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2001

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Repository Citation

Gould, I.; Lenhard, J. R.; Muentert, A. A.; Godleski, Stephen A.; and Farid, S., "New Approach to Silver Halide Photography Using Radical Cation Chemistry" (2001). *Chemistry Faculty Publications*. 5.
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Citation/Publisher Attribution:

Gould, I.; Lenhard, J.R.; Muentert, A.A.; Godleski, S.A.; Farid, S. New Approach to Silver Halide Photography Using Radical Cation Chemistry. *Pure Appl. Chem.* 2001, 73, 455-458. Available on publisher's site at: <http://iupac.org/publications/pac/>

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New approach to silver halide photography using radical cation chemistry*

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Abstract: A new mechanism for spectral sensitization of silver halide is described, which can potentially *double* the sensitivity of photographic emulsions. The photooxidized sensitizing dye is trapped using an organic donor molecule, which fragments to form a cation and a reducing radical, which injects an electron into the conduction band of the silver halide. In this way, two conduction-band electrons can be produced for each absorbed photon.

INTRODUCTION

The primary step in photography involves excitation of a sensitizing dye that is adsorbed to the surface of the silver halide crystal [1]. The excited dye injects an electron into the conduction band of the silver halide, which is trapped in the form of a metallic silver atom [1]. A single silver atom is unstable with respect to return electron transfer to the oxidized dye. With more photon absorption events, however, multiple electrons can be injected, and a cluster of silver atoms can form. A cluster as small as four silver atoms is stable and can function as a latent image [2]. In the development process, the latent image catalyzes a series of redox reactions resulting in reduction of the entire silver halide crystal and formation of millions of image dye molecules. It is this unique amplification process that distinguishes photography from other forms of imaging.

Despite the enormous inherent amplification, there remains a need for improvement in the sensitivity of silver halide materials. For example, the number of photons that are required to form the latent image is typically ca. 15–20, which means that most of the absorbed photons are wasted [3]. More efficient latent image formation would result in an overall increase in sensitivity without sacrificing grain size or other properties of the photographic emulsion. The standard approach to increasing photoefficiency of silver halide emulsions involves the addition of dopants to the silver halide crystal which trap the injected electrons, and thus minimize return electron transfer [4]. Much less attention has been paid to trapping the oxidized sensitizing dye to achieve the same effect. Here we describe a novel mechanism for increasing the photoefficiency of latent image formation based on trapping of the oxidized dye, two-electron sensitization, which has the potential for more than doubling the photosensitivity of silver halide emulsions.

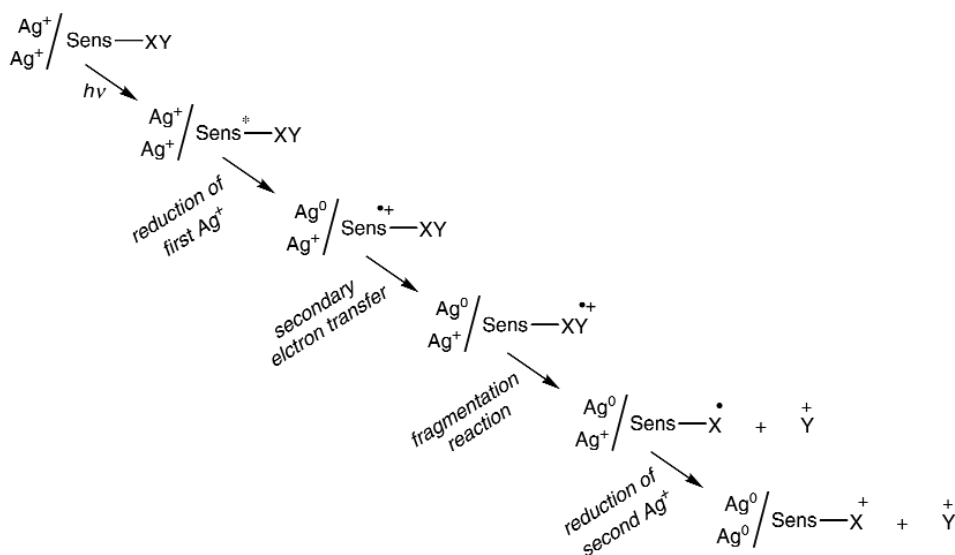
BASIC CONCEPT

In conventional photography, the oxidized sensitizing dye (Sens^{+}) can undergo return electron transfer in competition with latent image formation. The return electron transfer process wastes the photon ener-

