is the rate determining step. It was assumed that the chemisorbed hydrogen atoms on the catalyst arising from the presence of molecular hydrogen must be greater than that arising from the presence of water and therefore the second step should be much faster in the former case than in the latter. Actually we have found this to be the case in our exchange experiments with butane and water and butane and hydrogen so that the above conclusion that the second step cannot be the rate determining step can be upheld in its general form.

The experiments on the exchange of hydrogen atoms between ethylene and butene are of particular interest, in connection with the question as to whether or not unsaturated hydrocarbons undergo dissociation on the surface of the catalyst. Conn and Twigg[8] investigated the interaction of C_2H_4 and C_2D_4 on a nickel catalyst at 76° and 330-360°, but found that no ethylene molecules containing both hydrogen and deuterium atoms were formed, even if the time of interaction was much longer than the half life time of the exchange of ethylene with deuterium on the same catalyst. They considered these experiments as a direct proof that no dissociation of unsaturated compounds takes place to any appreciable extent, and concluded that the exchange of ethylene and deuterium must follow the associative mechanism.

It has been pointed out,[19] however, that this negative result might be due to the fact that under the experimental conditions of these authors the stationary concentration of hydrogen atoms on the surface of the catalyst was so low that the mutual exchange of C_2H_4 with C_2D_4 was inappreciable. The hydrogen concentration on the catalyst might be very low if the atoms formed by dissociation are removed from the catalyst by reaction with ethylene.

The present observations on the exchange of butene with ethylene show directly that unsaturated hydrocarbons can exchange their hydrogen atoms and although the observed rates were not very great (the same order of magnitude as the exchange rates with water) they show that there is only a quantitative difference in the behavior of unsaturated and saturated hydrocarbons. The negative result of the exchange experiment with ethylene and butane is presumably due to the displacement of the butane from the surface of the catalyst by ethylene.

Summary

The following exchange reactions of hydrogen atoms on palladium and nickel catalysts at pressures of 20-700 mm. and in the temperature range of 80-170° were investigated: water and ethylene, water and butene, water and butane, butene and ethylene and butane and ethylene.

It was found that exchange of hydrogen atoms between ethylene and water, butene and water and butene and ethylene does occur while under the same experimental conditions no exchange between butane and water or butane and ethylene was observed.

The experimental results are discussed and the importance of the mutual displacement of the reactants on the catalyst surface is emphasized. The two possible mechanisms for the exchange reactions are discussed in the light of the new experimental evidence.

JERUSALEM, PALESTINE RECEIVED SEPTEMBER 23, 1947

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[19] A. Farkas, *Trans. Far. Soc.*, **35**, 910 (1939).

[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS]

The Effect of Substituents upon the Rate of Fading of Some Sulfonphthalein Indicators in Alkaline Solutions

BY ELIZABETH E. SAGER, ARTHUR A. MARYOTT AND MARJORIE R. SCHOOLEY

I. Introduction

The usefulness of an indicator in the measurement of *p*H depends, in part, on its chemical stability. Phenolphthalein and some of the substituted phenolphthaleins show a pronounced tendency to fade, particularly in alkaline solutions. Replacement of the carboxyl group in the phenolphthaleins by the sulfonic acid group to form the phenolsulfonphthaleins greatly increases the stability. Sulfonphthaleins covering practically the entire useful *p*H range are available commercially and form one of the most satisfactory series of indicators for colorimetric and spectrophotometric measurements. In the course of a program concerning the application of precise spectrophotometric methods in the determination of ionization constants of indicators, it seemed desirable to examine quantitatively the alkaline stability of a rather complete series. Although the fading rates of certain of the sulfonphthaleins have been the subject of a number of investigations,[1-6] data are lacking in some cases and have been obtained under varied experimental conditions in others, so that an extensive intercomparison of the effect of substituents upon the fading rates cannot be made.

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[1] A. Thiel, *Monatsh.*, **54**, 1008 (1929).

[2] F. W. Panepinto and M. Kilpatrick, THIS JOURNAL, **59**, 1871 (1937).

[3] E. S. Amis and V. K. LaMer, *ibid.*, **61**, 905 (1939).

[4] S. Hochberg and V. K. LaMer, *ibid.*, **63**, 3110 (1941).

