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Mechanism and Kinetics of Electrocarboxylation of Aromatic Ketones in Ionic Liquid

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Abstract

The electrochemical carboxylation of a range of substituted benzophenones was studied in 1-butyl-1-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide ionic liquid (IL, ([Bmpy][NTf₂])). As expected, the aromatic carbonyls exhibited electrochemical reversibility for the first reduction to the radical anion at potentials which were a function of the sum of their Hammett substituent constants ($\Sigma\sigma$). However, in the presence of CO₂, the electrochemical reversibility was lost and positive shifts in reduction potentials were observed which were indicative of post-electron transfer chemical reaction which has been attributable to the nucleophilic radical anion/CO₂ coupling reaction.

Analysis of the positive potential shift a function of sweep rate (ν) indicated that the mechanism is either ECE or DISP1, or mixed ECE/DISP1. Also from the potential shift with ν , an apparent rate constant (k_{app}), and a pseudo-first order rate constant (k_1), for the coupling reaction was determined and compared to molecular solvent where the rate is over two orders of magnitude lower in IL compared to dimethylformamide (DMF). The low polarity of the IL compared to DMF appears to be the cause of slow kinetics. Finally, plots of k_{app} vs. $\Sigma\sigma$ were strictly linear indicating that IL does not preferentially interact with any of the electrogenerated radical anions thus implying that the electrocarboxylation reaction may be a useful probe of IL environments and structure on radical anion reactions.

Key words ionic liquid; organic electrochemistry; electro-carboxylation; mechanism; kinetics; Hammett

1. Introduction

The use of free and readily available atmospheric CO₂ as a chemical feedstock for synthesising value-added organic molecules has been the subject of intense research activity for many decades. Electrochemical reduction of CO₂ is energetically unfavourable due to the significant reorganisation energy associated with the transition from the linear O=C=O form to the bent radical anion form [1, 2] which has spawned a plethora of electrocatalytic [3-7] and redox catalytic approaches to effect CO₂ activation [8-11]. However, an alternative indirect approach is electrocarboxylation [12] which is the nucleophilic coupling of CO₂ to electro-generated radical anions: such reactions involving olefins, aldehydes and ketones are very well known [12].

A number of reports have already appeared detailing electrocarboxylation-type reaction in ILs [13-16] e.g. the electrosynthesis of carbamates [13], carboxylic acids [14-16] and dialkylcarbonates [17]. Of particular relevance to this study, is the preparative-scale electrocarboxylation of acetophenones [16].

The relatively simple and well understood electrochemistry of aromatic ketones is a powerful probe for investigating the effect of environment on electrochemical reactivity [18]. We have already shown [19] using comparative voltammetric and Hammett correlations studies [20] that the electrochemistry of a series of substituted benzophenones in aprotic ILs occurs as it does in aprotic organic solvents where the solvent parameter (ρ) of the Hammett relation is the same for [Bmpy][NTf₂] IL as for acetonitrile solvent indicating very similar solvent-solute / IL-solute interactions during reversible radical anion generation. Despite these observations, it is known that ILs can strongly influence chemical reactivity including electrochemical [21, 22]. The work reported here the results of a detailed mechanistic and kinetic examination of the electrocarboxylation of substituted benzophenones in [Bmpy][NTf₂] and comparing the results with previous studies performed in molecular solvent.

2. Experimental

Cyclic voltammetry (CV) was performed using a CHI600 potentiostat in the three-electrode configuration. A 0.3 cm diameter glassy disk acted as the working electrode (BAS Inc.), Pt wire (Goodfellow) acted as the counter electrode, and a home-made Ag/AgCl(sat) electrode was used as the potential reference (RE). To account for any drift of the RE potential, or varying liquid junction potentials, a small quantity of ferrocene (Fc, Aldrich) was added to the working solutions to provide an internal reference potential, all potentials are adjusted to Fc/Fc⁺ scale. All measurements were performed at room temperature (293 ± 1 K) in a sealed pear-bulb electrochemical cell under dry N₂ atmosphere.

