longer reaction times for completion of the reaction.

In conclusion, we feel that the present method, because of its simplicity, effectiveness, and mildness, will complement a number of previously known methods[11] for this conversion but the explosive nature of 1,1′-(thiocarbonyldioxy)dibenzotriazole limits further applications in various functional group conversions. Furthermore, it is highly recommended that the reaction should be carried out by one-pot procedure without the isolation of 1,1′-(thiocarbonyldioxy)dibenzotriazole for the safety purpose.

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Electrochemical Behaviour of Dibenzoylmethane on Mercury Film Electrode in Basic Ethanol-Water Solvent

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During the past two decades the electrochemical reduction of β-diketones has received considerable attention,[1-7] not only because of the numerous possibilities for reduction pathways, but also because of the large number of such compounds readily available and hence of potential synthetic use. Previous investigators[3-7] studied the electrochemical reduction of β-diketones by polarographic experiments. These included a study of 1,3-diphenyl-1,3-propanedione(or dibenzoylmethane), a typical symmetrical β-diketone, which was reported to give three different reduction waves under various conditions, thus suggesting at least three types of products and pathways. Evans[4] reported that three polarographic waves were observed and three reduction products of dibenzoylmethane could be obtained on mercury electrodes in slightly basic (pH < 10.0) ethanol-water solution. However, in more basic (pH greater than 10.0) solution the first two waves were fused to form one composite wave since the waves are quite close to one anothr on the potential axis. And reduction pathways were also proposed that reduction of the keto form of dibenzoylmethane to dimeric products occurred with two electron transfer process under the potential of the composite wave.

In this investigation cyclic voltammetry and kinetic measurements of electrochemical reduction of dibenzoylmethane on mercury film electrodes in basic ethanol-water solutions were made in order to elucidate the mechanism of the reduction reactions.

The mercury film electrodes were prepared by mere dipping of the platinum wire in mercury pool.[8] All of the experiments were performed in ethanol-water (50% by volume) solvent and the potential data given here are referred to the saturated calomel electrode (SCE). Dibenzoylmethane used in this investigation was found to exist almost entirely in th enol form by the measurement of IR and NMR spectra.

The pKa value of the dibenzoylmethane was measured to be 10.4 in 50% ethanol-water solution by pH-metric titration. Thus, the enolate form of dibenzoylmethane will be probably dominant over the enol form in the solution that pH is higher than 10.4.

The cyclic voltammograms of dibenzoylmethane in 0.10 M NaOH/ethanol-water solution were obtained and are shown in Figure 1. And the cyclic voltammetic data with various scan rates in unstirred solution are shown in Table 1. There are two reduction waves in both stirred and unstirred solutions, however in the unstirred solution the second reduction wave was decreased with decreasing scan rates.

Futhermore, the current ratio between two reduction waves (i_{p2}/i_{p1}) was increased up to 1.0 with increasing scan rates in unstirred solution but the ratio was measured to be nearly 1.0 and unchanged with scan rates in stirred solution. It seems that the two reduction waves are due to two consecutive reduction steps and the second reduction step is occurring with parallel chemical reaction.

When at the potential region of the first reduction wave the radical species is produced by one lectron transfer which will be followed by consecutive one electron transfer or coupl-

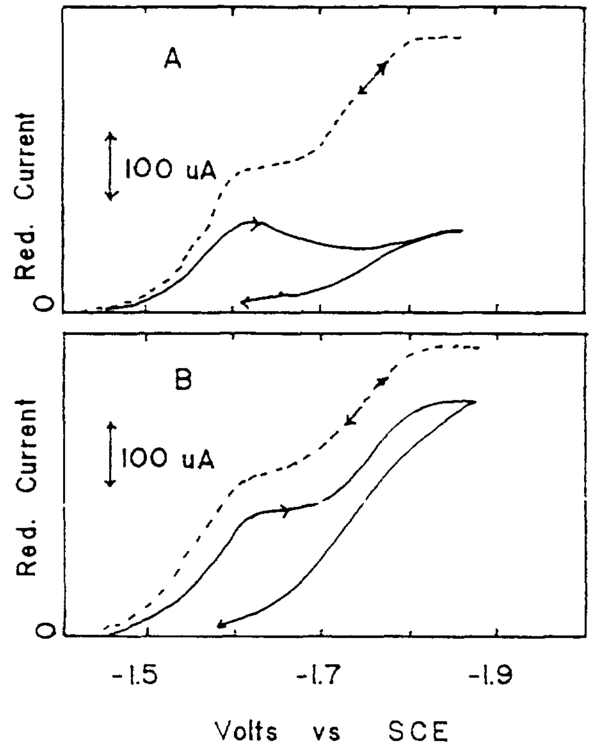


Figure 1. Cyclic voltammograms of 1.0×10^{-3}M dibenzolymethane in unstirred (solid line) and stirred (dashed line) solution of 0.10M NOH/ethanol-water. Scan rates were 19 mV/sec. (A) and 190 mV/sec. (B).

