Article

Electrochemical Behavior of 4-keto Isophorone in Non-Aqueous Medium in the Presence of Carbon Dioxide

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A cinética do acoplamento redutivo do CO_2 com o ânion-radical da 4-ceto isoforona (4KI) em meio de acetonitrila e eletrodo amalgamado de ouro foi analisada utilizando-se voltametria cíclica e cronoamperometria de duplo salto de potencial. A velocidade de acoplamento foi estimada em aproximadamente 0,35 s^{-1} e o mecanismo eletródico em velocidades de varredura baixas (v < 1 V s^{-1}) mostrou ser predominantemente DISP1.

The kinetics of the slow coupling of CO_2 with the anion-radical of 4-keto isophorone (4KI) in acetonitrile and on a gold/amalgamated electrode has been analyzed by using cyclic voltammetry and double potential step chronoamperometry. The coupling rate is estimated as 0.35 s^{-1} and the electrode mechanism at slow sweep rates (v < 1 V s^{-1}) is predominantly DISP1.

Introduction

The electrochemical reduction of activated olefins in non-aqueous solvents is well documented in the literature[1-5]. In the absence of a proton donor the reduction of these substrates normally occurs in two, well separated, one-electron transfers, were the anion-radical formed after the first electron uptake, is quite stable under these experimental conditions. These findings stimulated the investigation of the influence in the presence of traps capable of intercepting the radical intermediate. This is of practical importance for syntheses and C-C bond formation and functionalisation of activated olefins. Carbon dioxide has been widely used as an anion-radical intercepting agent. The electrochemical behavior of aromatic hydrocarbons[6-10] and quinones[11-13] in the presence of CO_2 has received special attention, probably due to the adequate stability of their electrogenerated anion-radical.

The limiting mechanism governing the electrode process in the presence of CO_2 strongly depends on the reduction potential of the substrate compared to the reduction potential of CO_2[6,11,14]. For aromatic hydrocarbons, experi-mental evidence clearly points to a limiting mechanism involving a coupling reduction between $CO_2^{-\bullet}$ and the aromatic hydrocarbon[6] (ECE mechanism) where the reduction potential of the substrate is more negative than the one of $CO_{2/}$ $CO_2^{-\bullet}$. It was demonstrated[14] in the case where the substrate is more easily reduced than CO_2($E^o_{substrate}$ < E^o_{CO2}) that homogeneous redox catalysis becomes a very important mechanistic step in the reductive addition of CO_2 to the aromatic hydrocarbon which is best described by a $DISP_1$ mechanism. In fact the ECE-DISP mechanism[15,16] are stated for a very large number of organic molecules and frequently are reported in the literature[17]. It is very important to discern between both mechanisms, especially when one wants to calculate the rate constant based on the theoretical equations. The use of the wrong equations can introduce a factor of two orders of magnitude error in the calculated rate constant[17].

The operative mechanism of the reductive addition of CO_2 to quinones is not yet completely elucidated[11,13]. The existence of a threshold potential governing the CO_2 addition at the first or the second voltammetric peak of the
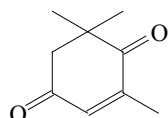
quinones was suggested by Nagaoka *et al.*[11]. These authors concluded that reductive addition of CO_2 to the quinones takes place at the first voltammetric peak where the $Q/Q^{\bullet-}$ couple has a reduction potential equal or more negative than -0.5 V (Ag/Ag$^+$ 0.01 mol dm^{-3}). In this case an ECEC electrode mechanism was proposed. For quinones having reduction potentials more positive than -0.5 V no addition at the first peak was observed. In this case a reductive dianion coupling with CO_2 is observed as supported by a positive shift of the dianion peak in the presence of CO_2. An EEC mechanism was proposed to describe this situation.

The potential for generating anion-radicals and their stability depend upon structure, as reported for aromatic compounds[6-10] and activated olefins[11-13]. Simpler conjugated olefins are less investigated[2,18]. In order to verify the influence of anion-radical stability on CO_2 addition, 4-keto-isophorone was chosen as a model. In this paper we report results from cyclic voltammetry, chronoamperommetry and controlled potential coulommetry.

