Voltammetric Behaviour of Benzil at a Glassy Carbon Electrode

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The voltammetric behaviour of benzil in DMF and in aqueous solutions on a glassy carbon electrode (GCE) was investigated and the results were compared with the reported voltammetric behaviour of benzil on a mercury electrode. Benzil gives two reversible 1e reduction peaks on a glassy carbon electrode in DMF. The apparent charge transfer rate constant for the first 1e step is found to be 2.819×10^{-3} cm s^{-1} which is much slower than reported on a mercury electrode. In DMF media, a surface prewave corresponding to the reduction of the species resulting from the slow time-dependent surface protonation of benzil is observed. A small anodic wave in the positive potential region corresponding to the oxidation of a small concentration of the isomeric semidione intermediate is also observed. In the presence of *o*-cresol, further reduction of the anion radical occurs in between the two cathodic peaks owing to simultaneous protonation and reduction. Benzoic acid protonates benzil itself, which results in a direct 2e reduction in the prewave region. In the presence of both *o*-cresol and benzoic acid, the benzoin formed from 2e reduction gives rise to a further reduction peak at a more negative potential. The benzil anion radical–Li^+ ion-pair also undergoes easier reduction than the free anion radical species.

In aqueous media an irreversible 2e reduction peak corresponding to the reduction of benzil to benzoin is observed. In neutral and alkaline media further reduction of benzoin to hydrobenzoin is also observed. In alkaline conditions at high sweep rates, oxidation waves corresponding to the *Z* and *E* forms of stilbenediolate are observed.

Benzil is a diketo compound that has been the subject of comprehensive polarographic and voltammetric investigations on mercury electrodes. Among the aprotic solvents, the voltammetric behaviour in dimethyl formamide (DMF) has received considerable attention over the past two decades.[1–6] In DMF and in other aprotic solvents, benzil is reduced in two one-electron steps to give the corresponding anion radical and dianion respectively. Both the anion radical and the dianion of benzil form ion-pairs with Li^+ ions.[2–4] These ion-pairs also show reversible redox behaviour with a shift in peak potential due to the ion-pair equilibrium. The voltammetric behaviour in other solvents such as acetonitrile,[7] dimethyl sulfoxide[4,8,9] and even molten salts[10–12] have been investigated. The anion radical and dianion formed during electrochemical reduction of benzil are quite stable and hence undergo *O*-alkylation and *C*-alkylation processes which are of some synthetic interest.[13–15]

The polarographic studies in aqueous media are even more exhaustive.[16–27] In general, benzil gives an overall two-electron wave over a wide pH range.[1,16,17] The two-electron reduction product is benzoin which is formed through tautomerisation of the (*E*)/(*Z*)-stilbenediol intermediate. The stereochemical aspects of this reduction process have thus received greater attention,[18,20,21] including spectrophotometric[22] and photochemical[23] investigations. Recent studies[26,27] have considered kinetic aspects and adsorption effects on mercury electrodes in detail. Apart from all the above investigations on mercury electrodes, some brief studies have also been performed on liquid[28] and solid[29] amalgamated electrodes. A brief note on the voltammetric behaviour of benzil on glassy carbon electrode (GCE) is also available.[30] No specific surface effects have however been observed on mercury films or other solid electrodes.

In a recent comprehensive investigation on the comparative voltammetric responses of aromatic carbonyl compounds[31] we found considerable surface effects of GCE when compared to mercury, which could be attributed to the interaction between acidic surface functional groups of GCE and the aromatic aldehyde bases. For example, the surface effects on the redox behaviour of benzaldehyde[32] and vanillin[33] are much weaker when compared to benzophenone[34] under identical conditions. Even stronger acidity effects are noticed in the benzil redox processes as reported in the present work. In addition we have also noticed some interesting *E–Z* isomeric transformations of benzoin intermediates as well as their tautomeric transformations on GCE which are reported here.

Experimental

The glassy carbon electrode (5 mm diameter, Tokai GCA) was fabricated, polished, cleaned and activated by an electrochemical cycling procedure as described elsewhere.[35] The electrode activity in aqueous solution was evaluated using the cyclic voltammetric response of the ferricyanide–ferrocyanide redox couple in 0.1 mol dm^{-3} aqueous KCl.[35] In non-aqueous solvents the voltammetric response depended very much on the level of polishing and pre-treatment. From a number of experiments it was found that a 'perfectly polished' GCE surface for non-aqueous studies was obtained by polishing GCE from $^1/0$ to $^4/0$ emery paper for 10 min each, washing with water, trichloroethene and the solvent supporting electrolyte (SSE) solution and introducing it into the cell in a wet condition and electrochemically activating it by cycling in the potential region of interest at 10 mV s^{-1} for 15 min without adding the compound. The electrode already activated according to this procedure produces the voltammetric responses of anthracene (An) reported in the literature for mercury[36] and platinum[37] electrodes in the same potential region.

