

## CYCLIC VOLTAMMETRIC STUDIES FOR DIFFERENT SUBSTITUTED BENZILS

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## ABSTRACT

The electroreduction of different substituted benzils was synthesized and studied in alcoholic and alkaline medium by cyclic voltammetry. In alkaline solutions, the reduction occurs in two reversible one-electron steps producing the anion radical and the dianion. In the presence of alcohol, the first reduction is unaffected and the second reduction wave becomes irreversible and is shifted toward positive potentials, following qualitatively the criteria for a rapid reaction of the dianion with the proton donor. The protonation can occur through the radical anion since it is not possible to observe the first step of the reaction to the radical anion.

**Keywords:** Cyclic voltammetric studies, Synthesized benzils, Electroanalysis.

## INTRODUCTION

Cyclic voltammetry (CV) is perhaps the most versatile electroanalytical technique for the study of electroactive species. Its versatility combined with the ease of measurements has served in the extensive use of CV in the field of electrochemistry, organic chemistry, inorganic chemistry, and biochemistry. Organic chemists [1,2] have applied this technique to the study of biosynthetic reaction pathways and to study the electrochemically generated free radicals. An increasing number of chemists have been using CV studies to evaluate the oxidation/reduction [3,4] potential of functional groups and the effects of other groups attached to them.

CV studies consist of cycling the potential of an electrode, which is immersed in an unstirred solution and measuring the resultant current. The potential of the working electrode is controlled versus a reference electrode (saturated calomel electrode or Ag/AgCl). The controlling potential which is applied across these two electrodes can be considered as an excitation signal. The potential range is scanned in one direction, starting at the initial potential and finishing at the final potential. A more commonly used variation of the technique is CV [5,6], in which the direction of the potential is reversed at the end of the first scan. Thus, the waveform is usually of the form of an isosceles triangle. This has the advantage that the product of the electron transfer reaction that occurred in the forward scan can be probed again in the reverse scan. In addition, it is a powerful tool for the determination of formal redox potentials, detection of chemical reactions that precede or follow the electrochemical reaction and evaluation of electron transfer kinetics [7-9]. The current now depends on the rate of mass transfer to the electrode surface and so the time dependence is  $\sqrt{t}$  resulting in an asymmetric peak shape.

In the electrochemical oxidation,

1. The initial electron transfer is carried out  
A suitable time gap allowing the chemical reaction to occur is provided

2. (set by the position of the switching potential)

The effects of the chemical reaction on the initial and subsequent electron

3. transfers are studied electrochemically.

Accordingly,  $i_p$  is directly proportional to concentration and increases with  $\gamma^{1/2}$ . The relationship to concentration is important in analytical applications and studies of electrode mechanism.

The value of  $i_{pa}$  and  $i_{pc}$  should be identical for a simple reversible couple, i.e.,

$$i_{pa}/i_{pc} = 1$$

However, the ratio of peak current can be significantly influenced by chemical reactions coupled to the electrode process. The peak current for a quasi-reversible system is not proportional to  $\gamma^{1/2}$  except when the peaks are so widely separated that the system is more appropriately described as totally irreversible. Although the average of peak potentials can be good estimate of the  $E^0$  for a reversible redox reaction, one must be careful not to attribute high accuracy to the determination. Estimating formal reduction potentials from quasi-reversible voltammograms is less reliable. Theoretical work shows that as the scan rate is increased, slow electron transfer kinetics can make the peak potential shift in such a manner that they are no longer symmetric about the  $E_{1/2}$  for the redox couple.

The response of a modified electrode will be quite different from that of solution behavior. At potentials far removed from formal potential, no current will flow through the electrode. As the potential reaches the formal potential, the current will increase to a maximum value, and a peak will be observed when the scale is over in one direction. Here, a symmetrical curve is obtained, as the rate of current decay will be equal to the rise of current. When the scale is reversed, again a peak is observed which will be the mirror image of the forward scan. This type of symmetric peaks is not observed in homogenous systems. This is because, in the case of modified electrodes, there is no diffusion of electroactive material, which undergoes changes at the electrode itself. A chemically reversible system will exhibit a ratio of peak current and  $\Delta E_p$  value as zero. Further, the peaks will be linearly dependent on the rate of a potential sweep. In general, though many immobilized redox couples exhibit symmetrical wave shape and linear dependence of peak current, with a rate of potential sweep, the  $\Delta E_p$  values are seldom zero but have small values.