Experimental

*Chemicals—*4-Keto-isophorone,4KI, (Fig. 1) was synthesized from isophorone (Aldrich) following a procedure described in the literature[19,20]. Spectroscopic grade acetonitrile, AN(Merck-Uvasol) was used as received. Tetrabutylammonium perchlorate, TBAP (Eastman) was vacuum dried at 100 °C for 48 h and stored in a desiccator over KOH. Since the cyclic voltammogram of the 0.1 mol dm^{-3} TBAP/AN solution, recorded at high sensitivity, resulted in a low, flat, baseline, TBAP was used without further purification. Before use, both N_2 and CO_2 (Air Liquid) were passed through a gas purification system made of a column containing BTS catalyst (BASF) followed by a series of washing bottles containing: H_2SO_4 (conc.), molecular sieve (3 Å) and activated silica. The residual water content of the final system (0.1 mol dm^{-3} TBAP/AN), determined by Karl Fisher titration, was found to be 30 mmol dm^{-3}. The maximum CO_2 concentration (saturation) dissolved in 0.1 mol dm^{-3} TBAP/AN, determined by acid-base titration, was found to be 0.14 mol dm^{-3}. This is a reasonable value when compared to the values of 0.20 mol dm^{-3} (0.1 mol dm^{-3} Et$_4$NClO$_4$/AN)[11], 0.24 mol dm^{-3} (Et$_4$NBF$_4$/AN)[12] and 0.15 mol dm^{-3} (Et$_4$NBr/DMF)[6.]

The CO_2 reduction wave in 0.1 mol dm^{-3} TBAP/AN is located very close to the discharge of the supporting elec-

trolyte where its beginning is estimated as -2.6 V *vs.* Ag/0.01 mol dm^{-3} Ag$^{+(\#)}$.

An EC&G PARC 273 potentiostat/galvanostat was used in all C.V. and double potential step chronoamperometric, D.P.S.C., experiments. The system was monitored by an IBM-PC compatible microcomputer controlled by the PARC m270 software. Controlled potential coulometric, C.P.C., experiments were performed using a 173 potentiostat/galvanostat equipped with a model 179 digital coulometer and a model 377 cell/synchronous stirrer (all EC&G PARC).

A commercial polarographic cell with five openings, adapted to receive three electrodes and the inlet/outlet for the gases, was used for C.V. and D.P.S.C. experiments. The working electrode was an amalgamated gold disc with a surface area of ~0.5 cm^2. The amalgam was removed daily from the gold surface using 40% (v/v) HNO_3. The gold surface was mirror polished using α-alumina (0.3-0.05 µm) before applying fresh Hg. The auxiliary electrode was a Pt wire spirally wound around the working electrode. All potentials are referred to a Ag/10 mmol dm^{-3} Ag$^+$ (0.1 mol dm^{-3} TBAP/AN) reference electrode; isolated from the bulk of the solution by a luggin capillary, located as close as possible to the working electrode. The ohmic resistance of the electrochemical system was found to be 75 Θ, the electronic internal compensation of the M270 interface was used as usual. For controlled potential coulometry experiments (CPC) a mercury pool (A = 12.5 cm^2) working electrode was used.

Results and Discussion

The cyclic voltammetric behavior of 4KI in the absence of CO_2 was investigated as a function of sweep rate, (0.01 < v < 50 V s^{-1}), and concentration (0.1-5 mol dm^{-3}, v = 0.1 and 5 V s^{-1}). A representative voltammogram is shown in Fig. 2A. During the cathodic sweep two well defined monoelectronic peaks are observed while only a single monoelectronic peak , corresponding to cathodic peak I, is observed during the anodic sweep. The analysis of the cyclic voltammograms recorded with the cathodic switching potential limited at -1.8 V furnished for the first monoelectronic process: $i_{pa}/i_{pc} < 1$ and $\Delta E_p = 72$ mV. The mechanistic criteria for these peaks are reported in Table 1. For the potential sweep rate analyzed, the first pair of peaks can be consider as a reversible monoelectronic process represented by the 4KI/4KI$^{\bullet-}$ couple.