A H-type cell with platinum counter electrode was used for voltammetric studies. The saturated calomel electrode (SCE) was connected to the working electrode compartment through a KCl-Agar luggin capillary. For cyclic voltammetry in DMF, the luggin capillary was equilibrated for 1 h in solvent supporting electrolyte mixture just before use. The solvent supporting electrolyte itself was kept over alumina for 24 h and filtered just before use. The working electrode compartment was deaerated with purified nitrogen until dissolved oxygen was completely

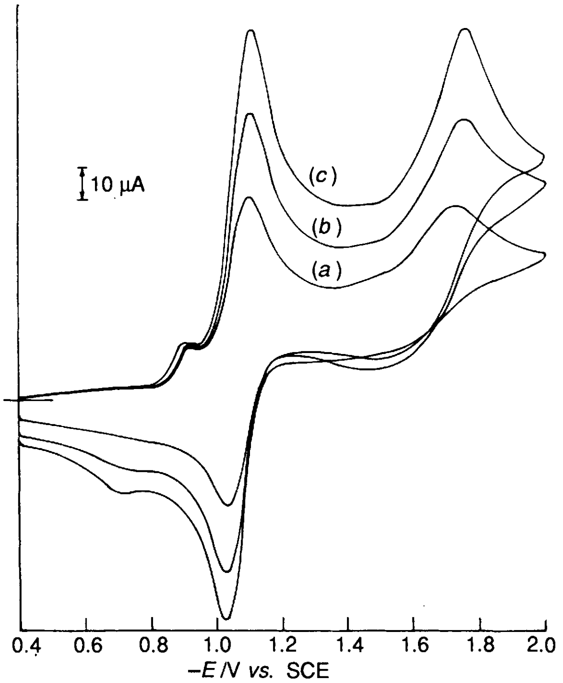


Fig. 1 Cyclic voltammograms for the reduction of benzil in 0.1 mol dm^{-3} TBAI/DMF on GCE at various concentrations at 20 mV s^{-1}. (*a*) 2, (*b*) 3 and (*c*) 4 mmol dm^{-3}.

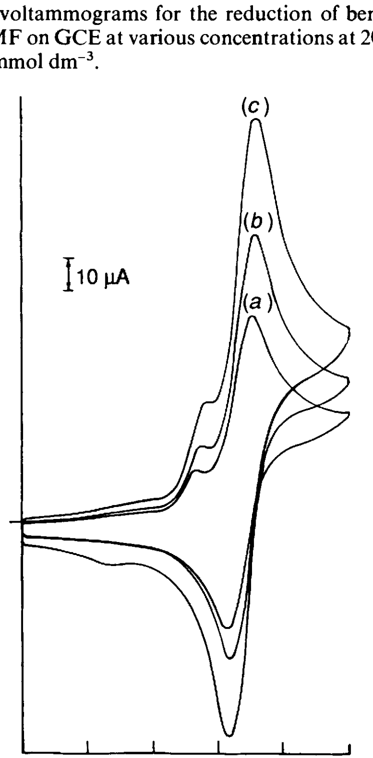


Fig. 2 Cyclic voltammograms for the reduction of benzil (2 mmol dm^{-3}) in 0.1 mol dm^{-3} TBAI/DMF on GCE at various sweep rates (first wave region only). (*a*) 20 mV s^{-1}, (*b*) 40 mV s^{-1} and (*c*) 80 mV s^{-1}.

removed (as indicated by the absence of a reduction peak at *ca.* -0.8 V). All experiments were carried out at 25 ± 1 °C. 50% ethanolic solutions were used. All chemicals were of AR grade.

Constant potential electrolysis in aqueous alcoholic acidic solution was carried out on a GC plate. The potential fixed for this experiment was around the first reduction peak potential namely -0.6 V. After electrolysis, the catholyte was evaporated to minimum volume and extracted with diethyl ether. The ether solution was dried with anhydrous sodium sulfate and evaporated, leaving a crude precipitate. The recrystallisation of crude precipitate from ethanol yielded a white precipitate which was identified as benzoin, m.p. 131 °C (lit., 130 °C); ν_{max}(KBr)/cm^{-1} 3400, 1660.

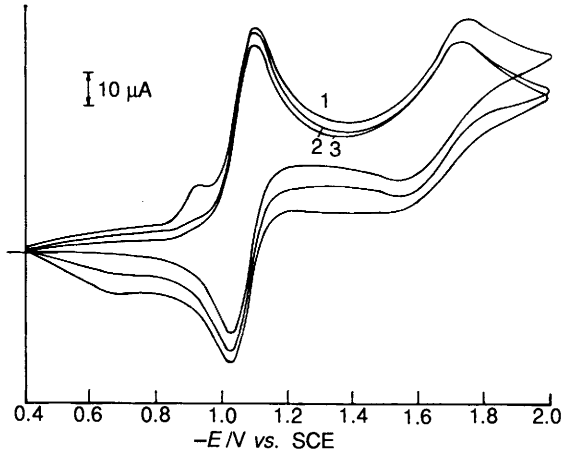


Fig. 3 Cyclic voltammograms for the reduction of benzil (2 mmol dm^{-3}) in 0.1 mol dm^{-3} TBAI/DMF on GCE in multisweeps. Sweep rate 20 mV s^{-1}. Numbers indicate the sweeps.

