

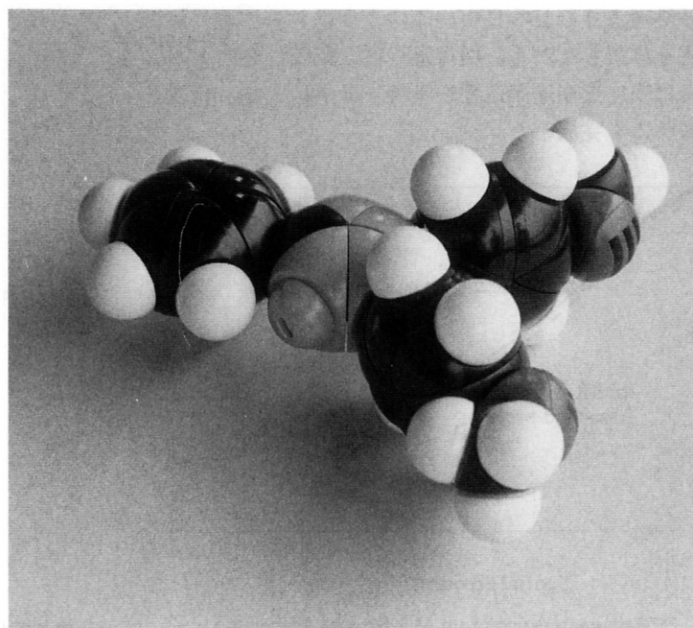
High Contrast Rapid Access Technology: The Effect of Tetrazolium Compounds

超硬調迅速処理技術: テトラゾリウム化合物の超硬調化作用

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Abstract:

Konica's RST system combines the processing speed and stability of rapid access processing with the high contrast of lith development. To achieve such high contrast, a tetrazolium compound is used to selectively retard development more in areas of low exposure than in areas of high exposure. The key to this is a compound whose reaction rate with the developer is bracketed by lower and higher silver halide reaction rates in lower and higher areas of exposure, respectively.

A precise knowledge of reaction rate thus being essential, we investigated ways beyond spectrometric measurement to determine it. A study of ten different tetrazolium compounds indicated that both Hammett's σ values and polaro half-wave potentials show strong promise as predictors of such compounds' reaction rates with a developer.

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Introduction

The Konica Corporation has succeeded in developing a new image forming system which provides very high contrast, the RST system. RST combines the high contrast of lith development with the processing speed and stability of rapid access development. In a single advance, the RST system has solved such traditional lith system problems as instability to aerial oxidation, processing exhaustion, and slow processing. The RST system was created by using photosensitive materials containing tetrazolium compounds and by processing these materials with a PQ developer, which contains phenidone and hydroquinone as developing agents, a large quantity of sulfite salt, and a heterocyclic compound.

The key to Konica's RST system is "selective development". In a previous report¹⁾, the mechanism of selective development's high contrast effect was indicated not to be caused by latent image bleaching, nor was it likely caused by the contrast increasing enhancement effect of semiquinone. The proposed hypothesis was that tetrazolium compounds competitively react with those developing agents which reduce silver halide. This hypothesizes that when the reaction rate of a tetrazolium compound with such developing agents is faster than the reduction rate of silver halide in lower exposure areas, but slower than that of developing agent in higher exposure areas, the development of the lower exposure area is selectively retarded. Since this implied that an optimum reaction rate would produce maximized contrast, the effects on contrast of three triphenyl tetrazolium compounds {p-iC₃H₇, p-CH₃, and non-substituted (H) compounds} of varying reaction rate were studied. The results supported the existence of an optimum reaction rate, but did not fully substantiate the mechanism.

In our own study, we dissolved various tetrazolium compounds in an aqueous solution containing an organic solvent and measured their reaction rates with a specially prepared, experimentally simplified PQ developer. Their correspondence to both Hammett's σ values and to the half-wave potentials in an alkaline solution of these compounds were investigated, as was their relationship to high contrast.