The small discrepancies from the theoretical values can be related to a chemical reaction occurring after the first electron transfer. Two possible explanations for this behavior can be found: (1) dimerization to a less extension of the anion-radical of 4KI as reported for isophorone in

Figure 1. 4-keto isophorone (4KI)
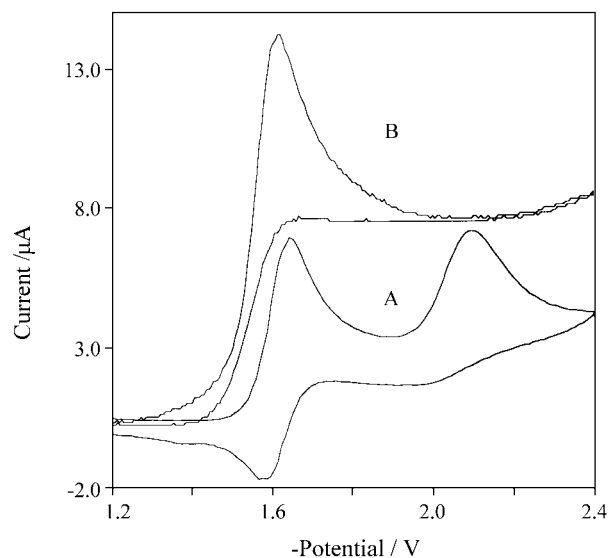
Figure 2. Cyclic voltammograms of 1.0 mmol dm^{-3} 4-keto isophorone in AN/0.1 mol dm^{-3} TBAP recorded at v = 0.1 V s^{-1}: (a) in the absence; (b) in the presence of CO_2 (0.14 mol dm^{-3}).

anhydrous DMF[3] or (2) irreversible protonation by residual water present in the solvent (30 mmol dm^{-3}). Since we did not have access to a totally reversible cyclic voltammetric behavior for the first cathodic peak, a diffusion coefficient of 9.05 x 10^{-5} cm^2 s^{-1} was calculated as a first approximate value.

No anodic counterpart for the second cathodic peak was observed (see Fig. 2A), even at the highest sweep rate investigated (50 V s^{-1}). A 30 mV anodic displacement of E_p^{II} was observed with increasing 4KI concentration. Addition, on purpose, of water resulted in an increase of i_p^{II} together with an anodic displacement of the peak potential. At the end, fusion between the two cathodic peaks occurred resulting in a single irreversible cathodic peak. This behavior of the second cathodic peak is well known and was observed for other conjugated ketones[3]. So, the electrode mechanism for the reduction of 4KI follows the well established EEC mechanism for activated olefins, the first voltammogram peak corresponding to the 4KI/4KI$^{\bullet}$ couple and the second peak to the 4KI$^{\bullet}$/4KI$^{=}$ couple.

Even with the proper care, no reproducible data were obtained if the voltammograms were recorded with E_λ at

-2.4 V. In this case it was necessary to renew the electrode surface in order to obtain reproducible curves. However, limiting E_λ at -1.8 V (potential corresponding to the first monoelectronic process) gave perfectly reproducible cyclic voltammograms. These results suggest adsorption on the electrode surface of the intermediate(s) and/or the product(s) formed after the second electron transfer. Further support for the occurrence of the adsorption is the rather symmetric shape of peak II (Fig. 2A). Based on these findings the electrode surface (Hg/Au) was renewed just before the recording of any cyclic voltammogram.

The cyclic voltammetric behavior of 4KI in the presence of CO_2 (saturated), when investigated as a function of v, shows some remarkable changes compared to its behavior in the absence of the anion-radical capturing agent. Two distinct sweep rate regions can be distinguished. For $v < 0.8$ V s^{-1} drastic changes in the C.V. behavior are observed: (1) The re-oxidation peak of 4KI$^{\bullet}$ as well as the second cathodic peak are no longer observed the C.V. shows a single irreversible peak in the presence of CO_2 (Fig. 2B); (2) The peak current is doubled ($i_{p,CO_2} = 2\ i_{p,N_2}$) suggesting the single cathodic peak to represent a two-electron uptake, which was confirmed by C.P.C. showing n = 2 in the presence of CO_2 and n =1 under N_2 atmosphere; (3). A $\Delta E_p/\Delta \log v$ value equal to -28 mV was found (see Fig. 3).
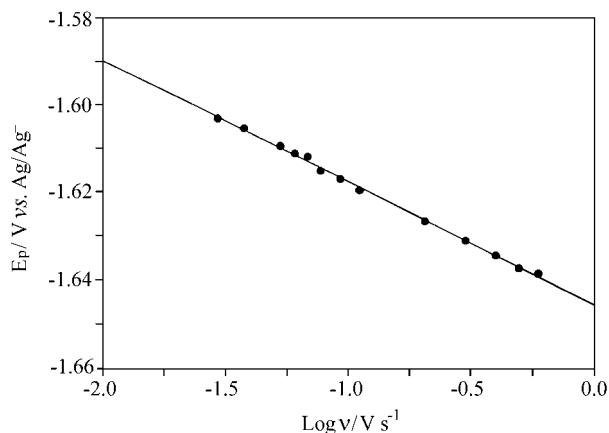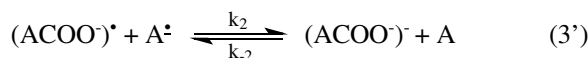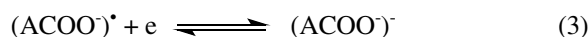

