

ELECTROCHEMICAL REDUCTION OF SUBSTITUTED α,α,α -TRIFLUOROACETOPHENONES. LINEAR RELATIONSHIP BETWEEN CYCLIC VOLTAMMETRIC PEAK POTENTIALS AND HAMMETT SUBSTITUENT CONSTANTS

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The peak potentials of substituted α,α,α -trifluoroacetophenones were measured in acetonitrile with 0.1 M tetrabutylammonium perchlorate. The cyclic voltammograms indicated an irreversible electrochemical process for the first wave (E_{pc1}) and a partially reversible one for the second wave (E_{pc2}) when the scan rate was slower than 100 mV s⁻¹. Excellent linear correlations were observed for E_{pc1} with σ constants ($\rho = 0.526$, $r = 0.999$) and for E_{pc2} with σ^- constants ($\rho = 0.605$, $r = 0.998$), respectively. Therefore, unknown σ values such as -0.36 for 3,4-ethyleneoxy can be estimated from these correlations. The mechanism of the electrode process probably involves a single electron transfer and the formation of a pinacol.

INTRODUCTION

Correlation of polarographic half-wave potentials ($E_{1/2}$) of organic compounds with a variety of parameters, e.g. ionization potentials (I_p),¹ electron affinities (EA)² and Hammett substituent constants,³ has long been an important subject in physical organic chemistry. Both theoretical considerations⁴ and empirical data¹⁻⁴ result in linear free energy relationships.³ Recently we observed⁵ an excellent correlation of ¹⁷O NMR chemical shifts with σ^+ substituent constants for substituted α,α,α -trifluoroacetophenones. The results raised the question of whether there is also a linear correlation between the half-wave potentials for these ketones and the Hammett-type substituent constants.

The half-wave potential ($E_{1/2}$) is usually obtained from polarographic measurement. From a cyclic voltammogram, $E_{1/2}$ can also be estimated in a reversible system by finding the mid-point of the cathodic peak potential (E_{pc}) and anodic peak potential (E_{pa}). In an irreversible system, $E_{1/2}$ cannot be obtained in the same way, because only E_{pc} or E_{pa} can be observed from the voltammogram. However, the difference in the peak potentials (ΔE_p) would be same as that in the half-wave potentials ($\Delta E_{1/2}$) for a series of compounds having the

same type of reducible centre under similar experimental conditions. This can be easily derived from the combination of equations (1)^{6,7} and (2)⁸ for a totally irreversible system in cyclic voltammetry (CV) and in polarography, respectively, to give equation (3), where the symbols in these equations have usual meaning.⁶⁻⁸ That is, the ΔE_p or $\Delta E_{1/2}$ will be directly related to the rate constant of heterogeneous electron transfer (k_f^0) at an electrode potential of 0 V as well as the free energy of activation for heterogeneous electron transfer (for the correlations using $E_{p/2}$ and E_p see, e.g., Refs 9 and 10, respectively), since the other parameters (v , αn_a , D_0 , t_1 and T) are assumed to be constant, as are R and F .

$$E_p = \frac{RT}{\alpha n_a F} \left[-0.780 + \ln k_f^0 - \frac{1}{2} \ln \left(\frac{\alpha n_a F D v}{RT} \right) \right] \quad (1)$$

$$E_{1/2} = \frac{RT}{\alpha n_a F} \ln 0.87 k_f^0 \sqrt{t_1 D} \quad (2)$$

$$\Delta E_p = \Delta E_{1/2} = \frac{RT}{\alpha n_a F} \Delta \ln k_f^0 \propto \Delta \Delta G^\ddagger(E) \quad (3)$$

The first CV study on α,α,α -trifluoroacetophenone in acetonitrile was reported by Andrieux and Saveant.¹¹ The results of the photochemical reaction involving charge-transfer (CT) quenching of several substituted α,α,α -trifluoroacetophenones were reported later¹² and the half-wave potentials of these ketones measured at a

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hanging mercury drop electrode by CV in acetonitrile, were also listed, but no further discussion about the correlation with the structures of the ketones was given.

Therefore, we undertook to examine the relationship between the reduction potentials of a number of substituted α,α,α -trifluoroacetophenones and the Hammett substituent constants in a CV study. In addition, the mechanism of the electrode process was also examined.

RESULTS AND DISCUSSION

Cyclic voltammetry of α,α,α -trifluoroacetophenones

A typical cyclic voltammogram for 2 mM substituted α,α,α -trifluoroacetophenones in acetonitrile solution with 0.1 M tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte is shown in Figure 1. The voltammograms of these ketones exhibit three distinct successive waves (E_{pc1} , E_{pc2} and E_{pc3}) in the potential range of -0.9 to -2.5 V. The reversibility of the first and second waves depends on the substituent. However, the third waves are usually too small and too broad to determine their peak potentials and reversibility.

