

configurations were used. For cation radicals, which are not sensitive to traces of oxygen, a cell (Figure 1) was constructed to allow simultaneous cyclic voltammetry, controlled potential electrolysis, and optical measurements. The working electrode consisted of a Pt basket with a mesh bottom into which was fitted a tube ending in a fritted glass disk. This tube contained a mesh Pt basket as a counterelectrode. This configuration offered large effective surface areas for both electrodes and allowed the flow of several milliamperes in a solvent of low dielectric constant such as dichloromethane ($\epsilon = 9$) containing 10^{-3} M reactant and 0.1 M ($\text{C}_3\text{H}_7\text{NClO}_4$) as electrolyte. A thin reference electrode fit directly into the top of the cell. The whole assembly was purged with dry nitrogen or argon and the flow of gas served both to stir the solution and to exclude oxygen and water. The stirred solution moved past the optical cell and allowed spectra to be recorded. (The entire cell assembly readily fit into the sampling compartments of Cary 17 or 219 spectrophotometers, and was small enough to be inserted into an optical dewar within the sampling compartments for low-temperature measurements.) At the end of the electrolysis, cyclic voltammetry could be performed on the product via the two Pt leads, which end in beads, inserted below the working electrode. The reversibility of the reaction could also be checked by regeneration of the parent compound simply by reversing the polarity of the working and counterelectrodes.

For anion radicals, which require rigorous exclusion of water and oxygen, solutions containing the solvent, reactant, and carrier electrolyte were contacted with molecular sieves, Al_2O_3 , and degassed on a vacuum line in a side arm of the cell shown in Figure 2. The cell assembly was then sealed off and the solution was poured into the cell. A Pt wire served as quasi-reference electrode. A magnetic stirrer, rotated by an outside magnet mounted on the flexible shaft of a stirring motor, pumped the solution over the working electrode and through an optical cell. For ESR measurements, the assembly shown in Figure 3 was used. Outgassed solutions, prepared as just described, were poured into the cell to cover the electrodes, and enough current was passed through the solution to convert 80–90% of the porphyrin to radical. (A more elaborate version employed a quasi-reference electrode.) After the cell was sealed off from the vacuum line, ESR and ENDOR measurements were obtained in the thin side arm, and the identity of the product was verified spectrophotometrically in the attached optical cell.

Chlorophyll and pheophytin were prepared by standard techniques (38). The syntheses of ^{15}N -tetraphenylporphyrin (95% ^{15}N), and of magnesium tetraphenylchlorin were reported (38, 41).

Methyl pyropheophorbide-*a*, deuterated at the 5-, 10-, and δ -positions (pyropheo-*d*₆, see Structure III) was prepared as follows: methyl pheophorbide-*a* (200 mg) was refluxed under nitrogen in 50 mL of dry collidine containing 4 mL of D_2O for 16 h. The solvents were removed under vacuum and the residue was crystallized from methanol–methylene chloride to give 196 mg (93%) of compound, partially deuterated at positions 5 and 10. To exchange the δ -position, this material was heated for 4 h at 110°C in 12 mL of deuterioacetic acid and 3 mL of dioxane, under nitrogen. The solution was diluted with methylene chloride; washed with water, then aqueous sodium bicarbonate; dried over anhydrous sodium sulfate; and evaporated to dryness. After crystallization from methylene chloride–methanol, a 96% recovery of methyl pyropheophorbide-*a* was obtained. NMR spectroscopy indicated that the δ -proton was >75% exchanged, that the 10-methylene was totally exchanged, but that the 5-methyl was only about 50% exchanged (labeled

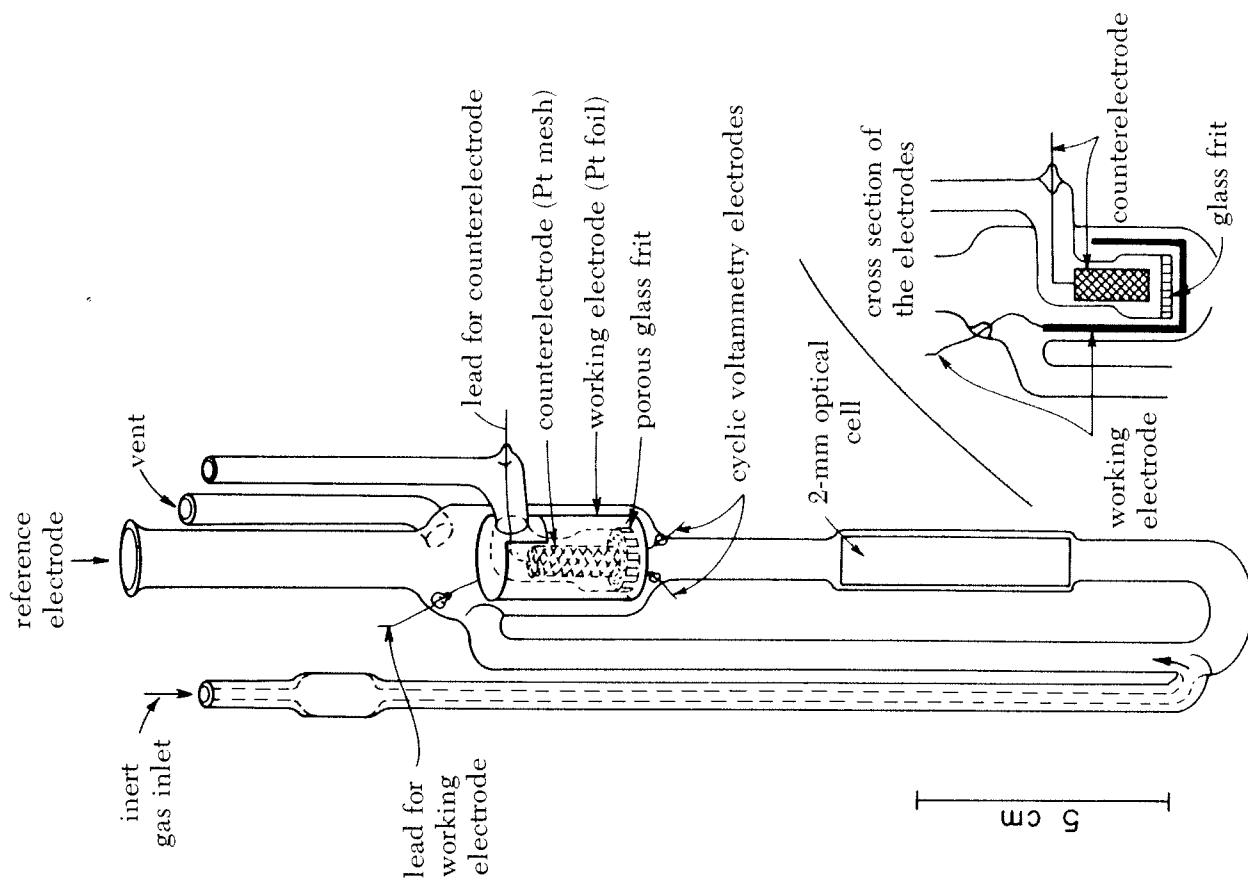


Figure 1. Electrooptical cell for controlled potential electrolysis, cyclic voltammetry, and optical measurements.