

MECHANISM OF THE ELECTROCHEMICAL CARBOXYLATION OF AROMATIC KETONES IN DIMETHYLFORMAMIDEAbdirisak A. ISSE¹ and Armando GENNARO^{2,*}

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Dedicated to Professor Sergio Roffia on the occasion of his retirement and in recognition to his contribution to molecular electrochemistry.

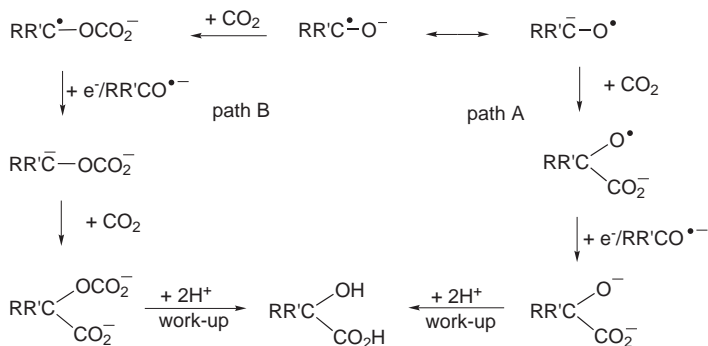
The mechanism of the electrochemical carboxylation of several benzophenones ($X\text{-C}_6\text{H}_4\text{COC}_6\text{H}_5$; $X = 4\text{-OCH}_3, 4\text{-CH}_3, \text{H}, 3\text{-Cl}, 3\text{-CF}_3, 4\text{-CF}_3$ and 4-CN) and several ring-substituted acetophenones ($Y\text{-C}_6\text{H}_4\text{COCH}_3$; $Y = 4\text{-OCH}_3, \text{H}, 3\text{-OCH}_3, 3\text{-Cl}, 3\text{-CF}_3, 4\text{-CF}_3, 3\text{-CN}$ and 4-CN) has been investigated by cyclic voltammetry in dimethylformamide. In the presence of CO_2 , all compounds exhibit a single irreversible peak representing a 2 e reduction process. The reaction mechanism has been analysed using the dependence of the peak potential E_p on various experimental parameters such as the concentrations of the reactant, the scan rate and the temperature. Also the kinetics of the electrocarboxylation reaction has been examined. The whole set of results has been carefully analysed in the framework of an ECE-DISP mechanism. It has been found that, under the conditions employed, the electrocarboxylation reaction is always under a mixed ECE-DISP1 kinetic control. The first step of the reaction is an attack, *via* the oxygen atom, of the electrogenerated ketyl radical anion $\text{RR}'\text{CO}^{\cdot-}$ at CO_2 . Further reduction of the carbonate-like adduct arising by such an attack followed by a second carboxylation reaction gives an arene-2-carboxylic acid.

Keywords: Cyclic voltammetry; Benzophenones; Carbon dioxide; Acetophenones; Ketyl radical anion; Electrocarboxylation; Electrochemistry; Carboxylic acids.

Electrochemical fixation of CO_2 in aromatic ketones has attracted a considerable interest as a method of obtaining 2-aryl-2-hydroxyalkanoic acids¹⁻⁶, which are intermediates in the synthesis of a variety of fine chemicals such as, for example, pharmaceutically active 2-arylpropanoic acids. Several groups have investigated the electrocarboxylation of aromatic ketones, with particular attention to the synthetic aspects of the process. Ikeda and Manda² have reported that electrocarboxylation of several substituted benzophenones carried out in dimethylformamide (DMF) and 1.71 M KI at a Hg electrode gives α -hydroxy acids with yields 62–92%. The process has

been further improved by Silvestri *et al.*³, who introduced the use of sacrificial aluminium anodes. Recently, Chan *et al.*⁵ have described the synthesis in high yields of two important intermediates in the manufacture of the drugs ibuprofen and naproxen by electrocarboxylation of 4-isobutylacetophenone and 2-acetyl-6-methoxynaphthalene, respectively, in a cell with unseparated cathode and anode compartments, with a sacrificial aluminium anode.

