Controlled Release Technology of Development Inhibitor Through a Series of Timing Groups

Keiji Mihayashi, Seiji Ichijima, Atsuhiro Ohkawa, Tatsuhiko Ohbayashi and Hiroyuki Watanabe
Ashigara Research Laboratories, Fuji Photo Film Co., Ltd.
210 Nakanuma, Minami-Ashigara, Kanagawa, JAPAN

Abstract

In order to achieve delayed release of development inhibitor from the DIR couplers, we have developed a new type of DIR Couplers which will be called a double-timing DIR couplers. In this report, the reaction mechanism of the double-timing DIR coupler and the releasing rate of development inhibitor from the coupler will be discussed and the chemistry of this system will be presented along with appropriate photographic data.

Introduction

The recent and still continuing advances in color negative film technologies have achieved remarkable improvements in image quality such as color saturation, image sharpness, graininess, etc., a major part of which owes much to DIR couplers. To meet ever-expanding requirements for better levels of image quality, a wider degree of development inhibition over a wider range of inhibition distance are expected. We have developed a new type of DIR coupler, called a double-timing DIR coupler, which releases a development inhibitor through a series of timing groups, in order to improve image sharpness and color saturation by the delayed release of the development inhibitor. The present research relates to the controlled delayed release technologies of development inhibitor.

Structures of double-timing DIR couplers and reaction mechanism

The double-timing DIR coupler is made up of four essential building-blocks; A coupler moiety(COUP), a first-timing moiety(T1), a second-timing moiety(T2) and a development inhibitor(DI). The double-timing DIR coupler releases development inhibitor through a three-step reaction.

(Scheme A) Reaction scheme of double-timing DIR coupler

\[
\text{COUP} \rightarrow \text{T1} \rightarrow \text{T2} \rightarrow \text{DI} \rightarrow \text{DYE (COUP/QDI)} + \text{T1} \rightarrow \text{T2} \rightarrow \text{DI}
\]

\[
(1) \quad \text{T1} \rightarrow \text{T2} \rightarrow \text{DI} \rightarrow \text{T2} \rightarrow \text{DI} \quad \text{with} \quad k_1
\]

\[
(2) \quad \text{T2} \rightarrow \text{DI} \quad \text{with} \quad k_2
\]

The first-step reaction is a ordinary coupling reaction; Coupler moiety is detached on reaction with the oxidized developer(QDI) to form a dye molecule(DYE) and a double-timing precursor(T1-T2-DI) for the development inhibitor. Then at a second-step[equation(1)], the double-timing precursor releases a single-timing precursor(T2-DI) which is still unable to work as a inhibitor. Finally, development inhibitor is released at the third-step reaction[equation(2)].

(Structures of double-timing DIR couplers)
Table 2 shows three different T2-DIs’ structures with different development inhibitors and those releasing rate. The linear correlation between pKa value of DI and the releasing rate of D (log k2) can be seen in Figure 1.

Table 2. The effect of DI structure on the releasing rate

<table>
<thead>
<tr>
<th>DI</th>
<th>The DI releasing rate at pH 10 (half life time)</th>
<th>pKa of DI2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>78 sec</td>
<td>4.64</td>
</tr>
<tr>
<td>2</td>
<td>1100 sec</td>
<td>6.69</td>
</tr>
<tr>
<td>3</td>
<td>8800 sec</td>
<td>9.16</td>
</tr>
</tbody>
</table>

1) Conditions were as follows : tetrahydrofuran: ac. carbonate buffer = 3:7, pH 10, T2 - DI 5 x 10^4 M, DI 5 x 10^4 M.
2) pKa was measured in tetrahydrofuran/H2O = 8/4.

Figure 1. The relationship between the pKa value and the releasing rate of DI (log k2)

To clarify the releasing mechanism of DI, the following experiments were carried out. N-methylated Compound 8 did not released DI (Scheme B), in contrast to the N-H Compound 1 (Table 1). Furthermore, in the presence of 2-mercapto-1,3,4-thiadiazole (MTD), the DI (PMT) of Compound 1 was exchanged by MTD under an alkaline solution (Scheme C). Figure 2 shows that the DI exchange reaction profile between Compound 1 and 6. Therefore, it is obvious that the DI releasing reaction is a reversible one. These results suggest that the releasing reaction of DI from T2-DI should not proceed by the nucleophilic substitution mechanism but electron transfer mechanism. From these observation, the releasing mechanism of DI from T2-DI is presumed as shown in Scheme D.
Scheme B) Reaction of N-methylated compound

\[
\text{(N - CH}_3\text{ Compound)}
\]

\[
\begin{array}{c}
\text{Nucleophile} \\
\text{DI was not Released}
\end{array}
\]