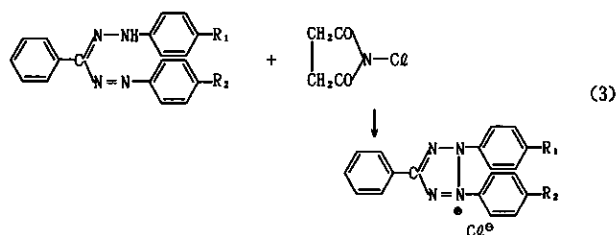
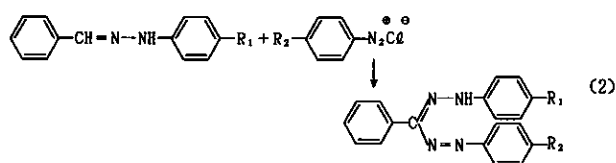
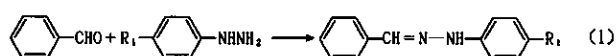
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Experimental

2.1 Synthesis of tetrazolium compounds

Employed were 2,3-position substituted diphenyl-5-phenyl tetrazolium salts. The compound substituents were Cl, F, CH₃, C₂H₅, iC₃H₇, OCH₃, OH, and N(CH₃)₂, as well as a non-substituted (H) compound. The tetrazolium compounds were synthesized following established procedures²⁾.

The reactions proceeded in three steps (where R₁ and R₂ indicate a pair of the same substituents):



As an example, the following were the procedures in synthesizing the p-OCH₃ substituted compound. A mixture of benzaldehyde (10.6g, 0.1mol) and p-methoxyphenylhydrazine hydrochloride (17.4g, 0.1mol) in methanol (200ml) was stirred in reflux for 2hours. The resulting solution was cooled to 20°C and filtered. The yield of benzaldehyde-p-methoxyphenylhydrazone (BMPH) was 19.2g(85%). In a mixture of p-anisidine (11.4g, 0.092mol) and hydrochloric acid (33.8g, 0.276mol) in water (200ml), sodium nitrite (6.4g, 0.093), cooled to 5°C, was added dropwise for 15minutes, stirred below 0°C for 25minutes, and obtained diazonium salts.

In a mixture of the above obtained BMPH (15.8g, 0.07mol) and 90 aqueous sodium hydroxide solution (12.6g, 0.3mol) in tetrahydrofuran (700ml), the above diazonium salt cooled to 5°C for 70minutes, was added dropwise and stirred for 4hours. The solution was poured into water, and the crystallized by-product was filtered off. The filtered solution was then neutralized with acetic acid to obtain the formazane.

Acetic acid (8ml) was then poured into a solution of the formazane (11.6g, 0.032mol) in chloroform (1.2l) and cooled to 5°C. To this solution, N-chlorosuccinimide (5.4g, 0.04mol) was added and stirred at 50°C for 3 hours. The precipitated crystals were filtered off and washed in ethylacetate. The yield was 8.7g (68%).

2.2 Emulsion, film coating, exposure, and development

The emulsions employed were composed of monodispersed cubic silver chloro bromide grains (chloride 65mole%) having diameters of about 0.3μm. The emulsions were prepared by a controlled double jet method and were used without any chemical or spectral-sensitization. Before coating, a triphenyltetrazolium derivative (6×10^{-3} mol/mol Ag), a surfactant, and a hardening agent were added to the emulsion. The emulsion was coated on a transparent support at 0.4mg Ag per cm². The prepared film was then exposed to an xenon lamp. The exposed film strips were developed at 28°C for 30 seconds in Konica CDM651K PQ developer.

2.3 Reaction of tetrazolium compounds with developing agents

Tetrazolium compounds form formazanes, which absorb light in the visible region by reacting with reducing agents. The reaction rates of the compounds in our study were measured spectrometrically. Solutions of the tetrazolium compounds (2.4×10^{-5} mol/l) were prepared composed of water and isopropanol (1:1) containing sodium carbonate(1g/l). The developer with which the tetrazolium compounds were reacted was composed of sodium sulfite anhydrous (40g/l), phenidone (0.5g/l), hydroquinone (15g/l), and sodium carbonate (50g/l), the pH was adjusted to 10.40. The reaction was carried out by mixing the above solution of the tetrazolium compound and the developer in a volume ratio of 19:1 (reaction mole ratio of tetrazolium compound : phenidone : hydroquinone = 1:6.8:300) at 25°C in a nitrogen atmosphere.

