

# The Kinetics of Silver Halide Conversion

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## Abstract

The reaction rate of halide conversion is dependent upon many factors, including the presence, method of addition, and concentration of many of the components used in silver halide precipitation and sensitization. We have studied the effect of many of these components on the reaction kinetics of halide conversion using a reflection spectrophotometric technique. The kinetics of halide conversion is a sensitive function of the source of halide, its solubility, the method of addition, and temperature. Halide sources include soluble halide salts, silver halides, and organic compounds that can act as halide releasing agents. The effect of grain size on halide conversion was also studied. Reaction rates for the halide conversion process can also be strongly influenced by the presence of ripeners, restrainers, and other common emulsion addenda.

## Introduction

Most photographic emulsions consist of mixed silver halide grains such as AgClBr, AgBrI, AgClI, or AgClBrI. These mixed halide grains and phases can be obtained by a variety of methods. Often, mixed halides are obtained by the introduction of a less soluble halide to a more soluble silver halide. This process is known as halide conversion<sup>1</sup>. Halide conversion is one of the most fundamental processes in the precipitation of silver halide emulsions. Particularly useful are silver halide grains which contain a heterojunction of different silver halide compositions<sup>2</sup>.

The conversion of AgCl to AgClBr, used extensively in color paper emulsions, has been studied by Sugimoto and Miyake<sup>3,5</sup>, and by Mydlarz<sup>6</sup>. These studies have suggested that conversion of AgCl to AgBr occurs by a multistep process comprising an initial reaction primarily at the corners of cubic AgCl emulsions, followed by a

(temperature dependent) slower process whereby the bromide rich phase spreads out over the faces of the substrate. These studies have been primarily based upon microscopic, diffraction, and electrochemical techniques.

In this work, we employ an *in-situ* spectrophotometric technique, which gives qualitative information about halide conversion rates. This technique allows halide conversion rates to be compared, and demonstrates the influence of other addenda on the conversion process.

## Experimental

Monodisperse AgCl and AgBr emulsions used in this study were prepared without organic ripeners using computer controlled double jet precipitation methods. The average grain size of the emulsions used were 1.0  $\mu\text{m}$  cubic edge length for AgCl, and 0.1  $\mu\text{m}$  cubic edge length for AgBr. Grain sizes distributions were determined by Electrolytic Grain Size Analysis<sup>7</sup>.

Spectral absorbances were determined using a Cary 100 UV/Vis spectrophotometer, equipped with a LabSphere DRA-300 Diffuse Reflectance integrating sphere. Spectra were typically obtained from 370-500 nm.

Reactions were conducted in a jacketed, controlled temperature vessel, and the emulsions were pumped through a 1 mm path length glass flow cell.

Tetramethyl thiourea (Acros Organic Chemicals, Fisher Scientific), 3,6-Dithia 1,8 octanediol (Acros Organic Chemicals, Fisher Scientific), and 4-Hydroxy-6-methyl-1,3,3a-tetraazaindene (Aldrich Chemical Company) were used as received.

## Results and Discussion

### Halide Source

The absorption behavior of AgCl and AgBr are well known<sup>8</sup>. The absorption edge of AgBr is at longer wavelength than that of AgCl. The absorption edge for mixed halides is intermediate between those of AgCl and AgBr.

The absorption spectra of a monodisperse 1  $\mu\text{m}$  AgCl emulsion and a 0.1  $\mu\text{m}$  monodisperse AgBr emulsion are shown in Figure 1. The concentration of AgBr used in this comparison was 5 mole % of the AgCl concentration. As expected there is very little absorption of the AgCl substrate at wavelengths  $> 425$  nm.

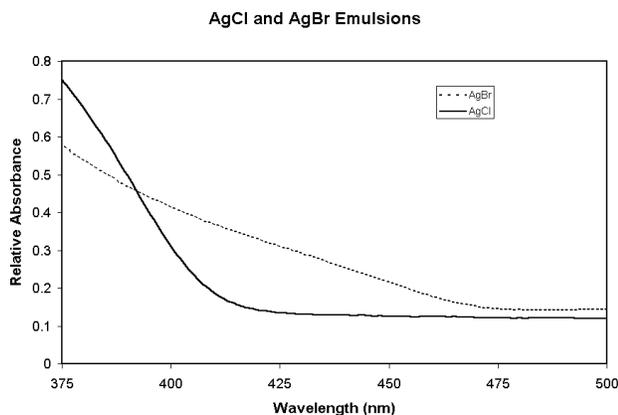


Figure 1. AgCl and AgBr

A variety of halide sources are commonly employed for halide conversion. Several different types were investigated in this study.