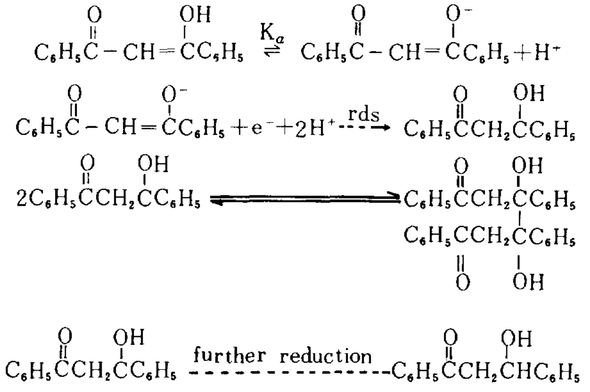
Table 1. Cyclic Voltammetric Data of 1.0×10^{-3}M Dibenzoylmethane with Various Scan Rates in Unstirred Solutions

Scan Rate mV/sec.	E_{p1} Volt	E_{p2} Volt	i_{p2}/i_{p1}
19	-1.61	-1.79	0.09
38	-1.62	-1.80	0.19
75	-1.64	-1.82	0.28
94	-1.65	-1.82	0.42
110	-1.66	-1.83	0.34
150	-1.68	-1.83	0.48
190	-1.68	-1.83	1.0

ing chemical reaction because of the chemical reactivity of radical species, the current ratio (i_{p2}/i_{p1}) are expected to increase up to 1.0 with increasing scan rates in unstirred solution.

The steady state current potential relationship for the reduction of dibenzoylmethane are shown in Figure 2. At low polarization region which controlled by charge transfer rates, Tafel slopes were about 110mV in both stirred and unstirred solutions and pH-dependance at constant current, was observed to be -80mV that means 0.7 order about the concentration of H^+. However, at higher polarization which controlled by diffusion rate the pH dependance, and current at fixed potential was observed to be independent of the concentration of H^+ in each solution used here.

Based on the above facts, the following mechanism is assumed;



$$C_6H_5\overset{O}{C}-CH=\overset{OH}{C}C_6H_5 \overset{K_a}{\rightleftharpoons} C_6H_5\overset{O}{C}-CH=\overset{O^-}{C}C_6H_5+H^+ \qquad (1)$$

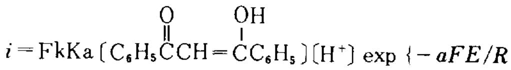
$$C_6H_5\overset{O}{C}-CH=\overset{O^-}{C}C_6H_5+e^-+2H^+ \xrightarrow{rds} C_6H_5\overset{O}{C}CH_2\overset{OH}{C}C_6H_5 \qquad (2)$$

$$2C_6H_5\overset{O}{C}CH_2\overset{OH}{C}C_6H_5 \rightleftharpoons \begin{array}{l} C_6H_5\overset{O}{C}CH_2\overset{OH}{C}C_6H_5 \\ \qquad\qquad\quad | \\ C_6H_5\underset{O}{C}CH_2\underset{OH}{C}C_6H_5 \end{array} \qquad (3)$$

$$C_6H_5\overset{O}{C}CH_2\overset{OH}{C}C_6H_5 \xrightarrow{\text{further reduction}} C_6H_5\overset{O}{C}CH_2\overset{OH}{C}HC_6H_5 \qquad (4)$$

Although the electrochemical reactions of (2) and (4) are consecutive, the fast chemical reaction of (3) is parallely occurring with step (4). Thus, it may be assumed that the polarization curve at less negative potentials coresponds to the combined steps (1) and (2) while at more negative potentials the current is controlled by diffusion rate.

The following relations are obtained from reactions (1) and (2):



$$i = FkKa[C_6H_5\overset{O}{C}CH=\overset{OH}{C}C_6H_5][H^+]\exp\{-\alpha FE/RT\}$$

where α is the transfer coefficient of reaction (2) and F is the Faraday constant. Thus, the logarithmic current for the reduction of dibenzoylmethane is at 298° K,

$$\log i = \log(\text{const.}) + \log([\text{enol}]) - \text{pH} - (\alpha/0.0592)E$$

