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Kinetic Investigation of Alkaline Decolorization of Crystal Violet in Ethanol-Water Mixtures

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ABSTRACT

The ability of scientists to control and manipulate chemical reactions requires detailed understanding of reaction mechanisms to account for the formation of identified products from known starting materials. In this paper, kinetics of crystal violet (CV^+) decolorization by hydroxide ion (OH^-) in aqueous binary mixtures of ethanol was studied spectrophotometrically with a view to describing the nature of the transition state involved in the reaction mechanism. The reaction was found to be first-order in each of $[CV^+]$ and $[OH^-]$. Investigation of primary salt effect and solvent effect on the rates of this reaction reveals that the reaction rates decrease with increasing ionic strength and solvent polarity. These findings suggest that the reaction of CV^+ with OH^- involves charge dispersal as the reactant species changed through the activated complex to the product, resulting in the reduction of charge density in the transition state. A concerted mechanism was proposed for the reaction.

Keywords: Crystal violet, Kinetics, Reaction mechanism, Salt effect, Solvent effect

Introduction

For over a century, scientists have been fascinated by the knowledge of how chemical transformation occurs at the microscopic (molecular or atomic) level. The microscopic steps in a chemical reaction which reflect how the reactant molecules interact with each other to form the product molecules are known as mechanism of the reaction (Sun, 2013). Knowledge of mechanism of a reaction enables scientists to tinker with the reaction conditions in a way that makes optimization of product yield and prediction of reaction rate possible. To understand completely the mechanism of a reaction, it is required to know, as a function of time, the precise positions of the atoms in the reactant molecules as

they are converted into products via any possible intermediates. According to Lewis (1961), a complete description of the state of a reacting system at every point from the beginning to the end of a reaction is practically impossible, and this task has never been achieved because the experimental techniques that are currently at the disposal of scientists are not well suited to follow the structural changes that occur within the timescale of most chemical reactions (that is, within 10^{-13} to 10^{-15} second). Therefore, knowledge of reaction mechanisms is mostly based on indirect experimental evidence.

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At the very minimum, a reaction mechanism must consist of a full description of all the intermediates and all the transition states encountered between the starting reactants and the final products (Lewis, 1961). Techniques, such as spectroscopic characterization, isotopic substitution, stereochemical study, product analysis, calorimetric method, kinetic investigation, and quantum computation, have been employed by scientists to study mechanism of reactions (Jackson, 1972; Bentley, 2006; Fischer and Hungerbuhler, 2006; Li *et al.*, 2010; Chen *et al.*, 2012). Among these techniques, the use of kinetics is the most popular. For reactions occurring in solution, kinetic investigations involving systematic manipulation of reaction variables provide very useful information about several features of reaction mechanisms. Investigation of medium effect on reaction rates is especially useful because such investigation provides information about transition state, a structural arrangement that is not amenable to direct observation (Morse, 1961; Kalidas *et al.*, 2000).

Crystal violet, a triarylmethane dye known chemically as hexamethylparosaniline chloride, is an antiseptic with selective action on Gram-positive organisms. It is used as histological stain and in the treatment of burns, boils, carbuncles, and mycotic skin infection (The Council of Pharmaceutical Society of Great Britain, 1973). In chemistry, the decolorization reaction of crystal violet with hydroxide ions has been used for over three decades by researchers to test theories of reactions in solutions. The frequent choice of this reaction for the aforementioned purpose may be due to the gradual disappearance of crystal violet color, which makes it easy and convenient to monitor the progress of the reaction. Although kinetics of decolorization reaction of crystal violet by hydroxide ions has been studied extensively by many researchers (Albrizzio, *et al.*, 1972; Mandal *et al.*, 1986; Talman *et al.*, 2005; Du *et al.*, 2013), no detail description of the transition state involved in the mechanism of the reaction is well documented in the literature. It is against this background that the present paper seeks

to study the kinetics of crystal violet decolorization by hydroxide ions with a view to describing the nature of the transition state involved in the reaction mechanism.