## METHODS

The general experimental procedure adopted in the CV studies of all the compounds is as follows. The CV experiments have been carried out with CH Instruments 760 C Electrochemical workstation, USA. About 5 mg of the substance was added to the ethanol for alcohol medium and then into sodium hydroxide solution for alkaline medium. It is then subjected to CV experiments. The total volume of the solution was 10 ml. Platinum electrode served as the counter electrode, Ag/Ag<sup>+</sup>

non-aqueous electrode as the reference electrode and glass carbon electrode is used as the working electrode.

## RESULTS AND DISCUSSION

The different substituted benzoils were synthesized, and the CV studies were carried out for the obtained compounds benzil, 4,4'-dibromo benzil, 2'-chloro-4-methoxy-3-nitro benzil, 2,2'-dichloro benzil, and its electroanalytical behavior is analyzed for the substituted benzil compounds. The behavior of the compound in the alcoholic and alkaline medium is also carried out for all the different benzil substituents.

### Cyclic voltammetric studies for the compound in alcohol and alkaline medium

The study of the electrochemical behavior of the compound benzil was carried out in the range of  $-0.50$ – $1.00$  V. From the range  $-0.50$ – $-0.66$  V, during which, no redox process is found to take place. In the forward scanning, a definite cathodic process is found to take place at  $-0.825$  V. In the reverse scan, in the anodic wave, an oxidative process is taking place at  $-0.75$  V (Fig. 1a). The peak currents  $i_{pa}$  and  $i_{pc}$  are  $-0.55$  and  $+1.75$ , respectively. The formal potential of the redox couple is  $-0.788$  V. This is indicative of an electrochemically irreversible redox process.

The study of the electrochemical behavior of the compound benzil in alkaline medium was carried out in the range of  $-0.20$ – $1.00$  V. From the range  $-0.20$ – $-0.66$  V, during which, no redox process is found to take place. In the forward scanning, a definite cathodic process is found to take place at  $-0.82$  V. In the reverse scan, in the anodic wave, an oxidative process is taking place at  $-0.72$  V (Fig. 1b). The formal potential of the redox couple is  $-0.76$  V. The peak currents  $i_{pc}$  and  $i_{pa}$  are  $+2.25$  and  $-0.49$ , respectively. These indicate that the redox system is electrochemically irreversible.

In the cyclic voltammogram of the compound 4,4'-dibromo benzil in alcoholic medium, two cathodic peaks and one anodic peak are seen. The clear cathodic peak occurs in the negative range at  $-0.35$  V with a peak current of  $i_{pc} +0.75$ . Another cathodic peak is observed at  $-1.0$  V with a peak current of  $i_{pc} +1.65$ . This indicates that a definite cathodic process is taking place at this potential (Fig. 2a). In the reverse scan, in the anodic wave, an oxidative process is found to occur at  $-0.21$  V with peak currents of  $i_{pa} -0.6$ . This shows that the redox process is chemically and electrochemically irreversible.

In the cyclic voltammogram of the compound 4,4'-dibromo benzil in alkaline medium, two cathodic peaks and one anodic peak are seen. The cathodic peak occurs in the negative range at  $-0.35$  V with a peak current of  $i_{pc} +0.85$ . Another cathodic peak is observed at  $-1.05$  V with a peak current of  $i_{pc} +2.2$ . This indicates that a definite cathodic process is taking place at this potential (Fig. 2b). In the reverse scan, in the anodic wave, an oxidative process is found to occur at  $-0.2$  V with peak currents of  $i_{pa} -0.6$ . This shows that the redox process is chemically and electrochemically irreversible.

The CV study of the compound 2'-chloro-4-methoxy-3-nitro benzil was carried out in the potential range of  $0.0$ – $1.2$  V. In the range from  $0.0$  V to  $-0.2$  V, there is no redox process found to take place. In the forward scanning, a definite two cathodic process is found to take place at  $-0.37$  and  $-0.82$  V. In the reverse scan, in the anodic wave, two oxidative processes were taking place at  $-0.32$  and  $-0.68$  V. The peak currents of  $i_{pa}$  are  $-2.4$  and  $-0.3$ , respectively. The peak currents for cathodic process  $i_{pc}$  were found to be  $+0.5$  and  $+3.7$ , respectively (Fig. 3a). This is indicative of an electrochemically irreversible redox process.