The working electrode was prepared by polishing to a mirror-like finish with an aqueous slurry of 0.015 μm γ-alumina followed by rinsing with deionised water and air drying. Occasionally, due to slight fouling of the electrode upon repeated potential cycling the working electrode was removed from the cell and polished as necessary to ensure a pristine surface.

The [Bmpy][NTf₂] was investigated due to its aprotic nature, general inertness, favourable physical properties and widespread popularity. It was synthesis according to the literature preparation [23] using methylpyrrolidinium and chlorobutane (Sigma-Aldrich) and lithium bis(trifluoromethane)sulfonimide (3M). Prior to use, the IL was dried under vacuum (0.2 atm.) for 24 hours at 80 °C. The dried IL was then transferred anaerobically to the electrochemical cell (with electrodes and solutes already *in situ* under flowing N₂ conditions.) For the “with CO₂” experimentation the gas flow to the cell was switched between N₂ and CO₂ as necessary. The CO₂ pressure was ambient atmospheric pressure.

To examine if the presence of dissolved CO₂ affected mass transport rates in the IL trial studies were carried out using 2mMol solution of ferrocene where CV currents were measures upon going form no CO₂ to saturation with CO₂, no significant difference was observed therefore have no reason to believe the ketones would behave differently in the CO₂-saturated IL.

The benzophenone derivatives investigated (from Sigma-Aldrich, used as received) are listed in Table 1 along with the sum of their Hammett substituent constants ($\Sigma\sigma$). Typical, concentrations (C°) were $0.010 \text{ mol dm}^{-3}$ while the concentration of CO_2 in $[\text{Bmpy}][\text{NTf}_2]$ at 1 atm. was calculated to be $0.078 \text{ mol dm}^{-3}$ using its reported Henry's constant H of 38.6 bar at 298K [24]. Since the concentration of CO_2 is in significant excess ($\times 7$) compared to benzophenones', pseudo-first order kinetic conditions are assumed to apply for electro-carboxylation reactions.

3. Results and discussion

The electrochemistry of substituted benzophenones in $[\text{Bmpy}][\text{NTf}_2]$ has already been detailed elsewhere [19] therefore the voltammograms shown here are for demonstrative and comparative purposes only. For all the benzophenones listed, reversible, one-electron ($n=1$) electrochemistry occurs for the electro-generation of the ketyl radical anion the half-wave potentials ($E_{1/2}$) of which vs. Fc/Fc^+ are given in Table 1.

Figure 1 shows cyclic voltammograms recorded at 0.050 V s^{-1} for the reduction of $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ 3-methylbenzophenone in $[\text{Bmpy}][\text{NTf}_2]$ in the absence and presence of CO_2 . In the absence of CO_2 , it is immediately obvious that the first reduction process, occurring at ca. -2 V vs. Fc/Fc^+ , is the expected electrochemically reversible $n = 1$ formation of stable radical anions. Also shown in Figure 1 is the expected 2nd irreversible $n=1$ reduction occurring at potentials ca. 0.6 V more negative than the initial parent reduction which corresponds to the formation of the di-anion species. Also evident in the voltammograms is the redox due to Fc/Fc^+ which is used to scale the voltammograms to 0.0 V . For all the benzophenones investigated, Randles-Sevcik plots (peak current vs. $\nu^{1/2}$) were linear indicating a single, uncomplicated, $n=1$ redox process is occurring. An example Randles-Sevcik plot is shown in Figure 2 for unsubstituted benzophenone in the absence of CO_2 for ν from 0.002 V s^{-1} to 25 V s^{-1} .

It is also immediately evident in Figure 1 that the addition of CO₂ results in the loss of electrochemical reversibility, a doubling of the reduction current, and a positive shift in the reduction potential. These observations are clear indications that a follow-up chemical reaction is occurring between the electro-generated radical anions and CO₂. Another clear indication of this apparent EC-type process is evident in the Randles-Sevcik plots in the presence of CO₂ (Figure 3) where two distance behaviours can be discerned depending on the time-scale of the measurements.