Results

Electrochemical Reduction of Benzil in DMF.—In contrast to the voltammetric behaviour of benzil on a mercury electrode, a new surface prewave is always noticed on glassy carbon electrodes. At low concentrations (< mmol dm^{-3}) a small irreversible surface prewave alone is noticed. Above this concentration, the peak height of this surface prewave becomes independent of concentration. In addition to this prewave, a reversible wave followed by an apparently irreversible wave are observed (Fig. 1). These two waves, which increase linearly with concentration of benzil, are subsequently referred to as the main waves. Another interesting feature is the appearance of a small anodic wave in the tail end of the main anodic peak (Fig. 1).

All these peaks in the voltammograms are found to depend on the sweep rate. The first main redox couple shows reversibility in all the sweep rate regions investigated (Fig. 2). The small anodic wave observed in the extreme positive potential region becomes even more apparent as the sweep rate is increased. This small anodic wave is not connected with the second main cathodic peak at all. The anodic peak is observed even when the cathodic limit of the cyclic voltammogram is set just beyond the first cathodic peak region (Fig. 2). The peak current (I_p) values of both first and second main peaks were found to increase linearly with the square root of the sweep rate ($V^{\frac{1}{2}}$) and concentration (C) of benzil. The peak current constant ($I_p/ACV^{\frac{1}{2}}$, A is the surface area of the electrode) is almost independent of sweep rate and concentration, especially for the first wave. A slight decrease in the peak current constant is noticed for the first peak at higher concentration and for the second wave in general. The cathodic prewave observed on GCE is quite surface sensitive. This is confirmed by multisweep cyclic voltammetric curves (Fig. 3). The prewave is present for the first cathodic sweep alone and in all subsequent sweeps this prewave is totally absent. Another interesting feature in Fig. 3 is the clear appearance of the reversibility of the second main wave. The small anodic wave at *ca.* -1.6 V on the reverse sweep is very sensitive to solvent properties and hence extreme precautions in terms of solvent supporting electrolyte purification as well as drying are required to achieve this reversibility of the second redox process.

Effect of Additives in Aprotic Media.—Addition of water (in

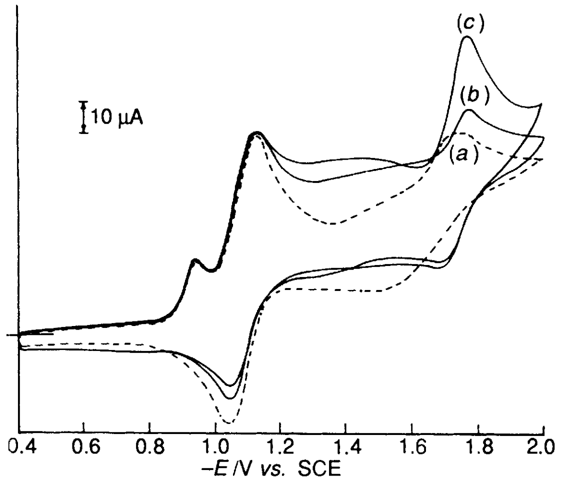


Fig. 4 Effect of *o*-cresol as proton donor on the reduction of benzil (2 mmol dm^{-3}) in 0.1 mol dm^{-3} TBAI/DMF on GCE at 20 mV s^{-1}. (*a*) No *o*-cresol, (*b*) 2.3 mmol dm^{-3} and (*c*) 4.4 mmol dm^{-3} *o*-cresol.

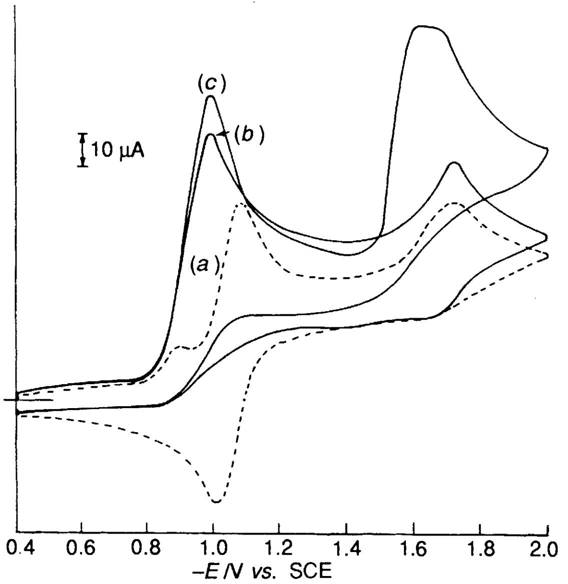


Fig. 5 Effect of benzoic acid as proton donor on the reduction of benzil (2 mmol dm^{-3}) in 0.1 mol dm^{-3} TBAI/DMF on GCE at 20 mV s^{-1}. (*a*) No benzoic acid, (*b*) 4.3 mmol dm^{-3} and (*c*) 6.4 mmol dm^{-3} benzoic acid.