Materials and methods

Reagents

All the reagents and solvent used were of high purity and were therefore used as supplied. Doubly distilled water was used to prepare the solvent mixtures. Stock solutions of crystal violet ($1 \times 10^{-4} \text{ moldm}^{-3}$), NaOH ($2 \times 10^{-2} \text{ moldm}^{-3}$) and KCl ($2 \times 10^{-1} \text{ moldm}^{-3}$) were prepared in aqueous binary mixtures of ethanol of varying compositions (mol-% of water = 10, 30, 50, 70, 90 and 100%) using standard procedure (Mendham *et al.*, 2000). All reagents were freshly prepared every day before the commencement of new experiment.

Kinetic Measurements

In all the kinetic experiments described in this paper, the progress of reaction was monitored by measuring the decrease in absorbance of crystal violet as a function of time using UNICO UV-2100 Spectrophotometer (UNICO Instrument Co., Ltd, Shanghai, China) maintained at a constant temperature of $28 \pm 0.1 \text{ }^\circ\text{C}$. All the kinetic measurements were carried out in triplicate and the total ionic strength of each solution was maintained at a constant value of 0.02 moldm^{-3} except where otherwise stated.

Kinetic experiment designed to determine the order of reaction with respect to crystal violet was carried out by mixing appropriate volumes of stock solutions of crystal violet, sodium hydroxide, potassium chloride, and aqueous solvent mixture in a 10 cm^3 flask to give a final mixture in which the concentration of OH^- ($2 \times 10^{-3} \text{ moldm}^{-3}$) is several fold higher than the concentration of CV^+ ($1 \times 10^{-5} \text{ moldm}^{-3}$). Under the condition of $[\text{OH}^-] \gg [\text{CV}^+]$, equation (1) is transformed into equation (2) and the

experimental data obtained for the change in crystal violet concentration as a function of time were fitted to pseudo-zero-order kinetic model (equation 5), pseudo-first-order kinetic model (equation 6), and pseudo-second-order kinetic model (equation 7). In order to determine the reaction order with respect to OH^- concentration, the experiment just described was carried out five times using different concentrations of OH^- (0.002, 0.004, 0.006, 0.008 and 0.010 $mol\ dm^{-3}$) while keeping the other reaction variables constant. To analyze the data obtained in these experiments, equation (3) was transformed into a linear form shown in equation (4), and this linear equation was used to construct a plot of $\log k'$ against $\log [OH^-]$ with the data obtained from the experiments.

The dependence of reaction rate on solvent polarity was investigated in a series of experiments by reacting CV^+ ($1 \times 10^{-5} \text{ mol}\ dm^{-3}$) with OH^- ($6 \times 10^{-3} \text{ mol}\ dm^{-3}$), changing the composition of ethanol-water solvent mixture in each experiment but keeping all other reaction variables constant ($\chi_{H_2O} = 0.3, 0.5, 0.7, 0.9$ or 1.0). Similarly, the dependence of reaction rate on the ionic strength of the reaction medium was investigated in a series of experiments by reacting CV^+ ($1 \times 10^{-5} \text{ mol}\ dm^{-3}$) with OH^- ($2 \times 10^{-3} \text{ mol}\ dm^{-3}$) in water ($\chi_{H_2O} = 1.0$), changing the total ionic strength of the medium in each experiment but keeping all other reaction variables constant ($I = 0.02, 0.04, 0.06, 0.08, 0.10, \text{ or } 0.12 \text{ mol}\ dm^{-3}$).

$$\text{Rate} = k[CV^+]^x[OH^-]^y \quad (1)$$

$$\text{Rate} = k'[CV^+]^x \quad (2)$$

$$k' = k[OH^-]^y \quad (3)$$

$$\log k' = y \log [OH^-] + \log k \quad (4)$$

$$[CV^+] = -k't + [CV^+]_0 \quad (5)$$

$$\ln [CV^+] = -k't + \ln [CV^+]_0 \quad (6)$$

$$1/[CV^+] = k't + 1/[CV^+]_0 \quad (7)$$

$$\ln k = \ln k_0 + 2z_A z_B A \sqrt{I} \quad (8)$$

Statistical Analysis

The data collected in this study were analyzed using simple linear regression method. The fitness of the regression models were statistically evaluated using R^2 values. All statistical analyses were carried out using Microsoft excel® 2010.