On increasing the scan rate, the reversibility increases for the first waves, but decreases for the second. It is likely that some coupled irreversible chemical reactions occur after the first electron transfer, and the rate constants (forward and backward) of the second electron transfer are finite. Therefore, at high scan rates the backward process of the first electrode reaction will compete with the following chemical reaction, whereas the second electrode reaction will no longer be able to

maintain equilibrium conditions as the potential changes.^{7,13}

The single-sweep CV data for substituted α,α,α -trifluoroacetophenones and the corresponding substituent constants are given in Table 1. Owing to the strong electron-withdrawing ability of CF_3 , the electrode processes are accelerated and a lower reduction potential for α,α,α -trifluoroacetophenone ($E_{1/2} = -1.42$ V vs SCE) than acetophenone ($E_{1/2} = -2.06$ V vs SCE)¹⁷ has been observed.

In this series of substituted α,α,α -trifluoroacetophenones, the near constancy of the current function $i_p/cv^{1/2}$ in Table 1 indicate¹⁰ that the diffusion coefficients are rather insensitive to structure. The values of the diffusion coefficients (D), measured by chronoamperometry, for certain ketones (Table 2) also show agreement.

Correlation of cathodic peak potentials with Hammett substituent constants

The reversibility of electrode processes in CV for these ketones not only changes with the scan rate, but also is different from one to another at different scan rates. Nevertheless, when the scan rate is slower than 100 mV s^{-1} , the first waves (E_{pc1}) in all of the cyclic voltammograms of these ketones change gradually from partial reversibility to total irreversibility (Figure 2). This irreversibility suggests that the rate process of the subsequent chemical reaction is much faster than the reverse electron transfer, so the rate of the forward electron transfer becomes rate limiting,^{7,13} and that the properties of the electrode process are now

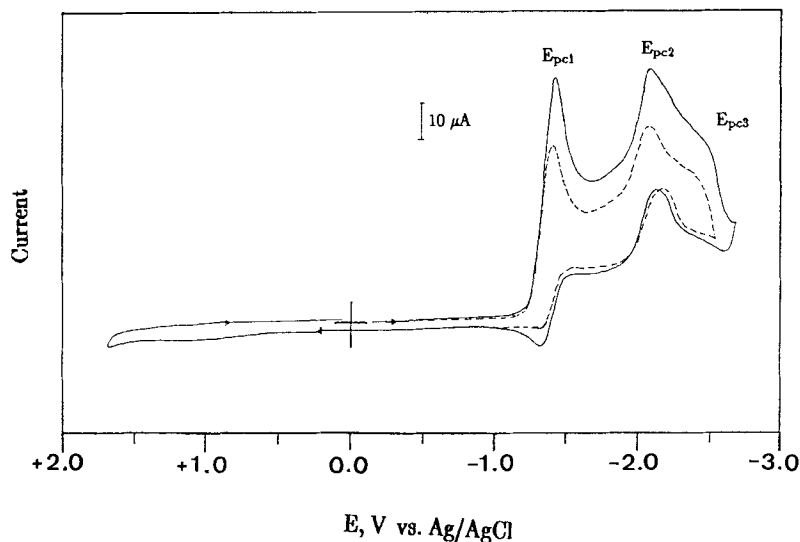
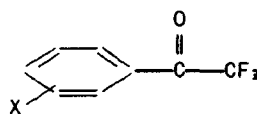


Figure 1. Cyclic voltammogram of 2 mM α,α,α -trifluoroacetophenone in acetonitrile with 0.1 M TBAP at a scan rate of 100 mV s^{-1} (full line) and 50 mV s^{-1} (dashed line)

Table 1. Cyclic voltammetric data^a and Hammett substituent constants for

X	σ^b	σ^-	E_{pc1}^c (V)	E_{pc2}^d (V)	$i_p/cv^{1/2e}$
3-CH ₂ CH ₂ O-4	-0.36 ^f	—	-1.593 -1.635 ^k	-2.275	0.0031
<i>p</i> -OCH ₃	-0.268	-0.20 ^b	-1.546 -1.582 ^k	-2.216	0.0028
<i>p</i> -CH ₃	-0.17	-0.14 ^g	-1.490 -1.505 ^k	-2.168	0.0028
3-OCH ₂ O-4	-0.16 ^h	—	-1.483 -1.490 ^k	-2.138	0.0031
<i>m</i> -CH ₃	-0.069	-0.069 ⁱ	-1.445 -1.463 ^k	-2.137	0.0023
<i>p</i> -OPh	-0.055 ^j	0.005 ^g	-1.431 -1.444 ^k	-2.073	0.0026
H	0	0	-1.398 -1.436 ^k	-2.073	0.0028
<i>m</i> -F	0.34	0.34 ⁱ	-1.234 -1.260 ^k	-1.890	0.0026
<i>m</i> -Cl	0.37	0.37 ⁱ	-1.219 -1.237 ^k	-1.853	0.0029
<i>m</i> -CF ₃	0.43	0.43 ⁱ	-1.169 -1.189 ^k	-1.819	0.0031
<i>p</i> -CF ₃	0.54	0.62 ^g	-1.111 -1.122 ^k	-1.725	0.0031
<i>mm'</i> -(CF ₃) ₂	0.82 ^f	—	-0.972 -0.992 ^k	-1.612	0.0025