The mechanism of electrocarboxylation of aromatic ketones has not been investigated in detail. Wawzonek and Gundersen¹ proposed the reaction mechanism shown in Scheme 1 (path A). In the course of mechanistic investigation of electrochemical reduction of aromatic ketones in DMF they found that benzoic acid and ethyl(diphenyl)methanol were formed when the ketyl radical anion $(C_6H_5)_2CO^{\bullet-}$ was made to react with CO_2 and ethyl iodide. These results led to the conclusion that the anion is a resonance hybrid and its reaction with the electrophilic CO_2 most probably takes place *via* the carbon atom. Because the reduction potential of the ensuing radical is less negative than that of the starting ketone, further electron uptake, either from the electrode or from $(C_6H_5)_2CO^{\bullet-}$ in solution, takes place to give a carboxylate anion. Also, Ikeda and Manda² invoked resonance structures of the ketyl radical anion to explain experimental results obtained for the reduction of a series of substituted benzophenones in CO_2 -saturated DMF. They found that the yield of carboxylic acid increased with increasing electron-withdrawing power of the substituents. The authors agreed to the above mechanism suggesting that the resonance structures shown in Scheme 1 lead to different reaction pathways. When electron-withdrawing groups are present in the phenyl rings, the structure with the negative charge localised on the carbon atom is likely to be predominant and hence



SCHEME 1

the carboxylation process is very efficient. When, instead, the molecule bears electron-donating substituents, both resonance structures are important. Thus, radical reactions leading to dimers and tars become important with a consequent decrease in the yield of carboxylation products.

More recently, a slightly different mechanism involving fixation of two CO_2 molecules, illustrated in Scheme 1 (path B), has been proposed^{5,7}. The ketyl radical anion reacts with CO_2 *via* the oxygen atom to give a species which, being more easily reducible than the starting ketone, undergoes immediate reduction and then incorporates a second CO_2 molecule. Note that the actual carboxylation product, which has been isolated by different workers, is not the dicarboxylate anion formed in the second carboxylation reaction but an α -hydroxy acid. The latter is assumed to form by hydrolysis of the dicarboxylate anion in the work-up procedure following electrolysis whereby strongly acid solutions are used²⁻⁶.

In this paper the results of mechanistic investigation of electrocarboxylation of several aromatic ketones are described. A series of benzophenones ($\text{X-C}_6\text{H}_4\text{COC}_6\text{H}_5$; X = 4-OCH₃, 4-CH₃, H, 3-Cl, 3-CF₃, 4-CF₃ and 4-CN) and ring-substituted acetophenones ($\text{Y-C}_6\text{H}_4\text{COCH}_3$; Y = 4-OCH₃, H, 3-OCH₃, 3-Cl, 3-CF₃, 4-CF₃, 3-CN and 4-CN) were studied.

EXPERIMENTAL

N,N-Dimethylformamide (Janssen, 99%) was kept over anhydrous Na_2CO_3 for several days and stirred from time to time. It was then twice fractionally distilled under reduced pressure under N_2 and stored in a dark bottle under N_2 . The supporting electrolyte, tetraethylammonium perchlorate (TEAP) (Fluka), was recrystallized from ethanol and dried in a vacuum oven at 60 °C. All the ketones were commercially available and were used as received. Carbon dioxide (99.998%) was supplied by SIAD (Italy). DMF solutions containing various concentrations of CO_2 were prepared by saturating the solvent with appropriate mixtures of CO_2 and argon. The CO_2 concentration was calculated from its solubility in DMF and partial pressure of CO_2 in the gas mixture⁸.

Electrochemical measurements were carried out using an EG&G Princeton Applied Research Model 173/179 potentiostat/coulometer, a universal programmer PARC Model 175, and a LeCroy LT322 oscilloscope. The mercury electrode prepared as previously reported was the working electrode⁹. The counter-electrode was a Pt wire while the reference electrode was $\text{Ag}[\text{Ag}][0.1 \text{ M Bu}_4\text{N}^+\text{I}^-]$ in DMF, calibrated after each experiment against the ferrocene/ferrocenium couple. All potential values are reported *versus* the KCl saturated calomel electrode (SCE), using $E_{\text{Fc}/\text{Fc}^+}^0 = 0.48 \text{ V vs SCE in DMF}$.

Digital simulations were performed using the program DigiSim 2.1 (Bioanalytical Systems).

RESULTS AND DISCUSSION

Cyclic Voltammetry of Ketones

In cyclic voltammetry (CV), all benzophenones give rise to two successive one-electron reduction peaks (Fig. 1), of which only the first is reversible in the whole range of scan rates employed (0.02–200 V s⁻¹). The mechanism of electroreduction of benzophenones in aprotic solvents has been previously investigated^{6,10} (Eqs (1)–(3)). The first electron uptake yields a stable ketyl radical anion which is further reduced at more negative potentials. The dianion formed in the second reduction step is a strong base and is therefore rapidly protonated by any proton donor HB present in solution. The standard potential of the first electron transfer (ET) was determined by cyclic voltammetry as the midpoint between the cathodic and anodic peaks. The values of E°_1 are collected in Table I.

