

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

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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

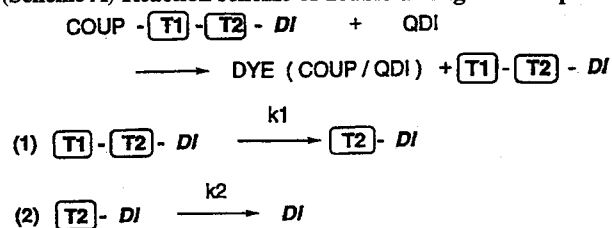
The recent and still continuing advances in color negative film technologies have achieved remarkable improvements in image quality such as color saturation, image sharpness, graininess, etc., a major part of which owes much to DIR couplers. To meet ever-expanding requirements for better levels of image 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-

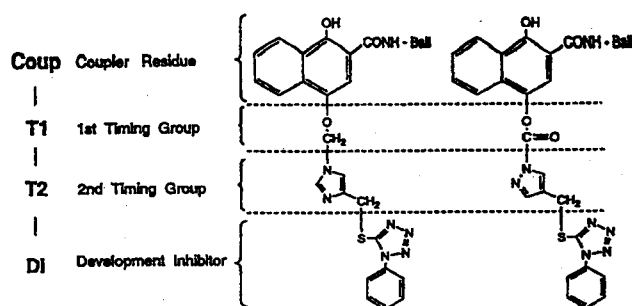
step reaction.

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

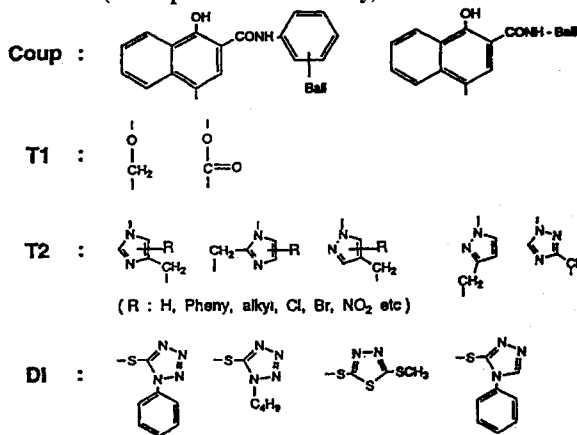


The first-step reaction is a ordinary coupling reaction; Coupler moiety is detached on reaction with the oxidized developer(QDI) to form a dye molecule(DYE) and a double-timing precursor(T1-T2-DI) for the development inhibitor. Then at a second-step[equation(1)], the double-timing precursor releases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



(Examples of Each Moiety)



Results and Discussion

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

T2-DIs with imidazole, pyrazole and 1,2,4-triazole moiety were synthesized. 1-phenyl-5-mercapto-tetrazole(PMT) was used as DI. The releasing rate of DI was measured in THF-aqueous carbonate buffer solution (3/7,vol/vol, at pH 10). The results were summarized in Table 1. As shown in the Table, the releasing rate of DI clearly depends on the structure of the T2(heterocycle). The imidazole derivatives(Compound 1 and 2) rapidly releases DI. The releasing rate from Compound 3 is smaller than those from imidazole derivatives. DI was not released from Compound 4 and 5. The releasing rate seems to be related the π -electron density on the heterocyclic ring of T2.

Table 1 also shows that the releasing rate is accelerated by the addition of sodium sulfite, hydroxylamine and silver chloride which are commonly contained in the photographic developer or the photographic layer.

Table 1. The releasing rate of DI from T2-DI and the effect of additives

Compound No	Structure (T2 - DI)	The DI releasing rate at pH 10 (half life time)			
		OH	Na ₂ SO ₃	NH ₂ OH	AgCl
1		78 sec	7 sec		
2		200 sec	25 sec	84 sec	28 sec
3		320 sec	120 sec	185 sec	
4		— ²⁾	— ²⁾		
5		— ²⁾	— ²⁾		

1) Conditions were as follows; tetrahydrofuran : aq. carbonate buffer = 3 : 7, pH10, T2-DI 0.5 mM, Na₂SO₃ 32 mM, NH₂OH 16 mM, AgCl 5 mM.

2) DI was not released.

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 k 2) can be seen in Figure 1.