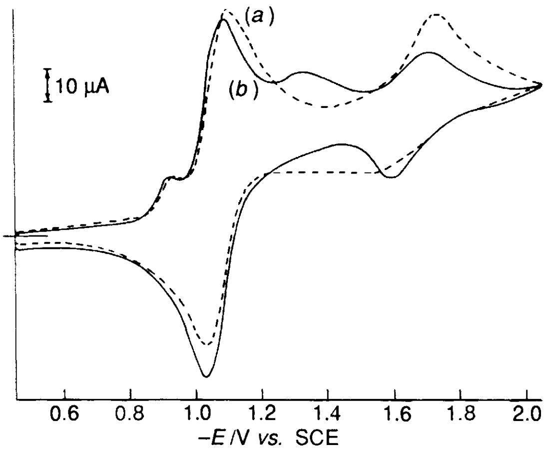


Fig. 6 Effect of Li^+ ion on the reduction of benzil (2 mmol dm^{-3}) in 0.1 mol dm^{-3} TBAI/DMF on GCE at 20 mV s^{-1}. (*a*) In the absence of Li^+. (*b*) In the presence of 1 mmol dm^{-3} $LiClO_4$.

millimolar concentrations) had no effect on the voltammetric behaviour of benzil in DMF. Even *o*-cresol had no effect on the first cathodic peak and prewave (Fig. 4). However, immediately after the first cathodic peak, changes in the voltammetric response are noticed (Fig. 4). A small wave is observed in between the first and second main cathodic peak. At higher *o*-cresol concentration, in addition to this change in the middle potential region, a substantial increase in the peak current in the second cathodic potential region (*ca.* −1.8 V) is also observed. With increasing *o*-cresol concentration, the anodic peak current in the first main cathodic potential region decreases slightly but the reversibiliity of the first redox couple is still observed.

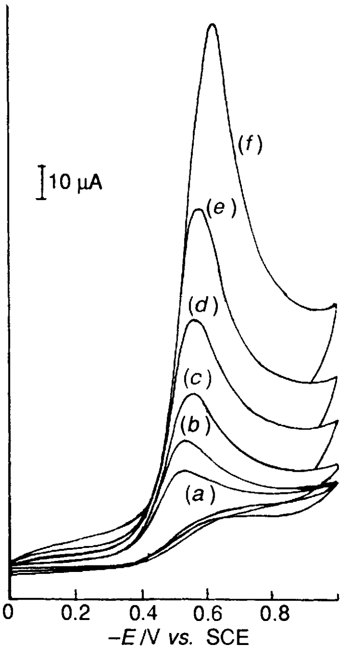


Fig. 7 Cyclic voltammograms for the reduction of benzil (1 mmol dm^{-3}) in 0.1 mol dm^{-3} H_2SO_4/50% EtOH on GCE at various sweep rates. (*a*) 10 mV s^{-1}, (*b*) 20 mV s^{-1}, (*c*) 40 mV s^{-1}, (*d*) 80 mV s^{-1}, (*e*) 160 mV s^{-1} and (*f*) 320 mV s^{-1}.

Benzoic acid also had a profound effect on the voltammetric response (Fig. 5). The first cathodic peak current increases in the prewave potential region itself and the anodic peak in the reverse sweep completely disappears. At sufficiently high concentrations of benzoic acid the peak current in the second main cathodic peak region increases substantially [Fig. 5(*c*)]. The new cathodic peak is quite broad indicating that it is in fact composed of two sharper peaks at closely spaced potential.

Li^+ ions also have no substantial influence on the prewave or the first redox process. However, a small reduction peak between the two main cathodic peaks is again observed in the presence of Li^+ ions (Fig. 6). In the presence of Li^+ ions, the second main peak apparently becomes reversible.

Butylbromide as a redox catalytic reagent also shows no catalytic influence on the prewave. There is however a small but noticeable increase in both the first and second main wave, probably due to the redox catalysis involving the anion radical and dianion respectively.

Voltammetry on GCE in Protic Media.—In 0.1 mol dm^{-3} aqueous sulfuric acid containing 50% EtOH, benzil gives a single well-defined irreversible voltammetric peak (Fig. 7). The peak current increases with benzil concentration as well as sweep rate. The peak current constant ($I_p/ACV^{\frac{1}{2}}$) remains fairly constant over the entire sweep rate and concentration ranges.

