

Table II. Rate Constants for the Racemization of Oxazolone I

Reagent causing racemization	Concn., <i>M</i>	$k_1 \times 10^{-2}$ min. ⁻¹	k_2 , l. mole ⁻¹ min. ⁻¹	$t_{1/2}$, min.
Pyridine	3.74	1.837 ± 0.043	0.012	2711
	4.30	2.480 ± 0.015		
	4.87	3.175 ± 0.014		
DL-Phe-OCH ₃	6.15×10^{-2}	4.438 ± 0.070	0.75	43.8
	9.23×10^{-2}	6.992 ± 0.077		
	12.3×10^{-2}	8.978 ± 0.066		
<i>p</i> -Nitro-phenylate ion	2.789×10^{-4}	1.410 ± 0.022	68.42	0.48
	5.579×10^{-4}	3.255 ± 0.012		
	8.368×10^{-4}	5.237 ± 0.031		

We prepared a more optically pure oxazolone using dicyclohexylcarbodiimide in ether to ring close the dipeptide acid; m.p. 115–119°; $[\alpha]^{25}_D -52.1^\circ$ (*c* 1.5, dioxane) (*Anal.* Calcd. for C₁₅H₁₈N₂O₄: C, 62.06; H, 6.20; N, 9.31. Found: C, 62.58; H, 6.43; N, 9.60); ν_{\max} 3260, 1823 (characteristic for oxazolone carbonyl group), 1715, 1662, 1540, 1308, 1262, 1112, 1079, and 1008 cm.⁻¹. All are intense peaks. Fractional crystallization of the optically active oxazolone II is difficult because it appears to have only a slightly lower melting point than the racemic compound.

Kinetic Studies. The rates of racemization of oxazolone I using certain nucleophiles in dioxane have already been observed. These nucleophiles were, in order of decreasing racemization rates: *p*-nitrophenylate ion, DL-phenylalanine methyl ester (DL-Phe-OCH₃), and pyridine. Second-order rate constants were calculated from three pseudo-first-order rate constants for each nucleophile. Ring-opening reactions were studied by following the disappearance of the intense oxazolone peak at 1825 cm.⁻¹. The same concentration of oxazolone, namely, 3.045×10^{-2} *M*, was used in both the racemization and ring-opening studies.

Table III. Rate Constants for Ring Opening of Oxazolone I

Reagent causing ring opening	Concn., <i>M</i>	$k_1 \times 10^{-2}$ min. ⁻¹	k_2 , l. mole ⁻¹ min. ⁻¹	$t_{1/2}$, min.
DL-Phe-OCH ₃	2.132×10^{-1}	1.443 ± 0.022	0.065	505
	3.780×10^{-1}	2.632 ± 0.044		
	7.590×10^{-1}	4.803 ± 0.072		
<i>p</i> -Nitro-phenylate ion	1.16×10^{-2}	1.984 ± 0.040	1.60	20.5
	1.74×10^{-2}	3.101 ± 0.055		
	2.32×10^{-2}	4.155 ± 0.086		

Our kinetic data support the concept that under peptide-coupling conditions a small steady-state concentration of oxazolone can form which subsequently racemizes much faster than it can ring open. Racemization depends on the concentration and basicity of the nucleophiles present in the reaction mixture. From the data in Tables II and III it can readily be shown that *p*-nitrophenylate ion can racemize the oxazolone 40 times faster than it can react with it to give ring-opened product. A weaker nucleophile such as DL-Phe-OCH₃ causes racemization to occur 11 times faster than ring opening.

In the course of our efforts to synthesize these oxazolones we uncovered some interesting chemistry in connection with the coupling of hindered peptides. We intend to publish a detailed account of these reactions together with complete results from kinetic studies on the racemization of peptide oxazolones in the near future.

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Book Reviews

Energetics of Propellant Chemistry. By BERNARD SIEGEL, Head, High Temperature Chemistry Section, and LEROY SCHIELER, Head, Chemical Propulsion Dept., Aerospace Corporation, Los Angeles, Calif. John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1964. xiii + 240 pp. 15.5 × 23.5 cm. \$10.00.

