

# PRESSURE AND TEMPERATURE EFFECTS ON THE KINETICS OF THE ALKALINE FADING OF ORGANIC DYES IN AQUEOUS SOLUTION<sup>1</sup>

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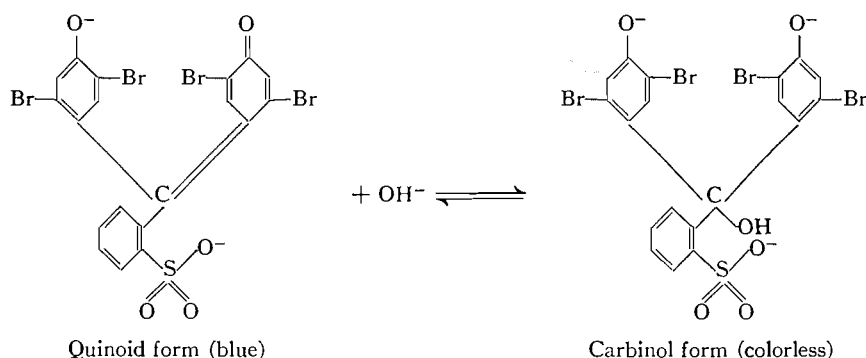
## ABSTRACT

The rates of the alkaline fading of bromphenol blue, phenolphthalein, crystal violet, and malachite green have been studied from atmospheric pressure to 16,000 pounds per square inch. The rates for phenolphthalein and malachite green were also measured over a range of temperatures in order to determine the activation energies and entropies. The reactions went essentially to completion with the exception of the fading of phenolphthalein, for which the effects of temperature and pressure on the back reaction and equilibrium constant were also studied. No effect of pressure was found for the fading of crystal violet, but the reactions of the other three dyes were accelerated by pressure, so that there are negative volumes of activation. These are correlated with the entropies of activation and are interpreted in terms of the reaction mechanisms.

## INTRODUCTION

Previous work (1, 2, 3, 4) has shown that for a number of reactions in aqueous solution the effects of pressure may be interpreted in terms of the electrostriction of the solvent around ions and dipoles. The present investigation consists of a study of reactions involving the attack by a hydroxide ion on large organic dye molecules. These reactions are of such a nature that electrostriction effects are not as powerful as in many of the previous reactions studied, so that structural effects are expected to play a part in determining the influence of pressure. Since the reactions chosen are structurally similar to one another, but are quite different electrically, they provide a useful means of separating the two effects. The dyes used were bromphenol blue, phenolphthalein, crystal violet, and malachite green, and of these the first two are negatively charged and the second two positively charged.

The kinetics of the alkaline fading of bromphenol blue were first studied under atmospheric pressure by Panepinto and Kilpatrick (5) and by Amis and La Mer (6). The results of these workers led to the following proposed mechanism, which was suggested by Amis and La Mer:



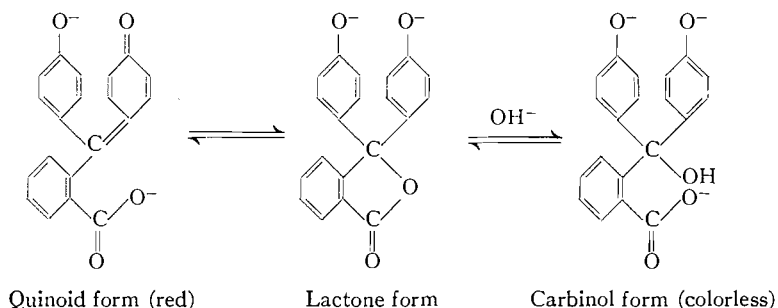
The reaction went to completion.

The alkaline fading of phenolphthalein was studied by Kober and Marshall (7), Biddle

<sup>1</sup>Manuscript received November 20, 1958.

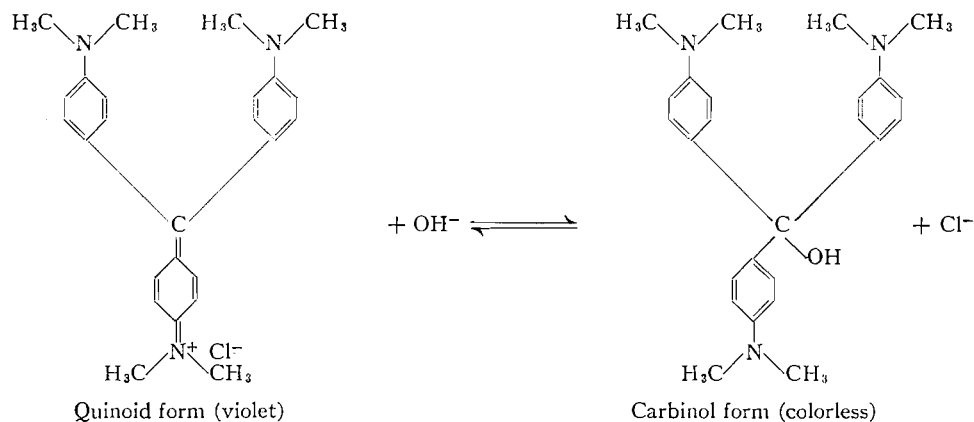
Contribution from the Department of Chemistry, University of Ottawa, Ottawa, Canada.

and Porter (8), Lund (9), Wygaerts and Eeckhout (10), and by Barnes and La Mer (11). The mechanism of the reaction can be represented by the following equations:

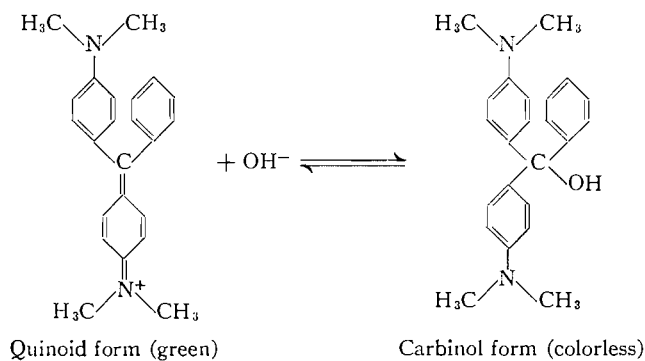


The reaction does not go to completion, and in our investigation the kinetics have been investigated in both directions over a range of temperatures and pressures.

