CHAPTER-VI

Experimental Part

Purification of Materials and Preparation of Solutions

The solvents and the acids were purified in a similar manner as described in the first section. All the experimental stock solutions of acids and carbinol base of crystal violet were prepared as described previously. The determination of total concentration of the dye was done by the same procedure as described in the first section. The same necessary experimental precautions and conditions of equilibrium studies were maintained in all kinetic studies.

Outline of the Experiment

It has been already discussed in the equilibrium section that the carbinol base of crystal violet reacted with an acid to give a coloured salt according to the equation

$$B + HA \rightleftharpoons BH^+A^-$$

in aprotic medium. In most cases the reactions were slow enough to be studied kinetically. Initially we started with a colourless solution which gradually developed colour with time till it reached a constant value at equilibrium. Therefore, the kinetics of these reactions could be easily followed by means of a spectrophotometer.
Procedure for Kinetic Experiments

Before starting with the actual experiment, the experimental solutions of both carbinol base and acid of desired strength were prepared from the stock solutions and were allowed to be cooled for about thirty minutes in a thermostat maintained at 6.5°C. When the solutions attained the temperature of the bath, they were mixed thoroughly and the mixing time was noted. Next the mixture was quickly transferred into a stoppered absorption cell (cooled at 6.5°C) and finally transferred into the cell compartment maintained at 6.5 ± 0.1°C. The mixing of the solutions and the transfer of the mixture to the cell compartment was finished in about one minute and first reading could be taken after about two minutes after the start of the experiments. Sufficient time was allowed for attaining the equilibrium before noting down the equilibrium reading. The spectrophotometric readings were taken at 610 mμ.

Similar experiments were performed at temperatures 10°, 15°, 20° and 25°C and the kinetic procedure was similar to that described above.

Two sets of kinetic experiments were done. In the first where the carbinol base concentration was varied acid concentration was kept fixed and in the second the acid concentration was varied while the carbinol base concentration being fixed.
Method of Calculation

Let us again consider the reaction

\[ B + HA \rightleftharpoons BH^+ A^- \]  

Since, in most of our experiments, the concentration of acid being very high compared to that of carbinol base (100 to 1000 times), the above reaction can be regarded as a pseudo unimolecular reaction. Writing equation (1) in the form

\[ A \xrightarrow{k_1} B \quad (2) \]

as expression for overall rate constant, \( k \) can be obtained in the following way.

Suppose the initial concentration of 'A' is 'a' and initially no 'B' is produced, then after time 't' the concentration of 'A' and 'B' are \((a-x)\) and \(x\) respectively.

Therefore, net rate of reaction at any instant,

\[ \frac{dx}{dt} = k_1 (a-x) - k_{-1} x \quad (3) \]

At equilibrium the rates of the two reactions are equal,

\[ \therefore \quad k_1 (a-x_e) = k_{-1} x_e \quad (4) \]

where \( x_e \) is equal to the amount of B at equilibrium and substituting the value of \( k_{-1} \) from equation (4) in equation (3) we get,

\[ \frac{dx}{dt} = k_1(a-x) - \frac{k_{-1} x}{x_e} (a-x_e) \]
or, \[
\frac{dx}{dt} = \frac{k_a}{x_e} (x_e - x)
\]

or, \[
\frac{dx}{x_e - x} = \frac{k_a}{x_e} dt
\]

On integrating we get,
\[
\ln(x_e - x) = \frac{k_a}{x_e} t + C
\]  \hspace{1cm} (5)

when \( t = 0, \ x = 0 \)
then \( C = - \ln x_e \)

By substituting the value of \( C \) in (5), we get,
\[
\frac{l}{t} \ln \frac{x_e}{x_e - x} = \frac{k_a}{x_e}
\]

but \( \frac{k_a}{x_e} = \frac{k_1}{x_e} + \frac{k_{-1}}{x_e} \) \hspace{1cm} \text{(from equation (4))} \quad \text{and}

let \( k = \frac{k_1}{x_e} + \frac{k_{-1}}{x_e} \)

then \( k = k_1 + k_{-1} = \frac{l}{t} \ln \frac{x_e}{x_e - x} \) \hspace{1cm} (6)

From equation (6) we can calculate the velocity constant, \( k \)
graphically. The specific rate \( k \) so obtained however, is the
sum of the rates for direct and reverse reaction.

Calculation of \( k_\alpha \), the Catalytic Constant

Since \( k \) depends on concentration of the acid, we have
followed Bell and calculated \( k_\alpha \) which is defined as \( \text{E} \)

\[
\lim_{C \to 0} \frac{k}{C} \quad \text{. The value of catalytic, constant} \ k_\alpha \text{ is}
\]
calculated graphically from the relation
\[
k = k_\alpha C - k_\beta C^2
\]
for most of acids and by relation

\[ k = k_\alpha C + k_\beta C^2 \]

or, \( \frac{k}{C} = k_\alpha + k_\beta C \)

for o-bromobenzoic acid. In the above relations

\[ k = k_1 + k_{-1}; \quad C = \text{acid concentration in moles/litre}; \]

\( k_\alpha \) and \( k_\beta \) are constant for each acid.