

Short Communication

Mechanisms involving the transient absorptions of cyanine dyes in gelatin and adsorbed to silver halide films: temperature dependence*

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Flash photolysis has enabled detection of transient species that might appear in the photographic process [1]. Four cyanine dyes were studied at 10^{-3} M in ~ 30 μ m thick gelatin films with and without AgBrI (0.05 μ m grains, S + Au surface treated): (1) ThC pts (3,3'-diethylthiacarbocyanine-*p*-toluenesulfonate); (2) 9-MeThCBr (3,3'-diethyl-9-methylthiacarbocyanine bromide); (3) 2,2'-cyanine (1,1'-diethyl-2,2'-cyanine chloride); and (4) sulfo-9-MeThC (anhydro-3-ethyl-9-methyl-3'-sulfobutylthiacarbocyanine hydroxide). In general, pulsed irradiation within the visible absorption bands temporarily bleached the ground-state absorption bands and formed transient absorptions at longer wavelengths (Figs. 1 and 2). Optical density changes after excitation were described by:

$$\Delta OD = A \exp(-k_2 t) + B \exp(-k_1 t) \quad (1)$$

Cyanine dyes dispersed in gelatin films

Steady state spectroscopy

West *et al.* [2] considered ThC pts to be a single isomer and 9-alkyl analogs (*e.g.*, 9-MeThCBr) exhibit two isomers with the *trans* configuration absorbing at longer wavelengths relative to the *cis* isomer. Their assignment has been reinforced in this study even though the geometrical isomers of sulfo-9-MeThC and 9-MeThCBr were not photoconvertible by exciting either within the *cis* or the *trans* isomer absorption bands (-80 °C to 23 °C).

Pulsed photolysis

The dark relaxation of optically induced transients for dyes in gelatin are described by two types of reactions having first-order rate constants: (1) $k = 10^{2.5} \exp(-500/RT)$ at -100 to 10 °C with a low energy of activation; (2) $k = 10^{8.5-10.4} \exp(-8000/RT)$ at 10 °C to 55 °C with a high energy of activation. Two distinct relaxation mechanisms are postulated:

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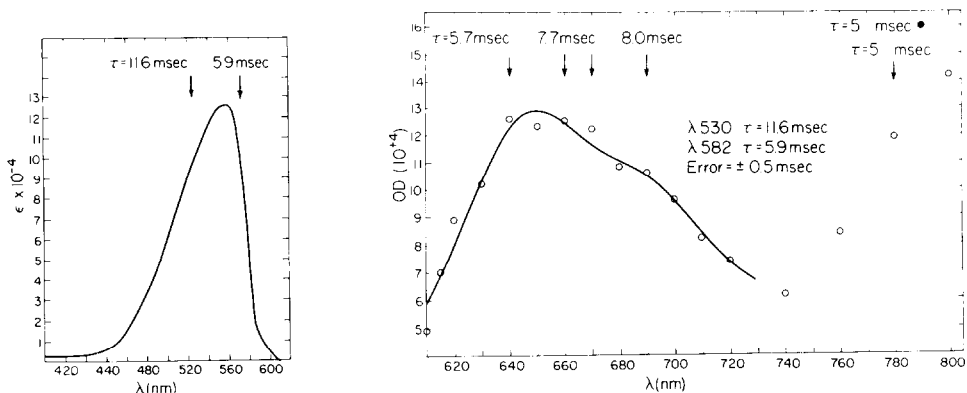


Fig. 1. (a) Absorption of ground state 9-MeThCBr in gelatin with regeneration lifetimes ($2.1 \times 10^{-3} M$, $27.6 \times 10^{-4} cm$). (b) Transient absorption of 9-MeThCBr in gelatin with relaxation lifetimes.

