An Electrochemical Cell for the Generation of Free Radicals for ESR Studies

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The design of a simple flow-through electrochemical cell for the generation of free radicals for esr studies is described in detail. The electrochemical cell has been found to be very satisfactory in the generation of different free radicals - anion, cation and neutral - and in carrying out various esr studies.

Free radicals (neutral, cationic and anionic radicals) belong to a very important class of chemical intermediates. One of the main challenges is the generation of free redicals - both in concentration and in time period - to enable one to carry out the investigations. Relatively unstable free radicals can be made stable by changing the environments and carry out the study [1]. Alternately, the unstable free radicals can be studied by fast techniques within the decay time of the free radical [1]. Otherwise, a steady state concentration has to be maintained to carry out the investigation.

One of the techniques, which has given immense information regarding the structure and reactivities of free radicals, is the electron spin resonance spectroscopy. Electrolytic production of a free radical is most common [2 - 10] both in closed (*in situ* as well as bulk) and flow systems. The use of high dielectric solvents - like water, acetonitrile, dimethyl formamide - pose technical problem of high dielectric loss (lossy solvent). Such solvents are and have been extensively used in generating and studying anions and cation radicals. Further, use of metals (platinum, gold etc.) in the cavity creates another problem - Q-loss (quality factor).

The present study concerns with the construction of an electrochemical cell for the generation of free radicals and testing its viability for the said purpose using nitrobenzene and 1,1 -dimethyl-4,4'-pyridinium dichloride (methyl viologen dichloride, $MVCl_2$) as testing compounds.

EXPERIMENTAL

Materials

The X-band JEO1 ESR spectrometer (model JES-FELXG) was used for recording the spectra. EG & G Princeton Applied Research Potentiostat/Galvanostat model 173 with 179 digital coulometer pulg-in was used for controlled potential electrolysis.

Nitrobenzene (Merck, BP 210°C), methyl viologen dichloride [$MV^{2+}(Cl^-)_2$] (BDH) and lithium chloride (BDH) were used as

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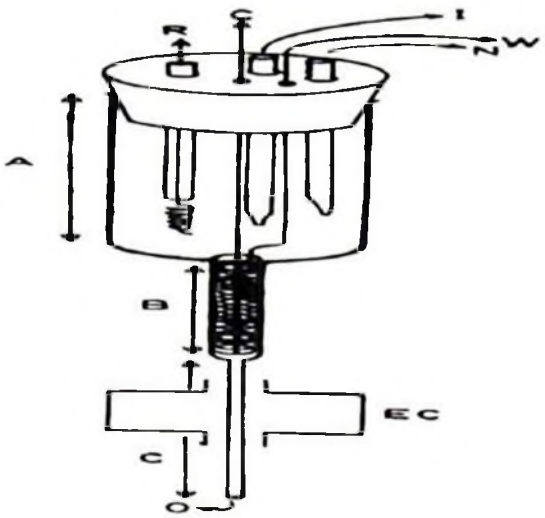


Fig.1 ESR-electrochemical cell
C = Counter Electrode (Pt-wire, W = Working electrode (Au - Wire) R = Reference electrode (Ag - Wire),
I = Solution inlet, N = Nitrogen Supply; O = outlet, EC = ESR cavity.

received. Tetra n-butyl ammonium perchlorate was prepared from the reaction of tetra n-butyl ammonium iodide (BDH) and magnesium perchlorate (Merck) in hot water. On cooling, tetra n-butyl ammonium perchlorate was obtained. This was filtered and thoroghly washed with cold water. It was recrystalized from ethanol, dried and kept in desiccator under vacuum. Acetonitrile was dried on alumina and distilled (BP 81.6°C). Ethanol of spectroscopic grade (Fluka) was used directly as received.

The cell - hereafter referred to as electrochemical esr cell (EESR) [11] - is shown in fig 1. It connsists of three parts. The upper part (A) consists of a wide pyrex glass tube of length 7-9 cm, an outer diameter of 2.8 cm and inner diameter of 2.4 cm. The mouth of the glass tube is fitted tightly with a rubber stopper containing five holes - for solution inlet, nitrogen gas bubbling and the three electrodes (W, C and R). The middle part (B), the main body of the cell, consists of a glass tubing of length = 6 cm, o.d = 0.8 cm and i.d = 0.6 cm. The lower part (C) is a glass capillary of length = 16.7 cm, o.d = 3.56 mm and i.d. = 1.2 mm. Several capillaries of varying internal diameter were tried but the best cavity response was shown by the capillary of above mentioned diameter.

The reference electrode was a helix of a silver wire (1.5 cm long, and 007 mm diameter). The working electrode W was a 6 cm long helix of 4.5 mm diameter made from pure (24 carat) gold wire (0.35 mm dia and 62 turn) obtained from local jewelary shop). The helix fitted tightly into the middle glass tube. The gold wire at one end of the helix was soldered to a copper wire in a plastic sheath. The soldered part was covered with a silicone rubber paste and dried. The copper wire formed one of the leads of the cell.

The counter electrode (C) was a platinum wire of length 11.6 cm and diameter 0.20 mm. (24 carat gold wire of the same dimension is equally good). One end of this wire was soldered to the copper wire and the joint was covered with the inert silicon rubber paste and dried. The counter electrode was placed inside a thin perforated tube of teflon and positioned at the center of the helix.