When source of soluble bromide (1 M KBr) is added to an AgCl emulsion, the bromide reacts very rapidly with the AgCl. Figure 2 shows the change in absorption behavior at 400 nm. A rapid increase in absorption at 400 nm is seen, followed by a much slower change. Since KBr does not absorb at 400 nm, this absorption increase is due to the rapid formation of AgClBr phases on the AgCl substrate. This absorption behavior is consistent with an initial rapid reaction of the KBr with AgCl, followed by a slower redistribution of the bromide rich phases over the surface of the grain.

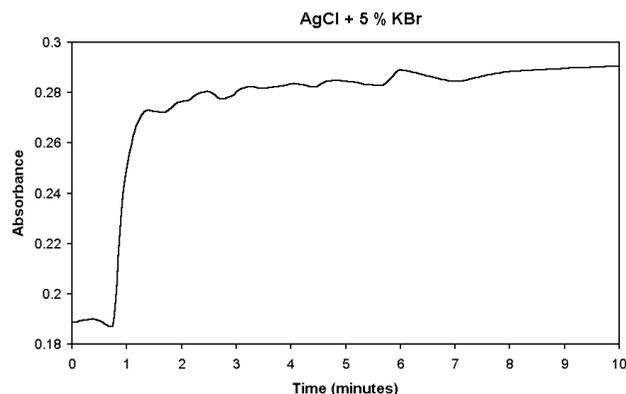


Figure 2. AgCl + KBr

As expected, the reaction of AgCl with AgBr occurs much more slowly. This can be seen in Figure 3, where a series of consecutive scans are plotted.

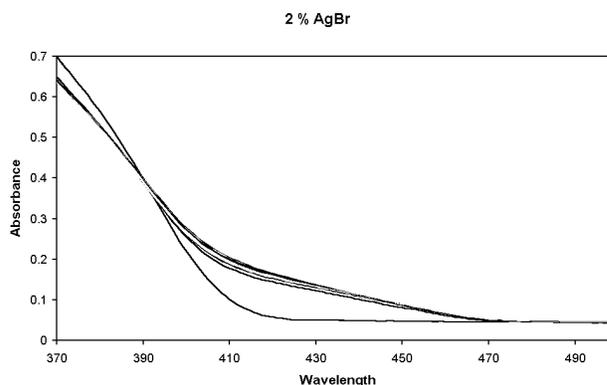


Figure 3. AgCl + AgBr

Similarly to the reaction of AgCl with KBr, soluble KI also reacts extremely rapidly. This is shown in Figure 4. The addition of even small amounts of KI to an AgCl emulsion causes very large absorption increases.

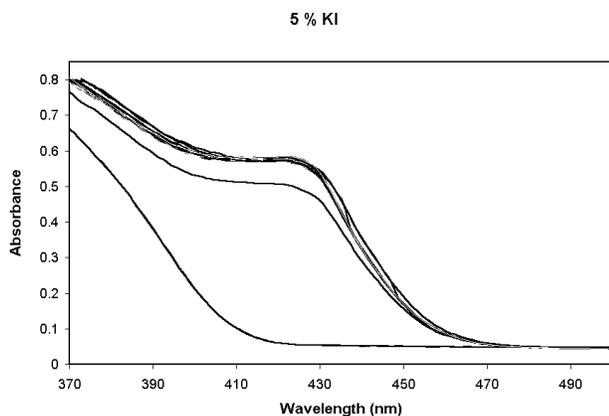


Figure 4. AgCl + KI

### Temperature

At 40 °C, the reaction of AgCl with AgBr is fairly slow. This can be seen in Figure 5, where the reaction of AgCl with AgBr at 40 °C and 70 °C are compared. At 40 °C, there is little additional absorption increase, over that caused by the addition of AgBr. At 70 °C however, there is a steady absorption increase, indicating reaction of the AgBr with AgCl. As seen in most other examples, the initial rapid reaction is followed by a slower reaction.

