{pK}_{a,2} = 9.6$; $K_{e,1}/K_{e,2} = 1$.

pH	6	7	8	9	10	11	12	13
%i ₁ /i	0.1	0	0	0	0	0	0	0
%i ₂ /i	99.9	100	100	100	100	100	100	100
%A	100	100	100	100	100	100	100	100
%AH ⁺	0	0	0	0	0	0	0	0
%A ⁻	0	0.3	2.5	20.1	71.5	96.2	99.6	100
%AH ⁻	100	99.7	97.5	79.9	28.5	3.8	0.4	0

The influence of several experimental parameters on the polarographic limiting current was investigated at pH 6.52, 9.20 and 12.44. Limiting current was found to be directly proportional to the 4-KKIS concentration over the complete concentration interval investigated (0.05-5 mM). It was also verified that the half-wave potential is independent of the concentration. These results suggest the limiting current to be diffusion controlled¹⁰.

A linear relationship between the limiting current and the temperature ($10 < t < 50$ °C) was observed for the pH values investigated. The temperature coefficients calculated from these results were 1.74, 1.68 and 1.18% °C⁻¹ for the pH values 6.52; 9.20; and 12.44, respectively. These values are characteristic for diffusion controlled currents¹³.

i-t Curves for the first drop, recorded immediately after

polarization of the D.M.E., were obtained at the pH values mentioned earlier. A straight line for the log i vs log t graph was obtained for all cases investigated. The slopes of these lines, as a function of the applied potential, are shown in Table 3.

Table 3. Slope, δ , of the log i vs log t graph. [4-KKIS] = 1 mM; $t = 25$ °C, $\mu = 1.0$.

pH 7.70		pH 9.20		pH 12.35	
E_{ap}/V	δ	E_{ap}/V	δ	E_{ap}/V	δ
-1.240	0.86	-1.328	0.82	-1.340	0.86
-1.320	0.57	-1.376	0.52	-1.440	0.39
-1.480*	0.32	-1.600*	0.27	-1.580*	0.26

* Values localized on the plateau of the polarographic wave.

The results in Table 3 show that on applying more negative potentials to the drop the value of the slope gets closer to the theoretically predicted value of 0.17 for a diffusion controlled current. These results can be explained assuming a chemical reaction, deactivating the radical formed, occurs after the first electron transfer. In fact, on applying more negative potentials to the drop the rate of charge transfer is increased exponentially. As a consequence, less time remains for the chemical reaction to occur, explaining why the slope of the log i vs log t graph approximates the theoretical value for a purely diffusion controlled current.

Ac polarography. All ac polarograms show three peaks, designated respectively I, II and III. A representative polarogram is shown in figure 1. Of these, peak I is localized in the same potential region as the dc wave, while peaks II and III have no counterpart in the dc polarogram. So peak I is a faradaic one while peaks II and III are non-faradaic peaks. The ac polarographic parameters, listed in table I, suggest the electron transfer not to be totally reversible^{14,15}. An alternative explanation is to assume a chemical reaction follows the first electron transfer. These hypothesis are supported by next experimental findings: (a) width at half height of peak I is significantly higher than the theoretical value of $92/n$ mV for a reversible electron transfer¹⁴; (b) a significant difference is observed between the peak potential and the half-wave potential ($E_p^I - E_{1/2}$); (c) the experimental slope resulting from logarithmic treatment is much higher than the theoretical slope of $118.2/n$ mV for a reversible electron transfer.

For all ac polarograms a much smaller peak current than limiting current ($i_p^I \ll i_l$) was found. Since, however, a significant ac current was observed, the possibility of the electron transfer to be totally irreversible is excluded, otherwise, under the experimental conditions used ([4-KKIS] = 1 mM), one should not observe any ac faradaic current¹⁶.

