

switching from E_c to anodic potentials, but shows a double or multipeaked pulse on switching back to E_c . Addition of up to 5% water to the DMF had no effect on the chemiluminescence. When tetra-*n*-butylammonium bromide (TBAB) is used as supporting electrolyte, luminescence is observed with the platinum electrode at potentials more positive than 0.9 v., but not with the mercury electrode, which oxidizes at considerably more negative potentials (*ca.* -1.0 v.). No luminescence is observed with tetra-*n*-butylammonium iodide as supporting electrolyte with either platinum or mercury (anodic limits of 0.1 and -0.4 v., respectively).

The results suggest that the chemiluminescence occurs only during the chemical reaction of the anion radical and an oxidant generated anodically and not during the direct electrooxidation of DPA^- . In TBAP solutions the oxidants are probably perchlorate radical or an oxidant derived from it at platinum, and mercury(II) at mercury. In TBAB solutions bromine is probably the oxidant. Since the potentials at which these ox-

dants are generated are sufficiently positive to allow DPA^- to be oxidized directly at the electrode, the reaction must occur some distance from the electrode surface and involve DPA^- diffusing toward the electrode and oxidant diffusing away from it. The results indicate that neither mercury salts of bromide or iodide nor iodine produce chemiluminescence in any reaction with DPA^- . One might question why the direct oxidation of DPA^- at the electrode, at potentials sufficiently positive to cause formation of DPA^* when produced by an electrogenerated oxidant, does not produce luminescence. Perhaps DPA species formed at the electrode surface rapidly dissipate any excess energy to the electrode. These chemiluminescent reactions, as well as those of other compounds, during electrolysis, is currently being investigated.

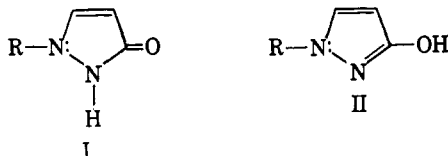
K. S. V. Santhanam, Allen J. Bard
 Department of Chemistry
 The University of Texas, Austin, Texas
 Received November 16, 1964

Book Reviews

The Chemistry of Heterocyclic Compounds. Pyrazolones, Pyrazolidones, and Derivatives. By RICHARD H. WILEY, University of Louisville, Louisville, Ky., and PAUL WILEY, Upjohn Laboratories, Kalamazoo, Mich. John Wiley and Sons, Inc., 605 Third Ave., New York 16, N. Y. 1964. xv + 539 pp. 16 × 23.5 cm. Price, \$26.00.

This volume is the twentieth in the series "The Chemistry of Heterocyclic Compounds" edited by Arnold Weissberger. It is divided into three main parts. Part I (142 pp.) deals with the chemistry of pyrazolinones and pyrazolidinones and their nitrogen and sulfur analogs. Part II (19 pp.) deals with uses of these compounds as medicinal agents, in color photography, as dyes, and as analytical reagents. The third part (322 pp.) is an appendix made up of tables listing the various pyrazolinones and pyrazolidinones which have been reported in the chemical literature.

This book might be of value to some as a rather complete compilation of the pyrazolinones and pyrazolidinones which have been reported in the literature up to 1956. With the exception of this prominent virtue, however, there seems to be little else about which one can comment very favorably. It is admitted that the great volume of literature must have posed a challenge to the authors. Yet it appears that they have largely avoided the greater challenges of critical comment and evaluation of data from the vantage point of current theory, which could have given rise to a really valuable treatise. Typical examples (many could be cited) illustrating this deficiency are: (1) classification of two canonical forms of 3-pyrazolin-5-one as "ionic tautomers" of 5-pyrazolinone (p. 63); (2) absence of discussion of factors known to affect orientation of alkylation (p. 22); and (3) rationalization of acidity of 3-pyrazolin-5-ones unsubstituted at N-1 (I) in terms of tautomerism to II (p. 49), when in actuality the same anion is obtained on removal of a proton from



either, and it is really the relative stability of this anion which is responsible for the observed acidity.

There is a substantial amount of repetition (*e.g.*, the discussion of ultraviolet spectra of 5-pyrazolinones on pp. 6, 10, and 19), yet

the regrettable practice of using numbers in place of structural formulas in depicting reactions, presumably in the interest of saving space, is commonplace. This practice is particularly annoying when one must scan back over several pages to locate the structure to which reference is being made.

Allusion is made to numerous reactions in the text of discussion (some of which, in the reviewer's opinion, were among the most interesting in the book), but depiction in terms of structures is lacking. Space considerations may have been the justification for this, but it seems to the reviewer that in a book of 500 pages, the inclusion of an additional 20 pages of text (added to the present total of 161 pages) would be justified in view of the great increase in readability to be gained.

One also wonders why an archaic style of printing and structural formulas were used in this volume when several of the preceding volumes in this series have print and formulas which are substantially easier to read.

Typographical errors and errors in formulas are relatively rare, but not absent. A check of 30 references randomly taken from the tables in the appendix revealed no discrepancies.

Richard C. Anderson
 Utah State University
 Logan, Utah

X-Ray Diffraction in Crystals, Imperfect Crystals, and Amorphous Bodies. By A. GUINIER, University of Paris. W. H. Freeman and Co., 660 Market St., San Francisco 4, Calif. 1963. x + 378 pp. 16 × 24.5 cm. Price, \$11.00.

Since the discovery and development of X-ray diffraction 50 years ago, the crystal structure problem has dominated research in this field. The basic physics of the interaction of X-rays with solids was fairly well understood by 1920, and a new breed of scientist, the X-ray crystallographer, recruited from the ranks of physics, chemistry, mineralogy, and somewhat later, metallurgy, began the accumulation of the great volume of structure determinations which remains today perhaps our most important deposit of knowledge of the nature of solids.

About 30 years ago a few crystallographers began to turn their attention to materials not perfectly periodic. Glasses and liquids were studied first, and the famous Guinier-Preston zones associated with age-hardened alloys were discovered. By 1950 the study