Spectroscopic Properties of Organic Photoconductors. III. Action Spectra for the Photoconduction of Cationic Dye Films

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The action spectra for photoconduction in solid films of four cationic dyes have been measured. Both the response and the quantum yield curves have maxima at the main absorption peaks, which correspond to the singlet-singlet transitions of the dye cations. The maximum efficiency of carrier production in rhodamine B is of the order of 0.1 electron excited per quantum absorbed.

IT is a first principle of photochemistry that light must be absorbed in order to cause photochemical effects. However, in general, not all wavelengths of *absorbed* radiation are equally effective in sensitizing a particular reaction, because a variety of electronic states may be excited. Each of these may be deactivated, with different probability, by various mechanisms such as luminescence, electron excitation, thermal degradation or bond rupture. Only the sum of these probabilities is the same, i.e., unity, for every energy level.

The relationship between exciting wavelength and the probability of the particular deactivation process in which one is interested is called an *action*, or *excitation spectrum* for this process. In the present communication we are concerned with the action spectra for photoconduction in some solid cationic dyes, whose absorption and reflection spectra[1,2] and kinetics[3] have been described previously in some detail. So far as we know, only one such action spectrum, that for trypaflavine, has heretofore been described in the literature.[4]

EXPERIMENTAL

The dye films to be studied were formed inside one window of a 1.0×1.0 cm square Pyrex absorption cell, which had been provided at its bottom with two thin platinum films, about 6 mm long and 1 mm apart. These electrodes were connected to external leads by tungsten wires, sealed vacuum-tight through the glass envelope. The dyes were deposited as uniformly as possible over the electrodes and the rest of the window, which was used for transmission and reflection measurements in the Beckman Quartz Spectrophotometer. Details of sample preparation and spectrophotometric measurements have already been published.[1,2] Films deposited from solution and by sublimation appeared to behave alike.

The fraction, A, of light incident on the cell, absorbed in the film, was computed by adding up all light entering the dye and subtracting the light leaving it, with due regard for multiple reflections. For illumination through the dye-vacuum interface of the film,

$$A = \left(\frac{T_{of}(1-T_d)}{T_d}\right)\left(\frac{1.02(1-R_{gg})(1+T_{of}R_{gg})}{(1+R_gR_f)}\right),$$

where the symbols are those used in references 1 and 2. An analogous formula was derived for illumination of the film through its glass backing.

For electrical measurements, the cell was placed in a bracket in thermal contact with a copper heating block of controlled temperature. The dye film was separated from the copper block by a thin layer of silicone grease and a 1-mm thick glass window; its temperature was therefore slightly lower than that measured by the thermocouple in the heating block. The electrode leads of the cell made contact with shielded springs, connected to a dry cell and a simple, balanced electrometer-tube preamplifier, having an input resistance of 10^{10} to 10^{11} ohms.[3] The preamplifier output was applied to a General Radio D.C. Amplifier and recorded by an Esterline-Angus recording milliammeter. The voltage gain of the entire apparatus (close to unity) was corrected for in the calculation of conductance. Because of the long time constants of the conduction processes in most of the dyes studied, only dc measurements were practicable.

Adequate illumination, at about 50 A band width, was provided by an $f/2.7$ grating monochromator, designed in this laboratory by R. C. Nelson.[5] At wavelengths in excess of 6000 A a Corning No. 3480 glass filter was inserted to absorb the second-order spectrum and stray light below 5700 A. The entire beam was focused on the film by a pair of fused silica lenses, with just sufficient blurring to provide fairly even illumination of the entire interelectrode gap. The output curve of the monochromator and its ribbon-filament source was measured by means of an Eppley thermopile of known sensitivity [see Fig. 1(a), curve I_0].