The slope at low potential sweep rates in the presence of CO₂ is *ca.* double that of observed in the complete absence of CO₂ (Figure 2), which indicates the $n = 2$ nature of the electrode process at slow sweep rates. At higher sweep rates in the presence CO₂ the slopes decrease towards the $n = 1$ value whilst partial reversibility emerges which indicates that the influence of the follow-up chemical reaction becomes diminished as the sweep-rate begins to out-pace the chemical kinetics.

In terms of elucidating the exact mechanism, three possibilities can be identified, these are ECE, DISP1 and DISP2, as described in Scheme 1. Seminal work by Saveant's group [25, 26] allows deconvolution of the different possibilities by analysing the shift (slope) of peak potential as a function of $\log_{10} v$ as shown in Scheme 1. Since the rate determining step (C) in an ECE process and a DISP 1 mechanism is the same they cannot be distinguished by this analysis but they can be distinguished from a DISP 2 mechanism. These authors have shown that for either a simple ECE or DISP 1 mechanism a slope of 29.6 mV / decade will be observed whereas a slope of 19.7 mV / decade will be observed for a DISP2 mechanism.

Figure 4 shows the E_p vs. $\log_{10} v$ plot for 4,4-dimethylbenzophenone where a $\partial E_p / \partial \log v$ of 28 mV / decade is observed which is consistent with an ECE or DISP1 type mechanism. The slopes for the other four benzophenones are given in Table 1 where values close to the theoretical value of 29.6 are reported thus indicating an ECE or DISP1 type mechanism for all benzophenones in the IL. These mechanistic observations are entirely

consistent with previous work in DMF by Isse *et al.* [27]. However, more detailed work by Isse determining $\partial E_p / \partial C^0$ along with the effect of temperature, indicated that a mixed ECE / DISP1 type mechanism was probably occurring in the DMF media.

As mentioned earlier, the positive shift in reduction potential can also be used to determine rate constants of follow-up chemical reactions [28]. As part of Isse's studies [27] of a mixed ECE/DISP1 mechanism in DMF digital simulation was used to determine an apparent rate constants, k_{app} , which is the produced, $K^{1/2} k_2$, where K and k_2 are the equilibrium constant, and 2nd order rate constants, respectively, for the C step in mechanism shown in Scheme 1. Under these conditions the $\partial E_p / \partial v$ is given by Equation 1.

$$\partial E_p = E^0 - 0.08 + 0.043 \log_{10} \left(\frac{K k C^{3/2}}{v} \right) \quad (1)$$

From the experimental data reported here, k_{app} was calculated using this expression, over a range of v for each benzophenone at C^0 of 0.01 mol dm⁻³ and the results are reported in Table 1 which are compared to a literature value [27] for benzophenone in DMF. From these data it is clear that k_{app} is at least two orders of magnitude lower in the IL environment compared to the molecular solvent environment.

Isse also speculated that for their system K lies between 0.5 and 20. If it is assume that similar behaviour pertains in IL here, the pseudo-first order rate constant for the radical anion – CO₂ coupling reaction, k_1 , can be estimate by assuming K to be 10 and multiplying k_{app} (M^{-3/2} s⁻¹) by $C^{3/2}$ (M^{3/2}). These calculated k_1 (s⁻¹) data are also presented in Table 1 where it can be seen that the rates are low and range from ca. 1 s⁻¹ to 1000 s⁻¹ with decreasing $\Sigma\sigma$. These low rate values also strongly indicate that the reactions cannot be diffusion-limited that might ordinarily be expected in viscous IL media.

Performing identical calculation on Isse's data for benzophenone in DMF reveals a k_1 value of ca. 21500 which is ca. 270 times larger than in the IL. The exact origin of this difference is unknown but may be due to viscosity affecting solvent reorganisation during the formation of the transition state, possible ion pairing [29] between the radical anion and the [Bmpy] cation, or some type of ionic liquid specific solute interaction (solvation) which affects