In an aqueous alcoholic neutral medium of 0.1 mol dm^{-3} tetraethylammonium toluene-*p*-sulfonate (TEATS) benzil gives two well-defined irreversible diffusion-controlled peaks at *ca.* −0.8 V and −1.5 V (Fig. 8). The peak currents again increase

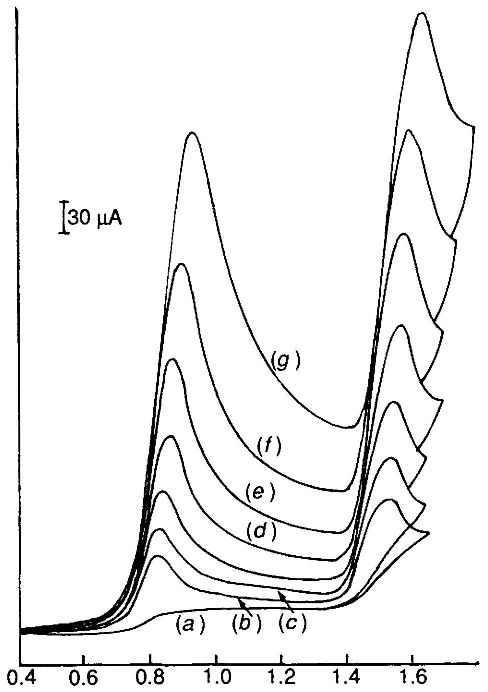


Fig. 8 Cyclic voltammograms for the reduction of benzil (2 mmol dm^{-3}) in 0.1 mol dm^{-3} TEATS/50% EtOH on GCE at various sweep rates. (*a*) 10 mV s^{-1}, (*b*) 20 mV s^{-1}, (*c*) 40 mV s^{-1}, (*d*) 80 mV s^{-1}, (*e*) 160 mV s^{-1}, (*f*) 320 mV s^{-1} and (*g*) 640 mV s^{-1}.

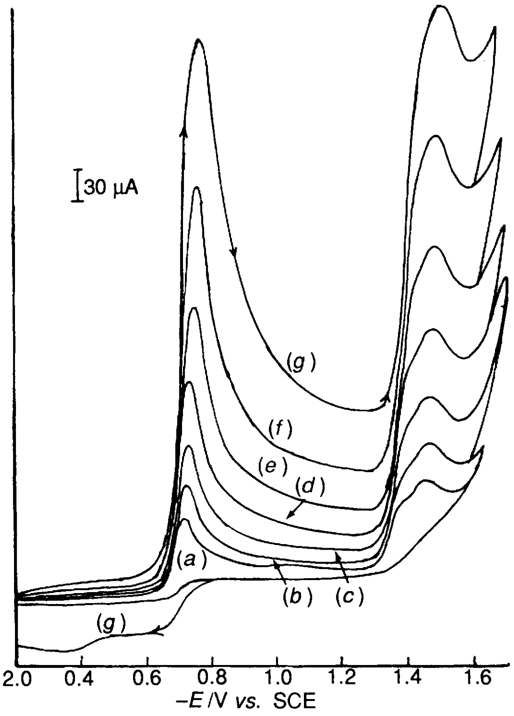


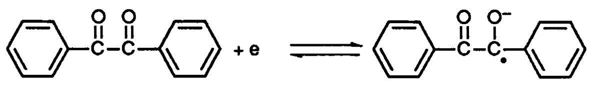
Fig. 9 Cyclic voltammograms for the reduction of benzil (1.8 mmol dm^{-3}) in 0.1 mol dm^{-3} TBAH/50% EtOH on GCE at various sweep rates. (*a*) 10 mV s^{-1}, (*b*) 20 mV s^{-1}, (*c*) 40 mV s^{-1}, (*d*) 80 mV s^{-1}, (*e*) 160 mV s^{-1}, (*f*) 320 mV s^{-1} and (*g*) 640 mV s^{-1}.

with sweep rate and with concentration of benzil. In all these cases, the peak current increases linearly with the concentration and the square root of the sweep rate.

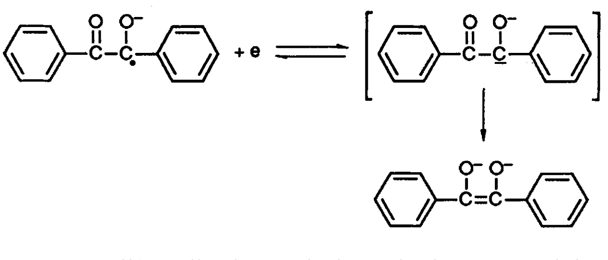
The voltammetric behaviour of benzil in 0.1 mol dm^{-3} tetrabutylammonium hydroxide (TBAH) containing 50% EtOH as alkaline solution is also quite similar to that in the neutral solution discussed above. Two well defined cathodic peaks (at −0.7 V and −1.35 V) are observed (Fig. 9). Compared to the voltammetric behaviour in a neutral medium, the voltammograms recorded in these alkaline solutions contain two distinct features. In the cathodic sweep a small post peak which is quite closely spaced with the second cathodic peak is observed. This 'post peak' is especially distinct when quite slow sweep rates are employed (Fig. 9). Secondly the anodic peaks are observed in the reverse sweeps when fairly high sweep rates (> 500 mV s^{-1}) are employed. These two anodic peaks, however, are not linked with the second cathodic peak observed at more negative potentials. A summary of voltammetric data for benzil reduction in aprotic and protic solvents is given in Table 1. Wherever possible the literature data on mercury electrodes under identical conditions are also reported for comparison.