The photoelectric response was measured by applying a potential of 1 to 45 volts and measuring the current as the sample was alternately illuminated with light of various wavelengths, and darkened. It was necessary to wait for periods of 30 seconds to about 30 minutes, for

[1] J. W. Weigl, J. Chem. Phys. **24**, 364 (1956).
[2] J. W. Weigl, J. Chem. Phys. **24**, 577 (1956).
[3] R. C. Nelson, J. Chem. Phys. **22**, 885 (1954).
[4] A. T. Vartanian, J. Phys. Chem. USSR **24**, 1361 (1950).
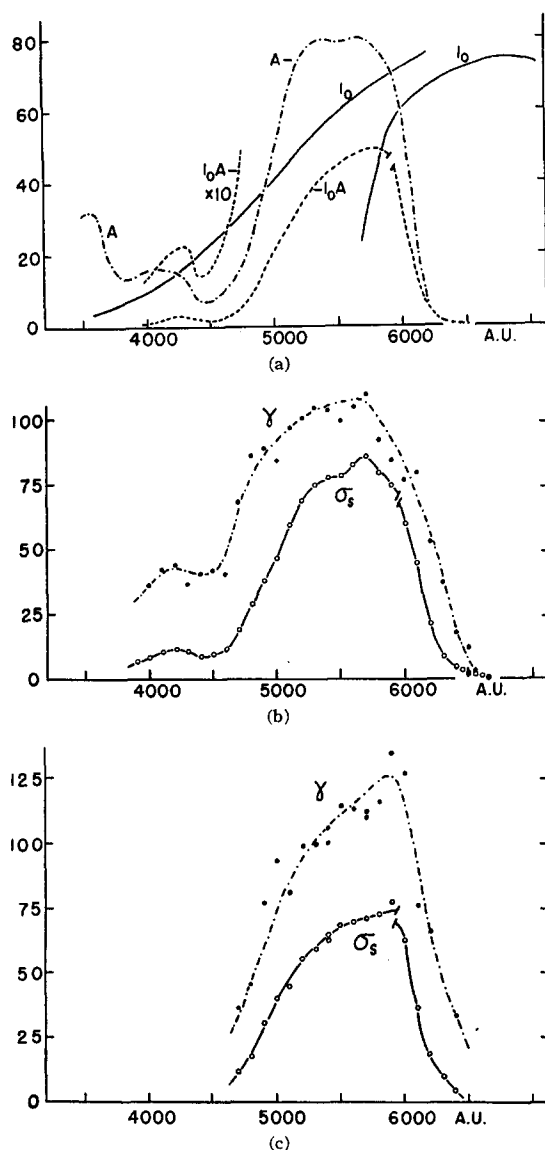[5] R. C. Nelson and R. Jenkinson, J. Opt. Soc. Am. **43**, 1181 (1952).

FIG. 1. Rhodamine B, thin film (deposited from alcohol). (a) A, percent absorption; I_0, light incident on film between electrodes ($\mu\mu$einsteins/sec); I_0A, light absorbed in film ($\mu\mu$einsteins/sec). (b) σ_s, steady-state conductance (1 unit $= 10^{-15}$ ohms^{-1}); γ, quantum yield (arbitrary units); temperature $= 36°$C. (c) same, temperature $= 52°$C. The curves of I_0, I_0A, and σ_s are broken at $\lambda6000$ A, due to the insertion of a cut-off filter.

