

constant for nucleus *i* on radical *j*, m_{ij}^k is the axial quantum number for nucleus *i* on radical *j* in the *k*th state, and β is the Bohr magneton. The data shown in Figure 2 were fitted to this function for $H > 2$ kG,¹⁵ giving the excellent fit shown with the solid line for the parameters in the figure caption. These values for kinetic and magnetic parameters compare very favorably with previous kinetic and ESR data on RCs,^{13,16} making us confident of the validity of the method. The details of this analysis and its implications for photosynthesis are the subject of a separate paper.¹²

The key point we wish to stress is that the analysis and method presented here should be generally applicable to many chemically interesting ET reactions. Figure 3 illustrates selected calculations of the dependence of ϕ_T on magnetic field strength between 5 and 100 kG for various values of Δg , *J*, and the recombination rates. It is evident that an appreciable ϕ_T can be generated at high field, even when ϕ_T is negligible at low field. In model systems, Δg and the hyperfine energies are generally known, thus it is straightforward to extract both recombination rate constants and exchange interactions from experimental data, as well as prove that ET must have occurred. This is a versatile method since the measurement of either ground-state absorption, triplet-triplet absorption, or delayed fluorescence provides the same information, and the method can be applied to the system in any physical state or at any temperature. Photosynthetic model systems are being investigated.

Acknowledgment. We thank Varian Corp. for loaning us the superconducting magnet used in these experiments. This work is supported by the NSF and the Science and Education Administration of the USDA under grants PCM7926677 and 78-59-2066-0-1-147-1, respectively. C.E.D.C. is an NSF Predoctoral Fellow and S.G.B. is a Sloan and Dreyfus Fellow.

(15) At 293 K the field ($B_{1/2}$), which gives a ϕ_T decreased from the zero-field value by half the low-field variation, is 42 G. ϕ_T at low field and the role of dipolar coupling are discussed elsewhere: Roelofs, M. G.; Chidsey, C. E. D.; Boxer, S. G. *Chem. Phys. Lett.*, in press.

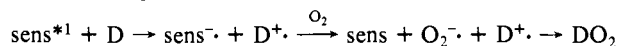
(16) (a) Okamura, M. Y.; Isaacson, R. A.; Feher, G. *Biochim. Biophys. Acta* 1979, 546, 394. (b) Parson, W. W.; Clayton, R. K.; Cogdell, R. J. *Ibid.* 1975, 387, 265.

Photooxygenation via Electron Transfer. 1,1-Dimethylindene

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Only a few examples of photooxygenation via electron transfer are known.¹⁻⁵ Although a variety of mechanisms are involved in these examples,^{1-3,5} reactions between a radical cation and



superoxide, formed by electron transfer from a sensitizer radical anion to oxygen, have been the most extensively studied.²⁻⁵ This area is currently of interest because it appears that photooxygenations involving electron-transfer processes may be more

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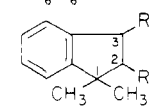
(2) Brown-Wensley, K. A.; Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* 1978, 100, 4162.

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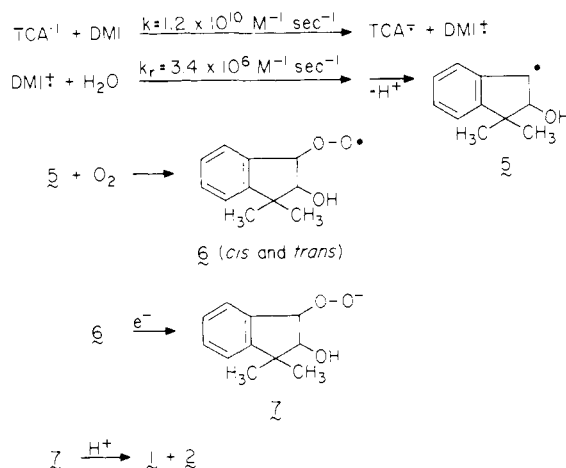
Table I. NMR Data of the Photoproducts and Their Reduction and Acetylation Products in C_6D_6 ^a



