Electroluminescence of Organic Compounds. The Role of Gaseous Discharge in the Excitation Process

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A study of the electroluminescence of fluorescent organic compounds is reported. Spectral observation showed the emitted radiation to be identical with the normal fluorescence spectrum. In addition nitrogen emission bands were invariably present in the spectra taken in air. No radiation was emitted from cells operated in a helium atmosphere. It is shown that all the experimental data are consistent with the hypothesis that ultraviolet emission from excited nitrogen molecules causes fluorescence excitation of the organic material. This is the sole source of the emitted radiation. Earlier work in this field is reviewed in the light of these findings.

Introduction

Since Destriau[1] first announced the discovery of electroluminescence, a multitude of papers has appeared on the subject and progress has been made toward elucidating the mechanism of light production. The phosphors used had been solely inorganic until the work of Bernanose and his collaborators[2-10] revealed the apparently general nature of organic electroluminescence. The technique developed by Bernanose[2] utilized a cellophane film impregnated with a solution of a fluorescent organic compound. The films were dried and embedded in molten paraffin wax to exclude air and tested for electroluminescent properties by sandwiching them between a transparent mica electrode, coated with a saline glycerol solution, and a metal electrode. Bernanose applied a sinusoidal voltage across the two electrodes and was able to show that the intensity of the light emitted was dependent on voltage and frequency in the same way as the emission from inorganic phosphors, except that much higher fields were necessary. Among the compounds found to emit under these conditions were acridine orange, carbazole, and various derivatives of 8-hydroxyquinoline. For each of these compounds, the spectrum of the electroluminescence emission appeared to be identical with the normal fluorescence spectrum, except for a few compounds where a new emission in the region of 4360 Å. was reported.[6,9] At high voltages dielectric breakdown occurred and a blue discharge was observed simultaneously with fluctuations of cell current. The fact that no fluctuations occurred at lower voltages

was cited as evidence that no discharge of any sort was taking place.[2]

An examination of possible excitation mechanisms was made by Bernanose.[7] It was pointed out that the electroluminescence of fluorescent dyes dispersed in cellophane could not be explained by mechanisms involving structure defects, activation centers, or crystal abnormalities. These and other considerations led Bernanose to postulate direct field excitation of the molecule as the operative mechanism.

Since the work of Bernanose, Namba and his co-workers[11] have repeated and confirmed his results. However, Lozykowski and Meczynska,[12] in agreement with Tumerman and Czayanov,[13,14] stated that no difference could be detected between the spectra of undyed films and films dyed with acridine orange, and they doubted the existence of organic electroluminescence. More recently, Kallmann, *et al.*,[15] have shown that a single crystal of anthracene will electroluminesce under certain conditions. Gurnee[16] has reported the electroluminescence of a thin layer of anthracene solidified from a melt with 1% carbon black added. This is essentially the technique of contact electroluminescence first reported by Lehmann,[17] who was able to excite many nonelectroluminescent materials after mixing them with a finely divided conductive powder. The validity of this technique has been strongly challenged by Morosin and Haak,[18] and defended by Lehmann.[19]

It is clear from the foregoing that considerable confusion exists with regard to the interpretation of organic electroluminescence. Accordingly, it seemed to be worthwhile to attempt to prove conclusively the existence of organic electroluminescence, in the same way in which Destriau[20] established that electroluminescent zinc sulfide emits light under the sole influence of an electric field, as distinct from the internal discharge mechanism proposed by Herwelly.[21]

Experimental

We have used several different methods in our attempts to obtain electroluminescence from organic

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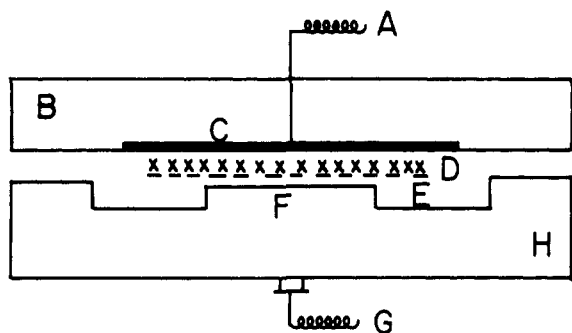(21) A. Herwelly, *Acta Phys. Austriaca*, **5**, 30 (1951).