Scheme C) DI Exchange reaction

\[
\text{THF-Carbonate buffer (3:7)} \\
pH 10
\]

1 \times 10^{-3} \text{M} \\
5 \times 10^{-3} \text{M}

The electronic effect of the imidazole ring's substitution on the releasing rate was investigated. The linear correlation between Hammett's \( \sigma_p \) constant of the substituent group and the DI releasing rate (log \( k_{\text{anion}} \)) from the anion form of T2-DI was observed (Figure 3). But in actual color negative developer solution, usually at pH 10, both anion and free form of T2-DI are present, so the practical DI releasing rate depends on both the dissociation constant of T2-DI and the releasing rate from anion species of DI (Scheme E). The relating values, pKa of T2-DI (the degree of T2-DI's dissociation), releasing rate from anion species and the resulting rate at pH 10 are listed in Table 3.

DI Releasing Rates from Anion Species

![Graph showing the relationship between Hammett's \( \sigma_p \) and the releasing rate from anion form of T2-DI](Image)

Figure 3. A linear relationship between Hammett's \( \sigma_p \) and the releasing rate from anion form of T2-DI

Scheme E) The releasing process consists of two reactions.

\[
\begin{array}{c}
\text{Releasing Rate at pH 10} \downarrow \\
\text{The Degree of dissociation} \downarrow \text{of Precursor at pH 10} \\
\text{Releasing Rate from} \\
\text{Anion species}
\end{array}
\]

(1) Reactions Proceed In Elimination Mechanism.

(2) The releasing reactions are reversible.
Table 3. Kinetic study on the DI releasing reaction

<table>
<thead>
<tr>
<th>R</th>
<th>pK a 1)</th>
<th>log k at pH 10</th>
<th>The Degree of Dissociation</th>
<th>log k anion</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃</td>
<td>15.1</td>
<td>0.2</td>
<td>10⁻⁶.¹</td>
<td>5.3</td>
</tr>
<tr>
<td>O</td>
<td>13.4</td>
<td>-0.9</td>
<td>10⁻³.⁴</td>
<td>2.6</td>
</tr>
<tr>
<td>H</td>
<td>14.9</td>
<td>-1.1</td>
<td>10⁻⁴.⁹</td>
<td>3.8</td>
</tr>
<tr>
<td>Cl</td>
<td>12.3</td>
<td>0.3</td>
<td>10⁻².³</td>
<td>2.6</td>
</tr>
<tr>
<td>Br</td>
<td>12.3</td>
<td>0.2</td>
<td>10⁻².³</td>
<td>2.5</td>
</tr>
</tbody>
</table>
| NO₂ | 9.3     | -4.5           | 0.8                         | -4.4        

1) These are following compound’s values:

The releasing mechanism and the releasing rate of T2 from T1-T2

We estimated the releasing rate of T2-DI from T1-T2-DI, by measuring the releasing rate of the heterocyclic ring(T2) from the model compound(T1-T2) in the Scheme D. When T2 is imidazole ring, T2 is split off quickly, regardless of the structures of T1 and T2, but when T2 is pyrazole or aniline ring, T1-T2 is gradually decomposed. Thus it is thought that the T1-T2 cleavage rate of methyloxy group or oxycarbonyl group can be controlled by the choice of T2’s structure bounded to methyloxy group or oxycarbonyl group. When T1 is oxycarbonyl group, the releasing rate of t2 can be controlled in wider rage, so it can be achieved the delayed release of development inhibitor.

Conclusion

We have achieved the delayed release of development inhibitor from the double-timing DIR coupler and we have found that -OCO-azo-C₃H₂-DI is a good precursor for the delayed controlled release. We can achieve the remarkably improved image sharpness and interlayer inter-image effect.

(Scheme F) T2 releasing rate from models of T1-T2

(T1 = -OCH₂-)

(T1 = -OC(-O)-)

References

2. S.Ichijima and N.Sasaki, USP 4,698,297 (1987)