

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

Adalgisa R. de Andrade*, José R. Romero and Julien F.C. Boodts.

*Faculdade de Filosofia Ciências e Letras de Ribeirão Preto-USP,
Departamento de Química, Av. Bandeirantes 3900
14040-901 Ribeirão Preto, SP, Brasil.*

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A redução eletroquímica do cetal da 4-ceto-isoforona, 4-KKIS, na região de pH entre 6,5 e 13, foi investigada por polarografia, dc e ac, voltametria cíclica, eletrólise e coulometria a potencial controlado. Uma única onda, de dois elétrons, foi observada para toda região de pH investigada. Os resultados experimentais são consistentes com um mecanismo eletródico do tipo ECE ou DISP1. Experimentos de eletrólise a potencial controlado mostraram uma alta seletividade (92%) na formação do monômero (produto de partida com a dupla ligação etilênica reduzida). O aumento da seletividade observada, quando comparada com outras carbonilas com estrutura similar, pode ser explicado pelo elevado grau de impedimento estérico da molécula de 4-KKIS.

The reduction of the ketal of 4-keto-isophorone, 4-KKIS, covering the $6.5 < \text{pH} < 13$ region, was investigated by polarography (dc and ac), cyclic voltammetry and controlled potential coulometry and electrolysis. A single two-electron transfer was observed over the pH region investigated. Experimental data are consistent with an ECE or DISP1 electrode mechanism. Controlled potential electrolysis experiments revealed an high selectivity (92%) for the monomer formation (original product with the ethylenic bond reduced) The increased selectivity observed compared with similar structures, can be explained by the higher degree of steric hindrance of 4-KKIS.

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

Introduction

The reduction of conjugated carbonyls is well documented in the literature, the reactional sequence of electron and proton uptake being well established¹⁻⁵. However because of structural features of the substrate and the influence of experimental parameters, such as the medium, electrode material, pH, etc., controlled potential electrolysis experiments normally result in a variety of reaction products without much selectivity being observed³. We therefore decided to investigate the aqueous electrochemistry of a series of simple, carefully chosen, α,β conjugated ketones showing structural variations which permitted to examine the influence of steric hindrance on the selectivity. In earlier papers we communicated the results of our investigation on isophorone⁶, a simple conjugated ketone, and 4-keto-isophorone⁷, a conjugated di-ketone of similar structure showing an higher degree of steric hindrance as a result of which better selectivity was obtained. These investigations also revealed that adequate choice of such parameters as pH and potential applied to the working electrode^{6,7} also permit

the selective synthesis of the monomer or dimer. To expand the series in order to find out how general this class of organic compounds behaves we investigated the ketal of 4-keto-isophorone, 4-KKIS. This substrate was chosen because the voluminous ketal group exerts a still more pronounced steric hindrance (compared to isophorone and 4-keto-isophorone) being the rest of the structure identical to the substrates investigated earlier^{6,7}. Since no electrochemical results with respect to 4-KKIS were found in the literature we also investigated the electrode mechanism. We now report the results of our investigation.

Experimental

Apparatus. Dc and ac^{*2} polarograms were recorded on a Polarecord E506 polarograph equipped with a model E505 D. M. E. stand (all Metrohm, Swiss). The amplitude of the ac signal used was 10 mV p/p while the frequency was 75 Hz. Drop time was controlled mechanically at 2s. All experiments were done at 25 ± 0.1 °C. Cyclic voltammetric experiments were done with a model 173 potentiostat/gal-

mination 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. 4-ketoisophorone, 4KIS, was synthesized according to a procedure described in the literature^{9,10} 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 and by 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 the desired pH and 4KIS concentration were prepared by transferring appropriate volumes of the stock solutions of the buffer components and of the 4KIS stock solution to a volumetric flask. The ionic strength of the working solutions was kept constant at 1.0 M through addition of NaCl. During the polarographic investigation the 4KIS concentration was maintained constant at 1.0 mM. Pre-purified nitrogen was used to deaerate all solutions.

Results and Discussion

Dc and ac polarographic investigation. Figure 1 shows some representative dc and ac polarograms of 4KIS. Polarograms were recorded covering the pH interval of 1-13. The analysis of Figure 1 shows distinct behavior according to the pH interval studied. We therefore decided to present the results and discussion by dividing the pH interval into three regions: (1) the acid interval (pH 5), (2) the weakly acid and neutral interval (5 pH 7.5), and (3) the basic interval (pH 7.5).

