

of literature searching involved in locating some of the data, especially when two identical compounds are reported independently by different investigators using different instruments. Hesse's arrangement deserves special comment since it makes it so convenient to find all constants together without having to look through several pages in order to find the Roman number accompanying the structure needed.

The merits of the compilation overshadow some errors which have been noticed. For instance, in the group of ajmaline alkaloids, Bartlett and co-workers [*J. Am. Chem. Soc.*, **84**, 622 (1962)] have shown that the ring B of ajmaline is *cis* fused to the chair piperidyl moiety, not *trans* as shown in the structure of ajmaline on page 71 and sandwicine and isoajmaline on page 72. The structure of quebrachidine on page 72 is correct (*trans* ring fusion of ring B and piperidine moiety).

The author is to be commended for having undertaken to compile all the data. It is hoped that this volume will be followed by a revised edition in order to keep up with the ever increasing number of publications in the area of indole alkaloids.

LILLY RESEARCH LABORATORIES
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NORBERT NEUSS

Spectroscopy and Molecular Structure. By GERALD W. KING, McMaster University. Holt, Rinehart and Winston, Inc., 383 Madison Ave., N. Y. 1964. xiv + 482 pp. 16 × 23.5 cm. Price, \$10.75.

There are many excellent texts on quantum mechanics which discuss a few applications to problems of spectroscopy. There are also several authoritative, but specialized volumes on spectroscopy. There are also several authoritative, but specialized volumes on spectroscopy. However, a well-balanced and self-contained treatment of the two closely connected areas has not been available in a text suitable for graduate students in physical chemistry. The present text should satisfy this need.

The quantum mechanical treatment is necessarily selective, with a concentration on interpretation, but the limited discussion is not superficial and forms an adequate background for the understanding of complex spectra. The theoretical treatment (Chapters 8 and 9) of rotation and vibration in polyatomic molecules is especially clear and concise. The theory of electronic spectra is less satisfying. Perhaps the treatment here is too concise, and a considerable amount of outside reading will be required to understand the many difficult topics which are included. The detailed illustrations chosen certainly are of current interest, but some appear rather sophisticated and may lead to some confusion to the beginner. However, the references are carefully chosen and will stimulate further reading. It is believed that the text serves admirably the purposes stated by the author, and the book is highly recommended to all who are interested in the fundamentals of spectroscopy.

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A. B. F. DUNCAN

Concepts in Photoconductivity and Allied Problems. By ALBERT ROSE, RCA Laboratories, Princeton, N. J. Interscience Publishers, John Wiley and Sons, Inc., 605 Third Ave., New York 16, N. Y. 1963. 168 pp. 14.5 × 21 cm. Price, \$5.95.

This book presents a phenomenological view of photoconductivity in solid materials. It attempts explanation of not only the simpler, but also some of the more complex aspects of photoconductivity in terms of a limited number of concepts. Primary among these concepts are those of trapping and recombination centers as differentiated by steady-state Fermi levels and demarcation levels. Within its restricted scope the treatment does attain some success. The most regrettable omissions are: the topics of carrier generation, carrier mobilities, scattering processes, and transport properties generally.

The subject of trapping and recombination has been dealt with in considerable detail, and, in fact, the discussion of Chapters 2 and 3 is by far the most lucid, informative, and credible

of the book. The models have been chosen well, and ultimately lead one to a system having a distribution of states throughout the forbidden zone. Many fundamental facts, such as the equality of lifetimes of both carriers, the nonrelation of temperature dependencies of semiconductivity and photoconductivity, etc., are emphasized, and the semiconductor-insulator transition is discussed clearly.

Chapter 3 must be contrasted with Chapter 9. This latter chapter, which is concerned with the energy levels of solids and electrolytes, eschews quantum mechanics and justifies its existence because, in the author's words, "the concepts are simple and provide a useful guide for exploratory work." This reader cannot agree. Vague, nonmathematical concepts are not simple; indeed, they are usually complex and frequently ambiguous. Furthermore, it is difficult to conceive of an association between ambiguity and utility, unless it be of an inverse nature.

Chapter 4 is concerned with space-charge-limited current flow and constitutes a good discussion. Chapter 5 discusses the gain-bandwidth product in a succinct fashion, and is marred only by the use of terminology which the book makes no pretense to define.

Chapter 6 discusses noise currents, and Chapter 7 provides a short discussion of capture cross sections. Both chapters are interesting, and probably do present some physical insights; on the other hand, they are overly heuristic and this reader did not find them useful.