2.4 Measurement of polarographic half-wave potentials of the tetrazolium compounds

The polarographic half-wave potentials were measured by a three pole direct current polarograph composed of a dropping mercury cathode (D.M.C.), a platinum anode, and a saturated calomel electrode (S.C.E.). The aqueous solutions of the tetrazolium compounds were prepared at concentrations of 1.5×10^{-3} mol/l and adjusted to pH10.40, employing an Atkins-

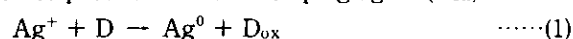
Pantin buffer solution. Oxygen-free nitrogen was introduced into the solution for 30 minutes before measurement. Measurement was carried out in a nitrogen gas atmosphere. The scan speed was 10mV/sec, with a current range of 10μA/V.

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Results and Discussion

The following competing reactions of the developing agent with the tetrazolium compounds and with silver halide were proposed in the report cited earlier¹⁾ to account for the high contrast effect.

Silver halide (Ag^+), reacting with the developing agent (D), is reduced to metallic silver (Ag^0), and yields an oxidized product of the developing agent (D_{ox}).



The developing speed in the higher exposure areas ($d \text{Ag}^0_{\text{h}}/dt$) is greater than that in the lower exposure areas ($d \text{Ag}^0_{\text{l}}/dt$). This relationship can be written.

$$(d \text{Ag}^0_{\text{h}}/dt) > (d \text{Ag}^0_{\text{l}}/dt) \quad \dots\dots(2)$$

The tetrazolium compounds react with the developing agent and form formazanes.



If the reaction rate of equation (3) is slower than the left-hand side of equation (2), but faster than that equation's right-hand side, then equation (4) follows;

$$d \text{Ag}^0_{\text{h}}/dt > d \text{T}^0/dt > d \text{Ag}^0_{\text{l}}/dt \quad \dots\dots(4)$$

While the tetrazolium compound in fact retards development in both high and low areas of exposure, it has a greater relative effect in the latter. In this way, development in the lower exposure areas is selectively retarded. It should be noted that no such selective retardation occurs if the compound's reaction rate is either higher or lower than that of silver halide in both high and low areas of exposure. It was anticipated, then, that there would exist an optimum reaction rate for high contrast.

3.1 Photographic effect of tetrazolium compounds

The average contrast values (\bar{G}) of the compounds were calculated from the characteristic curves shown in Fig. 1 to compare their high contrast effects. \bar{G} is the slope of the characteristic curve between the corresponding to densities of 0.1 and 1.0. Roughly speaking, the more highly retarded the emulsion, the higher the contrast, though this order is not absolute.

3.2 Influence of tetrazolium compound substituents on rates of reaction with the developer

The tetrazolium compounds were reduced to their

corresponding formazanes, splitting the bond of nitrogen at the 2 and 3-position. Thus, if, electron drawing substituents were introduced on the 2 and 3-positioned phenyl rings, the bond would be weakened and easily reduced. In contrast, if electron donating substituents were introduced, the bond would be strengthened, and the rate of reduction would be retarded.

The reaction rates of the tetrazolium compounds were measured spectrometrically, as exemplified by the non-substituted (H) compound in Fig.2

