

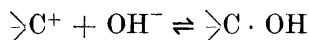
The Fading of Crystal Violet in Alkaline Solution

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When an aqueous solution of crystal violet ($(\text{CH}_3)_2\text{N} \cdot \text{C}_6\text{H}_4)_3\text{C} \cdot \text{Cl}$, is made alkaline, the colour gradually fades, but reappears on acidification. At very small hydroxyl ion concentrations a distinct violet colour remains indicating that the reaction does not go to completion, an equilibrium between the dye and the reaction product obviously being established.

This fading reaction is common to a great number of triphenyl methan dyes, amino compounds as well as hydroxy compounds (*e. g.* the phthaleins). The reaction taking place is the same in all instances and may be written:



As the absorption maximum of crystal violet in the visible region of light is found in the yellow-green part of the spectrum the fading reaction is very convenient for spectrophotometric rate measurements.

Since Brønsted¹ advanced his theory concerning the salt effect many chemists have contributed to the problem of ionic reactions, both theoretically and experimentally. It is generally assumed that the velocity constant at small concentrations of the reactants and small ionic strengths is given by^{2,4}:

$$\ln k = \ln k_0 - \frac{z_A z_B e^2 N}{\epsilon R T} \cdot \frac{1}{r_A + r_B} + \frac{z_A z_B e^2 N}{\epsilon R T} \cdot \frac{\kappa}{1 + a \kappa} \quad (1)$$

where k_0 is the molar rate constant extrapolated to $\epsilon = \infty$, z_A and z_B the valences of the reacting ions, e the electronic charge, N Avogadro's number, ϵ the dielectric constant, R the gas constant, T the absolute temperature, r_A and r_B the radii of the ions, a the distance of closest approach, and the Debye κ is given by

$$\kappa = \sqrt{\frac{8 \pi e^2 N}{1000 \epsilon k T}} \cdot \sqrt{I}$$

k being Boltzmann's constant and I the ionic strength. (The use of symbols employed in this article is that recommended by the "Commission on physico-chemical symbols and co-ordination of scientific terminologies" of the "International union of chemistry".)

Equation (1) is an approximation, and we may further neglect the term $a \kappa = 3.25 \cdot 10^7 \cdot a \sqrt{I}$ at $T = 300^\circ$ and $\epsilon = 80$; $a \kappa$ is thus of the same order of magnitude as \sqrt{I} , and we get the limiting law valid for small ionic strengths:

$$\ln k = \ln k_{0,\epsilon} + \sqrt{\frac{8\pi}{1000}} \cdot \frac{z_A z_B e^3 N^2}{(\epsilon RT)^{\frac{3}{2}}} \cdot \sqrt{I} \quad (2)$$

Omitting the term $a \kappa$ means that the dimensions of the ions are regarded negligible³.

For the fading of crystal violet the dependence of $\ln k$ on \sqrt{I} is linear until $\sqrt{I} = 0.15$, the slope of the curve being in accordance with the calculated value within about 5%. The reaction was studied in water at 25°C with the addition of sodium chloride, potassium sulphate and barium chloride as neutral salts. It is easily shown that the stoichiometric scheme above is also the kinetic equation of the reaction. Using hydroxyl ion concentrations 100 to 1000 times as great as the dye concentration, the logarithms of the extinctions plotted against the time give straight lines. This fact indicates that the reaction velocity is proportional to the dye concentration, and furthermore that the equilibrium concentration of the coloured form of the dye is very small. This is also demonstrated by measuring the equilibrium extinction, which in all cases was a few per cent of the initial extinction. On account of the smallness of the final extinction it was impossible to determine the equilibrium constant with any accuracy; it is however of the order of magnitude $2 \cdot 10^4$ at room temperature. When measured in solutions with different hydroxyl ion concentrations but identical and constant ionic strength (in casu 1.0 M NaCl) as suggested by Brønsted^{1, p. 205 f.} — the velocity constants proved to be proportional to the hydroxyl ion concentration.