The kinetics at atmospheric pressure of the fading of crystal violet in alkaline solution was studied by Biddle and Porter (8), Hockberg and La Mer (12), Goldacre and Phillips (13), and in great detail by Turgeon and La Mer (14). The reaction goes essentially to completion, and again involves the formation of a carbinol, as indicated below:

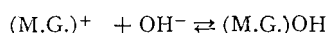
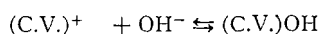
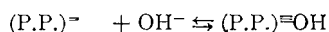
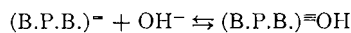


Very little work has previously been done on the fading of malachite green, which proceeds according to the equation:



In 1909 Sidgwick and Moore (15) made a few rate measurements, and Goldacre and Phillips (13) later made some studies in buffered solutions of pH 7.9.

It is to be seen that the four reactions may be represented schematically by the following equations:



The first two are reactions between ions of the same sign, the last two between ions of opposite sign. If electrostatic effects alone were important the first two reactions would therefore be expected to involve a decrease in volume during the activation process, and to be accelerated by pressure. The last two reactions, on the other hand, should involve an increase in volume and should be retarded by pressure. The results below show that these anticipations are realized in the first two cases, but that the third reaction is unaffected by pressure. The fourth reaction is accelerated by pressure. These results may be due to the fact that the charges do not approach very closely in the formation of the activated complex, and that structural effects are important.

#### EXPERIMENTAL PROCEDURE

##### *Materials*

The bromphenol blue used in the investigation was an Eastman Organics product. A stock solution was prepared by dissolving the dye in absolute ethanol, adding 0.01 *M* sodium hydroxide to convert it to the monosodium salt, evaporating the resulting solution in vacuum to dryness, and diluting with water to 1 liter. The phenolphthalein used was a C.P. grade Fisher product, and it was recrystallized three times from absolute methanol. The crystal violet used was an Anachemia Chemicals Ltd. product, and was purified by precipitating it as the carbinol, dissolving in hydrochloric acid, and recrystallizing the chloride twice; the crystals were dried in a vacuum desiccator. The malachite green used was a Fisher Scientific Company product (M-73), and was found by analysis to have the composition  $2[\text{C}_{23}\text{H}_{25}\text{N}_2]\text{C}_2\text{H}_2\text{O}_4 + \text{C}_2\text{H}_2\text{O}_4$  (mol. wt. 926.90). It was purified by recrystallizing it twice from water.

##### *High-pressure Technique*

The high-pressure technique used has been described in detail in a previous paper (4) in which a diagram of the apparatus is shown. In brief, the pressure vessel is designed so that the solutions are separated by mercury from the oil used in the rest of the apparatus, and so that samples can be introduced and withdrawn within a short period of time.

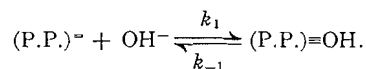
##### *Kinetic Procedure*

Since the sodium hydroxide was in all cases in excess of the dye, the reactions in the case of bromphenol blue, crystal violet, and malachite green were simple first-order reactions. The phenolphthalein reaction, on the other hand, had to be treated as consisting of opposing first-order reactions.

The first-order rate constants for the bromphenol blue reaction were obtained by plotting the logarithm of the photometric density *L* against the time and determining the slopes. The kinetic runs were carried out using a mixture that was  $2 \times 10^{-5}$  *M* in bromphenol blue and 0.2 *M* in sodium hydroxide. Five-milliliter samples were taken at

intervals of about 1500 seconds and delivered into a colorimeter tube containing 5 ml of water. The photometric densities of the solution were determined in an Evelyn photoelectric colorimeter using filter 565; the Lambert-Beer law was found to be obeyed by the dye solutions.

Since the phenolphthalein fading is reversible the mechanism must be represented as



The rate of disappearance of the dye is therefore given by

$$[1] \quad -\frac{d[(\text{P.P.})^-]}{dt} = k_1[(\text{P.P.})^-][\text{OH}^-] - k_{-1}[(\text{P.P.})=\text{OH}],$$

where  $k_1$  is the second-order rate constant for the forward reaction and  $k_{-1}$  is the first-order rate constant for the reverse reaction. Since  $[\text{OH}^-]$  is practically constant we can combine it with  $k_1$  to form a pseudo-first-order constant  $k_1'$ , the resulting equation being

$$[2] \quad -\frac{d[(\text{P.P.})^-]}{dt} = k_1'[(\text{P.P.})^-] - k_{-1}[(\text{P.P.})=\text{OH}].$$