Figure 1. Cross-sectional diagram showing details of electro-luminescence cell construction: A, electrical contact to conducting tin oxide layer; B, glass plate; C, tin oxide layer; D, phosphor layer; E, dielectric film; F, central platform for confining thicknesses in range 1–5 mils; G, electrical contact to steel plate; H, stainless steel plate electrode.
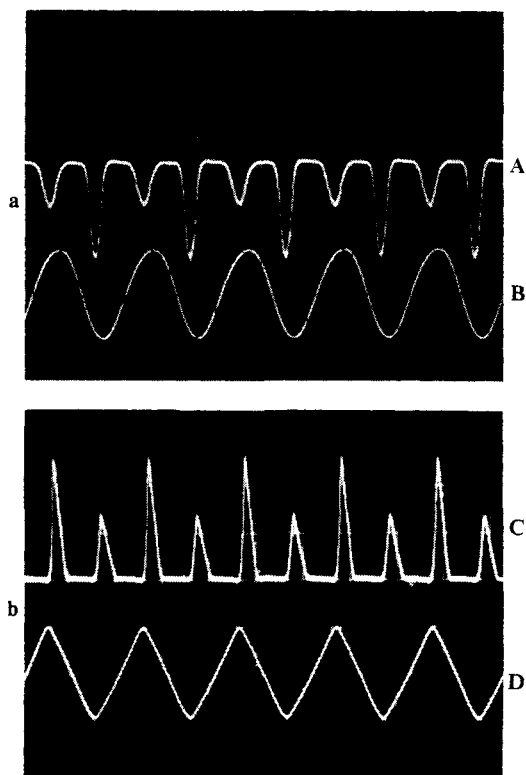

Figure 2. Typical output wave forms for sine and triangular excitation voltages. (a) Cell material, phenanthrene–tetrachlorophthalic anhydride charge-transfer complex: A, photomultiplier output, scale 2 v. cm.$^{-1}$; B, exciting voltage, sine wave, frequency 500 c.p.s., 2 kv. peak to peak. (b) Cell material, hexamethylbenzene-tetrachlorophthalic anhydride charge-transfer complex: C, photomultiplier output, scale 2 v. cm.$^{-1}$; D, exciting voltage, triangular wave, frequency 700 c.p.s., 2 kv. peak to peak.
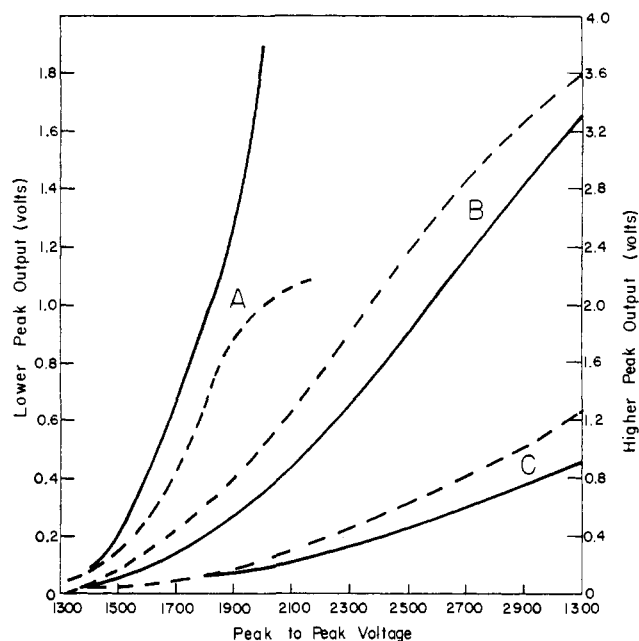

Figure 3. Effect of applied sinusoidal voltage and frequency on the electroluminescence intensity from a cell containing aluminum oxinate: lower peak heights, – – – –; higher peak heights, ————; A, 1000 c.p.s.; B, 200 c.p.s.; C, 80 c.p.s.

compounds, the methods differing in the way in which a thin layer was prepared and mounted between the electrodes. One electrode was made from stainless steel, the other from tin oxide coated glass. A series of the metal electrodes was made, each with a depressed central platform for electrical contact, so that a definite thickness of material could be accommodated when the glass electrode was compressed against it. The thickness ranged from 1 to 5 mils. Figure 1 shows the details of cell construction.