R	R'	trans			cis		
		H-2	H-3	$J_{2,3}$	H-2	H-3	$J_{2,3}$
OH	OOH	4.33	5.53	6.6	4.08	5.45	5.1
OH	OH	3.95	5.09	7.2	3.75	4.85	5.2
OCOCH ₃	OCOCH ₃	5.20	6.35	5.6	5.48	6.41	5.5
OCH ₃	OOH	3.85	5.45	5.5	3.33	5.32	5.1
OCH ₃	OH	3.39	5.00	6.9	3.24	4.90	5.1
OCH ₃	OCOCH ₃	3.69	6.40	5.9	~3.30	6.22	5.4
OOH	OCH ₃	4.50	4.71	5.8			
OH	OCH ₃	3.92	4.60	6.6			
OCOCH ₃	OCH ₃	5.46	4.72	4.7			

^a The H-3 signals are distinguished from those of H-2 by slight broadening due to long-range coupling with the aromatic proton(s). The structure of the cis diol was confirmed by comparison with an authentic sample prepared by OsO₄ oxidation of DMI.¹⁰ Reaction of the epoxide of DMI with NaOCH₃ gave a product identical with the reduction product of 12.

Scheme I



diverse and ubiquitous than the extensively studied singlet-oxygen processes. To define the scope of photooxygenation via electron transfer, we investigated the reactions of the cyclic, asymmetric olefin 1,1-dimethylindene (DMI)⁶ and report an electron-transfer-sensitized photooxygenation that is preceded by nucleophilic addition to the olefin radical cation⁷ and that gives products with regiochemistry opposite to that of products from a comparable singlet-oxygen reaction.

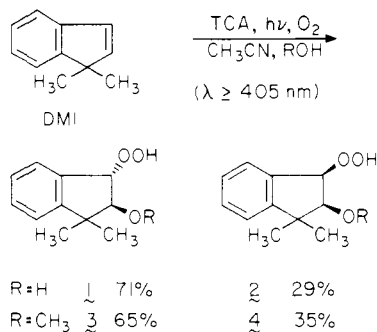
Irradiation of DMI, sensitized by 2,6,9,10-tetracyanoanthracene⁸ (TCA), in acetonitrile in the presence of oxygen and

(6) The dimerization of this olefin via its radical cation was investigated earlier: Farid, S.; Shealer, S. E. *J. Chem. Soc., Chem. Commun.* 1973, 677.

(7) A similar sequence of reactions has been postulated as a minor reaction path in the photooxygenation of 1,1-diphenylethylene in methanol; ref 5.

(8) This sensitizer was first used to study the photosensitized electron-transfer reactions of phenylacetylene: Mattes, S. L.; Farid, S. *J. Chem. Soc., Chem. Commun.* 1980, 126. It was prepared by allowing 2,6,9,10-tetrabromoanthracene (Grandmougin, E. C. R. *Hebd. Seances Acad. Sci.* 1921, 173, 1176) to react with 10 equiv of cuprous cyanide in refluxing *N,N*-dimethylacetamide for several hours. The copper complex of the product was destroyed with hydrogen sulfide, and the black solid which was collected by filtration was extracted repeatedly with boiling toluene. Concentration of the combined toluene extracts yielded crude 2,6,9,10-tetracyanoanthracene (TCA), which was purified by several recrystallizations from nitromethane: mp >345 °C; NMR (CF₃COOH) δ 8.21 (H-3), 8.86 (H-4), 9.20 (H-1) (ABX spectrum, $J_{1,3} = 1.5$ Hz, $J_{1,4} = 0.7$ Hz, $J_{3,4} = 9.05$ Hz); IR (KBr) 2225, 1625, 1460, 1365, 1258, 1172, 910, 822, 590, 438 cm⁻¹; absorption spectrum (C-H₃CN) λ_{max} 428 nm ($\epsilon = 11000$); mass spectrum, *m/e* (rel intensity) 279 (23, M + 1), 278 (100, M⁺), 252 (8), 251 (8), 250 (22, M - H₂CN), 249 (6), 224 (11), 223 (11), 222 (6), 200 (11), 199 (7); exact mass 278.0582 (calcd for C₁₈H₆N₄, 278.0592).

a nucleophile (water or methanol⁹) leads, in a very clean reaction, to the *cis* and *trans* hydroxy hydroperoxides **1** and **2** and to the *cis* and *trans* methoxy hydroperoxides **3** and **4**. The regiochem-



istry and stereochemistry of the products were established by NMR spectrometry, by their reduction products and acetate esters, and by comparison with authentic samples (Table I).

