

Applications of Pulse Radiolysis to Imaging Sciences

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Abstract

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 review, 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, flash photolysis vs. pulse radiolysis. The strength (and weakness) of the radiolytic techniques is their nonspecificity; the energy is always absorbed by the solvent not the solute. Radiation chemistry principles that were developed for one discipline are easily transportable to another. The pulse radiolysis technique with a wide arsenal of detection techniques 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 physical systems. We demonstrate the utility of the approach in several areas of interest to imaging sciences: clustering of silver atoms, growth of silver halides, and medium effects on these systems.

Introduction

Imaging packets of ionizing radiation, X-ray photons, or high-energy particles - electrons, protons, or other energetic particles, is a subdiscipline of imaging science with its own difficulties and 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 the imaging processes. Traditionally, one perceives the application of radiation chemistry mostly to conventional imaging, e.g., silver photography. However, its application to other materials and processes that become valuable in digital imaging is becoming more commonplace as the role of the latter grows. To understand the utility of the technique, we start with the basics but the interested reader is referred to more complete texts.¹

Radiation Chemistry

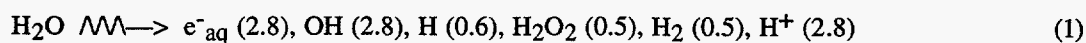
The major distinction between the effects of UV/visible photons and ionizing radiation, usually γ radiation or high-energy (1-50 MeV) electrons, is the nonspecificity of the latter. The energy in this radiation is sufficiently high to ionize many times any material that absorbs the radiation. Therefore, 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. Contrast this with the absorption of visible photons, where trace amounts of a dye may exclusively absorb all the incident light. Following the absorption act, however, the processes that ensue are very similar to those that occur in photolysis; mostly they lead to organic and inorganic radicals or metal ions at unusual oxidation states. To study the reactions of these short-lived intermediates, the equivalent of flash-photolysis, the pulse-radiolysis technique was developed in the mid-sixties. Today, ps pulses are routinely used to generate $>10^{-6}$ M radicals in aqueous solutions. Detection of the intermediates is done by spectrophotometric absorption, emission, conductivity, epr, and scattering techniques. Volumes of quantitative data collected using these techniques have been compiled and provide a wealth of spectral,² kinetic,³ and thermodynamic⁴ information on a large number of reactive intermediates.

Because the energy is absorbed predominantly by the medium, knowledge of the early events that follow the absorption of the energy in the medium allow application to many systems. In water, the consequences of the radiolysis are summarized in Eq. 1, where the numbers in parenthesis represent the yields in molecules per 100 eV of absorbed energy.

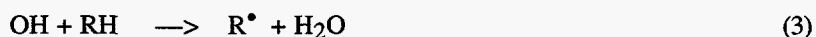
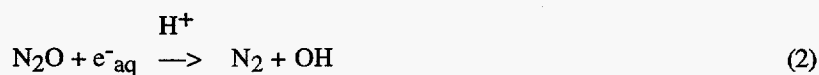
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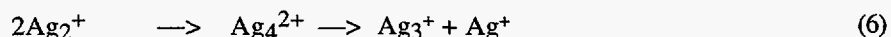
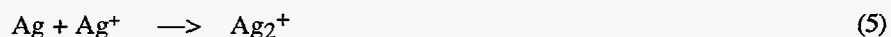
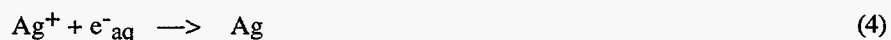


As in photolysis, equivalent amounts of oxidizing and reducing species (electrons and holes) are generated initially. In water, within less than a ps they include mostly OH and e^-_{aq} . However, well-tested techniques have been developed over the years to convert this mixture into a solution of either only oxidizing, or only reducing, radicals. Reactions 2 and 3 are most often utilized for this purpose. Reaction 2 leads exclusively to oxidizing radicals (OH) and Reaction 3 to reducing radicals, e^-_{aq} , and an organic reducing radical, R. Examples of strong reducing radicals are $\text{R} = (\text{CH}_3)_2\text{C}^{\bullet}\text{OH}$ or CO_2^- obtained from 2-propanol or formate, HCO_2^- , respectively. At times it is preferable to convert the OH to an inert radical, often using $\text{RH} = \text{t-butanol}$. In the following, we demonstrate the application of pulse radiolysis to fundamental questions relevant to silver photography. However, substantial contributions were made using this technique to many other issues of imaging, such as the detailed information collected on the properties of semiquinones and semireduced dyes.