the radical anion reactivity. The first two are probably not dominant since the rate is much slower than diffusional control and we have already shown that benzophenone redox behaves in [Bmpy][NTf₂] as it does in moderately polar molecular solvents [19] *i.e.* apparent absence of strong ion pairing. It is, however, very informative to consider recent work concerning the nature of ILs as solvents and their effect on reactivity. Firstly, Hapiot *et al.* [30] have shown that the rate of the acetophenone radical anion dimerization in imidazolium [NTf₂] type ILs is close to diffusional control (k_2 ca. 10^6 L mol⁻¹ s⁻¹), and that the bi-molecular dimerisation rate is enhanced relative to molecular solvent (k_2 ca. 10^5 L mol⁻¹ s⁻¹). Since the radical anion – radical anion dimerisation is strongly controlled by the coulombic repulsion between the radical anions and solvent polarity, these authors attributed the enhanced kinetics to strong charge stabilisation (termed “coulombic solvation”) of the electrogenerated radical anions with the imidazolium cations. Fry [29] previously also noted an ion pairing effect in imidazolium based ILs. Since benzophenone radical anions will delocalise charge much more effectively than acetophenone radical anions, and CO₂ is neutral, the benzophenone radical anion-CO₂ coupling is unlikely to be severely influenced by coulombic repulsion, therefore this effect is unlikely to be observed during electrocarboxylation.

Secondly, recent work [31] on weakly polar low dielectric constant aprotic ionic liquids such as [Bmpy][NTf₂] indicates that ionic species dissolved within such media are fully dissociated and behave as free ions which is an example of the “ionic liquid effect”, which is in keeping with our electrochemical observations. This suggests that the electrogenerated radical anion of the benzophenones exist as freely diffusing species which can react with dissolved CO₂ within the IL medium with the only apparent influence being the “polarity” (or medium effects) of the supporting IL.

In order to assess the medium effects on benzophenone electrocarboxylation reaction kinetics application of the Hammett relation [19, 20] is informative. A plot of log₁₀k_{app} vs. $\Sigma\sigma$, for the five benzophenones examined here, is shown in Figure 5 where it is immediately obvious that k_{app} increase logarithmically with increasing electron donating

ability of the substituents. This behaviour is expected since the substituents with $-\Sigma\sigma$ values donate charge density into the site of reduction making it more nucleophilic while substituents with $+\Sigma\sigma$ values withdraw charge density making it less reactive. In addition, the strict linearity of the plot indicates that the normal mesomeric behaviour of the substituents is maintained and that the IL-benzophenone and IL-radical anion interactions are similar for all benzophenones *i.e.* no substituent has a stronger or weaker affinity for the IL or vice versa.

Finally, the Hammett solvent parameter, ρ , (slope of the graph in Figure 5) which is an indicator of solvent “polarity”, was found to be 2 which is much smaller than the value of 4.4 found in DMF by Isse [27]. In simplistic terms, lower ρ values indicates a reduce influence of solvent “polarity” on the substituents’ mesomeric behaviour, and hence nucleophilicity. Although use of a single parameter such a ρ is wholly inadequate to describe “polarity” [31], it is worth considering the permeant dipolar nature of DMF with a moment, μ , of 3.86 D which, ultimately, gives rise to a donor number (DN) of 110 kJ mol⁻¹ while the DN for a polar IL such as [Bmim][NTf₂] is much smaller at 42.5 kJ mol⁻¹ [32]. It is, therefore, likely that the strong Lewis donating ability of DMF explains the faster reaction kinetics compared to the weakly polar [31] [Bmpy][NTf₂].

4. Conclusions

The electrocarboxylation of aromatic ketones in [Bmpy][NTf₂] ionic liquid media proceeds via an ECE and/or DISP1 type mechanism where the rate determining step is the radical anion/CO₂ coupling reaction. Rate data and Hammett considerations indicate that the radical anion react does not ion-pair with the [Bmpy] cation but acts as a free ionic species in conformation with the “ionic liquid effect” which is known to operate in aprotic ILs such as [Bmpy][NTf₂]. The apparent rate constants for the reaction in the IL are at least two orders of magnitude lower than those reported [27] in molecular solvent (DMF), the reason for which seems to be the significantly lower polarity of the IL compared to the DMF environment since mass transport and coulombic repulsive effects can be discounted.