The CV study of the compound 2'-chloro-4-methoxy-3-nitro benzil in alkaline medium was carried out in the potential range of  $0.0$ – $1.0$  V. In

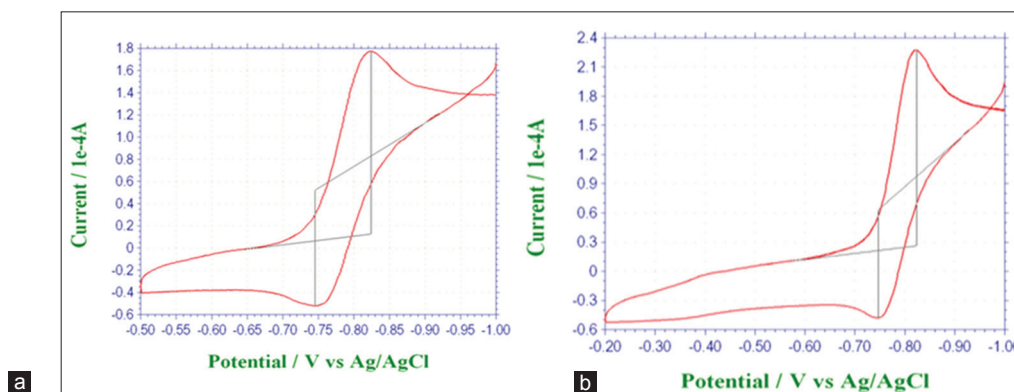


Fig. 1: (a) Cyclic voltammetry (CV) study for compound benzil in alcoholic medium. (b) CV study for compound benzil in alkaline medium

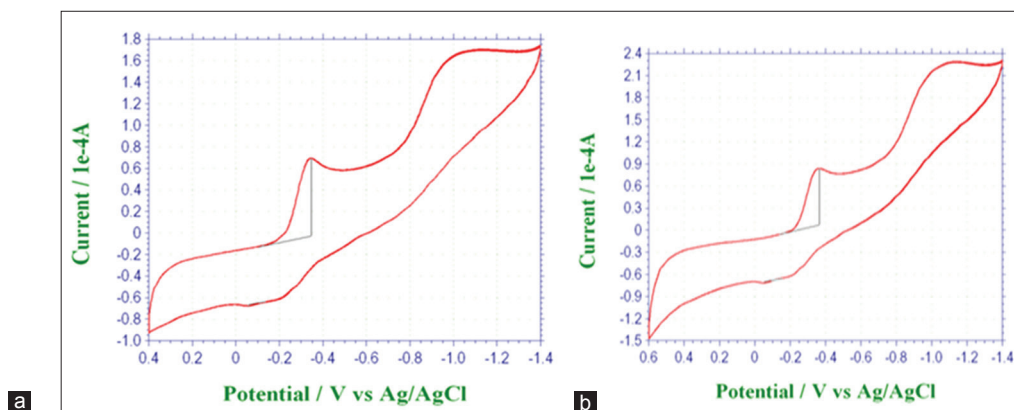


Fig. 2: (a) Cyclic voltammetry (CV) study for compound 4,4'-dibromo benzil in alcoholic medium. (b) CV study for compound 4,4'-dibromo benzil in alkaline medium