As already mentioned, peaks II and III have no counterpart in the dc polarograms suggesting those peaks to be connected with adsorption phenomena, being peak III the result of the

adsorption of the Ox-form of 4-KKIS and peak II its desorption. Since the desorption of the electro-active material occurs before the potential region is reached, where electron transfer takes place (peak I) one must conclude the charge transfer processes to occur without adsorption of the electro-active material. Further evidence for this behavior is obtained from comparison with the ac current of the pure supporting electrolyte. In fact, in the potential region between peaks II and III, the ac current in the presence of 4-KKIS is depressed when compared to the pure supporting electrolyte current. On the contrary, a perfect coincidence between both currents is observed in the potential region just before peak III, just after peak II and after peak I, indicating that, outside the potential region compressed between peaks III and II, the double layer structure is not modified by the presence of the electro-active material.

Controlled potential coulometry, C.P.C. C.P.C. experiments were executed at pH values of 9.20 and 12.50. At each pH value, a series of experiments were conducted gradually changing the applied working potential, E_{ap} , from a value localized at the foot of the i vs E curve to a value localized in the region of the limiting current. The results of these experiments are listed in Table 4.

Table 4. n_{ap} Values as a function of pH and E_{ap} [4-KKIS] = 0.05 mM, $\mu = 1.0$ M, $t = 25$ °C.

	E_{ap}/V vs Ag/AgCl, Cl ⁻	n_{ap}
pH 9.2	-1.320	1.47
	-1.340	1.66
	-1.370	1.87
	-1.390*	2.03
pH 12.5	-1.390	1.91
	-1.415	1.94
	-1.440	1.97
	-1.470*	2.03

* Values localized on the plateau of the polarographic wave.

The data of Table 4 clearly establish that at the more negative potentials two electrons participate in the electrode mechanism. When less negative working potentials (at the raising part of the i vs E curve) are used the apparent number of electrons transferred obeys: $n_1 < n_{ap} < n_1 + n_2$. This behavior suggests the reduction of 4-KKIS to follow an ECE type mechanism¹⁷. The chemical reaction, coupled to the first electron uptake, decreases the concentration of the radical formed explaining the fractional numbers obtained for n_{ap} .

The influence of the concentration of the electro-active material, at constant working potential, on the apparent number of electrons transferred was investigated at pH 9.20. The results of this study are shown in Figure 3, which clearly

shows that at the lower 4-KKIS concentrations the apparent number of electrons transferred tends to two. This behavior is characteristic of a process presenting a competition between the monomer formation (two-electron transfer) and dimer formation (one-electron transfer).

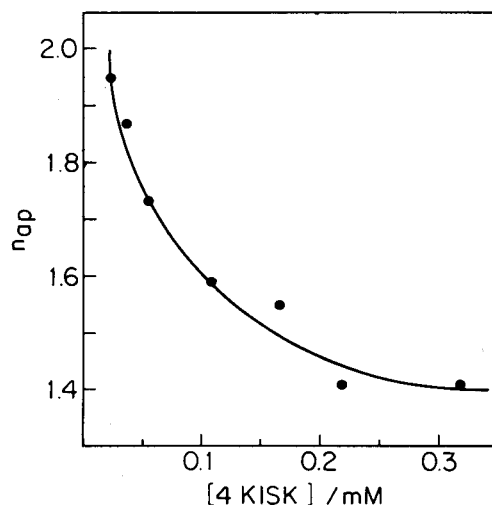


Figure 3. n_{ap} vs 4-KKIS concentration. pH = 9.20, $t = 25$ °C, $\mu = 1.0$ M.

Controlled potential electrolysis, C.P.E. Exhaustive controlled potential electrolysis experiments were executed at pH 9.20 and 12.20. For each pH value several C.P.E. experiments were done with the potential of the working electrode (Hg pool) chosen at different values of the i - E curve. The polarographic behavior of the solution was followed during the experiments. The polarographic current showed a regular decrease as a function of electrolysis time; no anodic current was observed at any time; at the end of the electrolysis the current coincided with the pure supporting electrolyte current. These findings suggest the intermediates, formed after the first electron transfer, are very reactive and that the final products are electro-inactive.