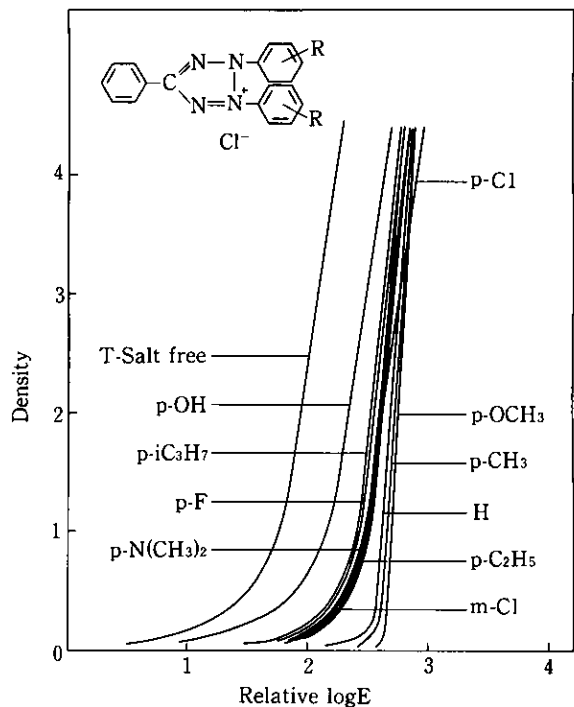


Fig. 1 Influence of tetrazolium compound substituents

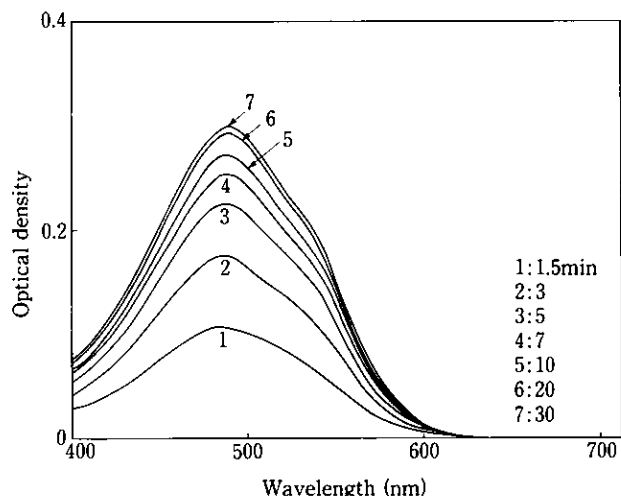


Fig. 2 Absorption spectra of non-substituted (H) compound with PQ Developer

3.2.1 Hammett's σ value

The relation between the reaction rate constants then derived and Hammett's σ values is shown in Fig.3. (The reaction rates of p-OH and p-N(CH₃)₂ substituted tetrazolium compounds were too low to determine.) A high coefficient (0.89) was obtained.

3.2.2 Polarographic half-wave potentials

A high degree of correlation between the reaction rate constant and the half-wave potential was observed as shown in Fig.4 for p-Cl, p-F, non-substituted (H), p-OCH₃, and p-CH₃ tetrazolium compounds, while m-Cl, p-C₂H₅ and p-iC₃H₇ shifted from these toward a higher half-wave potential. It seems that the half-wave

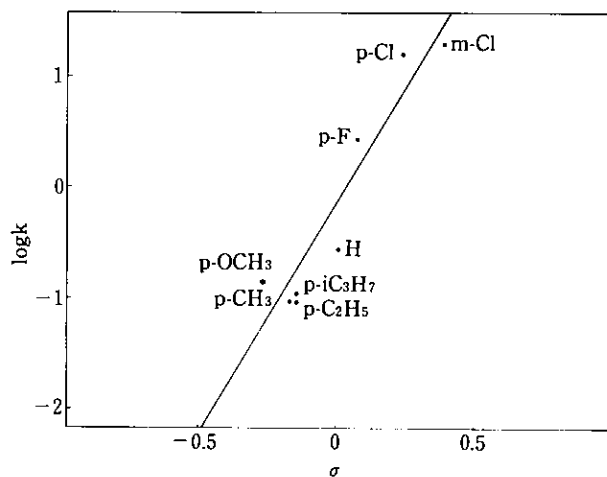


Fig. 3 Relation between reaction rate constant and Hammett's σ value

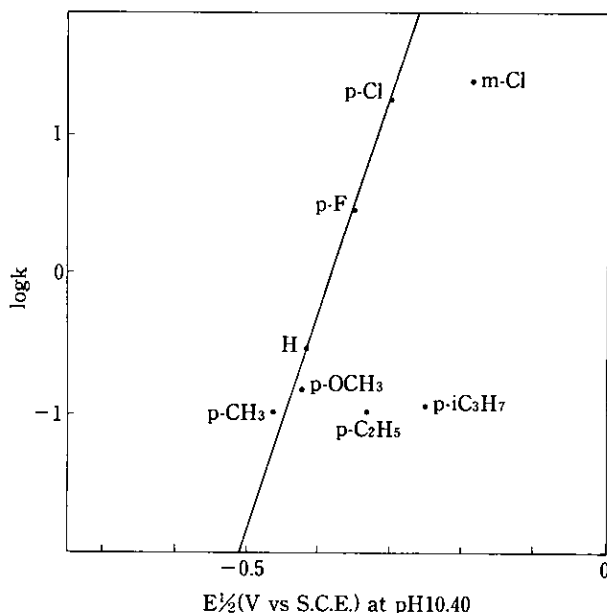


Fig. 4 Relation between reaction rate constant and half-wave potential

potentials of tetrazolium compounds are a promising indicator of the reactivity of these compounds, and can, to some degree, predict reaction rate constants. The potentials measured also confirm the fact that the high contrast effect is not due to latent image bleaching.