In order to check the Arrhenius equation

$$\log k = B - \frac{\Delta H}{2.3 R T} \quad (3)$$

the reaction was studied at 45° , 35° , 25° and 15°C . In La Mer's treatment of the problem⁴ he has derived the following equations for the dependence of ΔH and B on \sqrt{I} at 25°C :

$$\frac{\Delta H - \Delta H_0}{2.3 R T} = 0.51 z_A z_B \sqrt{I} \quad \text{and} \quad B - B_0 = 1.52 z_A z_B \sqrt{I} \quad (4)$$

At 30° C, the middle of the interval examined, the constants are found to be 0.59 and 1.59 respectively. The equations of La Mer are identical with those derived by Moelwyn-Hughes⁵. The variation of ΔH and B with the ionic strength only show a poor agreement with the theory, probably on account of the difficulty of keeping hydroxyl ion concentrations of the order of magnitude $10^{-3} M$ sufficiently constant in unbuffered solutions.

EXPERIMENTAL

Crystal violet was synthesised from 4,4'-bis(dimethylamino) benzophenone, dimethylaniline and phosphorus oxychloride⁶ and recrystallised 4 times from water. On drying in the air the product could not be obtained with a definite amount of water of crystallisation; but after drying for two weeks in a vacuum dessicator with phosphorus pentoxide the product was anhydrous and on analysis gave the following results:

| | | | |
|---------------------------|-------|----------------|--------------|
| $C_{25}H_{30}N_3Cl$ (408) | Calc. | N 10.30 | Cl 8.69 |
| | Found | » 10.16, 10.27 | » 8.82, 8.70 |

Nitrogen was determined by the micro-Dumas method according to Pregl, and chlorine was determined by semi-micro Volhard titration in the filtrate after precipitation of the carbinol with chlorine free sodium hydroxide and corrected for the solubility of silver chloride in the combined filtrate and wash water. A 10^{-4} molar stock solution was made by weighing the correct amount and dissolving in a calibrated flask with carbon dioxide free water. This solution as well as all the others used were kept protected against the carbon dioxide in the atmosphere.

Sodium hydroxide, carbonate free, was prepared from 16–18 normal NaOH (Merck zur Analyse) which was filtered from the insoluble sodium carbonate through a sintered glass filter with protection against the carbon dioxide in the air. The stock solution was made up from carbon dioxide free water to about 0.02 *N* and kept in a paraffin lined bottle provided with a buret and soda lime tubes. It was standardised against hydrochloric acid, which in turn was standardised against borax (Kahlbaum zur Analyse).

Barium hydroxide (Kahlbaum z. A.) was dissolved in water, filtered, standardised, and preserved like sodium hydroxide.

Sodium chloride, *potassium sulphate* and *barium chloride* (Kahlbaum z. A.) were accurately weighed, dissolved in carbon dioxide free water in calibrated flasks.

Water. It was found, that a carbon dioxide free sample could be prepared by bubbling air, which had passed a washing bottle with diluted sulphuric acid and a large tower with soda lime through a 6 l pyrex flask with distilled water from the laboratory still at a rate of two bubbles per second for 24 hours. The pH of the water used was between 6.5 and 7.5 measured with a glass electrode. By controlling the pH after two months' storage it was found, that the flask, which for some years had been used for storing water, gave off no alkali to the water.

The spectrophotometer used was a Hilger Nutting spectrophotometer with the absorption tubes placed in a metal box, through which water from the thermostat was circulated. The temperature was constant within $\pm 0.01^\circ C$, and the thermometer used was controlled against a standard thermometer.

All the volumetric instruments were calibrated by weighing out with water.

Procedure. The various ingredients for a run except the dye solution were measured into a 100 ml measuring flask, which was then filled up with water until about 5 ml below the mark and placed in the thermostat. When temperature equilibrium was reached the requisite amount of crystal violet solution, as a rule 4 ml, was added so as to make the solution $4 \cdot 10^{-6}$ molar in respect to the dye. Simultaneously the stop watch was started. The solution was made up to 100 ml with water and again placed in the thermostat. By siphoning the solution into the absorption tube under protection against the atmospheric carbon dioxide the tube was rinsed five times with the solution and finally filled. The comparison tube was constantly filled with distilled water. Now the thermostat box with the absorption tubes was placed in position and the pointolite lamp lighted. The time elapsed after the start of the stop watch amounted to about 6 minutes. The extinction D was measured at intervals of 1, or in the slower experiments 2, 3, or 5 minutes at 586 $m\mu$ wavelength (absorption maximum of crystal violet). In a series of experiments with identical composition the solution was constantly irradiated in some of them, while in the others it was screened from the light except in the 10 second periods of measuring. The differences in the velocity constants lay within the experimental error, so it is concluded, that the light does not influence the reaction.