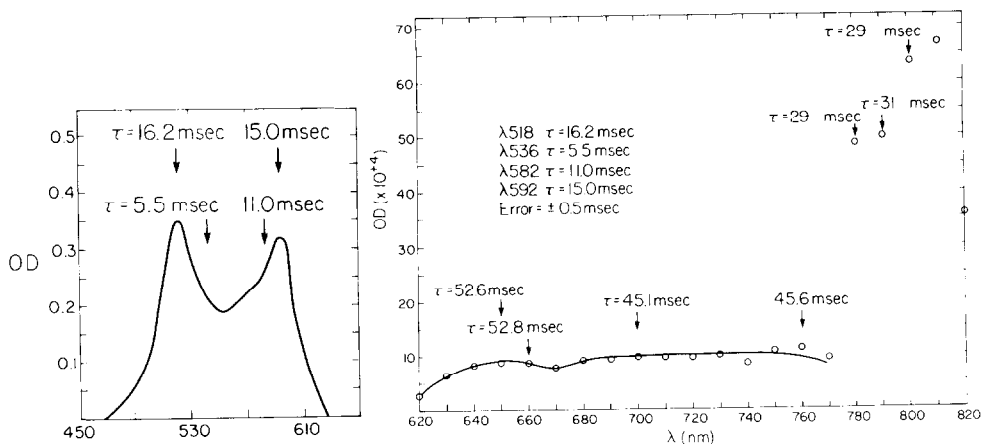


Fig. 2. (a) Absorption of ground state 9-MeThCBr on AgBrI (S + Au) in gelatin with regeneration lifetimes ($1.83 \times 10^{-3} M$, $31.0 \times 10^{-4} cm$). (b) Transient absorption of 9-MeThCBr on AgBrI (S + Au) in gelatin with relaxation lifetimes.

(1) A torsional movement about a double bond resulting from a "forbidden" transition; a low frequency factor and low energy of activation are manifest at low temperatures (183 - 294 K).

(2) A torsional movement about a double bond subsequent to an allowed transition; a high frequency factor and high energy of action are observed at higher temperatures (294 - 325 K).

It is known from X-ray analysis that ThCBr displays one configuration within the crystalline state, the extended all-*trans* configuration [3]. It is by analogy to the crystalline configuration that the relaxation lifetime of 5.2 ms is assigned to the *trans* configuration within gelatin and longer lifetimes of the analogs to the mono-*cis* configuration at 23 °C.

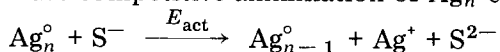
ThC pts τ_{cis} = not present; τ_{trans} (576 nm) = 5.2 ± 0.3 ms;
 9-MeThCBr τ_{cis} (550 nm) = 18.2 ± 0.5 ms; τ_{trans} (582 nm) = 6.5 ± 0.3 ms;
 sulfo-9 MeThC τ_{cis} (530 nm) = 19.4 ± 0.5 ms; τ_{trans} (584 nm) = 6.5 ± 0.3 ms.

The substituents, 3-sulfobutyl in sulfo-9-MeThC *versus* 3-ethyl in 9-MeThCBr or the anions (sulfo *versus* bromide) do not significantly affect the relaxation lifetimes when comparing similar geometrical isomers. The larger, bulkier 3-sulfobutyl, relative to the ethyl group of the *cis* configuration does not restrict the arrangements of the energy levels by crowding or displacing the planarity of the atoms in the methine chain. It is postulated that the *cis* isomer is less hindered than the *trans* configuration within the sulfo-9-MeThC and 9-MeThCBr.

Additional analytical data, including the delocalized transit distances for each isomer (particle in the box model), the free energy ΔG° , and calculations based upon spectroscopic evidence reinforce the kinetic observations by showing the equilibrium constant favoring the unhindered *cis* configuration.

Transient absorption spectra of 0.05 M AgBrI (S + Au) dispersed in gelatin

Figure 3 shows the transient absorption spectra produced by pulsed irradiation of undyed, unsensitized AgBrI (520 nm) and peak absorptions at 640 nm are significantly shifted and intensity enhanced by surface chemical treatment of sulfur and gold. The contribution of sulfur and gold to the overall transient absorption is described by the subtractive spectra, AgBrI (S + Au) minus AgBrI absorption coefficients (cm^{-1}) *versus* wavelength. Prominent shifted new absorptions are observed at 490 and 700 nm. These are a direct result of crystal surface sensitization, and are assigned to a sulfur hole (S^-). This sulfur hole complements the halogen, X° , hole of the AgBrI assigned to 520 and 620 nm spectral regions. A proposed mechanism is discussed in the next section. An activation energy, 0.033 ± 0.002 eV, at 490 and 680 nm of AgBrI (S + Au) is assigned to S^- trapped hole, and the long lifetimes of 89 - 92 ms describe the migration of S^- and Ag^+ in the competitive annihilation of Ag_n° centers, eqn. (12),



Cyanine dyes adsorbed to AgBrI (S + Au) crystals dispersed in gelatin

Initial observations

The relaxation lifetimes of induced absorptions (30 - 50 ms) for cyanine dyes complexed to the grain surface are *not* the same as lifetimes for regeneration of the ground state (5 - 16 ms) (Figs. 1 and 2). This observation is due to the formation of the sulfur, S^- , or halide, X° , hole, eqns. (8) - (10), absorptions overlapping the induced transient absorptions