[5] M. D. Barnes and V. K. LaMer, *ibid.*, **64**, 2312 (1932).

[6] M. H. Hubacher, *ibid.*, **65**, 2097 (1943).

The mechanism of the fading reaction has been established.[3] A study of the Brønsted primary salt effect showed that the bivalent, alkaline form of the indicator, $[R^{=}]$, adds a hydroxyl ion to form the colorless carbinol, $[ROH^{=}]$. As the reaction is reversible, the extent of fading depends on the alkali concentration. The equilibrium between the colored and faded forms is illustrated for phenolsulfonphthalein in Fig. 1. The bimolecular rate constants, k_1 and k_2, represent the fading and color-regenerating reactions, respectively.

In the present work, phenolsulfonphthalein and nine of its derivatives which have various substituents in the two chromophoric rings were studied.

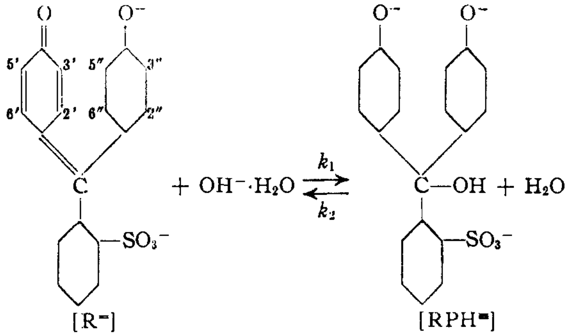

Fig. 1.—Alkaline fading of the phenolsulfonphthaleins.

II. Experimental

Brom phenol red was obtained from Hynson, Westcott and Dunning and the other indicators were obtained from W. A. Taylor and Company. Preliminary experiments were first made to determine the limiting spectral curves which represent the neutral yellow form and the reddish purple to blue alkaline form of each indicator. The molar absorbancy index, a_M, is calculated for any given wave length according to the equation

$$a_M = -\log_{10} T_s/(b \times M) \qquad (1)$$

in which T_s is the transmittancy of the solution, b is the length of the absorbing path between the boundary layers of the solution (cell-length in cm.), and M is the molar concentration of the indicator.

The maximum values of a_M were found for the alkaline forms of the indicators and vary from about 36,000 for thymol blue to 73,000 for brom cresol purple. As two-cm. absorption cells were used for the experiments, odd concentrations of each indicator were used to give an initial transmittancy value of 25 to 30% at the wave length of maximum absorption.

All of the fading reactions were conducted in relatively strong alkali, 1.12 *M*. At lower concentrations of alkali, the time required to follow some of the fading reactions is prohibitively long. The spectral transmittancies at the wave length of maximum absorption were observed throughout the course of the reactions at various intervals of time depending upon the rates of fading. The duration of the reactions ranged from less than an hour for brom phenol blue to a month and more for the more stable indicators. The transmittancies were measured with a Beckman quartz photoelectric spectrophotometer after revision of the cell compartment as described in a previous publication.[7] The temperature of the room containing the spectrophotometer and the solutions was maintained at 25° to within ±1°. In several instances the fading reaction continued to completion, but in a majority of cases a finite equilibrium between colored and colorless forms was reached. When there was no further change in the transmittancy at the wave length of maximum absorption, the spectral curve was taken at 5 mμ intervals from 220 to 750 mμ. These curves represented either the colorless carbinol form in cases of complete fading or an equilibrium mixture of colored and colorless forms. The solutions were again examined later to determine whether any changes in the spectral curves had occurred which might indicate irreversible decomposition.

III. Calculation of Rate Constants

Where the fading continues only until some definite equilibrium is established between the colored and the colorless forms of the indicator, the rate of disappearance of the colored form is given by

$$-d[R^{=}]/dt = k_1[R^{=}][OH^{-}] - k_2[ROH^{=}] \qquad (2)$$

As the alkali concentration is much greater than that of the indicator and does not change much during the reaction, the bimolecular rate constant, k_1, may be replaced by the first-order rate constant, $k_1' = k_1[OH^-]$. The integrated rate equation is then

