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Selforganization and silver halide photolysis

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We show that certain criteria for selforganizing systems, namely thermodynamic control and structural specificity of the products, determined by weak bonding therein, are met by the photolabile silver halides which yield Ag^o_n clusters on irradiation. Laser flash photolysis (35 ps pulse, 355 nm) of sub-μm, cubic photographic emulsion grains, AgBr and Ag(I)Br, dispersed in gelatin, leads to reversible formation of light absorbing transients assigned to these clusters. Under our conditions two unique values, or, at least, narrow distributions of cluster nuclearity appear to obtain. Nucleation and cluster growth occur at the grain surfaces, i.e. AgBr-gelatin interface. Further studies are required to establish size and structure of the clusters which evolve under these conditions to see if the criterion of modular construction, as envisioned in the clusters of clusters model[1], is actually realized in this chemistry.

INTRODUCTION

In recent work[1] Teo and Zhang have described the formation of high-nuclearity hetero- and homoclusters of coinage metals in terms of a "clusters of clusters" approach based on original proposals of Hoare and Pal[2] and Briant and Burton[3]. Nuclearities of clusters formed by this growth sequence correspond to "magic numbers", which confer a unique level of stability on the clusters according to quantum chemical prediction[4]. Teo uses the term "selforganization" in connection with the formation of such supraclusters.

Hallmarks of selforganizing systems include thermodynamic control of assembly, weak bond formation, structural specificity and modular assembly of components. If we envision nucleation and formation of an Ag^o phase from, e.g. AgBr, under irradiation, the ionic bonds of the crystal lattice are replaced by relatively weak, pseudo-metallic bonds and the coordinate covalent bonds of cluster-stabilizing ligands. Ag^o_n cluster stabilization energies, E_s, should conform to the formula of Freund and Bauer[5]

$$E_s/n = E_\infty(1 - n^{-0.25}) \qquad (1)$$

where E_∞ is the lattice energy for metallic silver, 2.62 eV. Thus for the icosahedral Ag_{13} cluster, which is a key intermediate in the clusters of clusters model, $E_s/n = 1.24$ eV, substantially less than typical covalent bonds, and consistent with operation of selforganization.

The primary consequence of photolysis of AgBr may be considered to be supersaturation of the AgBr host in dissolved atomic Ag^o [6]; this supersaturation expresses itself in the formation of clusters which represent local minima on the system potential energy surface. Size and distribution of clusters is determined not only by thermodynamics of the clusters themselves, but by degree of supersaturation and ability of ligands, which correspond to surface sites on the AgBr particles and, in the case of photographic emulsion, functional groups associated with the gelatin dispersant, to stabilize the cluster surface.

For spherical clusters the free energy of formation has been proposed[6] to be

$$\Delta G = 4\pi r^2\sigma - (4/3\pi r^3(RT/V_{Ag})n\ c_s \qquad (2)$$

where σ is the surface free energy of Ag^o at the site of separation (which may be strongly influenced by the presence of gelatin[6c,7], the usual dispersant for the silver halide microcrystals in photographic "emulsions"), V_{Ag} is the molal volume of Ag^o and c_s is the supersaturation in atomic Ag^o of the AgBr phase corresponding to a particular photoexcitation density, n, i.e. exposure level. Thermodynamic control of cluster size distribution for a given n thus corresponds to the case, $\Delta G = 0$, whereby

$$r = (\sigma V_{Ag}/RT)(-n\ c_s) \qquad (3)$$

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If evolution of Ag^o clusters occurs according to the clusters of clusters model, the supraclusters should be built up in modular fashion from smaller clusters, with icosahedral Ag_{13} as a key intermediate[1]; the arrangement of silver atoms in these clusters is thus very specific but does not correspond to that of bulk metallic Ag. Eqs. 1 and 2 thus do not apply as written though the general principles underlying them may yet be relevant. In summary, photolysis of AgBr should lead to evolution of Ag^o clusters whose size and structure is thermodynamically controlled and which represent iterations of fundamental building blocks, e.g. icosahedral Ag_{13}.