Polarographic results for the acid region (pH 5). All dc_{last} polarograms show a single polarographic wave. The polarograms, for solutions with pH less than 3.5, show a maximum of the first kind, which was observed even at concentrations as low as 5.0×10^{-5} M. A concentration of 0.002% Triton X-100 was used to eliminate the maximum. It is known from the literature that the use of a tenso-active substance can affect the electrochemical behavior.^{11,12} Therefore, this aspect was investigated in more detail. It was found that the half-wave potentials were not affected whereas

the currents decreased with increasing Triton X-100 concentration.

The behavior of the half-wave potential, $E_{1/2}$, as a function of pH is shown in Figure 2.

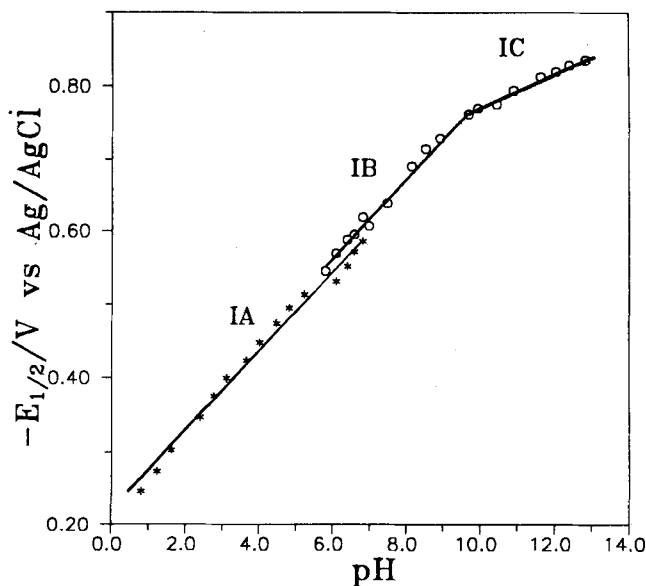


Figure 2. Half-wave potentials as a function of pH. 4KIS = 1 mM, $t = 30^\circ\text{C}$, $\gamma = 1.0$, (pH 4 values obtained in presence of 0.002% Triton X-100).

The $E_{1/2}$ vs pH graph clearly shows that with increasing pH the half-wave potentials are displaced to more negative values, suggesting that protons participate in the electrode mechanism. A straight line, designated IA, having a slope of 55 mVpH^{-1} is obtained for the pH region between 1 and 7.5. It is worthwhile to mention that the polarograms with pH < 3.5 were recorded in the presence of Triton X-100 (0.002%). As can be seen from Figure 2 their half-wave potentials fall on the straight line defined by the half-wave potentials of the polarograms recorded in the absence of Triton X-100 ($3.5 < \text{pH} < 7.5$). Since the number of electrons participating in the reduction is two (see coulometry results), a slope of 55 mVpH^{-1} for line IA suggests, polarographically, that two

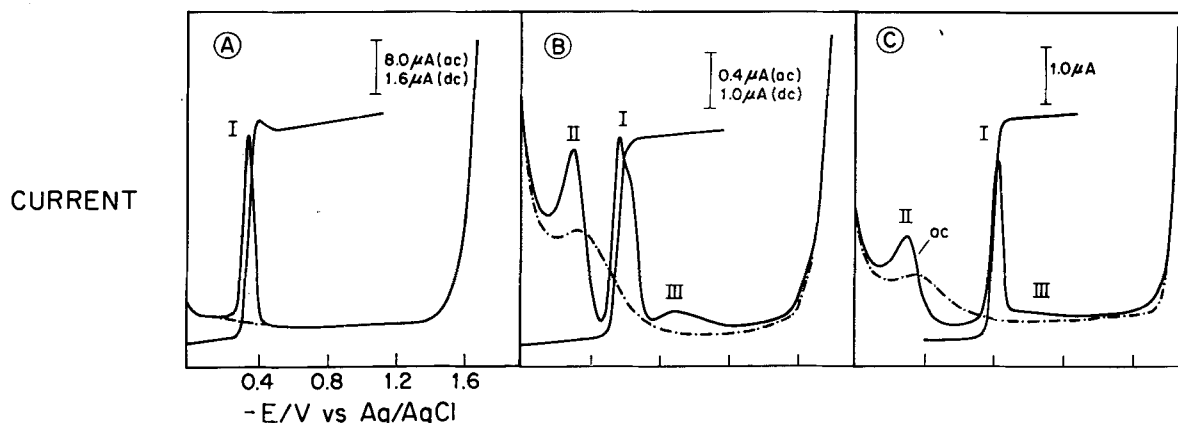


Figure 1. Dc and ac polarograms as a function of pH. (A) 2.43, (B) 6.08, (C) 10.90. 4KIS = 1 mM, $t = 30^\circ\text{C}$, $\gamma = 1.0$, (-.-) supporting electrolyte.