Paper, typography, and binding are of reasonably good quality. Typographical errors have been found in equations 2.12 and 3.12, the caption of Fig. 5.3, and on pages 33, 66, 80, 120, 121, 135, and 154. There is a minor inconsistency between equations 3.32 and 3.33, and a constant is neglected in one of the equations (4.25).

A number of hypothetical models have been proposed to explain various types of behavior. Experimental results typifying all such behaviorisms are lacking in reference, and it is not possible to decide on the general validity of the proposed models. This is not a fault of the book since it makes no pretense to a description of experiment; this latter fact, however, implies that the book will not serve as an introductory reader. Indeed, it would not be going too far to assert that the present volume and that of Bube (R. H. Bube, "Photoconductivity of Solids," John Wiley and Sons, Inc., New York, N. Y., 1960) are largely complementary. Both books are valuable in that together they point out very well the present lack of understanding of the field of photoconductivity.

The average physical chemist will have no difficulty in reading this book; he probably will not want to do so unless he is engaged in or associated with photoconductor research. It presents a good, although uneven, summary of the phenomenological point of view, its strengths and its weaknesses; it will probably convince the reader that there must be a more satisfying way of understanding the various aspects of photoconductivity.

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S. P. MCGLYNN

Colorimetric Determination of Elements. Principles and Methods. By G. CHARLOT, Professor of Analytical Chemistry, Faculte des Sciences, Ecole Superieure de Physique et de Chimie Industrielles, Paris. American Elsevier Publishing Co., Inc., 52 Vanderbilt Ave., New York 17, N. Y. 1964. ix + 449 pp. 17.5 × 25 cm. Price, \$18.00.

This book is an English translation (by the Express Translation Service, London) of the second French edition of 1961. Some sections of the latter have been revised for the English edition. The book consists of two parts. The first, comprising a little more than a third of the whole, deals with the theoretical foundations of colorimetry and spectrophotometry and with principles of separation. The second part is a compilation of selected methods of separation and colorimetric determination of approximately 65 elements. The treatment tends to be condensed, e.g., six pages for aluminum, three and one-half for beryllium, six for sulfur, three for the rare earths, and five lines for hydrogen.

The chief usefulness of the book probably lies in its unitary survey of a rather wide field, sections of which have received fuller treatment in a number of earlier books. It contains compara-

tively little new material. A census of the first 20 chapters of Part II ("Estimation of the Principal Elements"), making up the alphabetical sequence aluminum to gold, yields an average of a little more than one reference per chapter (24 altogether) dated later than 1959. Purchasers of scientific books have by

this time become hardened to their prices, so that the price of this volume may occasion only mild surprise.

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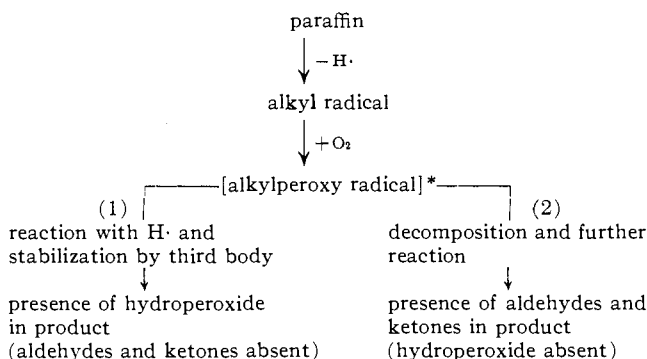
E. B. SANDELL

ADDITIONS AND CORRECTIONS

1950, Volume 72

Elmer J. Badin: The Low Temperature, Low Pressure, Hydrogen Atom Initiated Combustion of Hydrocarbons.

Page 1552. At the end of column 2, replace the simplified reaction mechanism by the following mechanism.

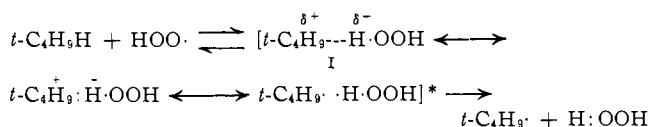


Page 1553. At the end of column 2 before the Summary, the following should be inserted (any part of the paper at variance with the addition should be regarded as having been modified): Only three paraffins (methane, propane, and isobutane) in Table III are unique in that each has a specific type of C-H bond (primary, secondary, or tertiary) at only one carbon. Hence, rates in Table III [see also *J. Am. Chem. Soc.*, **83**, 5045 (1961)] may be used to demonstrate two previously unreported empirical correlations for rate of conversion of paraffin (0.03 ml. STP CH₄ per min., 0.19 ml. STP C₃H₈ per min., and 0.57 ml. STP *i*-C₄H₁₀ per min.) to aldehyde and ketone.