Methods of obtaining a thin layer of organic material included deposition from a hot saturated solution, solidification of a melt, embedding in resin, and evaporation of a suspension. The latter method was found to be the most generally useful. A Wig-L-Bug shaker was used to disperse the material in the presence of ethanol. In all cases a layer of polystyrene was placed between the two electrodes to provide a high resistance. In some cases silicone oil or a purified acid-free castor oil was used in attempts to exclude air from the cells.

The exciting voltage was applied *via* a high voltage amplifier capable of a maximum output of 5 kv. over a frequency range from 50 to 2000 c.p.s. in sine, square, pulse, and triangular wave forms. The cells were mounted rigidly and the light output, if any, was monitored by an IP21 photomultiplier tube and a Tektronix dual beam oscilloscope simultaneously with the cell current or voltage. Provision was also made for conducting runs at low pressure or in the presence of gases other than air. Electroluminescence and fluorescence spectra were taken on Kodak 103_{a-F} plates using a Bausch and Lomb medium quartz spectograph, with exposure times of up to 2 hr. The compounds used in our tests for electroluminescence included aromatic hydrocarbons, inorganic chelates, and organic charge-transfer complexes. They were prepared from reagent grade material purified by recrystallization and vacuum sublimation techniques.

Results and Discussion

In general, those cells from which radiation was emitted showed characteristics similar to cells containing inorganic phosphors, with the exceptions that higher voltages were needed to stimulate emission, and no secondary peaks were ever observed. Figure 2 shows typical oscilloscope traces obtained using triangular- and sine-wave excitation voltages. The light output increased with voltage and frequency, and there was evidence of saturation at high voltages, as shown in Figure 3. In agreement with many authors, we
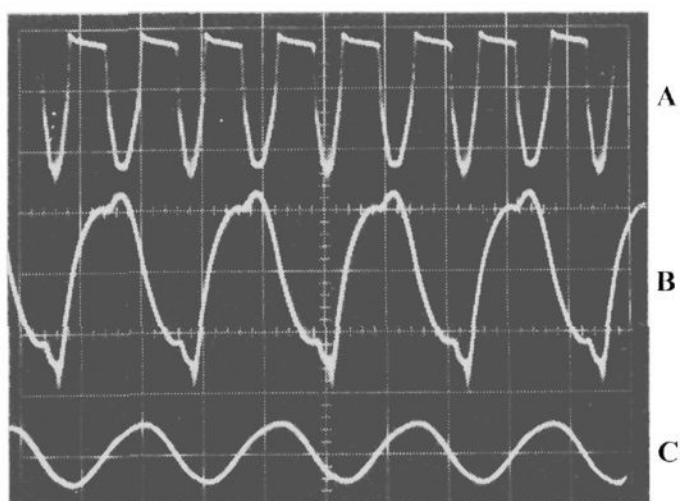
Figure 4. Photograph of wave forms showing relationship between intensity of emitted radiation, cell current, and exciting voltage for a cell containing only a polystyrene film: A, photomultiplier output, scale, 5 v. cm.$^{-1}$; B, cell current; C, exciting voltage, sine wave, frequency 230 c.p.s., 2 kv. peak to peak.

Figure 5. Proportion of ultraviolet radiation from a cell containing hexamethylbenzene–tetrachlorophthalic anhydride (λ_{max} ~5000 Å.) excited by a sinusoidal voltage at 300 c.p.s.: O, without ultraviolet filter; ×, with ultraviolet filter (cut-off, λ 4000 Å.).

found that two peaks of unequal size were obtained for each complete wave cycle, except from those cells which did not contain any phosphor material, but contained only polystyrene sheet. The higher peak corresponded to a cathodic potential on the metal electrode. In most cases the ratio, higher peak: lower peak, increased with voltage and frequency. Observation of the current through the cell revealed that each light flash was accompanied by a current increase superimposed on the normal current wave form, in phase with the light emission as shown in Figure 4. Using 0.10-μsec. voltage pulses, the decay time of the emission was shown to be less than 10^{-7} sec.

