

Some Unexpected Observations in Cyclovoltammetric Investigations of Chromogenic Coupling

Peter Bergthaller
Agfa-Gevaert AG, Research & Development
Leverkusen, Germany

Ulrich Nickel
University of Erlangen-Nürnberg, Institut für Physikalische Chemie
Erlangen, Germany

1. The Coupling Reaction: Current View

The current view of chromogenic coupling as an electrophilic substitution of the coupler anion followed by either a dehydrogenation (in the case of the four-equivalent coupler) or the elimination of a leaving group (in the case of a two-equivalent coupler) describes dye yield mainly as the consequence of a stoichiometric relationship between coupler and available oxidized colour developer.

Poor dye yield is regarded as the consequence of insufficient reactivity of the coupler anion towards the quinone diimine formed at the developed silver halide. However, it must be taken into account that any step of the coupling process may be rate-determining, and deficits in dye yield may result from any kind of unrecognized shortage in the overall reaction.

Among the factors determining the size and density of the dye cloud forming around a developing silver halide grain the following are regarded as the most important ones.

- size of the silver halide grain,
- amount of available coupler,
- amount of Quinone diimine (QDI) formed in the course of development,
- desamination and sulfonation,
- rate of coupler deprotonation (formation of the active species of the coupler) during the initial phases of development,
- nucleophilic reactivity of the coupler anion (charge density on carbon),
- access of QDI to the coupler,
- electron donating properties of the leuco dye intermediate,
- basicity of the leaving group,
- energetic stabilization of the chromophor,
- solvation energy of the dye as a whole.

2. Investigation of Dye Formation Rates

Dye formation rates and dye yields may be determined by different methods.

Non-Photographic Methods

- Spectrophotometric method (stopped flow measurements),
- Potentiometric Method,
- Cyclovoltammetric Method: measurement of developer oxidation (anodic wave) and consumption of QDI (cathodic wave).

Photographic Methods

- Competitive coupling in the presence of dissolved coupler,
- Competitive Coupling in the presence of an efficient competitive coupler.

Any of the methods has advantages and limitations of its own and may provide a different answer to the same question: What determines the photographic result: coupling rate or dye formation rate?

3. Some Special Features of the Cyclovoltammetric Method

In the cyclovoltammetric method, colour developer is first oxidized at the electrode in the presence of the coupler, and the oxidation products are then reduced by varying the electrode potential.

The diagnostic value of the cyclovoltammetric method may be underestimated, as it is the only method providing insight into the electrochemical course of the coupling process under conditions very close colour photography. In particular, an evaluation of the cathodic wave gives insight into the rate of QDI consumption, while an evaluation of the anodic wave may disclose an unknown consecutive electrochemistry by primary coupling products.

The evaluation of cyclic voltammograms of water soluble model couplers and dispersed colour couplers as well shows that coupling is not the only process occurring under photographic conditions, and that side reactions or escape reactions may predominate if the reactants or the conditions are improperly chosen. These reactions may lead to

extensive loss of dye, thus providing an explanation for the "weak equivalency problem".

It is shown that the coupling equivalency problem is more one of intermediate stability than one of overall coupler reactivity: in the four-equivalent yellow coupler series, and to a smaller extent in the four-equivalent magenta coupler series, the dye yield may strongly depend on the amount of available quinone diimine.

4. Reactive Intermediates

There are good arguments for a key role of the highly reactive semiquinonoid intermediate between leuco compound and azomethine dye, the "Leuco-semiquinone Diimine", and it is proposed that an extended formulation of the coupling scheme may be favorably applied to four-equivalent coupling.

5. Outlook

Of course, the combined results of kinetic and electrochemical experiments have consequences on the adoption of competitive coupling as an exclusive method for determining coupler reactivity.

Unfortunately, coupler reactivity has as many aspects as single reaction steps are involved, and high coupler reactivity may escape detection in any kind of experiments based on competitive coupling, especially if the formation of dye is inhibited by sluggish leuco dye oxidation. Thus, in competitive coupling experiments where the amount of available quinone diimine is reduced, four equivalent couplers may be classified erroneously as couplers of low activity.

There are good arguments for assessing coupler reactivity under the aspect of initial reactivity and dye yield as well.