The behavior is therefore that of reversible first-order reactions, which obey the kinetic law

$$[3] \quad k_1' + k_{-1} = \frac{2.303}{t} \log \frac{c_e}{c_e - c}.$$

Here  $c_e$  is the equilibrium concentration of the carbinol form of phenolphthalein, and  $c$  is the concentration of the carbinol form at any time  $t$ . Let  $c_r$  be the total concentration of phenolphthalein,  $c_e'$  the equilibrium concentration of the pink form of phenolphthalein, and  $c'$  the concentration of the pink form at any time  $t$ . Then since

$$[4] \quad c_e = c_r - c_e'$$

and

$$[5] \quad c = c_r - c',$$

equation [3] becomes

$$[6] \quad k_1' + k_{-1} = \frac{2.303}{t} \log \frac{c_r - c_e'}{c' - c_e'}.$$

The absorption of light by the substance was found to obey the Lambert-Beer law, and the concentration of the colored substance is therefore directly proportional to the photometric density  $L$  according to the expression

$$[7] \quad c' = L/K_1.$$

Here  $K_1$  is the calibration constant whose value depends on the nature of the colored substance and the characteristics of the filter used.  $L$  is the photometric density, equal to  $\log(I_0/I)$ , where  $I_0$  is the intensity of the incident light and  $I$  that of the transmitted light. Equation [6] therefore becomes

$$[8] \quad k_1' + k_{-1} = \frac{2.303}{t} \log \frac{L_r - L_e}{L - L_e},$$

where  $L_e$  is the photometric density of the solution at equilibrium,  $L_r$  is the photometric density of the solution when all its phenolphthalein is in the pink form, and  $L$  that at any time  $t$ .  $L_r$  and  $L_e$  are constants. From equation [8] it can be seen that a plot of  $\log (L - L_e)$  against the time should result in a straight line with a slope equal to

$$-\frac{k_1' + k_{-1}}{2.303},$$

so that the value of the combined rate constant ( $k_1' + k_{-1}$ ) can be calculated. The individual rate constants  $k_1$  and  $k_{-1}$  can be found from the equilibrium constant  $K$ , which is equal to  $k_1/k_{-1}$ . If ( $k_1' + k_{-1}$ ) is called  $k_e$  then

$$[9] \quad k_1 = \frac{k_1'}{[\text{OH}^-]} = \frac{k_e - k_{-1}}{[\text{OH}^-]} = \frac{k_e - k_1/K}{[\text{OH}^-]}.$$

From this

$$[10] \quad k_1 = \frac{k_e}{[\text{OH}^-] + (1/K)}$$

so that

$$[11] \quad k_{-1} = k_e - k_1'.$$

The kinetic runs with phenolphthalein were carried out using a solution that was  $1.00 \times 10^{-5} M$  in phenolphthalein and  $0.01 M$  in sodium hydroxide. Ten-milliliter samples were taken at about 2000-second intervals and the photometric densities of the samples were determined in the Evelyn photoelectric colorimeter using filter 540 (the absorption maximum is at  $550 \mu$ ). The photometric density at equilibrium was determined in each case by allowing the reaction mixture to remain under the experimental conditions for at least 24 hours. The value of the combined rate constant  $k_e$  was determined by plotting  $\log (L - L_e)$  against the time.

The procedure with crystal violet was similar to that with bromphenol blue. The dye shows an adsorption maximum at  $590 \mu$  and the best filter was No. 565. The Lambert-Beer law was again obeyed. The kinetic runs were carried out in a mixture that was  $5.0 \times 10^{-6} M$  in dye and  $2.0 \times 10^{-3} M$  in sodium hydroxide. Samples were withdrawn at intervals of about 900 seconds and the photometric densities  $L$  determined using the colorimeter. The values of  $\log L$  were plotted against the time, and straight lines obtained in each case. The apparent first-order rate constants were calculated from the slopes of the lines.

The kinetic procedure with malachite green was similar to that with crystal violet. The solutions used were  $0.0004 N$  in NaOH and  $0.00002 M$  in malachite green. Owing to the much lower concentration of NaOH used the solutions were protected from  $\text{CO}_2$  with a soda-lime tube. For runs under pressure, 40 ml each of the reacting solution were mixed and introduced into the pressure vessel. Ten-milliliter samples were taken at about 1000-second intervals and the photometric density measured as before using filter No. 565. In each case the logarithms of the photometric densities were plotted against the time.

## EXPERIMENTAL RESULTS

### *Bromphenol Blue*

Rate constants for the bromphenol blue reaction were determined at a temperature of  $25.0^\circ \text{C}$  and at pressures varying from atmospheric to 16,000 pounds per square inch. Typical plots of  $\log L$  against time are shown in Fig. 1, and the rate constants,

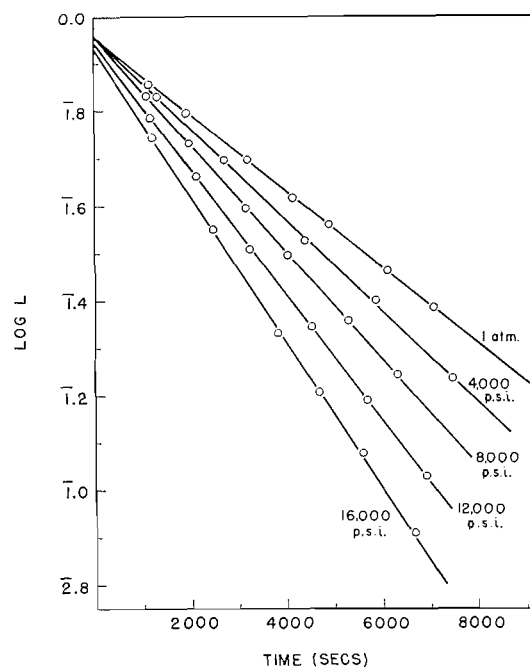


FIG. 1. Plots of  $\log L$  against time for the fading of bromphenol blue at various pressures.

