Pulse Radiolysis in Imaging Sciences: Silver, Silver Halides, and Other Clusters

Dan Meisel*

Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439

Pulse radiolysis has been utilized over the last three decades to study a variety of physical and chemical systems, including those relevant to imaging processes. In this overview, we outline the similarities between photolysis and radiolysis and highlight the differences. In particular, we focus on the time-resolved variants of the two disciplines: pulse radiolysis versus flash photolysis. The strength (and weakness) of the radiolytic techniques is their nonspecificity; the energy is always absorbed by the majority medium, the solvent and not the solute. Therefore, once thermalization occurs (<< 1 ps), the primary reactive intermediates are the same regardless of the solute. From this time on, the chemistry that follows is the chemistry of radicals, radical ions, excited states, metal ions at unstable oxidation state, and other reactive molecular products such as metallic and semiconductor clusters. Thus, radiation chemistry principles that were developed for one discipline are easily transportable to another. The pulse radiolysis technique with a wide arsenal of detection methodologies is currently used to identify short-lived intermediates and to determine their kinetic and thermodynamic properties. Together these studies provide mechanistic insight into the behavior of many chemical and physical systems. We demonstrate the utility of the approach in several areas of interest to imaging sciences, in particular, clustering of silver atoms, growth of silver halides, and medium effects on these systems. Other systems of relevance to imaging sciences include reactivity and redox potentials of quinone and one-electron reduced/oxidized dyes.

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Introduction

Imaging of wave packets of ionizing radiation, x-ray photons, and high-energy particles (such as electrons, protons, or heavier particles) is a subdiscipline of imaging science with its own requirements. This is not the subject of our discussion. Rather, we draw attention to the use of ionizing radiation to assist in unraveling details and mechanisms of imaging processes. Traditionally, one perceives the application of radiation chemistry mostly to the physical chemistry of conventional imaging, i.e., to silver photography. However, application of radiation chemistry to other materials and processes valuable in digital imaging is becoming more commonplace as the role of digital imaging grows. To understand the utility of the technique, we start with the basics of radiation chemistry and pro-

* IS&T Member

istry of imaging processes.

ceed with specific examples relevant to the physical chem-

Essentials of Radiation Chemistry

Only a brief description of the physical and chemical consequences of the deposition of ionizing radiation is possible here. The interested reader is referred to more complete texts on radiation chemistry in general^{1,2} and the pulse radiolysis technique in particular.^{3,4} The major distinction between the effects of UV/visible photons and ionizing radiation, usually γ radiation or high-energy (1 to 50 MeV) electrons, is the nonspecificity of the latter. The energy that each particle carries is sufficiently high to ionize many times any molecule that absorbs the radiation. Therefore, the medium absorbs most of the ionizing radiation while any solute (or dopant) that may be present at low concentrations absorbs only a negligible fraction of the energy. Contrast this with the absorption of visible photons, where trace amounts of a dye may exclusively absorb all of the incident light. At higher solute concentrations, the solute will appreciably absorb the energy but this "direct effect" will become significant only in the mole/ liter concentration range. The distribution of energy among the two components is proportional to the electron density of each.⁵ Therefore, from the density and total composition of the material, one can calculate the dose absorbed by each component.

Because the energy is absorbed predominantly by the medium, knowledge of the early events that follow the absorption of energy in the medium allows application to many and varied systems. Figure 1 illustrates the sequence of events that occurs following the deposition of energy in matter, using water as the most commonly studied solvent. An electron-hole pair is generated from the original particle (e.g., electrons at relativistic energies of several mega electron volts in a pulse radiolysis accelerator). A few tens of electron volts are delivered to the medium molecule in each such ionization event and that energy is transferred to the ejected electron, which may in turn cause one or, a few, more ionization events. The next ionization event caused by the same energetic electron occurs several thousand angstroms away from the previous event and each of these electrons creates a large number of ionizations. Thus, small volumes (~40 Å in diameter⁶) that contain fragmentation products are generated and they initially are well separated from one another. These volumes, labeled "spur" (or "tracks" for heavier particles), are the analog of the photochemical cage in a photolytic event.