protons participate in the reduction mechanism in the pH region below 7.5. The slopes of the logarithmic analysis, as well as the half-width of the faradaic ac peaks are presented in Table 1.

Table 1. Dc slopes and width at half-height of the ac peak as a function of pH. $[4kis] = 1 \text{ mM}$, $t = 25 \pm 0.1 \text{ }^\circ\text{C}$, $\mu = 1.0 \text{ M}$.

pH	Dc wave IA slope/mV	DC wave IB slope/mV	ac peak IA $E_{p/2}/\text{mV}$	ac peak IB $E_{p/2}/\text{mV}$
0.80	36 ^a	-	60	-
1.98	41 ^a	-	72	-
2.76	42 ^a	-	68	-
3.37	47 ^a	-	64	-
4.01	32	-	62	-
4.47	29	-	62	-
4.81	33	-	72	-
5.23	47	-	b	-
5.80	28	33	b	-
6.10	28	33	b	-
6.41	26	27	b	-
6.60	45	48	b	-
6.83	37	45	b	-
8.54	-	42	-	88
9.23	-	35	-	69
10.39	-	34	-	76
10.91	-	27	-	70
11.50	-	32	-	72
12.41	-	36	-	80
12.73	-	40	-	76

a-Values obtained in the presence of 0.002% Triton-X-100.

b-Splitting of ac peak is observed.

The logarithmic analysis of the dc polarograms of solutions with pH = 4-5, recorded in the absence of Triton X-100, gives results close to the theoretically predicted values for a reversible two-electron uptake (29.6 mV). In the presence of Triton X-100 (pH 0.8-3.4) the polarograms furnish a slope higher than the theoretical value. Guidelli et al.¹² showed that a decrease in the velocity of electron transfer takes place when a tenso-active substance is adsorbed on the mercury surface. Under these circumstances, processes well known as reversible (e.g., cadmium ion reduction in acid medium) behave as quasi-reversible or even irreversible reactions. So the observed deviation of the slopes from the theoretical value for the dc polarographic waves recorded in presence of Triton X-100 must be attributed to the effect of the tenso-active substance since the electron transfers are in fact reversible. Further support for the reversibility of the electron transfer in acid medium is obtained from the ac polarograms, recorded in the absence of a tenso-active substance. The values found for the width at half-height, $E_{p/2}$, of the ac peaks are reasonably close to the theoretical value of 46 mV for a reversible two electron transfer.¹³ A single ac peak, designated peak I, is observed in the acid region (pH < 4). In this pH region the peak potential coincides perfectly

with the half-wave potential ($E_{1/2} = E_{p/2}$). These results suggest that the electron transfers behave reversibly. The reversibility of the electron transfer for acid conditions is also supported by the fact that the peak currents are of much higher intensity than the corresponding limiting current ($i_p \gg i_l$). Figure 1A shows the current outside the peak region to coincide with the current of the pure supporting electrolyte, suggesting that the electroactive material is not adsorbed onto mercury in the acid pH region. This behavior is different from the one shown by isophorone, IS,⁶ investigated earlier by us, where a strong adsorption of the oxidized form was observed. Both ketones being protonated in the acid pH region, this difference in adsorption behavior can be explained on the basis of the observed reduction potentials. Reduction of IS occurs at potentials around -1.0 V (vs Ag/AgCl), so the negatively charged mercury favours the adsorption of RH^+ . Reduction of the more easily reduced conjugated diketone, 4KIS, occurs around -0.3 V (vs Ag/AgCl). At these less negative potentials, where the double layer is positively charged, adsorption of the protonated 4KIS species is not favoured, which explains why adsorption phenomena are not observed with this compound.