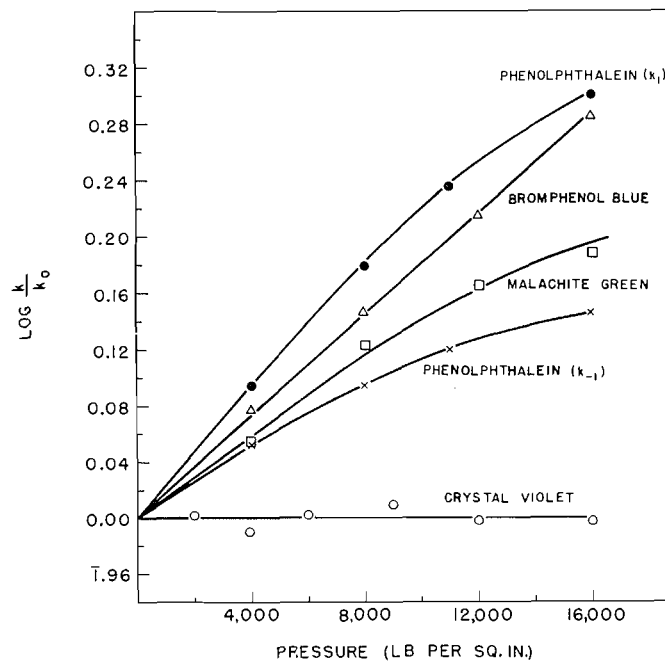


FIG. 2. Van't Hoff plots of the logarithms of  $k/k_0$  against the hydrostatic pressure.

obtained from the slopes, are listed in Table I;  $k_1'$  represents the apparent first-order rate constant and  $k_1$  the second-order rate constant. Figure 2 includes a plot of  $\log k/k_0$  against the pressure for this reaction. The relationship is seen to be quite linear, and the

slope of the line corresponds to a volume of activation of  $-14.9$  cc per mole. The energy of activation for the reaction was determined by Amis and La Mer (6), and the results at zero ionic strength are

$$\begin{aligned}\Delta S^* &= -13.34 \text{ calories per degree per mole,} \\ E &= 12.2 \text{ kcal per mole,} \\ A &= 2.04 \times 10^{10} \text{ liters per mole per second.}\end{aligned}$$

TABLE I  
Summary of results for the alkaline fading of bromphenol blue ( $T = 25.0^\circ \text{C}$ )

$P$ (lb/in. <sup>2</sup> )	$k_1'$ (sec <sup>-1</sup> )	$k_1$ ( $M^{-1}$ sec <sup>-1</sup> )	$k/k_0$	$\log k/k_0$
14.7	0.0001860	0.0009298	1	0
4000	0.0002226	0.001113	1.197	0.0781
8000	0.0002609	0.001305	1.404	0.1473
12000	0.0003056	0.001528	1.643	0.2156
16000	0.0003588	0.001794	1.929	0.2853

$$\Delta V^* = -14.90 \text{ cc/mole.}$$

### Phenolphthalein

Since an activation energy for the phenolphthalein reaction had not previously been determined, the rates of the reaction in both directions were measured over a range of temperatures. From the slopes of plots of  $\log (L - L_e)$  against time, the values of  $k_1' + k_{-1}$  can be calculated, and the results are included in Table II. By allowing the mixtures to

TABLE II  
Rate and equilibrium constants for the fading of phenolphthalein at various temperatures

Temperature ( $^\circ \text{C}$ )	$k_1' + k_{-1}$ (sec <sup>-1</sup> )	$K$ ( $M^{-1}$ )	$k_1'$ (sec <sup>-1</sup> )	$k_1$ ( $M^{-1}$ sec <sup>-1</sup> )	$k_{-1}$ (sec <sup>-1</sup> )
9.7	0.0000412	74.0	0.0000262	0.00262	0.0000151
20.0	0.0000960	86.9	0.0000446	0.00446	0.0000513
25.0	0.000143	66.7	0.0000572	0.00572	0.0000858
34.6	0.000311	41.8	0.0000917	0.00917	0.000219

$$\Delta H = -9.97 \text{ kcal/mole.}$$

$$E_1 = 8.59 \text{ kcal/mole.}$$

$$E_{-1} = 18.47 \text{ kcal/mole.}$$

$$\Delta F = -2.49 \text{ kcal/mole.}$$

$$\Delta S_1^* = -41.94 \text{ cal/deg-mole.}$$

$$\Delta S_{-1}^* = -17.12 \text{ cal/deg-mole.}$$

$$A_1 = 1.14 \times 10^4 M^{-1} \text{ sec}^{-1}.$$

$$A_{-1} = 3.06 \times 10^9 \text{ sec}^{-1}.$$

stand for over 24 hours at the four temperatures the equilibrium constants were determined, and are also shown in the table. The separated values of  $k_1'$  and  $k_{-1}$  are also shown and from  $k_1'$  the values of  $k_1$  are calculated, and are shown in the table. Figure 3 shows a van't Hoff plot of the logarithm of the equilibrium constant against the reciprocal of the absolute temperature, and it is seen that a straight line is obtained. The thermodynamical values obtained from this plot are as follows:

$$\Delta H = -9.97 \text{ kcal per mole,}$$

$$\Delta F = -2.49 \text{ kcal per mole,}$$

$$\Delta S = -25.1 \text{ cal mole}^{-1} \text{ deg}^{-1}.$$

Figures 4 and 5 show plots of  $\log k_1$  against  $1/T$  and of  $\log k_{-1}$  against  $1/T$ . The Arrhenius law is seen to be obeyed accurately, and the frequency factors and energies and entropies of activation obtained are:

$$\begin{aligned}
 E_1 &= 8.59 \text{ kcal per mole,} \\
 A_1 &= 1.14 \times 10^4 \text{ liters mole}^{-1} \text{ sec}^{-1}, \\
 \Delta S_1^* &= -41.49 \text{ cal mole}^{-1} \text{ deg}^{-1}, \\
 E_{-1} &= 18.47 \text{ kcal per mole,} \\
 A_{-1} &= 3.06 \times 10^9 \text{ sec}^{-1}, \\
 \Delta S_{-1}^* &= -17.12 \text{ cal mole}^{-1} \text{ deg}^{-1}.
 \end{aligned}$$

Table III shows the results obtained at 25.0° C and at the various pressures employed. Figure 6 shows a plot of the logarithm of the equilibrium constant against the pressure and from the slope of the straight line a value of  $\Delta V$  of 8.7 cc per mole was calculated. The plots of the logarithms of  $k_1$  and  $k_{-1}$  against the pressure are included in Fig. 2, and from the initial slopes values of -19.7 and -11.0 cc per mole are calculated for the volumes of activation for the forward and reverse reactions.