*Lecture presented at the XVIIIth IUPAC Symposium on Photochemistry, Dresden, Germany, 22–27 July 2000. Other presentations are published in this issue, pp. 395–548.

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gy and reduces the overall photographic sensitivity. In contrast, the two-electron concept uses the chemical potential contained in the Sens^{*+} in a productive way. The concept is illustrated in Scheme 1. Excitation of the sensitizing dye as in conventional photography, results in formation of a reduced silver ion and the radical cation of the sensitizer, Sens^{*+} . In the two-electron sensitization scheme, an electron donor compound, X–Y, is added, which can reduce the Sens^{*+} to form the radical cation X–Y $^{*+}$. This reaction physically separates the oxidized species and the trapped electrons, and thus could slow return electron transfer. In photographic systems, however, return electron transfer may occur over many timescales, from fractions of seconds to days. Thus, it seems unlikely that this simple charge-separation process alone will be particularly beneficial. In the subsequent step, however, the X–Y $^{*+}$ undergoes fragmentation to form a radical X $^{\bullet}$ and a cation Y $^{+}$. If the cation Y $^{+}$ is sufficiently stable, return electron transfer can be endothermic and thus be essentially eliminated. Finally, if the X–Y molecule is properly designed, the radical X $^{\bullet}$ is highly reducing and can irreversibly inject another electron into the silver halide conduction band. In this way, *two* electrons can be injected into the silver halide for each absorbed photon.



Scheme 1

ENERGETIC, KINETIC, AND STRUCTURAL REQUIREMENTS

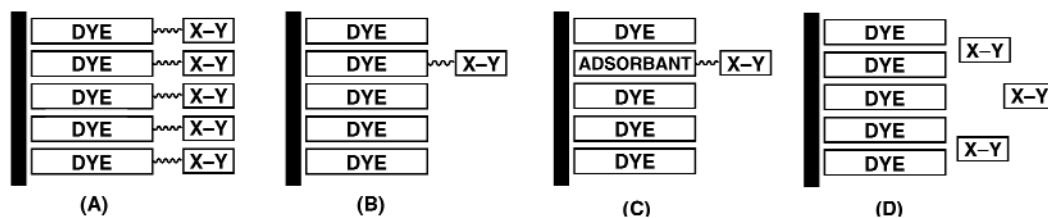
For the two-electron sensitization scheme to work, the X–Y molecule must satisfy three requirements. The first is that it must donate an electron to the oxidized dye. This is easily accomplished by ensuring that the oxidation potential of the X–Y molecule is lower than that of the sensitizing dye. For example, sensitizing dyes that absorb in the blue region of the spectrum typically have oxidation potentials around 1.4 V vs. SCE [5]. The oxidation potential should not be too low, however, since the compound might then be susceptible to oxidation by air or other adventitious oxidants. Also, X–Y compounds with low oxidation potentials may be unreactive and thus not meet the second requirement, which is that the X–Y $^{*+}$ be capable of undergoing fragmentation within a reasonable timescale to form a stable cation Y $^{+}$. The rate of fragmentation of the X–Y $^{*+}$ should be high enough so that it can react before being reduced by an electron donor in the matrix, or by return electron transfer from the silver halide. The timescales for these processes are not known, but it would seem reasonable that the lifetime of X–Y $^{*+}$ should be less than a millisecond. As discussed below, the most likely structure class for X–Y is an amine. Fragmentation reactions that have been reported for amine radical cations which take place on various

timescales include deprotonation, desilylation, decarboxylation, and carbon–carbon bond cleavage [6]. Importantly, these different reactions occur via different mechanisms, and respond to external conditions such as solvent polarity, nucleophilicity, and basicity in different ways. This suggests that a range of different X–Y molecules could be used, and that the reactivities of these molecules can be manipulated to suit the conditions of the silver halide gelatin matrix.

