Red Chemiluminescence of Pyrene

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Light emission has been reported to occur by the reaction of aromatic hydrocarbon radical anions with various oxidants.[1,2] The emission thus produced has been interpreted as resulting from the formation of an excited singlet, since the spectrum of the emission corresponds to the normal fluorescence of the parent hydrocarbons. The electrical generation of a triplet has also been indicated for the explanation of a delayed electroluminescence in anthracene crystals,[3] and of a green emission from phenanthrene in solution.[4] We wish to report here the observation of a red emission, together with a blue emission during direct-current electrolysis of a solution of pyrene at room temperature.

Two platinum-wire electrodes separated from each other by about 1 cm were immersed into a 10^{-3} M solution of pyrene in anhydrous dimethylformamide, which included 10^{-3} M tetraethylammonium bromide as supporting electrolyte. When a direct-current voltage of about 7.5 V was switched on, a blue emission was detected on the electrode surface with negative polarity. The emission had extremely short duration, and then changed its color to red under the constant current passage. The blue emission was dim, but it was visually identified as the fluorescence of pyrene. The red emission, on the other hand, was clearly visible in a dimly-lit room, and occurred continuously with a constant brightness as long as the constant current passed through. At the same time gas was evolved from a cathode, and the emitting species diffused upwards along streams of gas. When the applied voltage was turned off, the evolution of gas stopped immediately, but the emission continued to occur in a solution for more than 5 sec.

Pyrene is essential for the red emission because no red emission was observed at the same current when only supporting electrolyte and solvent were used, or when phenanthrene, perylene, *p*-quarterphenyl, 9,10-diphenylanthracene, or rubrene was used in place of pyrene. The possibility that the emission originated from a singlet state of dissolved oxygen was ruled out by the observation of the same emission from a carefully deoxygenated solution. The emission from oxygen, *e. g.*, the emission produced by the reaction of hydrogen peroxide with sodium hypochlorite in aqueous solution shows a different tint. The red emission was also observed by employing tetraethylammonium iodide or tetra-*n*-butylammonium bromide as supporting electrolyte. The applied voltage was far beyond the decomposition potentials of dimethylformamide and of supporting electrolyte, so that carbon monoxide would be evolved from a cathode,[5] and some kind of oxidant would be generated at an anode.

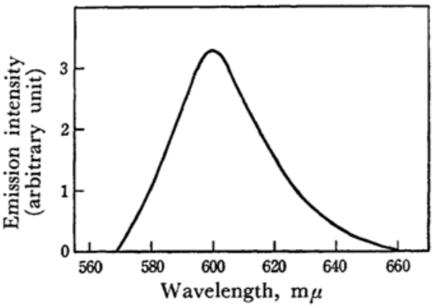

Fig. 1. Chemiluminescence spectrum of pyrene in dimethylformamide.

As shown in Fig. 1, the spectrum of the red emission recorded with a spectrophotometer was found to range from 570 to 660 mμ with a maximum around 600 mμ. This corresponds to the emission range of pyrene phosphorescence in rigid glass reported by Hochstrasser.[6]

From these observations, it is concluded that the red emission was derived from a pyrene molecule in a triplet state, resulting from the reaction of an electro-generated pyrene anion with an electrochemically generated oxidant.

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