We have demonstrated the utility of time-resolved laser flash photolysis coupled with transient absorption for observation of early events in the photoreaction of silver iodide organosols[8,9] and liquid photographic emulsions[10]. An important inference from these studies, especially in comparison with similar studies on silver halide nanoparticles formed in glass matrices[11], i.e. photochromic glasses, is that on the time scale probed in the experiments (0.1 – 10 ns) the photochemistry is localized on the surface of the particles. By comparison, the photochemical process involved in the photographic silver halide technology can occur in the bulk of the AgBr crystals as well as at the surface, but it is thought to be gated by lattice relaxations which occur on the time scale of microseconds[12]. The present report relates results obtained on the silver halide system by this technique to the issue of selforganization, as proposed by Teo.

RESULTS AND DISCUSSION

Experimental details. Experimental procedures for preparation and characterization of micro-crystalline AgBr and Ag(I)Br photoemulsions[10,13], time-resolved transient absorption[14] and emission[15] spectroscopy have been described previously. The emulsions comprise aq. gelatin dispersions of cubic microcrystals ("grains") with mean grain size of (0.4 – 0.5) µm, prepared according to the method of Hill[13]. Steady-state emission spectra were obtained on a Perkin-Elmer MPF-44B fluorescence spectrometer and corrected for wavelength dependent variation in Xe lamp power and detector response.

Luminescence Spectroscopy. Steady-state fluorescence spectra for the liquid emulsions ("pure" AgBr and $AgI_{.05}Br_{.95}$) obtained at room temperature with 355 nm incoherent excitation are shown in Fig. 1. Emission from both materials is comparable in intensity and distribution, comprising two bands with onsets at 2.78 and 2.38 eV. The former is commonly observed and attributed to recombination at I^- centers[16]. Berry[17] suggests that the green emission corresponds to recombination at I^- centers in the crystal bulk, while the orange luminescence occurs at I^- centers at the surface; this interpretation is supported by systematic study of relative intensities of the two emissions as a function of crystal size[18]. Based on low temperature measurements, Czaja[19] assigns I^- centered, phonon-assisted emission to 2.51 eV, however; he identifies the 2.38 eV emission with I^- pair emission, corresponding to recombination at a defect center formed by association of 2 I^- ions in the coordination sphere of the same Ag^+ ion, designated $(I^-)_2$. The threshold for observation of $(I^-)_2$ centered emission corresponds to ca 10 ppm I^- which is not an unusual level to obtain adventitiously in nominally pure AgBr[19]. As relative contributions of I^- and $(I^-)_2$ centered recombinations should, however, reflect I^- concentration in the non-stoichiometric solids, our observation of essentially equivalent spectral distribution of emission from our two samples (Fig. 1) is more consistent with Berry's interpretation. Similar spectra have recently been reported for size-restricted AgBr sols[20].

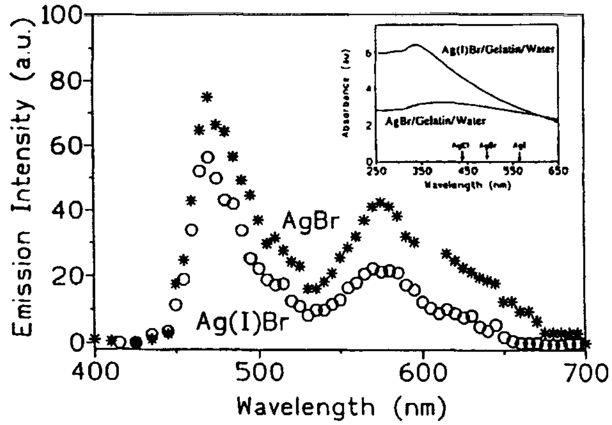

Figure 1 Photoluminescence spectra for AgBr and Ag(I)Br photoemulsions at ambient temperature; $[AgX] = 5 \times 10^{-4}$ M.