"The Energetics of Propellant Chemistry" is stated by the authors to be an introduction to propellant chemistry for chemists or advanced chemistry students. This is an appropriate description of the level of difficulty of the contents. References throughout the book to "the student" indicate that the author had use as a textbook in mind. For this purpose the instructor would be forced to provide his own problem assignments as there are no exercises given. However, there are in the appendices and in Chapter 5 fairly extensive tables of data suitable for calculating specific impulse and rocket engine performance, with suggestions for using them.

The function of a propellant is to power a rocket. This function is in the background of the discussion of particular substances or classes of substances throughout the book, and the discussion of every topic turns ultimately to its relationship to specific impulse or

other rocket performance parameter. Nevertheless the book is not primarily a propellant engineer's textbook or handbook. It is primarily a book of physical chemistry limited in scope to the gross measurable properties (thermodynamics) and the theoretical molecular interpretation of these properties (principally in terms of binding energies) of a selected group of elements of low atomic weight and their compounds. A background equivalent at least to a good course in physical chemistry will be necessary for the reader to follow the arguments readily.

The main body of the book is a detailed analysis of binding energies and other molecular properties that lead to desirable propellants. Beginning with Chapter 2, the authors deal with energies of formation of combustion products, the energetics of working fluid gases, and the binding energies of fuels and oxidizers, to each of which a chapter is devoted. The final chapter of text is a discussion of real propellant systems. The customary limitation to elements of low atomic weight is strictly adhered to. All the reactive elements up to and including potassium are considered. In the discussion of products, the major emphasis is on oxides, fluorides, and hydrogen compounds. Bond types of typical molecules are discussed and a rationale for comparative strengths of bonds

is presented. These same substances are then treated as working fluid gases, and a survey of the dissociation equilibria that occur in them at various elevated temperatures is presented. Among the reactants treated separately are hydrides and organic fuels, peroxides, oxyfluorides, oxychlorides, fluoramines, and nitro compounds. Various combinations of these, together with polymeric binding materials, hydrogen, oxygen, fluorine, and several metals are taken up in the real propellant systems.

These four chapters provide a very good survey of current propellant chemistry. The authors are knowledgeable and full of enthusiasm. They present their material in the easy colloquial style of successful practitioners of the art they are describing. They are fully aware of both standard formulations and unproved but promising propellant candidates. What their presentation may lack in precision of statement, it more than makes up in the drive and enthusiasm with which it is written. A picture of the factors that must be taken into account and of the current mode of thinking about them emerges which fairly represents the complicated, unsettled, and highly competitive field of propellant chemistry.

The authors have decided to treat products and ingredients separately, and certainly a case can be made for this approach in terms of the different energetic attributes, molecular weight requirements, and phase stabilities desirable in the two categories. Nevertheless they repeatedly acknowledge the fact that products cannot be treated as completely independent of the reactants because the same elements must be present in each, and because the energy change that occurs is more important than are the high energy level of reactants or the low energy level of products separately. The BN concept, to which they are partial, is a typical case in which they find such cross connection necessary.

The opening chapter of the book is on the calculation of propellant performance, and gives a brief introduction to rocket propulsion parameters. The relationships of the thermal parameters, temperature, pressure, heat capacity, and heat of reaction, to the performance parameters, thrust, specific impulse, exhaust velocity, and weight are given in this chapter. A brief outline of general methods of calculating combustion-product temperature and composition is also given here.

This chapter is the least polished of the book and gives evidences of lack of editorial care in proofreading and lack of attention to detail in the formulation of equations and the structure of sentences. Examples, which probably would cause no difficulty for the student in the class of a competent instructor, but might somewhat frustrate a person working through the text alone, are the lack of dimensional balance of equation 1-1, and the units applied to the mechanical equivalent of heat, J , used throughout Chapter 1. This type of loose construction has the unfortunate effect of making the reader skeptical about the validity of these and hence of other constructions which are not readily understood on first reading. A sentence such as the following from the top of page 24 is enough to cause the uninitiated to ponder for some time: "Additionally it can be seen the presence of condensed phases is undesirable since the enthalpies of condensed phases are generally higher than for the ideal gas as well as lowering the average molecular weight of the working fluid." Here we have an unfortunate editorial error in the use of *lowering* when *raising* is intended, and a statement about enthalpy that can only be true if enthalpy of vaporization is ignored. These are by no means all of the examples of poor construction that could be listed in the first chapter, in addition to which numerous typographical errors are present.