Measurements

Constant potential electrolysis of the flowing solutions for generating ion radicals was performed just above ESR cavity. The performance of the

cell was tested by recording the ESR signal of stable methyl viologen cation radical ($MV^{+\cdot}$) and nitrobenzene anion radical ($NB^{-\cdot}$) generated by controlled potential electrolysis.

In general, a known volume (10-15 ml) of solution of concentration 1 mM or less was deaerated by passing purified N_2 gas and was put into the electrolytic cell. In case of MV^{2+}, a solution of methyl viologen dichloride in ethanol with 1.0 M LiCl supporting electrolyte was electrolysed while in the case of nitrobenzene, a solution in acetonitrile with 0.1 M tetrabutyl-ammonium perchlorate as supporting electrolyte was used. Controlled potential electrolysis of the flowing solution was carried out with silver wire electrode as reference (at -0.81 V for $MV^{2+\cdot}$ and at -1.15 V for NB) to generate the respective ion radicals: $MV^{+\cdot}$ and $NB^{-\cdot}$. During electrolysis an atmosphere of N_2 was maintained in the electrolysis cell. The flow rate of solution was controlled with the help of a stopper put in the outlet passage. Good response was observed at flow rate of 0.6 ml/min.

The ESR signal was observed on the oscilloscope screen of the spectro-photometer and measurement conditions were set to optimize the signal. A typical setting for a scan was: Field 3375 Gauss, sweep width ±25 G, microwave power 0.1 μw, frequency 9.430 GHZ, Mod width 0.63x0.1 G, response 0.3 sec, amplitude 4x1000; sweep time 16 min.

DISCUSSION

Geski and Maki [2] were the pioneers of the electrolytic generation of free radicals (anion radicals) for the purpose of esr studies. Their electrochemical-esr cell was an *in situ* cell. Though successful in obtaining the esr signals and hyperfine spliting constants of some anion radicals derived from nitroaromatics, the cell was beset with various problems associated with the power loss (Q-loss) and frequency instabilities. Furthermore, the polarographic technique used by Geske and Maki was a rather specialized technique in those days (1950's-1960's). The bulk electrolysis was a successful technique but not suited to unstable free radicals. The Geski-Maki cell was improved upon and modified by Bard [12]. Albery [4] used tubular working electrode positioned just outside the esr cavity. Such an arrangement is suited for flow-cell. Since flow-through cells require large effective area of working electrode, tubular design satisfies the requirement. Allendorfer [3] and later Ohyn Nishiguchi [5] used helical working electrode. Such electrode fitted tightly against the inner wall of the 6 mm i.d. quartz esr tubing. The presence of the metal in the cavity creates problem - the Q-factor as well as volume of solution are affected. It was a good attempt but needed improvement and better design.

When the cell in our laboratory was almost completed and was being tested, a report of an electrochemical-esr cell by Bond appeared [13]. Bond's cell is perhaps so far the most versatile but a very specialised SEESR (Simultaneous Electrochemical ESR) *in situ* cell which requires special skill in fabrication and handling. It has a

Table 1

Hyperfine Splitting Constants (in Guass)

Radical	A^N	A^H_2	A^H_3	A^H_4 / $A^H(CH_3)$
NB$^-$	10.86[a]	2.74	1.15	3.87
ref[4]	10.32	3.79	1.09	3.97
MV$^{\bullet+}$[b]	4.23	1.33	1.57	3.99

(a) observed/ simulation
(b) values were taken from ref. 15 for simulation of the recorded esr spectra.

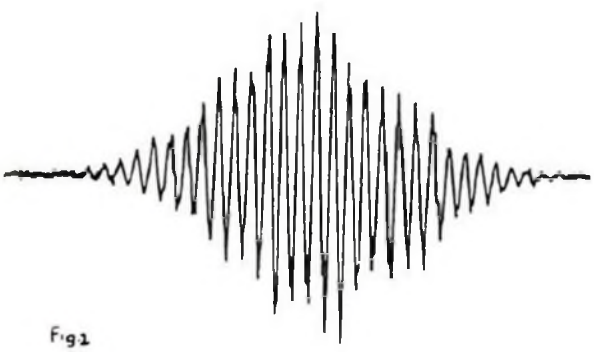


Fig.2

Fig. 2 ESR - spectrum of MV.'

limitation - it is useful for stable free radical. Further, the working electrode is of micrometer dimension; so a high concentration of parent compound (1 mM or higher) has to be taken to obtain good esr signal. The presence of high concentration of parent compound could result in exchange broadening. This Bond Cell however, has great advantage of low temperature operation. Nevertheless, we do feel that an alternative cell design be also available to the workers in the field of free radical chemistry and hence this report.

The reduction reaction may be represented as:

$MV^{2+\bullet} + e \leftrightarrows MV^{\bullet+}$ (1)

$NB + e \leftrightarrows NB^-$ (2)

The esr spectra obtained by electrochemical reduction of $MV^{2+\bullet}$ and NB are recorded. The ESR spectra of $MV^{\bullet+}$ are given in Fig.2. These esr spectra were simulated with the hyperfine splitting constants A^x (X=H,N) collected in Table 1. The literature values are also given in the table.

From the recorded esr spectra (with hyperfine structure) and the hyperfine splitting constants values agreeing with the literature values, it is clear that the electrochemical cell developed in our laboratory gives perfectly satisfactory results. Through the use of this electrolytic cell, free radicals (both anion and cation radicals) could be generated and esr spectra could be recorded. The disagreement in

the A^{II}_2 from the literature values of $NB^{\cdot}$, be due to the accuracy of the simulation method employed in the assignment of A^{II}_2.

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