Our proposed mechanism for the formation of **1** and **2** is shown in Scheme I. The first step in this reaction is an exothermic electron transfer from DMI ($E^{\text{ox}} = 1.68$ V vs. SCE, in CH_3CN) to singlet-excited TCA ($E^{\text{red}} = -0.45$ V vs. SCE, in CH_3CN ; singlet excitation energy $\Delta E_{\text{O-O}} = 2.90$ eV). As expected, this exothermic reaction is diffusion controlled (Stern–Volmer slope for TCA fluorescence quenching by DMI in N_2 -saturated $\text{CH}_3\text{CN} = 242 \text{ M}^{-1}$; $\tau_{\text{TCA}}^* = 19.6$ ns; i.e., $k_q = 1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$).

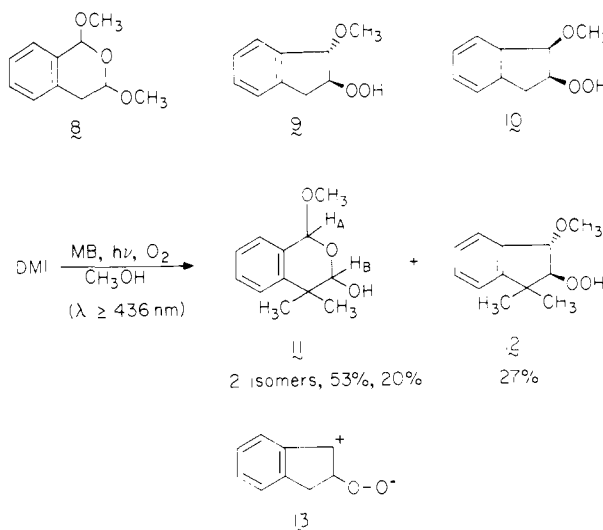
The regiochemistry of the products, with the hydroxy or methoxy group in the 2 position, suggests that nucleophilic addition to the olefin radical cation precedes oxygenation. This view is strongly supported by quenching experiments. Addition of 1,4-dimethoxybenzene (DMB) ($[\text{DMB}] = 2\text{--}6 \times 10^{-4} \text{ M}$), which has a lower oxidation potential ($E^{\text{ox}} = 1.34$ V vs. SCE, in CH_3CN) than DMI, to an acetonitrile solution of DMI (0.04 M) containing water (0.32 and 0.64 M) lowers the quantum yield of **1** and **2**. The Stern–Volmer slopes (13.8×10^3 and $6.8 \times 10^3 \text{ M}^{-1}$), which vary by a factor very close to 0.5 as the water concentration is doubled, show that water and the quencher, DMB, compete for reaction with the DMI radical cation and, furthermore, that all other reactions of $\text{DMI}^{\cdot+}$ are negligible compared to its reaction with water at the given concentrations, i.e., the SV slopes are equal to $k_q/k_r[\text{H}_2\text{O}]$. Assuming that the quenching reaction, which represents an exothermic electron transfer, proceeds at the diffusion-controlled rate of ca. $1.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, the reaction constant for the nucleophilic addition of water to $\text{DMI}^{\cdot+}$ is ca. $3.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$.

As for most reactions of free radicals with O_2 , the oxygenation of **5** is expected to be very fast or even diffusion controlled. Reduction of the peroxy radical **6**, probably through electron donation from the sensitizer radical anion ($\text{TCA}^{\cdot-}$), and protonation¹¹ of the resulting anion **7** are the likely sequence of reactions to give the hydroperoxides **1** and **2**.

A similar sequence of reactions is expected with methanol as a nucleophile. The reaction constant for the nucleophilic addition of MeOH to $\text{DMI}^{\cdot+}$ was determined to be ca. $9.6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ from the product distribution **1** + **2** vs. **3** + **4** when mixtures of water and methanol, in acetonitrile, were used.