5. Acknowledgments

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6. References

- [1] W. Li, Electrocatalytic Reduction of CO₂ to Small Organic Molecule Fuels on Metal Catalysts, in: Yun Hang Hu (Ed.), *Advances in CO₂ Conversion and Stabilization*, ACS Symposium Series, 2010, Vol. 1056, pp 55 – 76.
- [2] Y. Kushi, H. Nagao, T. Nishioka, K. Isobe, K. Tanaka, *J. Chem. Soc., Chem. Commun.* (1995) 1223 – 1224.
- [3] Y. B. Vassiliev, K. Bagotzky, N. A. Mayorova, *J. Electroanal. Chem.* 189 (1985) 295 – 309.
- [4] V. U. Kaiser, E. Heitz, *Ber Bunsen-Ges Phys. Chem.* 77 (1973) 818 – 823.
- [5] R. Kortlever, J. Shen, K. J. P. Schouten, F. Calle-Vallejo, M. T. M. Koper, *J. Phys. Chem. Lett.* 20 (2015) 4073 – 4082.
- [6] C. M. Sánchez-Sánchez, V. Montiel, D. A. Tryk, A. Aldaz, A. Fujishima, *Pure Appl. Chem.* 73, (2001) 1917 – 1927.
- [7] M. Todoroki, K. Hara, A. Kudo, T. Sakata, *J. Electroanal. Chem.* 394 (1995) 199 – 203.
- [8] A. Gennaro, A. A. Isse, J. M. Saveant, M. G. Severin, E. Vianello, *J. Am. Chem. Soc.* 118 (1996) 7190 – 7196.
- [9] J. L. Qiao, Y. Y. Liu, F. Hong, J. J. Zhang, *Chem. Soc. Rev.* 43 (2014) 631 – 675.
- [10] F. Ungvary, *Coordination Chemistry Reviews* 160 (1997) 129 – 159.
- [11] X. L. Yin, J. R. Moss, *Coordination Chemistry Reviews* 181 (1999) 27 – 59.
- [12] D. A. Tyssee, M. M. Baizer, *J. Org. Chem.* 39 (1974) 2819 – 2823.
- [13] M. Feroci, M. Orsini, L. Rossi, G. Sotgiu, A. Inesi, *J. Org. Chem.* 72 (2007) 144 – 149.
- [14] H. Wang, G. Zhang, Yingzi Liu, Y. Luo, J. Lu, *Electrochem. Comm.* 9 (2007) 2235 – 2239.

- [15] Q. Feng, S. Liu, *Asia Journal of Chemistry* 23 (2011) 4823 – 4826.
- [16] Q. Feng, K. H., S. Liu, J. G. Yu, F. Liu, *Electrochim. Acta* 56 (2011) 5137 – 5141.
- [17] L. Zhang, D. F Niu, K. Zhang, G. Zhang, Y. Luo and J. Lu, *Green Chemistry* 10 (2008) 202 – 206.
- [18] P. Zuman, D. Barnes; A. Ryvolova-Kejharova, *Disc. Farad. Soc.* 45 (1968) 202 – 226.
- [19] S. O'Toole, S. Pentlavalli, A. P. Doherty, *J. Phys. Chem. B* 111 (2007) 9281 – 9287.
- [20] L. P. Hammett, *J. Am. Chem. Soc.* 59 (1937) 96 – 103.
- [21] M. J. Earle, S. P. Katfare, K. R. Seddon, *Org. Let.* 6 (2004) 707-710.
- [22]. C. L. Lagrost, D. Carrié, M. Vaultier, P. Hapiot, *J. Phys. Chem. A*, 107 (2003) 745 – 75.
- [23] D. R. MacFarlane, P. Meakin, J. Sun, N. Amini, M. Forsyth, *J. Phys. Chem. B* 103 (1999) 4164 – 4170.
- [24] J. L. Anthony, J. L. Anderson, E.J. Maginn, J. F. Brennecke, *J. Phys. Chem. B* 109, (2005) 6366 – 6374.
- [25] L. Nadjo, J. M. Saveant, *J. Electroanal. Chem.* 33 (1971) 419 – 451.
- [26] C. P. Andrieux, J. M. Saveant, *J. Electroanal. Chem.* 33 (1971) 453 – 461.
- [27] A. A. Isse, A. Gennaro, *Coll. Czech. Chem. Commun.* 68 (2003) 1379 – 1394.
- [28] A. J. Bard, L. R. Faulkner, *Electrochemical Methods, Fundamentals and Applications*, John Wiley and Sons, New York, 1981, pp 452 – 454.
- [29] A. J. Fry, *J. Electroanal. Chem.* 546 (2003) 35 – 39.
- [30] F. Andre, P. Hapiot, C. Lagrost, *Phys.Chem.Chem.Phys.* 12 (2010) 7506 – 7512.
- [31] M. A. Ab Rani, Crowhurst, B. A., A. Dolan, N. H. Hassan, J. P. Hallett, P. A. Hunt, H. Niedermeyer, J. M. Perez-Arlandis, M. Schrems, T. Welton, R. Wilding, *Phys.Chem.Chem.Phys.* 13 (2011) 16831 –16840.
- [32] M. Schmeisser, P. Illner, R. Puchta, A. Zahl, R. van Eldik, *Chemistry – a European Journal*, 18 (2012) 10969 – 10982.

