CHAPTER VI

Kinetic Parameters
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Many charge-transfer complexes exhibit a change in absorbance in the CT band with time, the colour fading in some cases and changing in others, indicative of some chemical reaction taking place. Some attention has been paid to the kinetics of these changes but the reports have been far in between and much less numerous compared with those on the formation constants. And unfortunately, the kinetic scene is as confused as the equilibrium picture, with conflicting views frequently expressed.

Reid and Mulliken [108] reported in 1954 that the absorbance of the pyridine - iodine complex in pure pyridine (K = 290) in the 422 nm band shifts slowly, increasing in intensity. They attributed it to the conversion of the initially-formed CT complex (which they named an "outer complex") into an "inner complex".

\[
\text{Py} + \text{I}_2 \rightleftharpoons \text{PyI}_2 \rightarrow (\text{PyI})^+ \text{I}^-
\]

They gave no rate data.
In the same year, Rose et al. [109] by determining argentimetrically the rate of the reaction of triethylamine with picrylchloride in the presence and in the absence of hexamethylbenzene, evaluated the formation constant of the hexamethylbenzene – picryl chloride complex, but this value turned out to be ten times that determined spectrophotometrically; they conjectured that the former K might include interactions other than the pure charge-transfer interaction. The actual reason may lie in the possibility that what they determined kinetically could have been the extent of binding in an “inner complex” formed from an initial “outer complex”.

Andrews and Keefer [110] in 1955 found that a molecular complex is largely formed first between anthracene and maleic anhydride in the Diels-Alder reaction. They obtained simple first-order plots for the change in absorbance of the diene with time for two-thirds of the complexation reaction when excess dienophile was present, from which they calculated second order rate coefficients.

Colter et al suggested the involvement of change-transfer complex in the catalysis of the acetolysis of some tosylates by phenanthrene [111] and by other arene donors [112]. They observed first-order rates in the presence of a stoichiometric concentration of
the donor [111]. Rappoport in 1963 identified the "outer" complex initially formed between a π-donor and electron-acceptor as a π-complex and the "inner complex" as a σ-complex formed by the lone pair of electrons to form a normal covalent bond with an atom in the acceptor, often leading to a charged or ionic species, as reflected in the reaction investigated earlier by the Reid and Mulliken [108].

Investigating the reaction of N, N- dimethylaniline [113] with tetracyanoethylene in chloroform, Rappoport found that the reaction proceeds in three steps:

\[
\text{N,N-dimethylaniline} + \text{TCNE} \rightarrow \pi\text{-complex} \rightarrow \sigma\text{-complex} \rightarrow \text{N,N-dimethyl-4-tricyano-vinylaniline.}
\]

with the elimination of a HCN molecule. He was able to monitor the π → σ transformation at 675 nm and considered it irreversible. The conversion of the σ complex to the product, which was observed at 515 nm, was very slow compared with the collapse of the π-complex. The π-σ conversion was first-order in the π-complex and first-order in dimethylaniline suggesting 'exchange' between the complex and the donor by the involvement of the donor molecule during the conversion. Rappoport and Horowitz [114] found a similar solution to
prevail in the reaction N-methylaniline with TCNE, and rates second order.

Nogami et al [115] in 1968, following the interaction of aniline with chloranil [2,3,5,6-tetrachlorobenzoquinone], found the π-complex to be stable below -78°C, the interaction being studied down to 36K [-187°C] in 75% ether -25% isopropyl alcohol medium. With increasing temperature, the π-complex decomposes to give a disubstituted product, 2,5-dichloro-3,6-dianilino-p-benzoquinone. They suggested two possible mechanisms

\[ D + C \rightleftharpoons \pi\text{-complex} \xrightarrow{\text{direct conversion}} \text{product} \quad \text{...(a)} \]

and

\[ D + C \rightleftharpoons \pi\text{-complex} \rightarrow \text{intermediate} \rightarrow \text{product} \quad \text{...(b)} \]

and gave integrated rate equations for both the mechanisms.

