

followed by



with equal probability. We have used this reaction to assess the yield of benzene triplets under different conditions of irradiation.

Benzene solutions with varying concentrations of *cis*-butene-2 were irradiated with γ -rays from a 500-curie cobalt-60 source. Considerable isomerization of the butene-2 was observed, the $G(\text{trans-C}_4\text{H}_8\text{-2})$ values ranging from 0.18 to 2.3, the latter being the value for all solutions with butene-2 concentrations greater than 0.1 *M*. Energies absorbed were measured by the Fricke dosimeter ($G_{\text{F}_2^{3+}} = 15.6$).

No isomerization was observed when similar experiments were carried out in *n*-hexane. However, when mixtures of *n*-hexane, benzene and *trans*-butene-2 were irradiated, even though the $G(\text{H}_2)$ values decreased with increasing benzene concentration due to the latter's protective action, the $G(\text{cis-C}_4\text{H}_8\text{-2})$ values increased to that for pure benzene solutions.

When iodine was introduced into the benzene-*cis*-butene-2 system, the $G(\text{trans-C}_4\text{H}_8\text{-2})$ values decreased slightly but the side products found in iodine-free systems were absent. This, combined with the evidence from the hexane experiments, rules out the possibility of the isomerization proceeding by a free radical mechanism.

Mixtures of cyclohexene, benzene and *cis*-butene-2 also were examined and as in the hexane experiments $G(\text{H}_2)$ values dropped with increasing mole fraction of benzene while the $G(\text{trans-C}_4\text{H}_8\text{-2})$ values increased from 0 for pure cyclohexene to 0.55 for a 3:1 benzene-cyclohexene mixture. The isomerization does not proceed *via* a charge transfer mechanism since this would be enhanced by increasing cyclohexene concentration.³

If the isomerization takes place by an energy transfer mechanism involving the benzene triplet, another material with a triplet energy lower than those of both benzene and butene-2 should decrease the amount of isomerization. The addition of anthracene to benzene *cis*-butene-2 solutions lowered the $G(\text{trans-C}_4\text{H}_8\text{-2})$ values.

The data obtained are exemplified in Table I.

(3) J. Manion and M. Burton, *J. Phys. Chem.*, **56**, 560 (1952).

TABLE I

THE RADIATION INDUCED *cis-trans* ISOMERIZATION OF BUTENE-2

Solution	Mole fraction of benzene	Concn. of butene-2 moles/l.	$G(\text{H}_2)$	$G(\text{C}_4\text{H}_8\text{-2})$ isomerization
Pure benzene		0.0027(<i>cis</i>)	0.0375	1.18(<i>trans</i>)
		.047 (<i>cis</i>)	.038	1.33(<i>trans</i>)
		.122 (<i>cis</i>)	.038	2.30(<i>trans</i>)
		.179	.038	2.29(<i>trans</i>)
Benzene-hexane	0	.018(<i>trans</i>)	3.93	— (<i>cis</i>)
	0.593	.033(<i>trans</i>)	0.52	0.31(<i>cis</i>)
	.814	.018(<i>trans</i>)	.28	1.05(<i>cis</i>)
Benzene + I ₂ (0.0076 g. mole. l. ⁻¹)		.03 (<i>cis</i>)	.038	0.89(<i>trans</i>)
		.13 (<i>cis</i>)	.038	1.90(<i>trans</i>)
Cyclohexene-benzene	0	.27 (<i>cis</i>)	1.20	— (<i>trans</i>)
	0.276	.27 (<i>cis</i>)	0.77	— (<i>trans</i>)
	.533	.27 (<i>cis</i>)	.44	— (<i>trans</i>)
	.774	.27 (<i>cis</i>)	.3	0.55(<i>trans</i>)
Benzene-anthracene (0.056 g. mole. l. ⁻¹)		.0475(<i>cis</i>)	.038	0.50(<i>trans</i>)
	^a	.0475(<i>cis</i>)	.038	1.48(<i>trans</i>)
		.0924(<i>cis</i>)	.038	0.85(<i>trans</i>)
	^a	.0924(<i>cis</i>)	.038	2.30(<i>trans</i>)
	^a	.118 (<i>cis</i>)	.038	1.10(<i>trans</i>)
	^a	.118 (<i>cis</i>)	.038	2.30(<i>trans</i>)

^a Pure benzene.

These experiments demonstrate that large amounts of benzene triplets are formed during irradiation of benzene and that the $G(\text{C}_6\text{H}_6 \text{ triplet})$ must be about 4.60, a value comparing very closely with $G(\text{H}_2)$ for pure *n*-hexane (4.0).⁴ The protective action of the benzene evidently involves processes producing the triplet state of benzene. The specific sensitizing effect of the benzene makes an electron transfer mechanism⁵ for the isomerization unlikely. The work is being extended.

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(4) W. H. T. Davison, *Chem. Ind. (London)*, 662 (1957).

