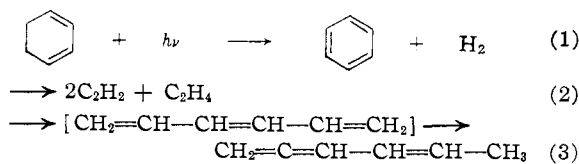


**INTERNAL CONVERSION IN THE
PHOTOCHEMISTRY OF DI- AND TRIOLEFINS**

Sir:

Franck and Sponer pointed out¹ that "since by internal conversion exceedingly "hot" molecules are produced, chemical reactions occur which equal thermochemical reactions rather than photochemical ones." It was demonstrated² recently that in the photochemistry of 1,3,5-cycloheptatriene, the isomerization to toluene, which has a quantum yield of unity at zero pressure, probably occurs from a vibrationally excited ground state molecule, which in turn originates by internal conversion from the initially formed electronically excited singlet state.

It now has been realized that similar arguments may apply to the photochemistry of other aliphatic di- and triolefins. Photolysis of 1,3-cyclohexadiene in the vapor phase³ is known to lead to the reactions



We now have obtained quantum yields for these products at 2600 Å. over an 80-fold pressure range which extended down to 0.3 mm. The processes which decreased with an increase in pressure were (1) and (2). These reactions are known to be important in the vapor phase pyrolysis of 1,3-cyclohexadiene.⁴ A plot of the reciprocal of the quantum yield for hydrogen *vs.* pressure was a straight line over the whole pressure range. The quantum yield at zero pressure was 0.16. The uncorrected radiative lifetime of the molecule in the first singlet excited state was calculated by the integration of the absorption band to be 4×10^{-9} sec. Crossover from this state to a long-lived state has not been observed, so that only one excited state needs to be taken into consideration.⁵ Since the lifetime represents an upper limit, as fluorescence has not been observed even under extreme conditions,⁶ it can be calculated that below a pressure of 1 mm. the excited molecule may not last long enough to undergo deactivating collisions with surrounding molecules.⁷ The observed pressure dependence of reactions (1) and (2) suggests that these two reactions probably originate from a vibrationally excited ground state molecule which arises by internal conversion from the initially formed electronically excited molecule.

(1) J. Franck and H. Sponer, "Volume Commemoratif V. Henri," Maison Desoer, Liège, 1948, p. 169.

(2) R. Srinivasan, *J. Am. Chem. Soc.*, **84**, 3432 (1962).

(3) R. Srinivasan, *ibid.*, **82**, 5063 (1960).

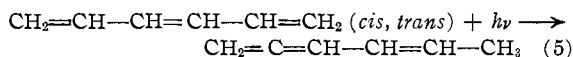
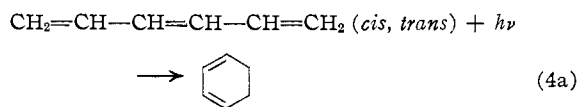
(4) F. O. Rice and A. L. Stallbaumer, *ibid.*, **64**, 1527 (1942).

(5) The non-existence of a triplet state is almost impossible to prove experimentally. In this instance, apart from the absence of phosphorescent light emission,⁸ the basis for this statement is the principle that crossover from singlet to triplet is unfavorable when the energy gap is large, which is the case in dienes and trienes. Gouterman (*J. Chem. Phys.*, **36**, 2864 (1962)) recently has provided a theoretical basis for this idea.

(6) R. J. De Kock, Ph.D. Thesis, Rijksuniversiteit Te Leiden, 1959, p. 66.

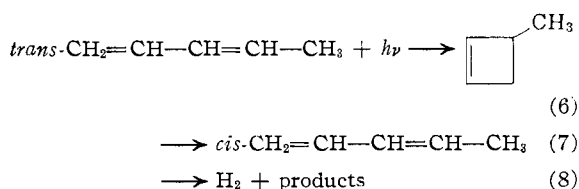
(7) This is based on calculations from kinetic theory. However, wall effects may be important at low pressure.

In the case of 1,3,5-hexatriene (*cis*, *trans*) the photochemical processes (4a), (4b) and (5) are known⁸ to occur in the vapor phase. We have now



obtained quantum yields for hydrogen and 1,2,4-hexatriene at 2600 Å. over a pressure range from 0.3 to 16.8 mm. Reaction (4a) which is the only process known in the pyrolysis of 1,3,5-hexatriene, will be followed by (4b) through a carryover of energy from the first step. It was found that the quantum yield for hydrogen decreased with an increase in pressure. A plot of the reciprocal of the quantum yield *vs.* pressure was a straight line over the whole pressure range. The quantum yield at zero pressure was 0.24. The radiative lifetime of the excited singlet state was calculated to be 3×10^{-10} sec.⁹ No other electronically excited state has been observed in the photochemistry at this wave length. By the application of the same arguments as in 1,3-cyclohexadiene, it can be concluded that 1,2,4-hexatriene may originate from an electronically excited molecule while benzene and hydrogen (through 1,3-cyclohexadiene) occur from a vibrationally excited ground state molecule formed by internal conversion from the electronically excited molecule.

We have also studied the photochemistry of *trans*-1,3-pentadiene in the vapor phase at pressures down to 0.8 mm. The reactions that were observed at wave lengths below 2500 Å. were



Hydrogen was found to decrease with an increase in pressure while the other two reactions showed a slight increase in yield under the same conditions. Since the calculated radiative lifetime which is about 10^{-9} sec. is too short to allow deactivating collisions with the electronically excited molecule below ~ 1 mm., the pressure quenching probably is not from a molecule in the upper singlet state. On the other hand, reaction (6) must originate from this state as it is exactly the reverse of the reaction that is observed thermally. Lack of knowledge of the modes of pyrolysis of 1,3-pentadiene makes it difficult to interpret the photochemistry. While it is attractive to suggest that hydrogen originated

(8) R. Srinivasan, *J. Am. Chem. Soc.*, **83**, 2807 (1961).