Figures

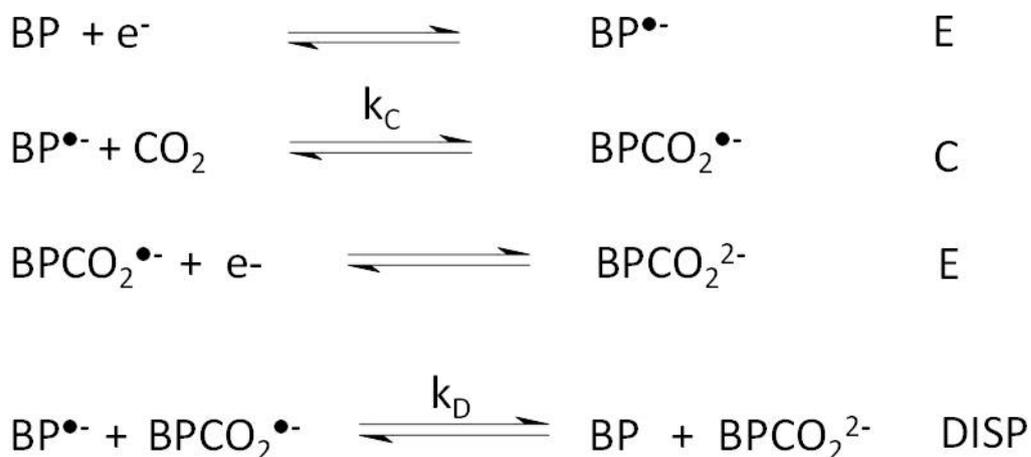
Table 1. List of substituted benzophenones studied, their Hammett substituent constants ($\Sigma\sigma$), mechanistic and kinetic data. $E_{1/2}$ is the half-wave potential on the absence of CO_2 , E_p is the first reduction peak potential in the presence of CO_2 , v potential sweep-rate, K and k_2 are the equilibrium and 2nd order rate constants ($\text{mol L}^{-1} \text{s}^{-1}$) for the radical anion- CO_2 coupling reaction and k_1 is the equivalent 1st order-rate constant (s^{-1}).

Benzophenone	$\Sigma\sigma$	$E_{1/2}$ vs. Fc/Fc^+	$\partial E_p / \partial \log v^* / \text{mV}$	$\log_{10} K^{1/2}k_2 (\text{M}^{-3/2} \text{s}^{-1})^\S$	k_1 / s
4-Cyan-	1.0	-1.75	30	3.0	1
BP	0.0	-2.07	32	4.9 (7.10 [§])	79 (21500 [§])
3-Methyl	-0.07	-2.09	32	5.1	140
4,4-dimethyl	-0.34	-2.17	28	5.7	500
4,4-dimethoxy	-0.54	-2.27	30	6.0	111

*[25]

§ [27]

Scheme 1. Possible reaction mechanisms for the ketyl radical electrocarboxylation reaction.



