or M(I) to M(II) or M(III), respectively.

$$2CO_2 + 2e^- \rightarrow CO_3^{2-} + CO \qquad (2)$$

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Orbital Correlation Barrier between the Reaction Channels for the Combination and Disproportionation of Radical Pairs

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The self termination reaction of organic free radicals have received increased attention in the recent literature. Experimental studies by Fischer,[1,2] Ruchardt,[3] Golden[4] and others have suggested that certain radicals recombine without activation. Theoretical work has suggested that recombination without activation may not be general.[5,6] Several experimental studies confirm this.[7]

In this paper, we present orbital correlation arguments that indicate that combination and disproportionation of radical pairs should occur by separate, nonconverting reaction paths. These paths are illustrated by AM1[8] calculations on ethyl radical termination reactions.

The SOMO (singly occupied molecular orbital) of the ethyl radical is illustrated in pairs oriented for recombination and disproportionation in Figure 1. The topology of this orbital is evident from the fact that it is similar to the LUMO (lowest unoccupied orbital) of the ethyl cation, which is the antibonding combination of a carbon p-orbital with the methyl group orbital of correct (π) symmetry. It is immediately apparent that the phase is inverted in passing from C_1 to C_2 on the same face of the radical. Any incoming radical that came along the path toward combination with C_1 would begin to overlap with the part of the SOMO localized on the C_1 p-orbital. Since the part of the SOMO localized on the adjacent methyl hydrogen, which would be the hydrogen abstracted in a disproportionation reaction, is of opposite sign to that on C_1, the radical approaching C_1 would necessarily have opposite sign to that of the SOMO on this hydrogen. Clearly, the interaction of the incoming radical to the methyl hydrogen would be antibonding. Consequently, a HOMO/LUMO crossing of the interacting radical pair would be necessary for the conversion of an approach along the combination path to an approach along the disproportionation path. The converse is obviously true by analogous arguments (see Figure 1 for the two approaches).

Figure 1. Ethyl radical orbitals oriented for combination and disproportionation.

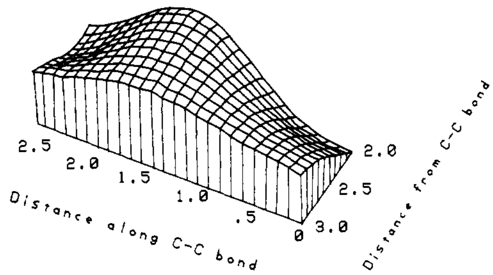

Figure 2. Potential surface for the approach of a hydrogen atom to an ethyl radical showing the two reaction channels. The energy is plotted vs. distance parallel to the C–C bond in the plane of the C–H bond and the nonbonding p-orbital of the ethyl radical (zero is defined as exactly above the methylene carbon) and the distance from the C–C bond (from 2 to 3 Å) in the same plane. Each division represents 0.1 Å. The height of the surface is 3.0 kcal/mol.

As a probe of this phenomenon, AM1 molecular orbital calculations[8] were performed on the approach of a hydrogen atom to the ethyl radical. The ethyl radical was, first, completely optimized using the half electron method.[9] A test hydrogen atom was then placed at various positions with respect to the ethyl radical. The energies for the resulting radical pairs were calculated by an open-shell SCF technique and 3 × 3 CI. The utility of these procedures for the calculation of bond dissociations in small molecules has been previously discussed.[10,11] It is worth noting that the artifacts reported with the MNDO techniques[10] all disappear when the calculations are repeated with AM1, for the cases containing only C, H, N, and O (the only elements for which AM1[11] parameters were available). The results are displayed in Figure 2, which is an energy surface for the radical pair with the H atom positioned in the plane of the two carbons and perpendicular to the methylene group.

The barrier between the two paths is clearly observable in Figure 2. In addition, one can see that the downward slope of the energy with approach of the radical pair is initially greater for attack at the hydrogen (disproportionation) than for attack at carbon (combination). This seems reasonable as the methyl hydrogen protrudes in the direction of the incoming radical. Upon further approach, however, the valley leading to combination deepens more than that leading to recombination.