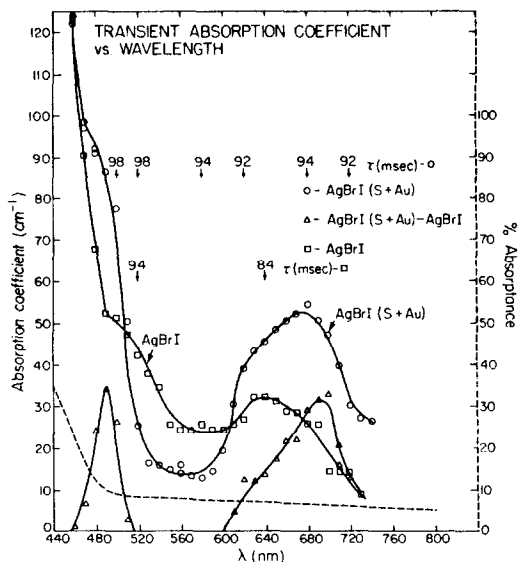
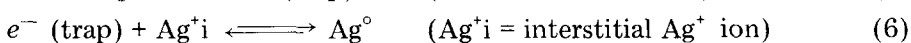
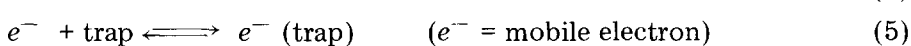


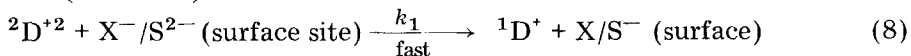
Fig. 3. Transient absorption coefficient *vs.* wavelength.

from the dye-grain complex. The regeneration of the ground state is described by three concurrent reactions involving surface sites, electron traps, and sub-latent image sites, Ag_n° [eqns. (8) - (10)]. The overall review of the proposed mechanisms [1], consistent with observed transient absorptions for dyes adsorbed to AgBrI (S + Au) grains can be described by eqns. (2) - (14). Reactions (3) - (7) and (14) lead to latent image formation, while reactions (8) - (12) and the reverse of (5) - (7) are sources of inefficiency.

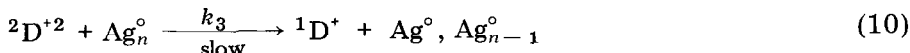
A. The excitation and electron transfer process of the dye on silver bromide grains.†



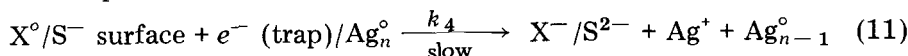
B. A simple model for the regeneration of the ground state via competing reactions (5 - 16 ms).



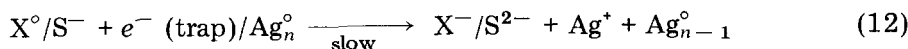
†The simplified notation refers to an isolated dye molecule, but in reality there is mixing of wavefunctions of adsorbed dye on grain surfaces.



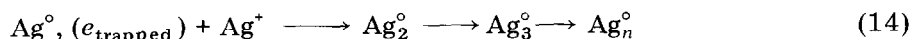
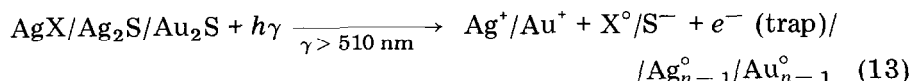
C. Relaxation model for the induced transient spectrally overlapping the radical absorption. Annihilation of sub-latent image center, Ag_n (30 - 50 ms).



D. Relaxation model for the induced (Au + S) sensitized grain transient (92ms).



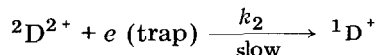
E. Alternate process leading to transient species.



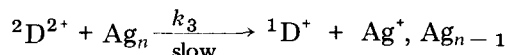
Temperature dependence

The activation energies relating to the temperature dependence for regeneration of the ground state (Table 1) were divided into two categories.

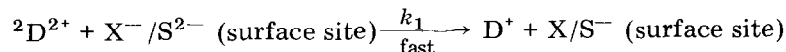
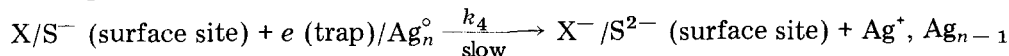
(1) Relatively high activation energies corresponding to thermal de-trapping of the electron (eqn. 9) (2.3 - 5.7 kcal):



or annihilation of the subimage, Ag_n° , via dissociation and electron transfer to the recombination site (eqn. 10):



(2) Low activation energies attributed to the halogen or sulfide hole capture of the electron or dissociation of Ag_n° , (eqn. 12), (0.60 - 0.80 kcal) and rapid regeneration of the ground state (eqn. 8).



