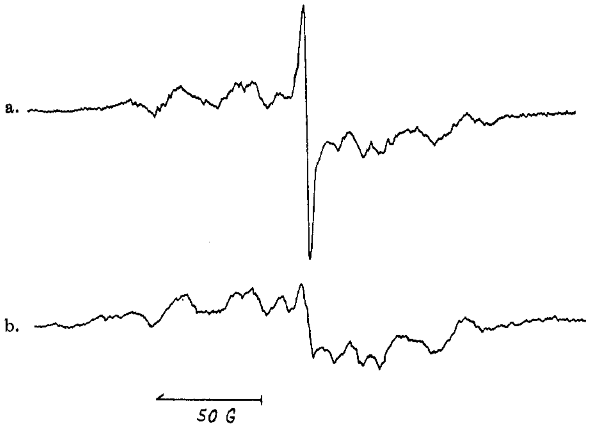

Figure 1. Esr spectra of *n*-decane γ irradiated at 77°K in the dark: (a) immediately after irradiation; (b) after bleaching with a 300-W tungsten lamp using a Toshiba IR-D1B filter. Measurements were made at 77°K in the dark with a microwave power of about 0.03 mW (The wavelength ranged from 1 to 3μ.)

was thermally stable at 77°K, and the appreciable decrease of the intensity was not found during 0.5 hr. The yield of the trapped electrons was of comparable order with that for the 3-methylpentane or 3-methylhexane glasses, which were purified by the same procedures and were irradiated at the same condition, but the sensitivity to the infrared light illumination seems higher in the polycrystalline case of *n*-decane, although the quantitative comparison is not made yet. The similar sharp singlet was also observed in *n*-nonane and *n*-hexadecane.

Our experiments strongly suggest that the nonpolar organic crystalline solids are capable of trapping the electrons produced by irradiations, even if the actual reason for the appearance of the signal of the trapped electrons was some impurities in the samples. Nevertheless, our results clearly indicate that the glassy matrix is not always necessary for trapping electrons. The experiments using the crystalline solids may give some other information about the trapping sites of the electrons.

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Electrogenerated Chemiluminescence. II. The Rotating-Ring-Disk Electrode and the Pyrene-N,N,N',N'-Tetramethyl-*p*-phenylenediamine System[1]

Sir: In conventional studies of electrogenerated chemiluminescence (ECL), both anion and cation radicals of an appropriate fluorescer are alternately generated at a single electrode, thereby producing luminescence in the subsequent reaction of these ionic species within the diffusion layer about the electrode. One common method employs an unreferenced sinusoidal potential as a means of generating ionic species;[2,3] another uses a double (or multiple) potential step between known oxidative and reductive potentials.[4,5] While the former technique is probably the simplest means of observing the electroluminescent phenomenon, it is undesirable from an electrochemical standpoint, because accurate potentials are not known; hence it is possible that dianions or dications are formed or that the decomposition of the solvent or supporting electrolyte at unknown potentials forms agents which inhibit the desired chemiluminescent reaction. Even if this difficulty can be eliminated by employing the latter technique, the current–time–intensity behavior obtained is observed to be quite complex because of the diffusional nature of the processes involved so that mathematical description of these processes is extremely difficult. In addition, large nonfaradaic double-layer charging effects inevitably result when a high-frequency alternating potential is applied to a cell having large uncompensated resistance. Most importantly, no alternating-potential process can achieve a true steady state; the intensity of chemiluminescent emission always varies with time.

These problems may be surmounted throngh the somewhat novel use of the ring–disk electrode[6] for the simultaneous generation of the anionic and cationic precursors of the chemiluminescent product. This type of electrode is particularly convenient for quantitative work because the solutions of the hydrodynamic equations which describe mass transfer as a function of rotation rate are known.[7] Since the steady state may be attained quickly at even moderate rotation rates, the potentials of both the ring and the disk may be set independently, thereby resulting in constant-current levels at both electrodes; this, in turn, results in the steady-state emission of chemiluminescence (unless the bulk concentration of the fluorescer is depleted or sufficient quantities of quenching agents are generated so as to

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[1] This research was supported by the Robert A. Welch Foundation and the National Science Foundation (GP 6688X).

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[3] C. A. Parker and G. D. Short, *Trans. Faraday Soc.*, **63**, 2618 (1967).

[4] D. M. Hercules, R. C. Lansbury, and D. K. Roe, *J. Amer. Chem. Soc.*, **88**, 4578 (1966).

[5] A. Zweig, A. K. Hoffmann, D. L. Maricle, and A. H. Maurer, *ibid.*, **90**, 261 (1968).

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deactivate the excited state of the chemiluminescent product). Because there is no alternation of potential at either electrode, charging currents are negligible once the steady state is attained. As an added advantage, the typically larger electrode area of the rotating ring–disk results in greater quantities of chemiluminescent emission.