(5) J. H. Baxendale and F. W. Mellows, *J. Am. Chem. Soc.*, **83**, 4720 (1961).

BOOK REVIEWS

The Chromatography of Steroids. By I. E. BUSH, M.A., Ph.D., M.B., B.Ch. (Cantab.), Bowman Professor of Physiology, The University of Birmingham. Pergamon Press Ltd., Headington Hill Hall, Oxford, England. 1961. xxi + 437 pp. 16 × 23.5 cm. Price, \$12.50.

This monograph despite its general title deals primarily with paper chromatography. Column chromatography is adequately treated but the newer techniques of thin layer and vapor phase chromatography are not covered at all. The author has departed from the conventional description of techniques, solvent systems and mobilities and instead has approached the subject mainly from the theoretical point of view. One of the author's aims was "to show that the behavior of steroids in chromatographic systems is a consequence of general laws and that it can be treated quantitatively with reasonable accuracy." For this purpose nearly half of the book is devoted to the basic theory of chromatography, the quantitative treatment of chromatographic behavior of steroids and the use of chromatography for structure analysis. The chapter on techniques and apparatus is very informative and includes many innovations introduced by the author. Methods for the preparation of ex-

tracts for chromatography are also found in this chapter. There is a chapter on various colorimetric and radioactive techniques for quantitation including the direct scanning of paper chromatograms, both manual and automatic. Typical analytical problems in steroid biochemistry such as hydrocortisone in human blood and urinary steroids are dealt with in a special chapter. The appendices are full of useful information on purification of reagents and materials, microchemical reaction and methods for detection.

The theoretical and quantitative treatment of organic compounds in chromatographic systems, has been studied in other fields. The author believes, and the reviewer agrees, that further extension of these studies would be very fruitful in the field of steroids with the variety and number of functional groups and known stereochemistry. The term R_M , defined earlier by Bates-Smith and Westall as $R_M = \log(1/R_F - 1)$ is introduced into steroid chromatography. Theoretically, the change in R_M is a constant. The ΔR_M due to substitution (H → R) or due to reaction (*i.e.*, OH → = O) at a given position was found to be reasonably constant in a given solvent system for a series of steroids where reliable R_F values were available. Similarly, the ΔR_M due to a change in solvent systems for a particular group was

also reasonably constant. Thus the use of ΔR_M for characterization of a steroid in much the same manner as molecular rotation difference, ΔM_D , is very promising. However, the unwary should be warned that rigid and precise conditions must be employed to obtain the R_F value.

The book is interestingly written and very readable. The author makes critical evaluation of methods and techniques and, although everyone may not always agree with him, it is very useful to the investigators new in the field. The book is highly recommended to everyone actively engaged in steroid research and to investigators interested in the quantitative behavior of organic compounds in chromatographic systems.

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Wissenschaftliche Forschungsberichte. Naturwissenschaftliche Reihe. Band 70. Einführung in die Raman-spektroskopie. By Dr. JOSEF BRANDMÜLLER, Professor der Physik, Phil.-theol. Hochschule Bamberg, and Dr. HERBERT MOSER, Privatdozent für Experimentalphysik, Universität München. Dr. Dietrich Steinkopff Verlag, Holzhofallee 35, Darmstadt, Germany. 1962. xv + 515 pp. 15 × 21 cm. Price, Brosch., DM. 90.; geb., DM. 94.

The authors have succeeded in their principal objects: to present a clear introduction into the basic theory of Raman spectra and a detailed description of experimental techniques.

The theoretical part starts from the general properties of scattered radiation and furnishes a good presentation of Placzek's theory and his results regarding intensity, polarization and the influence of symmetry. The theory of rotational lines by Placzek and Teller is also discussed in some detail. Further theoretical results, including Volkenshtein's theory, are more briefly reported.

The experimental part is, quite naturally, a collection of rather disparate, but in general thorough and well substantiated reports and advice on specific experimental problems, ranging from mercury arcs and photomultiplier cells to the description of cells for liquids, crystals and gases and the measurement of frequency, intensity and degree of depolarization.

The last quarter of the text discusses applications and results. In the preface the authors point out that this part covers only a very small and, in addition, somewhat subjective selection. In fact, a number of useful discussions of several specific subjects (e.g., analysis of organic compounds and mixtures) are presented in this part.

Since Herzberg's books furnish a rather complete systematic discussion of vibrations, the authors are justified in presenting only a few examples of vibration problems, but even in a brief discussion of specific applications (e.g., H-bonding, dissociation of strong acids) a survey of concordant or discordant results obtained by other methods, or at least suitable references, would be desirable. Quoting old literature on a specific problem and at the same time omitting very important, more recent contributions (T. F. Young, J. Chédin and their co-workers on the structure of strong acids) is likely to mislead the reader.

On the whole, this book is an excellent aid for the active worker in the field of Raman spectroscopy.

