



Figure 1. Plot of the log of the second-order rate constants for catalysis of aromatization of phenanthrene 3,4-oxide (\square), phenanthrene 1,2-oxide (Δ), naphthalene 1,2-oxide (\circ), phenanthrene 9,10-oxide (\bullet), and benzene oxide (∇) vs. the pK_a of the acid catalyst: H_3O^+ (pK_a -1.74), acetic acid (pK_a 4.71), cacodylic acid (pK_a 6.23), $H_2PO_4^-$ (pK_a 6.42), imidazole (pK_a 7.14), Tris (pK_a 8.25), and H_2O (pK_a 15.75). Insert to figure: Plots of the observed first-order rate constants vs. total concentration of phosphate buffer for the aromatization of naphthalene 1,2-oxide at three pH values.

cal and a free energy minimum exists between A and D which provides for concerted general acid catalysis. From II it may be seen that this minimum corresponds to a transition state associated with ca. 60% C-O bond scission and 60% H-O bond scission ($-\alpha = 0.6$). General acid catalysis of carbocation formation is, therefore, anticipated in the aromatization of the arene oxides. The experimental results reported herein support these quasi-theoretical predictions.

Jencks and co-workers have recently established Bronsted relationships extending from $\beta = +1$ to 0 for general base-assisted acyl transfer to α -effect amines.⁸ The present

study represents the first instance of a range of possible transition states in a general acid catalyzed reaction.

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References and Notes

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- (6) The method of alternate routes assumes that the free energy contour map is formed by addition of the weighed contribution of the edge reaction coordinates to each point on the map (B. M. Dunn, *Int. J. Chem. Kinet.*, **6**, 143 (1974)). The treatment differs from that applied by More O'Ferrall (R. A. More O'Ferrall, *J. Chem. Soc. B*, 274 (1970)) and Jencks (W. P. Jencks, *Chem. Rev.*, **72**, 705 (1972)) to their transect diagrams in that these authors create the interior of the map by a process of ratiocination based on details of experimental results (i.e., the interior of the transect diagrams are not computed from the edge free energy values and, thus, there is allowed an increasing degree of latitude in moving from the edge towards the center for the inclusion of concepts as the triple potential) (see T. C. Bruice, *Annu. Rev. Biochem.*, in press). The advantage of "MAR" awaits further exploration. Structures I, II, and III were generated by a computer program written by Dr. R. F. Williams (R. F. Williams, W. Paik, and T. C. Bruice, to be submitted for publication) which assumes that all reactions are Hammond-like (G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955)) and that the influence of each edge on any point on the map is the reciprocal of some function of the distance of the point from the edge.
- (7) Edge free energy reactant coordinates were constructed by assuming that: (a) the pK_a of oxide is -2; (b) the pK_a of the alcohol moiety of state D is 10.7 (calculated by the method of J. P. Fox and W. P. Jencks, *J. Am. Chem. Soc.*, **96**, 1436 (1974)); (c) proton transport is diffusion-controlled in the thermodynamically favored direction; (d) thermodynamically favored ring closure of carbonium ions to oxide is associated with a ΔG^\ddagger of 3.8 kcal M^{-1} ; and (e) the value of $\Delta G^\ddagger_{B \rightarrow D}$ approximates that of k_H and $\Delta G^\ddagger_{A \rightarrow C}$ that of k_0 .
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Book Reviews*

The Chemist in Industry (2): Human Health and Plant Protection. By E. S. STERN, J. F. CAVALLA, and D. P. JONES. Oxford University Press, New York, N.Y. 1974. viii + 87 pp. \$9.75 (cloth); \$4.95 (paper).

This is the second book of a series having the aim of giving to the college graduate background information needed to appreciate current developments and philosophy in the chemical industry. The title is potentially misleading, for the book is concerned with the nature of pharmaceutical and agrochemical industries, and has nothing to do with health conditions and security in a chemical plant.

The first half of the book starts with drug design, discusses specific types of biological effects, and continues through development to screening, clinical trial, formulation, and marketing. The second half begins with a general discussion of research on agrochemicals, followed by discussions of pesticides, control of plant diseases, plant growth regulators, fertilizers, and finally agrochemicals and the environment. Each half has a concluding essay entitled "The Future of the Industry"; these are frank and do not shrink from controversial issues.