The purpose of this communication, then, is to report the use of a rotating-ring–disk electrode for the study of ECL phenomena in an attempt to overcome the difficulties encountered in the single-electrode experiment. The cell shown in Figure 1 has features which include an exterior compartment in which either a platinum or a mercury-pool auxiliary electrode is separated from an interior compartment with fritted disks, a Luggin compartment extending into the interior compartment and fitted with an aqueous saturated calomel reference electrode, and a side arm for the attachment of the sealed cell to a vacuum–helium line for the purposes of solution deaeration.[8] The ring–disk electrode assembly shown consists of a platinum ring and disk separated by a 0.02-mm Teflon insulator and independently connected to stationary leads through loop brushes. The entire assembly extends into the central cell compartment where it may be rotated at a preset rate by means of a Motomatic Model E150 tachometer–generator motor using feedback control. When the electrode is rotated in an appropriate fluorescer–supporting electrolyte solution and appropriate oxidative and reductive potentials are applied to the disk and ring by means of a dual-channel potentiostat,[9] chemiluminescence is observed at the ring. This emission then passes through a Pyrex flat at the bottom of the cell to a reflecting prism mounted in the cell cavity of an Aminco-Bowman spectrofluorimeter. The prism is turret mounted in a platform of variable height, so that optimum emission may be directed into the detector of the spectrofluorimeter. This apparatus has been used in the study of a variety of compounds known to yield chemiluminescence, and it has been found that, in addition to steady-state spectra, current-potential-intensity relationships are also quite readily obtained. While the ring and disk currents are generally observed to increase with the square root of rotation rate at fixed potentials,[7] the intensity of emitted light is found to vary directly with rotation rate at low and intermediate rates. This latter observation is in accord with preliminary results obtained upon treating ECL at the ring–disk theoretically with digital simulation techniques similar to those previously employed by Feldberg[10] in treating ECL obtained by the double-potential step. The details of these experiments and calculations will be presented in a subsequent communication.

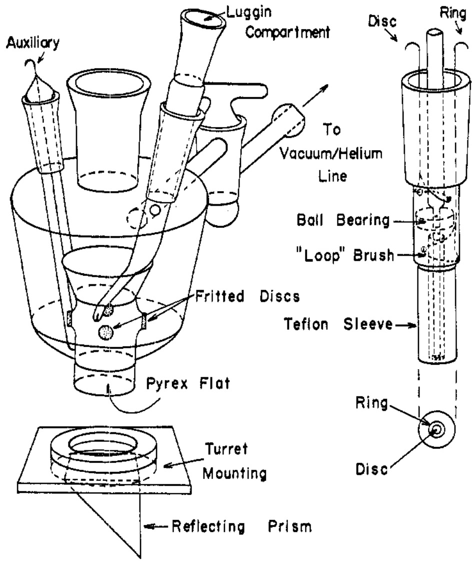

Figure 1. The rotating-ring–disk electrode, the electrochemical cell, and the auxiliary optical system used in the study of electrogenerated chemiluminescence.

The observation of ECL from pyrene, however, is of immediate interest to workers in this field because delayed fluorescence studies of this compound have shown the existence of the triplet state in solution[11] and because its fluorescent emission is observed not only from the excited monomer but also from an excimer.[12] Repeated attempts in this laboratory to obtain ECL from solutions of pyrene by ring–disk and alternating-potential methods always have failed to yield measurable emission, however, presumably owing to an extremely short-lived cationic species and also because the dication forms at potentials close to those at which the cation radical is produced. The addition of N,N,N′,N′-tetramethyl-*p*-phenylenediamine (TMPD) to an N-N-dimethylformamide solution of pyrene and tetra-N-butylammonium perchlorate supporting electrolyte yields a solution from which pyrene ECL may be observed using either technique; from the electrochemical behavior of this mixed system, it is clear that the TMPD is oxidized to its cationic form (Wurster's blue) and that this species serves as a stable oxidant for pyrene anion. This observation is in general agreement with those of Weller and Zachariasse,[13] who have observed pyrene chemiluminescence in solutions of the pyrene anion in contact with solid Wurster's blue perchlorate. In addition, their conclusion about the energetic in-

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feasiblility of the direct formation of the excited singlet state of the monomer has been substantiated by potential measurements made with the ring–disk electrode; measurable chemiluminescent pyrene emission at 400 mμ (3.09 eV) was detected when the potential difference between the ring and disk was only 2.10 V. The observed spectra also show both excited monomer (418 mμ) and excimer (468 mμ) bands, as observed in the chemiluminescent reaction in ethereal solution[13] and in the fluorescence of pyrene alone. The ECL process appears perturbed by intervening chemical reactions, however, and somewhat different results are obtained depending upon whether the pyrene anion is generated at the ring or at the disk. This process and related ones are currently being investigated.

The application of the ring–disk electrode for these studies also suggests that it may be useful for chemical experiments in which unstable or reactive species are generated at both the disk and the ring with a second (outside) ring employed as a detector electrode (*i.e.*, a disk–ring–ring electrode). The theory and application of this electrode are being investigated.

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