Design and principles of two-electron sensitization by fragmentable electron donors

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Abstract

Fragmentable two-electron donors are molecules that have been designed to undergo a bond fragmentation reaction after capturing the hole created by photoexposure of AgX. As part of the design, the radical remaining after fragmentation is made sufficiently reducing that it can inject an electron into the AgX conduction band. Use of these compounds thus allows creation of two electrons for each absorbed photon. This two-electron release mechanism has been extensively studied by flash photolysis measurements in solution and the creation of a strongly reducing radical after fragmentation has been convincingly demonstrated. In addition, EPR measurements have shown that the reaction sequence also takes place for a fragmentable two-electron donor compound adsorbed to AgBr, creating a second electron. Photographic results confirm that two-electron sensitization can yield the expected 2X gain in photosensitivity.

Introduction

Improvement in the basic photosensitivity of silver halide materials continues to be a goal pursued by photographic researchers. While the electron created by photoexposure of AgX is directly used in the formation of the latent image, the photohole is generally agreed to be a source of inefficiency.[1] Recombination of the hole with the electron is one loss pathway; regression of the latent image by reaction with the hole is another. Consequently, pursuit of novel processes that irreversibly destroy the hole represents a pathway for improving photoefficiency. If processes can be designed such that the destruction of the hole leads to injection of an electron into the AgX conduction band, significantly improved photoefficiency can be expected.

We have developed a class of compounds, fragmentable electron donors (FEDs), designed to capture the photohole and then undergo a bond fragmentation reaction to give a neutral radical and a stable cation.[2-5] This irreversible reaction removes the hole from the latent image

formation cycle. In favorable cases, termed fragmentable two-electron donors, the radical created is sufficiently reducing that it injects an electron directly into the silver halide conduction band. In effect, the chemical energy stored in the bond has been used to convert the hole into a conduction band electron, yielding two conduction band electrons for each absorbed photon.

The sequence of photoinduced reactions for a fragmentable two-electron donor X–Y at a dyed AgBr interface can be summarized as follows:

First electron in C.B.:   (1)

$$AgBr/dye/X\text{–}Y + h\nu \Rightarrow AgBr/dye^*/X\text{–}Y \Rightarrow e^-_{CB} + AgBr/dye^+/X\text{–}Y$$

Oxidation of X–Y: (2)

$$AgBr/dye^+/X\text{–}Y \Rightarrow AgBr/dye/X\text{–}Y^{\bullet+}$$

Bond fragmentation: (3)

$$AgBr/dye/X\text{–}Y^{\bullet+} \Rightarrow AgBr/dye/X^{\bullet} + Y^+$$
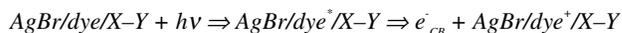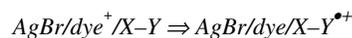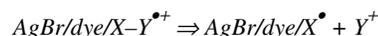
Second electron in C.B.:   (4)

$$AgBr/dye/X^{\bullet} \Rightarrow e^-_{CB} + AgBr/dye/X^+$$
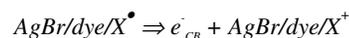
Energetic, Kinetic and Structural Requirements

In order to meet the energetic and kinetic requirements for this two-electron sensitization scheme, three criteria must be satisfied:

(i) the oxidation potential E1 of the electron donor X–Y must be low enough to allow it to capture a hole from the AgX valence band or from an adsorbed sensitizing dye.

(ii) the bond fragmentation reaction of the radical X–Y$^{\bullet+}$ must be fast enough to outrun competing reactions that consume the radical

(iii) the electrochemical potential E2 of the resultant neutral radical X$^{\bullet}$ must be negative enough that transfer of an electron to the AgX conduction band is energetically favorable

Of these thermodynamic and kinetic requirements, the reducing power of the radical X$^{\bullet}$ is the most difficult to

meet. Of the radicals that were previously studied by various transient techniques, those with heteroatoms in the α positions were found to be the strongest reducing agents.[6,7] Specifically, α-amino radicals were found to have oxidation potentials in the necessary range of ca. – 0.9 V, the estimated potential threshold corresponding to the AgBr or AgBrI conduction band. This observation suggested that the radical cations of amines were likely to be the best candidates for X–Y$^{\bullet+}$.[6]

A number of known fragmentation reactions of radical cations were considered for X–Y$^{\bullet+}$, including decarboxylation, desilylation, C–C bond cleavage, and deprotonation. Of these, it seemed that decarboxylation might be the most useful, both because this reaction appeared to be fairly efficient for amine radical cations, and because of the ready access to carboxyl substituted amines.[8] The only potential problem with the use of amines is that they should not be protonated under the aqueous conditions of silver halide photography. This final requirement precludes the use of simple aliphatic amines.