Fig. 2 shows time-resolved emission data excited with a 355 nm laser pulse (35 ps fwhm) for both emulsions; rise and decay kinetics are essentially indistinguishable in the two cases. Consider a mechanism according to which light absorption creates bound excitons, E, insofar as AgBr is an indirect band material with a dissociation energy of 4.0 eV, greater than the photon energy, 3.5 eV, used in these studies. Such an excitation model has been described by Dexter[21]. A lifetime of ca 1.5 ns can be calculated for these excitons at room temperature[22]. The excitons are dissociated at isoelectronic acceptor centers, e.g. I^- or $(I^-)_2$, with liberation of photoelectrons which can diffuse rapidly to the microcrystal surface and creation of trapped photoholes[22]. Alternatively the excitons may be formed bound to the I^- or $(I^-)_2$ centers. Localization of excitation at the I^- centers is consistent with the observation of lattice-encapsulated I_2 as the

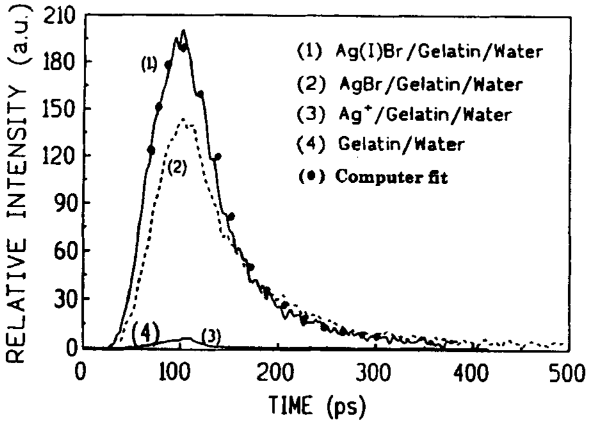

Figure 2 Time-resolved emission from AgBr and Ag(I)Br with 355 nm laser excitation; conditions are as in Fig. 1. Individual data points correspond to computer fit in accord with mechanism of eqs. 4–6 (see text).

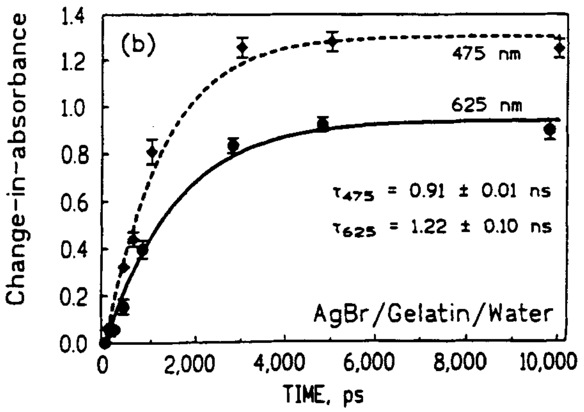

Figure 3 Transient absorption spectra recorded at the indicated delay times following pulsed laser excitation (2.5 mJ, 355 nm) of the AgBr photoemulsion.

principal halogen product of photolytic decomposition of Ag(I)Br[23], as well as with the data of Fig. 2 which indicate that there is no strong dependence of emission rise or decay rates on the level of I^- in the grains. In either case the pseudo-first order rate constant for exciton dissociation is designated k_1. The I^- or $(I^-)_2$ trapped photoholes can then catalyze luminescent recombination.

$$E + I^- \rightarrow e^- + p^+(I^-) \qquad (4)$$
$$E + p^+(I^-) \rightarrow I^- + p^+ + h\nu \qquad (5)$$
$$p^+ + I^- \rightarrow p^+(I^-) \qquad (6)$$

The second order rate constant for the emissive process of eq. 5 is designated k_2. A computer fit of the experimental data according to this mechanism requires two parameters (along with a scaling factor), k_1 and k_2/n, respectively, where n is the excitation density achieved during laser excitation and corresponds to the initial concentration of bound excitons. The tail of Fig. 2, corresponding to conditions where the process of eq. 3 should be rate limiting with respect to luminescence decay, can be fit to $k_1 = (3.2 \pm .7)\ \mathrm{x}10^9\ s^{-1}$. Data points in Fig. 2 were obtained using this experimental value and a "best fit" value of $k_2/n = 4.5 \times 10^6\ s^{-1}$.