There is a simple experimental demonstration of this phenomenon. Upon heating, alkanes generally are thought to first break their C–C bond to form two alkyl radicals, which can then react further by disproportionation, combination, or other reactions. The activation energy is equivalent to the bond dissociation energy. If a viable path that allowed interconversion from the path of combination (the reverse of dissociation) to disproportionation were to exist, alkanes could be converted directly into disproportionation products with an activation energy significantly lower than that for bond dissociation.

The implication of these results, that once embarked along one of the two reaction paths, a radical pair can no longer be diverted to the other product, requires some rethinking of theories of radical self-reactions that depend only upon consideration of steric factors.

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In addition radical pair intermediates that are bound together (i.e., biradicals) may have allowable conformations that strongly favor internal combination (cyclization) or disproportionation. Recent reports of the relative combination/disproportionation ratios might be reconsidered in this light.[12,13]

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Book Reviews

Topics in Current Chemistry. Volume 130. Springer-Verlag: New York. 1986. 209 pp. $53.00. ISBN 0-387-15810-3.

This volume contains six diverse and generally readable chapters under the heading of Synthetic Organic Chemistry.

Chapter 1: Steric and Electronic Substituent Effects on the Carbon–Carbon Bond, by C. Rüchardt and H.-D. Beckhaus, reviews the application of experimental and computational techniques toward the elucidation of the factors influencing the bond dissociation energies of C–C bonds.

Chapter 2: Selective Hydroboration and Synthetic Utility of Organoboranes Thus Obtained, by A. Suzuki and R. S. Dhillon, provides a selective account of this large area with a focus on hydroboration of molecules containing several reactive functional groups and options for further manipulations of the so-formed products. Organization is by the nature of the target functional group in the final product.

Chapter 3: Synthesis of Ynamines, by J. Collard-Motte and Z. Janousek, provides a good comprehensive review of available methods for formation of ynamines. The chemistry of ynamines is not discussed, except where relevant to the preparation of other ynamines.

Chapter 4: Electrochemically Reduced Photoreversible Products of Pyrimidine and Purine Analogues, by B. Czochralska, M. Wrona, and D. Shugar, outlines the photoreversible dimerization and related reactions observed when a variety of purine/pyrimidine-related compounds are subjected to reduction at a mercury electrode.

Chapter 5: High Pressure Synthesis of Cryptands and Complexing Behavior of Chiral Cryptands, by J. Jurczak and M. Pietraszkiewicz, provides a brief survey of usual methods for cryptand formation followed by a description of the application of high-pressure techniques to the preparation of these important macrocycles.

Dennis P. Curran, *University of Pittsburgh*

Ring–chain Tautomerism. By R. E. Valters and W. Flitsch. Plenum Press: New York and London. 1985. xi + 278 pp. $45.00. ISBN 0-306-41870-3.

This review of ring–chain tautomerism is an English translation of a book by Valters, "Ring–chain Isomerism in Organic Chemistry", Zinatne, Riga, 1978, which has been revised and updated. The authors state that coverage includes the literature until the end of 1982, and there is some supplementary literature beyond that appended at the end of various chapters. The review is intended to bridge the gap since an earlier review of the topic in 1963. Some of the examples from the earlier review are repeated; on the other hand, these authors have incorporated information from work before 1963 missed by the earlier reviewer. Inevitably, some literature since 1963 has been overlooked. In particular the present treatment covers information based on NMR spectroscopy, a method which was in its infancy for determination of ring–chain structures and equilibria 30 years ago. The development of phosphorus chemistry in the interim is also reflected in the inclusion of several classes of these compounds in Chapter 4.

