Pure & Appl. Chem., Vol. 49, pp. 353-356. Pergamon Press, 1977. Printed in Great Britain.

AROMATIC ALDEHYDE-LEUCO DYE PHOTOXIDATION

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Abstract - Tris(dimethylaminophenyl) methane leuco dyes undergo rapid photoxidation together with aromatic aldehydes. Quantum yields for dye formation in film media are ~750. A practical photoimaging system based on this chemistry was developed. The chemical aspects of sensitization, achievement of dark stability, and the rendering of the films photo-insensitive after imaging are discussed.

The conventional estimate of the amplification achieved in the development of an exposed grain of silver halide is of the order of 10^9 atoms of silver per quantum of light. Few free radical chain reactions have chain lengths near that number and one that does ($H_2 + Cl_2$) has to date resisted practical application in a photoimaging mode.

Thousands of ideas of utilizing light to cause the recording of information have been investigated. No known non-electronic practical system to date has achieved the speed of silver halide photography, although many commercially important systems - photopolymerization, photo insolubilization, dye imaging, electrostatic and magnetic toning - have been realized.

This work represented an attempt to obtain a fast photoimaging system by coupling two types of amplification: the optical density of a photochemically formed dye, in a chain reaction process. The photoxidation of aromatic aldehydes in the presence of oxidizable leuco dyes has been investigated. In addition to establishing the chemistry which occurs, this paper will describe sensitization, dark reactions and dark stability, inhibition, oxygen effects, plasticization, and fixation (rendering photoinsensitive after exposure).

Aromatic aldehyde photoxidation has long been known as a free radical chain reaction since the work of Backström (Ref. 2). The long chain length (10^4) and the operability in air make this an attractive reaction for use in a photoimaging system. The chain carrying steps of the oxidation are generally accepted:

$$R-\overset{\overset{O}{\parallel}}{C}\cdot + O_2 \longrightarrow R-\overset{\overset{O}{\parallel}}{C}-O-O\cdot$$

$$R-\overset{\overset{O}{\parallel}}{C}-O-O\cdot + RCHO \longrightarrow R-\overset{\overset{O}{\parallel}}{C}-O-OH + R-\overset{\overset{O}{\parallel}}{C}\cdot$$

We thought it likely that a reduced leuco dye could participate in the oxidation and, perhaps, form dye with the same quantum yield. When a benzene solution of benzaldehyde and leuco crystal violet is irradiated in air, dye is formed in an exceptionally fast photochemical reaction.

$$\text{ØCHO} + (Me_2N\text{-}C_6H_4)_3CH \xrightarrow[h\nu]{O_2} (Me_2N\text{-}C_6H_4)_3C^+ + \text{ØCO}_2^- + H_2O$$

Most of what follows deals with the transfer of this chemistry to a film matrix, the optimization of variables such as photospeed and dark stability, and the attempt to obtain a detailed understanding of the chemistry involved.

For reasons to be discussed we arrived at a system containing 4-formylphenoxyacetic acid, benzophenone, diisopropylethyl amine, a hexaarylbiimidazole (HABI) photoinitiator, 3-chloro-4-dimethylaminophenyl-bis-(4-dimethylaminophenyl)-methane, a sodium salt of ethylene-diamine tetraacetic acid and tricresyl phosphate in a cellulose acetate butyrate binder. This composition was coated on paper or plastic film to give photosensitive materials.

Upon light exposure these systems achieved an optical density of 1.0 at an incident energy of $50 \mu j/cm^2$. Discernible images were seen at $4 \times 10^{-3} \mu j/cm^2$. This is slow in photographic terms but is comparable in speed to commercially available dry silver systems. It means a quantum yield of dye formation of approximately 750 in the film-based medium.

Aldehyde

Changes in aldehyde structure caused changes in photoimaging speed by factors greater than 10^5. Aldehydes with multiple hydroxy or methoxy substituents actually slowed dye formation, a not surprising result since they are structurally similar to known antioxidants. Optimum results were obtained from 2,4-dichlorobenzaldehyde and ortho- and para-formylphenoxyacetic acids. The latter was chosen because of an occasional inhibiting impurity in the dichloro-benzaldehyde. The relative speeds of dye formation in solution generally paralleled relative speeds in polymeric film binders.