The fate of the electron-hole pairs depends on the identity of the medium. In water, the hole dissociates to produce H^+ and the oxidizing OH radicals and the electrons thermalize and solvate within less than 1 ps. Although the precursors to the solvated electrons are beyond the

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Figure 1. Schematic illustration of the early events following the deposition of high-energy electrons in water.

direct observation of the current time resolution of pulse radiolysis (they were detected on photoionization, however^{7,8}), the efficiency of their reactions with various scavengers were determined.⁹ Within the first picosecond we thus obtain a thermalized, but spatially nonhomogeneous distribution of e^-_{aq} , OH, H, and H⁺ fragments, as well as the molecular products H₂ and H₂O₂. The production of H⁺ is significant because it may lead to changes in the original solution acidity if the solution pH was near neutral. Buffers may restore the pH to its original value but this process may take some time depending on initial pH and buffer concentrations.

Three processes now compete with one another as the system evolves toward equilibrium. The radicals in the spur may diffuse away from the original location of their production, they may react with one another, and they may react with solutes in the solution. Soon the identity of the spurs is lost as they expand and their product distribution homogenizes across the solution. Within 10 to 100 ns the distribution is homogeneous. At low (<10⁻² M) solute concentrations, the yield of the various fragmentation products has dropped to approximately one third of their initial yield and the yield of molecular products has doubled. For water, the consequences of the radiolysis at this time are summarized by Eq. 1:

$$\begin{array}{l} H_2 O \quad \Lambda \Lambda \Lambda_{\rightarrow} \\ e^-{}_{aq}(2.8), OH(2.8), H(0.6), H_2 O_2(0.5), H_2(0.5), H^+(2.8), \end{array}$$

where the numbers in parenthesis represent the yields in molecules per 100 eV of absorbed energy at the time that the spurs had homogenized.

Well-tested techniques have been developed over the years to convert this mixture into a solution of mostly oxidizing, or mostly reducing, radicals. Reactions 2 and 3 are most often utilized for this purpose. Reaction 2 converts hydrated electrons to the oxidizing OH radicals, and Reaction 3 converts the latter to the reducing organic radical, R:

$$N_2O + e^-_{aq} \xrightarrow{H^+} N_2 + OH,$$
 (2)

$$OH + RH \to R^{\bullet} + H_2O. \tag{3}$$

Examples of strong reducing radicals are $R = (CH_3)_2 C^{\bullet}OH$ or $C^{\bullet}O_2^{-}$ obtained from 2-propanol or formate, HCO_2^{-} , respectively. Sometimes it is preferable to convert the OH to an inert radical, often using RH = t-butanol. Substantial contributions to many systems of relevance to the chemistry of imaging were made using this technique such as the detailed information collected on the properties of semiquinones, nitrocompounds, and semireduced dyes.^{10,11}

Experimental Details

To study reactions of short-lived intermediates, an equivalent of flash photolysis, the pulse radiolysis technique was developed in the mid-1960s. The pulsed source is a linear accelerator, Bevatron, or Van de Graaff. At present, pulses of a few pico seconds are routinely used to generate >10⁻⁶ M radicals in aqueous solutions. At Argonne National Laboratory, a linear accelerator provides pulses of up to 21-MeV electrons that can be extracted in pulse widths of 5 ps to 10 µs to generate radical concentrations from 10^{-5} M to 2×10^{-2} M in aqueous solutions. Volumes of 1 to 10 ml are commonly used for irradiation but various arrangements provide great flexibility in the design of the experiment. Detection of intermediates is done by spectrophotometric absorption, emission, conductivity, electron paramagnetic resonance (EPR), or light-scattering techniques. In most institutions the experiment is completely interfaced to a computer for data acquisition and analysis. Volumes of quantitative data that were collected using these techniques have been compiled and provide a wealth of spectral,^{12,13} kinetic,^{14,15} and thermodynamic¹⁶ information on a large number of reactive intermediates.