RESULTS

Among the three kinetic models tested in this paper, a plot of $\ln [CV^+]$ against time was found to be almost linear ($R^2 = 0.998$), indicating that the reaction of crystal violet with hydroxide ion is first-order with respect to crystal violet concentration (Figure 1). Values of pseudo-first-order rate constants (k') obtained at various hydroxide ion concentrations are presented in Table 1 and these data were used to construct a plot shown in Figure 2. As displayed in Figure 2, a plot of $\log k'$ against $\log [OH^-]$ gives a linear plot ($R^2 = 0.948$) with a slope that is equal to 0.921. This implies that the reaction under investigation is first-order with respect to hydroxide ion concentration because the value of the slope obtained in the plot is approximately equal to one. On the basis of these findings, the differential rate law expression for the reaction between crystal violet and hydroxide ion can be written as equation (9), suggesting that this reaction is second-order overall.

$$-\frac{d[CV^+]}{dt} = k[CV^+][OH^-] \quad (9)$$

Presented in Table 2 are the second-order rate constants and the relative rate constants for the reaction of crystal violet with hydroxide ions at various compositions of the solvent mixtures. Using these results to construct a plot of $\log k$ versus E_T^N (normalized $E_T(30)$ values) shown in Figure 3, an inverse correlation (see the negative slope of the plot in Figure 3) which deviates slightly from linearity ($R^2 = 0.936$) was observed. Comparison of the relative rates displayed in Table 2 also indicates that there is consistent but slight decrease in the reaction rates

on increasing the composition of water in the aqueous binary mixtures from 30% in the least polar solvent system to 100% in the most polar solvent system.

As shown in Table 2, the reaction rate observed when the reaction was conducted in the least polar solvent system is approximately nine times faster than the reaction rate when the reaction was conducted in the most polar solvent system. Results for the variation of second-order rate constants with ionic strengths of the reaction medium are presented in Table 3, and these data were fitted to equation (8) to obtain the plot of $\ln k$ versus \sqrt{I} shown in Figure 4. As shown in Figure 4, the reaction rates for the decolorization of crystal violet cation (CV^+) by hydroxide ion (OH^-) were retarded as the ionic strength of the reaction medium increases.

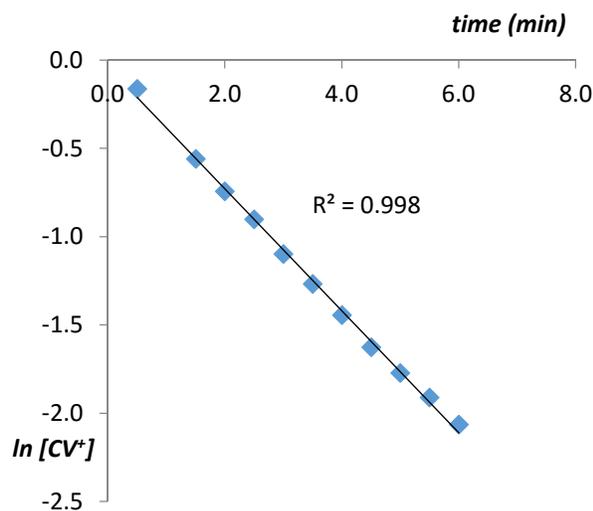


Figure 1: Pseudo-first order plot for the reaction of crystal violet with excess OH^- concentration

Table 1: Variation of pseudo-first-order rate constants with OH^- concentrations

$[OH^-]$ ($mol\,dm^{-3}$)	k' (min^{-1})
0.002	0.154 ± 0.044
0.004	0.405 ± 0.025
0.006	0.525 ± 0.072
0.008	0.589 ± 0.083
0.010	0.707 ± 0.084