FIG. 2. Trypaflavine, thin film (deposited from alcohol). Temperature $= 49°$C. I_0A, light absorbed in film ($\mu\mu$einsteins/sec); σ_s, steady-state conductance (1 unit $= 10^{-15}$ ohms^{-1}); γ, quantum yield (arbitrary units).
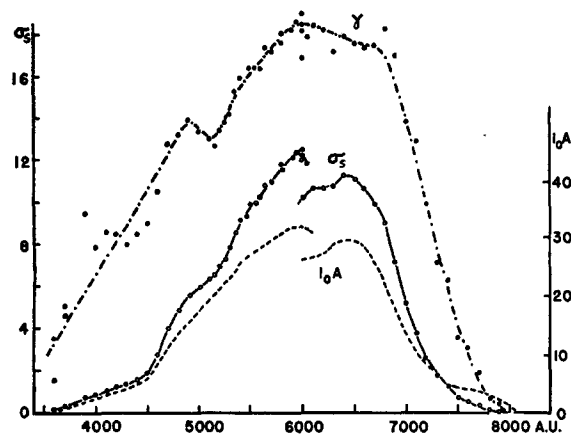
FIG. 3. Pinacyanole, thin film (deposited from alcohol). Temperature $= 35°$C. I_0A, light absorbed in film ($\mu\mu$einsteins/sec); σ_s, steady-state conductance (1 unit $= 10^{-15}$ ohms^{-1}); γ, quantum yield (arbitrary units). Cut-off filter inserted at $\lambda6000$ A.
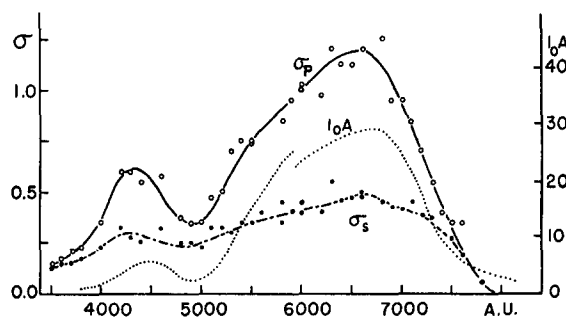
FIG. 4. Malachite green, thin film (deposited from alcohol under air, then evacuated). Temperature $= 36°$C. I_0A, light absorbed in film ($\mu\mu$einsteins/sec), σ_P, peak conductance; σ_s, steady-state conductance (1 unit $= 10^{-15}$ ohms^{-1}); cut-off filter inserted at $\lambda6000$ A.

different dyes, for a steady state conductance to be attained in light or darkness. The steady dark current, largely due to leakage through the glass blank, was subtracted from the photocurrent.

Calculations

The dependence of the steady-state conductance upon the light intensity was determined by means of calibrated screens, inserted in the light beam. In the relationship, $\sigma_s{}^p \propto I$ the exponent, p, was found to be 2.0, 1.75, and about 1.25, respectively, for rhodamine B, trypaflavine, and pinacyanole.
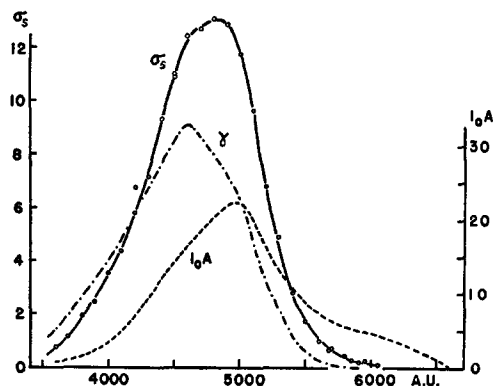
The quantum yield of *photoconduction*, γ, was computed from the illumination absorbed per unit volume, I_0A/V, the measured exponent, p, the steady-state conductance, σ_s, and its second-order dark decay constant, a, by the formula for steady-state conductance:

$$\gamma I_0A/V = a\sigma_s{}^p.$$

TABLE I. Absolute quantum yields.