Though they could not observe the σ-complex spectroscopically suggesting that it might be too short-lived, they conceded that the reaction probably proceeds via its formation. They identified the product by its UV-visible and infra-red spectra. They found that the increase of absorbance with time was initially linear and quadratic. They did not resolve the rate coefficients, but Fig. 3 in their paper, showing the time dependence of the absorbance due to
the product has a clear induction period lasting extending to about 200 minutes, the distinct mark of a consecutive process.

Litt and Summers [22] in 1973 found that the polymeric complexes formed by 10-methyl-phenothiazine and p-(methylthio)anisole acting as donors, with acceptors such as TCNE, decomposed with absorbance changes which gave first-order plots.

Shah and Murthy [116] followed spectroscopically the kinetics of the interaction of excess tertiary aliphatic amines with chloranil in different solvents and used the simple equation

\[ k = \frac{1}{t} \left[ \frac{Z_\infty - Z_0}{Z_\infty - Z_t} \right] \]

where \( Z_0 \), \( Z_t \) and \( Z_\infty \) are, respectively, the absorbances of the reaction mixture at \( t = 0 \), \( t = t \) and at the end of the reaction, to evaluate the first-order rate coefficient. They found the reaction to proceed in two stages, the complex decomposes first giving chloranil anion radical and then the monosubstituted product; in the case of triethylamine and tri-isopropylamine, the reaction stopped at the first stage. For the triethylamine - chloranil reaction, they estimated first-order rate coefficients of 8.2 per sec for the anion radical formation and 3.1 per sec for the formation of the product.
Dwivedi and Banga [117, 118] found that the reaction of aliphatic primary amines and aniline with DDQ proceeded in two stages, involving the formation of the mono-substituted intermediate and then the di-substituted (final) product. The first could be monitored in the case of aliphatic amines at 289 nm and the first-order rate coefficient calculated using the equation

$$k = \frac{1}{t} \ln \frac{Z_0}{Z_t}$$

... (55)

and the second reaction at 354 nm using eqn. (54). Thus for n-propylamine in chloroform at 299k, they found $k_1 = 4.03 \times 10^{-3}$ per s, for the first stage and $k_2 = 3.84 \times 10^{-3}$ per s for the sec. It is to be noted that $k_1$ and $k_2$ differ barely by ±25% from the mean. Similar results were obtained for all the four aliphatic amines in each of the three solvents.

Dwivedi et al. [119] found much the same to obtain in the reaction of substituted anilines with DDQ, but here the reported values of $k_1$, and $k_2$ (for the two steps) differ by a factor of 2 to 2.5.

Srinivasan et al [120-123] have studied spectroscopically the kinetics of the interaction of substituted amines which chloranil
in a number of solvents. With Mahalatchoumy [120] he attempted to apply the method of residuals, which is dealt with in the next chapter. Srinivasan and Couppammalle [121] have investigated solvent effects on the first-order kinetics of the reaction of N,N-dimethylaniline with chloranil. Srinivasan and Sindhujayarajan [122] have calculated the apparent first-order rate coefficients of the reaction of substituted anilines with chloranil in THF medium. Srinivasan and Sivasankari [123] have used the first-order rate coefficients of the reaction between m-toludine and chloranil to interpret solvent effects.

2. The Kinetics of Consecutive, First-order Reactions.

Most reactions in chemistry, including the familiar ones, proceed in a number of steps or stages, each step is characterized by a rate-coefficient ("rate constant") which, for a given reaction, is actually a function of many factors including the temperature, presence or otherwise of catalysts and inhibitors, solvent, ionic strength, etc. All these must be clearly specified to make a stated value of the rate-coefficient meaningful.

The actual kinetic situation in any reaction becomes complicated if all the steps are taken into account, but the concept
of 'the rate-determining step' (or, the rate limiting step) has been very helpful in simplifying the situation: the slowest of the steps generally determines the overall rate of the reaction, provided that all other steps are significantly faster. Further simplification is possible if the reaction is carried out with one reactant alone in a low concentration compared with the others, whereby the order of the reaction in numerically lowered. The most familiar of these are the pseudo-first order reactions.