Nature of the Emitted Radiation. The intensity of the emitted radiation was such that the emitting area was easily visible in a darkened room. There was a correlation between the fluorescence efficiency of the organic material and the observed electroluminescence intensity. To the eye the electroluminescence appeared to be identical with the fluorescence of the compound concerned. Microscopic examination revealed that over most of the emitting area light emission was steady, but in some places particles emitted in regular flashes. The number of such particles increased with increasing frequency. In the cases where cells were prepared by using only films of polystyrene, cellophane, or Teflon between the electrodes, *i.e.*, containing no fluorescent material, a blue glow was seen. The wave forms obtained from such cells tended to show no difference between anodic and cathodic peaks and the light outputs were relatively high. The wave forms for light output and current were essentially the same as in the cases where fluorescent material was present. An ultraviolet filter showed that a high proportion of the light emitted was in the ultraviolet region of the spectrum, as shown in Figure 5.

Prolonged excitation of any given cell was deleterious to its performance and the light output steadily decreased. In some cases there were signs that some chemical change had occurred indicated by color changes in the surface layers of the organic material. Generally, however, after a rest period the brightness was mostly restored, although never reaching the original intensity.
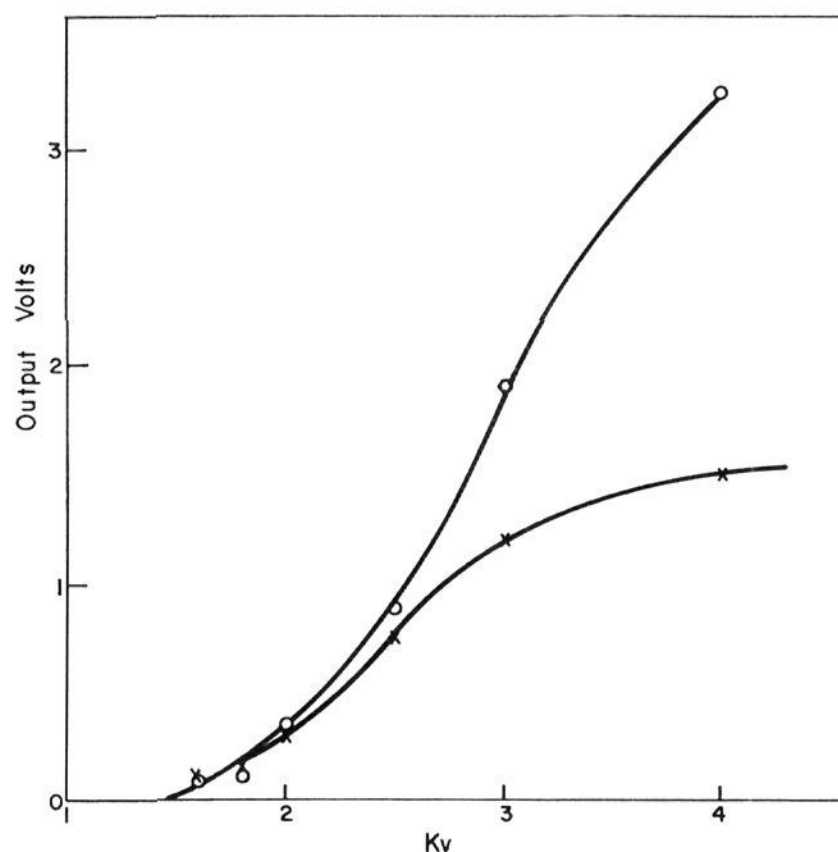
Spectroscopic Data. At first on visually observing the emitted radiation, it was thought that genuine electroluminescence was being observed. However, spectroscopic examination of radiation emitted from the electrochemical cell revealed that in every case there were bands present in the region 3000–5000 Å. in addition to the normal fluorescence spectrum of the compound studied. These additional bands were unambiguously identified with the second positive series of nitrogen, which is the spectrum obtained from the positive column of discharge tubes containing air or nitrogen at low pressure. No lines were obtained which could not be identified with this nitrogen series. Furthermore, cells prepared and run in the complete absence of air yielded no electroluminescence on excitation. For example, cells where the phosphor was embedded in resin or oil would not emit, whereas those cells where traces of air were present emitted strongly.