^a Measured with a glassy carbon electrode at a scan of 50 mV s⁻¹ in acetonitrile with 0.1 M TBAP at 22 °C unless stated otherwise.

^b Ref. 14.

^c Reproducible within ± 0.005 V.

^d Reproducible within ± 0.010 V.

^e In units of A l mol⁻¹ (s/mV)^{1/2}.

^f Extrapolated from E_{pc1} vs σ plot (Figure 3).

^g Ref. 15.

^h Ref. 3.

ⁱ Value as σ used.

^j Ref. 16.

^k Potential was measured at a scan rate of 100 mV s⁻¹.

just like those of a totally irreversible system. Hence a linear relationship between E_{pc1} and σ in terms of equation (3) would be expected. Indeed, an excellent linear relationship ($\rho = 0.526$, $r = 0.999$, s.d. = 0.008) in correlating E_{pc1} with σ at $v = 50$ mV s⁻¹ is realized (Figure 3). At $v = 100$ mV s⁻¹, the linear E_{pc1} vs σ plot ($\rho = 0.532$, $r = 0.996$, s.d. = 0.016) supports our assumption that the first electrode process in CV could be treated as an irreversible process for these ketones at scan rates slower than 100 mV s⁻¹. Worse correlations with σ^0 ¹⁸ ($\rho = 0.561$, $r = 0.981$, s.d. = 0.039) and with σ^- ¹⁴⁻¹⁶ ($\rho = 0.535$, $r = 0.991$, s.d. = 0.027) have been observed at $v = 50$ mV s⁻¹.

Some quantitative criteria^{7,10} for total irreversibility in cyclic voltammetry have been developed which also

support our assumption. One of the principal tests for electrochemical reversibility rests on the constancy of the transfer coefficient from various properties of the CV wave. The transfer coefficients calculated from equations (4),^{7,10} (5)⁷ and (6)^{7,10} are listed in Table 3. The internal consistency in these values confirms that the first wave exhibits total irreversibility at scan rates slower than 100 mV s⁻¹.

$$E_p = \frac{2.3RT}{2\alpha n_a F} \log v + \text{constant} \quad (4)$$

$$E_p - E_{p/2} = 1.857(RT/\alpha n_a F) \quad (5)$$

$$E_p = \frac{2.3RT}{2\alpha n_a F} \log i_p + \text{constant} \quad (6)$$

Table 2. Diffusion coefficients (D)^a and coulometric n values^b for selected ketones

Substituent	$10^5 D$ ($\text{cm}^2 \text{s}^{-1}$)	$n_1 (E)$	$n_2 (E)$
H	2.9	1.09 (-1.70)	—
<i>p</i> -CH ₃	2.8	1.11 (-1.70)	—
<i>m</i> -CH ₃	2.6	1.05 (-1.65)	—
<i>p</i> -CF ₃	2.9	—	2.12 (-1.85)
<i>p</i> -OPh	2.8	1.04 (-1.40)	—
<i>m</i> -F	2.9	1.04 (-1.40)	2.21 (-2.00)

^a Measured by chronoamperometry.^b Measured by chronocoulometry.

The magnitude of the slope of the plot of E_p or $E_{p/2}$ vs $\log v$ is another probe for this purpose.¹⁰ Figure 2 shows the negative shift of peak potential when the scan rate changed from 10 to 100 mV s^{-1} . The values (42–48) of slopes (m) for these ketones shown in Table 3 are consistent with $30/\alpha$ mV negative shift per decade for a one-electron-transfer irreversible wave.⁷

The positive value of 0.526 for the reaction constant ρ indicates a nucleophilic reaction¹⁹ and the aromatic ring has a higher electron density in the transition state than in the starting material. The electron on the electrode is probably the nucleophilic agent.