In contrast to the electron-transfer-sensitized photooxygenations, the singlet-oxygen reactions of indene and DMI are quite different. The methylene blue sensitized oxygenation of indene^{12–14} in

methanol gives, besides the acetal **8** and other minor products,



a *trans* and *cis* mixture of the methoxy hydroperoxides¹⁵ **9** and **10** having regiochemistry opposite to that of **3** and **4** from the electron-transfer-sensitized reaction of DMI. We have also studied the singlet-oxygen reaction of DMI, in which the somewhat similar products **11**¹⁶ and **12** were formed.

The difference in regiochemistry between the singlet-oxygen and electron-transfer-sensitized photooxygenations arises from the difference in the sequence of addition of oxygen and the nucleophile as a result of diverse reactivities of the intermediates. In the electron-transfer reaction, addition of ground-state oxygen to $\text{DMI}^{\cdot+}$ is too slow to compete with the nucleophilic addition of water or methanol. Thus, in that reaction, the products result from nucleophilic addition followed by oxygenation. In the singlet-oxygen reaction, however, an oxygenated intermediate is formed first by the addition of $^1\text{O}_2$ to the olefin. The perepoxide,¹² the 1,4-peroxide,¹³ the dioxetane,¹³ and their zwitterionic ring-cleavage product **13**¹⁴ have been postulated as the initial oxygenated intermediate, which undergoes nucleophilic attack by the solvent to give **9** and **10**. The acetal **8** is presumably formed from the bis(aldehyde) obtained from the dioxetane.¹³ The reaction of DMI with singlet oxygen is analogous to that of indene.¹⁷

The difference in regiochemistry between electron-transfer-sensitized photooxygenation and singlet-oxygen reactions reported here is expected to hold for related reactions of other asymmetric olefins and dienes.

Further studies are in progress on the photooxygenation of DMI with 9,10-dicyanoanthracene (DCA) as the sensitizer, in which superoxide is expected to play an important role. These results will be presented in another paper.

Registry No. **1**, 80721-69-3; **2**, 80721-70-6; **3**, 80721-71-7; **4**, 80721-72-8; *trans*-**11**, 80721-73-9; *cis*-**11**, 80721-74-0; *trans*-**11** diacetate, 80721-75-1; *cis*-**11** diacetate, 80721-76-2; **12**, 80721-77-3; DMI, 18636-55-0; TCA, 80721-78-4; *trans*-2,3-dihydro-3,3-dimethyl-1*H*-indene-1,2-diol, 80721-79-5; *cis*-2,3-dihydro-3,3-dimethyl-1*H*-indene-1,2-diol, 80721-80-8; *trans*-2,3-dihydro-3,3-dimethyl-1*H*-indene-1,2-diol

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(16) The signals of the ring protons of **11** appear as singlets (C_6D_6): major isomer, δ 5.47 (H_A) and 5.15 (H_B); minor isomer, δ 5.44 (H_A) and 4.85 (H_B). The signals of the monoacetate derivative of the major isomer are at δ 5.52 (H_A) and 6.36 (H_B); those of the minor isomer are at δ 5.43 (H_A) and 6.03 (H_B).

(17) The difference in product distribution between the singlet-oxygen reactions of indene and DMI can be attributed to steric hindrance.

(9) The presence of a small amount of a base (10^{-4} M NaOH or NaOCH_3) is required in the reaction with methanol (0.5–2 M) to obtain **3** and **4** as exclusive products. One explanation for this effect is that the base stabilizes the sensitizer radical anion ($\text{TCA}^{\cdot-}$) by preventing its protonation. $\text{TCA}^{\cdot-}$ may be needed to reduce the peroxy radical, which otherwise leads to other products.

(10) Van Rhee, V.; Kelly, R. C.; Cha, D. Y. *Tetrahedron Lett.* **1976**, 1973.

(11) This sequence of reactions has been postulated for the addition of nucleophiles to radical cations in the absence of oxygen: Neunteufel, R. A.; Arnold, D. R. *J. Am. Chem. Soc.* **1973**, *95*, 4080. Shigemitsu, Y.; Arnold, D. R. *J. Chem. Soc., Chem. Commun.* **1975**, 407.