Laser Flash Photolyses. Transient absorption spectra recorded after 355 nm laser flash photolysis of the aq. AgBr emulsion (2.5 mJ/pulse, [AgBr] = 5 x 10^{-4} M) are shown in Fig. 3. Similar results for the $AgI_{.05}Br_{.95}$ emulsion are shown in Fig. 4. Absorption bands in both cases are genuine transients which are completely discharged within seconds. After exposure to 50 pulses of this energy, an 0.6 cm^3 sample of the AgBr emulsion exhibited no permanent, spectroscopically detectable changes. Under these conditions then, photographic emulsions are photochromic, as were the AgI nanosols we previously investigated[8,9]. Similar regression of photolytic silver has been observed[23] in the case of large tabular Ag(I)Br crystals photolyzed at low intensity and attributed to reoxidation of Ag^o species by photoholes thermally liberated from iodide trapping states, formed according to eq. 4.

$$p^+(I^-) \rightarrow p^+ + I^- \qquad (7)$$
$$p^+ + Ag^0n \rightarrow AG^+ + Ag^0(n-1) \qquad (8)$$
$$Ag^+ + I^- \rightarrow AgI \qquad (9)$$

We accordingly assign the transients to Ag^o species: small Ag^o clusters, e.g. associated with reduction sensitization centers in AgBr photoemulsions, thought to be Ag_2, yield broad absorption bands in the visible region[24], as do more massive metallic Ag^o deposits formed by photolysis of silver halides of various compositions[25]. It is thus not possible to draw detailed inferences concerning size and/or structure of the Ag^o clusters to which the absorptions are assigned. There do however appear to be at least two components to the transient absorption, centered on 475 and 625 nm, respectively. In both cases the

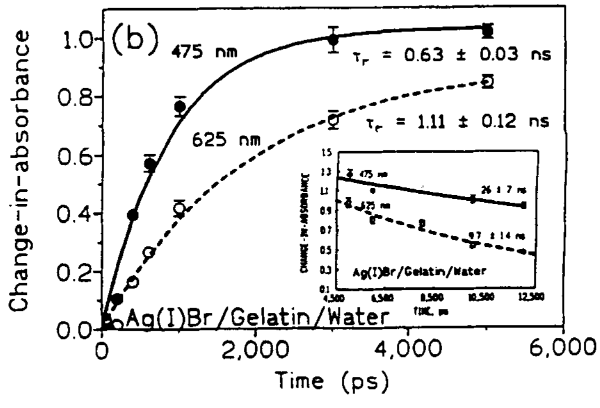

Figure 4 As Fig. 3 for Ag(I)Br emulsion.

latter evolves somewhat more slowly than the former (see Figs. 5 and 6, below). We infer formation of two kinds of Ag° clusters, each characterized by a unique (or narrowly distributed) nuclearity.

From the traces of Figs. 3 and 4 kinetic plots were constructed as shown in Figs. 5 and 6, respectively; in both cases growth of the transients at 475 and 625 nm followed pseudo-first order kinetics after brief induction periods, t_i. Note that in Fig. 6 onset of the regression process is observable; the species responsible for the 625 nm transient apparently regresses faster than that responsible for the 475 nm absorption. Its decay lifetime, ca. 10 ns, sets an upper limit on the lifetime of the trapped photoholes, i.e. a lower limit on the rate constant associated with eq. 7. Kinetic parameters, t_i and pseudo-first order rate constants, k, obtained by analysis of transient absorption spectra recorded after excitation with laser pulse energies, I = 1 mJ and 2.5 mJ, are given in Table 1. Little pulse energy dependence of either parameter, outside of experimental error, is apparent. The t_i's are comparable to the 300 ps time constant for photoelectron liberation (eq. 4).