Discussion

Electrochemical Reduction of Benzil in DMF.—Benzil gives two one-electron reduction waves in aprotic solvents such as DMF on a mercury electrode.[1–6] The first and second main reduction peaks obtained on GCE correspond to those reduction processes observed on mercury electrodes. The first and second reduction peak potentials on mercury and GCE are more or less the same (Table 1). Hence we may assume that these two 1e processes correspond to the formation of anion radical and dianion respectively [eqns. (1) and (2)].



(1)



(2)

The benzil/benzil anion radical couple gives a reversible peak even under the slowest sweep rate conditions. The anion radical is stable even towards protonating agents like *o*-cresol, ion-pair forming agents like Li^+ ions and radical scavangers like butyl bromide. Similar behaviour with regard to anion radical stability has also been observed on a mercury electrode.

The anion radical/dianion redox couple [eqn. (2)] is also apparently quite stable. The anodic oxidation peak due to the dianion oxidation at *ca.* −1.6 V is distinctly observed only during multisweep experiments (Fig. 3) and in the presence of protonating agents (Fig. 4) and Li^+ ions (Fig. 6). On a mercury electrode it has also been reported that a reversible anion radical/dianion couple redox peak could be obtained only by *in situ* alumina treatment.[4]

The cathodic and anodic potentials are found to shift in opposite directions with sweep rate for the benzil/benzil anion radical redox couple (Fig. 2). The increase of ΔE_p with sweep rate suggests a quasi reversible nature for the charge transfer. Using the value of 1.1×10^{-5} cm^2 s^{-1} for the diffusion coefficient[4] and on α value of 0.5 and Nicholson's dimensionless parameter ψ,[38] the apparent charge transfer rate constant for this redox process on GCE was calculated. The average rate constant obtained is 2.819×10^{-3} cm s^{-1}. On a mercury electrode[4] it is suggested that the charge transfer rate constant, k_h^0 is greater than 1 cm s^{-1}. This trend of slower apparent charge transfer rate constant on GCE compared to a mercury electrode is in agreement with the general trend.[39,40] Linear dependence of I_p on $V^{\frac{1}{2}}$ as well as C, and the constancy of peak current

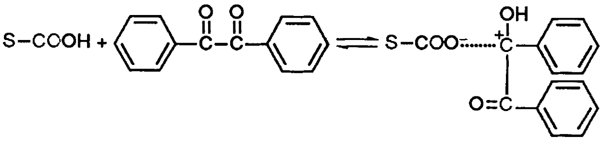
Table 1 Voltammetric behaviour of benzil (2 mmol dm^{-3}) in aprotic and protic media. Sweep rate = 20 mV s^{-1}.

Medium	Additive (concentration/mmol dm^{-3})	Glassy carbon electrode			Mercury electrode	
		$-E_{p/2}/V$	$I_p/\mu A$	$I_p/ACV^{\frac{1}{2}}$	$-E_{\frac{1}{2}}/V$	$I_p/ACV^{\frac{1}{2}}$
0.1 mol dm^{-3} TBAI/DMF	None	0.930 (prewave)	12	—	—	—
		1.040	52	942.97	1.0[a]	890.00[b]
		1.620	34		1.6	
	H_2O (millimolar)	—	—	—	—	—
	o-Cresol (6.4)	1.040	55	—	—	—
		1.720[c]	50	—	—	—
	Benzoic acid (6.4)	0.920	84	—	—	—
		1.540[c]	70	—	—	—
	$LiClO_4$ (2.19)	1.040	52	—	—	—
		1.225[c]	—	—	—	—
	Butyl bromide (11.7)	—	—	—	—	—
0.1 mol dm^{-3} H_2SO_4/50% EtOH	None	0.410	70	1313.37	0.310[d]	—
0.1 mol dm^{-3} TEATS/50% EtOH	None	0.780	96	1745.62	0.760[e]	—
		1.450	129	2339.30	—	—
0.1 mol dm^{-3} TBAH/50% EtOH	None	0.690	100	1813.40	0.815[f]	—
		1.360	102	1849.68	—	—
		1.430 (postwave)	—	—	—	—

[a] Ref. 2. [b] Ref. 4. [c] New peak. [d] pH 1.3, ref. 16. [e] pH 8.6, ref. 16. [f] pH 11, ref. 23.