TABLE III

Rate and equilibrium constants for the fading of phenolphthalein, at various pressures ( $T = 25.0^\circ \text{C}$ )

$P$ (p.s.i.)	$k_1' + k_{-1}$ ( $\text{sec}^{-1}$ )	$K$ (liters $\text{mole}^{-1}$ )	$k_1'$ ( $\text{sec}^{-1}$ )	$k_1$ (liters $\text{mole}^{-1} \text{sec}^{-1}$ )	$k_{-1}$ ( $\text{sec}^{-1}$ )	$k_1/k_0$	$k_{-1}/k_0$
14.7	0.000143	66.7	0.0000572	0.00572	0.0000858	1	1
4000	0.000168	73.6	0.0000712	0.00712	0.0000967	1.245	1.127
8000	0.000193	81.2	0.0000865	0.00865	0.000107	1.512	1.241
11000	0.000212	87.3	0.0000986	0.00986	0.000113	1.724	1.317
16000	0.000232	98.0	0.000115	0.0115	0.000120	1.993	1.398

$$\Delta V_1^* = -10.66 \text{ cc/mole.}$$

$$\Delta V_{-1}^* = -10.98 \text{ cc/mole.}$$

$$\Delta V = -8.68 \text{ cc/mole.}$$

#### Crystal Violet

Rate constants for the fading of crystal violet were measured at a temperature of 25.0° C and at pressures varying from atmospheric to 16,000 lb per sq. in. The results are summarized in Table IV, which shows the apparent first-order constants  $k_1'$  and the true second-order constants  $k_1$  obtained by dividing  $k_1'$  by the concentration of hydroxide ions.

TABLE IV

Summary of results for the alkaline fading of crystal violet ( $T = 25.0^\circ \text{C}$ )

$P$ (p.s.i.)	$k_1'$ ( $\text{sec}^{-1}$ )	$k_1$ (liters $\text{mole}^{-1} \text{sec}^{-1}$ )	$k_1/k_0$	$\log k_1/k_0$
14.7	0.000520	0.260	1	0
2000	0.000522	0.261	1.004	0.0017
4000	0.000509	0.255	0.981	-1.9917
6000	0.000522	0.261	1.004	0.0017
9000	0.000532	0.266	1.023	0.0098
12000	0.000518	0.259	0.996	-1.9983
16000	0.000518	0.259	0.996	-1.9983

$$\Delta V^* = 0.$$

Pressure is seen to have essentially no effect on the rates, a conclusion that is verified by the plot shown in Fig. 2.

The results obtained by Turgeon and La Mer (14) at atmospheric pressure are, at an ionic strength of 0.0011  $M$ ,



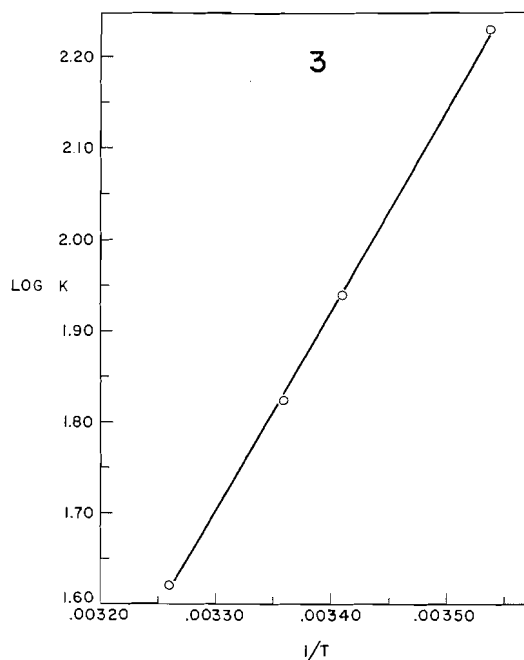


FIG. 3. Plot of the logarithm of the equilibrium constant against  $1/T$ , for the fading of phenolphthalein.

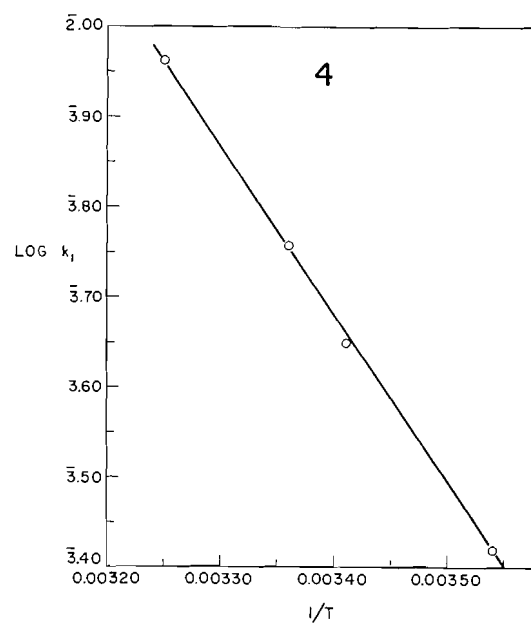


FIG. 4. Plot of  $\log k_1$  against  $1/T$ , for the fading of phenolphthalein.