Figure 3. Dependence of E_p on log v for 1 mmol dm^{-3} of 4KI in AN/0.1 mol dm^{-3} TBAP in the presence of CO_2 (0.14 mol dm^{-3}).

Table 1. Kinetic parameters for the first 4-keto isophorone reduction wave in the presence (0.14 mol dm^{-3}) and in the absence of CO_2 in 0.1 mol dm^{-3} TBAP/AN; WE: amalgamated gold disc; [4KI] = 1 mmol dm^{-3}.

Kinetic parameter	4KI reduction without CO_2 / mV	4KI reduction with 0.14 mol dm^{-3} of CO_2 / mV
$\partial E_p/\partial \log v$	0.0	28.0
$\partial E_p/\partial \log C_A$	0.0	0.0
i_{pa}/i_{pc}	0.7	no anodic peak
$\Delta E_{pc}/E_{pa}$	72	no anodic peak

Experiments varying the 4KI concentration did not show any dependence of E_p on C_A in the range analyzed, $C_A = 0.05\text{-}5$ mol dm^{-3}, $\nu = 0.1$ V s^{-1}, (see Table 1) while the peak current was found to be proportional to $\nu^{1/2}$.

This behavior of 4KI at low sweep rates is indicative of a coupling of the anion-radical, $A^{\bullet-}$, to CO_2. The experimental results show that the coupling can be described by an ECE (steps 1, 2, 3, and 4) or DISP1 (steps 1, 2, 3', and 4) mechanism (see below), the fundamental difference being the way the second electron uptake occurs: heterogeneous (ECE) or homogeneous (DISP). The ECE-DISP1 problem has been the subject of detailed theoretical analysis for several electrochemical techniques[6,15,16]. Cyclic voltammetry is a very powerful technique in mechanistic analysis but, in this particular case it is not able to discriminate between ECE/DISP1, this impossibility results from the fact that the rds (step 2) is the same for both mechanisms as stated below.

$$A + e \rightleftharpoons A^{\bullet-} \qquad (1)$$

$$A^{\bullet-} + CO_2 \xrightarrow{k_1} (ACOO^-)^{\bullet} \qquad (2)$$

$$(ACOO^-)^{\bullet} + e \rightleftharpoons (ACOO^-)^- \qquad (3)$$

$$(ACOO^-)^{\bullet} + A^{\bullet-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} (ACOO^-)^- + A \qquad (3')$$

$$(ACOO^-)^- + CO_2 \longrightarrow A(COO^-)_2 \qquad (4)$$

Further advance in the mechanistic formulation was attempted by performing double potential step chronoamperometric experiments. The potential was stepped from an initial resting potential of -1.20 V to a potential of -1.70 V, where it was kept for a time θ, finally being stepped back to -1.20 V. Figure 4 shows the theoretical i(2)/i(θ) *vs.* log θ curves for the ECE/DISP1 cases[22] as well as the experimental data obtained for 4KI + CO_2. The experimental results were fitted to the working curve by displacement of the x axis. While no acceptable fit can be obtained between the experimental data and the theoretical curve for an ECE mechanism, a more than reasonable fit, at least in the log θ -2,0 region, is obtained for the DISP1 mechanism. Comparison of the theoretical working curve and the experimental points leads to $k_1 = 0.35$ s^{-1}. DISP1 kinetics were observed for the reductive coupling of other classes of compounds with CO_2[14,24]. The reduction of 1,4-benzoquinone[24] showed an even slower coupling constant. When we compare the radical-anion formed in the first electron transfer of both compounds one can conclude that 4KI is much more unstable than the BQ, so the coupling constant is related to the life time of the anion-radical. This slow coupling reaction with the CO_2 molecule is predicted by Marcus theory. The coupling rate of the anion-radical (step 2) is subject to large charges due to the reorganizational energy of the solvent as the linear CO_2 molecule will have to bend in order to react with the anion-radical.