The first empirical correlation is *linearity* of log rate of conversion of paraffin to aldehyde and ketone *vs.* values of C-H bond dissociation energy (CH₃-H, 102 kcal. per mole; *i*-C₃H₇-H, 94 kcal. per mole; *t*-C₄H₉-H, 89 kcal. per mole). Values of bond dissociation energy are those compiled by Cottrell [T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd Ed., Butterworths, London, England, 1958, pp. 177, 182, 183].

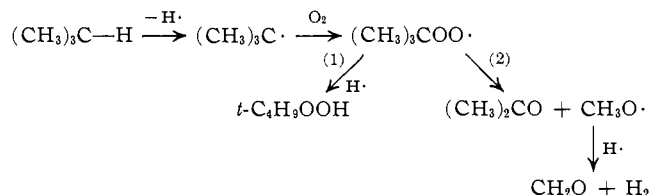
The second empirical correlation is *linearity* of log rate of conversion of paraffin to aldehyde and ketone *vs.* values [R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 619] of the polar substituent constant σ^* (CH₃, 0; *i*-C₃H₇, -0.19; *t*-C₄H₉, -0.30). Inclusion of *n*-butane (rate of conversion is 0.34 ml. STP *n*-C₄H₁₀ per min., σ^* for *sec*-C₄H₉ is -0.21) results in some deviation from the line, the reason probably being that *n*-butane contains secondary C-H bonds at two different carbons.

These correlations suggest there are carbonium ion contributions to the activated complex in the hydrogen-abstraction step, e.g., as in reaction of HOO· radical with isobutane.



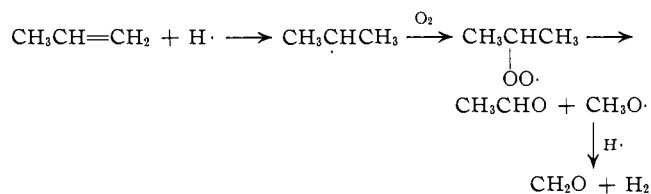
The hypothesis is made that the weakest C-H bond forms a dipole as in I, such a dipole being caused inductomerically by the HOO· radical.

These correlations also suggest that (2) is the main reaction path. The oxidation of isobutane is described below, path 1 functioning to only a minor extent and path 2 functioning to a major extent with formation of about 12 mole % each of acetone and formaldehyde.



This mechanism is somewhat analogous to Semenov's "delayed branching" mechanism as described by Minkoff and Tipper [G. J. Minkoff and C. F. H. Tipper, "Chemistry of Combustion Reactions," Butterworths, London, England, 1962, p. 129] and to the chemical steps suggested by Lewis and von Elbe [B. Lewis and G. von Elbe, "Combustion, Flames and Explosions of Gases," 2nd Ed., Academic Press Inc., New York, N. Y., 1961, p. 174].

Oxidation of olefins under these conditions most probably involves addition of H· followed by further reaction leading to oxidative scission at the double bond.

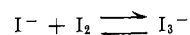


This differs slightly from initial addition of HOO· as suggested by Minkoff and Tipper (p. 173).—ELMER J. BADIN.

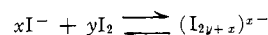
1952, Volume 74

Mansel Davies and Emrys Gwynne: The Iodine-Iodide Interaction.

Page 2748 ff. The title should read "The Iodide-Triiodide Equilibrium in Aqueous Solutions." In addition, the systems



and the further possible equilibria



have been the subject of very many studies in aqueous solutions (L. I. Katzin and E. Gebart, *J. Am. Chem. Soc.*, **77**, 5814, (1955), and references therein). Dr. Ramette of the Chemistry Department, Carlton College, Northfield, Minn., has recently brought to our attention the presence of a number of numerical errors in the Tables I and II of our paper. These errors must be admitted and the senior author (M. D.) must accept the fact that he had not checked all the arithmetical detail.

These details have now been reworked on the same assumptions as previously—in particular, that there is no appreciable variation of K_1 with ionic strength (for which our own specific experiments provide strong support) over the concentrations ranges and for the ionic types relevant to our conditions. The over-all effect of the recalculations is to leave all our previous conclusions unchanged but the new figures show that the uncertainties in K_3 (for equilibrium (1)) extrapolated to zero [I₂] (free iodine concentrations) are larger than previously represented.

Briefly, the revised K_3 values and their estimated uncertainties are:

T, °C.	25	38	49	63
K_3	764.3 ± 2.0	589.0 ± 2.0	500 ± 10	413 ± 2

Thus, for 0.1 M KI at 25° the extreme limits on the extrapolated K_3 give 764.3 ± 2.5 . The over-all best value of ΔH_3 is now