Temperature Series 400 nm

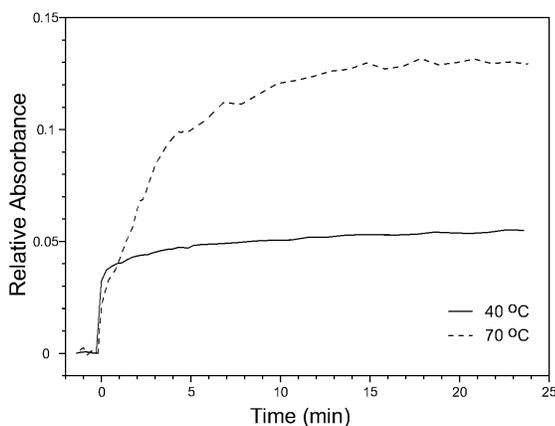


Figure 5. AgCl + AgBr, 400 nm

Interestingly, Figure 6 shows complimentary absorption behavior can be seen at 450 nm. At 450 nm, there is almost no absorption by AgCl. This suggests that the absorption at 450 is predominantly caused by AgBr. This suggests that the absorption profile at 400 nm qualitatively shows the formation of AgClBr, whereas the absorption profile at 450 nm shows the disappearance of AgBr. In this way, absorption profiles at two different wavelengths can be used qualitatively to monitor the rates of different processes. In this case, both the disappearance of reactants and the formation of products can be observed.

Temperature Series 450 nm

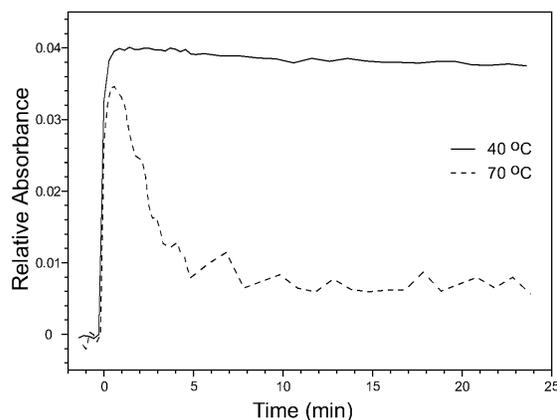


Figure 6. AgCl + AgBr, 450 nm

### Ripeners

The influence of chemical ripeners can have a marked effect on the rate of halide conversion. This is clearly shown in Figure 7, where the concentration of Tetramethyl thiourea (TMTU) is increased. As was observed before, little reaction of AgBr with AgCl occurs at 40 °C. In the presence of ripener, the rate of this reaction can be greatly increased. Similar behavior was observed with 3,6 Dithia 1,8 octanediol. The exact cause of this rate increase is not known, but could be due to the increased halide solubility, morphological changes, or both. Once again, complimentary behavior is observed at 450 nm (Figure 8).