METHOD OF CALCULATION

According to Christiansen ⁷ the uncertainty of the rate constants is smallest, when calculated from observations made between 20 and 60 % conversion, and in most cases the reaction is only followed in this interval. In some cases the measurements were continued to a higher degree of conversion, and it was found that the points were still distributed at random about the same straight line, but the deviations were larger. Only in a few of the slow experiments the plot showed a faint curvature indicating a decrease in the rate constant. The slope of the plot of $\log D$ against t , and the intersection with the ordinate axis determining k and $\log D_0$ in the equation

$$\log D = \log D_0 - kt$$

were calculated by means of the method of least squares, using the Gaussian normal equations

$$\begin{aligned} n \log D_0 - k \Sigma t &= \Sigma \log D \\ \log D_0 \Sigma t - k \Sigma t^2 &= \Sigma t \log D \end{aligned}$$

In solving the equations it is a great facilitation, that when the t values constitute an arithmetical progression with the difference 1, the determinant $n\Sigma t^2 - (\Sigma t)^2$, as can be easily shown, is equal to $\frac{1}{12} (n^2 - 1) n^2$, where n is the number of observations. It should be noted, that the k thus calculated is not the true velocity constant but differs from it by the factor 2.30259, and it will be designated k' in the following.

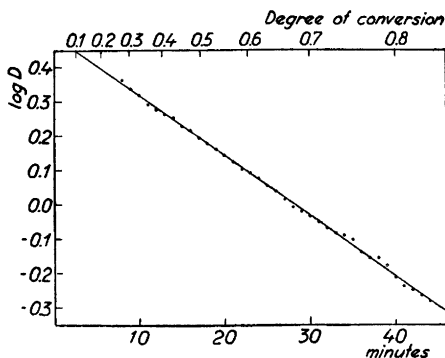


Fig. 1. 0.004 M NaOH, 0.025 M NaCl and $3.5 \cdot 10^{-6}$ M crystal violet at 25° C.

RESULTS

Fig. 1 shows the plot of a single measurement at 25° C. The straight line is drawn according to the values $\log D_0 = 0.493$ and $k' = 0.01750$ calculated by the above method including all observations. At the top of the diagram is marked the degree of conversion. When calculated from the first 16 observations ($0.2 < \alpha < 0.6$) $\log D_0$ is found to be $= 0.495$ and $k' = 0.01763$; the mean error of the $\log D$ values is 0.0047. In the same way the last 21 observations ($\alpha > 0.6$) give $\log D_0 = 0.493$ and $k' = 0.01748$, and the mean error 0.0084.

Table 1 shows the dependence of the velocity constant on the hydroxyl ion concentration in a series of measurements in 1 M sodium chloride.

Fig. 2 shows a plot of $\log (k'/[\text{OH}^-])$ against \sqrt{I} . The straight line has the theoretical slope 1.018. It is seen, that the limiting law holds until $\sqrt{I} \sim 0.15$. There is obviously no difference between the effect of univalent and divalent ions.

Table 1. k' in 1 M NaCl at 25° C as a function of $[\text{OH}^-]$.

| $[\text{OH}^-]$ | k' | $\frac{k'}{[\text{OH}^-]}$ | Deviation |
|-----------------|--------|----------------------------|---------------|
| 0.002 | 0.0044 | 2.200 | - 0.118 |
| 0.003 | 0.0059 | 1.967 | + 0.115 |
| 0.004 | 0.0086 | 2.148 | - 0.066 |
| 0.005 | 0.0106 | 2.120 | - 0.038 |
| 0.006 | 0.0126 | 2.100 | - 0.018 |
| 0.007 | 0.0145 | 2.071 | + 0.011 |
| 0.008 | 0.0169 | 2.113 | - 0.031 |
| 0.010 | 0.0208 | 2.080 | + 0.002 |
| 0.012 | 0.0236 | 1.967 | + 0.115 |
| 0.016 | 0.0329 | 2.056 | + 0.026 |
| Mean: | | 2.082 | 0.073 ~ 3.5 % |