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Molecular Structure. The Physical Approach. By J. C. D. BRAND and J. C. SPEAKMAN, University of Glasgow. St. Martin's Press, Inc., 175 Fifth Avenue, New York 10, N. Y. 1961. viii + 300 pp. 15 × 23.5 cm. Price, \$6.00.

This book presents a broad coverage of physical methods useful in the determination of molecular structure, directed toward honors students in physical chemistry and research workers in other fields. In this country it should prove most useful to undergraduates in honors sections in physical chemistry, and to intermediate-level graduate students in all fields of chemistry.

The coverage provided is quite broad, and includes treatments of molecular rotation and vibration, dipole moments, nuclear magnetic resonance, nuclear quadrupole resonance, infrared and Raman spectra, Kerr effect, X-ray diffraction and crystal structure analysis and electron diffraction. Chapters are provided on symmetry (point-group and space-group), and on elementary quantum mechanics. The elements of group theory are treated in an appendix, as are the applications of the Wilson FG matrix method to normal coordinate calculations.

The presentations are clear and carefully prepared; the text appears to contain few errors. As was intended, the emphasis

is on principles rather than on practice; the value of the book would be increased significantly by an increase in the number of references to articles illustrating applications of the principles discussed or extending the coverage to a more advanced level. In terms of current interest, the treatment of high resolution nuclear magnetic resonance spectroscopy is least satisfactory, as it does not properly reflect the state of the art even as of 1957.

The emphasis on symmetry considerations and applications of group theory should certainly be commended. The problem of providing coverage in such condensed form has led to some difficulties. For example, the definition on p. 25 specifies that "a representation Γ of a group is a set of *numbers* that multiply in accordance with the group multiplication table," and again (p. 256) "the *characters* of the matrices of a group of operations are said to form a representation Γ of the group." There should also be noted the statement (p. 78) that all asymmetric top molecules have a permanent dipole moment.

On the whole, this book can be highly recommended to its intended users. It has been carefully written and edited, and appears at a price which makes it an attractive investment.

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Werkstoffe des Reaktorbaues mit besonderer Berücksichtigung der Metalle. By KARL LINTNER, Dr. phil., a. o. Professor, II. Physikal. Institut der Universität Wien, and ERICH SCHMID, Dr. phil. Dr. mont, h.c., o. Professor, Ausw. wissenschaft. Mitglied d. Max Planck-Instituts für Metallforschung, Stuttgart, Vorstand d. II. Physikal. Instituts der Universität Wien. Springer-Verlag, Heidelberger Platz 3, Berlin-Wilmersdorf, Germany. 1962. viii + 592 pp. 16.5 × 23.5 cm. Price, DM. 78.

As the title points out, the book deals with materials for nuclear reactors, with special consideration given to metals. In the two opening chapters the authors make a valiant effort to review the fundamentals of nuclear physics and of metallurgy. As is often the case, the value of such short reviews might be questioned. Those unfamiliar with this background are unlikely to grasp it in 40 pages; those most likely to find the book useful would be well grounded in these fundamentals.

Perhaps the most outstanding feature of the book is the extensive treatment of the influence of radiation on the properties of solids. The references in this section represent a very thorough coverage of the field and the review is well organized in a logical summary. Too often such reviews are limited to only one type of material with the effect of losing the general features of radiation/lattice interactions. The authors in this case treat metals, oxides, semiconductors and hydrocarbons in the same chapter with pleasing results.

The greater part of the book deals with the metals used as reactor fuels: uranium, plutonium and thorium. The special technological problems involved in the use of these metals are not lost in the very successful discussion of fundamental properties. Ceramic fuels, by the authors' choice, were not given broad coverage. A more extended treatment of the ceramic fuels might have been desirable since the metallic fuels will probably be less and less important in future reactor developments.

The concluding chapters deal with materials for reactor application as moderators, coolants, control elements and structural materials. These final chapters are somewhat brief compared to the fine treatment of radiation effects and of the metallic fuels. Control materials, for example, are covered in only nine pages.

The book is generally thorough and well written. The extensive literature references constitute a required reading list for the materials scientist approaching reactor technology. As is typical of this publisher, the book is handsomely printed. The reviewers would rate the book as a valuable technical reference on nuclear reactor materials.

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Solvolytic Displacement Reactions. By ANDREW STREITWIESER, JR., Associate Professor of Chemistry, University of California, Berkeley, California. McGraw-Hill Book Company, Inc., 330 West 42nd Street, New York 36, N. Y. 1962. ix + 214 pp. 15.5 × 23.5 cm. Price, \$5.00.

This book is a direct reprint of Prof. Streitwieser's well known article in *Chem. Rev.*, 56, 571(1956), with the addition of a 22-page Supplement covering selected topics since 1956.

A large amount of valuable information about non-solvolytic displacement reactions is presented first, followed by data on solvolytic reactions. Sections on the S_N1 mechanism, mechanis-