The σ value of the 3,4-ethyleneoxy group could be estimated from coumaranyl trifluoromethyl ketone as -0.36 by extrapolation on the basis of the excellent linear E_{pc1} vs σ plot (open circle in Fig. 3). In addition, the σ value of 0.82 for the *m,m'*-bis(trifluoromethyl) group obtained by this method seems to be more appropriate than that usually suggested as double that of $\sigma_m(\text{CF}_3)$, 0.86.

Although the different reversibility in E_{pc2} suggested that the correlation with σ might not be good, the E_{pc2} vs σ plot showed the contrary [$\rho = 0.582$, $r = 0.994$,

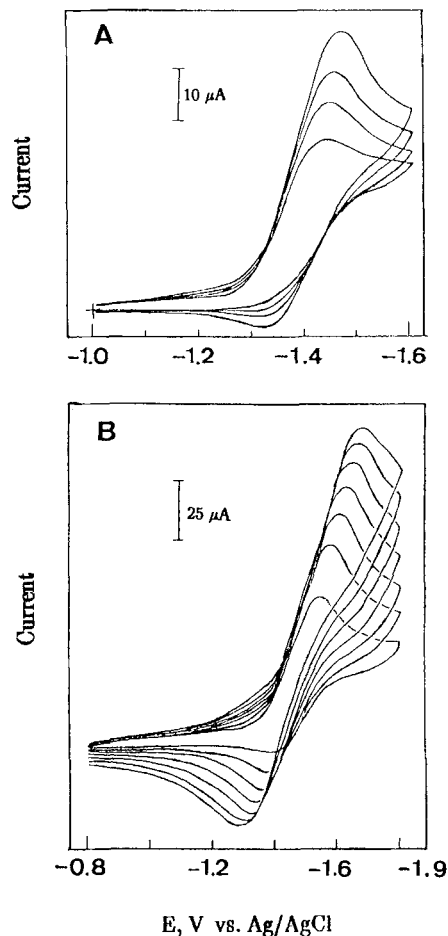
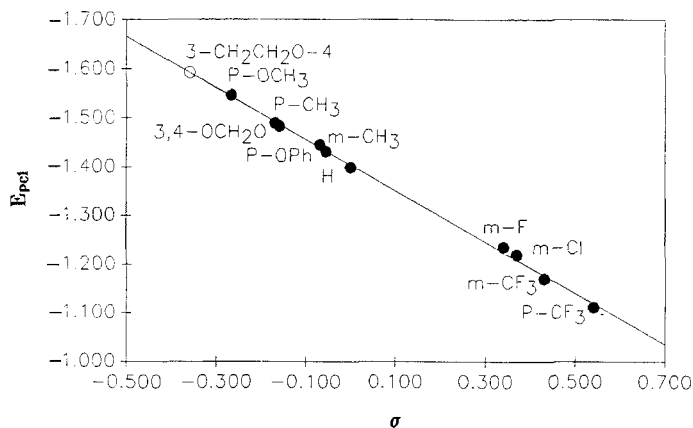
Figure 2. Dependence of peak potential of the first wave (E_{pc1}) of 3-methyl- α,α,α -trifluoroacetophenone on scan rate: (A) $30 < v < 100 \text{ mV s}^{-1}$ and (B) $100 < v < 700 \text{ mV s}^{-1}$ Figure 3. E_{pc1} vs σ plot for substituted α,α,α -trifluoroacetophenones

Table 3. Transfer coefficients determined by independent methods^a

Substituent	m^b	Transfer coefficient			Av. ^c
		E_p vs $\log v$	$E_p - E_{p/2}$	E_p vs $\log i_p$	
H	45	0.65	0.66	0.57	0.63
<i>p</i> -OCH ₃	45	0.65	0.62	0.54	0.60
<i>m</i> -CH ₃	47	0.62	0.62	0.57	0.60
<i>m</i> -Cl	42	0.70	0.65	0.70	0.68
<i>m</i> -F	48	0.61	0.65	0.55	0.60
<i>m</i> -CF ₃	46	0.64	0.65	0.58	0.62

^a E_p refers to E_{pc1} .

