Physical Organic Chemistry

The Fundamental Concepts

Second Edition, Revised and Expanded

Calvin D. Ritchie

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Second Edition, Revised and Expanded

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PREFACE

The first edition of this book evolved from a set of notes for a one-semester course offered to senior undergraduate and first-year graduate students in the Department of Chemistry, State University of New York at Buffalo. The first edition has been used for more than ten years in that course with only minor changes. In that time, the background education of students, the hot areas of physical organic chemistry, and the author's interests and perceptions have all undergone some changes. For these reasons, it was felt that a thorough revision of the entire book might be useful. The result of this revision is substantially different from the first edition, but the rigor of the material has not changed; it is not intended for bedtime reading. Even the very best students should read with pencil and paper at hand.

The book strongly reflects my own philosophy of science. Much of the difficulty in learning science arises from the fact that the concepts and theories have developed over a long period of time and that approximations and shortcuts which were introduced during that development, and which frequently resulted from much trial and error rather than straightforward logic, lead to a terrifying amount of detailed esoterica. For example, molecular orbital theory at the *ab initio* Hartree-Fock level is very easily developed from first principles. If, however, one looks at some of the semi-empirical methods, such as CNDO, MINDO, etc., the amount of detail and complexity due to the approximations which are used is beyond anyone but the true practitioners of the methods. To the best of my ability, within the confines of reasonable time and space, I have tried to present all concepts at the most fundamental level. Not only is the material easier to learn when presented in this way, but it stays longer.

Several friends at other universities have commented that their students found the problems given at the ends of the chapters of the first edition to be impossibly difficult. After using the text for some time, I must agree that average students seem unable to complete other than the simplest ones. At least some of the trouble is that students frequently have not learned how to approach complex problems in a logical, stepwise fashion. It is probably also true that a lack of confidence prevents serious attempts to think about such problems. In order to build confidence and provide simple reinforcement of text material, I have added a number of easy problems at the end of each chapter. To help students learn how to approach problems, hints are now given with most problems to get the student started on the correct path. I still believe that the only way to learn the material in the text is to spend the time necessary to work the difficult problems. They do require considerable time.

It is assumed that students using this book have a working knowledge of calculus through simple differential equations and have completed the first three years of a normal chemistry curriculum including a full year of study of physical chemistry. Courses in linear algebra, thermodynamics, and quantum mechanics would certainly be useful, but the essential background in these subjects is presented in the text.

The purpose of the book is to introduce the most important of the fundamental concepts of physical organic chemistry. In my opinion, this requires a heavy emphasis on the physical side of the subject rather than on reaction mechanisms. I recognize, however, that students at the level taking this course are more comfortable with reaction mechanisms than with, for example, the operator formalism applied to a harmonic oscillator. For this reason, I have attempted to give the book a "story line" involving thorough studies of mechanisms. There is no intent to present a survey of mechanisms of organic reactions.

The material is divided roughly into two major mechanistic themes. Chapters 1 through 5 develop the topics of kinetics, salt, solvent, and structural effects on reactions in the loose context of SN1 and SN2 type reaction mechanisms. In Chapter 5, the context begins to move to other types of reactions, and Chapter 6 deals with acid-base reactions; the concepts of catalysis, reaction rate theories, and isotope effects are presented primarily in that context in Chapters 7 through 9.

Matrix algebra is introduced early in Chapter 1 in the context of kinetics and is then used throughout the text, particularly in the discussions of quantum mechanics and normal mode analysis. Sufficient introduction to the basics of matrix algebra is given so that diligent students with no prior knowledge of the subject should be able to understand the material presented. It is hoped that the examples of applications of matrix algebra will provide sufficient motivation for the students to spend the time necessary to develop a facility with this valuable tool.

My debts to my own teachers are enormous. Among these teachers, in addition to Profs. W. F. Sager and E. S. Lewis with whom I have been privileged to have had extended personal contact, I include Profs. L. P. Hammett, A. Frost and R. G. Pearson, and S. Glasstone, whose texts *Physical Organic Chemistry*, *Kinetics and Mechanisms of Reactions*, and *Theoretical Chemistry*, respectively, have greatly influenced my thinking.