Experimental Section

Details of the syntheses of the compounds, the electrochemical measurements, and the flash photolysis measurements have been previously published.[2-5] Photo-EPR spectra at 9.3 GHz were measured on a Bruker ESP 300E spectrometer fitted with a helium gas-flow cryostat. *In situ* irradiations were performed with the output of a 200 W super pressure Hg/Xe light source passing through a combination of a 1/8 m monochromator and appropriate interference and long-pass filters.

The photographic data reported here used simple black and white format coatings, exposed at 365 nm, and processed in Kodak Rapid x-ray developer. The emulsions studied included a 1.2 μm by 0.12 μm AgBrI tabular emulsion (4.05% total I with a central 1.5% I region and higher iodide in the perimeter), an AgBr cubic emulsion with a cubic edge length of 0.52 μm, a doped AgBr cubic emulsion with a cubic edge length of 0.11 μm (used for the EPR experiments), and an AgBr octahedral emulsion with an octahedral edge length of 0.45 μm. In some cases, the antifoggants 2,4-disulfo-catechol and/or tetraazaindene were added to the coating melt before addition of the FED compounds. The samples used for EPR measurements were in the form of degelled powders produced by standard techniques.[9]

Solution Studies

In designing compounds for use as fragmentable electron donors, it has been important to have methodologies to measure whether compounds of potential interest, in fact, met the criteria defined above. Measurements of the oxidation potential of the parent electron donor X–Y can, in principle, be approached by standard electrochemical techniques. However, the fast fragmentation reactions of the radical cations X–Y$^{\bullet+}$, while desirable for the electron hole separation at the dye/silver halide interface, make an exact experimental determination of the formal oxidation potentials of the X–Y molecules difficult to obtain. Such fast follow-up reactions usually lead to significant shifts in the peak potentials to values lower than the formal potentials. Nevertheless, the peak potentials can serve as a guide for rank ordering potentials of related compounds and were extensively used in our efforts to identify desirable structural variations. In addition, we obtained upper limits for the oxidation potentials of the various classes of compounds from measurements of structurally related compounds that could not fragment.

For determination of the rate of fragmentation of the radical cations X–Y$^{\bullet+}$ and the energetics of the resulting radical X$^{\bullet}$, transient optical absorption spectroscopy and an "energy bracketing" approach was used. In this scheme, the compound X–Y is oxidized by an electron transfer reaction initiated by a short laser pulse. The resulting X–Y$^{\bullet+}$ radical undergoes the bond fragmentation reaction to give the radical X$^{\bullet}$. X$^{\bullet}$ is then allowed to interact with various electron acceptor compounds of known reduction potential. The ability of X$^{\bullet}$ to reduce a given electron acceptor compound indicates that the oxidation potential of X$^{\bullet}$ is nearly equal to (or more negative than) the reduction potential of that electron acceptor.

Specifically, electron transfer between an optically excited acceptor, A, and a high oxidation potential donor acting as a cosensitizer, C, was used to form separated "free" radical ions, A$^{\bullet-}$ and C$^{\bullet+}$, at a high efficiency. Most studies were carried out using 9,10-Dicyanoanthracene, DCA, as A and biphenyl as C. The reduction potential of DCA is very close to the value of ca. –0.9 V, the electrochemical threshold corresponding to the silver halide conduction band. In a typical experiment, the DCA is optically excited by a nanosecond laser pulse and the initial photoinduced electron transfer from biphenyl to the DCA forms DCA$^{\bullet-}$, which is observed at its characteristic absorption maximum at 705 nm. In the presence of X–Y, which has a lower oxidation potential than C, secondary electron transfer occurs to generate free X–Y$^{\bullet+}$ in high yield. The X–Y$^{\bullet+}$ then fragments to give X$^{\bullet}$. A slow (ca. 1 μs) growth in adsorption is observed at 705 nm, due to reduction of a second DCA molecule by the X$^{\bullet}$. If this slow-growing absorption signal is equal in magnitude to the initially observed DCA$^{\bullet-}$ signal, every X$^{\bullet}$ has reduced a DCA molecule, indicating that the oxidation potential of X$^{\bullet}$ is more negative than −0.9 V. Consequently, these X$^{\bullet}$ radicals should presumably also be able to inject electrons into silver halide. If the oxidation potential of X$^{\bullet}$ was not sufficiently negative to reduce DCA, an estimate of its oxidation potential was obtained by using other cyanoanthracenes as acceptors.