Above pH 4 two new peaks, designated II and III, are observed (Fig. 1B), besides the principal faradaic peak, I. No waves in the dc polarograms, coinciding with ac peaks II and III, are observed. Furthermore, the current in the potential region between peak I and II is lower than the current observed for the pure supporting electrolyte in the same potential region. These experimental results suggest that peaks II and III are non faradaic adsorption peaks. Figure 3 shows some representative ac polarograms for different concentration at pH 4.8.

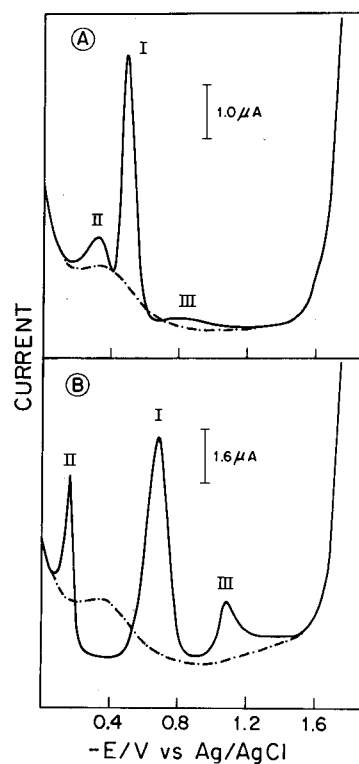


Figure 3. Ac polarograms as a function of 4KIS concentration. (A) 0.77 mM, (B) 7.00 mM. pH 4.86, $t = 30 \text{ }^\circ\text{C}$, $\mu = 1.0$, (---) supporting electrolyte.

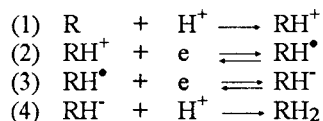
For dilute 4KIS solutions ($C < 0.4$ mM) peak III is almost imperceptible. Peak II is observed over the complete concentration interval investigated. At higher concentrations both peaks become very sharp and show a high current intensity. This behavior further supports the adsorptive nature of peaks II and III.

The behavior of the 4KIS dc polarographic wave was studied as a function of concentration (0.05-2.0 mM) at pH values of 1.10 and 4.88. A linear dependency between the limiting current and the concentration was observed for pH 1.10 and 4.88. The half-wave potentials were found to be independent of the 4KIS concentration.

The dependency of the limiting current on the temperature was studied in the 5-60 °C interval using the same pH values mentioned above. For all pH values investigated a linear relationship was obtained for the i_l vs T curve. Temperature coefficients obtained were 1.2 and 1.5 %°C⁻¹ for pH values of 1.10 and 4.88, respectively.

For the same pH values, the dependence of the limiting current on the height of the mercury column and the drop time was also investigated. For all cases a linear relationship between the limiting current and $h_{Hg}^{1/2}(t^{1/6})$ was observed. The linear relationship was not observed when other values were used for the exponent. All of these criteria support the conclusion that the electrode process is diffusion controlled.

The experimental data can be rationalized assuming reduction of 4KIS in acid region follows a CEEC mechanism:



For pH < 4, no evidence of adsorption of the species involved in the reduction was found. For pH 4, however, experimental evidence supports the adsorption of R, peak II represents the $R \rightarrow R_{ad}$ process.

The 55-mV slope of the $E_{1/2}$ vs pH graph indicates that the second electron-transfer (step 3) is reversible, otherwise the participation of a single proton in the reduction mechanism would be observed by the polarographic technique.¹⁴ The controlled potential-electrolysis and coulometric experiments (see later) also support a reversible electrode process without kinetic complications coupled to it.

Polarographic results for the basic region (pH > 7.5). In this pH region all dc_{fast} polarograms show a single polarographic wave. The $E_{1/2}$ vs pH plot presents two straight lines IB and IC (Figure 2), having slopes of 56 mV pH⁻¹ and 24 mV pH⁻¹, respectively. Since two electrons are involved in the 4KIS reduction these slopes suggest participation of two and one proton, respectively in the electrode process.

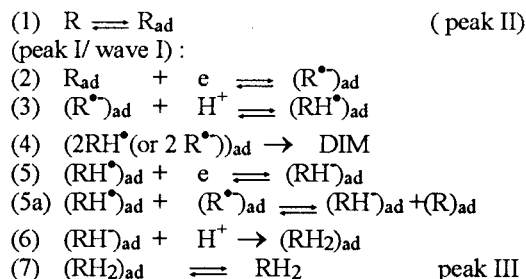
The slopes of the logarithmic treatment and $E_{p/2}$ values (Table I) are higher than the values theoretically predicted for a reversible electron transfer without kinetic complications coupled to it. The values, however, do not change significantly with increasing pH. Comparison of the ac peak potential with the corresponding dc half-wave potential shows a 10-30 mV cathodic displacement to occur in the basic pH region, contrary to the behavior for pH 4.0 where both parameters coincide. Also, peak currents are smaller than the corresponding dc limiting currents. This experimental behav-

ior suggests that the electrode process is no longer totally reversible as was observed for pH 5.0.

