

# **FREE RADICALS**

**VOLUME I**

**Part I: Dynamics of Elementary Processes**

**Edited by**  
**JAY K. KOCHI**

# FREE RADICALS

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**JAY K. KOCHI**

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**VOLUME I**

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## **Introduction to the Series**

Reactive intermediates have always occupied a place of importance in the spectrum of organic chemistry. They were, however, long considered only as transient species of short life-time. With the increase in chemical sophistication many reactive intermediates have been directly observed, characterized, and even isolated. While the importance of reactive intermediates has never been disputed, they are usually considered from other points of view, primarily relative to possible reaction mechanism pathways based on kinetic, stereochemical, and synthetic chemical evidence. It was felt that it would be of value to initiate a series that would be primarily concerned with the reactive intermediates themselves and their impact and importance in organic chemistry. In each volume, critical, but not necessarily exhaustive coverage is anticipated. The reactive intermediates will be discussed from the points of view of: formation, isolation, physical characterization, and reactions.

The aim, therefore, is to create a forum wherein all the resources at the disposal of experts in the field could be brought together to enable the reader to become acquainted with the reactive intermediates in organic chemistry and their importance.

As the need arises, it is anticipated that supplementary volumes will be published to present new data in this rapidly developing field.

## Preface

When asked to organize a monograph on free radicals, I agreed to do it because I believed that this type of book would fill a definite need. The object was to present an up-to-date and authoritative account of free radicals written by a group of experts active in the field. It soon became apparent, however, that the organization of the subject was not as trivial as I had imagined, and none of the usual classifications was adequate. I finally decided that a multifaceted approach was feasible in which five major areas would be covered:

- Structure and Energetics
- Free Radicals with Heteroatoms
- Dynamics of Elementary Processes
- Free Radical Chain Reactions
- Synthesis

The first four categories are included in the present book. The last, which has, alas, fallen by the wayside, is perhaps the hardest to write about and was intended as a distillation of our knowledge about free radicals, to exploit them for chemical synthesis. Unfortunately, synthetic chemists have by and large eschewed this intermediate as being too reactive for their designs. Quite the contrary is true, and we wish to show in the following pages that free radicals as reactive intermediates do offer a number of unique advantages. One of our hopes for this book, therefore, is to stimulate chemists into expanding their repertoire of synthetic methods and their approaches to synthetic problems to include this versatile intermediate.

Overlapping coverage and duplication are inevitable in a book such as this, and no doubt detract from a unified presentation and lead to inefficiency. I believe, however, that each author has a message to convey and must feel free to develop it as he perceives it. No two authors approaching a problem from different points of view will interpret the data in the same way. Hopefully, such occurrences will be sufficiently minimal to augment rather than weaken the presentation. Most of the chapters were written as self-contained entities and are intended to be read as such. The treatment of free radicals in this book is not necessarily comprehensive, since the emphasis is primarily directed toward a critical analysis and unification of what is known and pointing out the direction for future developments.

I wish to express my thanks to all of the participants whose contributions made this endeavor possible.

*Bloomington, Indiana*  
*April 1972*

JAY K. KOCHI

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## CHAPTER 1

# Rate Processes in the Gas Phase

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England*

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## I. INTRODUCTION

This chapter summarizes the present state of knowledge of quantitative kinetics of free radical reactions in the gas phase. In essence it presents an up-to-date version of an earlier summary<sup>1</sup> entitled "Reactions of Alkyl Radicals" with the modification of including reactions of other radicals as well as alkyls.

Two significant changes have occurred in the decade following the previous article. The first is the enormous increase in the amount of quantitative kinetic data that has become available. Whereas ten years ago it was feasible to list all the rate constants of the reactions of alkyl radicals larger than methyl in a review of this type, to attempt the analogous task here would be formidable. The days have passed when textbooks and broadly based reviews can summarize all the measured rate constants. The classic monograph<sup>2</sup> of E. W. R. Steacie, *Atomic and Free Radical Reactions*, which dealt with the whole of quantitative gas kinetics at that time, would now run to several volumes. This large increase in the number of measurements has led to the development of compilations and evaluations of kinetic data. The former consist of logically and consistently arranged sets of tables of experimental kinetic data, sometimes with brief comments, while the latter attempt a

critical assessment of data concerned with a limited number of reactions. So far three compilations dealing with radical reactions have appeared<sup>3-5</sup> and one evaluation of unimolecular reactions, a section of which covers decompositions of radicals.<sup>6</sup> It is clear that this type of effort will become increasingly important.\* In this article selections of rate constants and Arrhenius parameters for the various types of radical reactions are given with a view to illustrating any general trends that exist. The reactions are limited to polyatomic monoradicals and concentrate on alkyl and substituted alkyl radicals but with some mention of heterocentered radicals. Lack of space precludes any discussion of biradicals or carbenes.