$$k_1' + k_2 = 2.303/t \log [x_e/(x_e - x_t)] \qquad (3)$$

where x_t is the fraction of $[R^{=}]$ which has reacted at time, t, and x_e is the fraction reacted at equilibrium. From the relationship between the concentration and spectral transmittancy in accordance with Beer's law

$$x_e = \frac{\log T_{s,o} - \log T_{s,e}}{\log T_{s,o}}$$

and

$$x_t = \frac{\log T_{s,o} - \log T_{s,t}}{\log T_{s,o}}$$

where $T_{s,o}$, $T_{s,t}$, and $T_{s,e}$ are the transmittancies at zero time, at time t, and at equilibrium, respectively. Equation 3 then becomes

$$k_1' + k_2 = \frac{2.303}{t} \log \frac{\log T_{s,o} - \log T_{s,e}}{\log T_{s,t} - \log T_{s,e}} \qquad (4)$$

From the transmittancies measured at intervals during the course of the fading and the observed equilibrium transmittancy, the forward and reverse rate constants and the equilibrium constant were evaluated in the following manner. The composite rate constant, $k_1' + k_2$, was determined from the slope of the straight line obtained by

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[7] Elizabeth E. Sager, Marjorie R. Schooley, Alice S. Carr and S. F. Acree, *J. Research N. Bur. Standards*, **35**, 521 (1945), RP1686.

TABLE I

Common name	Abbr.	Substituents	Fading rates $k_1 \times 10^3$ min. × M	Fading rates $k_2 \times 10^3$ min. × M	Substituent effect A_x Obsd.	Substituent effect A_x Calcd.	Equilibrium constant K	Ionization constant pK^*	$\frac{[ROH^=]}{[R^=]}$[a]
Brom phenol blue	BPB	3′,5′,3″,5″ Br	84	....	+1.69	+1.78	(34,000)	4.0	0.003
Chlor phenol red	CPR	3′,3″ Cl	12.5	....	+ .86	....	(500)	6.0	.005
Brom phenol red	BPR	3′,3″ Br	13.5	....	+ .89	....	(540)	6.2	.008
Brom cresol purple	BCP	3′,3″ CH_3; 5′,5″ Br	1.87	0.06	+ .03	+0.03	33	6.3	.001
Phenol red	PR	None	1.73	.25	....	....	7.9	7.9	.006
Brom cresol green	BCG	2′,2″ CH_3; 3′,5′,3″,5″ Br	0.80	....	− .32	− .08	(10,000)	4.7	.005
Cresol red	CR	3′,3″ CH_3	.24	.52	− .86	....	0.5	8.3	.001
Brom thymol blue	BTB	2′,2″ CH_3; 3′,3″ Br; 5′,5″ C_3H_7	.0280	.0016	−1.79	−1.79	20	7.0	.002
Meta cresol purple	MCP	2′,2″ CH_3	.0261	.0085	−1.82	....	3.1	8.3	.006
Thymol blue	TB	2′,2″ CH_3; 5′,5″ C_3H_7	(.004)	....	−2.6	−2.68	(.22)	8.9	.002

[a] At pH = pK^* + 3.

plotting log (log $T_{s,e}$ − log $T_{s,t}$) as a function of time according to equation 4. The equilibrium constant was evaluated from

$$K = \frac{[ROH^=]}{[R^=][OH^-]} = \frac{\log T_{s,0} - \log T_{s,e}}{\log T_{s,e}\,[OH^-]} \qquad (5)$$

In general $T_{s,0}$ could not be obtained directly because measurable fading occurred during the time interval between the start of the reaction and the first experimental observations. It was obtained from the intercept of the above plot corresponding to zero time. The separate rate constants were then obtained from the equations

$$k_1 = \frac{k_1' + k_2}{[OH^-] + 1/K} \text{ and } k_2 = k_1/K$$

In cases where fading goes practically to completion, equation 4 assumes the simplified form