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

DI	The DI releasing rate at pH 10 (half life time) ¹⁾	pKa of DI ²⁾
I:	78 sec	4.64
II:	1100 sec	6.69
III:	8800 sec	9.16

1) Conditions were as follows; tetrahydrofuran : aq. carbonate buffer = 3 : 7, pH 10, T2-DI 5 x 10⁻⁴ M

2) pKa was measured in tetrahydrofuran/H₂O = 6/4.

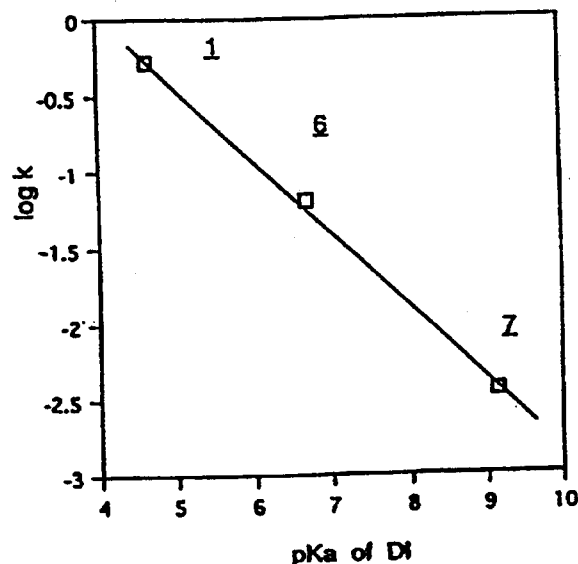
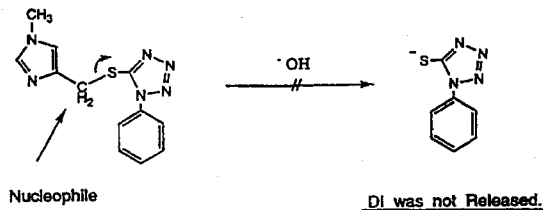


Figure 1. The relationship between the pKa value and the releasing rate of DI(log k 2)

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(Table1). 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

(N-CH₃ Compound)



(Scheme C) DI Exchange reaction

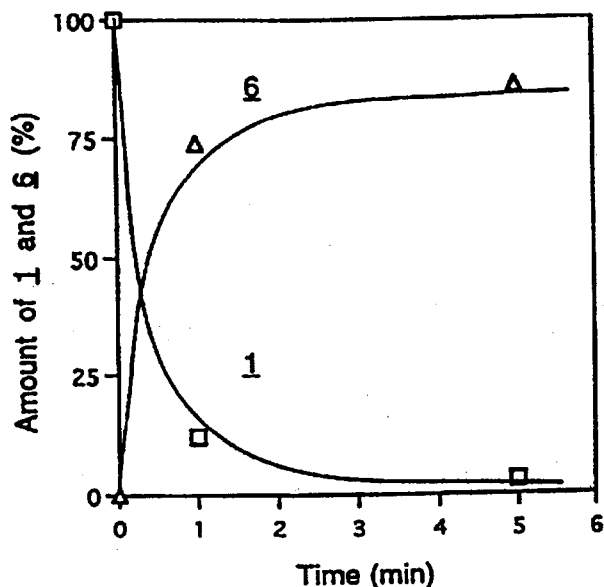
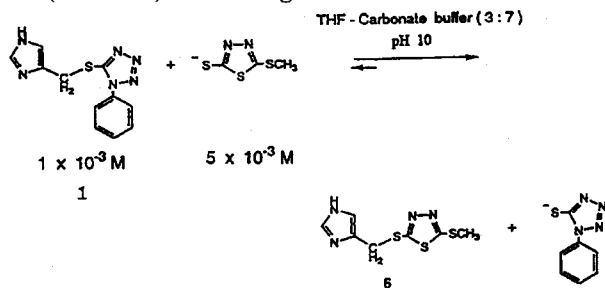
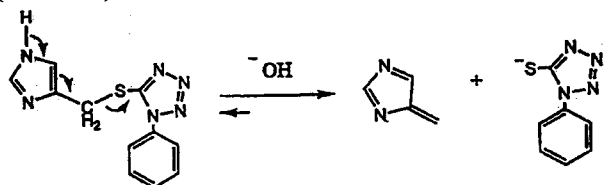


Figure 2. The change in amount of Compound 1 and Compound 6 with time

(Scheme D) Presumable mechanism of DI releasing reaction



- (1) Reactions Proceed in Elimination Mechanism.
 - (2) The releasing reactions are reversible.