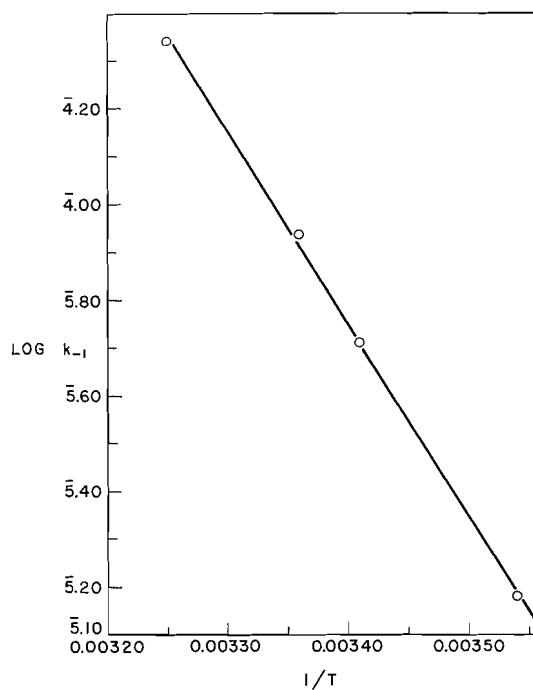


FIG. 5. Plot of  $\log k_{-1}$  against  $1/T$ , for the fading of phenolphthalein.

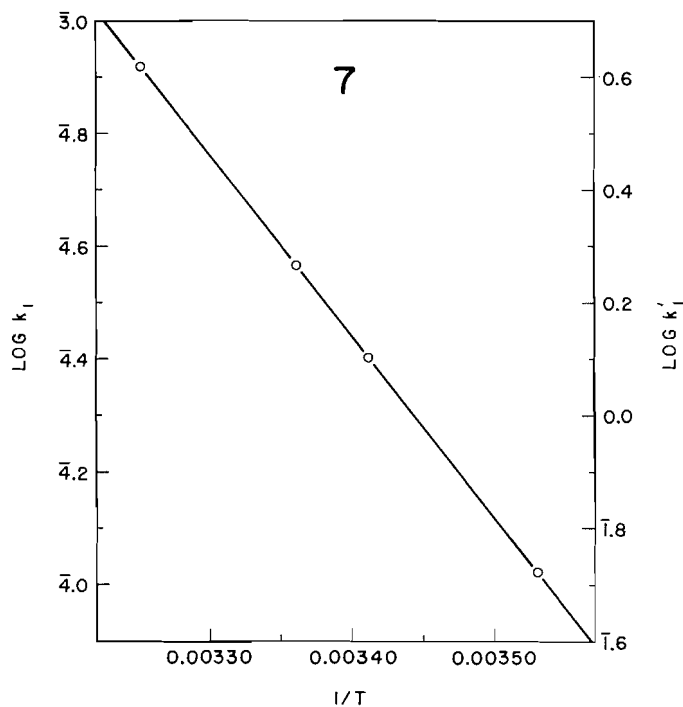
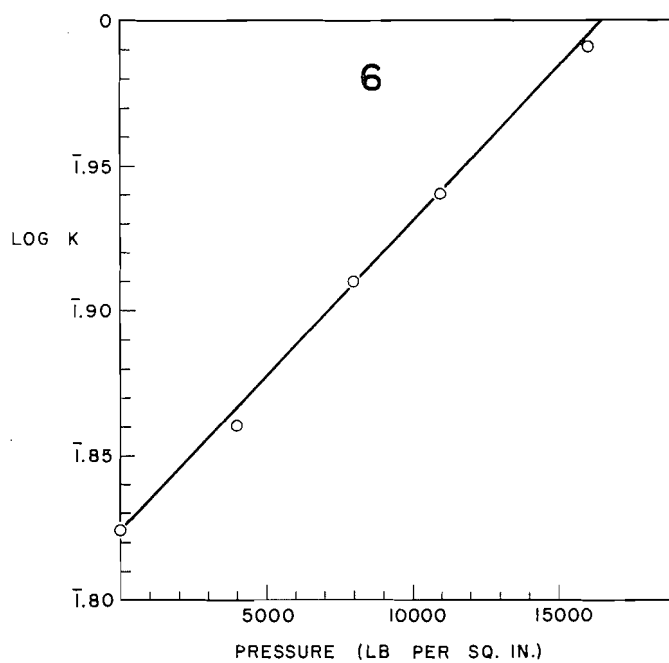


FIG. 6. Plot of  $\log K$  against the pressure, for the fading of phenolphthalein.  
 FIG. 7. Plot of  $\log k_1$  against  $1/T$  for the fading of malachite green.

$$\begin{aligned}
 E &= 15.1 \text{ kcal mole}^{-1}, \\
 A &= 3.13 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}, \\
 \Delta S^* &= -12.3 \text{ cal deg}^{-1} \text{ mole}^{-1}.
 \end{aligned}$$

### Malachite Green

Rate constants under atmospheric pressure and at the various temperatures employed are summarized in Table V, in which  $k_1'$  represents the apparent first-order rate constant

TABLE V  
Summary of results for the alkaline fading of malachite green  
under atmospheric pressure

Temperature ( $^{\circ}\text{C}$ )	$k_1'$ ( $\text{sec}^{-1}$ )	$k_1$ ( $\text{M}^{-1} \text{sec}^{-1}$ )
10.2	0.0001053	0.5265
20.0	0.0002533	1.267
25.0	0.0003684	1.842
34.9	0.0008291	4.146

$$\begin{aligned}
 E &= 14.65 \text{ kcal/mole.} \\
 A &= 1.023 \times 10^{11} \text{ M}^{-1} \text{ sec}^{-1}, \\
 \Delta S^* &= -10.15 \text{ e.u.}
 \end{aligned}$$

and  $k_1$  the true second-order rate constant. The corresponding Arrhenius plot is shown in Fig. 7. The energy of activation, frequency factor, and entropy of activation obtained are:

$$\begin{aligned}
 E &= 14.65 \text{ kcal mole}^{-1}, \\
 A &= 1.023 \times 10^{11} \text{ M}^{-1} \text{ sec}^{-1}, \\
 \Delta S^* &= -10.15 \text{ e.u.}
 \end{aligned}$$

Table VI shows the rate constants obtained at  $25.0^{\circ}\text{C}$  and under various pressures. The corresponding van't Hoff plot is included in Fig. 2; the curve is seen to be not linear. From the slope at the lower pressures we calculate a volume of activation of  $-12.0$  cc per mole.