Binder

When one changes from a fluid organic solution to a viscous, polymeric film base, great changes in rates of chain propagation and termination occur. As one might expect, the dye formation reaction is greatly slowed. Speed can be partially regained by adjustment of relative concentration of reactants and by plasticization. Cellulose acetate butyrate was chosen as a film vehicle to contain the chemistry because of its known permeability to oxygen. Oxygen permeability may be unimportant, for imaging speeds in air and in oxygen were identical, but imaging occurred more rapidly in cellulose acetate butyrate than in any other binder investigated.

Plasticization

Photoimaging speeds are markedly affected by viscosity. One will probably never achieve solution photospeeds in condensed phases such as film bases, but plasticization of the film does help. Plasticizers which are inert to free radicals are useful in our system and tricresyl phosphate was normally used. The tertiary amine also functions as a plasticizer. Plasti-cizers do, however, cause a problem once a film is imaged. The dye is mobile and can diffuse causing loss of resolution. This can be overcome by insolubilizing the dye with a mordant or by removing plasticizers during the fixing process.

Sensitization

Most imaging systems involving free radical reactions operate in vacuum to avoid oxygen interference. Obviously this cannot be done with a photoxidation. Operating in air raises a problem, however, with most photoinitiators. The triplet states of aromatic ketones are rapidly quenched by oxygen. We have found that this can be obviated by the faster electron transfer from tertiary amines. Using benzophenone as initiator the addition of diisopropyl-ethylamine gave significant increases in photospeed. Similar increases in speed of photo-polymerization have been reported (Ref. 3).

The chemistry of photoinitiation by benzophenone and tertiary amines is well known and is known to be faster than oxygen quenching of benzophenone triplet (Ref. 4).

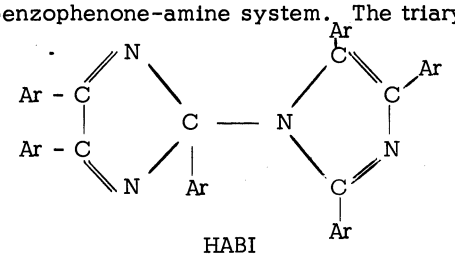
$$\emptyset CO\emptyset \xrightarrow{h\nu} \emptyset CO\emptyset^{*1} \longrightarrow \emptyset CO\emptyset^{*3}$$

$$\emptyset CO\emptyset^{*3} + EtN\underline{i}Pr_2 \longrightarrow \emptyset_2\dot{C}\text{-}\bar{O} + Et\overset{+\cdot}{N}\underline{i}Pr_2$$

$$\emptyset_2\dot{C}\text{-}\bar{O} + Et\overset{+\cdot}{N}\underline{i}Pr_2 \longrightarrow \emptyset_2\dot{C}OH + EtN\underline{i}Pr\,(\cdot C(CH_3)_2)$$

We confirmed the electron transfer mechanism by comparing imaging speeds with benzo-phenone and p-phenylbenzophenone (with the amine). While the former ketone has a $n\text{-}\pi^*$ triplet state, the latter has a $\pi\text{-}\pi^*$ triplet which abstracts hydrogen atoms at a rate 10^{-3} that of benzophenone (Ref. 5). We found identical imaging speeds with the two systems.

We achieved greater imaging speed by using hexaarylbiimidazoles (HABI) (Ref. 6) in addition to the benzophenone-amine system. The triarylimidazoyl radicals



HABI

obtained from HABI by photodissociation are known to undergo rapid hydrogen abstraction and electron transfer reactions (Ref. 7). Another important advantage of HABI in a viscous film medium is the slow rate of cage recombination of the radicals. Electron transfer from amine to the triarylimidazoyl radical followed by proton transfer is the probable mechanism in our system.

Dark Stability

Any satisfactory system must avoid color formation in the dark for at least six months to one year. We initially observed color formation in stored films arising from point sources. This suggested a catalytic reaction. The catalysis of autooxidation by transition metal ions is well documented (Ref. 8) and the deliberate addition of Co^{+2} accelerated color formation dramatically. We overcame this catalytic oxidation by adding a small amount of a metal sequesterant - the sodium salt of ethylenediamine tetraacetic acid.

Slow oxidation and color formation still occurred in the dark. The dark stability of leuco crystal violet alone in cellulose acetate binder is only approximately three months. This led to a study of substituent effects on the leuco dye. It seemed likely that only peroxy radicals were involved in the dark reaction while many different radicals (acyl, aminoalkyl, hydroxyalkyl) were involved in the photoimaging abstraction of hydrogen from the leuco triarylmethane dye. The two color formation reactions (dark vs. light) did respond differently to substituents on the leuco dye. Substitution with halogen atoms slowed both reactions, but the dark reaction was slowed to a much greater extent. The final choice (one meta-chlorine substituent) was a compromise between the two rates.