Since regeneration of the ground state and the decay of the induced transient exhibit different lifetimes, additional transients were formed [eqns. (8), (11), (13), (14)] absorbing primarily in the 600 - 700 nm and 440 - 520 nm regions.

The different activation energies for the regeneration of the dye are related to the additional transients formed. This is particularly true near 520 nm and 595 nm, where 9-MeThCBr shows the low activation energies attributed to trapped halogen or sulfide holes.

A trapped electron model

The very large negative values for the ΔS^{\dagger} (act) described a more random

TABLE 1

Activation energies of regeneration of dye adsorbed to 0.05 μm AgBrI (S + Au) dispersed in gelatin films

| Dyes | Regeneration to ground state (nm) | Lifetime (ms) | E_{act} (kcal) | W ($E_{\infty}=1.2$ eV) (\AA) | W ($E_{\infty}=0.56$ eV) (\AA) | $\Delta S_{\text{act}}^{\neq}$ (cal/deg) |
|-------------------------|-----------------------------------|---------------|-------------------------|---|--|--|
| ThC pts | 565 | 4.3 | 3.7 | 4.4 | 11.4 | -37 |
| | 594 | 9.4 | 2.5 | 4.2 | 9.9 | -41 |
| 9-MeThCBr | 518 | 16.2 | 0.73 | 3.9 | 8.6 | -49 |
| | 536 | 5.5 | 5.7 | 4.8 | 14.6 | -30 |
| | 592 | 15.9 | 0.73 | 3.9 | 8.6 | -49 |
| sulfo-9-MeThC | 522 | 10.5 | 3.3 | 4.3 | 10.9 | -38 |
| | 570 | 25.0 | 2.7 | 4.2 | 10.3 | -42 |
| | 594 | 14.9 | 2.4 | 4.1 | 9.9 | -42 |
| | 622 | 24.5 | 2.3 | 4.1 | 9.9 | -44 |
| AgBrI (S + Au) (no dye) | 490 | 92 | 0.76 | | | -51 |
| | 680 | 92 | 0.86 | | | -51 |

arrangement in the transition state [${}^2\text{D}^{2+}\text{X}^- \text{---} e$ (trapped) --- $\text{Ag}_n^+\text{X}_n^-$] as compared to the ground state, [${}^1\text{D}^+\text{X}^- \text{---} \text{Ag}_n^+\text{X}_n^-$] indicative of the localization of the electron near the recombination center of the ${}^2\text{D}^{2+}$. For two isolated traps, the magnitude of the barrier between them may be described as a simple function of the distance, W , between them, using eqn. (15):

$$W = \frac{e^2}{(E_{\infty} - E_{\text{act}})} \left\{ \left[\frac{Z}{Z'} \right]^{\frac{1}{2}} + 1 \right\} \left\{ Z' + (Z'Z)^{\frac{1}{2}} \right\} \quad (15)$$

The distance, W , from ${}^2\text{D}^{2+}$ is described as a function of activation energies, E_{act} , dielectric constant, K , and, $Z \approx 0.1$, the charge of the traps, neglecting screening constants, $Z' = 1 - Z$, the charge of the recombination center ${}^2\text{D}^{2+}\text{X}^-$, and E_{∞} , the energy of an electron in an isolated trap (representing bulk trapping parameters). Appropriate E_{∞} values [4] range between 0.56 eV for the latent sub-image center, $\text{Ag}^+ \text{---} e \text{---} \text{Ag}^+$, and 1.2 eV (stable latent image) $e/\text{Ag}^+ \text{---} e/n \text{---} \text{Ag}^+$. The following values of W (E_{act} , E_{∞}) were calculated: 3.9 - 4.8 \AA (0.7 - 5.7 kcal, 1.2 eV) and 8.6 - 14.5 \AA (0.70 - 5.7 kcal, 0.56 eV).

Extended lifetimes quenching of relaxation signals, initial experiments of thermally stimulated current, and ionic thermocurrent measurements suggest that induced transient relaxations within dye adsorbed to grain surfaces are due to radical formation rather than excited species within gelatin films.

- 1 S. H. Ehrlich, Vogel Centennial Dye Sensitization Past and Future, Putney, Vermont, 1973 (Aug. 26 - 30); *Photogr. Sci. Eng.*, 18 (2) (1974) 18 (1974) 179.
- 2 W. West, S. Pearce and F. Grum, *J. Phys. Chem.*, 71 (1967) 3116.
- 3 P. J. Wheatley, *J. Chem. Soc.*, (1959) 3245, 4096.
- 4 C. R. Berry, *J. Photogr. Sci.*, 18 (1970) 169.