3.3 Effect of reaction rates of tetrazolium compounds with developer

The relation between \bar{G} and reaction rate is shown in Fig. 5. Substantial high contrast effects were found, from highest to lowest, in p-OCH₃, p-CH₃, and non-substituted (H) tetrazolium compounds. Both substituents leading to higher reaction rates such as p-Cl, m-Cl, and p-F, and those leading to lower reaction rates such as p-OH, and p-N(CH₃)₂, show almost no contrast effect. As anticipated by the proposed mechanism of selective development, the results here suggest the existence of an optimal reaction rate to achieve high contrast.

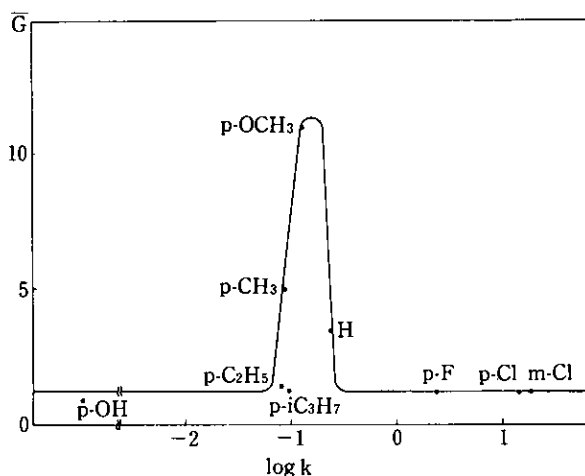


Fig. 5 Relation between \bar{G} and the reaction rate constant

It appears, however, that the proposed mechanism, while perhaps a major element in achieving high contrast, is not sufficient in itself to account for that effect. This becomes clear when considering that p-C₂H₅ and p-iC₃H₇ have no high contrast effect even though their reaction rates are nearly the same as those of p-CH₃ and p-OCH₃.

At first, this might be thought to be explained by noting that the experiments providing this reaction data were conducted with a homogenous reaction system containing no silver halide. It might be assumed that in an actual photographic system reaction would be more complicated, and that the compounds would effect high contrast due to such factors as the steric hindrance of substituents.

This, however, is not the case. Returning to Fig. 1, these substituents still fail to produce high contrast even in such a silver halide-containing system. A simple principle of tetrazolium compounds competing with silver halide in reacting with the developer to selectively retard development does not, then, compose the entire mechanism. Further factors appear to be involved. For example, it may be that formazanes, which form during the development process, have an effect on development retardation leading to high contrast.

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Conclusion

It has been suggested that the mechanism of RST's high contrast effect lies in the competing developer reaction of silver halide and tetrazolium compounds, where such compounds' reaction speed must be bracketed by higher and lower silver halide reaction speeds in areas of higher and lower exposure, respectively. While it has been found that this suggestion and its implication of an optimum compound reaction rate do not alone explain the high contrast effect, they do appear to reflect a major factor in the actual mechanism. Thus, determining the reaction rate constants of tetrazolium compounds is highly significant to the design of a high contrast system such as the RST system.

Such design aided by our finding that such reaction rate constants can be derived not only from spectrometric measurement, but also possibly be projected in part from Hammett's σ values and from polarographic half-wave potentials. These positive findings encourage further investigation, so that a study of additional factors may establish reliability and refine the accuracy of a model of the high contrast mechanism in a practical system.

Acknowledgements

The authors wish to express their appreciation to Prof. Nobuo Mii and Dr. Kenichi Kuge (Department of Natural Science, Chiba University) for their helpful discussion and suggestions, and to Mr. Kunio Ueda (Faculty of Engineering, Chiba University) for his valuable assistance with experiments.

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