The final requirement is that the X[•] radical should inject an electron into the conduction band of silver halide. Experiments with sensitizing dyes of varying redox potentials have shown that silver halide has an effective reduction potential of ca. –0.9 V vs. SCE [4b]. From this we can assume that if X[•] has an oxidation potential of –0.9 V or more negative, it will be capable of injecting an electron. Measurements of oxidation potentials for radicals have been reported by Griller and Wayner *et al.* [7]. Typical hydrocarbon radicals such as benzyl are not very reducing, having positive oxidation potentials (0.73 V vs. SCE). A significant increase in reducing power is obtained by the addition of an oxygen atom in the position α to the radical center. To lower the reduction potential to –1.0 V, however, the literature data suggest that a nitrogen atom has to be present in the α position. α -Amino radicals are highly reducing because the products of their oxidation are the very stable iminium ions. To generate an α -amino radical, the molecule X–Y should clearly be an amine. The pK_a's of most aliphatic amines are typically in the range of 9–10, whereas those for aromatic amines are lower, typically 3–4 [8]. At the pH of the gelatin medium (ca. 5.5) [9], most aliphatic amines will be protonated, which suggests that the amine should be aromatic.

BINDING MODES

For the X–Y molecule to be effective, it should be physically located close to the silver halide surface, so that it can reduce the oxidized dye and inject the second electron. This could be accomplished in several ways, as illustrated in Scheme 2. The X–Y molecule could be covalently attached to each dye molecule (A). Electron transfer between moieties separated by a few atoms has been shown to be quite efficient and can occur in picoseconds [10]. Trapping of the oxidized dye should occur with very high efficiency under these conditions. Alternatively, the X–Y molecule could be attached to only a few of the dye molecules, (B). In this case, the “hole” on the oxidized dye has to migrate among the dyes until it arrives at the one with the X–Y, where rapid electron transfer to form X–Y^{•+} would occur. This scheme has the advantage that most of the sensitizing dyes are “conventional”, and need not be subject to the synthetic procedure required for the linked molecules. Additionally, less disruption of dye aggregation by the attached X–Y groups may occur. Also, because it would be present in sufficiently low concentrations, the dye to which the X–Y is linked need not be identical to the other sensitizing dyes. In a third scheme (C), the X–Y is covalently attached to a compound that adsorbs to the surface of the silver halide crystal. This scheme also relies on hole hopping, but has the advantage that the X–Y compound is not attached to a light absorbing molecule. Finally, the X–Y molecule can simply be added at relatively high concentration (D), with the assumption that the molecule itself will adsorb sufficiently to the surface of the silver halide, or that it will be present at a sufficiently high concentration so that electron transfer to the oxidized dye can take place.



Scheme 2

SUMMARY

A fundamentally new mechanism for spectral sensitization of silver halide is proposed which has the capability of delivering two conduction-band electrons per absorbed photon. The scheme uses an organic electron donor compound X–Y which must meet the following criteria: 1) the oxidation potential must be lower than that of the sensitizing dye, 2) the radical cation of X–Y must undergo fragmentation with a faster rate than those of competing electron-hole recombination reactions, 3) the oxidation potential of the radical X^{*} must be more negative than the effective electrochemical potential of the silver halide conduction band, and 4) the pK_a of the X–Y compound must be such that at the pH of the gelatin medium, it is not protonated.

Details of the thermodynamic and kinetic properties of X–Y compounds which meet these requirements and can be used in the two-electron sensitization scheme, together with photographic evaluations of their effectiveness, are given elsewhere [11].

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