For the fast potentiostatic step region (0.1 < θ < 10 ms) a mixed behavior is observed. In this region, besides the slow reductive addition of CO_2 (step 2) the reverse reaction (step 1 of the mechanism) starts to compete with the CO_2 addition explaining the not totally satisfactory fitting observed for θ < -2 between the experimental data and the DISP1 simulated curve (Fig. 4). The cyclic voltammetry for high sweep rates, discussed below, showed the same evidences.

For higher sweep rates (ν > 0.8 V s^{-1}) less drastic changes are observed in the C.V. in the presence of CO_2. The duplication of the current of the first cathodic peak, verified at lower sweep rates (see Fig. 2B), is no longer observed approaching the peak current values much closer to the ones obtained in the absence of CO_2. A perfect fit between curves A and B (Fig. 5) is not observed because it was not possible to achieve high enough sweep rates to
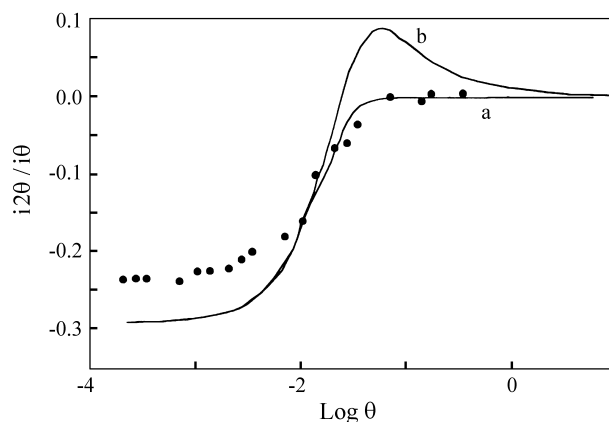
Figure 4. Dependence of i(2θ)/iθ on log θ. (•) experimental data for 1 mmol dm^{-3} 4KI in AN/0.1 mol dm^{-3} TBAP in the presence of CO_2 (0.14 mol dm^{-3}). Continuous curves: theoretical behavior for: (a) DISP 1; (b) ECE mechanisms.
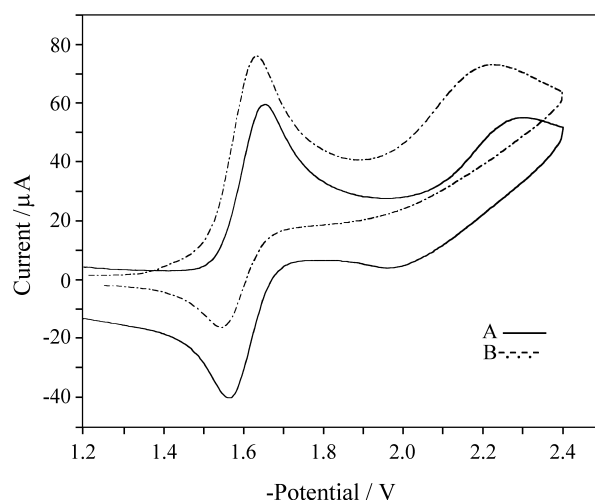
Figure 5. Cyclic voltammograms of 1 mmol dm^{-3} of 4KI in AN/0.1 mol dm^{-3} TBAP: (a) in the absence; (b) in the presence of 0.14 mol dm^{-3} CO_2, $\nu = 5.0$ V s^{-1}.

completely eliminate the influence of step 2 on the voltam-metric behavior of 4KI. Simultaneously an anodic displace-ment of E_p^{II} is observed under these experimental conditions (Fig. 5). An identical experimental behavior[11] was reported for the addition of CO_2 to a series of quinones in acetonitrile.

Based on the anodic displacement of E_p^{II} and in the absence of substantial changes in the first peak, the authors assumed the addition of CO_2 to occur between the dianion and CO_2 and proposed an EEC mechanism to represent the electrode mechanism. So our experimental results at the higher sweep rates ($v > 0.8$ V s^{-1}) seem to follow the same electrode mechanism[11].

Acknowledgments

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