Reduction and Clustering of Silver

Using the principles outlined above, the one-electron reduction of many metal ions has been investigated from the early days of pulse radiolysis. By far the most intensively studied is the reduction of silver ions.¹⁷ A silver ion is an attractive target because the one-electron reduction by e_{aq} (or a few other strong reducing radicals) cleanly generates the metal atom, Ag⁰. Early studies have identified the spectrum of monomeric Ag atoms in water¹⁸ and a more recent excursion to the same system has refined the value of its extinction coefficient and kinetic parameters.¹⁹ Because the one-electron reduction leads to the generation of metallic silver atoms, this reaction opens up an opportunity to study in detail the growth processes of silver clusters and the properties of the intermediates involved. Little doubt exists regarding the initial reactions and the identity of the early species. These are illustrated in Reactions 4 through 6:

$$Ag^{+} + e^{-}_{ag} \to Ag, \qquad (4)$$

$$Ag + Ag^+ \to Ag_2^+, \tag{5}$$

$$2Ag_{2}^{+} \to Ag_{4}^{2+} \to Ag_{3}^{+} + Ag^{+}.$$
 (6)

But, as the clusters grow and the system evolves away from the original starting state, identification becomes increasingly difficult, especially because the only characterization that is commonly utilized is spectrophotometric. Nonetheless, models to describe the growth processes, the spectral evolution of the intermediates, and the increase in the redox potential of the clusters, from -1.8 V for the atom eventually to 0.79 V for the large particles, have been suggested.²⁰⁻²⁸ Figure 2, taken from Ref. 29, shows the dependence of the redox potential of silver clusters on aggregation number. These were calculated from the



Figure 2. Redox potential of silver clusters as a function of the number of Ag atoms in the cluster (from Ref. 29).

enthalpy of sublimation of bulk silver and solvation energies of the various ions. For the larger aggregates, reduction by one-electron redox couples of known potential ($V^{-/o}$, e.g., viologens or $Cu^{2/1+}$) was used to determine approximate potential. As the clusters grow and their redox potential becomes more positive, the reference couple intervenes to reduce additional Ag⁺ ions (Reaction 7):

$$Ag_n + V^- \leftrightarrows Ag_n^- + V^o \tag{7a}$$

$$Ag_n^- + Ag^+ \to Ag_{n+1} \tag{7b}$$

net:
$$Ag_n + V^- + Ag^+ \hookrightarrow Ag_{n+1} + V^o$$
 (7)

The redox potential of the cluster, whose size is estimated from kinetic modeling, is then assumed to equal that of the reference couple.²⁰ Reaction 7a is similar to the charging reaction that was invoked in the electrochemical model for redox catalysis on metallic particles.^{30–32} The latter demonstrates the common principles that underlie energy conversion photocatalytic systems and imaging processes, which is a theme that has been emphasized in earlier meetings of this forum.³³

The nucleation growth of the cluster is often described as a diffusion-controlled process among all of the existing species in the solution.³⁴ Whereas this approach provides some insight into the dynamics of the process, its validity is sometimes questioned because of the uncertainty of the reacting species. In particular, the charge on the particle, Ag_n^{m+} , is often unknown and may affect the rate of reaction of various species, especially the charged ones, by orders of magnitude. Indeed, this is partially the reason for the strong dependence of the rate of the growth processes on ionic strength of the solution. In addition, specific complexation of the parent Ag⁺ ions, and perhaps its reduced products, will change the rate and energetics of the process significantly. The presence of local modifier concentrations such as polyelectrolytes,^{35,36} polymeric membranes,³⁷ micelles and crown ethers,³⁸ gelatin, or the surface of colloidal silica particles also affects the observed rate of the reduction as well as growth processes.^{39,40} Radiolytically initiated reduction and agglomeration of