At pH 12.20 color of the solution changed from uncolored at the initial stages of the experiment to yellow (after exhaustive C.P.E.). This yellow color disappears when the solution is neutralized (pH ~7). The reduction products were isolated after adequate processing of the reactional mixture and identified by spectroscopic techniques (i.r., ¹H.M.N.R.). Product A was identified as 2,2,6 trimethyl-4-dioxolone-cyclohexanone, so the starting material with the double bound in the ring reduced (two electron transfer). Product B, obtained in a very small quantity (8%), was not characterized. However, based on the coulometric results one can suppose it to be a dimer (one electron transfer). It was also shown that the products formed are identical for both pH values investigated. The number of products formed is a function of E_{ap} . With the potential of the working electrode localized in the limiting current region of the i - E curve only product A is formed. When less negative potentials are used a mixture of A and B is obtained. At pH 9.20 formation of the product B was only observed if the working potential applied corresponds to a value for which $i_j/4$.

Cyclic voltammetry Cyclic voltammetric experiments were

executed at pH 9.20. 4-KKIS yields a single reduction peak corresponding to the dc polarography. No oxidation peak was observed for the scan rates investigated ($0.01 < v < 50$ V/s). A typical voltammogram is shown in Figure 4.

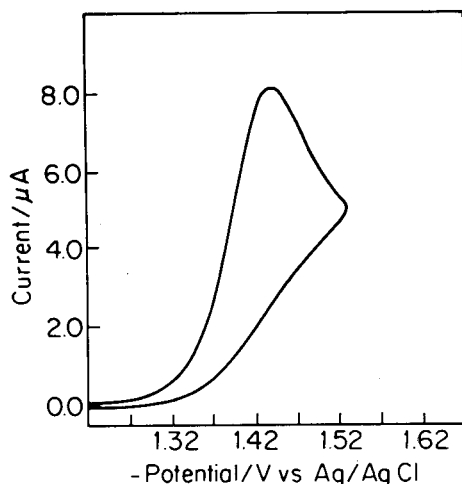


Figure 4. Cyclic voltammetry of 4-KKIS at mercury electrode. $[4\text{-KKIS}] = 1.0 \text{ mM}$, $\text{pH} = 9.20$, $t = 25^\circ\text{C}$, $v = 1.0 \text{ M}$, $\nu = 0.5 \text{ Vs}^{-1}$.

The variation of the peak potential with $\log v$ is linear with a slope of -30 mV . Peak potential is independent of 4-KKIS concentration over the range investigated ($0.1 \text{ mM} < C_A < 5.0 \text{ mM}$). The reduction mechanism is therefore of ECE or DISP1 type, i.e. the rate determining step is the protonation of the 4-KKIS radical¹⁸⁻²⁰

Conclusions.

Ac polarographic results clearly demonstrate that at the less negative potentials 4-KKIS is adsorbed at the mercury surface. However, in the potential region where the faradaic process occurs, 4-KKIS is already completely desorbed.

Based on the experimental results obtained we propose next reduction mechanism for the pH region between 6.0 and 10.0.

- (1) $\text{R} + \text{e}^- \rightleftharpoons \text{R}^\cdot$
- (2) $\text{R}^\cdot + \text{H}^+ \longrightarrow \text{RH}^\cdot$
- (3) $2\text{RH}^\cdot \longrightarrow \text{DIM (product B)}$
- (3') $2\text{R}^\cdot \longrightarrow \text{DIM (product B)}$
- (4) $\text{RH}^\cdot + \text{e}^- \longrightarrow \text{RH}^-$
- (4') $\text{RH}^\cdot + \text{R}^\cdot \longrightarrow \text{RH}^- + \text{R}$
- (5) $\text{RH}^\cdot + \text{H}^+ \longrightarrow \text{RH}_2 \text{ (product A)}$

Cyclic voltammetric experiments show an ECE (step 4) or DISP1 (step 4') type mechanism to be operative, being the rate determining step the protonation of the 4-KKIS radical (step 2). Unfortunately, we are unable to decide if the second electron transfer is heterogeneous (ECE) or homogeneous (DISP1) in nature.

