

## ELECTROCHEMICAL EQUIPMENT FOR GENERATION OF RADICALS AND RECORDING ELECTRONIC SPECTRA

P. HOBZA, I. NYKL\* and K. UHLÍŘ

*J. Heyrovský Institute of Physical Chemistry and Electrochemistry,  
Czechoslovak Academy of Sciences, Prague 2*

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An equipment permitting continuous measurement of optical absorption spectra of both cation and anion radicals is described. Reduction of anthracene in acetonitrile and oxidation of perylene in methylene chloride were chosen as representative examples of application.

Electrolysis is one of the most popular methods of generation of radicals. Most of the papers concerning electrochemically generated radicals were devoted to ESR spectroscopy, whereas the optical properties of radical ions were investigated rather rarely<sup>1-5</sup>. In spite of several reported designs of electrochemical equipment<sup>6-10</sup>, the majority of spectroscopic data on radical ions originates from chemical oxidation-reduction treatments.

In this paper we present an electrochemical apparatus which is advantageous for its simplicity and for convenience in generation of radicals.

### DESCRIPTION OF THE APPARATUS

*Electrochemical cell.* The electrochemical cell is presented in Fig. 1. In the generation of anion radicals (*i.e.* reduction), the dropping mercury electrode served as indication electrode. As working electrode a mercury pool electrode was used.

In the generation of cation radicals (*i.e.* oxidation), the rotating wire Pt electrode (length 5 mm, diameter 0.5 mm) as indication electrode was used, the working electrode was realized by the Pt sheet (3 . 1 cm) placed in the cell. The sheet was arranged in such a way as not to shield the light beam passing through the cell. The reference and auxiliary electrode were common in reduction, oxidation, and polarography. Working and auxiliary electrodes were separated by sintered glass disc.

The electrochemical cell was inserted either into a commercially available quartz or glass optical cell (with a joint of 10 mm diameter) of different optical path length. This electrochemical cell is placed directly in a cell compartment of a spectrophotometer.

*Instrumentation.* A schematic diagram of the electrochemical apparatus is shown in Fig. 2. A Radelkis OH 102 polarograph in three-electrode operation and a SVUOM Pie 60 model potentiostat permitting compensation of the IR voltage drop during the electrolysis up to  $\pm 75$  V were used. The potential of the working electrode was maintained at a chosen value by means of the potentiostat. The lead-in wire to the reference electrode was shielded. In order to avoid any possible reversal voltage shock at the beginning of the operation of the potentiostat, a silicon

\* Predoctoral Fellow, Faculty of Science, Charles University, Prague.

diode KY 725 was placed in series with the auxiliary electrode. The switch  $S_{2A,B}$  was necessary for reversal of the polarity of the diode because, when changing the operation modes *reduction-oxidation*, the voltage on the socket A changed its polarity. Selection between electrolysis and polarography was made possible by means of the switch  $S_{1A,B,C}$ . The auxiliary and reference electrodes were connected by the switch  $S_{3A,B}$  ("Off-On"). The current flowing during generation of radicals was recorded by an EZ-2 strip-chart recorder Metra so that it was possible to calculate the charge that had flown into the cell.

*Determination of concentration.* The concentration of radical ions was determined from the height of polarographic waves<sup>11</sup>, from the time-dependence of absorption curves and by coulometry<sup>12</sup>. In coulometric measurements a correction for the tentatively estimated decay of radicals to the parent compounds was made.

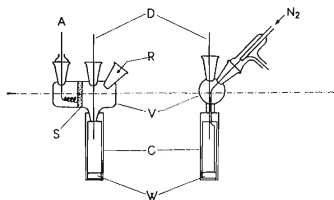


FIG. 1

Electrochemical Cell Used for Generation of Radicals and Recording Electronic Spectra and Polarograms

A Auxiliary electrode (Pt wire), R reference electrode (Ag/AgCl), W working electrode, D indication electrode, V electrochemical cell, C optical cell, S sintered glass disc.