$$k_1' = \frac{2.303}{t} \log (\log T_{s,0}/\log T_{s,t}) \qquad (6)$$

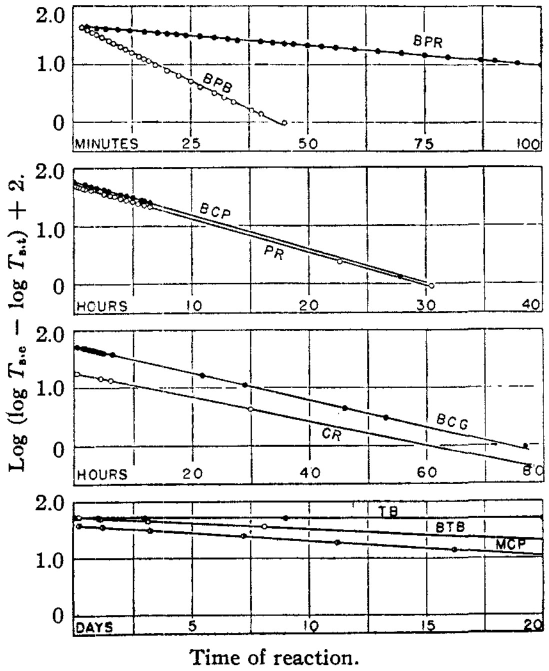

Fig. 2.—Rate of fading of phenolsulfonphthalein indicators in 1.12 M NaOH: log (log $T_{s,e}$ − log $T_{s,t}$) + 2 plotted as a function of time.

IV. Experimental Results

The ten sulfonphthaleins are listed in Table I and their common names as indicators, substituent groups, fading rates, effect of substituents upon the fading rates, as well as their equilibrium and ionization constants are also given. The indicators are given in the order of their fading rate constants, k_1, and the reverse rate constants, k_2, are calculated for the cases where they could be obtained. The substituent effects are defined and discussed in the next section. The experimental data plotted in accordance with equation 4 or equation 6 are shown in Fig. 2. The plots are linear over the entire range of fading. Additional data for TB, BTB, and MCP extended well beyond the twenty days given in the figure. TB fades extremely slowly and only an approximate value of k_1 could be obtained. Data for CPR are not shown. In this case the plot was linear only up to about 50% faded. Beyond this region the points fell above the straight line in a manner suggesting a small amount of colored impurity, presumably some other sulfonphthalein, having similar absorption but greater alkaline stability. In this case k_1 was evaluated from the initial, linear portion of the curve.

In addition to reversible fading similar to the sulfonphthaleins, the phenolphthaleins undergo gradual irreversible decomposition which has been attributed to oxidation by the air.[8] No definite evidence of irreversible decomposition, however, was found for any of the sulfonphthaleins during the course of the present observations. Any substantial irreversible change should be apparent as a gradual change in the transmittancy curves after fading had become complete or had reached an equilibrium. Figure 3 shows the spectral curves for BCG during various stages of the fading. In this case the fading goes to completion. Curves numbered 4 and 5 were taken after five and thirteen days, respectively, and indicate that no detectable change in spectral absorption of the colorless carbinol had occurred during this interval. Corresponding data for PR, which does not fade completely, are shown in Fig. 4.

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[8] E. S. Amis and R. G. Overman, THIS JOURNAL, **66**, 941 (1944).

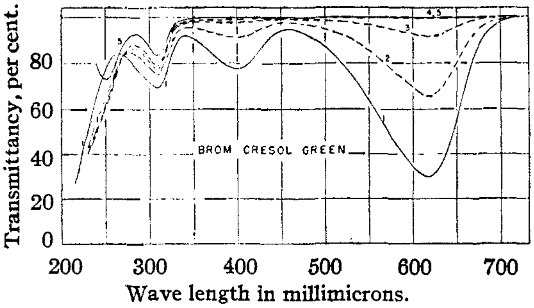

Fig. 3.—Per cent. transmittancy of brom cresol green in alkaline solutions plotted as a function of wave length: curve 1, unfaded at pH 8.2; curves 2, 3, 4 and 5, fading in 1.12 M NaOH after one, five, seven and thirteen days, respectively.

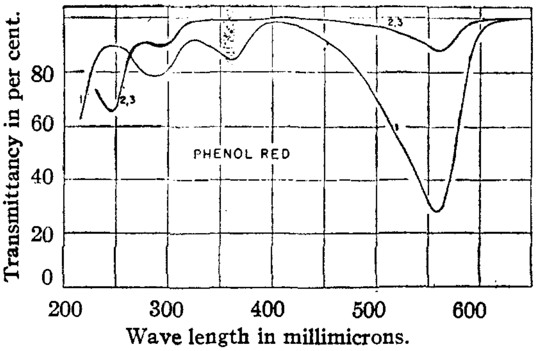

Fig. 4.—Per cent. transmittancy of phenol red in alkaline solutions plotted as a function of wave length: curve 1, unfaded at pH 11.8; curves 2 and 3, partially faded in 1.12 M NaOH after seven and twelve days, respectively.