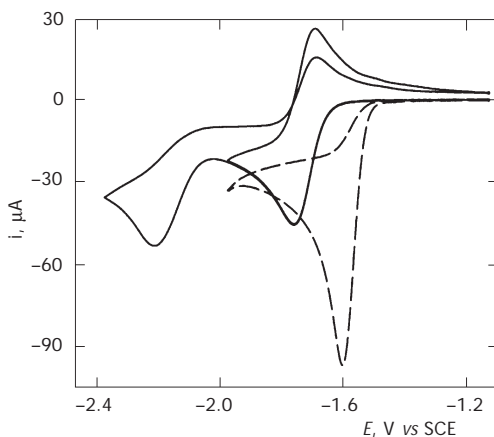
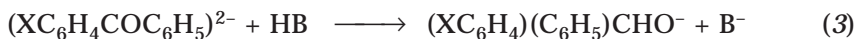


FIG. 1

Cyclic voltammetry of 2.22 mM benzophenone in the absence (—) and presence (---) of 0.2 M CO₂ in DMF containing 0.1 M TEAP at Hg electrode at $\nu = 0.2 \text{ V s}^{-1}$

Two successive one-electron reduction processes leading to a radical anion and then to a dianion were observed also for the acetophenones ($\text{XC}_6\text{H}_4\text{COCH}_3$), but the ketyl radical anions formed in this case were less stable than those obtained from benzophenones. An example of the voltammetric behaviour of these compounds is illustrated in Fig. 2, which

TABLE I
Electrocarboxylation of benzophenones ($\text{X-C}_6\text{H}_4\text{COC}_6\text{H}_5$) in DMF containing 0.1 M TEAP at Hg electrode at 25 °C

X	E° V vs SCE	$\partial E_p/\partial \log v$ mV	$\partial E_p/\partial \log c_c^\circ$ mV	$\log k_{\text{app}}^a$
4-OCH ₃	-1.835	-28	48	7.83
4-CH ₃	-1.792	-28	46	7.50
H	-1.730	-28	41	7.10
3-Cl	-1.600	-26	47	5.62
3-CF ₃	-1.563	-27	42	4.47
4-CF ₃	-1.503	-29	42	3.90
4-CN	-1.343	-	-	-

^a Calculated from Eq. (13).

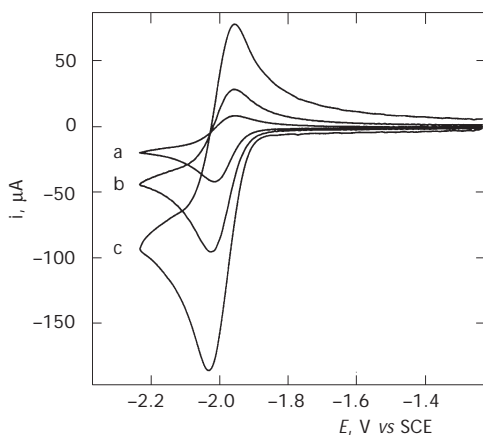


FIG. 2
Cyclic voltammetry of 1.71 mM acetophenone in DMF containing 0.1 M TEAP at Hg electrode at different scan rates (in V s^{-1}): 0.2 (a), 1 (b), 4 (c)

shows some voltammograms encompassing the first reduction wave of acetophenone at different scan rates. The ratio of the anodic to cathodic peak current (i_{pa}/i_{pc}) is smaller than unity at slow scan rates. As the scan rate (ν) is raised, i_{pa}/i_{pc} increases, approaching unity at moderate values of ν . The current function ($i_{pc}/\nu^{1/2}$) of the first cathodic peak is practically independent of ν even though this reduction peak is not fully reversible, indicating that the number of exchanged electrons is always one. Similar results have been previously reported for the electroreduction of several arylmethyl ketones^{7,11}. The ketyl radical anion undergoes dimerisation to give pinacol. The general reduction process for this class of compounds is consistent with the mechanism proposed for benzophenones (Eqs (1)–(3)), with the exception that a radical–radical coupling reaction now occurs (Eq. (4)).



The standard potential of the first reduction step of each arylmethyl ketone $\text{XC}_6\text{H}_4\text{COCH}_3$ was measured by CV at high scan rates, where complete chemical reversibility was found, and the values obtained are reported in Table II. Figure 3 shows plots of E° versus Hammett substituent constants.