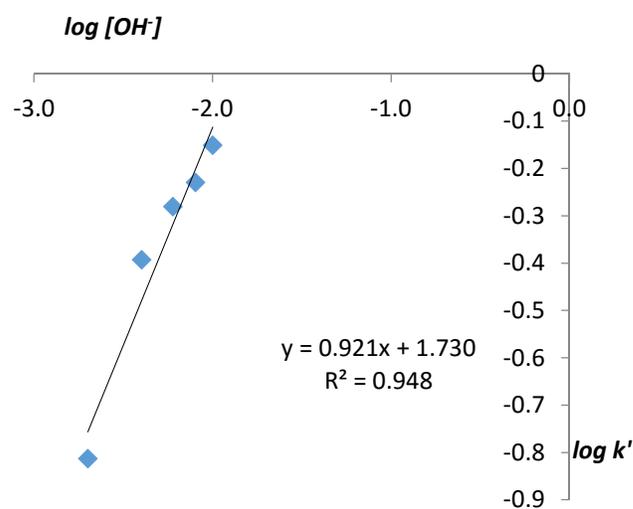
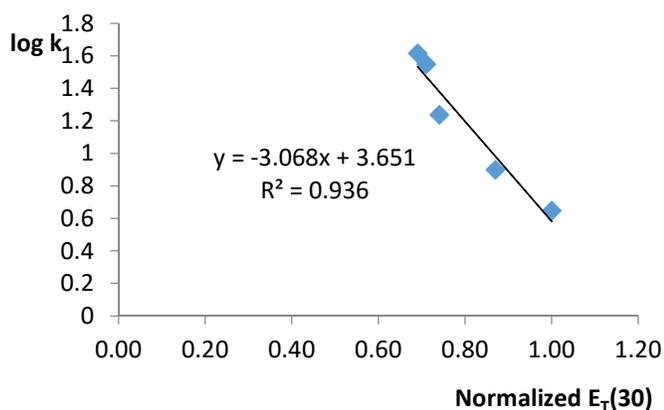


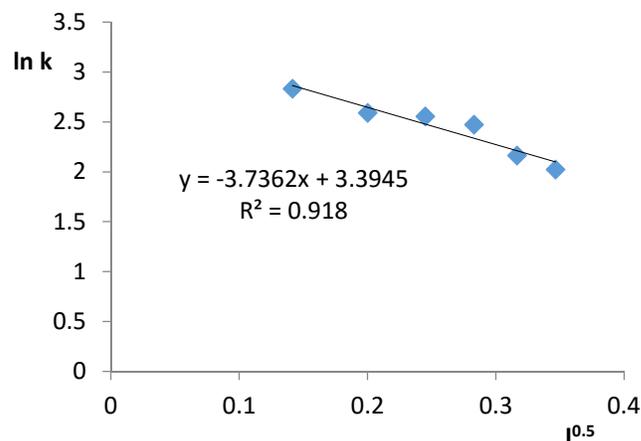
Figure 2: $\log k'$ versus $\log [OH^-]$ plot for determining the order of reaction with respect to $[OH^-]$

Table 2: Variation of second-order rate constants and relative rate constants with normalized $E_T(30)$ of the solvent mixtures

Ethanol-Water mixture		
(mol-% H_2O)	E_T^N k ($mol^{-1}dm^3min^{-1}$)	$k_{rel.}$
30	$0.6941.32 \pm 1.74$	9.29
50	$0.7135.43 \pm 1.84$	7.96
70	$0.7417.30 \pm 0.29$	3.89
90	$0.877.95 \pm 0.54$	1.79
100	$1.004.45 \pm 0.11$	1.00

**Figure 3:** $\log k$ versus E_T^N plot for determining the effect of solvent polarity on reaction rate**Table 3:** Variation of second-order rate constants with ionic strengths of the reaction medium

I ($mol\,dm^{-3}$)	k ($mol^{-1}dm^3min^{-1}$)
0.02	17.02 ± 1.16
0.04	13.33 ± 0.86
0.06	12.88 ± 1.44
0.08	11.85 ± 0.77
0.10	8.72 ± 0.43
0.12	7.58 ± 1.33