^b The slope of E_{pc1} vs $\log v$ for $v < 100 \text{ mVs}^{-1}$

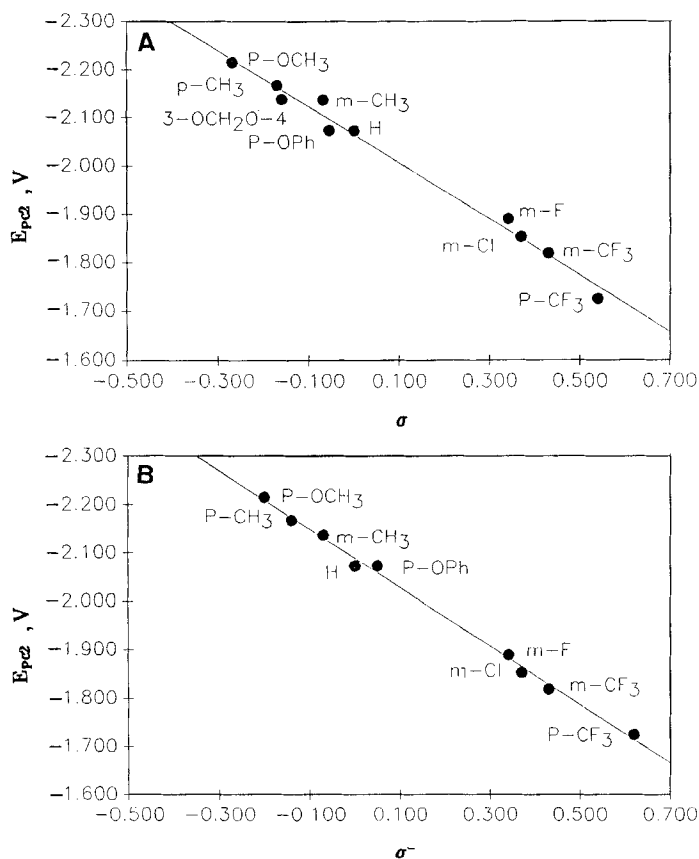
^c Average: ± 0.05 .

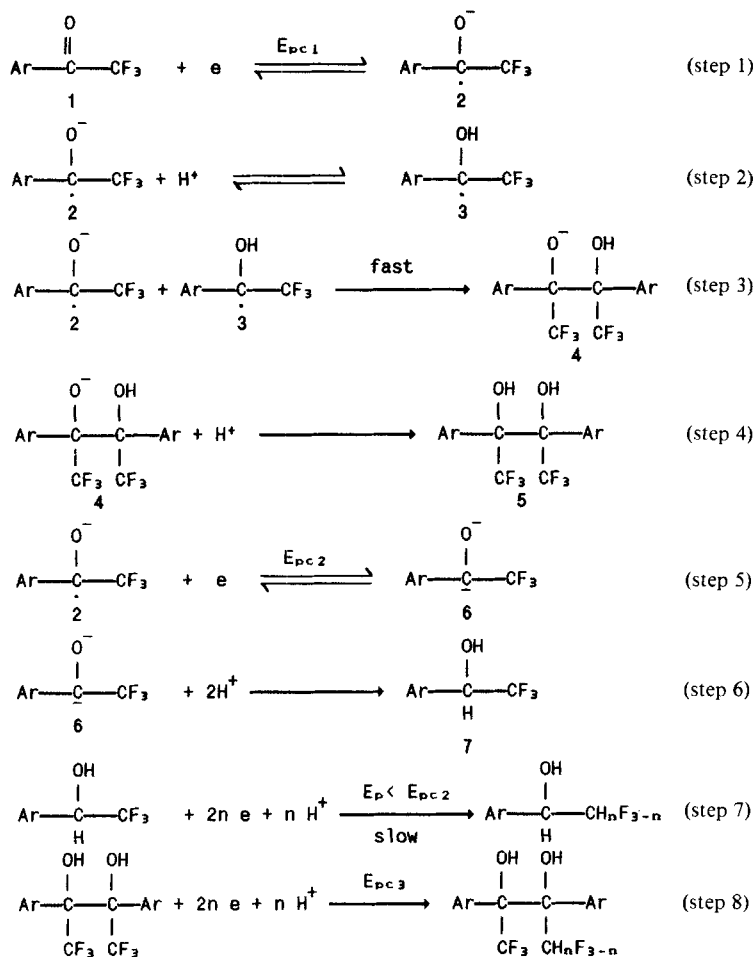
s.d. = 0.023, Figure 4(A)). If the second peak potentials were plotted against σ^- instead of σ , an even better correlation [$\rho = 0.605$, $r = 0.998$, s.d. = 0.015], Figure 4(B)] resulted.

Mechanism of the cyclic voltammetric electrode process

A number of possible processes for the electroreduction of carbonyl compounds have been summarized,²⁰ and a series of papers and a broad survey of the literature on early work on the reduction of aromatic carbonyl compounds are available.²¹ The reduction of α,α,α -trifluoroacetophenone has also been studied.^{11,22} Based on our findings, the overall mechanism of the CV of α,α,α -trifluoroacetophenones in acetonitrile with 0.1 M TBAP as supporting electrolyte could be as illustrated in Scheme 1.