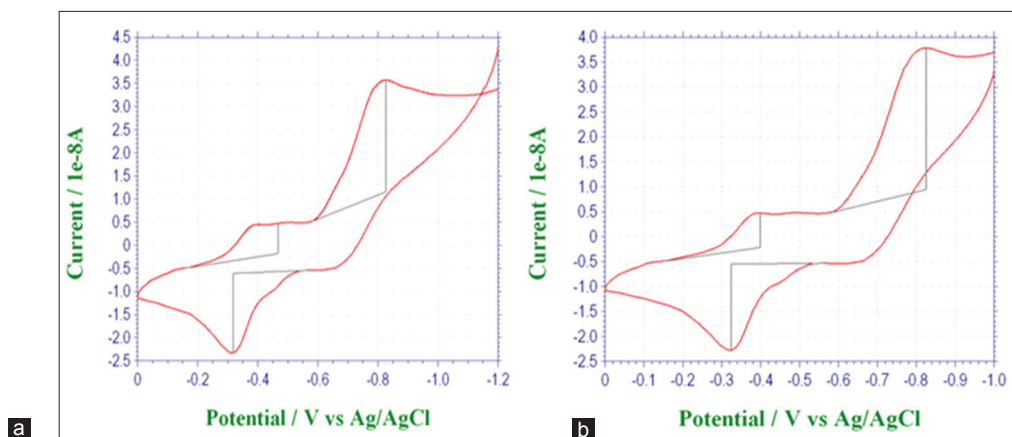


Fig. 3: (a) Cyclic voltammetry (CV) study for compound 2'-chloro-4-methoxy-3-nitro benzil in alcoholic medium. (b) CV study for compound 2'-chloro-4-methoxy-3-nitro benzil in alkaline medium

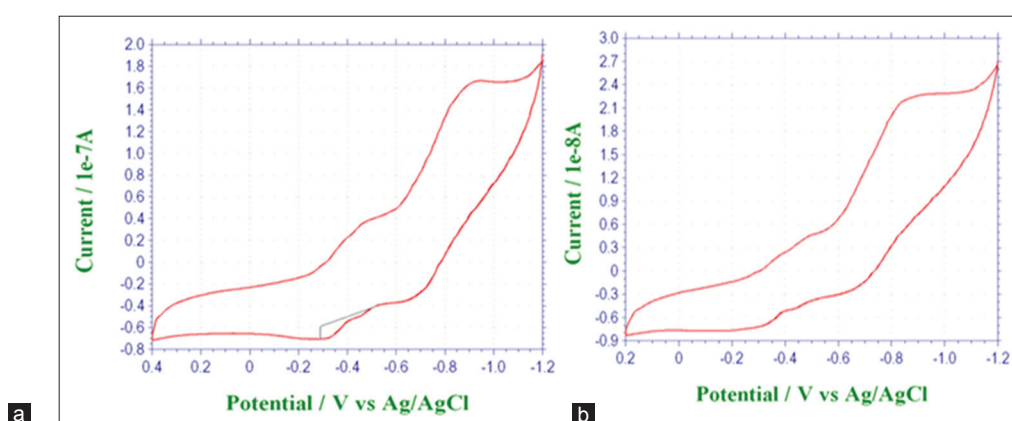


Fig. 4: (a) Cyclic voltammetry (CV) study for compound 2,2'-dichloro benzil in alcoholic medium. (b) CV study for compound 2,2'-dichloro benzil in alkaline medium

the range from 0.0 V to -0.2 V, there is no redox process and is found to take place. In the forward scanning, a definite two cathodic process is found to take place at -0.38 and -0.82 V. In the reverse scan, in the anodic wave, two oxidative processes are taking place at -0.325 and -0.68 V. The peak currents  $i_{pa}$  are -2.3 and -0.5 and for  $i_{pc}$  were found to be +0.5 and +3.8, respectively (Fig. 3b). This is indicative of an electrochemically irreversible redox process.

In the cyclic voltammogram of the compound 2,2'-dichloro benzil in alcoholic medium, two cathodic peaks and two anodic peaks are seen. A poorly defined cathodic peak at -0.45 V, with a peak current  $i_{pc}$  of +0.4, is also found. The clear cathodic peak occurs in the negative range at -0.95 V with a peak current of  $i_{pc}$  +1.7 is obtained. This indicates that a definite cathodic process is taking place at this potential. In the reverse scan, in the anodic wave, an oxidative process is found to occur at -0.32 V. Another anodic peak is observed at -0.65 V. Both these anodic processes occur at peak currents of  $i_{pa}$  -0.7 and -0.35, respectively (Fig. 4a). This suggests that the redox process is chemically and electrochemically irreversible.

In the cyclic voltammogram of the compound 2,2'-dichloro benzil in alkaline medium, two cathodic peaks and two anodic peaks are seen. The clear cathodic peak occurs in the negative range at -0.87 V with a peak current of  $i_{pc}$  +2.3, and another poorly defined cathodic peak appears at -0.52 V. This indicates that a definite cathodic process is

taking place at this potential. A poorly defined anodic peak at -0.30 V is also found. In the reverse scan, another anodic peak is observed at -0.68 V. Both these anodic processes occur at peak currents of  $i_{pa}$  -0.75 and -0.25, respectively (Fig. 4b). This suggests that the redox process is chemically and electrochemically irreversible.

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