Scheme 1. The effect of an interacting species L (a ligand, polymer, substrate particle, etc.): $\Delta E^{\circ} = \text{redox}$ potential of Ag^{+}/Ag , $\Delta E_{L} = \text{redox}$ potential of $\text{Ag}L^{+}/\text{Ag}L$, $\Delta G_{L}^{+} = \text{free}$ energy of complexation of the ion, and $\Delta G_{L} = \text{free}$ energy of complexation of the atom.

silver has also been studied in solid matrixes such as zeolites or low-temperature matrixes using primarily EPR detection. $^{41-44}$

The effect of medium and complexing agents on the reduction of silver ions and the growth processes that follow were studied soon after the observation of Ag^o atoms by pulse radiolysis.⁴⁵ Several generic questions may be asked in this situation: How does the complexation affect the kinetics of the reduction? Does the reduced species retain the same ligand? What is the stability of the reduced complexed silver atom and how fast does it lose its ligand, if at all? How does the presence of the ligand either on the ion or on the reduced atom affect the growth of clusters. Answers to these questions will depend on the specific ligand but several generalizations can easily be drawn.

The effects of the complexation on thermodynamic properties are quite predictable. Generally speaking, the interacting system tends to stabilize the ion more than the atom, therefore, the redox potential will become more negative in the presence of the interacting agent. This is illustrated in Scheme 1, where L is a chelating agent or any other interacting species such as a polymer, silica particle, etc.

Easily seen from the cycle of Scheme 1 is that the change in redox potentials will be equal to the difference in the free energy of the interaction (i.e., the stabilization energy) between the two oxidation states. From the cycle $\Delta G_L^+ - \Delta E_L = \Delta G_L - \Delta E^\circ$, and thus

$$\Delta E_L - \Delta E^o = \Delta G_L^+ - \Delta G_L. \tag{8}$$

Because stabilization of the ion is invariably larger than that of the atom, $\Delta G_L^+ < \Delta G_L$, the right side of the equation is negative, hence the redox potential of the complexed species is more negative than the "naked" couple. Often the reduction of AgL⁺ leads to its dissociation from *L* (the diagonal in Scheme 1), but the dissociation might be slow enough to allow the identification of AgL. Indeed, pronounced effects of *L* on the kinetics of the growth process were observed and these are very sensitive to the specific *L* and strongly depend on ionic strength. Studies of the effects of *L* = silica, gelatin, polyacrylate, and the chelates NH₃ and CN⁻ were reported. Solvation by a polar solvent will exert a similar effect and has been discussed by Belloni and colleagues.⁴⁶

The case of complexation by CN⁻ is interesting because a doubly negatively charged species is generated in that case from a singly charged ion (Reaction 9):

$$Ag^{1}(CN)_{2^{-}} + e^{-}_{aq} \rightarrow Ag^{o}(CN)_{2^{-}}.$$
 (9)

The thermodynamics of this system, and of the corresponding naked aqueous system, is shown in Scheme 2,



Scheme 2. Energy levels of the $Ag^{\scriptscriptstyle +\!/\!o}$ and $Ag(CN)^{2\cdot}_{2\cdot}$ in aqueous solutions taken from Ref. 47.

taken from a recent study by Remita, Mostafavi, and Amblard.⁴⁷ The ⁺¹ state is indeed more stabilized by complexation than the atom (1.22 and 0.41 eV, respectively). The ionization potentials according to this study are 2.7 and 1.9 eV for the hydrated species and cyanide complex, respectively, and thus their redox potentials are –1.8 and –2.6 V versus NHE, respectively. The latter is only slightly more positive than the redox potential of the hydrated electron (–2.9 V).