For determination of the fragmentation rates of the oxidized donors X–Y, the scheme described above was used to produce the radical cations X–Y$^{\bullet+}$ and the time evolution of their optical absorption was followed in the visible region of the spectrum. In these experiments, the concentration of the X–Y parent and the DCA acceptor were adjusted to

minimize interference of the DCA$^{\bullet-}$ spectrum with the desired signal from the X–Y$^{\bullet+}$ radical cation. In cases where the fragmentation rates were either too fast or too slow to be conveniently determined at room temperature, the rate constants were measured as a function of temperature and the room temperature constant determined by extrapolation.

Photographic Studies

In parallel with the solution studies, photographic experiments were carried out to determine whether gains in sensitivity were obtained. The general structures of the FED compounds that were initially studied did not contain any moieties to promote adsorption to the silver halide surface. Consequently, these compounds were studied by adding them at relatively high concentrations to emulsion melts to assure that some molecules were close to the surface of the emulsion grains. Most of the screening studies were done on versions of emulsions with a sulfur chemical sensitization, which provided a reasonable starting sensitivity with essentially no fog. Table 1 illustrates data obtained on the undyed tabular AgBrI emulsion for one of the compound series. All three compounds have similar values E1, the peak potential for oxidation of the parent X–Y compound. These values indicates that the compounds can accept photoholes from the AgBrI valence band. Further, the X–Y$^{\bullet+}$ radical cations derived in each case have fragmentation rates k_{fr} that are quite rapid. However, the X$^{\bullet}$ radical formed after fragmentation of compound **1** has an oxidation potential E2 that is less negative than –0.4 V, well below the expected –0.9 V threshold value for the AgBrI conduction band, while compounds **3** and **5** give X$^{\bullet}$ radicals with values of E2 more negative than –0.9 V. The data clearly indicate that a larger speed gain is obtained with compounds **3** and **5**, lending support to the operation of the two-electron sensitization scheme in the silver halide environment.

$$Me_2N - \langle C_6H_4 \rangle - C(R_1)(R_2) - CO_2^-$$
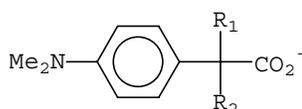
Table 1.

Cmpd	R1,R2	E1	E2	k_{fr}	Log rel sens
		(V)	(V)	(sec^{-1})	(365 nm)
None					1.00
1	H,H	0.53	>-0.4	4.3 x 10^4	1.06
3	OH, H	0.52	<-0.9	5 x 10^5	1.26
5	OH, Me	0.51	<-0.9	6.7 x 10^5	1.24

The effect of varying E1 on the photographic behavior of the FED compounds was examined for a variety of series, one of which is shown in Table 2. Figure 1 illustrates the sensitivity gains and fogs obtained for the members of this series, coated at a range of concentrations on the S sensitized, undyed AgBrI tabular emulsion. As can be seen from the figure, the FED compounds with the higher

oxidation potentials give a larger speed increase for a given amount of fog. Consequently, a more positive value of E1 is seen to be a generally desirable design characteristic for these compounds, as long as this value does not become so large that the compounds are no longer hole trapping with respect to the sensitizing dyes to be used in the system.

$$R_4 - \langle C_6H_4 \rangle - N(H) - CH(R_3) - CO_2^-$$
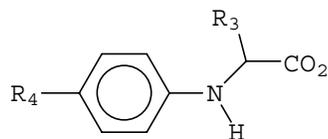
Table 2

Cmpd	R3	R4	E1
			(V)
24	Me	H	0.52
26	Me	Cl	0.51
30	CH$_2$CO$_2^-$	H	0.60
25	Me	CO$_2^-$	0.62
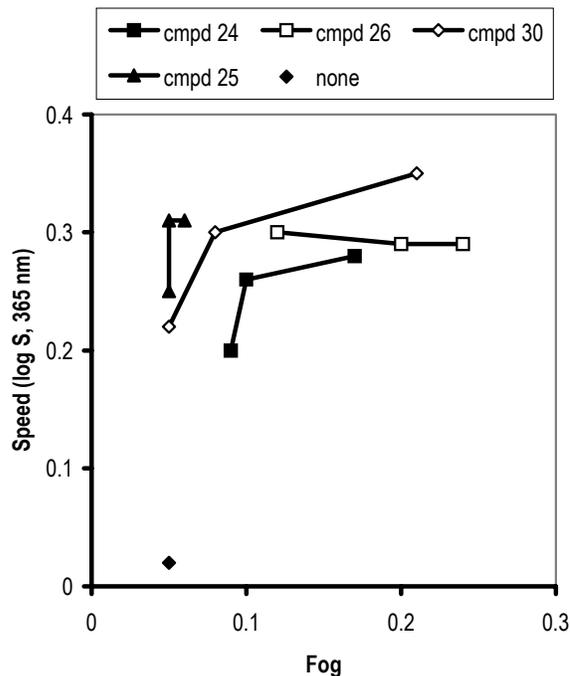
Figure 1. Speed vs fog for FEDs with varying E1