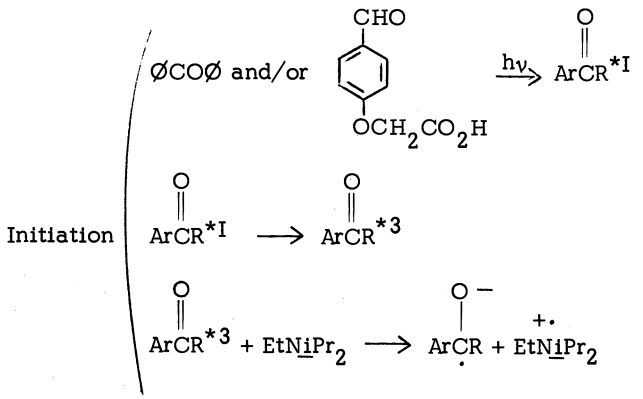
Fixing

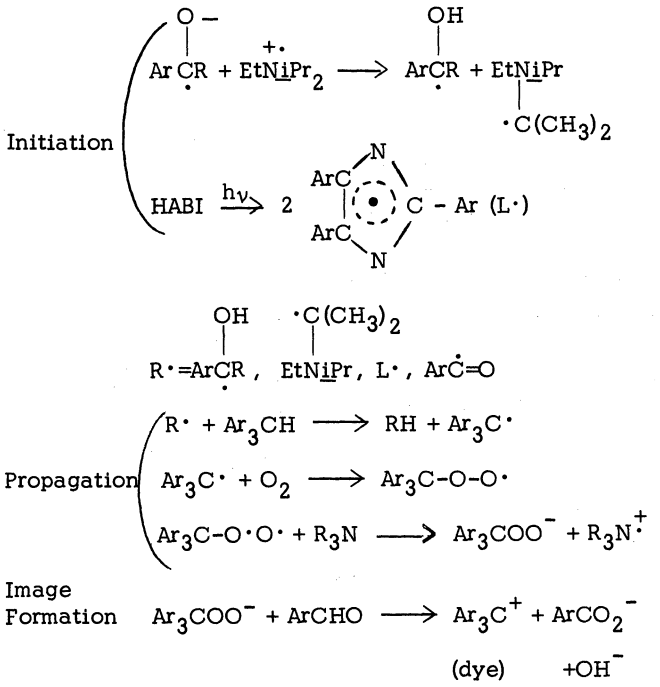
After photoexposure, films need to be made photoinsensitive. This can easily be done by immersing the exposed films in 1:1 hexane-toluene. Unoxidized leuco dye is extracted along with plasticizers. The resultant film is now not only photochemically inert, but the dye is immobilized and resolution is maintained.

For most practical applications wet processing is undesirable and completely dry methods of fixing are required. Our best method at this time is the application to our films of a wax topcoat which contains a free radical inhibitor such as a hindered phenol. After exposure the film is warmed to soften the wax and rolled to allow interpenetration of the two layers.

Mechanism

Our data to date are consistent with the following mechanism for image formation





It seems likely that the long-lived $Ar_3C\cdot$ radical picks up most of the oxygen. The triarylmethyl hydroperoxy radical, however, should be as reactive as any hydroperoxy radical and readily undergo electron transfer and hydrogen abstraction reactions. It is possible that $Ar_3C\text{-}OO\cdot$ is really $Ar_3C^+ + O_2^{\cdot-}$, but the details of image formation are unknown. Aryl carboxylate corresponding to the aromatic aldehyde was isolated in yields approximately that of the dye. Amine oxide has never been observed. The termination reaction is also speculative.

Conclusion

We have discussed several factors which are of importance in attempting to achieve a practical photoimaging system. The factors are obviously interrelated and one cannot solve one problem while sacrificing other necessary features. Changes made to effect dark stability almost certainly change photospeed. Compromises were frequently made.

The net result is a system which is fast in comparison with nonsilver systems, which has nearly molecular resolution, and which gives an image immediately on exposure. The system is operable in air and is not sensitive to changes in relative humidity. Acceptable dark stability and image stability have been achieved. The system has not been commercialized. Such a development would occur only if other technical problems were solved and if economic circumstances were favorable.

Acknowledgment

Dr. R. L. Ellis assisted in the optimization of the aldehyde and the leuco dye.

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