TABLE II
Electrocarboxylation of acetophenones ($\text{X-C}_6\text{H}_4\text{COCH}_3$) in DMF containing 0.1 M TEAP at Hg electrode at 25 °C

X	E° V vs SCE	$\partial E_p/\partial \log \nu$ mV	$\partial E_p/\partial \log c_c^\circ$ mV	$\log k_{app}^a$
4-OCH ₃	-2.170	-28	42	9.41
H	-1.998	-27	43	8.04
3-OCH ₃	-1.985	-30	48	7.79
3-Cl	-1.804	-28	44	5.66
3-CF ₃	-1.766	-28	43	4.60
3-CN	-1.693	-29	43	3.89
4-CF ₃	-1.665	-28	39	3.74
4-CN	-1.462	-	-	-

^a Calculated from Eq. (13).

For both series of aromatic ketones, good linear correlations of E° with σ^- were obtained ($R^2 = 0.995$). Correlations of E° with the more common Hammett constants σ did not give satisfactory results. Good linear correlations were obtained if the electron-donating groups and only moderately electron-withdrawing substituents were considered. With the strongly electron-withdrawing *para* substituents such as CF_3 and CN, remarkable deviations of E° from the linear Hammett plots were observed. The reaction constants ρ calculated from the correlations of Fig. 3 have considerably large positive values, *i.e.*, 6.4 for $\text{XC}_6\text{H}_4\text{COC}_6\text{H}_5$ and 9.5 for $\text{XC}_6\text{H}_4\text{COCH}_3$, indicating that electron transfer (ET) to ketones in both series is very sensitive to the electron-withdrawing power of the substituents.

These results suggest that conjugation of the substituent with the carbonyl group accommodating the incoming electron plays an important role in the ET. Such a conjugation stabilises the ketyl radical anion through delocalisation of the negative charge on the phenyl ring and substituent. This means that the negative charge of the ketyl radical anion does not reside almost exclusively on the oxygen atom but is distributed in the entire molecule. Molecular orbital calculations on reduced benzophenones and acetophenones have shown that only 40–50% of the total charge on the ketyl radical anions is associated with the carbonyl group¹².

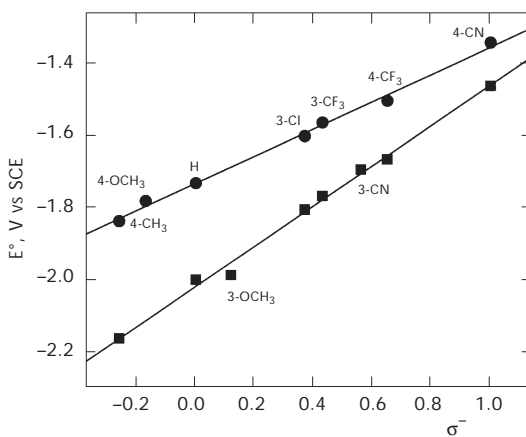


FIG. 3

Dependence of the standard reduction potential of benzophenones (●) and acetophenones (■) on Hammett substituent constants. Data were obtained in DMF containing 0.1 M TEAP at 25 °C

Cyclic Voltammetry of Ketones in the Presence of CO₂

Typical examples of the effect of CO₂ on the voltammetric pattern of the ketones are illustrated in Figs 1 and 4. In CO₂-saturated DMF, a rapid reaction takes place between CO₂ and the ketyl radical anion. For all the compounds examined, the first reduction peak shifts to less negative potentials and becomes irreversible. Also the cathodic peak current becomes twice the value in the absence of CO₂. It is well established that electrocarboxylation of ketones is a 2 e process and gives α-hydroxy acids with high yields²⁻⁶. It is also assumed that the initial product of the reaction is a dicarboxylate ion, which hydrolyses in the work-up to α-hydroxy acid. The overall reaction underlying the irreversible peak observed in the presence of CO₂ is therefore



Mechanism of Electrocarboxylation of Ketones

Let us now examine in more detail the mechanism of electrocarboxylation. There are two possible reaction pathways for the nucleophilic attack of RR'CO^{•-} on CO₂ (Scheme 2), both leading, however, to the same overall reaction (Eq. (5)) after further reduction followed by second CO₂ fixation. At the moment, we are unable to discriminate between these reaction path-