$$k_C \ll k_D \Rightarrow \text{DISP1} (-29.4 \text{ mV } E_{pc} \text{ shift})^{32}$$

$$k_C \gg k_D \Rightarrow \text{DISP2} (-19.4 \text{ mV } E_{pc} \text{ shift})^{32}$$

Figure 1. CVs of $1.0 \times 10^{-2} \text{ mol L}^{-1}$ 3-methylbenzophenone in [Bmpy] [NTf₂] performed at a glassy carbon working electrode at 50 mVs^{-1} , versus ferrocene redox couple, before and after CO₂ addition at 1 atm.

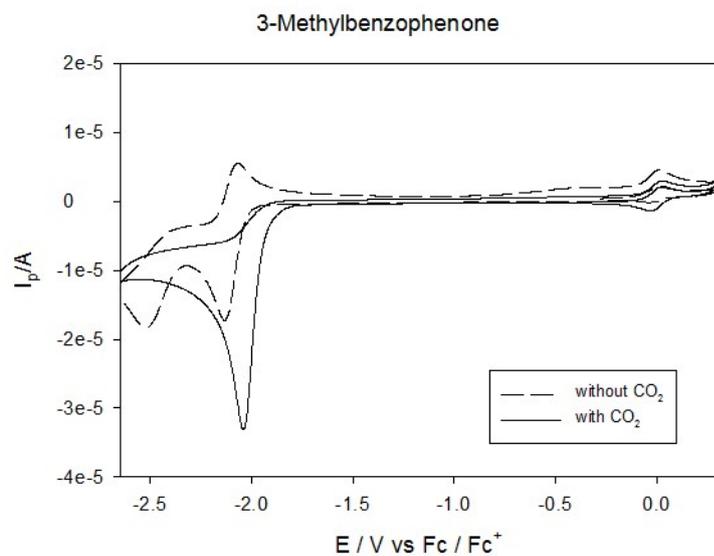


Figure 2. Randles-Sevcik plot for the reduction of unsubstituted benzophenone under N₂ atmosphere in [Bmpy] [NTf₂] at a glassy carbon electrode.

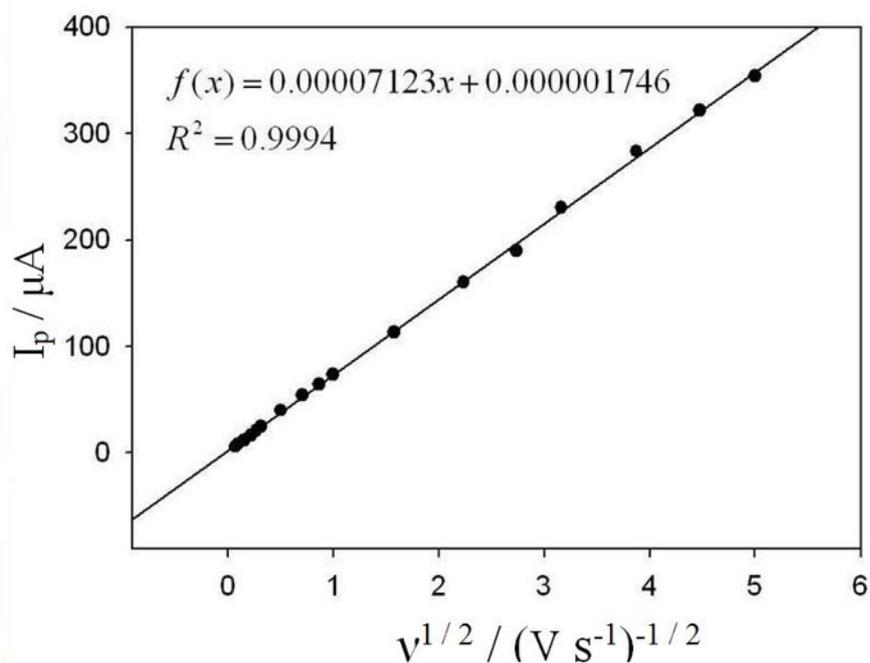


Figure 3. Randles-Sevcik plot for the reduction of unsubstituted benzophenone under CO₂ atmosphere (1 atm) in [Bmpy] [NTf₂] at a glassy carbon electrode.