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I have been fortunate in having had, for many years, two exceptionally gifted departmental colleagues. Profs. Harry King and Jim McIver have been responsible for my education in mathematics and modern quantum mechanics, and have read and criticized sections of this book; their knowledge, patience, enthusiasm, and general intellectual abilities are greatly appreciated. Chapters 5, 8, and 9 could not have been written without many sessions spent with Harry King; the original material on tunneling, in Section 9.6, was developed in close collaboration with him.

Calvin D. Ritchie

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CHAPTER 1

Kinetics: Integration of Rate Equations

1.1 Introduction

Among other things, physical organic chemistry is concerned with the study of all factors, structural or environmental, which affect the rates and equilibria of organic reactions. This sub-area of physical organic chemistry includes a tremenduous range of interests, but the first step in the study of a reaction, regardless of final interest, nearly always involves some consideration of *mechanism* of the reaction. At the most elementary level, the *mechanism* of a reaction will specify any intermediates involved in the overall reaction. This specification of intermediates usually involves the determination of the empirical rate law for the reaction.

An empirical rate law states how the rates of formation of products, and rates of disappearance of reactants, depend on the concentrations of reactants, products, and catalysts, while all other variables, such as temperature, pressure, and ionic strength, are held constant. The empirical rate law allows us to begin testing postulated mechanisms.

The testing of a postulated mechanism using knowledge of the empirical rate law depends on the concept of an *elementary step* of a reaction. The essential feature of an *elementary step* of a reaction is that the rate law for that step must be directly related to the stoichiometry of that step. That is, if the reaction:

$$wA + xB \underset{k_r}{\overset{k_f}{\rightleftharpoons}} yC + zD \tag{1.1}$$

is an elementary step, then the rate law for this step must be:

$$\begin{aligned} \frac{1}{z}\frac{d[D]}{dt} &= \frac{1}{y}\frac{d[C]}{dt} = -\frac{1}{w}\frac{d[A]}{dt} \\ &= -\frac{1}{x}\frac{d[B]}{dt} = k_f[A]^w[B]^x - k_r[C]^y[D]^z . \end{aligned} \tag{1.2}$$

More practically, if the empirical rate law for some reaction does not correspond to the stoichiometry for the reaction, the reaction must

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involve more than one elementary step, and ***must involve at least one intermediate.***

This characteristic of an elementary step of a reaction can be deduced from any of the theories of reaction rates. At the simplest level, the frequencies of encounters of particles are directly proportional to the concentrations of the particles, and if any type of particle is required for some reaction, then it must encounter the other types required for the reaction.

We write some postulated set of elementary steps for a reaction of interest, and see if the resulting implied rate law is consistent with the empirical rate law. In some cases, we can integrate the rate laws, such as Eq. (1.2), to obtain expressions for concentrations of the various species as functions of time. These expressions can then be compared with actually measured concentrations as functions of time as the reaction proceeds. In the general case where a reaction may consist of several elementary steps, the rate laws for the elementary steps form a set of simultaneous differential equations which must be integrated to obtain expressions for concentrations as functions of time.

Let's start with some cases of reactions involving a single elementary step.

1.2 Simple First-Order Reactions

The simplest case is that of a reversible first-order reaction, such as an isomerization reaction:

$$A \underset{k_{-1}}{\overset{k_{+1}}{\rightleftharpoons}} B \tag{1.3}$$

with the rate law given by:

$$\frac{d[B]}{dt} = -\frac{d[A]}{dt} = k_{+1}[A] - k_{-1}[B]. \tag{1.4}$$

The integration of the last equation can be done quite easily. Suppose the concentrations of A and B at time equal zero are $[A]_0$ and $[B]_0$, respectively. Since reaction of one mole of A produces one mole of B, the concentrations of A and B, at any time, are related by:

$$[A] + [B] = [A]_0 + [B]_0 \quad \text{or} \quad [A] = [A]_0 + [B]_0 - [B] \tag{1.5}$$