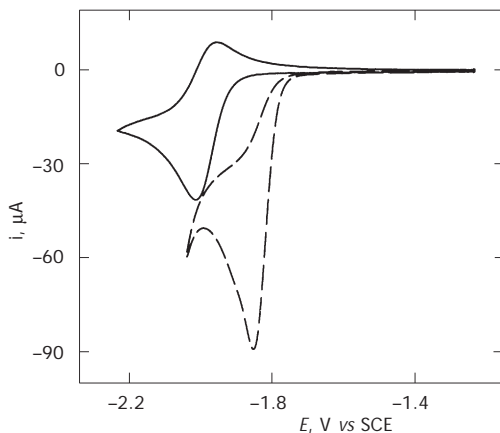
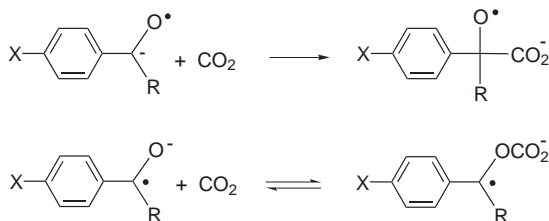
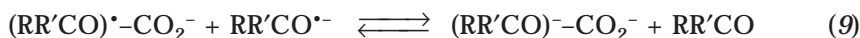
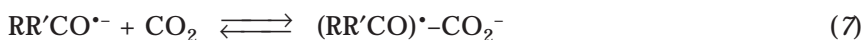


FIG. 4
Cyclic voltammetry of 1.71 mM acetophenone in the absence (—) and presence (---) of 0.2 M CO₂ in DMF containing 0.1 M TEAP at Hg electrode at $\nu = 0.2 \text{ V s}^{-1}$



SCHEME 2

ways, so we will start our analysis with a general reaction scheme without any reference to the exact position of the carboxylation of $\text{RR}'\text{CO}^\bullet$. A reasonable starting point seems to be the ECE-DISP mechanism reported in Scheme 3, which is quite frequently observed in organic electrochemistry.



SCHEME 3

Theoretical treatment of this mechanism has been already presented for cyclic voltammetry¹³. Five kinetic limiting zones were defined: two ECE regimes where reaction (9) is negligible compared with reaction (8) and reaction (7), either reversible (EC_rE) or irreversible (EC_iE) is the rate-determining step, and three DISP regimes where the second ET occurs only in solution and the rds is either reaction (7) (DISP1), reaction (9) (DISP2) or reaction (10) (DISP3). Theoretical equations, predicting the variation of E_p as a function of scan rate, initial concentrations of ketone (c°) and CO_2 (c_c°) and equilibrium as well as kinetic constants of the pertinent reactions of each kinetic regime, were given^{13b}. Our own data based on digital simulations led to the same results. At 25 °C, $\partial E_p / \partial \log v$ is -30 mV for EC_iE , EC_rE and DISP1, and -20 mV for DISP2 and DISP3. Variation of E_p with $\log c_c^\circ$ has

the following slopes: 59 mV for EC_rE, 40 mV for DISP3, 30 mV for EC_iE and DISP1, and 20 mV for DISP2. The peak potential shows a dependence on c° only in the case of DISP2 with a $\partial E_p/\partial \log c^\circ$ value of 20 mV.

The results of voltammetric analysis of the reduction of benzophenones and acetophenones in the presence of CO₂ are reported in Tables I and II. For all compounds, the peak potential varies linearly with ν and c° but is independent of the concentration of the ketone. This analysis could not be carried out with the 4-CN-substituted compounds because carboxylation of the ketyl radical anions derived from such ketones is not very fast and hence the process is only partly kinetically controlled by the carboxylation reaction. In fact, complete irreversibility of the peak is observed only at very slow scan rates under CO₂ saturation. A comparison of the experimental slopes of E_p versus $\log \nu$ and $\log c^\circ$ with those predicted for the various limiting cases shows that the DISP2 and DISP3 cases can be safely ruled out. The values of the slopes $\partial E_p/\partial \log \nu$ are consistent with DISP1 as well as with both ECE kinetic limiting cases. The electrocarboxylation mechanism of various unsaturated compounds has been analysed in the framework of the ECE-DISP mechanism^{13d,14}. In all cases the possibility of the occurrence of the EC_rE mechanism has been discarded because it is known that carboxylates are stable products that do not readily undergo decarboxylation. It has been found that the electrocarboxylation of several compounds follows a pure DISP1 mechanism. Thus, in analogy with other unsaturated compounds, a reaction mechanism based on DISP1 or EC_iE might be assumed for the aromatic ketones.