(9) This value leads to an unreasonably high figure for the oscillator strength. A more realistic value for the lifetime may be four or five times larger. The arguments that follow will not be significantly affected by this change.

from a ground state molecule which is formed by internal conversion, it is not known whether such a reaction can occur thermally. The stereoisomerization reaction (7) is known as a thermal process but its pressure dependence does not show the expected trend. The reaction is known even in solution,¹⁰ which suggests that it may not be subject to collisional quenching at all. But it should also be borne in mind that the large spectral shifts

(10) N. I. Shuikin and V. A. Tulupov, *Vestnik Moskov Univ.* **9**, No. 8, Ser Fiz-Mat.; *Estesven Nauk*, No. 5, 91 (1954); *C. A.* **49**, 3776 (1955); R. Srinivasan, *J. Am. Chem. Soc.*, in press.

displayed by dienes and trienes in going from the vapor phase to even a hydrocarbon solution make a correlation between the photochemistry in the two phases rather obscure.

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BOOK REVIEWS

The Wave Mechanics of Electrons in Metals. BY STANLEY RAIMES, Reader in Mathematics, Imperial College, University of London. Interscience Division, John Wiley and Sons, Inc., 440 Park Avenue South, New York 16, N. Y. 1961. xi + 367 pp. 15.5 × 23.5 cm. Price, \$13.00.

This is an unusual book among the many recent volumes on solid state physics. Some 350 pages are devoted to discussion of what most solid state physics books take for granted or else discuss briefly in perhaps one third to one tenth the space. The author makes his purpose completely clear in his preface, and the potential reader is advised not to ignore it.

This is *not* the place to seek a complete picture of band structures of solids, nor a description of transport phenomena. What this book does present is a fairly detailed mathematical treatment of elementary aspects of the behavior of electrons in a periodic potential.

The level is such that a well-trained physics major in his senior year should have no difficulty in reading it from cover to cover. The required quantum mechanical aspects are covered in early chapters and where needed. I found the writing clear and self-contained.

The point of view is distinctly theoretical, and much pertinent experimental material is not mentioned. This is quite consistent with the avowed purpose of the text.

A reviewer's criticism of specific sections seems irrelevant. When a book is unique it will be used (or not) because of its uniqueness, and not because it is (or is not) the best possible treatment of the material included. A more relevant question to be discussed here would seem to be the potential uses of this book in contemporary American education. Certainly this will not be widely selected as a text book for a first course in solid state physics; there is insufficient coverage of experimental aspects, and no pretense of covering perhaps ninety per cent. of solid state material. The elementary nature of the treatment will also prevent it from being chosen as a text book for an advanced course in theory of solids. Where it may well find popular usage is as a supplementary text in elementary courses at points where a simple but rigorous treatment is wanted for some aspect of electrons in solids, either in courses on solids or in modern physics.

Particularly worthy of note is the chapter on plasma oscillations. I know of no other text which contains such a lucid, modern, and complete treatment of this topic. The footnote on p. 197 will also be welcomed as containing the essence of a decent proof of Bloch's theorem.

A clear and fairly complete treatment of the Wigner-Seitz "cellular" method is presented in Chap. 9. The author gives enough detail so that anyone should be able to understand it on his first encounter, and indeed one wishes that he had chosen also to discuss some of the newer techniques such as the OPW and APW methods.

The strongest impression that this reviewer received from the book is that every topic included is discussed right from the beginning, with no steps omitted. As a result some fairly sophisticated material is reached without the reader becoming aware that he is learning anything "hard." I think it is an excellent book to learn from, and students who use it will be grateful to the writer for his great care to make it comprehensible in every respect.

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Acids, Bases, and the Chemistry of the Covalent Bond. BY CALVIN A. VANDERWERF, Professor of Chemistry and Chairman of the Department, University of Kansas. Reinhold Publishing Corporation, 430 Park Avenue, New York 22, N. Y. 1961. ix + 117 pp. 12.5 × 18.5 cm. Price, \$1.95.

This book is one of the first two titles to appear in the publisher's series "Selected Topics in Modern Chemistry." The stated main purpose of both this volume and the series as a whole is to serve as supplementary material for the first-year college chemistry course.

The present volume is devoted to the chemistry of ionic reactions at the covalent bond. The treatment begins with Brønsted-Lowry acid-base theory, continues with Lewis theory, and concludes with base displacement and acid displacement and addition reactions. These are developed successively in a logical fashion, each as an extension of the previous concept.

The book consists of six chapters, the first of which is introductory. Chapter 2 is concerned with the Brønsted-Lowry concept of acids and bases. This is the one part of the book in which the treatment is not above the level of that in the usual modern first-year college chemistry textbook. Although acidity constants are mentioned, there are essentially no examples of calculations involving them. The over-all pattern of the book does not really suffer from the lack of such calculations, but in their place is presented, without any qualifications, the idea that equilibrium in the reaction of any acid with the conjugate base of a weaker acid will lie at least 50% to the right. This concept comes to grief in even the elementary example of a very dilute aqueous solution of an acid such as acetic acid, and is likely to cause future difficulties if taken too seriously by the student. The presentation of the Brønsted-Lowry concept is done in a fashion which permits its use as a foundation for the remaining material in the book.

Chapter 3 deals with the effect of structure on relative acid and base strengths. The roles of relative electronegativity, of ion sizes and of resonance are presented in an effective manner. As seems customary in elementary treatments, the relative electronegativity concept is stretched a bit be-