The influence of the drop time and height of the mercury column on the dc limiting current were investigated at pH 9.9. Linear relationships were only obtained for $t^{1/6}$ and $h_{Hg}^{1/2}$, suggesting that currents are diffusion controlled. The temperature coefficient was investigated at the same pH resulting in a 1.9%°C⁻¹ value. Albeit slightly higher than the value for the acid region it still falls in the range normally accepted for diffusion-controlled currents.¹⁴

The influence on the dc limiting current of the 4KIS concentration was studied in the 0.1 to 3 mM interval. A negative deviation from linearity was observed for [4KIS] 1.5 mM. Half-wave potentials were independent of concentration. This behavior can be understood assuming that dimerization of the anion radical, formed after the first electron uptake, occurs at the higher 4KIS concentration as was indeed observed under controlled-potential electrolysis conditions, where higher 4KIS concentrations, favouring second-order kinetics, are used. On the basis of other criteria investigated, dimerization is only of minor importance under polarographic conditions.

The experimental results can be rationalized assuming that an ECEC^{3,15} process with adsorption is operative in basic region.



So the reduction mechanism of 4KIS, in the basic pH region, follows the one proposed for isophorone, a similar, conjugated ketone, recently investigated by us.⁶ Step (5a) was included in the mechanism as a possible alternative to step (5). With the data available it is not possible to distinguish between them.

Contrary to the acid pH range, where no evidence supporting adsorption of the several species involved in the reduction mechanism was found, for the intermediate and basic regions it must be assumed that all species are adsorbed as denoted by the ac polarograms (Figs. 1B and 1C). Indeed for these regions, two extra peaks, II and III, having no counterpart in the dc polarogram, are observed. Peaks II and III are adsorption-desorption peaks delineating the potential interval where adsorption of the species occurs.

From the intersection of lines IB and IC (Figure 2) an apparent value of 9.2 can be obtained for equilibrium (6). So for solutions with pH 9.2 step (6) does not occur, explaining why only the participation of a single proton ($E_{1/2}/pH = 24$ mV) is observed polarographically. This is quite reasonable since the proton concentration at these higher pH values is very low, so the anion, formed after the second electron uptake, is stable. For pH 9.2 the proton concentration in solution is already adequate for step (6) to occur, explaining

the participation in the electrode mechanism of two protons ($E_{1/2}/\text{pH} = 56 \text{ mV}$) as observed polarographically.

Electrode mechanism in the intermediate region (5.5 pH 7.5). For the 5.5 pH 7.5 region the faradaic peak (peak I) in the ac polarogram clearly shows a deformation on its more negative side (Figure 1B) whereas the corresponding dc polarograms continue to show a single wave. The logarithmic treatment of these dc waves, however, did not result in a straight line but in two straight segments connected by a sloping region. This behavior, characteristic of a composite wave ($E_{1/2}/E_p$ small)¹⁶ confirms the ac behavior and shows the wave (peak) to represent two overlapping electrode processes. The analysis of these experimentally unfavourable data was recently solved by one of us using the Gauss-Newton algorithm.¹⁷ Excellent convergence of the experimental data was obtained for the 5.80 pH 6.80 region. For extremely unfavorable situations (5.5 pH 5.8 and 6.80 pH 7.5) where $0.1 < i_{1,1}/i_{1,2} < 0.9$ the algorithm no longer handles the problem. The half-wave potentials obtained for the intermediate region were plotted on Figure 2 and do fit lines IA and IB.

The splitting as a function of pH of the polarographic waves of conjugated ketones is a process frequently reported in the literature^{3,4} and is explained as a consequence of the rate at which the acid-base equilibrium is established. So, at these intermediate pH values, the rate of protonation of R leading to RH^+ is no longer fast enough so both R and RH^+ exist simultaneously in the double layer, leading to two waves (peaks). Because RH^+ is more easily reduced, it gives rise to the less cathodic wave (peak) whereas R is responsible for the more cathodic wave (peak).