There are, however, two results which strongly contrast with the occurrence of a pure DISP1 or EC_iE kinetic regime. First, the dependence of E_p on c° is significantly different from that expected for either the EC_iE or DISP1 kinetic regime. In fact, $\partial E_p/\partial \log c^\circ$ slopes of around 45 mV were observed for all compounds whereas a 30 mV shift of E_p per unit $\log c^\circ$ is expected for both EC_iE and DISP1 limiting cases. The experimental $\partial E_p/\partial \log c^\circ$ slopes lie somewhere between the values predicted for EC_rE and for EC_iE or DISP1. It seems that the process is under mixed ECE-DISP1 kinetic control.

A second point of contrast with the EC_iE or DISP1 limiting case is given by the effect of temperature on the kinetics of the process. The rate constant (k_7) of the carboxylation reaction can be calculated from Eqs (11) and (12) in the case of EC_iE and DISP1, respectively.

$$E_p = E^\circ - \frac{0.78RT}{F} + \frac{1.152RT}{F} \log \left(\frac{RTk_7c^\circ}{F_0} \right) \quad (11)$$

$$E_p = E^\circ - \frac{1.127RT}{F} + \frac{1.152RT}{F} \log \left(\frac{RTk_7 c_c^\circ}{Fv} \right) \quad (12)$$

Although the two equations give very similar results and either one could be used for the purpose of our analysis, we used the kinetic zone diagram reported in ref.^{13b} to discriminate between them. We measured k_7 at different temperatures from 25 down to -31 °C for a few representative benzophenones and acetophenones (Fig. 5). As shown in Fig. 5, k_7 is virtually independent of T , which is quite unusual with a rate constant. Again, a reasonable explanation of this discrepancy is that we are not in a pure kinetic limiting zone. The process is perhaps under mixed ECE-DISP1 kinetic control and what we measure is not a true rate constant but a kinetic parameter containing an equilibrium constant of an exothermic reversible reaction. To check this possibility, we simulated the voltammetric response of the reaction sequence of Scheme 3 by varying all relevant parameters such as c° , c_c° , v , K_7 , k_7 , and k_9 . The equilibrium and kinetic constants K_7 , k_7 , and k_9 were varied so as the system remained under mixed kinetic control and the slopes of the linear variation of E_p with $\log c^\circ$, $\log c_c^\circ$ and $\log v$ were those experimentally observed, *i.e.*, 0, 45 and -30 mV, respectively. These conditions were actually fulfilled with a quite narrow range of K_7 values from 0.5

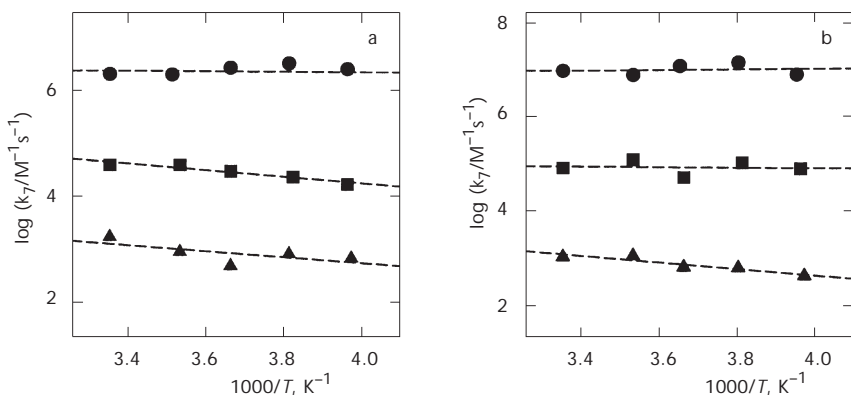


FIG. 5

Dependence of the rate constant (k_7) of carboxylation of X-C₆H₄COC₆H₅ (a) and Y-C₆H₄COCH₃ (b) on temperature. The lines were drawn to show the experimental trends of the rate constants, which were obtained in DMF containing 0.1 M TEAP according to an EC₁E or DISP1 limiting case. X: H (●), 3-Cl (■), 4-CF₃ (▲); Y: H (●), 3-Cl (■), 3-CN (▲)

to 20. When K_7 assumes values outside this range, the system tends to a pure kinetic control by one of the limiting cases EC_rE , EC_iE and $DISP1$. In the mixed kinetic zone, the dependence of E_p on the various parameters is given by the following equation (at 25 °C):

$$E_p = E^\circ - 0.08 + 0.03 \log (K_7^{1/2} k_7 c_e^{\circ 3/2} / v). \quad (13)$$

Thus, only a kinetic parameter or an apparent rate constant, which is the product of the square root of the equilibrium constant and the forward rate constant of reaction (7), can be calculated from the experimental data. The values obtained for such a kinetic parameter, which we denote k_{app} , are reported in Tables I and II (last column). Correlation of the apparent rate constant with the substituent constants is illustrated in Fig. 6. The reaction constants ρ calculated from k_{app} versus σ^- plots are 4.4 and 6.8 for the benzophenone and acetophenone series, respectively. Such high and positive reaction constants indicate that both polar and mesomeric effects of the substituent are important.