First order kinetics and the relatively straightforward evolution of the spectral bands appear to be inconsistent with continuous evolution of cluster nuclearity. We prefer a model according to which number of Ag^o_n species increases with time: following rate determining nucleation at pre-existent nucleation centers, D, on the microcrystal surface, clusters grow rapidly to a thermodynamically predetermined size (nuclearity = n), consistent with principles of selforganization. Precedent for this sort of phase formation mechanism involving ongoing renucleation of the new phase is found in the base-catalyzed reduction of Ag^+ in isopropanol solution[26] and in the thermolysis of $Ag_2(C_2O_4)$[27]. High diffusibility for atomic Ag° on the AgBr surface has already been posited by Malinowski and co-workers[28] to account for observations made in the course of studying deposition of silver on an AgBr substrate. Thus

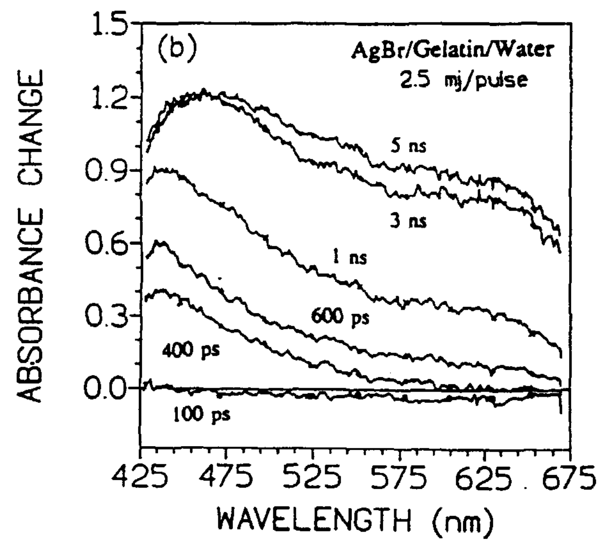

Figure 5 Computer fits of data from Fig. 3 at the indicated wavelengths to pseudo-first order kinetics.

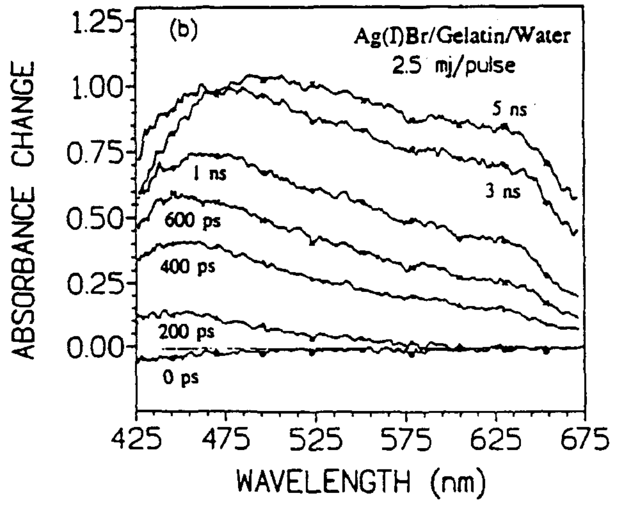

Figure 6 As Fig. 5 for data from Fig. 4. Inset shows regression of transient absorption at both wavelengths at longer delay times.

$$Ag^0 + D \rightarrow {}^{\cdot}AgD \qquad \text{rate constant} = k \qquad (10)$$

$$n\,Ag^0 + AgD \rightarrow AG^0n \qquad \text{fast} \qquad (11)$$

According to this mechanism two types of nucleation site, D_a and D_b, correspond to rate constants, k_a and k_b, and equilibrium nuclearities, n_a and n_b, respectively, thus giving rise to two unique cluster populations.