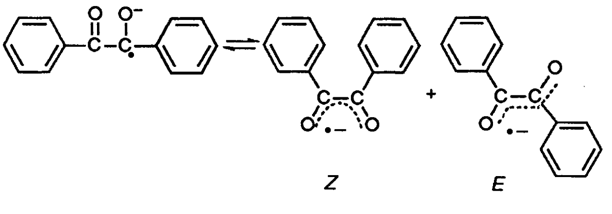
constant $I_p/ACV^{\frac{1}{2}}$ indicate that both the electrochemical reduction processes are diffusion controlled. A small but noticeable decrease in the peak current constant value at high sweep rates, the shift of cathodic peak potential with increase in concentration and the variation of apparent charge transfer rate constant with benzil concentration, *etc.* are linked to the blocking effects observed on solid electrodes in general.

Two specific voltammetric features observed in the case of benzil reduction on GCE which are absent in the voltammograms recorded on mercury and platinum electrodes should receive special attention. The first feature is the appearance of the prewave even on a perfectly polished GCE which still contains some surface acidic functional group such as COOH, or phenolic OH in low concentrations.[41] The appearance of a prewave at low concentrations, its concentration independence beyond 1 mmol dm^{-3} of benzil, its sweep rate dependence and its absence in the second and subsequent sweeps in multisweep experiments indicate that this prewave is due to some specific interaction between electrode surface functional groups and the reductant molecule, namely benzil. It may be assumed that this interaction is between acidic functional groups present on GCE and the basic carbonyl function in the benzil molecule leading to a surface protonation prewave. The slow time-dependent surface protonation process for benzil may be represented by eqn. (3). In this scheme S denotes the GCE surface. Since this surface protonated species is more easily reduced than the unprotonated species, the prewave is observed. This type of surface protonation on GCE in DMF has also been observed for other carbonyl compounds like benzaldehyde,[32] vanillin[33] and benzophenone.[34]



(3)

Another feature is the appearance of the small anodic wave at *ca.* −0.7 V. This anodic wave is certainly not linked with the cathodic prewave discussed above. If the potential is reversed in the prewave region alone, this anodic peak does not appear. Fig. 2 also suggests that this anodic wave appears whenever the anion radical is generated in the first main cathodic region. It is probable that the anion radical delocalises its charge between the two carbonyl groups and forms a semidione type of anion radical which can exist in *Z* and *E* forms [eqn. (4)].[42]

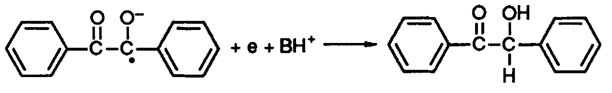


(4)

Although the *E* form of the benzil anion radical is likely to be the predominant species, the presence of a small concentration of the *Z* form cannot be ruled out on short time scales (fast sweep rates). The oxidation of this minor constituent is probably responsible for the appearance of a small anodic peak at more positive potentials when high sweep rates are employed (Figs. 1 and 2).

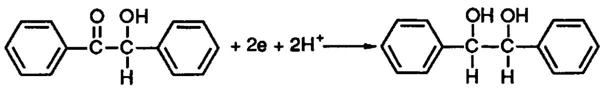
Influence of Additives on the Electrochemical Reduction of Benzil in DMF.—Water in millimolar level concentrations seems to be a poor protonating agent for benzil and hence it has no effect on the voltammetric response.

o-Cresol also does not influence the benzil/benzil anion radical redox process (Fig. 4). However, the protonated benzil anion radical seems to undergo further facile reduction at *ca.* −1.4 V which is between the two main reduction peaks. Since this reduction process takes place between the falling portion of the first cathodic peak and the rising portion of the second cathodic peak, it is quite difficult to quantify the voltammetric response properly. However, a small decrease in the anodic peak current due to benzil anion radical oxidation in the presence of *o*-cresol whenever the middle potential region is crossed in the cathodic sweep substantiates this view. *o*-Cresol also seem to have another interesting effect on benzil reduction. At *ca.* −1.8 V (corresponding to the reduction of the unprotonated benzil anion radical) one should not expect a reduction peak if the protonated anion radical undergoes reduction at *ca.* -1.4 V as suggested above. However, we observed a distinct peak at *ca.* -1.8 V which increases substantially with *o*-cresol concentration (Fig. 4). It is tempting to suggest that the first 2e reduction product benzoin [eqn. (5)] undergoes a further 2e reduction in the more negative potential region [eqn. (6)].



(5)

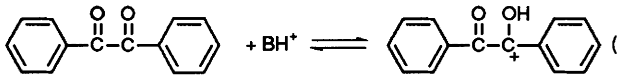
(BH$^+$ refers to *o*-cresol)



(6)

It has been reported that benzoin itself undergoes reduction[1] at *ca.* -1.8 V on a mercury electrode which lends support to this view. In aqueous conditions we also observed the reduction of benzoin at more negative potentials.