Dye	Rhodamine B	Rhodamine B	Trypaflavine	Units
Temperature	36	52	49	°C
Wavelength of max yield	5700	5900	4600	A
Volume of film[a]	0.1×0.6×d	0.1×0.6×d	0.1×0.6×d	cm³
$I_0 A$	47.0	48.0	22.3	$\mu\mu$einst/sec
$I_0 A/V$	47.2/d×10¹³	48.2/d×10¹³	22.4/d×10¹³	quanta absorbed/cm³ sec
σ_s	$\begin{cases} 8.55\times10^{-14} \\ 89.0/d\times10^3 \end{cases}$	7.60×10⁻¹⁴ 79.0/d×10³	1.23×10⁻¹⁴ 13.0/d×10³	ohms⁻¹ conduction electrons/volt sec cm
a (rate constant)	$\begin{cases} 3.0\times10^{11} \\ 28.8d\times10^{-8} \end{cases}$	8.3×10¹¹ 79.5d×10⁻⁸	5.0×10¹² 48.0d×10⁻⁷	ohms/sec volt cm/electron
p (exponent)	2.0	2.0	1.75[b]	...
γ	0.48×10⁻¹¹	1.0×10⁻¹¹	0.35×10⁻¹¹	$\left(\dfrac{\text{conduction electrons}}{\text{quantum absorbed}}\right)\left(\dfrac{\text{cm}^2}{\text{volt sec}}\right)$ electron volts
E_{act} (trap depth)	0.55[c]	0.55[c]	0.50[d]	electron volts
η [e]	$\begin{cases} 0.5\times10^{-2}/\mu_{free} \\ 0.10 \end{cases}$	0.4×10⁻²/μ_{free} 0.16	1.5×10⁻⁴/μ_{free} ...	total electrons excited per quantum absorbed
η or γ	108	125	9.05	arbitrary units on graph

[a] Film thickness, d, cancels out in the calculation.
[b] For this calculation, p was set equal to 2.0 in order to preserve reasonable units.
[c] R. C. Nelson, J. Chem. Phys. 22, 888 (1954) (this value was confirmed for the present sample).
[d] A. T. Vartanian, J. Phys. Chem. USSR 24, 1361 (1950).
[e] Using $\mu_{free} \approx 0.03$ cm²/volt sec for rhodamine B (see text).

Here γ is expressed in (cm² ohms⁻¹ photon⁻¹), or in electronic units of (conduction-electrons/photon X cm²/ volt sec); it is proportional to the quantum efficiency, η. for excitation of charge carriers to traps *and* to the conduction band: $\gamma = \eta\mu_{drift} = \eta\mu_{free}\exp(-E/kT)$. The constant, μ_{drift} (in cm²/volt sec), is the mean drift mobility, averaged for *all* carriers, trapped and mobile; μ_{free} is the free, or "microscopic," mobility of *untrapped* carriers in the conduction band.[6] The Boltzmann factor accounts for that great majority of carriers which have been excited by the light, but cannot contribute to conduction because they are reversibly trapped, E electron volts below the conduction band.[3]

RESULTS

Thin Films

Figures 1 to 4 show action spectra for photoconduction of four cationic dyes: a xanthene, an acridine, a cyanine, and a triphenyl methane derivative. In "thin" films, such as those shown, having a peak absorption of less than about 80%, the light is absorbed fairly homogeneously throughout the sample at all wavelengths, and the results may be interpreted in a straightforward manner. In general, illumination of the dye film between electrodes causes a more or less gradual rise of photocurrent, followed by a leveling-off when the carriers are destroyed by recombination as quickly as new ones are formed by the light. In the dark, the photoconductance falls off at a rate approximately proportional to its square, indicating decay via an electron-hole recombination process. The kinetics of excitation and decay are independent of whether any voltage is applied at the electrodes; hence electrical energy is not required for the excitation of carriers.[3,7]

[6] William Shockley, *Electrons and Holes in Semiconductors* (D. van Nostrand Company, Inc., New York, 1950), p. 211
[7] A. T. Vartanian, Acta Physicochimica URSS 22, 201 (1947).

The results may be discussed in terms of a simple band scheme, proposed by Nelson[3] on the basis of extensive kinetic data on rhodamine B and triphenylmethane dyes.

It is evident that the photosensitivity in each case closely parallels the absorption curve. Carriers are produced, with comparable efficiency, by light absorbed in all singlet-singlet bands observed, whether the transitions lead directly to the lowest excited level or to states nearly degenerate with it (as at the short-wavelength shoulder of the peak in rhodamine B) or, instead, to higher singlet levels of different polarization (e.g., the short-wavelength bands of pinacyanole and malachite green).