Substitution of this result into the rate law gives:

$$\begin{aligned}\frac{d[B]}{dt} &= k_{+1}\Big([A]_0 + [B]_0 - [B]\Big) - k_{-1}[B], \\ &= -\{k_{+1} + k_{-1}\} \cdot [B] + k_{+1}\Big([A]_0 + [B]_0\Big)\end{aligned} \tag{1.6}$$

which can be put into standard form by defining:

$$k_\psi \equiv \{k_{+1} + k_{-1}\} \quad \text{and} \quad X \equiv k_\psi[B] - k_{+1}\Big([A]_0 + [B]_0\Big)$$

so that:

$$\frac{d[B]}{dt} = \frac{1}{k_\psi}\frac{dX}{dt} \quad \text{and} \quad \frac{dX}{X} = -k_\psi dt$$

which integrates immediately to:

$$\ln(X) = -k_\psi t + \ln(X_0) \quad \text{or} \quad \frac{X}{X_0} = \exp(-k_\psi t)$$

where $\ln(X_0)$ is the constant of integration.

After substituting for X in terms of the original parameters, and rearranging, we obtain:

$$\{k_{+1} + k_{-1}\}[B] - k_{+1}\Big([A]_0 + [B]_0\Big) = X_0 \exp(-k_\psi t) \tag{1.7}$$

The appearance of the left-hand side of this equation may be simplified by noting:

$$K_{eq} = \frac{k_{+1}}{k_{-1}} = \frac{[B]_\infty}{[A]_\infty} \tag{1.8}$$

This equation may be solved for k_{-1} in terms of the concentrations at infinite time and the result substituted in Eq. (1.7). After a little algebra involving the fact that $[A]_\infty + [B]_\infty = [A]_0 + [B]_0$:

$$[B] - [B]_\infty = \frac{X_0[B]_\infty}{k_{+1}\Big([A]_\infty + [B]_\infty\Big)} \exp(-k_\psi t) \tag{1.9}$$

Noting that at $t = 0$, $[B] = [B]_0$ we can deduce that the entire term multiplying the exponential and involving X_0 must be equal to $[B]_0 - [B]_\infty$, so that we obtain the final form:

$$\frac{[B] - [B]_\infty}{[B]_0 - [B]_\infty} = \exp(-k_\psi t) \tag{1.10}$$

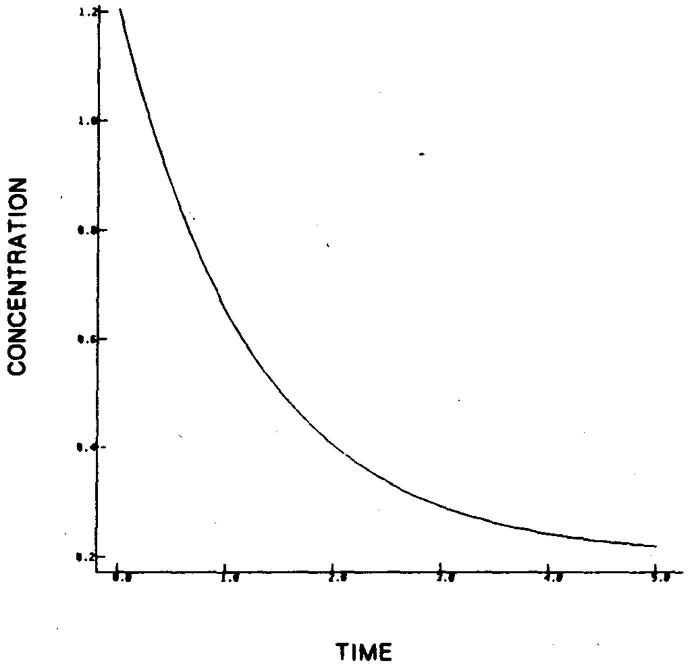

Figure 1.1: *First-order Decay. Plot of Eq.(1.11) with* $\beta_0 = 1.2$; $\beta_\infty = 0.2$; $k_\psi = 0.8$.

It is particularly convenient that any variable which is linearly related to the concentration of B can be substituted for [B] in this last equation; that is, for any constants a and c:

$$\text{If} \quad \beta = a[B] + c, \quad \text{then} \quad \frac{\beta - \beta_\infty}{\beta_0 - \beta_\infty} = exp(-k_\psi t) \qquad (1.11)$$

Figure 1 shows a typical plot of concentration as a function of time for a first-order process.

In the next few pages, it will become apparent that Eq. (1.11) is far more generally useful than one would expect if it applied only to the relatively few true first-order reactions. Because of the general utility, it is worth considering how one might examine experimental data to see whether or not the equation applies.