Origins of the Emitted Radiation. A possible explanation of the origin of the radiation emitted by organic compounds in an electric field could be that the normal fluorescence emission of such compounds is excited by the ultraviolet radiation emitted by excited nitrogen molecules. This could occur when very small amounts of nitrogen are present in the cell even when steps have been taken to exclude nitrogen. In order to test this hypothesis, it is necessary to distinguish excitation by nitrogen discharge from genuine electroluminescence, even though the two emissions may show identical spectral characteristics. That this is no simple task may be seen from the controversy between Morosin and Haak[18] and Lehmann,[17,19] which will be discussed later.

From the theory of glow discharge, the voltage at which emission first occurs is dependent on the ionization energies of the gas present. Accordingly, runs were conducted in nitrogen (15.7 e.v.), argon (15.7 e.v.),

and helium (24.5 e.v.), at atmospheric pressure. No difference could be detected between the spectra taken in nitrogen and those in argon. However, Cooke[22] has observed very efficient transfer of energy from excited argon atoms to nitrogen molecules in a discharge tube, and a small impurity content of nitrogen can account for the presence of nitrogen bands in an argon atmosphere. *In helium, however, no light emission was observed from any cells except those in which a standard commercial electroluminescent zinc sulfide phosphor was used.* This seems to be conclusive evidence that the glow emission excitation mechanism at least predominates to a large extent over any genuine electroluminescence under our conditions of excitation.

It remains to be shown that all the observed experimental data are consistent with the glow mechanism. First, a decay time of 10^{-7} sec. or lower would be expected for a mechanism involving simple fluorescence emission by an organic compound. In addition, the general features of the wave forms obtained for cells containing fluorescent organic compounds were identical with those obtained with polystyrene alone, where the occurrence of glow discharge is unequivocal. The small current pulses coincident with light emission, shown in Figure 4, can be attributed to the onset of the discharge. The unequal heights of successive light peaks can also be explained on the basis of glow discharge. The anode region in a glow discharge tube exhibits the greatest light intensity[23]; hence it would be expected that a higher light output would be obtained from a cell when the transparent electrode was anodic, because most of the emitted light does not have to traverse the layered phosphor material. It has been noted above that this is indeed the case. Figure 2 shows the magnitude of the difference in output. The fact that there is no peak-height difference in the cases where transparent dielectric material alone is used is readily explained by the same method. This is illustrated in Figure 4.

Further indirect evidence for the glow emission–fluorescence mechanism may be cited. The facts that only fluorescent compounds will emit light and that the most efficient fluorescers show the brightest emission are consistent with the hypothesis. The decreasing light output of a given cell with time can be attributed to the chemical action of radicals generated in the glow discharge on the surface of the phosphor; and the subsequent partial regeneration of light emission can be attributed to the reversibility of such reactions. The failure of Bernanose to observe the emission bands of the second positive series of nitrogen may be attributed to the high absorbance of the mica he used as the transparent electrode. We have measured the transmittance of mica sheet and found 50% transmittance at 4400 Å., as compared with 3200 Å. for the tin-coated glass.

Conclusion

The general, and somewhat surprising, effect of the glow emission mechanism is that the electrical properties exhibited are very similar to those observed for genuine inorganic electroluminescence. It is this fact that has led to most of the confusion with regard to differentiating between glow discharge excitation and true electroluminescence of organic materials. Moreover, we regard it as doubtful if the method of "contact electroluminescence" is successful when applied to organic phosphors, although Lehmann seems to have shown fairly conclusively that the method works in the case of inorganic phosphors.[19] The only case in which genuine organic electroluminescence appears proven is for anthracene using Kallmann's techniques.[15] It is noteworthy that Kallmann's results were obtained from single crystals under conditions very dissimilar to those used by other investigators. To the authors' knowledge, no case of "organic electroluminescence" has been observed in which the spectrum differs from the normal fluorescence spectrum, apart from Bernanose, who observed a new blue line from carbazole which can be attributed to glow emission. Inorganic phosphors, on the other hand, frequently show wave lengths differing from fluorescence wave lengths and often change color with voltage and frequency. An equivalent finding for organic phosphors would represent the most acceptable and convincing type of evidence for genuine electroluminescence; unfortunately, such a finding has yet to be reported.

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