Experiments were carried out in which the laser pulse energy, I, dependence of the amplitude of the maximum observable transient (5 ns delay) was evaluated. Little change in spetral distribution of transient absorption with I was observed, indicating that cluster nuclearity is not controlled by excitation density. Data are shown in Figs 7 and 8 for AgBr and Ag(I)Br respectively. Accordingly cluster size distributions are not controlled by supersaturation, n_s, as suggested by eqs. 2 and 3.

Table 1 Kinetic parameters for Ag° transient growth

Emulsion	*I (mJ/pulse)*	t_i *(ps)*	*k (475) (s^{-1})*	*k(625) (s^{-1})*
AgBr	2.5	250	1.1×10^9	0.82×10^9
AgBr	1.0	300	1.6×10^9	1.1×10^9
Ag(I)Br	2.5	175	1.6×10^9	0.90×10^9
Ag(I)Br	0.9	275	0.75×10^9	0.68×10^9
Avg.		(250 ± 48)	$(1.26 \pm .35) \times 10^9$	$(0.88 \pm .15) \times 10^9$

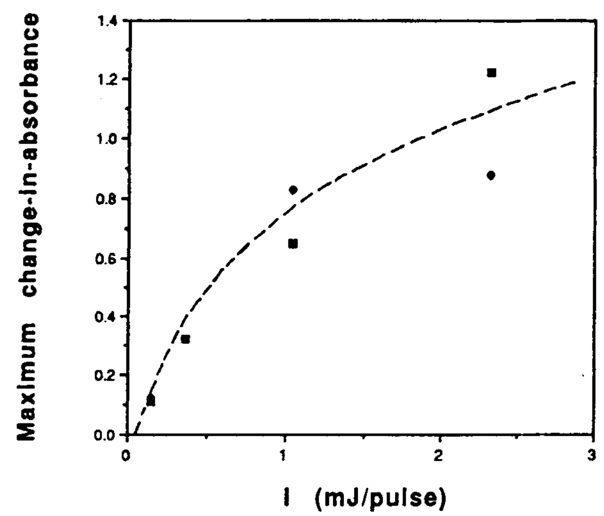

Figure 7 Analysis of maximum transient absorption, ΔA_{max}, observed following 355 nm laser excitation with pulse energy, I, of AgBr photoemulsion at (◆) 475 nm and (□) 625 nm according to two-level model of a saturable absorber. See text (Table 2) for fitting parameters.

Under conditions of intense coherent excitation, the AgBr and Ag(I)Br microcrystals are saturable absorbers, and excitation density achieved on excitation with incident pump pulse irradiation, I (photons), can be given in a simple two-level approximation[29] as

$$n = (I - I_O)f_{abs}/\{v[1 + (I - I_O)/I_{sat}]\} \qquad (12)$$

where I_o is a threshold for onset of the observable photoeffect and I_{sat} is an exposure corresponding to saturation of absorption of the sample. The transient amplitude, ΔA, measured at wavelength λ is then

$$\Delta A = 1000\, n\Phi\varepsilon l/N \qquad (13)$$

where ε is the molar extinction coefficient of the photoproduced Ag^o species, formed with quantum efficiency, Φ, l is the effective sample length along the measuring axis (determined by the concentration of the sol, and ca. 3 x 10^{-6} cm in the present experiments), and N is Avogadro's Number. Combining eqs. 12 and 13 we obtain

$$\Delta A = 1000\, \Phi\varepsilon l(I - I_O)f_{abs}/\{vN[1 + (I - I_O)/I_{sat}]\} \qquad (14)$$