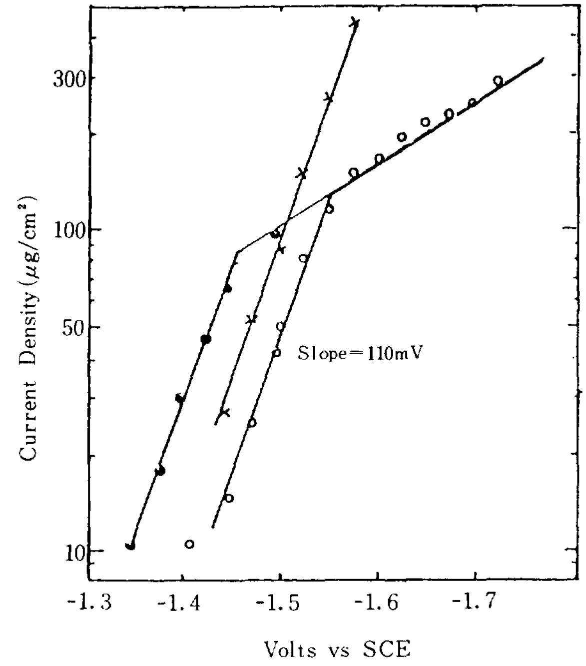


Figure 2. Steady state polarization curves for 1.0×10^{-2}M dibenzoylmethane. O-O-O-O-O pH=13.6, Unstirred solution. ×—×—×—× pH=13.6, Stirred solution. ●-●-●-●-● pH=12.6, Unstirred solution.

If α is considered to be about ½ as usual, the Tafel slope and pH dependance of current will be 120 mV and − 1 respectively. The observed values in Fig. 2. are in agreement with this prediction within the experimental error.

The cyclic voltammetry data of Figure 1 and Table 1 can be also interpreted by the reaction scheme (1) to (4). If the two reduction waves are corresponding to reaction (2) and (4), respectively, the height of the second wave presumably increases with increasing scan rate because dimerization of radical (reaction(3)) is fast enough. Furthermore, when the potential sweeping rate is very slow the second wave is to be probably disappeared.

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Studies of Induced Electron Transfer Reaction: Kinetics of the Oxidation of Cu(phen)$_2^+$ by Co(TrDTA)$^-$ Ion

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The unusal redox reactivity of Co(EDTA)$^-$ with reduced stellacyanin has been attributed to the formation of an oxidant protein precursor complex in which overlap between the donor redox orbital of the distorted tetrahedral type Cu(I) center and the e_g acceptor orbital of the oxidant is poor; it is reported that nonadiabacity is not a requisite feature of the outer sphere oxidation of Cu(I) by Co(EDTA)$^-$ complex ion.[1-5]

In order to determine the reactivity of the electron transfer from Cu (phen)$_2^+$ to Co(TrDTA)$^-$, we have investigated the oxidation of the bis(1,10-phenanthroline) copper(I) ions by trimethylenediaminetertraacetato Co(III) ions. The trimethylenediaminetetraacetato Co(III) complex and bis(1,10-phenanthroline) copper(I) complex ions were prepared by literature methods.[6-8] The kinetics of oxidation of Cu(phen)$_2^+$ by trimethylenediamine tetraacetato Co(III) complex ion was monitored by following the absorbance decrease at 435 nm. Pseudo-first order conditions were employed, maintaining the concentration of the cuprous complex at ca. 10-25 M and varying the oxidant concentration from 2.5×10^{-4} to 2.5×10^{-2}M.

Observed first order rate constants, k_{obs}, were derived from the slopes of linear $\ln(A_t-A_\infty)$ vs. time plots for the oxidation of Cu(phen)$_2^+$ by Co (TrDTA)$^-$ as shown in Fig. 1 and 2. For all the redox reactions considered, plots of k_{obs} (25°C) vs. oxidant were found to be linear with small positive intercepts (0.04-0.23 s^{-1}) over 50-100 fold concentration ranges covered. it is clear that electron transfer from Cu(I) to Co(III) obeys that rate law: $-d[Cu(I)]/dt = k[Cu(I)]\,[Co(III)]$.

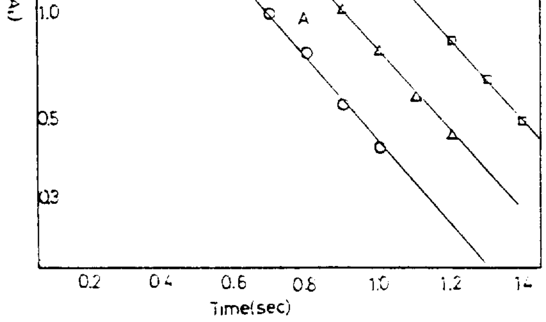

Figure 1. Plot of $\ln(A_\infty - A_t)$ vs time for the oxidation of Cu(phen)$_2^+$ by Co(TrDTA)$^-$. pH 6, μ 0.5, 25°C, 5×10^{-3}M