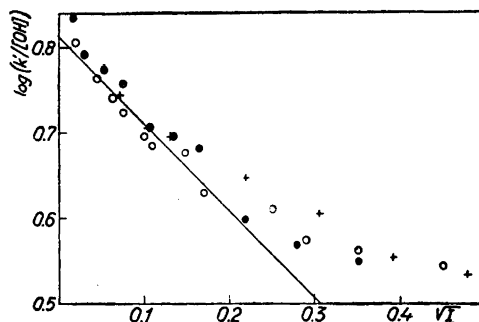


Fig. 2. Measurements at 25° C. Open circles: NaOH with and without NaCl; filled circles: Ba(OH)₂ with and without BaCl₂; crosses: NaOH with K₂SO₄.

Table 2 comprises the logarithms of the velocity constants measured at different temperatures and ionic strengths; each value is mean of 2—4 measurements. The table includes the terms *C* and *A* calculated by the method of least squares from the equation

$$\log \frac{k'}{[\text{OH}^-]} = C + A \sqrt{I}$$

which is identical with equation (2). In the last column are stated the theoretical values of *A*.

Table 2. Log (*k'*/[OH⁻]) as a function of temperature and ionic strength.

| | $\sqrt{I} = 0.0316$ | 0.0707 | 0.1000 | <i>C</i> | <i>A</i> | <i>A</i> (theor.) |
|-------|---------------------|--------|--------|----------|----------|-------------------|
| 15° C | 0.386 | 0.343 | 0.312 | 0.420 | - 1.09 | - 1.00 |
| 25° C | 0.773 | 0.731 | 0.695 | 0.810 | - 1.14 | - 1.02 |
| 35° C | 1.128 | 1.085 | 1.063 | 1.156 | - 0.96 | - 1.04 |
| 45° C | 1.498 | 1.471 | 1.423 | 1.539 | - 1.00 | - 1.06 |

In Fig. 3 is shown a plot of log (*k'*/[OH⁻]) against 1/*T* at different ionic strengths including the extrapolated values at $\sqrt{I} = 0$ (the column headed *C* in Table 2). The straight lines representing the equation

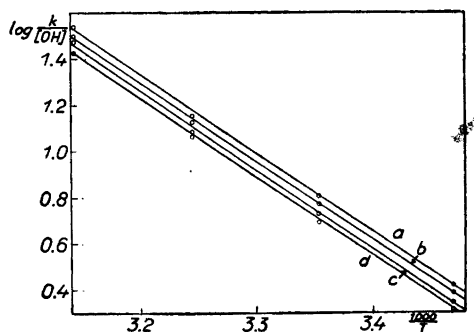


Fig. 3. Relation between log (*k'*/[OH⁻]) and 1/*T*. \sqrt{I} is for curve a 0.000, b 0.0316, c 0.0707, and d 0.1000.

Table 3. B' and ΔH as functions of the ionic strength.

| \sqrt{I} | B' | ΔH |
|------------|-------|------------|
| 0.0000 | 12.20 | 15530 cal |
| 0.0316 | 12.13 | 15490 — |
| 0.0707 | 12.23 | 15680 — |
| 0.1000 | 12.08 | 15530 — |

$$\log \frac{k'}{[\text{OH}^-]} = B' - \frac{\Delta H}{2.3 RT}$$

are calculated by the method of least squares, and in succession from above correspond to $\sqrt{I} = 0.000, 0.0316, 0.0707$ and 0.1000 .

The values of B' and ΔH calculated for these lines are shown in Table 3. They obviously do not satisfy equation (4) p. 301, in which $z_A z_B = -1$ must be inserted for this reaction.

SUMMARY

The reaction between crystal violet and hydroxyl ions in pure water and dilute salt solutions has been studied at $15^\circ, 25^\circ, 35^\circ,$ and 45°C . It is found that the salt effect is in accordance with Brønsted's theory, provided that the ionic strength is less than 0.02. The velocity constants found satisfy the Arrhenius equation in the interval examined, but the accuracy of the measurements is insufficient to verify the relation between the Arrhenius constants and the ionic strength as derived by La Mer.

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