The two possible reaction pathways of $RR'CO^{\cdot-}$ with CO_2 (Scheme 2) may be discriminated on the basis of some chemical considerations. Although the negative charge on $RR'CO^{\cdot-}$ is distributed in the entire molecule, the oxygen atom presumably bears greater charge density than the carbon atom. Thus, an oxygen attack of the ketyl radical anion at CO_2 seems more

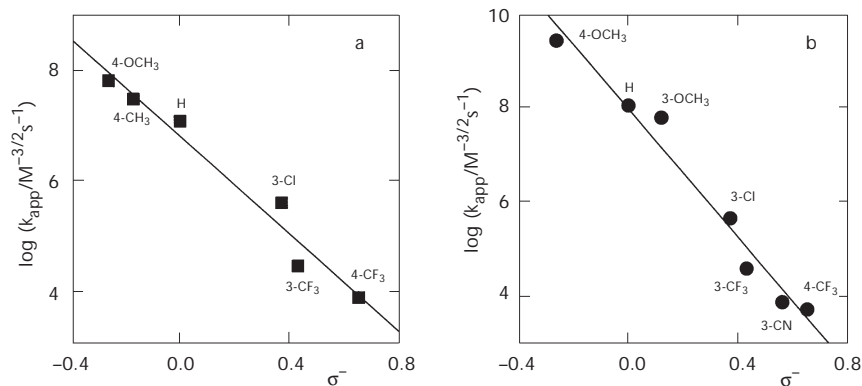


FIG. 6

Correlation of the apparent rate constant (k_{app}) for the electrocarboxylation of benzophenones (a) and acetophenones (b) with the substituent constants. The data were obtained in DMF containing 0.1 M TEAP at 25 °C

likely than a carbon one. Such a hypothesis is strongly supported by the fact that the mixed kinetic zone, where Eq. (13) is valid, requires K_7 to be fairly small ($0.5 \leq K_7 \leq 20$). If the ketyl radical anion $RR'CO^{\cdot-}$ reacted via the carbon atom, a quite stable carboxylate ion with a new carbon-carbon bond would be formed. In that case we expect the equilibrium in reaction (7) to be shifted far to the right, in clear contrast with the low K_7 domain defined by the above analysis. A nucleophilic attack of $RR'CO^{\cdot-}$ on CO_2 via the oxygen atom, on the other hand, would give rise to a carbonate-like species (Scheme 2) that may easily undergo dissociation back to the reagents.

The case against the carbon attack mechanism becomes more evident if one considers the decarboxylation rate constants (k_{-7}) imposed by the experimental data, *i.e.*, K_7 and k_{app} . Since $k_{app} = K_7^{1/2}k_7$ and K_7 is defined as $K_7 = k_7/k_{-7}$, the decarboxylation rate constant is given by $k_{-7} = k_{app}/K_7^{3/2}$. The calculation of k_{-7} was carried out using only the two extreme values of K_7 . When $K_7 = 0.5$, decarboxylation rate constants lying in the 2×10^4 – 2×10^8 s^{-1} range and in the 2×10^4 – 7×10^9 s^{-1} range were found for benzophenones and acetophenones, respectively. When the higher limit of K_7 is used, the ranges of k_{-7} values become 9×10^1 – 8×10^5 s^{-1} and 6×10^1 – 3×10^7 s^{-1} for benzophenones and acetophenones, respectively. The carboxylated intermediate obtained in reaction (7) decomposes very rapidly as compared with the decarboxylation of common carboxylates, which involves the rupture of a carbon-carbon bond. In fact, it is well known that the latter is a very slow reaction, which is often carried out using catalysis or drastic conditions such as high temperature¹⁶. The kinetics of decarboxylation of the carboxylate systems under discussion has not been studied before. It has been shown that the rate of decarboxylation of several carboxylic acid salts depends on the stability of the anion formed. A carbon attack of $RR'CO^{\cdot-}$ at CO_2 in reaction (7) would yield an arylacetate anion, which may be compared with the triphenylacetate ion $Ph_3CCO_2^-$ for which decarboxylation rate constants in various polar solvents of the order of 10^{-4} s^{-1} have been reported¹⁶. Since decomposition of the intermediate species formed in reaction (7) is very fast, k_{-7} being at least 5 orders of magnitude greater than the decarboxylation rate constant of $Ph_3CCO_2^-$, it is very unlikely that the acetate ion is formed in the first carboxylation step (Eq. (7)).