(12) Fenical, W.; Kearns, D. R.; Radlick, P. *J. Am. Chem. Soc.* **1969**, *91*, 3396.

diacetate, 80721-81-9; *cis*-2,3-dihydro-3,3-dimethyl-1*H*-inden-1,2-diol diacetate, 80721-82-0; *trans*-2,3-dihydro-2-methoxy-3,3-dimethyl-1*H*-inden-1-ol, 80721-83-1; *cis*-2,3-dihydro-2-methoxy-3,3-dimethyl-1*H*-inden-1-ol, 80721-84-2; *trans*-2,3-dihydro-2-methoxy-3,3-dimethyl-1*H*-

inden-1-ol acetate, 80737-15-1; *cis*-2,3-dihydro-2-methoxy-3,3-dimethyl-1*H*-inden-1-ol acetate, 80721-85-3; *trans*-2,3-dihydro-1-methoxy-3,3-dimethyl-1*H*-inden-2-ol, 80721-86-4; *trans*-2,3-dihydro-1-methoxy-3,3-dimethyl-1*H*-inden-2-ol acetate, 80721-87-5.

Book Reviews

Interpretation of Mass Spectra. Third Edition. By F. W. McLafferty (Cornell University): University Science Books, Mill Valley, California. 1980. xvii + 303 pp. \$13.00.

The third edition of Professor McLafferty's popular text continues the excellent pragmatic approach used in the earlier two editions: instruction via challenging involvement in the practical interpretation of many unknown spectra. This reviewer has made extensive use of both earlier editions in short courses on mass spectrometry and the interpretation of mass spectra and is as enthusiastic about this new edition as he was of the previous ones. It is anticipated that the students will be as complimentary in their evaluation of this third edition as they have been of the earlier ones.

Although high-resolution mass spectrometry can provide ion compositions rather easily, a relatively small fraction of the mass spectrometers in use have a resolution that exceeds 1000. Thus, Professor McLafferty's text continues to emphasize the importance of the use of isotopic abundances in mass spectral interpretation. However, the instructor will have to provide the student more information concerning the basis for the isotopic calculations; progressively less dependence should be developed on the use of the tables provided. Recognition of "cluster" patterns can be most useful in interpretation and this feature continues to be given appropriate attention by the author.

Much of the content has been reorganized in this new edition. A major organizational change intends to separate basic from more advanced material; at least a partial success has been achieved in this tantalizing goal. An expanded treatment of mechanisms of ionic fragmentations is provided in this new edition and the author attempts further to classify and relate these to principles drawn from physical-organic chemistry. A new short chapter on computer identifications of unknowns has been included that, while interesting, is much too brief to be of significant value to the beginning student. The number of unknown spectra included has been decreased by about one third from the number offered in the second edition, but with no loss in the pedagogical goals. Literature references have been nearly completely revised; about 70% of the references are to works published in the past 7-8 years. Another important change made by the author has been to use m/z (M/z would have been still better) rather than m/e almost uniformly throughout the book. All of these changes have been made with little change in the size (or cost!) of this text—quite a feat.

The easy, lucid style of the author makes the book enjoyable reading. Only a few typographical errors were noted; in most instances, these are of an obvious nature and will cause the reader no serious problem. The book is a good source of general information and is valuable as a reference of the specialist in mass spectrometry as well as for introducing beginning students to the interpretation of mass spectra.

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Nonlinear Optics of Free Atoms and Molecules. By David C. Hanna and Michael A. Yuratich (The University of Southampton) and David Cotter (Max Planck Institut für biophysikalische Chemie). Springer-Verlag, New York. 1979. ix + 351 pp. \$44.00.

This book provides a review of the theory and covers many experimental aspects of nonlinear optical processes in atomic vapors, molecular gases, and cryogenic liquids. Chapter 1 contains a clear introduction to the topic. A general theoretical framework is developed in Chapters 2 and 3 and applied in a unified interpretation of nonlinear processes including: stimulated electronic Raman scattering (termed SERS, but not to be confused with surface-enhanced Raman scattering), the optical and DC Kerr effects, two-photon emission, absorption and ionization, third harmonic generation, coherent anti-Stokes Raman scattering (CARS), and several higher-order nonlinear processes. Chapters 4-7 deal with specific experimental results; with the exception of two sections in Chapter 4 (4.2 Theory of Optimum Focussing and Phase Matching, and 4.3.2 Contribution of Autoionizing Transitions to the Susceptibilities), they can be understood without detailed knowledge of the earlier chapters.