* Unsigned book reviews are by the Book Review Editor.

The emphasis of the authors naturally reflects their British background, and some allowance must be made for differences when transferring the discussions to American industry. Nevertheless, it is a helpful and interesting orientation piece. It is quite short, but the brevity has the merit of encouraging one to read it.

Residue Reviews. Volume 55. Edited by F. A. GUNTHER and A. D. GUNTHER. Springer Verlag, New York, N.Y. 1975. vi + 152 pp. \$16.80.

This volume in this series of reviews on pesticides and other contaminants is largely analytical in emphasis. More than half the book consists of a chapter on "Automation in the Pesticide Analytical Laboratory" by Daniel E. Ott (Department of Entomology, University of California, Riverside). Another long chapter is "Pesticides in Air: Sampling Methods", by L. P. van Dyk and K. Visweswariah (Plant Protection Research Institute, Pretoria, South Africa, and Central Food Technological Research Institute, Mysore, India, respectively). The last chapter is a short one, but not the less important: "Polychlorinated Biphenyl Residues in Silos in the United States", by L. B. Willett (Ohio Agricultural Research and Development Center) and J. F. Hess, Jr. (American,

Burt and Jones Co.). As in earlier volumes, each review is extensively documented, and there is an excellent index.

Technique of Electroorganic Synthesis. Parts I and II (Techniques of Chemistry, Volume V). Edited by NORMAN L. WEINBERG (Hooker Chemical and Plastics Corp.). John Wiley & Sons, Inc., New York, N.Y. 1974. viii + 1987 pp. \$92.50.

Eight books on organic electrochemistry have appeared in the past three years. This avalanche was largely triggered by the virtual void left since Fichter's "Organische Electrochemie", published in 1943. The volumes under review here, like Fichter's work, treat electrosynthesis in an encyclopedic fashion. The wealth of material available can be judged by the size of this two-part work: it totals 1987 pages, 3411 references, and 2811 g.

The books contain eleven chapters by authors who are considered expert in the various areas. Part I begins with 228 pages on preparative methods and on mechanistic techniques and principles. The remaining pages cover oxidation reactions. Part II treats both oxidation and reduction reactions and has chapters dealing specifically with halogenation, organometallic compounds, and polymers. Finally, there is a very useful 389-page tabulation of oxidation and reduction potentials. Because of the organization and the extensive use of tables throughout, it is easy to locate information. Therefore, this should be the most useful reference book for those working in the field. In this regard it cannot be faulted except for its lack of an author index and the fact that virtually no references later than 1970 are included.

The books will not be very useful to a beginner who wants a little information. As indicated above, the treatment is exhaustive and as might be expected it sometimes becomes exhausting for the reader as well. In the chapter on reduction reactions, for example, the text is badly fragmented and the novice will not easily grasp the basic principles and potential utility of the method. This reviewer found the chapters on oxidations particularly well done. The mechanistic discussions in the chapters on the oxidation of carboxylates and amines are, for example, written critically and are quite readable. In contrast the introductory survey of mechanisms and mechanistic methods in the second half of Chapter III is written uncritically and in places unclearly.

These books are, however, primarily meant to review electroorganic synthesis. A number of unique and apparently general functional group transformations as well as several high-yield carbon-carbon bond formation processes are described and several recipes are included. The text demonstrates, however, that electrosynthesis should still be considered a pubescent science since these reactions have not generally been applied to the synthesis of complex molecules and often have been performed on a small scale.

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The Chemistry of the Isoquinoline Alkaloids. Volume 2. Edited by TETSUJI KAMETANI. The Sendai Institute of Heterocyclic Chemistry, and Kinkodo Publishing Co., Sendai, Japan. 1974. vii + 359 pp. \$30 (paperback).

It is pleasing that Kametani has undertaken the task of continuing this series with a second volume, which, besides a general introduction into the chemistry of isoquinoline alkaloids, lists new alkaloids isolated between 1967 and 1972 in the same way as in his first volume (names, structures, physical, and botanical data). It is especially noteworthy that great care has been given in presenting the alkaloids with known absolute configurations with their correct absolute structures. The book gives the expert in the field all the necessary information which he needs to keep him up to date. This excellent compilation is an important dictionary for all scientists interested in isoquinoline alkaloid chemistry. It is hoped that Kametani and his coworkers will continue this series in the same fashion.