A further confirmation of the validity of the mixed kinetic regime comes from the analysis of the peak current as a function of scan rate. In fact, the ECE and DISP1 limiting cases can be distinguished by observing the variation of the current ratio i_p/i_p° (where i_p and i_p° are the peak currents measured in the presence and absence of CO_2 , respectively) in dependence on v

and the rate constant (k_7) of the carboxylation reaction^{13a}. Figure 7 shows some theoretical curves pertaining to ECE and DISP1 limiting cases as well as to a mixed EC₁E-DISP1 kinetic regime. The simulations were carried out for a system consisting of a ketone (ca 1 mM) with a five-fold excess of CO₂, assuming equilibrium constant $K_7 = 10$ for the carboxylation reaction (Eq. (7)). Other simulations carried out under the same conditions except for the value of K_7 , which was varied between 20 and 0.5, gave similar results. The experimental data to be compared with the theoretical curves can be obtained by measuring the peak current, first of the ketone alone, under the conditions where complete reversibility is attained, and then in the presence of CO₂, as a function of v . Since acetophenones do not exhibit completely reversible voltammograms up to moderately high scan rates, this analysis has been applied only to the benzophenones. Figure 7 shows fitting of the experimental data obtained for a few benzophenones on the theoretical curves. As shown in the figure, the best fittings were obtained with the mixed kinetic regime. Similar results were obtained when fitting of the data was attempted on theoretical curves calculated using other values of K_7 in the 0.5–20 range. In all cases, the mixed EC₁E-DISP1 curve could fit the data better than the corresponding pure EC₁E, EC₁E and DISP1 curves.

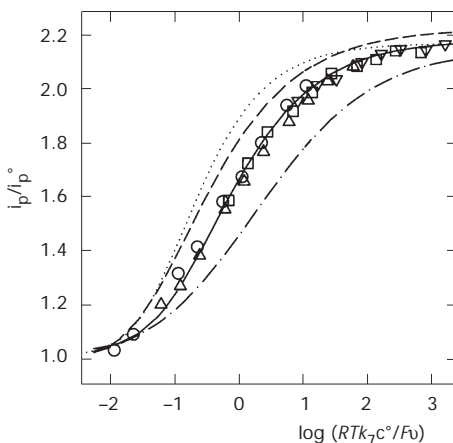


FIG. 7

Variation of the current ratio i_p/i_p^0 as a function of $\log(RTk_7c^0/Fv)$ for the electrocarboxylation of X-C₆H₄COC₆H₅ in DMF containing 0.1 M TEAP at 25 °C. The experimental points were obtained for X = H (□), 4-OCH₃ (∇), 3-Cl (Δ) and 3-CF₃ (○) whereas the lines show theoretical curves calculated for EC₁E (⋯), DISP1 (---), EC₁E with $K_2 = 10$ (- · -) and mixed EC₁E-DISP1 (—)

CONCLUSIONS

The electrochemical reduction of aromatic ketones in the presence of CO₂ follows an ECE-DISP mechanism. Voltammetric analysis of the process under different experimental conditions gives results consistent with the reaction mechanism shown in Schemes 1 (path B) and 3. The first step is a nucleophilic attack of the electrogenerated ketyl radical anion on CO₂ leading to a reversible carboxylation of the ketone at the oxygen atom of the carbonyl group. Further reduction of the ensuing radical at the electrode or in solution followed by a second CO₂ capture yields a 2-arylalkanoic acid. The whole process was found to be under mixed ECE-DISP1 kinetic control. This makes impossible determination of the true values of the carboxylation rate constant (k_7); only an apparent rate constant given by $k_{app} = K_7^{1/2}k_7$ can be obtained from the experimental data. However, it is interesting to note that K_7 is restricted to a quite narrow range ($0.5 \leq K \leq 20$) so that a rough estimate of k_7 can be made from k_{app} with a reasonable error.

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