The reviewer was somewhat misled by the discussion leading up to equations 1-39 to 1-46, in which specific impulse and exhaust velocity are related to molecular weight, temperature, and pressure in terms of an adiabatic coefficient γ . In the discussion phrases such as, "approximate equations," "outdated computation concepts," "lead to erroneous conclusions when improperly applied," are used. The reviewer was then somewhat surprised to discover that these equations which had been so disparaged were the only bases referred to throughout the remainder of the text for the part played by molecular weight and temperature of the combustion gases.

The book is replete with tables and diagrams, which comprise about 40% of the book's 240 pages and add considerably to its interest. The diagrams illustrate comparative thermodynamic information for particular substances in several classes of combustion product gases, and equilibrium dissociation behavior of selected gaseous product species as functions of temperature. Of interest in the chapter on real propellant systems are extensive tables of the compositions of combustion product gases for various oxidizer-propellant combinations.

A list of symbols and their units of measurement is included and is essential because few symbols are defined in the text. The units of measurement listed illustrate a dilemma of the propellant chemist, who is pulled on the one hand by the prevalence in the chemical literature of thermodynamic data, heats of formation, binding energies, and so on, given in the c.g.s. system, and on the other hand by the propulsion engineer who demands his parameters in English units. Thus, we find densities in g. cc.⁻¹, and mass of propellant in lb.; energies in kcal. mole⁻¹, and velocities in ft. sec.⁻¹. Perhaps the most curious use of units in the table is erg cal.⁻¹ for the mechanical equivalent of heat. These units are quite irreconcilable with the usage of J in equations throughout Chapter 1.

Despite the shortcomings of the first chapter, on the whole the book is to be recommended. The chemist entering the field of propellant chemistry or wishing to increase his awareness of it will find it a worthwhile introduction to the subject. It will give him the principal commonly used or seriously considered major propellant components, factors (aside from kinetics) that must be taken into account in considering potential propellant ingredients, qualitative discussions of how these factors apply to particular components, and qualitative theoretical consideration of the properties of these compounds in terms of molecular binding concepts. It will also provide him with some tables of thermodynamic data and instructions in their use for the illustrative calculation of equilibrium compositions and propellant performance characteristics. The book is not a definitive study of the best methods of calculating these parameters, nor should it be considered a replacement for the massive and reliable tables of thermal properties which now exist in the field of propellant engineering and chemistry.

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Positronium Chemistry. By JAMES GREEN, The University of New South Wales, Sydney, Australia, and JOHN LEE, New England Institute for Medical Research, Ridgefield, Conn. Academic Press Inc., 111 Fifth Ave., New York, N. Y. 1964. xii + 105 pp. 16 × 24 cm. \$5.50.

A great many fundamental and extremely interesting problems in chemical structure and the nature of chemical reactions are not amenable to study with conventional chemical techniques. The subtle problems involving the electronic structure of molecules, the nature of atomic wave functions, electron-transfer mechanisms, etc., require a knowledge of several disciplines and probes of high resolution for their elucidation. When such a probe is discovered, and its potential realized, a rash of new activity in the field is to be expected. Such discoveries as electron and nuclear magnetic resonance, the hydrated electron, and the Mössbauer effect are obvious examples.

Too often, however, the literature in which such discoveries and the progress in the development of the techniques are reported is not regularly read by scientists who could apply them in their own areas of research. Moreover, experimental difficulties and the lack of an adequate background in physics and electronics may dampen the enthusiasm some chemists and biologists might otherwise express.

Positronium, the transient bound system of a positron and an electron, may be considered an isotope of hydrogen. It has essentially half the reduced mass of the normal hydrogen atom and hence, twice the Bohr radius and half the ionization potential. It was discovered by physicists through observation of the longer annihilation lifetime of the triplet state. The rate of conversion of triplet to singlet states ("quenching") gives information on the chemical nature of the medium in which positronium is formed.

The authors of "Positronium Chemistry" are to be commended for supplying a well-organized, very readable account of the present status of a potentially important chemical species and for choosing a title that will attract the nonphysicist.

After a very brief, but clear and adequate description of the basic physics of the positron and the bound states of positronium, the authors describe the experimental techniques involved in making measurements with positronium. Block diagrams and a few electronic circuits are presented, but the descriptions of the coincidence counting technique and the functions of the various components are so simply and clearly described as to be intelligible even to a novice in the use of such equipment. (As the authors point out in the Pref-