The $E_{1/2}$ vs pH graph denounces the participation of only one proton in the reduction mechanism which is a sure indication for step (4) or (4') to be irreversible. In fact, if we consider step (4) or (4') to be reversible, polarographically

a 60 mV slope should be obtained for the $E_{1/2}$ vs pH graph¹⁰. Further support for this proposal is obtained from the fact that at these moderately alkaline solutions protonation of the carbanion, RH^- , is extremely favored²¹. Consequently the RH^- anion rapidly abstracts a proton from the medium displacing equilibrium (5) completely to the right.

Polarographic results do not furnish sure evidence for the dimerization step in the reduction mechanism. Unambiguous evidence for the dimerization step is obtained from the coulometric and CPE experiments. This is understandable considering the much higher area of the working electrode used in the latter experimental techniques. The fact that monomer formation (two electron transfer) is favoured on applying more negative potentials to the working electrode is easily understood taking into account that the charge transfer rate is an exponential function of applied potential, while rate of dimerization is independent of the potential. So on applying more negative potential to the working electrode an experimental situation is created where less time is allowed for the radical to dimerise while speeding up the acceptance of the second electron. As a result monomer formation is favoured.

Under more strongly alkaline conditions ($\text{pH} > 10$) polarographic results showed the reduction mechanism to occur without participation of protons ($dE_{1/2}/d\text{pH} = 0$). Controlled potential electrolysis results suggest a quite stable dianion is formed as denounced by the yellow color formed which only disappears on neutralization of the solution. Therefore the following mechanism adequately represents the 4-KKIS reduction in more alkaline medium:

- (1) $\text{R} + \text{e}^- \rightleftharpoons \text{R}^\cdot$
- (2) $\text{R}^\cdot + \text{R}^\cdot \longrightarrow \text{Dimer (Product B)}$
- (3) $\text{R}^\cdot + \text{e}^- \rightleftharpoons \text{R}^{\cdot-}$
- (4) $\text{R}^{\cdot-} \longrightarrow \text{RH}_2 \text{ (product A)}$
 $2\text{H}^+ \text{ (neutralization)}$

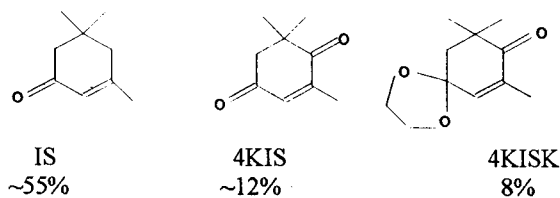
Controlled-potential electrolysis shows an interesting results from the synthetic point of view. Normally, electrolysis on a mercury pool electrode (non-renewed electrode surface) of unsaturated carbonyls results in a monomer/dimer mixture due to highly reactive intermediates formed. The results of 4-KKIS investigation showed, for the complete pH region investigated (pH 6.5-13), dimer formation is only of minor importance in the overall reduction mechanism and can be controlled by appropriate choice of the potential applied to the working potential.

In two earlier papers the results of the investigation of the reduction mechanism of two other conjugated ketones were published^{6,7}. Increasing the basicity of the solution favours dimer formation for all the conjugated ketones investigated. Dimer formation is also favoured applying less cathodic potentials to the working electrode. However, significant differences in the dimer yield were observed, as shown in Table 5.

These results can be understood in the light of the structural features of the conjugated ketones. Examination of the structures presented in Table 5 shows dimer formation to decrease with increasing steric hindrance.

Carefully choice of the medium, pH and working potential, permits an excellent selectivity for the monomer synthesis, in line with the results observed in earlier work^{6,7}. So of

Table 5. Percentage of dimer obtained for a series of, conjugated ketones. $pH = 9-10$; $[ketones] = 10 \text{ mM}$; $\mu = 1.0 \text{ M}$.



IS: isophorone⁶; 4KIS: 4-Keto-isophorone⁷; 4-KKIS: ketal of 4-keto-isophorone.

the series of compounds investigated, electro-synthesis is an excellent alternative to obtain selectivity of the dihydro derivatives.

Acknowledgments

Financial support from the FAPESP and CNPq is gratefully acknowledged.

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