Benzoic acid, a more powerful protonating agent than *o*-cresol, protonates the reactant benzil itself. A single wave due to the 2e reduction of benzil to benzoin is observed in the prewave region [eqn. (7)]. Since the prewave observed in the absence of protonating agents is also due to surface protonated benzil species, the reduction potential of bulk protonated benzil species (due to benzoic acid) is likely to be very close to the potential region of the first wave. This is found to be the case. Merging of the main reduction wave of benzil in the presence of benzoic acid with the prewave thus lends support to the assumption that the prewave is due to the reduction of surface protonated species. It may also be noted that the anodic peak corresponding to the first main cathodic peak is absent. This is due to the non-availability of the anion radical formed in the first step because of its protonation and subsequent reduction in the same potential region leading to the formation of benzoin. The appearance of another reduction peak at *ca.* -1.8 V in the presence of benzoic acid (Fig. 5) is again related to the further reduction of benzoin as discussed above for *o*-cresol.



(7)

(BH$^+$ refers to benzoic acid)

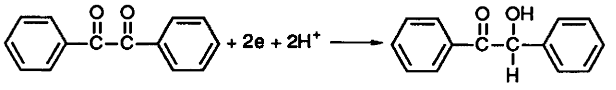
Li$^+$ ions also do not influence the prewave process or the first redox process substantially (Fig. 6). However, the lithium–benzil anion radical ion-pair gives rise to an early reducible redox couple which shows the reduction peak at *ca.* -1.4 V. At sufficiently high concentrations of Li$^+$ ions, the redox peaks in the middle potential region reach their maximum value and the redox peaks at more negative potentials disappear completely. All these facts substantiate the ion-pair fermation effect of Li$^+$ as well as the reversibility of the second electron transfer step. A similar voltammetric response showing two peaks for the anion radical in presence of Li$^+$ ion has also been reported on a mercury electrode.[4]

Electrochemical Reduction of Benzil in Protic Media.—Studies of the polarographic and voltammetric behaviour of benzil on a mercury electrode in aqueous solution have been confined to the first reduction peak alone (reduction of one carbonyl group). Although benzil contains two carbonyl groups, the possibility of the reduction of the second carbonyl group has not received the attention it deserves.[16–27] In acid medium on GCE, benzil gives only a single irreversible 2e diffusion controlled wave within the available potential region (Fig. 7). Formation of the 2e reduction product benzoin is also confirmed by constant potential electrolysis. In acid medium on mercury a single 2e wave has also been observed.

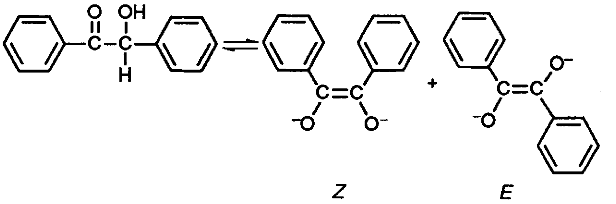
In neutral or in alkaline media, two 2e reduction waves corresponding to the reduction of the first and second carbonyl groups respectively are clearly noticed on GCE (Figs. 8 and 9). The linear variation of I_p with C and $V^{\frac{1}{2}}$ and the constancy of the peak current constant suggest that these processes are irreversible diffusion controlled 2e reduction processes. On a mercury electrode the second reduction process was found to merge with the background reduction.[27] This is probably due to the fact that this study[27] employed only sodium hydroxide as the supporting electrolyte. Since we have employed tetraalkyl ammonium salts as supporting electrolyte in the present work, the second reduction step has also been clearly observed (Fig. 8).

In the case of a number of aromatic carbonyl compounds investigated, namely benzaldehyde,[32] benzophenone[34] and vanillin,[33] a prewave due to reduction of surface protonated species (similar to the process observed in DMF) was also observed along with the main reduction peak in neutral media. This type of prewave is not observed for benzil reduction (Fig. 9). Compared to other carbonyl compounds mentioned above, benzil, even in the unprotonated form, is more easily reduced in the potential region of -0.7 V and hence no surface protonation effect has been observed in neutral aqueous solution.

Two observations on the voltammetric response of benzil in tetrabutylammonium hydroxide medium deserves a special mention. At high sweep rates whenever the potential is reversed beyond the first cathodic reduction peak, two anodic oxidation peaks are observed. These probably correspond to the oxidation of small concentrations of (*Z*)- and (*E*)-stilbenediolate anions formed from the two electron reduction product of benzil, namely benzoin [eqns. (8) and (9)]. Similar oxidation behaviour of the *Z* and *E* isomers has also been investigated on a mercury electrode.[21] The 'post peak' observed on the second reduction peak is probably linked with the reactant adsorption process which is quite often encountered in the electroreduction of larger organic compounds.[43,44]



(8)



(9)

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