In the days before computers, Eq. (1.11) was usually written in the logarithmic form:

$$\ln(\beta - \beta_\infty) = -k_\psi t + \ln(\beta_0 - \beta_\infty).$$

A value for β_∞ was obtained from a final experimental determination when the reaction had essentially reached equilibrium. The values of $\ln(\beta - \beta_\infty)$ were then plotted vs time. A straight line plot indicated adherance of the data to first-order behavior, and the slope of the plot gave a value for k_ψ. This is an extremely easy treatment of data, and would be perfectly correct if the data were exact. Major practical problems arise because the logarithmic term "blows up" as β approaches β_∞ since $\ln(0) = -\infty$. As a result, small errors in β or β_∞ can cause extreme curvature in the plots. The situation is particularly bad in cases where β_∞ is difficult to obtain accurately because of instabilities of products. In all cases, it is improper to use a linear-least-squares fitting of the semi-logarithmic plot to obtain a value for k_ψ since errors in $ln(\beta - \beta_\infty)$ are not random.

With the availability of computers, it is now quite easy to be more correct in the data treatment. If a reaction is followed, for example, by observation of absorbance of the reaction solution as a function of time, Eq.(1.11) with β equal to the absorbance will apply for any case where the absorbances of reactants and products differ at the wavelength of observation. For reasonable absorbances from ca. 0 to 1.0, the expected errors is absorbance measurements will usually be nearly independent of the actual absorbance. The treatment of data can then involve a direct application of non-linear-least-squares fitting. We would have n values of β_i obtained at times t_i, and would like to choose values of k_ψ, β_0, and β_∞ such that the sum of the squares of the differences between observed β_i and those calculated from Eq.(1.11) using the values of t_i would be as small as possible.

Defining $\Re$ as the sum of the squares of the differences between observed and calculated absorbances:

$$\Re \equiv \sum_{i=1}^{n} [\beta_i - \Delta\beta_0 \exp(-k_\psi t_i) - \beta_\infty]^2 \, , \qquad (1.12)$$

$$\text{where } \Delta\beta_0 \equiv \beta_0 - \beta_\infty \, ,$$

the *best* values for k_ψ, $\Delta\beta_0$, and β_∞ will be such that the three partial derivatives, $\partial\Re/\partial k_\psi$, $\partial\Re/\partial(\Delta\beta_0)$, and $\partial\Re/\partial\beta_\infty$ are equal to zero. Defining the sums:

$$\overline{B} = \sum_{i=1}^{n} [\beta_i] \, ; \quad \overline{\mathcal{E}} = \sum_{i=1}^{n} [exp(-k_\psi t_i)] \, ; \quad \overline{B\mathcal{E}} = \sum_{i=1}^{n} [\beta_i \exp(-k_\psi t_i)] \, ;$$

$$\overline{T\mathcal{E}} = \sum_{i=1}^{n} [t_i \exp(-k_\psi t_i)] \, ; \quad \overline{\mathcal{E}\mathcal{E}} = \sum_{i=1}^{n} [\exp(-2k_\psi t_i)] \, ;$$

$$\overline{BT\mathcal{E}} = \sum_{i=1}^{n} [\beta_i t_i \exp(-k_\psi t_i)]\,; \quad \overline{T\mathcal{E}\mathcal{E}} = \sum_{i=1}^{n} [t_i \exp(-2k_\psi t_i)]$$

and taking partial derivatives of $\Re$, we obtain:

$$\frac{\partial \Re}{\partial k_\psi} = 2\Delta\beta_0 \left\{ \overline{BT\mathcal{E}} - \Delta\beta_0 \overline{T\mathcal{E}\mathcal{E}} - \beta_\infty \overline{T\mathcal{E}} \right\} = 0$$

$$\frac{\partial \Re}{\partial(\Delta\beta_0)} = -2 \left\{ \overline{B\mathcal{E}} - \Delta\beta_0 \overline{\mathcal{E}\mathcal{E}} - \beta_\infty \overline{\mathcal{E}} \right\} = 0$$

$$\frac{\partial \Re}{\partial \beta_\infty} = -2 \left\{ \overline{B} - \Delta\beta_0 \overline{\mathcal{E}} - n\beta_\infty \right\} = 0$$