The response of crystal violet and basic fuchsin films is too slow to permit investigation at many wavelengths. It was established, however, that in these dyes, as in the others, the red threshold of photoconduction coincides with the absorption edge of the first singlet-singlet band of the solid dye. The malachite green film illustrated in Fig. 4 was deposited from solution under air, instead of nitrogen, prior to the usual evacuation. This "oxidation" caused the usually sluggish response of this dye to become sufficiently fast for an experiment requiring repeated illumination, but also produced a transient "peak" response, which exceeded the steady-state photoconductance. This complication, which appeared to be due to a photovoltaic effect, made a quantitative yield calculation impossible. However, it was observed that here, too, the response followed the entire spectrum, with roughly equal efficiency of excitation in the two absorption peaks.

Quantum yields for photoconduction were computed for the other three dyes and plotted, in arbitrary units, in Figs. 1 to 3. It is clear that the quantum efficiencies, too, follow the absorption curves, with peaks in the vicinity of the absorption maxima. For rhodamine B
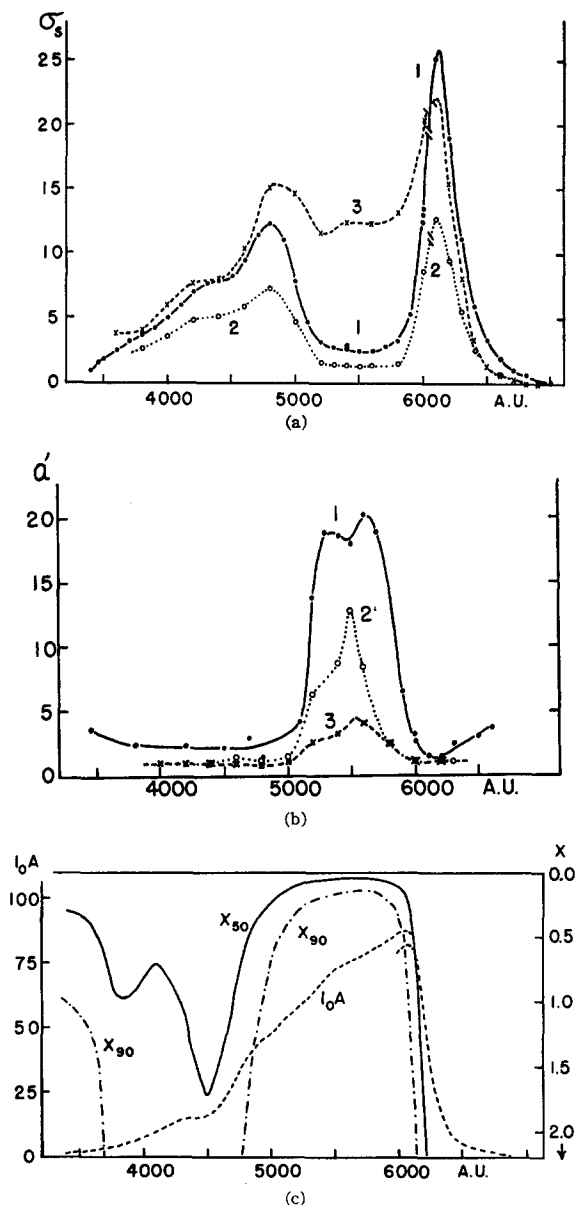
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FIG. 5. Rhodamine B, thick film (deposited by sublimation). (a) σ_s, steady-state conductance (1 unit $= 10^{-13}$ ohms^{-1}). (b) a', second-order rate constant for transient rapid decay, immediately after illumination (1 unit $= 10^{10}$ ohm/sec). Curves 1: 51°C, illumination from vacuum side of film. Curves 2: 30°C, illumination from vacuum side of film. Curves 3: 30°C, illumination through glass backing of film. (c) Light distribution within film. I_0A, total light absorbed in film; X_{50}, X_{90}, the depth in the film, measured in microns, downward from the illuminated face, above which 50% and 90%, respectively, of the incident radiation has been absorbed. These curves show the locus of light absorption in the film.