The book is divided into five chapters: Introduction; Intramolecular Reversible Addition Reactions to the C=O Group; Intramolecular Reversible Addition Reactions to the C=N Group; Intramolecular Reversible Addition Reactions to Other Groups; and Generalizations Concerning the Influence of Structural and External Factors on the Relative Stability of Ring and Chain Isomers. Except for the last chapter, the information is presented rather uncritically according to functional groups undergoing interaction. In the last chapter the authors endeavor to draw generalizations about structure–reactivity relationships from the information presented in earlier chapters. Most of the conclusions are based on equilibrium behavior, not on rates or thermodynamic data, which, as the authors point out, are sparse.

The English text is a translation by the coauthor of a Russian draft and, perhaps for this reason, contains awkward or archaic passages, which are sometimes unclear. ["...adjustment of the equilibrium affords more drastic conditions..."; "...the free energy difference enthalpy and entropy components..."] These interruptions do not, however, detract seriously from the reader's overall comprehension of the subject. In some instances the organization is confusing and does not follow clearly from the table of contents or subheadings. More serious for interested researchers is the lack of literature citations for many of the tables. Some errors were noted in references, particularly the spelling of authors.

The index, organized according to generic functional groups, is sparse and therefore not very useful for searching. Unfortunately, there is no author index.

After one reading the outside cover had already begun to deteriorate, so it can be expected that copies purchased for general library use will soon be in need of rebinding.

Paul R. Jones, *University of New Hampshire*

Nonsteroidal Antiinflammatory Drugs. Edited by J. G. Lombardino (Pfizer, Inc.). John Wiley & Sons: New York. 1985. xix + 442 pp. $99.50. ISBN 0-471-89803-1.

The book presents an overview of different aspects related to nonsteroidal antiinflammatory drugs (NSAID). It is organized into four chapters that cover the different areas now under scientific investigation.

Chapter one describes the physiology of normal synovial joints and the alterations that occur during joint diseases, especially osteoarthritis.

Chapter two reviews recent concepts of biochemical processes involved in initiating and promoting inflammation and the role of different biologically active medicators and possible pharmacological interventions.

In Chapter three laboratory models to characterize antiinflammatory and analgesic effects as well as renal and gastric side effects of NSAIDs in acute and chronic inflammation are introduced and their applications, limitations, and predictive values are discussed. QSAR considerations demonstrate the use of these animal models to predict clinical safety and efficacy of NSAIDs.

Chapter four covers the medicinal chemistry, pharmacology, and metabolism as well as the clinical aspects of the acidic NSAID that have been administered to humans. This chapter includes an excellent literature review for a total of 67 different acidic NSAIDs.

The book is written by experts with hands-on experience; its content is very well organized and presented, and the literature references of each chapter are quite extensive. The book is the ideal reference book for pharmacologists and medicinal chemists involved in NSAID research.

Hartmut Derendorf and Jurgen Venitz, *University of Florida*

Treatise on Analytical Chemistry. 2nd Edition. Edited by P. J. Elving (University of Michigan), V. G. Mossotti (U.S. Geological Survey), and I. M. Kolthoff (University of Minnesota). John Wiley & Sons: New York. 1984. xxix + 675 pp. $75.00. ISBN 0-471-01836-8.

The "Treatise on Analytical Chemistry" has long been THE authoritative source for serious students of the discipline. The present addition to that series, Part 1, "Theory and Practice", Volume 4, Section E, Principles of Instrumentation for Analysis, is therefore a great disappointment.

The sections dealing with hardware, such as analog electronics, operational amplifiers, interfacing principles, and digital electronics, are finely done. But much of the material is available elsewhere, where it is not embedded in such an expensive surrounding.

The sections dealing with transducers and process control equipment are somewhat dated. The sections on computer systems and programming are limited in scope and are not current. These areas are particularly difficult to write about because of the short half-life of the technology. The first manuscripts for this volume were solicited in 1974 and due in 1975. One suspects that many of the authors submitted their material at that time and then periodically attempted to update it as publication of the volume was repeatedly delayed.

Of most concern is the section titled Automation: Instrumentation for