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Topics in Current Chemistry (Fortschritte der Chemischen Forschung). Volume 54. Triplet States I. Springer-Verlag, Berlin, Heidelberg, New York. 1975. 163 pp. \$29.30.

The latest volume in this series consists of three reviews concerning triplet states: "Quantum-Mechanical Calculations of the Potential Energy Surfaces of Triplet States" by A. Devaquet;

"Photochemistry of β,γ -Unsaturated Ketones" by W. G. Dauben, G. Lodder, and J. Ipaktschi; and "Protein Triplet States" by A. H. Maki and J. A. Zuclich. Each review deals with recent developments in research in an area of photochemistry and/or photophysics of intensive current interest. The treatments are all of high quality, they are well written, and the literature coverage up to early 1974 is as good as can be expected. These reviews should prove of value to chemists who have interests in one or more of these areas, but will be of limited interest to nonspecialists. Since the state of knowledge in each of these areas is expanding rapidly, this is not a volume which will be a valuable addition to personal libraries, especially considering its cost in relationship to the number of pages, but will be consulted mainly in institutional collections. The value of the second review is also mitigated by the circumstance that a much more complete and comprehensive review on the same subject by K. N. Houk has been published in the February 1976 issue of *Chemical Reviews*.

Despite the high quality of this volume, both in the writing and the presentation, I have distinct reservations about this type of book. There are many review journals and books available to the scientific public these days. Those relevant to the present volume would include *Chemical Reviews*, *Accounts of Chemical Research*, *Advances in Photochemistry*, *Annual Reviews*, and the various Specialist Periodical Reports published by the Chemical Society. With the availability of the above publications at much lower cost, considering the range of subject matter in each volume as well as the cost per page, I frankly see no scientific justification for an expensive book of the type reviewed here. Each of these reviews could just as well have appeared in one of the aforementioned publications, or could have been collected with several other papers (note that this is designated "Triplet States I") in a much larger volume produced at lower cost. It is, of course, the institutional libraries, which are very hard-pressed for funds these days to keep up with the mounting costs of books and journals which are considered to be essential, who will have to pay for this and similar volumes and keep these series afloat financially. I submit that there are better uses for these limited funds. Pressure to buy such volumes will understandably come from the specialists who would like the material to be available to them, regardless of cost to the institution. It is time that the editorial boards and publishers took a good look at the purpose of such volumes, the availability of alternative less expensive outlets for the material, and the nature and priorities of the potential purchasers of their product.

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Combustione e Inquinamento. By U. GHEZZI and C. ORTOLANI (Politecnico di Milano). Tamburini Editore, Milan, Italy. 1974. v + 320 pp.

In reducing the rather broad title to the specific problem of hydrocarbon combustion and pollutant formation and control in the internal combustion engine, the authors attempt to present the state of the art in this area.

The first two chapters present an abbreviated introduction into classical chemical kinetics and thermochemistry which is followed in the subsequent chapters by the description of the kinetics and mechanisms of hydrocarbon combustion and pollutant formation with emphasis on carbon monoxide, nitric oxide, carbon dioxide, and hydrocarbon emission characteristics. Chapters 6 through 12 consider the technical aspects of the combustion and control processes in the actual engine and its accessories such as the carburetor with some details of the authors' own research. Such highly important aspects as exhaust gas recirculation, thermal and catalytic reactors, and combustion chamber modifications are highlighted and give the reader a good introduction into the existing and considered possibilities for control. The final four chapters are reserved for the analysis of Wankel, Diesel, and gas-turbine engines with a special description of the determination of the air/fuel ratio.

Emphasizing some of the relevant publications of recent years, the book represents a fairly good introduction into the field. Unfortunately, some rather important areas and new developments such as numerical modeling, new diagnostic techniques, importance of alternative fuels, and others are missing. Still, the reader should find this text useful as both a learning source and for reference work. As such, the language (Italian) should not be a major barrier.

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