From theoretical considerations, the m values (the slope of the E_p vs $\log v$ plot) for α,α,α -trifluoroacetophenones (Table 3) fit the diagnostic criteria of a so-called 'ePrrec' mechanism.²³ According to this reaction pathway, the rate-determining step is the forward reaction of the preceding proton transfer equilibrium (step 2) after a rapid reversible electron transfer (step 1) and then a fast radical-radical coupling (rrc) reaction (step 3). That is, once the neutral


 Figure 4. (A) E_{pc2} vs σ plot and (B) E_{pc2} vs σ^- plot for substituted α,α,α -trifluoroacetophenones

Scheme 1. Mechanism of electrode reactions and chemical reactions in CV of substituted α,α,α -trifluoroacetophenones

radical **3** forms in the neighbourhood of the electrode, it couples with the newly formed radical anion **2** to give a pinacol **5** after the protonation step (step 4). The irreversibility of the first waves could be due to the competition of a moderately fast and irreversible rrc reaction. The proton source may be the trace amount of water present in the solvent.²⁴ When the concentration of proton increases in the solution, the preceding proton transfer would be more favourable and then a more irreversible wave would be observed (see below). The n values for some ketones, listed in Table 2, also indicated that the first wave, in addition to the second wave, was a one-electron transfer process (steps 1 and 5). Moreover, the observed linear correlation with σ^- for E_{pc2} suggests that the aromatic ring would have a partial negative charge in the transition state in the second electrode process (step 5), and eventually the

dianion would be protonated^{21,24} to give the alcohol **7** (step 6).

The third wave (Figure 1) could be due to the reduction of the C—F bond in the α,α,α -trifluoro-methyl group. The electrolytic reduction of the C—F bond in α,α,α -trifluoroacetophenone had even been noted in protic solvent.²² Figure 5 shows the cyclic voltammograms of α,α,α -trifluoroacetophenone, 1,1,1,4,4,4-hexafluoro-2,3-diphenylbutane-2,3-diol and 1-phenyl-2,2,2-trifluoroethanol. The last two compounds did undergo electrode reactions, which should come from the reduction of the C—F bond in the CF_3 group, whereas the broad and low current peaks might be due to the slow rate of electron transfer and the complicated electrode processes, producing different F-containing alcohols or pinacols (steps 7 and 8). On the other hand, from a comparison of their

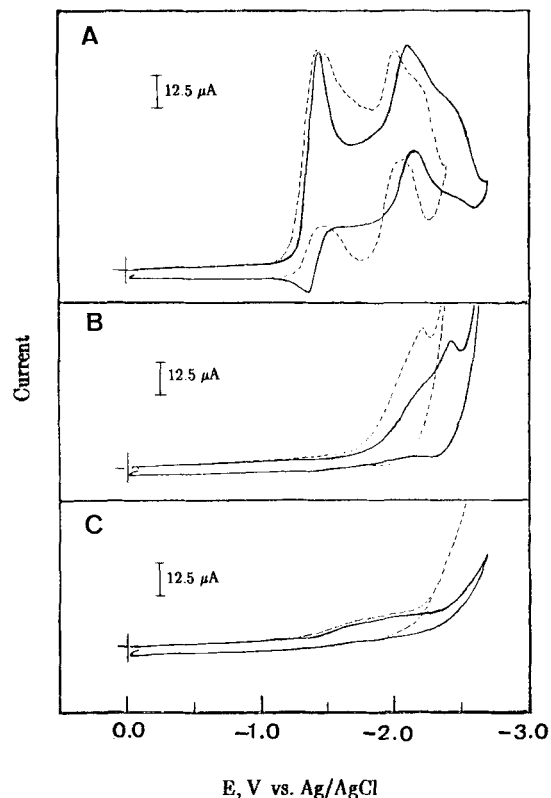
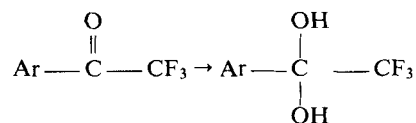


Figure 5. Cyclic voltammograms of (A) α,α,α -trifluoroacetophenone, (B) 1,1,1,4,4,4-hexafluoro-2,3-diphenylbutane-2,3-diol (pinacol **5** in Scheme 1) and (C) 1-phenyl-2,2,2-trifluoroethanol (alcohol **7** in Scheme 1) in acetonitrile with 0.1 M TBAP (full line) and with 2% water added (dashed line) at a scan rate of 100 mV s^{-1}

relative peak potentials, it seems that the third wave just represents the reduction of pinacols formed after the first reduction in the carbonyl group of ketones (step 8), whereas the reduction of alcohols is probably immersed in the second wave (step 7).