V. Discussion of Results

Substituents introduced into the rings of the parent substance, PR, have pronounced effects upon both the forward and the reverse rate constants, as shown in Table I. Qualitatively, the variations in k_1 are in accord with the general inductive influences of these substituents. Replacement of a hydrogen atom by the more electronegative halogen makes the effective charge on the reactive central carbon atom more positive, and thus increases its rate of reaction with the negative hydroxyl ion. The opposite inductive effect of a methyl or other alkyl group leads to a decrease in the rate of reaction, compared to PR. The inductive influence of a given substituent should have opposite effects upon the forward and reverse rate constants. An increase in effective positive charge on the reacting carbon atom should make more difficult the removal of the hydroxyl ion from the carbinol and thus decrease k_2. For substituents sufficiently removed from the point of reaction, that is, in the meta position with respect to the central carbon atom, such is the case. For example, CR, with a meta methyl group in each of the chromophoric rings, has a lower value of k_1 and a higher value of k_2 than PR. On the other hand, MCP, with a methyl group in the ortho position, has lower values for both k_1 and k_2, indicating that some other factor predominates over the inductive effect. In terms of the collision theory, this behavior would be attributed to a steric effect associated with the proximity of the substituent to the reacting center of the molecule, which would play a similar role in lowering both k_1 and k_2.

In the cases of the indicators which have more than one substituent in the chromophoric rings, it is of interest to ascertain whether they act more or less independently of each other in influencing the rate constants. According to the method of Hammett,[9] the effect of a substituent upon a given type of reaction may be defined by $A_x = \log k_x - \log k_0$, where k_0 is the rate for the unsubstituted compound, and k_x is the corresponding rate constant when a given substituent is introduced. On the basis of the transition state theory, A_x is related to the change in free energy of activation, ΔF, by $A_x = \Delta F/(2.3RT)$ and consequently reflects a change in either the energy of activation or the entropy of activation, which is characteristic of the nature and location of the substituent introduced. It has been found that, in general, substituents relatively far removed from the reacting center affect primarily the energy of activation, whereas neighboring groups influence both the energy and the entropy of activation. For example, from a thermodynamic study of the alkaline fading of several sulfonphthaleins Hochberg and LaMer[4] found that meta substituents influenced the energy of activation while ortho substituents influenced both the energy and the entropy of activation.

Only three substituents need be considered for the present comparisons. These are a bromine in the meta position, an alkyl group (methyl or isopropyl) in the meta position, and a methyl group in the ortho position. No distinction is made between a methyl and an isopropyl group in the meta position, because their inductive effects should be practically the same and they are sufficiently removed from the reacting center to minimize any differences due to size. Only the fading rates will be considered in detail since the values of k_2 are more approximate and could not be obtained in some instances.

From the values of k_1 for BCP, CR, MCP, and PR the separate substituent effects are given by $A_{m\text{-Br}} = +0.89$, $A_{m\text{-alkyl}} = -0.86$, and $A_{o\text{-CH}_3} = -1.82$. These values represent the effect of two identical substituents, one in each of the chromophoric rings. For the five remaining cases which have two or three substitutents in each ring, the observed values of A_x should be the same as the values calculated by summation of the individual substituent effects provided these groups exert independent effects on the reaction. The seventh and eighth columns of Table I show a comparison of the observed and calculated values of A_x. The

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[9] Louis P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940.

agreement is exact for BCP and BTB, both of which have two groups of opposite inductive effect, bromine and alkyl, in the meta positions. For BPB and BCG with two bromines in the meta positions, the observed values of A_x are lower than the calculated values by 0.09 and 0.24, respectively, and suggest a tendency toward saturation when both meta substituents have inductive influences in the same direction. As the fading of TB was extremely slow it is conceivable that some mechanism other than the formation of the carbinol, which might be too slow to be observable in the other cases, might be the controlling factor. That the mechanism is the same, is supported by the agreement between the observed and calculated values of A_x. The reasonably good agreement between the two values of A_x for the five cases listed shows that the total change in the free energy of activation is nearly an additive function of the contributions of the separate substituents. It should be possible to make satisfactory estimates of the alkaline stability of other poly-substituted sulfonphthaleins from a knowledge of the individual substituent effects.

