Photoconductivity of Benzene Solutions of Pyranthrene

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Photoconductivity of pyranthrene solutions in benzene under 436 nm radiation has been observed[1] and reported to vary linearly with light intensity for incident flux below 3×10^{17} photons$\cdot$sec^{-1} cm^{-2}. For the same system using a different type of cell and higher field strengths we have observed much larger photocurrents which depend on the square root of light intensity for the range of incident flux from 10^{14} to 10^{16} photons sec$^{-1}\cdot$cm^{-2}. The large photocurrents were obtained using a cell in which solution touched only glass, stannous oxide coated quartz and rhodium plated brass. The cell is shown in Fig. 1. The stannous oxide coated quartz flat presses against the ground and polished base to make a leakproof fit. Electrode spacing is variable from 0.010 cm to 0.036 cm, and the stannous oxide electrode is made negative. Fluorometry grade benzene is distilled over the pyranthrene from an all glass system in an atmosphere of oxygen-free nitrogen. Pyranthrene (K and K Laboratory) was chromatographed by the method of Sangster and Ervine[2] using silica gel and benzene as the eluant. The product consisted of orange needle-like crystals. Solution concentration was around 2×10^{-4} molar.

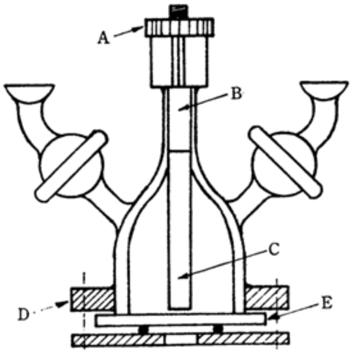

Fig. 1. Photocell.

A. Micrometer, B. Precision bore tubing, teflon seal, C. Rhodium plated brass, D. Clamp ring, E. Quartz flat with stannous oxide coating.

The apparent specific conductance of the benzene at 23°C was around 3×10^{-16} ohm^{-1}cm^{-1} as measured with a field strength of 3100 V/cm; apparent conductivity of the pyranthrene solution was around 6×10^{-15} ohm^{-1}cm^{-1}, for applied field strength of 3100 V/cm. For an incident flux of 10^{16} photons sec^{-1}cm^{-2} and for field strength of 3100 V/cm, the photocurrent was two orders of magnitude larger than the dark current; intensity dependence is shown on Fig. 2. The dependence of photocurrent on light intensity is seen to be nearly square root.

Experiments were carried out using pyranthrene as received also, with similar results for applied field strength of 3100 V/cm. Also shown in Fig. 2 are results for applied fields of 310 V/cm and for 1.1×10^4 V/cm. The square root dependence is developed only at the higher field strengths.

Rotating sector experiments were done to determine the rise time of the photocurrent. The light was chopped using an eight inch sector rotating at 30 cps and the rise time was observed to be less than 3×10^{-3} sec under applied field of 3100 V/cm; instrument response time set the upper limit on photocurrent rise time. This time is more than an order of magnitude longer than the transit time of a pyranthrene ion according to the estimate $t=d/\mu E$, where d is the plate separation distance, μ is mobility, and E is applied field strength which is taken as the geometric field. Transit time is about 10^{-1} sec for spacing of 0.36 mm, mobility of 3.6×10^{-2} cm^{2}V^{-1}sec^{-1} based on a Stokes' law friction

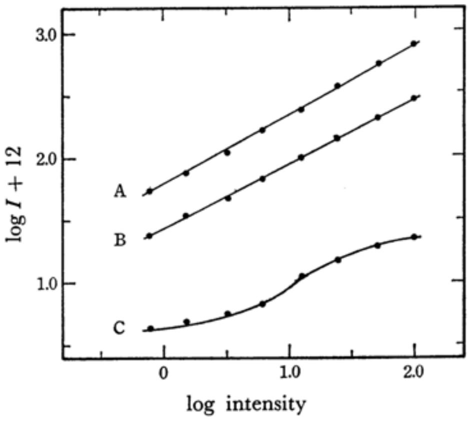

Fig. 2. Log of photocurrent *vs.* log of intensity (436 nm band).

A. Chromatographed pyranthrene, applied field 3100 V/cm, slope 0.55, B. Pyranthrene, applied field 1.1×10^4 V/cm, slope 0.51, C. Pyranthrene, applied field 310 V/cm.

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1) M. Sano and H. Akamatu, This Bulletin, **36**, 480 (1963).

2) R. C. Sangster and J. W. Ervine, Jr., *J. Chem. Phys.*, **24**, 670 (1956).

factor for ionic radius of 10^{-7} cm, and a field strength of 3100 V/cm. Photoconductivity is therefore not limited by photoionization growth time in the steady state experiments but is a measure of steady state carrier concentration. Square root dependence of photocurrent on light intensity suggests that the carriers are probably pyranthrene radical cations and anions generated at a rate proportional to light intensity and destroyed in bimolecular collisions.

That pyranthrene and not benzene radical anions are formed follows from the comparison between electron affinities and solvation energies of the two species. Electron affinities are -1.40 eV for benzene and 1.61 eV for pyranthrene,[3,4] and the sum of electron affinity and solvation energy is -2.19 eV for benzene and -3.51 eV for pyranthrene for a 75% dioxane-water mixture.[4] As some recent work indicates, this sum will not be much different for benzene solution.[5] Neglecting differences in solvation entropy between radical anions of benzene and pyranthrene and assuming an energy difference of 1 eV between them, then only one ion in 10^{12} would be a benzene radical anion in a 10^{-4} molar solution of pyranthrene in benzene.

Finally an energy balance indicates that a photon of 436 nm radiation has ample energy (2.7 eV) to make up the deficit in the reaction

$$\begin{array}{ll}
M_g \rightarrow M_g^+ + e & \Delta E = 6.69\ \mathrm{eV} \\
M_g + e \rightarrow M_g^- & \Delta E = -1.61\ \mathrm{eV} \\
M_g^+ + M_{sol} \rightarrow M_{sol}^+ + M_g & \Delta E = -1.9\ \mathrm{eV} \\
M_g^- + M_{sol} \rightarrow M_{sol}^- + M_g & \Delta E = -1.9\ \mathrm{eV} \\
\hline
2M_{sol} \rightarrow M_{sol}^+ + M_{sol}^- & \Delta E = 1.3\ \mathrm{eV}
\end{array}$$

where M is pyranthrene and the solvation energy is taken as -1.9 eV. From this result it is reasonable that rate of cation and anion generation can be proportional to incident light intensity.

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[3] R. S. Becker and E. Chen, *J. Chem. Phys.*, **45**, 2403 (1966); absolute electronegativity of 4.15 ± 0.05 eV and ionization energy of 6.69 eV for pyranthrene gives 1.61 eV for EA.

[4] F. A. Matsen, *J. Chem. Phys.*, **24**, 602 (1956).

[5] A. Prock, to be published.