tained by Vartanian,[4] in that the response and quantum efficiency curves approximately match the absorption spectrum. The peak of our quantum yield curve (4600 A) coincides more closely with the absorption maximum (4560 A)[1,4] than his (4900 A). A further, and possibly related, discrepancy between his results and ours lies in the relationship between illumination and steady-state conductance: he found exponent p to be 1.0, while our preparation showed $p = 1.75$, a value more nearly consistent with the observed second-order dark decay. (Nonintegral dependence of steady-state conductance upon illumination is, in general, an indication that first- and second-order decay processes of comparable magnitudes are present.[8])

Thick Films

Figure 5(a) shows an example of the confusing results which can be obtained on thick samples. The photoresponse of the rhodamine B film illustrated showed a deep *depression*, rather than a maximum, at the absorption peak.[9] The conductance in the trough was comparable to that of much thinner films. In addition, the dark decay after illumination was complicated by a transient rapid decay process, having an apparent rate constant a', which varied sharply with wavelength [Fig. 5(b)]. Its duration was about the same at all wavelengths (approximately 23 seconds at 51°C and 40 seconds at 30°C), except for an extension at the very peak of the absorption curve. Furthermore, even the steady-decay constant, a, was enhanced near the absorption maximum.

The dip in the steady-state response curve could be accounted for by the increase observed in the effective decay constants at corresponding wavelengths, especially if it is remembered that the recombination rates prevailing during the photosteady state must have been even higher than the transients measured subsequently [Fig. 5(b)].[10]

This complex behavior may be explained in terms previously used to account for analogous effects in cadmium sulfide crystals.[11] The rhodamine film in question was about 2.2 microns thick and had a peak optical density of about 16.3. Hence, at the absorption maximum, about 10^{16} times as many quanta were absorbed, per unit volume, at the illuminated surface as at the back of the film. In regions of low extinction, on the other hand, the light was absorbed fairly homogeneously throughout the film. A graphic illustration of the variation in the locus of light absorption with wavelength is provided in the transmission contours

and trypaflavin these relative yields may be converted to absolute values by the factors computed in Table I. Unfortunately, the conduction of pinacyanole decays too rapidly in the dark to permit the evaluation of the rate constant, a, and, hence, its absolute efficiency of photoexcitation.

Our results for trypaflavin are similar to those ob-

[8] A. Rose, RCA Rev. 12, 397 (1951).

[9] A similar effect in thick films of trypaflavine has been reported by Vartanian.[4]

[10] The following argument does not explain the discrepancy between curves 2 and 3 of Figs. 5(a) and 5(b). The difference in response, at the same temperature, to illumination through the vacuum and glass interfaces of the film is presumably due to some refractive index or structural effect at the surface.

[11] See reference 8, p. 402.

(X_{50}, X_{90}) of Fig. 5(c); near 5700 A, essentially all the light was absorbed in the 0.2-micron layer nearest the light source, the remaining 2 microns of film thickness being effectively shaded. Since, on the average, electrons are excited within about 0.1μ of the site of light absorption,[12] and since, furthermore, the diffusivity of the carriers is low, the steady-state illumination produced an enormously concentrated thin layer of carriers at the surface. The nonhomogeneous carrier population of the film, taken as a whole, recombined about 10 times faster than an equal number of uniformly distributed electrons and holes. The abnormally high decay rate of the carriers near the surface, in turn, depressed the steady-state photoconductance at the absorption peak. In other words, in this spectral region the sample behaved like a 0.2μ thick film, while in regions of low absorption its depth permitted greater response.

When the light was turned off, the excess of carriers near the surface disappeared by quick recombination and by diffusion to other portions of the film; after this transition period, recombination proceeded at a rate commensurate with the measured conductance. A rough estimate of carrier mobility could be made from the observed transient times and conductances: $\mu_{\text{free}} \approx 3 \times 10^{-2}$ cm²/volt sec. The corresponding peak quantum yield for carrier excitation is of the order of 0.1 electron excited per photon absorbed (see Table I).