Reduction and Clustering of Silver

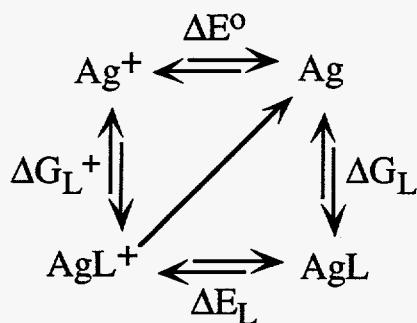
Using the principles outlined above, the one-electron reduction of many metal ions has been investigated. By far the most intensively studied is the reduction of silver ions.⁵ Because the one-electron reduction leads to generation of metallic silver atoms, this reaction opens up an opportunity to study in detail the growth processes of silver clusters and the properties of the intermediates involved. There is little doubt regarding the initial reactions and the identity of the early species. These are illustrated in Reactions 4-6. But, as the clusters grow and the system evolves away from the original starting materials, identification becomes increasingly difficult, especially because the only characterization that is available is spectrophotometric. Nonetheless, models to describe the growth processes, the spectral evolution of the intermediates, and the increase in the redox potentials of the clusters, from -1.8 V for the atom to 0.79 V for the large particles, have been described.



Current efforts focus on the effects of the medium and complexing agents on these processes. The thermodynamic effects are easy to predict. Generally speaking, an 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 particles, etc. It is easily seen from the cycle of Scheme 1 that the change in redox potentials will be equal to the difference in the free energy of the interaction between the two oxidation states: $\Delta G_L^+ - \Delta E_L = \Delta G_L - \Delta E^0$, thus:

$$\Delta E_L - \Delta E^0 = \Delta G_L^+ - \Delta G_L \quad (7)$$

Because the stabilization of the ion is larger than that of the atom, $\Delta G_L^+ < \Delta G_L$, the right-hand side of the equation is negative, hence the redox potential of the interacting 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 NH_3 and CN^- were reported.



Scheme 1: The effect of an interacting species.
L (a chelating agent, polymer, substrate particle, etc.).
 ΔE° = Redox potential of Ag^+/Ag .
 ΔE_L = Redox potential of AgL^+/AgL .
 ΔG_L^+ = Free energy of complexation of the ion.
 ΔG_L = Free energy of complexation of the atom.

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.⁶ In these studies, halide ions, X^- in Reaction 8, were radiolytically released by dissociative electron transfer into a solution containing silver ions. The ensuing growth of the silver halide particles 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 above 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 9 were measured and were found to increase in the usual order, $\text{I}^- > \text{Br}^- > \text{Cl}^-$. However, for the chloride, the equilibrium is strongly shifted to the left even at relatively high Cl^- concentrations generated in the pulse (sub mM, though). The rate of the forward and backward reactions of Equilibrium 9 were also measured. In all cases, as expected, the forward reaction is diffusion controlled. The dissociation reaction, however, changes among the halides and the rate of this reaction essentially controls the equilibrium. This inherent instability of the early species in the growth process creates a bottleneck in the dynamics of the evolution of the solid particles. Whether the mechanism of growth is monomer-aggregate or aggregate-aggregate processes, the small concentration of the early clusters hinders their further evolution.



Another point of interest in studying the evolution of silver halides is effect of size on their spectra. Early studies of the spectral changes with time, following the initiation pulse, revealed the quantum size effect on the energy of states. 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.

Conclusions

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

Acknowledgment

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References

1. a. Farhataziz and M. A. J. Rodgers, *Radiation Chemistry: Principles and Applications*, VCH Publishers, 1987.
b. R. V. Bensasson et al., *Flash Photolysis and Pulse Radiolysis*, Pergamon Press, 1983.
c. M. S. Matheson and L. M. Dorfman, *Pulse Radiolysis*, MIT Press, Cambridge, 1969.
2. A. Habersbergerova, Absorption spectra of intermediates formed during radiolysis and photolysis, *Rad. Res. Rev.* 1: 109-181 (1968).
3. a. G. V. Buxton et al., Critical review of rate constants for reactions of e-aq, H atoms and OH/O⁻ radicals in aqueous solutions, *J. Phys. Chem. Ref. Data* 17: 513-886 (1988).
b. P. Neta et al., Rate constants for reactions of inorganic radicals in aqueous solution, *J. Phys. Chem. Ref. Data* 17: 1027-1284 (1988).
4. P. Wardman, Reduction potentials of one-electron couples involving free radicals in aqueous solution, *J. Phys. Chem. Ref. Data* 18: 1637-1755 (1989).
5. a. A. Henglein, Physicochemical properties of small metal particles in solution: "microelectrode" reactions, chemisorption, composite metal particles, and the atom-to-metal transition, *J. Phys. Chem.* 97: 5457-571 (1993) and references therein.
b. J. Khatouri et al., Kinetics of cluster growth by aggregation, *Z. Phys. D* 34: 57-64 (1995) *ibid* 47-56.
6. a. K. Schmidt et al., Growth of silver halides from the molecule to the crystal. A pulse radiolysis study, *J. Am. Chem. Soc.* 110: 4882-4884 (1988), *ibid*, *J. Phys. Chem.* 93: 6100-6109 (1989).

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