The second important change to occur in free radical kinetics during the past ten years is the development of quantitative approaches to the relations between kinetics and thermodynamics. While the existence of such connections has been recognized for some time, it is only by the recent work of Benson and co-workers<sup>6-9</sup> that they have been applied in a systematic way. This has come about by the development of straightforward and reliable methods of estimating the enthalpies, entropies, and heat capacities of molecules and free radicals. At the same time this group has fostered the application of transition state theory, again in a systematic way,<sup>10</sup> and although the main effort here concerns unimolecular reactions of molecules, some significant applications arise in free radical chemistry. These methods and general underlying philosophy are dealt with in Chapter 17, but their importance is worth emphasizing here and they do crop up at various points in this chapter.

## II. MEASUREMENTS OF RATE CONSTANTS

The first point to note is that little data exist on absolute measurements of rate constants of free radical reactions in the gas phase. Most of the absolute data have been obtained for combination and disproportionation reactions by the rotating sector technique. This experimental approach is well documented and it suffices to say here that the method is not very accurate and not well suited to measuring temperature coefficients, particularly of low activation energy reactions. Errors in determining rate constants by rotating sector experiments in excess of  $\pm 20\%$  are not uncommon.<sup>11</sup>

Absolute rate constants for the combination of methyl radicals have been measured by a variety of techniques<sup>1,12</sup> but seldom have they been exploited to study other reactions. The method most likely to be developed is that

\* The International Council of Scientific Unions has set up a committee on data for science and technology (CODATA), and a task force in chemical kinetics under the chairmanship of S. W. Benson (Stanford Research Institute) has been created to coordinate data projects in chemical kinetics.



involving kinetic spectroscopy whereby the methyl combination reaction<sup>13,14</sup> and reaction with nitric oxide<sup>14</sup> have been studied by making direct measurements of methyl concentrations via their absorption at 216.4 nm in flash photolyses experiments. The absorption coefficients for methyl radicals at 216.4 nm have been measured and it is probable that absorptions of other radicals will be identified and measured in this way.

So far no gas-phase rate constants have been reported from ESR determinations of concentrations of polyatomic radicals, but considering the wealth of data derived by this method on atomic reactions, an eventual breakthrough seems likely.

The vast majority of rate constants discussed in this chapter have been measured relative to some other reaction of the radical, often the combination reaction. Where the rates of combination of the radicals have not been measured they are usually assigned a value based on the results of analogous reactions. The importance of the absolute measurements of the rates of radical combinations can hardly be overemphasized.

As regards the accuracy of rate constant measurements of free radical reactions in the gas phase, it has to be admitted that these are not among the most accurate measurements in physical chemistry. There are very few free radical reactions for which the activation energy is known to better than  $\pm 0.5$  kcal/mole with a corresponding error in the  $A$  factor [ $\pm 0.4$  to  $\pm 0.2$  in  $\log A$  (liters/mole-sec) for second-order reactions over the temperature range 300–500°K]. Most measurements of Arrhenius parameters of free radical reactions involve considerably larger errors than those quoted above. The precision of the data, as reflected in the standard deviations of least-mean-squares treatments, is usually considerably better than these errors; the differences arise from systematic errors which are particularly difficult to detect. Usually several independent determinations of the Arrhenius parameters for a radical reaction are necessary before reasonable estimated errors can be assigned with confidence.

Fortunately the position is much better for relative rate constants for a series of related reactions since many of the systematic errors are canceled. It is thus possible to make meaningful interpretations of the factors affecting the relative rates of related reactions.

### III. SOURCES OF RADICALS

On the whole, ketones and aldehydes<sup>1</sup> have lost favor to azo compounds for the production of thermally equilibrated alkyl radicals.<sup>15</sup> A range of azo compounds is now commercially available and they are excellent clean sources of the corresponding alkyl radicals which can be generated in relatively high concentrations from high-intensity photolyses in the near