Having established the general structural properties required for parent FED moieties to give beneficial speed increases, a further goal of the synthetic team was to create FED molecules containing a group that would promote adsorption to the silver halide surface. Several different approaches were taken to accomplish this. Compounds were made where the FED moiety was attached to a sensitizing dye, utilizing a linking group attached to one of the nitrogens of the general cyanine dye structure. In addition, compounds were synthesized where the linking group was

attached to a molecule known to adsorb strongly to silver halide. Examples included a thiourea or a phenyl-mercaptotetrazole. Finally, it also proved possible to make compounds where the FED moiety was incorporated within the structure of the adsorbing molecule, as shown below for the FED compound PMT-6:
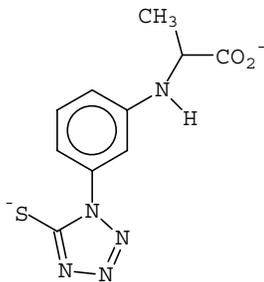
Figure 2 illustrates the photographic behavior obtained for a common FED moiety (shown in Table 3), linked to three different adsorbing molecules: a monomethine benzothiazole cyanine, a phenyl mercaptotetrazole, and a thiourea. The emulsion used for this evaluation was the 0.52 μm AgBr cube with a sulfur sensitization, dyed with the same blue-absorbing monomethine cyanine that is a component of the FED compound, DFED-8. (When DFED-8 was added to this dyed emulsion, a corresponding amount of the blue sensitizing dye was omitted.) As can be seen from the figure, all three of these adsorbable FED compounds give similar, large increases in photographic sensitivity for this emulsion. For comparison, DFED-8E, the nonfragmenting analog of DFED-8 where the carboxylate group on the FED moiety is replaced by the corresponding ethyl ester, was also added to the emulsion at varying levels. As expected, speed increases from the presence of this compound were very small.
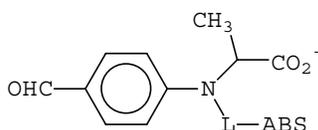
Table 3

Cmpd	ABS
DFED-8	Monomethine benzothiazole
PMT-3	Phenyl mercaptotetrazole
TU-3	Alkyl thiourea

The ability of appropriate FED compounds to give significant speed increases in the presence of green and red sensitizing dyes is shown in Fig. 3. This figure contains data for the FED compound PMT-3, added at various concentrations to the S sensitized AgBrI tabular emulsion dyed with typical blue, green, and red sensitizing cyanine dyes. As can be seen from the figure, significant sensitivity gains can be obtained for each of the dyed emulsions but this sensitivity increase is accompanied by some fog increases in the presence of the green or red dyes.
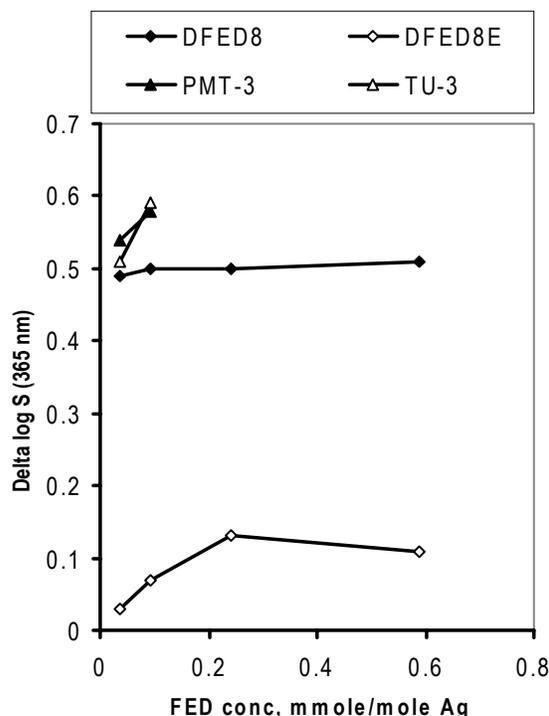
Figure 2. Speed gains with adsorbable FED compounds
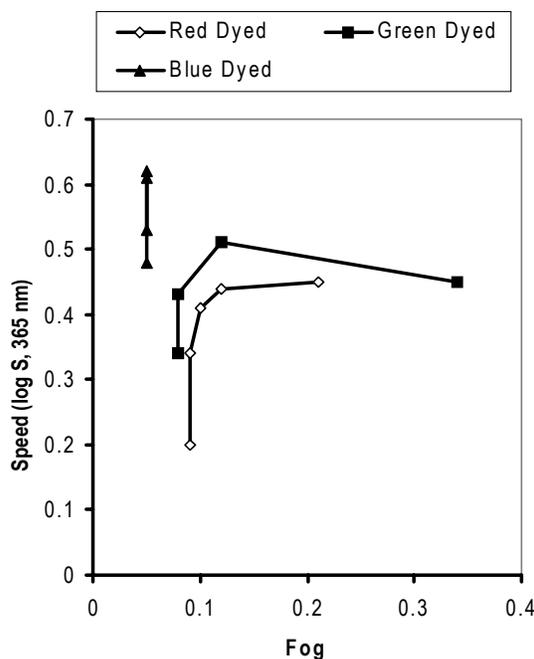
Figure 3. Speed v. fog for PMT-3 with various sensitizing dyes