However, the simple equations of kinetics fail when two or more steps in the reaction sequence are comparable in magnitude, say, by a factor of 20 or less. Under these circumstances, when the rates of these steps together determine the overall rate (of formation of the final product), it is labelled a consecutive reaction system. The simplest of all these is the two-step, consecutive first-order reaction, which may be generalized as:

\[
\begin{align*}
A & \xrightarrow{k_1} B \xrightarrow{k_2} C \\
\end{align*}
\]

The treatment of this reaction system and the derivation of the integrated rate equations for the reactant A, the intermediate B and
the product C, are covered in all standard books, including [124, 125]: if B and C are initially absent,

\[ A = A_0 \exp(-k_1 t), \]

\[ B = A_0 \frac{k_1 [\exp(-k_1 t) - \exp(k_2 t)]}{(k_2 - k_1)} \]

\[ C = A_0 \frac{[1 - \exp(-k_2 t) - k_2 \exp(-k_2 t)]}{(k_2/k_1)} \]

The overall kinetic profile is determined by the relative magnitudes of \( k_1 \) and \( k_2 \) (or by the \( k_2/k_1 \) rate ratio). When \( k_2 \sim k_1 \), the general profiles for the time-dependence of the relative concentrations of the reactant (A), intermediate (B) and the product (C) are as in Fig. 2, the actual profiles depending on the magnitude of the rate ratio, \( k_2/k_1 \).

![Figure 2](image_url)

Generally, the concentration of the reactant decreases in an exponential manner; that of the intermediate first increases,
reaches a maximum and then decreases; meanwhile the concentration of the product increases very slowly at first, marking an induction period (the end of which coincides with the appearance of the maximum in the concentration curve of the intermediate), and then increases fast before leveling off. The appearance of an induction period in product formation is diagnostic of a series of consecutive reactions preceding it.

The situation, and the equations for A, B and C become complicated when either of the two steps or both, become reversible. And if there are more than two steps of comparable velocities in the reaction sequence, the equations become more formidable [126]. But this thesis is limited in scope to irreversible, two-step, consecutive first-order reactions the rate equations of which are given above. In these equations A, B and C are the formal concentrations of the three species, determined by a conventional method such as titrimetry.

The equation for the disappearance of the reactant is simple first-order in A and contains only one rate-coefficient, $k_1$. It can be readily solved for $k_1$. However, the equations for the intermediate B and the product C contain the difference between two
exponential terms of the parameters $k_1$ and $k_2$, and are transcendental. Estimates of $k_1$ and $k_2$ can be obtained from B versus t or C versus t data only by iterative methods.

3. Evaluation of Consecutive Reaction Rate-coefficients from Spectrophotometric Data.

When a spectrophotometer is employed to estimate concentrations of a species in a solution, the observed absorbance is the algebraic sum of the contributions by all the absorbing species at the given wavelength:

$$Z = \ell \sum C_i E_i$$ ---- (59)

Where $\ell$ is the path length, $C_i$ is the concentration of the $i$th species and $E_i$ its molar extinction coefficient at that wavelength. The equation for the absorbance of a mixture containing the three species, A, B and C, of a consecutive reaction system at a given time t, is a complicated one, but can be represented as

$$\frac{Z}{A_0} = L \exp(-k_1t) + M \exp(-k_2t)$$ ..... (60)

where L and M are constant coefficients containing the parameters $k_1$, $k_2$, $E_A$, $E_B$ and $E_C$. In the general situation when all the three
species absorb, fitting of $\frac{Z}{A_o}$ data by the least-squares method requires the simultaneous adjustment of these five parameters. If only one of the three species absorbs, then three parameters have to be determined. Evaluation of rate coefficients from spectrophotometric data, therefore, always involves the optimization of more parameters than from data such as those determined by, say, titrimetry, and to that extent more cumbersome. Hence they yield less accurate results than do direct concentration estimates.

However, the spectrophotometer has become very convenient tool in the hands of the chemist and has largely replaced conventional methods in the field of research in kinetics. Accordingly, optimization methods have been developed to evaluate kinetic and related parameters from absorbance data. These are useful in many situations, but have not been applied, surprisingly, to a significant extent in the study of the rates of reactions of charge-transfer complexes, except for the evaluation of the rate coefficient of a process assumed to be taking place in a single step, by using the simplest first-order equations outlined in section 1