Table 2 Onset and saturation of photoeffects in AgBr and Ag(I)Br

Parameter	*AgBr*	*Ag(I)Br*
I_o	0.05 mJ	0.10 mJ
	8.5 x 10^{13} photons	1.7 x 10^{14} photons
n_o	4 x 10^{19} cm^{-3}	1 x 10^{20} cm^{-3}
I_{sat}	1.7 mJ	2.0 mJ
	2.9 x 10^{15} photons	3.4 x 10^{15} photons
n_{sat}	1.5 x 10^{21} cm^{-3}	2.2 x 10^{21} cm^{-3}

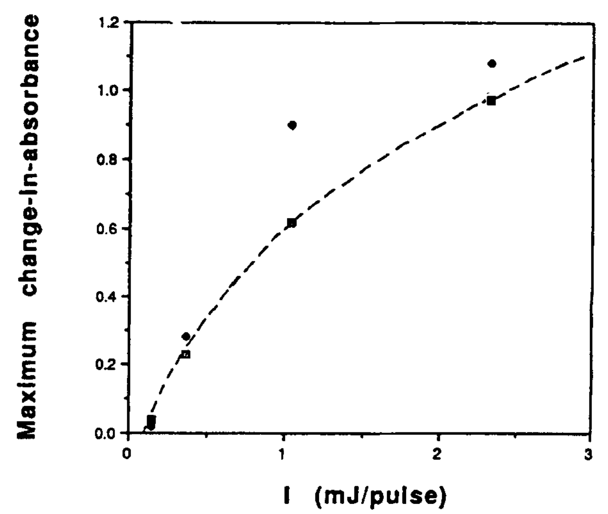

Figure 8 As Fig. 7 for Ag(I)Br.

The data of Figs. 7 and 8 were fit to eq. 14 with values of I_o and I_{sat} given in Table 2. The excitation densities, n_o and n_{sat}, corresponding to these exposures were estimated on the assumption

$$f_{abs} \cong 1/d = 0.06 \qquad (15)$$

where d is the average AgBr grain dimension (0.5 μm), insofar as direct estimation of f_{abs} from extinction spectra is not usually possible in heterogeneous samples comprising light scattering particles[30]. These density of states estimates are also included in Table 2. The product εΦ is, of course, not factorable on the basis of the data shown in Figs. 7 and 8; both fits correspond to reasonable values of the product, εΦ = 2 x 10^5 M^{-1}cm^{-1}, however, which suggests high quantum efficiency for the cluster forming process.

The estimates of n_o correspond approximately to n_{Mott} for AgBr[31], the excitation density at which Coulombic forces between carriers and between carriers and charged defects are effectively screened, thereby allowing interaction with isoelectronic defects to proceed efficiently, e.g. eq. 4. Estimates of n_{sat} correspond approximately to those for surface density of states in microcrystals of the size employed here, consistent with the preconception, above, that photochemistry should be confined to particle surfaces.

CONCLUSIONS

Certain criteria for selforganizing systems, namely thermodynamic control and structural specificity of the products, determined by weak bonding therein, are met by the photochemistry of the silver halides. Laser flash photolysis (35 ps pulse, 355 nm) of cubic photographic emulsion grains leads to reversible formation of light absorbing transients assigned to Ag^o_n clusters. While the present data do not permit detailed structural characterization of the clusters, kinetics of their formation are consistent with a model of rate limiting nucleation at pre-existing nucleation sites (defects) on the grain surfaces, followed by rapid growth of clusters to an equilibrium size.

Two unique, narrow distributions of cluster nuclearity appear to obtain. Nucleation and growth occur at grain surfaces, i.e. AgBr-gelatin interface. The cluster sizes are thus apparently not determined by supersaturation, i.e. excitation density, of the AgBr host in Ag^o as expected *a priori*, but rather by the chemical potential of Ag^o at the surface, which may, in turn, be controlled by chemisorbed gelatin[31]. Further studies, currently underway, are required to establish size and structure of the clusters which evolve under these conditions to see if the criterion of modular construction, envisioned in the clusters of clusters model[1], is actually realized in this system.

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NOTES AND REFERENCES

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