Mechanism and Theory in Food Chemistry

Dominic W. S. Wong

MECHANISM AND THEORY IN FOOD CHEMISTRY

DOMINIC W.S. WONG, Ph.D.
Cornell University

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MECHANISM AND THEORY IN FOOD CHEMISTRY

To
My Wife, Eleanor,
and Children, Jacob, Joshua, Jessica

FOREWORD

This is a unique book on food chemistry. Textbooks on food chemistry are written generally in a descriptive manner, with tables of comparative data and sometimes from the functional aspects of the food ingredients. They rarely place emphasis on modern mechanisms underlying the chemical reactions that occur in food during processing and storage nor do they treat interactions among the components of foods. The present book, *Mechanism and Theory in Food Chemistry,* is an exception. The author has stressed the principles of the reaction mechanisms, carefully detailing what is known to occur or is expected to occur based on his detailed understanding of organic chemical reactions. This unifies the themes of oxidation, reduction, hydrolysis, structure, polymerization, emulsification, etc., that are key to the conceptual approach used. Students are challenged to understand and explain the chemical reactions in food systems, based on their background in chemistry. The textbook covers the important topics of food chemistry, based on the more traditional organization around the general types of components found in foods—the proteins, lipids, carbohydrates, enzymes, vitamins—but also expands the content to include both naturally occurring as well as added colorants, flavors, sweeteners, and other food additives. Each chapter includes sections on how the constituents covered interact with other compounds in the food, as well as discussions of effect of temperature, pH, metal ions, oxygen, and other constituents on the roles of the reactions and interactions.

The book should be a valuable text for a more advanced course in food chemistry, probably at the graduate level, or as an adjunctive text for an undergraduate junior or senior course, as well as a valuable reference for researchers.

Robert E. Feeney
John R. Whitaker
Department of Food Science and Technology
University of California, Davis

PREFACE

The primary objective of this book is to focus on the reaction mechanism and theory essential to understanding the many chemical processes occurring in food and food systems. Too often, food chemistry courses tend to be descriptive and require mere memorization of unrelated chemical structures. It is the author's firm belief that an adequate comprehension of the principles of food chemistry is based on a thorough knowledge of the reaction mechanisms and theories under a coherent theme. For every phenomenon or change observed in food or food systems, there is a corresponding chemical equation or model. Most of the presentations in this book are found in reaction mechanisms explained in equations or figures.

The book is organized in ten chapters: (1) Lipids, (2) Proteins, (3) Carbohydrates, (4) Colors, (5) Enzymes, (6) Flavors, (7) Sweeteners, (8) Natural Toxicants, (9) Additives, and (10) Vitamins. The first three chapters constitute the foundation of food chemistry and hence require a broad coverage. Other chapters are slightly more selective in the presentation of the materials. The references at the end of each chapter is by no means encyclopedic, but provide a guide to those who would like to obtain more information on a particular area discussed in the text. Selected references are included mainly for certain topics the author finds interesting and deserving further reading.

There are three appendixes: (1) General kinetics of olefin autoxidation, (2) Singlet oxygen, and (3) Where do the radicals come from? These were written to cover certain chemical principles that students are normally expected or assumed to, but rarely actually understand. The latter two are especially important, since they contain information basic to the numerous chemical reactions often discussed in food systems.

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CONTENTS

1 LIPIDS

Dietary lipids supply approximately 35–40% of the total calories taken by an average adult and exhibit the most efficient energy conversion, yielding 9 calories per gram, twice as many calories supplied by carbohydrates or proteins. The large consumption of fats and oils necessitates better understanding of the basic chemistry that underlines the various changes, both under natural conditions and during food processing.

The oxidation of unsaturated lipids has been one of the most extensively studied areas and will remain so, since it is related to the deterioration of foods, the production of both desirable (e.g., flavor, color) and undesirable breakdown products (e.g., toxic dimers), and the numerous reactions associated with other food constituents. The problem is further complicated by the fact that these reactions can be initiated, inhibited, or altered by many factors, including metal, enzymes, antioxidants, temperature, light, and pH.

The physical chemistry of lipids is another important area of great interest to food chemists. The polymorphic property and crystal habits of fat are of great importance in the formulation of various fat and oil products such as margarine, ice cream, and mayonnaise. Knowledge on the formation and breakdown of emulsions is required for the effective application of emulsifiers in many food-processing systems.

The chemistry of lipids and the mechanisms of the various reactions that occur in processing, including lipid degradation, via oxidation, thermal and radiolytic reactions, hydrogenation, interesterification, and polymorphic changes, are presented. A significant portion of the discussion will be devoted to the theory and applied chemistry of emulsions in food systems.

LIPID OXIDATION

Lipid oxidation in foods is associated with the reaction of oxygen with unsaturated lipids in two different pathways, (a) autoxidation and (b) photosensitized oxidation.

Autoxidation

Autoxidation is a free-radical chain reaction involving the following steps (see Eq. 1-1).

$$\mathrm{LH} \xrightarrow[\text{initiator}]{k_i} \mathrm{L\cdot} + \mathrm{H\cdot} \qquad 1\text{–}1.1$$

$$\mathrm{L\cdot} + \mathrm{O_2} \xrightarrow{k_o} \mathrm{LOO\cdot} \qquad 1\text{–}1.2$$

$$\mathrm{LOO\cdot} + \mathrm{LH} \xrightarrow{k_p} \mathrm{LOOH} + \mathrm{L\cdot} \qquad 1\text{–}1.3$$

$$\mathrm{LOO\cdot} + \mathrm{LOO\cdot} \xrightarrow{k_t} \text{Non-radical products} \qquad 1\text{–}1.4$$

$$\mathrm{LOO\cdot} + \mathrm{L\cdot} \xrightarrow{k_{t'}} \text{Non-radical products} \qquad 1\text{–}1.5$$

$$\mathrm{L\cdot} + \mathrm{L\cdot} \xrightarrow{k_{t''}} \text{Non-radical products} \qquad 1\text{–}1.6$$

Eq. 1-1

1. *Initiation:* Homolytic abstraction of hydrogen to form a carbon-centered alkyl radical in the presence of an initiator.
2. *Propagation:* The free radical reacts with O_2 to form peroxy radical which reacts with more unsaturated lipids to form hydroperoxide. The lipid free radical thus formed can react with O_2 to form peroxy radical. Hence, autoxidation is a radical chain process.
3. *Termination:* The chain reaction can be terminated by the formation of nonradical products.

The overall reactions follow rate equation 1-2. (Refer to Appendix 1.) Under normal oxygen pressure, the alkyl radical reacts rapidly with oxygen to form the peroxy radical (Rxn 1-1.2). The rate of reaction 1-1.2 is fast, and most of the free radicals are in the form of the peroxy radical. Consequently, the major termination takes place via reaction 1-1.4 by peroxy radical combination. The reaction follows rate equation 1-3 (*1*).