It is of interest to note that the accelerating effect of a *m*-halogen on the fading rate of a sulfonphthalein is practically the same as the retarding effect of a *m*-alkyl group. On the basis of the generally observed inductive influences of these groups, a much larger effect might be expected from the *m*-halogen atom. Hammett correlated substituent effects quantitatively for a wide variety of aromatic reactions where the substituent is in the meta or para position, so that the entropy of activation remains substantially independent of the nature of the substituent for a given type of reaction. A_x may then be regarded as the product of two factors, $A_x = \rho\sigma_x$, where ρ is characteristic only of the type of reaction and σ_x depends only on the nature of the substituent. If the reaction under consideration conformed to this general rule, the observed values of A_x, $A_{m\text{-Br}} = +0.89$, $A_{m\text{-Cl}} = +0.86$, and $A_{m\text{-alkyl}} = -0.86$ should be proportional to the substituent constants listed by Hammett which are $\sigma_{m\text{-Br}} = +0.39$, $\sigma_{m\text{-Cl}} = +0.37$, and $\sigma_{m\text{-alkyl}} = -0.07$. Although the relative values for the two halogen atoms are normal with bromine having a slightly larger effect, the proportionality does not hold when the halogen and alkyl groups are compared. That Hammett's rule does not apply is not surprising in view of the high degree of benzenoidal–quinoidal resonance in the indicator ion. This resonance affects and may largely determine the effective charge on the central carbon atom. A given substituent, consequently, may influence this effective charge not only by exerting its normal inductive effect but also by modifying the resonance. Since the possibilities for this sort of resonance do not exist in the carbinol, the individual effects of the meta substituents in the case of k_2 might be expected to follow the order observed by Hammett. From the reverse rate constants, $A'_{m\text{-Br}} = -1.0$, $A'_{m\text{-alkyl}} = +0.3$, and $A'_{o\text{-methyl}} = -1.5$. Although the agreement is none too good, possibly because of the greater experimental uncertainties in determining k_2, a meta bromine has a definitely greater effect than a meta alkyl group in accordance with the general inductive influences of these groups.

The rate studies may be used to make a rough estimate of the maximum amount of reversible alkaline fading which might be encountered during the normal use of these indicators in the measurement of *p*H. The upper limit of the interval of color transformation may be taken as a *p*H three units higher than the pK^* of the indicator corresponding to 99.9% of the colored alkaline form. The values for pK^*, representing the ionization constants for each indicator, are given in Table I, column 10. The ninth column lists the values of K for the equilibrium eventually established between the colored alkaline form and the colorless carbinol form. The values in parentheses could not be determined directly from the experimental data but are approximate values obtained from the known values of k_1 and values of k_2 estimated from the substituent constants listed in the preceding paragraph. The eleventh column shows the ratio of carbinol to colored form of each indicator, $[\text{ROH}^=]/[\text{R}^=]$, which would be reached at the above limit of *p*H after sufficient time had elapsed for the equilibrium to be established. The extent of reversible fading is of the same order for all of the indicators and does not exceed 1% in any case although the fading rate constants vary by a factor greater than 10^4. It is evident that the indicators which fade the most rapidly and have the largest equilibrium constants have a compensating factor in that their color transformations occur at lower values of *p*H.

Summary

A quantitative examination by precise spectrophotometric methods of the stability in 1 M alkali of phenolsulfonphthalein and nine of its derivatives with alkyl and halogen substituents in the ortho and meta positions has been made. Some of the indicators faded completely, but in general the reaction continued only until some finite equilibrium was established between the colorless carbinol and the colored quinoid forms. The fading rate constants k_1, and, where possible, approximate values of the color regenerating rate constants, k_2, were calculated. The substituents were found to exert nearly independent effects upon the fading rate constants in cases where more than one substituent was present in the two chromophoric rings.

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