Henglein and coworkers studied the effect of various adsorbed nucleophiles on the spectral features of small silver clusters.^{17,48-51} The particles are commonly produced as a precolloidal suspension in water by radiolytic reduction (Reactions 1 and 3), but their size and charge at their surface is not precisely characterized. They probably all contain silver ions at their surface. The presence of nucleophiles, such as I⁻, SH⁻, or $C_6H_5S^-$, causes a red shift and broadening in addition to decreased intensity in the surface-plasmon band of the small particles. The reasons for this shift are not clear and may result from increased electron density on the particle or from complex formation at the surface. The more negative redox potential of the small particles can be utilized to reduce a variety of acceptors that cannot be reduced by bulk silver, including other metal ions.⁵²⁻⁵⁴ The external shell of a metal affects the absorption by the core particle, but a physical model to describe this effect is still to come.

Growth of Silver Halides

Another process that was studied using pulse radiolysis is the growth of silver halides from the molecular stage to the large particle.^{55,56} In these studies, halide ions, X^- in Reaction 9,

$$RX + e_{aa}^{-} \to X^{-} \tag{9}$$

$$Ag^+ + X^- \hookrightarrow AgX, \tag{10}$$

were radiolytically released by dissociative electron transfer into a solution containing silver ions. The ensuing growth of the silver halide particles, Reaction 10, was then followed using spectrophotometric, conductivity, and light-scattering detection techniques. Several notable points can be reiterated here. Just as the silver atoms and clusters discussed in the previous section lack the stabilization of the lattice energy that exists for the bulk, so do the halides. As a result, the molecule, AgX, is much less stable than the bulk material. Equilibrium constants for Reaction 10 were measured and are summarized in Table I. They were found to increase in the usual order, $I^- > Br^- > Cl^-$. However, for chloride, the equilibrium is strongly shifted to the left even at the relatively high Cl concentrations generated in the pulse (\leq mM concentrations, though).

The rate of the forward and backward reactions of Equilibrium 10 were measured and are also given in Table I. As expected, the forward reaction is diffusion controlled for all the halides. The dissociation reaction, however, changes among the halides and the rate of this reaction essentially controls the magnitude of the equilibrium. The inherent instability of the early nucleation species in the growth process creates a bottleneck in the dynamics of the evolution of the solid particles. Whether the mechanism of growth in the following steps is a monomer-aggregate or an aggregate-aggregate process, the small concentration of the early clusters hinders their further growth.

Another interesting point in studying the evolution of silver halide particles is the effect of size on their spectra.^{55,56} Early studies of the spectral changes with time, following the initiation pulse, revealed the quantum size effect on the energy of the transition. As the particles grow, their lowest excited state, or the bottom of their conduction band, continuously shifts to lower energy, asymptotically approaching their energy in the bulk. This is shown in Fig. 3 for the growth of AgI. At early times, <100 μ s after the pulse, various complexes of the Ag_mI_n group are formed and they all absorb at wavelengths shorter than 320 nm. A few hundred microseconds later, a well-defined exciton band appears. A similar band was also observed for the growth of AgI particles that were stabilized, and whose growth was slowed, by poly(ethyleneimine).⁵⁷ As time progresses and sizes increase, this band continuously shifts to lower energies and higher wavelengths. This is a manifestation of the now-well-documented quantum size effect on the electronic levels of the material. For larger particles, independent size determination using light scattering was feasible. From the absorption edge seen in Fig. 3, and using the Particle in the Box model developed by Brus and coworkers,^{58,59} the size of the particles could also be calculated from Eq. 11:

$$E = E_g + \frac{\hbar^2 \pi^2}{2R^2} \left[\frac{1}{m_e} + \frac{1}{m_h} \right] - \frac{1.8e^2}{\epsilon R},$$
 (11)

where m_e and m_h are the reduced masses of the electron and hole, respectively; R is the particle radius, E_g is the bandgap energy for the bulk material, and the rest of the signs have their usual meaning. Sizes obtained from light scattering agree quite well with those calculated from the absorption edge. Although the quantum-size silver halide particles can be stabilized (e.g., using polymeric stabilizers) and thereby become long-lived, relatively little research has been performed on them using radiolytic techniques. This is perhaps because the issues involved in these particles are of interest specifically to the silver photography community and less so to the radiation chemistry community. Nonetheless, it was shown that stabilization by poly(ethyleneimine) may drastically change the redox chemistry of the clusters.⁵⁷



Figure 3. Spectra of growing AgI particles in solutions containing $[Ag^+]_o = 1 \times 10^{-4} \text{ M}$ and $[I^-]_o = 2 \times 10^{-4} \text{ M}$. Note the continuous shift to lower energies as the particles grow with time.