Controlled-potential coulometry and electrolysis. Controlled-potential coulometric experiments were conducted at pH values 4.8 and 11.7. Twenty milliliters of $4.84 \times 10^{-2} \text{ mM}$ 4KIS were electrolysed with the potential of the working electrode controlled at the plateau of the i vs E curve. Values of 1.95 ± 0.04 (pH 4.8) and 1.83 ± 0.02 (pH 11.7) were obtained for the apparent number of electrons transferred. These values are in line with the controlled-potential electrolysis results (see below) where for the basic pH value a small quantity of dimer was found.

To isolate and identify the reduction products, exhaustive electrolysis experiments were carried out with a large mer-

cury pool working electrode ($A=23 \text{ cm}^2$). Experimental details and results are collected in Table II.

To secure adequate buffering capacity the concentration of the buffer component, present at the lowest concentration, was increased and kept at least 20 times the 4KIS concentration. Progress of the electrolysis was followed polarographically and by uv spectroscopy. Polarographic limiting current showed a continuous decrease with increasing electrolysis time, at the end of the experiments coinciding with the residual current of the pure supporting electrolyte. No anodic wave was observed at any time. This result was confirmed by uv spectra where a continuous decrease of the intensity of the conjugated carbonyl band at 240 nm as a function of electrolysis time was observed.

Products were separated by TLC after neutralization and adequate processing of the reaction mixture. Products, identified by common spectroscopic techniques, are shown in

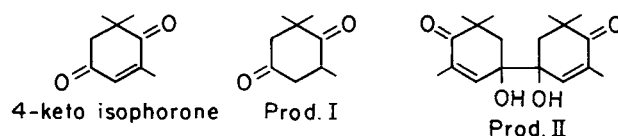


Figure 4. Structural formula of the substrate and electrolysis products.

figure 4. For acid conditions only a single product was found, identified by i.r and ¹HNMR

as 1,1,3-trimethylcyclohex-2,5-dione, so the starting material with the ethylenic double bond reduced (product I, Fig.4). For alkaline conditions, besides the monomer, a dimer is obtained (product II, Fig.4).

Conclusions

The experimental results of our investigation show that the reduction of 4KIS on mercury follows the general mechanism of this class of compounds,³ in particular the one for isophorone investigated earlier by us.⁶ Compared to the latter compound, the difference is that no adsorption of 4KIS on mercury is observed for pH 4.

The controlled-potential electrolysis results are interesting from the synthetic point of view because of the excellent selectivity obtained. Normally, electrolysis on a mercury pool electrode (non-renewed electrode surface) of α,β -unsaturated carbonyls results in a monomer-dimer (and polymer) mixture due to the highly reactive intermediates formed. As a result of our isophorone⁶ investigation, we already emphasized the importance of the control of pH and E_{ap} to assure selectivity. The results of the 4KIS investigation not only confirmed the selectivity, but also showed monomer selectivity to be more easy for the diketone. In fact while for isophorone a strongly acid medium (pH~1) is required to obtain the monomer as the sole reduction product for 4KIS, choosing the right E_{ap} , the monomer is obtained as the only product even at pH~5. Increasing the basicity of the solution favours dimer formation for both ketones investigated; however, $[\text{DIM}]_{\text{IS}} > [\text{DIM}]_{\text{4KIS}}$. These results can be understood in light of the structural features of the diketone where the

Table 2 - Distribution of the products as a function of pH as obtained from controlled-potential electrolysis. [4KIS] = 10 mM; $t = 25 \pm 0.1$ °C; $\mu = 1.0M$.

pH	$-E_{ap}$ vs Ag/AgCl	Products
1.0	0.61	100% monomer
4.9	0.64	100% monomer
4.9	1.14	100% monomer
9.9	1.14	80% mon./20% dimer
10.5	0.96	80% mon./20% dimer
10.5	1.61	80% mon./20% dimer

* All potentials are controlled at a value in the plateau region of the i vs E curves.

rad-rad couple suffers more accentuated steric hindrance. Steric hindrance being less pronounced with isophorone(IS), it is reasonable that more dimer is obtained with this structure, specially under basic pH conditions where the radical intermediate is more stable.

Finally, the good selectivity obtained with 4KIS, confirming identical conclusion with IS, points to a general behavior of these , unsaturated ketones in aqueous medium when adequate control of pH and E_{ap} is maintained.

Acknowledgments

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