Wawzonek and Gundersen²⁵ suggested that the positive shift of peak potentials on the addition of water could be used to detect the different influences of radical anion **2** and dianion **6** in studying the polarography of acetophenone. Andrieux and Saveant also studied¹¹ the effect of the addition of water in linear voltammetry. Figure 6 shows the positive shift of peak potential for the *m*-CF₃-substituted ketone on addition of 2% of water. The larger shift of the second wave ($E_{pc2} \rightarrow E'_{pc2}$) (180 mV) than the first ($E_{pc1} \rightarrow E'_{pc1}$) (100 mV) indicates that the second wave should be the reduction of the radical **2** (step 5), and not the neutral radical **3**.^{21,25,26} It is worth noting that a new peak is present, designated E_{pw} , between E'_{pc1} and E'_{pc2} in Figure 6, in addition to Figure 5(A). This phenomenon was observed for all the ketones, but the degree of decay of E_{pc1} or the growth of E_{pw} were different. It is known^{11,27} that these ketones are apt to undergo hydration to form *gem*-diols:



Thus the stronger the electron-withdrawing substituent, the easier was *gem*-diol formation and then the more decay in E_{pc1} was observed, as predicted. This electrode

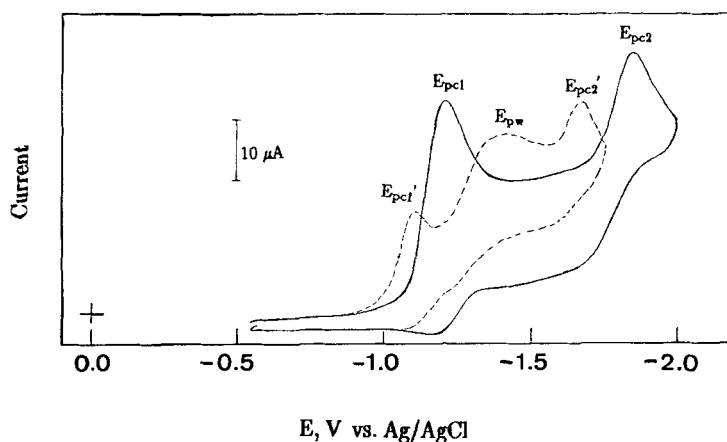


Figure 6. Cyclic voltammograms of 3-methyl- α,α,α -trifluoroacetophenone in acetonitrile with 0.1 M TBAP (full line) and 2% water added (dashed line) at a scan rate of 100 mV s^{-1}

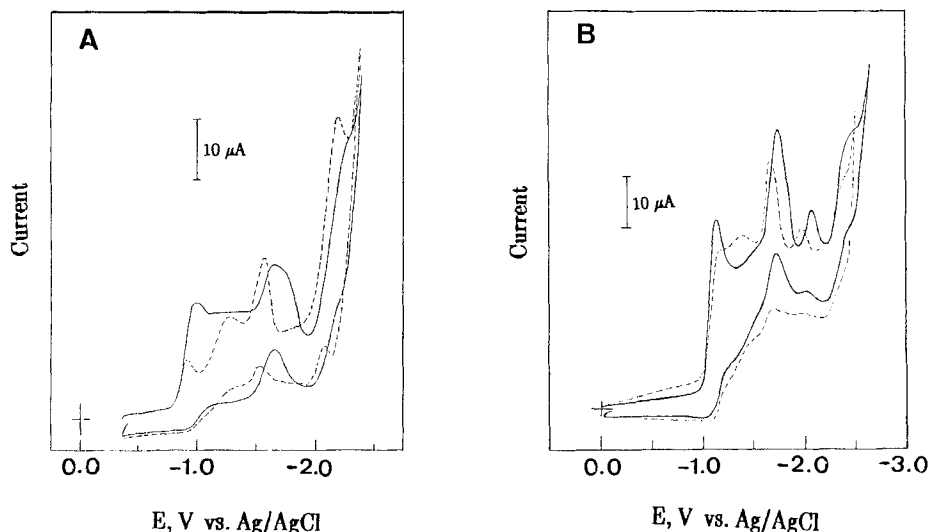
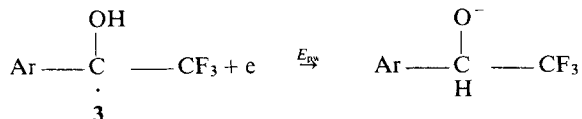


Figure 7. Cyclic voltammograms of (A) 3,5-bistrifluoromethyl- α,α,α -trifluoroacetophenone and (B) 4-trifluoromethyl- α,α,α -trifluoroacetophenone in acetonitrile and 0.1 M TBAP (full line) and 2% water added (dashed line)

reaction may be the reduction of the neutral radical 3:



since the dimerization process shifts the first wave (E_{pc1}) towards more anodic potentials and then two separated waves (E'_{pc1} and E_{pw}) can be observed even if the standard potential of the latter is more positive than that of the former.²¹ The reason why this electrode reaction was insignificant in anhydrous acetonitrile could be attributed to the low concentration of proton source in the solution. When water is added, the third wave in Figure 5(A) is influenced even more than the second, which indicates that the fission of the C—F bond becomes easier in the presence of water.²⁸