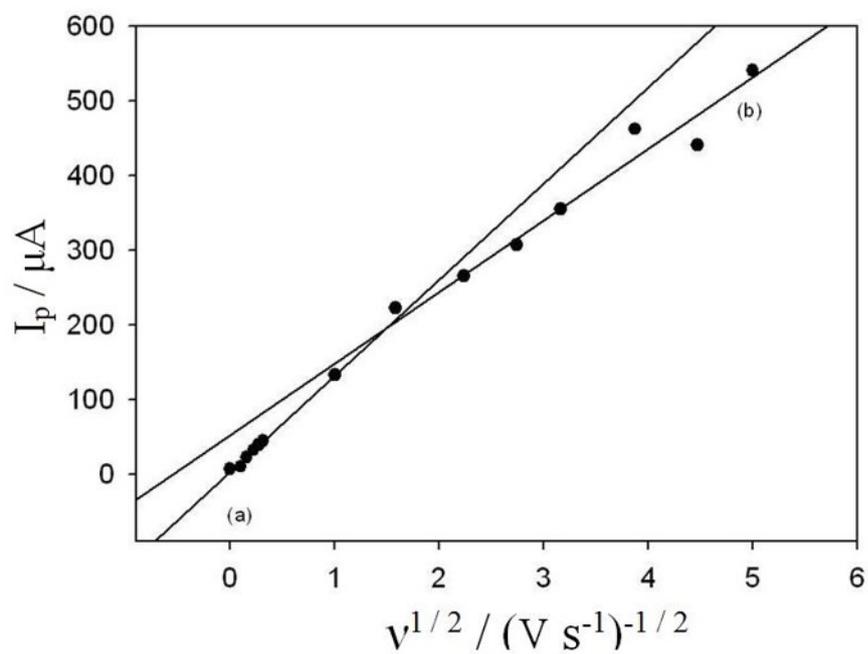


Figure 4. A plot of E_p vs. $\log u$ for 4,4-methylbenzophenone.

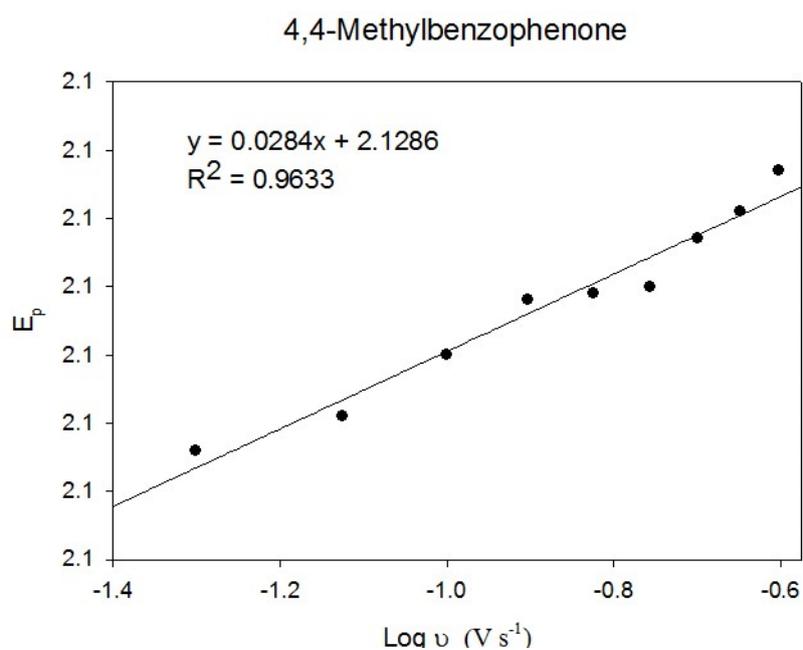


Figure 5. Apparent rate constant (k_{app}) vs. $\Sigma\sigma$ Hammett plot for the electrocarboxylation of substituted benzophenons in [Bmpy] [NTf₂].