Anion Effects

In a series of experiments on several salts of crystal violet (the fluoride, chloride, iodide, oxalate, and sulfate) it was shown that, although the ionization potentials of the anions vary widely and the sulfate and oxalate are semiconductors,[13] all exhibit about the same sensitivity to white light, and all have similar absorption spectra. In addition, the iodide, chloride and sulfate were shown to respond strongly to sodium light, whose wavelength (5893 A) coincides with the main absorption peak of the cation. In no dye examined was there any evidence of photosensitivity beyond the long-wavelength limit of the first singlet-singlet transition. Even optical untrapping of carriers, when it occurs, appears to require primary excitation of the electronic levels of the dye.

DISCUSSION

The action spectra for photoconduction of solid cationic dyes match their absorption spectra. Electrons may be excited to the conduction band, or to traps in thermal equilibrium with it, by any of the observed singlet-singlet transitions of the cations, quite independently of the nature of the associated anions. Therefore, these dyes may be considered to be homogeneous photoconductors, whose properties are stoichiometrically determined by their chemical composition.

In a discussion of the absorption curves of these compounds in the solid state[1] it was pointed out that the spectra correspond essentially to the transitions of *individual* cations, except for the lowest excited state, which is strongly perturbed by dipole-dipole interaction among lattice neighbors. All higher singlet states are internally degraded to the lowest one, in times apparently less than 5×10^{-15} sec.[14] The interaction was postulated to lead to *exciton* migration from the site of absorption through the crystal, at a rate of one lattice spacing per $\sim 5 \times 10^{-15}$ sec. It was estimated that after some 20 000 jumps the exciton would be trapped at some molecule, there to be degraded thermally, by light emission, or by electron excitation. For rhodamine B, the efficiency of the latter process appears to be of the order of 10%.

The present results are generally consistent with this picture. The quantum yield vanishes at the long-wavelength edge of the first singlet band, as it does for practically all other photoeffects in dyes. The only puzzle is why it should also decrease in the regions of low absorption, to the *short*-wavelength side of the main visible absorption bands. One possible explanation is, that such absorption leads to states which are degraded by competing processes before they can cause the excitation of carriers to the conduction band.[15]

These might possibly be *triplet* levels, reached by transitions which are weak in the isolated molecules, but somewhat enhanced in the crystal. Triplets cannot interact with neighboring ground-state molecules of different multiplicity by dispersion forces,[16] and hence could not give rise to mobile excitons of the type discussed above. In addition, one would expect them to be quickly degraded to the lowest *triplet* level, which might well be energetically or otherwise unable to cause electron excitation. This otherwise unsupported hypothesis may help to explain the observation of Vartanian[4] that oxygen has photochemical effects on trypaflavine films only at wavelengths shorter than the main absorption peak: this paramagnetic gas might well interact preferentially with triplet states of the solid dye molecules.

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[12] In reference 1 it was estimated that light absorption leads to the formation of *excitons*, having a lifetime of the order of 10^{-10} sec and a mobility of one lattice spacing (~ 8.5 A) per $\sim 5 \times 10^{-15}$ sec. The mean range for $10^{-10}/5 \times 10^{-15} = 2 \times 10^4$ jumps, taken at random in three directions, is $(8.5)(\frac{2}{3} \times 10^4)^{\frac{1}{2}} \approx 700$ A. Thus most carriers are formed within 0.1μ of the locus of light absorption.

[13] R. C. Nelson, J. Chem. Phys. **20**, 1327 (1952).

[14] It is hard to imagine how a simple vibration mechanism could account for degradation times, so short compared to 10^{-13} sec.

[15] The same sort of result was obtained by Vartanian[4] for trypaflavine. Unfortunately, there are as yet no data on the yield of carrier production from the ultraviolet absorption bands.

[16] P. P. Feofilov, Doklady Akad. Nauk. SSSR **44**, 147 (1944).