Since the emulsions described above are not optimized for sensitivity (having only a sulfur sensitization), the question arises as to whether speed increases will be seen for the FED compounds when used in a highly efficient

emulsion. One such benchmark emulsion is the 0.48 μm octahedral AgBr emulsion that has been extensively used for studies of latent image formation mechanism and shown to have a quantum sensitivity of about 8 photons/grain when optimally sensitized with sulfur and gold.[10] Addition of the FED compound PMT-6 to an undyed, S + Au sensitized version of this emulsion was carried out and a sensitivity gain of 0.30 log units was obtained—exactly what would be expected if the expectation of two electrons for each absorbed photon was realized.

EPR Studies

Although the photographic data strongly suggests that the FED compounds can provide two-electron sensitization as envisioned in the mechanism given in Eqs. 1 to 4, it is not possible to prove from photographic data alone that the photoinduced reactions shown to take place in solution actually occur at the silver halide surface. To provide photophysical evidence of the mechanism in a silver halide system, we have utilized electron paramagnetic resonance techniques. For these studies, a small (0.11 μm) AgBr cubic emulsion was precipitated containing the known electron-trapping dopant, $[OsCl_5NO]^{2-}$. The trapping of electrons at this dopant can be monitored by the appearance of the characteristic low-temperature EPR signature of $[OsCl_5NO]^{3-}$.[9] The blue dye linked compound DFED-11 was added to the emulsion at roughly ½ monolayer coverage. (The structure of DFED-11 is identical to DFED-8 except that the phenyl ring of the aniline part of the FED moiety has a methyl instead of a formyl substituent. This structural change gives a lower oxidation potential E1 for the FED moiety in DFED-11 compared to DFED-8.) In addition, a control sample was prepared with DFED-11E, the nonfragmenting, ester version of DFED-11, added to the emulsion at the same surface coverage. When either sample at 8 K was illuminated in the EPR spectrometer with light absorbed by the blue dye, a signal corresponding to an organic radical and electrons trapped at the Os nitrosyl dopant was observed. These results indicate that excitation of the dye resulted in the production of electrons in the AgBr conduction band and a radical in the dye, probably localized on the aniline in the FED moiety. When the sample containing the nonfragmenting DFED-11E was warmed in the dark to 200 K, held briefly, and then recooled to 8 K, the spectrum of the organic radical did not change, while the spectrum of the electron trapped at the Os nitrosyl dopant shifted in a manner corresponding to a known change in geometry of this trapped electron center.[9] The overall integrated intensity of the total combined spectrum also did not change. When the sample containing DFED-11 was given the same temperature cycle, the overall integrated intensity of the EPR spectrum again did not change. However, in this case, the integrated intensity of the spectrum corresponding to the organic radical decreased dramatically, while the portion of the spectrum corresponding to the trapped electron at the Os nitrosyl increased by nearly 2X. This change in the distribution of the EPR signal indicates that the FED moiety fragmented at the higher temperature, producing the energetic radical that was destroyed when it injected a second electron into the AgBr conduction band.

Summary

Fragmentable two-electron donors represent a novel class of photographic sensitizers with the capability of doubling photographic sensitivity by producing two electrons for each photon absorbed by a silver halide emulsion grain. Synthesis of a large variety of these compounds, together with electrochemical and photophysical measurements, have been used to design compounds that can give significant speed increases in real photographic materials. Recent EPR measurements confirm that the two-electron sensitization scheme operates as envisioned at the silver halide surface.

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