The last two equations may be solved for $\Delta\beta_0$ and β_∞:

$$\Delta\beta_0 = \frac{n\overline{B\mathcal{E}} - \overline{B}\cdot\overline{\mathcal{E}}}{n\overline{\mathcal{E}\mathcal{E}} - \overline{\mathcal{E}}\cdot\overline{\mathcal{E}}} \tag{1.13}$$

$$\beta_\infty = \frac{\overline{\mathcal{E}}\cdot\overline{B\mathcal{E}} - \overline{B}\cdot\overline{\mathcal{E}\mathcal{E}}}{\overline{\mathcal{E}}\cdot\overline{\mathcal{E}} - n\overline{\mathcal{E}\mathcal{E}}} \tag{1.14}$$

Substitution of these results into the first of the three equations results in a single equation which must be satisfied by the *best* value for k_ψ:

$$\begin{aligned} \overline{BT\mathcal{E}} \left\{ n\overline{\mathcal{E}\mathcal{E}} - \overline{\mathcal{E}}\cdot\overline{\mathcal{E}} \right\} - \overline{T\mathcal{E}\mathcal{E}} \left\{ n\overline{B\mathcal{E}} - \overline{B}\cdot\overline{\mathcal{E}} \right\} \\ + \overline{T\mathcal{E}} \left\{ \overline{\mathcal{E}}\cdot\overline{B\mathcal{E}} - \overline{B}\cdot\overline{\mathcal{E}\mathcal{E}} \right\} = 0. \end{aligned} \tag{1.15}$$

A reasonable algorithm for finding k_ψ would involve the following steps:

- Choose an initial value for k_ψ equal to $0.69/t_{1/2}$, where $t_{1/2}$ is the approximate time at which the concentration is half-way between its initial and final values. Calculate the value of the left-hand-side of Eq.(1.15).
- Halve the value of k_ψ and recalculate the left-hand-side of the equation. If this value is larger magnitude and of the same sign as the first value, double the original value of k_ψ and again calculate the left-hand-side of the equation. Repeat the halving, or doubling, until the value calculated for the left-hand-side of the equation changes sign.
- Use repeated linear interpolations of k_ψ vs. the calculated value of the left-hand-side of the equation to whatever precision in k_ψ is desired.

In actual practice, Eq.(1.15) is a well-behaved function of k_ψ for reasonable data covering at least several half-lives of reaction, and convergence of the linear interpolations is quite rapid.

In order to judge whether or not the reaction is actually first-order, at least two tests should be applied: first, the root-mean-square error, $[\Re/n]^{1/2}$, should be no larger than the expected error in β; and, second, a plot of the experimental β_i against the values calculated using the selected parameters should show only random scatter from a straight line and no systematic curvature.

1.3 Second-Order Reversible Reactions

Now, let's consider the reaction:

$$A + B \underset{k_r}{\overset{k_f}{\rightleftharpoons}} C + D, \tag{1.16}$$

which, if it is an elementary step, gives the rate law:

$$\frac{d[D]}{dt} = \frac{d[C]}{dt} = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k_f[A][B] - k_r[C][D]. \tag{1.17}$$

In order to integrate the rate law, we will follow essentially the same steps as we did above:

- Use the stoichiometry of the reaction to write the rate law in terms of a single variable concentration;
- write the differential equation in standard form with separated variables and integrate;
- eliminate the reverse rate constant by using $k_f/k_r = K_{eq}$, with K_{eq} expressed in terms of concentrations at equilibrium;
- evaluate the constant of integration from conditions at time equals zero.

For simplicity, we will assume that only A and B are present at $t = 0$, with concentrations $[A]_0$ and $[B]_0$ respectively. We then have the stoichiometric relationships:

$$[B] = [B]_0 - [A]_0 + [A]; \quad [C] = [D] = [A]_0 - [A]$$

which are substituted into the rate law to give:

$$\frac{d[A]}{dt} = -k_f[A]\{[B]_0 - [A]_0 + [A]\} + k_r\{[A]_0 - [A]\}^2,$$

and, sorting out powers of $[A]$:

$$\frac{d[A]}{dt} = -(k_f - k_r)[A]^2 - \{k_f([B]_0 - [A]_0) + 2k_r[A]_0\}[A] + k_r[A]_0^2.$$

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