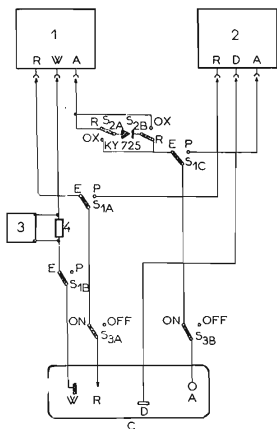


FIG. 2

Circuit Configuration of Electrochemical Apparatus

1 Potentiostat, 2 polarograph, 3 strip chart recorder, 4 measuring resistor, C electrochemical cell, W working electrode, R reference electrode, D indication electrode, A auxiliary electrode,  $S_1, S_2, S_3$  switches. Position of the switches:  $S_1$ : E electrolysis, P polarography;  $S_2$ : R reduction, OX oxidation;  $S_3$ : ON electrodes in connection with the apparatus, OFF electrodes disconnected.

*Course of electrolysis.* After removing the dissolved oxygen by passing pure dry nitrogen through a polyethylene capillary into the cell, the absorption spectrum and polarogram were recorded. The free radical was prepared at a potential corresponding to the limiting current of the first polarographic wave of the respective hydrocarbon. During the electrolysis a nitrogen atmosphere was kept in the electrochemical cell to prevent any access to air. The absorption curve of the solution of the radical was measured. After desactivation of the radical (exposure to air), the absorption spectrum was measured again.

*Substances and solvents.* Perylene and anthracene were obtained commercially, the latter was purified by vacuum sublimation. Tetrachloromethane was dried over  $P_2O_5$  for a day and distilled from  $P_2O_5$ . Acetonitrile was purified by refluxing with  $CaH_2$ , followed by fractional distillation from  $CaH_2$ <sup>13</sup>. Tetrabutylammonium perchlorate was prepared by neutralization of tetrabutylammonium hydroxide with perchloric acid; the precipitate was recrystallized from ethyl acetate and vacuum dried. Tetrabutylammonium tetrafluoroborate was prepared by neutralization of tetrabutylammonium hydroxide with tetrafluoroboric acid; the precipitate was recrystallized from aqueous methanol and vacuum dried<sup>14</sup>.

### Examples of Application

*Oxidation of perylene.*  $0.1M-Bu_4NBF_4$  in dichloromethane appears to be the most convenient system for electrochemical oxidations<sup>12</sup>. Oxidation of perylene (initial concentration  $2-5 \cdot 10^{-5}M$ ) at  $+1.1 V$  vs  $Ag/AgCl$  electrode yielded a red solution of the perylene cation radical (Fig. 3). The highest concentration of the radical was reached after 40 minutes after the beginning of electrolysis, the conversion of perylene being 45% (determined by coulometry) and 47% (determined from the time-dependence of absorption curves of perylene). On exposing the solution to air, the absorption bands of the radical disappeared within ten minutes probably owing to moisture in air.

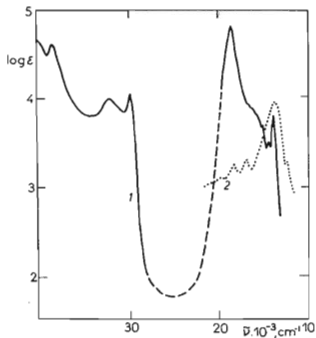


FIG. 3

Electronic Spectra of the Perylene Cation (1) and Anthracene Anion Radicals (2)

The spectrum of perylene cation radical (1) between  $20000-29000\text{ cm}^{-1}$  (dashed curve) could not be measured because of high absorbance of the parent hydrocarbon.

*Reduction of anthracene.* Electrochemical reduction at  $-1.8$  V vs Ag/AgCl electrode performed in acetonitrile, using  $0.1\text{M-Bu}_4\text{NClO}_4$  as a supporting electrolyte resulted in a blue solution of the anthracene anion radical (Fig. 3). With an initial concentration of  $5 \cdot 10^{-3}\text{M}$ , the conversion of anthracene, determined from the height of the polarographic anodic oxidation wave after 50 minutes after the beginning of electrolysis, was about 2%. On interrupting the electrolysis the absorption bands of the radical disappeared.

The recorded absorption curves of the two radicals are in good agreement with similar curves of the anthracene anion radical<sup>15</sup> and the perylene cation radical<sup>16</sup> generated by chemical methods.

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