Ripener 400 nm

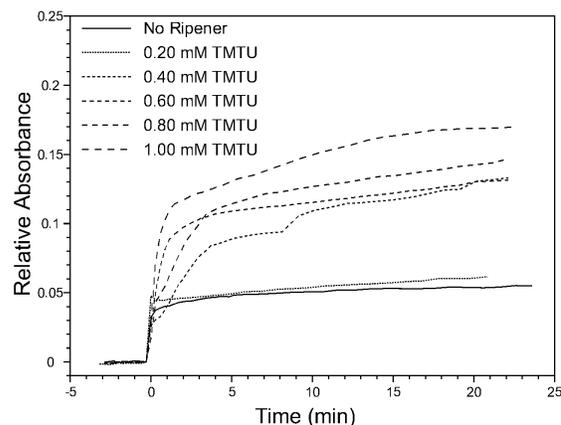


Figure 7. Ripener level series, 400 nm

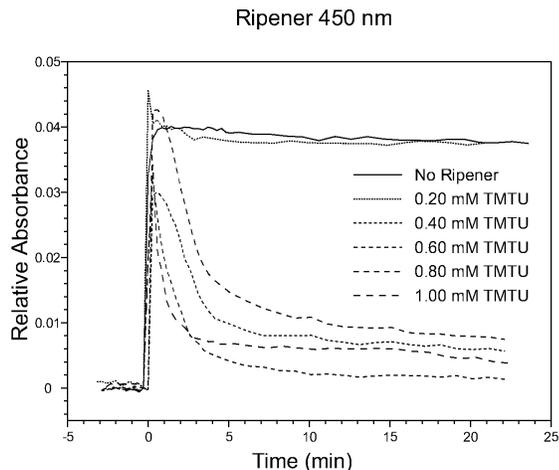


Figure 8. Ripener level series, 450 nm

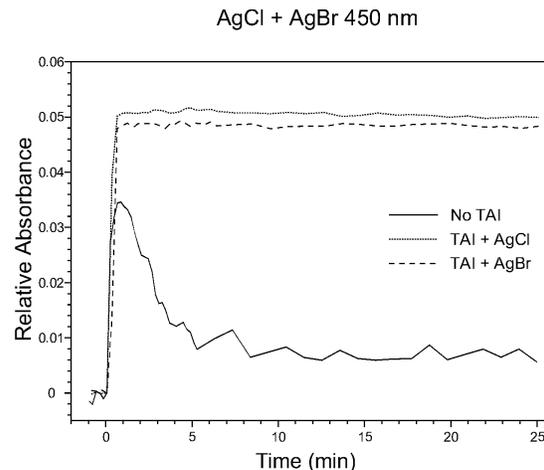


Figure 10. AgCl + AgBr + TAI, 70 °C, 450 nm

### Restrainers

Compounds which strongly adsorb to silver halide surfaces, can also greatly influence the rate of halide conversion. 4-Hydroxy-6-methyl-1,3,3a-tetraazaindene (TAI) is commonly used as an antifoggant and crystal growth restrainer<sup>9</sup>. When a monolayer of TAI is added to AgCl prior to the addition of AgBr, the reaction of AgBr with AgCl can be completely suppressed. This can be seen in Figures 9 and 10. SEM images of this emulsion mixture clearly shows the presence of both AgCl and AgBr crystals, confirming the reaction suppression. Furthermore, if a monolayer of TAI is added to the AgBr prior to addition of AgBr to AgCl, the reaction can also be completely suppressed. In this latter instance, much less TAI is required, since the molar amounts of AgBr are only a few percent of the amount of AgCl.

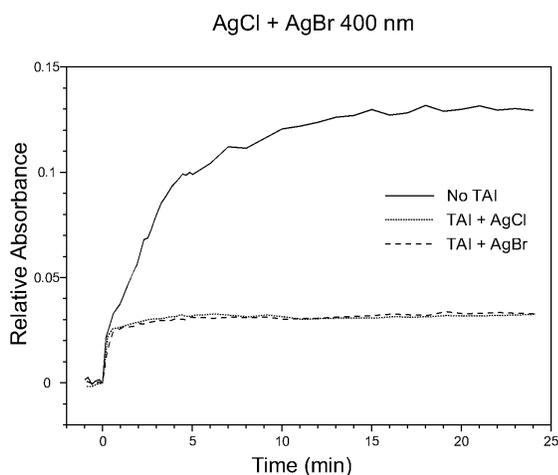


Figure 9. AgCl + AgBr + TAI, 70 °C, 400 nm

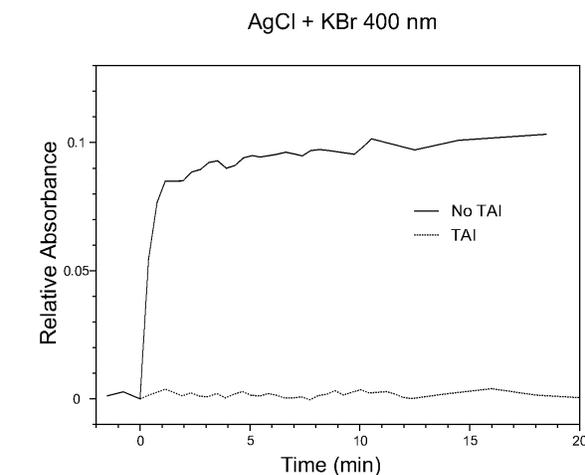


Figure 11. (AgCl + TAI) + KBr, 40 °C, 400 nm

## Summary

The halide conversion process was followed spectrophotometrically for a number of halide sources and addenda. For most conversion reactions, two processes were seen – a fast initial reaction followed by a slower reaction. Soluble halides like KBr and KI react extremely quickly with AgCl, whereas the relatively insoluble AgBr reacted much more slowly. The addition of various addenda greatly affected the halide conversion rate. Ripeners increased the reaction rate, whereas restrainers were able to completely suppress it.

## References

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