TABLE VI  
Summary of results for the alkaline fading of malachite green  
( $T = 25.0^{\circ}\text{C}$ )

$P$ (p.s.i.)	$k_1'$ ( $\text{sec}^{-1}$ )	$k_1$ ( $\text{M}^{-1} \text{sec}^{-1}$ )	$k_1/k_0$
14.7	0.0004789	2.395	1
4000	0.0005422	2.711	1.132
8000	0.0006358	3.179	1.327
12000	0.0007014	3.507	1.464
16000	0.0007384	3.692	1.542

$$\Delta V^* = -12.0 \text{ cc/mole.}$$

## DISCUSSION

### Comparison with Previous Work

It is difficult to compare the rate constants obtained in the present investigation with those obtained by previous workers, owing to the different conditions employed. The following comparisons may, however, be of interest.

For bromphenol blue the value of the rate constant obtained at  $25.0^{\circ}\text{C}$  and 1 atm pressure was  $0.000932 \text{ M}^{-1} \text{ sec}^{-1}$ . Extrapolation of Amis and La Mer's (6) results to the same ionic strength (0.2 M) gives  $0.000854 \text{ M}^{-1} \text{ sec}^{-1}$ .

For the fading of phenolphthalein the present values of  $K$ ,  $k_1$ , and  $k_{-1}$  at 25° C and 1 atm pressure are as shown below:

$$\begin{aligned} K &= 65.25 \text{ } M^{-1}, \\ k_1 &= 0.00572 \text{ } M^{-1} \text{ sec}^{-1}, \\ k_{-1} &= 0.0000858 \text{ sec}^{-1}. \end{aligned}$$

The values obtained by Barnes and La Mer (11) under the same conditions are:

$$\begin{aligned} K &= 66.70 \text{ } M^{-1}, \\ k_1 &= 0.00634 \text{ } M^{-1} \text{ sec}^{-1}, \\ k_{-1} &= 0.0000972 \text{ sec}^{-1}. \end{aligned}$$

For crystal violet the value of  $k_1$  obtained in the present work was  $0.260 \text{ } M^{-1} \text{ sec}^{-1}$  at 25.0° C. The value of Turgeon and La Mer (14), corrected to the same ionic strength, was  $0.256 \text{ } M^{-1} \text{ sec}^{-1}$ . It was found that for this reaction there was some catalysis by the mercury in contact with the solution in the case of the work done in the high pressure vessel; the rate constant in the absence of mercury was  $0.207 \text{ } M^{-1} \text{ sec}^{-1}$ .

On the whole the agreement between the results of the present work and those of the previous workers is quite satisfactory.

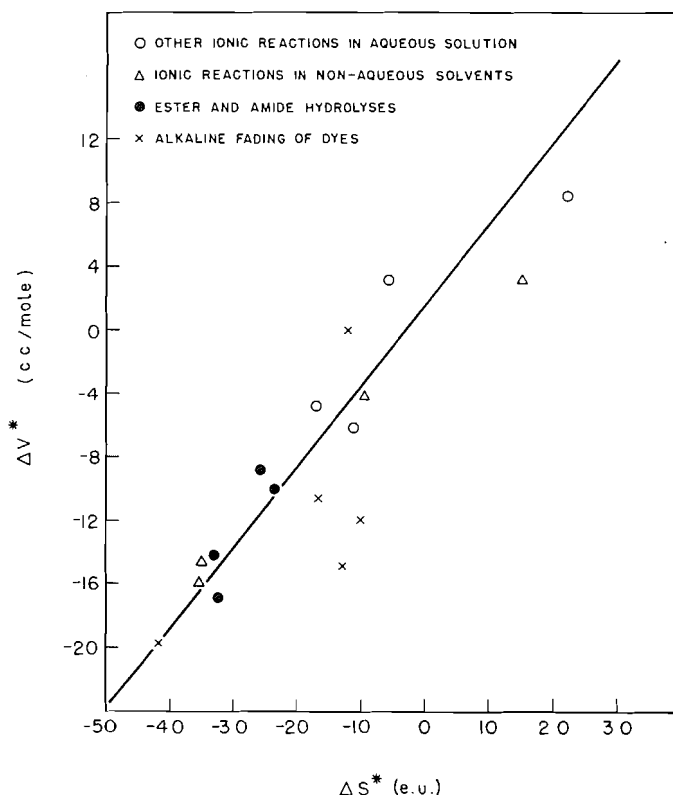
#### Significance of the $\Delta V^*$ Values

The  $\Delta V^*$  values obtained in the present investigation are listed in the last column of Table VII, which also gives the values of  $E$ ,  $A$ , and  $\Delta S^*$ . Also included in this table are the data for a number of other reactions; the last four are in solvents other than pure water.