The electronic effect of the imidazole ring's substitution on the releasing rate was investigated. The linear correlation between Hammett's σ_p constant of the substituent group 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

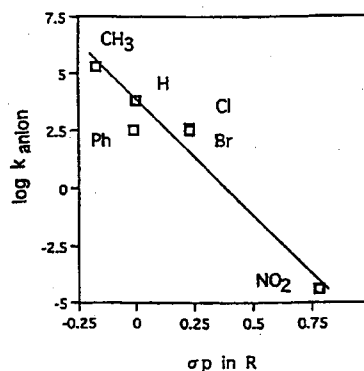
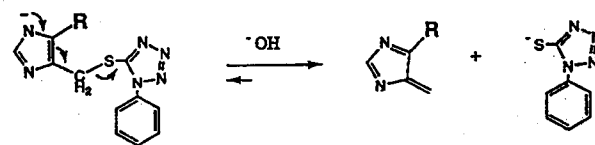


Figure 3. A linear relationship between Hammett's σ_p and the releasing rate from anion form of T2-DI

(Scheme E) The releasing process consists of two reactions.

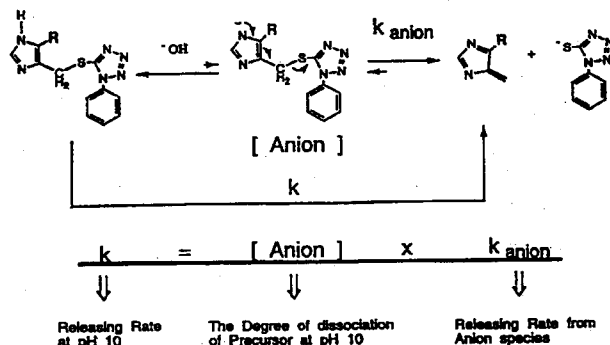



Table 3. Kinetic study on the DI releasing reaction

R	pKa ¹⁾	log k at pH 10	The Degree of Dissociation	log k _{anion}
CH ₃	15.1	0.2	10 ^{-5.1}	5.3
	13.4	-0.9	10 ^{-3.4}	2.6
H	14.9	-1.1	10 ^{-4.9}	3.8
Cl	12.3	0.3	10 ^{-2.3}	2.6
Br	12.3	0.2	10 ^{-2.3}	2.5
NO ₂	9.3	-4.5	0.8	-4.4

¹⁾ These are following compound's values:



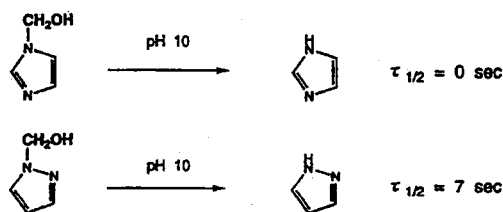
The releasing mechanism and the releasing rate of T2 from T1-T2

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 methylol group or oxycarbonyl group can be controlled by the choice of T2's structure bounded to methylol group or oxycarbonyl group. When T1 is oxycarbonyl group, the releasing rate of t2 can be controlled in wider range, so it can be achieved the delayed release of development inhibitor.

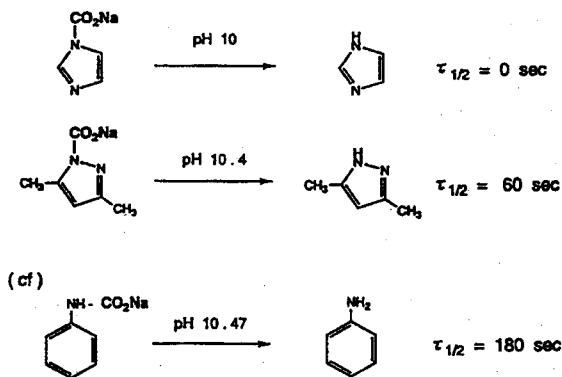
Conclusion

We have achieved the delayed release of development inhibitor from the double-timing DIR coupler and we have found that -OCO-azole-CH₂-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)-)



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