Moreover, the CV behaviours of the *p*-CF₃- and *m,m'*-(CF₃)₂-substituted ketones shown in Figure 7 are different from the others, with more waves at the more cathodic potential, and this might have resulted from the reduction of CF₃ in aryl groups (for previous instances of the electrochemical reduction of trifluoromethyl compounds see Refs 29 and 30). However, this reduction would be more difficult³⁰ in the *m*-CF₃-substituted ketone and therefore similar reduction peak(s) was not observed in the potential window.

It has been established¹¹ that pinacol is produced in the presence of lithium cation in the large-scale electrolysis of α,α,α -trifluoroacetophenone. In order to examine the pinacol formation in the solution system without Li⁺, large-scale electrolysis of α,α,α -trifluoroacetophenone at E_{pc1} was carried out and the

product analysis showed about a 10% yield of a pinacol, CF₃CPh(OH)CPh(OH)CF₃, detected by gas chromatography, together with a large amount of intractable tars. On controlling the potential at E_{pc2} , the same pinacol was also obtained (*ca* 4%), which suggested further electron transfer in the radical anions 2. No defluorinated product²² was detected, probably owing to the different reaction conditions employed.

EXPERIMENTAL

Materials. Acetonitrile (Hayashi), employed as a solvent, was purified³¹ by heating under reflux with calcium hydride for at least 8 h under nitrogen, followed by distillation prior to use. The potential window with 0.1 M TBAP was found to be from +1.7 to -2.7 V vs a Ag/AgCl (KCl saturated) reference electrode.

Tetrabutylammonium perchlorate (TBAP) (Tokyo Kasei), the supporting electrolyte, was recrystallized from absolute ethanol followed by drying *in vacuo* at room temperature for 24 h.

Commercial α,α,α -Trifluoroacetophenone (Merck) was used without further purification. All of the substituted ketones were prepared from the reaction of the appropriate arylmagnesium bromide in diethyl ether with 1.2 equiv. of trifluoroacetic anhydride under reflux. The ketones were isolated by vacuum distillation (30–60%) and then further purified by column chromatography on silica gel.^{5,32}

1,1,1,4,4,4-Hexafluoro-2,3-diphenylbutane-2,3-diol, m.p. 152–153 °C (uncorrected; lit.,^{33,34} 155–156 °C) and 1-phenyl-2,2,2-trifluoroethanol, the GC standards, were prepared from α,α,α -trifluoroacetophenone by

photochemical irradiation³⁴ and by sodium tetrahydroborate reaction, respectively.

Electrochemical instruments. A glassy carbon electrode (BAS GCE-63 grade carbon) was used for CV experiments with an area of $7.05 \times 10^{-2} \text{ cm}^2$, measured from the analysis of the chronoamperometric $i-t$ transient of 4 mM hexacyanoferrate(III) in 1.0 M KCl solution,³¹ in which the diffusion coefficient is $D = 0.763 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. In every experiment, the electrode was newly hand-polished with aluminium oxide (first 0.3 μm and then 0.05 μm) and felt pads (Buehler) on a flat glass plate to a mirror-like finish, rinsed with distilled water, cleaned ultrasonically for 2 min, rinsed with distilled water and then dried at 100 °C.

Reticulated platinum electrodes were used as cathodes for chronocoulometry and large-scale controlled-potential electrolysis. A platinum wire was used as the auxiliary electrode and an Ag/AgCl electrode as the reference electrode in all electrochemical experiments.

In performing CV experiments, a three-electrode, single-compartment cell was used. Prior to use, the reference electrode was calibrated with an aqueous saturated calomel electrode (SCE). The measurements were carried out with a BAS Model CV-27 394 potentiostat and a BAS Model C1B-120 267 cell stander. Cyclic voltammograms were obtained with a BAS Model RXY 226 X-Y recorder in a solution of 2 mM ketones in acetonitrile containing 0.1 M TBAP at room temperature (ca 22 °C). All potentials were recorded with respect to the reference electrode.

The chronoamperometric $i-t$ curves and chronocoulometric curves were recorded with a BAS Model RYYT-DP 182 recorder with the same solution as in CV.

For large-scale electrolyses (3 mmol) at a reticulated carbon electrode, a two-compartment H-cell was used. The same solvent and supporting electrolyte as in CV were used.

Product analysis. Gas chromatographic analysis was performed on a 10-m Carbowax 20M column using a Hewlett-Packard Model 5890 instrument.

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