TABLE VII  
Summary of data for reactions in aqueous solution

Reaction	$E$ (kcal)	$A$	$\Delta S^*$ (e.u.)	$\Delta V^*$ (cc per mole)	Ref.
Bromphenol blue + OH <sup>-</sup>	12.2	$2.0 \times 10^{10}$	-13.3	-14.9	Present work
Phenolphthalein + OH <sup>-</sup> ( $k_1$ )	8.6	$1.1 \times 10^4$	-41.9	-19.7	Present work
Phenolphthalein + OH <sup>-</sup> ( $k_{-1}$ )	18.5	$3.1 \times 10^9$	-17.1	-10.6	Present work
Crystal violet + OH <sup>-</sup>	15.1	$3.1 \times 10^{10}$	-12.3	0.0	Present work
Malachite green + OH <sup>-</sup>	14.7	$1.0 \times 10^{11}$	-10.2	-12.0	Present work
Methyl acetate + OH <sup>-</sup>	12.0	$9.3 \times 10^7$	-24.1	-9.9	4
Ethyl acetate + OH <sup>-</sup>	11.6	$3.2 \times 10^7$	-26.2	-8.8	4
Acetamide + OH <sup>-</sup>	14.2	$9.5 \times 10^6$	-33.5	-14.2	4
Propionamide + OH <sup>-</sup>	14.6	$1.5 \times 10^6$	-32.6	-16.9	4
CH <sub>2</sub> BrCOO <sup>-</sup> + S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	13.3	$1.6 \times 10^9$	-17.0	-4.8	2
CH <sub>2</sub> ClCOO <sup>-</sup> + OH <sup>-</sup>	22.7	$5.7 \times 10^{10}$	-11.6	-6.1	16, 17, 18
CH <sub>2</sub> BrCOOCH <sub>3</sub> + S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	17.2	$1.0 \times 10^{14}$	-5.7	+3.2	2
Co(NH <sub>3</sub> ) <sub>5</sub> Br <sup>++</sup> + OH <sup>-</sup>	23.6	$5.0 \times 10^{17}$	21.7	8.5	2
(CH <sub>3</sub> )(C <sub>6</sub> H <sub>5</sub> )(C <sub>6</sub> H <sub>5</sub> )(C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> )N <sup>+</sup> Br <sup>-</sup> → (CH <sub>3</sub> )(C <sub>6</sub> H <sub>5</sub> )(C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> )N + C <sub>2</sub> H <sub>5</sub> Br	29.7	$3.1 \times 10^{16}$	14.9	3.3	17, 18
C <sub>2</sub> H <sub>5</sub> O <sup>-</sup> + C <sub>2</sub> H <sub>5</sub> I → C <sub>2</sub> H <sub>5</sub> OC <sub>2</sub> H <sub>5</sub> + I <sup>-</sup>	20.7	$2.1 \times 10^{11}$	-9.7	-4.1	16, 18, 19
C <sub>6</sub> H <sub>5</sub> CCl <sub>3</sub> → C <sub>6</sub> H <sub>5</sub> CCl <sub>2</sub> <sup>+</sup> + Cl <sup>-</sup>	15.0	$3.5 \times 10^6$	-35.0	-14.5	1, 2
C <sub>6</sub> H <sub>5</sub> N + C <sub>2</sub> H <sub>5</sub> I → C <sub>6</sub> H <sub>5</sub> N <sup>+</sup> (C <sub>2</sub> H <sub>5</sub> )I <sup>-</sup>	14.4	$3.6 \times 10^6$	-35.4	-15.8	18, 19

Figure 8 shows a plot of  $\Delta V^*$  against  $\Delta S^*$  for all of the reactions listed in Table VII. As previously shown (4), there is a fairly good correlation between the values, although the reactions studied in the present work show greater deviations than do the other reactions. This is presumably due to the fact that structural factors are playing a more important role. When electrostatic interactions are predominant a correlation is expected, for reasons discussed in a previous paper (3), but structural effects may introduce deviations.

FIG. 8. Plot of  $\Delta V^*$  against  $\Delta S^*$  for a number of reactions.

The values of  $\Delta V^*$  obtained in the present investigation will now be discussed with reference to the mechanisms. The negative volumes of activation obtained for the fading of bromphenol blue and of phenolphthalein are consistent with the fact that there is an approach of charges of the same sign. However, since the hydroxide ion approaches the uncharged central carbon atom, a strong electrostatic effect is not to be expected. It therefore seems likely that structural effects contribute, and some evidence with regard to this is referred to below.

With crystal violet there is no volume of activation in spite of the approach of ions of opposite sign. The hydroxide ion, however, attacks the central carbon atom which is separated by several Ångströms from the three nitrogen atoms which share the positive charge. Electrostriction effects are therefore unimportant, and the zero value of  $\Delta V^*$  suggests that there is no volume change due to structural effects.

This conclusion gives the clue to the negative volumes of activation found with the other three fading reactions. The crystal violet ion is the only one of the four investigated in which the three benzene rings lie in a plane. This arises because the resonance involving the quinoid forms of the rings can occur with all three rings.\* In the case of bromphenol blue, phenolphthalein, and malachite green only two of the three rings can be involved

\*Spectroscopic results (20) have in fact indicated that, owing to repulsion between hydrogen atoms on neighboring rings, the crystal violet ion is not quite planar but that the three rings are twisted slightly out of the plane. This is not found with malachite green and other molecules in which one ring does not enter into the resonance and is therefore out of the plane of the other two rings.

in such resonance. The third ring may therefore be twisted out of the plane of the rest of the molecule, and the molecule may occupy a somewhat greater volume relative to the carbinol form.

The suggestion is therefore that in the bromphenol blue, phenolphthalein, and malachite green reactions the quinoid forms of the dyes may structurally be somewhat larger (relative to the carbinol forms) than in crystal violet, so that the fading reaction involves a decrease in volume. In the bromphenol blue and phenolphthalein reactions there may also be small contributions from electrostriction effects; these, however, will be unimportant for malachite green for the same reason as for crystal violet.

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