**Figure 4:** $\ln k$ versus \sqrt{I} plot for determining the effect of ionic strength on reaction rate

DISCUSSION

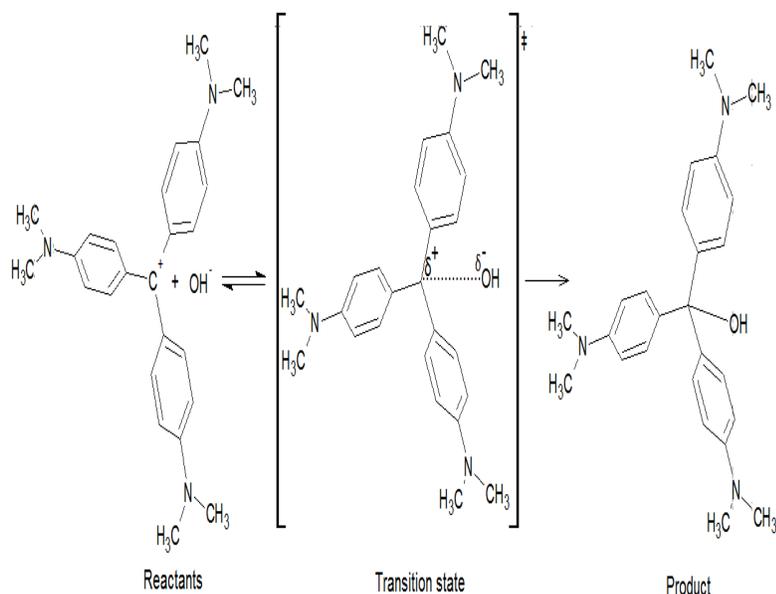
The rate law obtained in this study (equation 9) indicates that the reaction under investigation is first-order in each of $[CV^+]$ and $[OH^-]$. This is consistent with the findings reported in literature for alkaline fading reactions of crystal violet and other triarylmethane dyes (Mandal *et al.*, 1986; Du *et al.*, 2013). As pointed out by Edwards *et al.* (1968), information about elemental composition and charge of the transition state in the rate-determining step can be obtained from empirical rate law. For the reaction between crystal violet and hydroxide ions, it can be inferred that the transition state contains twenty-five carbon atoms, thirty-one hydrogen atoms, three nitrogen atoms and one oxygen atom, obtained by simple combination of all the atoms in crystal violet cation and hydroxide ion.

The progressive decrease in the rate of reaction observed between crystal violet and hydroxide ions on moving from solvents of low polarity to solvents of high polarity is an indication that the initial reactant species were more stabilized by solvation in the more polar solvents than the activated complex (Reichardt, 1982; Sun, 2013). This suggests that there is a reduction in charge density as the reactant species changed through the activated complex to the product (Jackson,

1972; Canle *et al.*, 2006; Meek *et al.*, 2016). Reactions involving charge creation or destruction during activation process are usually affected to a greater extent by solvent polarity than reactions in which there is charge dispersal (Shorter, 1973; Reichardt, 2003). Since the magnitude of the rate deceleration observed in the results reported in this paper is small, it can be deduced that only charge dispersal occurred during the activation process.

The retardation observed for the rates of alkaline decolorization of crystal violet cation in medium of high ionic strength is in agreement with well-established chemical principle. According to this principle, reactions between ions of like charge (product of z_A and z_B in equation 8 is positive) are usually accelerated by an increase in ionic strength whereas reactions between ions of opposite charge (product of z_A and z_B in equation 8 is negative) are usually retarded by an increase in ionic strength (Reichardt, 2003). The reaction rates when one or both of the reactants is neutral (product of z_A and z_B in equation 8 is zero) are expected to be independent of the ionic strength. An increase in ionic strength of a reaction medium leads to an increase in the polarity of the medium (Reichardt, 2003). The observed kinetic salt effect reported in this paper can be explained since ions of opposite charge (such as CV^+ and OH^- studied here) react more slowly in solutions of high ionic strength because the charges cancel out and the activated complex formed has a less favorable interaction with its atmosphere than the separated ions (Canle *et al.*, 2006; Atkins and de Paula, 2010).

On the basis of the kinetic results presented and discussed in the preceding paragraphs, it may be suggested that the mechanism of the reaction between CV^+ and OH^- to form colorless carbinol occurs in a single concerted step, forming an activated complex with a reduced charge density along the reaction pathway (Scheme 1).



Scheme 1: A proposed single-step mechanism for the conversion of crystal violet to carbinol

CONCLUSION

Rate of chemical reaction between crystal violet and hydroxide ions was studied in aqueous binary mixtures of ethanol at constant temperature by monitoring the decrease in crystal violet concentration using spectrophotometric method. The reaction was found to be second-order overall and the reaction rate was found to display an inverse relationship with both solvent polarity and ionic strength. Interpretation of the results in the light of transition-state theory led to the conclusion that the initial reactant species were more stabilized by solvation than the activated complex because of the reduction in charge density as the reactant species undergoes transformation through the activated complex to the product. The reaction mechanism was considered to occur in a single concerted step.

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Conflict of Interests

The authors declare that there is no conflict of interest

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