Chapter 2 is particularly good as a supplement to the literature in the treatment of three topics: nonlinear polarization in nonmonochromatic fields, the numerical factors $K(-\omega_i, \omega_1, \dots, \omega_n)$ in equations relating the n th order polarization and n th order susceptibilities, and secularity. The

relation of the susceptibility formalism to the adiabatic ("dressed states") formalism and to the vector model is also considered in some detail. The treatment of damping and multipolar nonlinearities, on the other hand, is quite limited, and the density matrix is not used as extensively as in N. Bloembergen's "Nonlinear Optics". Propagation of plane waves in nonlinear media is covered in Chapter 3, with a clear explanation of phase mismatch and optimum power generation; discussion of focussed (Gaussian) beams is postponed to Chapter 4.

In chapters on experimental results, the sections on phase matching techniques (4.4 and 6.3), saturation, and limiting mechanisms (4.6 and 5.4) are of broad interest. Data and references have been compiled in several very useful tables: Table 2.1. Processes of importance in free atoms and molecules; Table 2.2. Two-photon resonant third-order nonlinear susceptibilities; Table 2.3. Three-photon resonant fifth-order nonlinear susceptibilities; Table 4.4. Summary of results (up to early 1979) for uv harmonic and sum-frequency generation; and appendices (Universal Constants, and a List of Major Symbols and Acronyms). The text includes 469 references, many of these from 1977-79.

"Nonlinear Optics of Free Atoms and Molecules" is a valuable supplement to Bloembergen's treatise mentioned above. It is well-organized and carefully written—on a level appropriate to researchers in nonlinear optics and related fields. (Other texts must be consulted by those who wish a general introduction.) The monograph contains substantial background and explanatory material on a subject of growing interest, and it will retain its utility as a reference text.

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Introduction to Applied Solid State Physics: Topics in the Applications of Semiconductors, Superconductors and the Nonlinear Optical Properties of Solids. By Richard Dalven (University of California Berkeley). Plenum Press, New York. 1980. vii + 329 pp. \$27.50.

In spite of the pervasive presence of solid-state devices in the professional and private life of every scientist, there is almost no treatment of the fundamental theory of such devices in the texts which are widely used to introduce people to solid-state physics. Thus Richard Dalven's clear and well-written text fills a definite need.

Approximately two-thirds of the book deals with semiconductor devices. Dalven starts with a careful discussion of the pn junction and proceeds to a treatment of transistors, MIS and MS devices, and the use of semiconductors in the generation and detection of electromagnetic radiation. The exposition is aided by a wealth of clear and useful diagrams. Superconductivity—particularly Josephson junctions and their applications—forms the basis of one chapter and the book concludes with a discussion of the nonlinear optical properties of solids which goes far beyond anything previously available at the introductory level. Throughout the book, typical physical parameters are presented (usually in the body of the text rather than in tables). Readers will find the generally extensive and current bibliography at the end of each chapter particularly valuable; the references seem to be chosen for easy availability to people with access to a medium-sized university or laboratory library. There are also a few problems at the end of each chapter, although a teacher using this as a text would probably supplement these.

A word of warning is needed, however. This is *not* a book for a casual reader with a limited physics background. The book arose from Dalven's introductory graduate course at the University of California at Berkeley. The background explicitly assumed is a knowledge of electricity and magnetism, wave mechanics, and solid-state physics comparable to that which a good undergraduate physics major would possess. Without such a background, much of the book would be rough going indeed! (The chemist reader should not develop, however, an inferiority complex. Where it intersects current chemistry, Dalven's book is rather deficient.) These features regrettably mean comparatively few experimental chemists will be able to use this volume to better understand the fundamental science underlying much of their equipment and general scientific and personal environment. In summary, we recommend that the reader expend the necessary effort to read and use this book but suspect few chemists will.

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Baltimore County*