Other Systems

Several other systems of specific interest in imaging sciences were studied using radiation chemistry techniques. The effect of gelatin in aqueous solutions on the rates of several radiolytically induced reactions was studied using pulse radiolysis.⁶⁰ Little effect of the increased macroviscosity on the rate of the reaction of OH radicals was observed when the concentration of the gelatin was increased. This led to the conclusion that local viscosity and connectivity among water channels within the gel network are not significantly affected even at high concentrations. Relevant to the development process in silver photography is the oxidation of hydroquinones. A large body of literature has accumulated on the one-electron reduction of guinones and the corresponding oxidation of hydroquinones. Spectra, redox potentials, and rates of redox reactions were collected using the pulse radiolysis technique.^{11,16}

Finally, radiolytic techniques are currently utilized in the pursuit of understanding the physics and chemistry of nanomaterials. The interest in these materials is not limited to imaging devices but includes a broad range of observations of significance in conventional as well as digital imaging. Many studies using pulse radiolysis have been reported on the reactions of small particles with various reactive intermediates usually in aqueous solutions. These include redox reactions on noble metal particles other than silver, on transition metal oxides, and on II-VI semiconductor particles.⁶¹ Often the question addressed is what are the consequences of the injection of excess charge into the particle? How does it affect the surrounding environment and how does it affect the particle itself? For many particles in aqueous suspension, excess charge in the particles leads to charge compensation by various counterions from the solution, notably protons. This can be studied by following changes in the ionic conductivity of the solution following the pulse. On the other hand, injection of electrons into chalcogenide particles often leads to a shift in the absorption edge of the particles. Henglein and colleagues were able to show that a single excess electron in a small particle of several hundred CdS molecules causes a complete bleaching of the absorption by all of the molecules of that particle.⁶² This amounts to a strong nonlinear optical effect in these materials. However, the explanation for this effect is still under debate in the literature.63-65

To summarize, the pulse radiolysis technique has been applied to a large number of colloidal (and, of course, molecular) systems, although not necessarily in the context of

TABLE I. Stability Constants and Rate Constants for the Formation of AgX in Aqueous Solutions. Reaction 10 was Initiated Pulse Radiolytically Using Dissociative Electron Attachment, Reaction 9. The Constants were Determined by Following the Conductivity Changes in the Solution.⁵⁶

Halide	<i>K</i> , M ⁻¹	<i>k</i> _f , M ⁻¹ s ⁻¹	<i>k</i> _b , s ^{-1*}	
AgCl	$2.0 imes10^3$	$\sim \! 2.0 imes 10^{10\dagger}$	$9.1 imes10^6$	
AgBr	$2.9 imes10^4$	$1.3 imes10^{10}$	$4.6 imes10^5$	
Agl	$3.8\times10^{6\ddagger}$	$8.1 imes10^9$	$2.1 imes10^3$	

Calculated from the equilibrium, K, and rate constant k_{f} .

Assumed based on results from the other halides.

From A. E. Martel, and R. M. Smith, *Critical Stability Constants*, Plenum Press, N.Y., 1982.

imaging technologies. The mechanism of redox catalysis on noble metal particles, the mechanism of oxidative degradation of organic pollutants, the mechanism of growth of II– VI materials, the effects of charges on the electronic energy levels in semiconductor particles, and the fundamentals of electron-transfer processes among particles were all issues addressed with this technique. Clearly, the technique could be further utilized in imaging sciences, in particular, in the study of interfacial processes.

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