

The preparation of pentamethoxyphosphorane and II by the phosphite-dialkyl peroxide route indicates its generality.<sup>9</sup> The physical properties are in accord with those predicted. The chemical reactions illustrate their sensitivity toward acids and suggest possible applications as low-temperature alkylating agents.<sup>10</sup> Extensions of these studies are now in progress.

**Acknowledgment.** We wish to thank Dr. John R. Van Wazer and the Monsanto Company for their determination of the P<sup>31</sup> n.m.r. spectrum.

(9) In this connection it should be noted that no difficulty has been experienced in preparing diethyl peroxide whereas two violent explosions have taken place during the work with dimethyl peroxide.

(10) V. A. Kukhtin and K. M. Orekhova [*Zh. Obshch. Khim.*, **29**, 1687 (1959)] have reported that the 1:1 adduct of biacetyl and triethyl phosphite reacts with acetic acid to give ethyl acetate in 60% yield.

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Received October 8, 1964

### Chemiluminescence of Electrogenerated 9,10-Diphenylanthracene Anion Radical<sup>1</sup>

Sir:

Hercules has discussed possible mechanisms for the chemiluminescence of electrogenerated species based on qualitative electrochemical experiments with a platinum electrode in deoxygenated nonaqueous solvents.<sup>2</sup> Chandross and Sonntag have recently shown that chemiluminescence occurs when 9,10-diphenylanthracene anion radical (DPA<sup>-</sup>) is treated with the 9,10-dichloride of DPA or a variety of oxidizing agents.<sup>3</sup> They proposed that oxidation of DPA<sup>-</sup> produces DPA in an excited state (DPA\*) which emits light in returning to the ground state. These results suggest two possible mechanisms for the chemiluminescent reaction occurring during electrolysis of aromatic hydrocarbons. The radical anion R<sup>-</sup> formed at the cathode is oxidized directly to an excited state R\* at the anode surface, or an oxidant is produced at the anode which reacts with R<sup>-</sup> to form R\*. Either of these mechanisms could occur depending upon the potential of the anode.

To elucidate the mechanism of the chemiluminescent process during electrolysis, the electrochemistry of DPA in deoxygenated dimethylformamide (DMF) solutions of several supporting electrolytes at a hanging mercury drop and a platinum wire electrode was investigated. Typical results of cyclic voltammetric experiments of a 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) solution in the presence and absence of DPA are shown in Figure 1. At mercury the reduction of DPA to DPA<sup>-</sup> and DPA<sup>-2</sup> occurs well before discharge of the supporting electrolyte and follows the usual mode of electroreduction of aromatic hydrocarbons in aprotic solvents.<sup>4</sup> At a platinum electrode only the wave for the reduction to DPA<sup>-</sup> occurs before the final current rise. With both electrodes no separate wave for the oxidation of DPA is observed. The luminescence

(1) This research was supported by the Robert A. Welch Foundation.

(2) D. M. Hercules, *Science*, **145**, 808 (1964).

(3) E. A. Chandross and F. I. Sonntag, *J. Am. Chem. Soc.*, **86**, 3179 (1964).

(4) "Advances in Polarography," I. S. Longmuir, Ed., Pergamon Press, New York N. Y., 1960: (a) P. H. Given and M. E. Peover, p. 948; (b) A. C. Aten and G. J. Hoijtink, p. 777, and references contained therein.

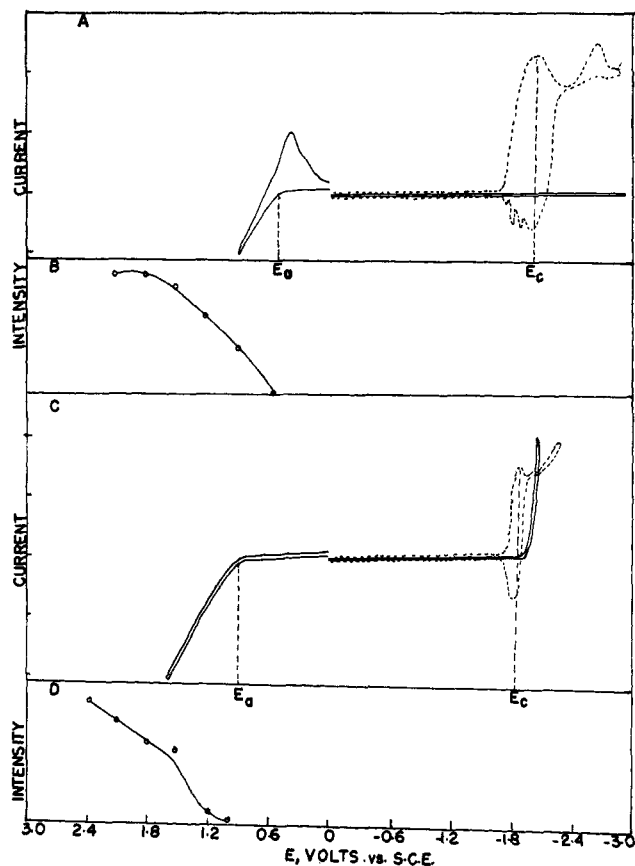


Figure 1. Cyclic voltammetric curves and light emission during electrolysis of 9,10-diphenylanthracene. A and C: the dimethylformamide solutions were 0.1 M in tetra-*n*-butylammonium perchlorate, without (solid lines) and with (dashed lines) 3 mM DPA at hanging mercury drop (A) or platinum wire electrode (C). B and D: light emission upon holding electrode potential at  $E_c$  for 1–2 sec. and then switching to various positive potentials, using hanging mercury drop (B) or platinum wire electrode (D).

reaction was studied by holding the potential of the working electrode at a potential,  $E_c$ , where reduction to DPA<sup>-</sup> occurs, for several seconds, and then switching the potential to various more positive values and observing the occurrence and intensity of light emission. The potentials were controlled with an electronic potentiostat; a platinum auxiliary electrode in a separate chamber and an aqueous saturated calomel electrode (s.c.e.) were used. Emitted light was measured using a Dumont 6467 photomultiplier tube with an output to either a sensitive galvanometer (0.003  $\mu$ a./mm.) or an oscilloscope.<sup>5</sup> Typical results are shown in Figure 1. No emission results until the potential of the working electrode is switched to a threshold potential,  $E_a$ , at which oxidation of the supporting electrolyte or electrode occurs, 0.51 v. vs. s.c.e. with the mercury electrode and 1.00 v. with the platinum electrode in TBAP. Beyond  $E_a$  the intensity of the emitted light increases with increasing potential. Upon switching back to  $E_c$ , light emission is again observed, as Hercules reported.<sup>2</sup> The light emission, when observed on an oscilloscope, is in the form of a single sharp pulse on

(5) (a) The technique of monitoring emitted light during electrolysis has been described by T. Kuwana, B. Epstein, and E. Seo, *J. Phys. Chem.*, **67**, 2243 (1963); *J. Electroanal. Chem.*, **6**, 164 (1963). (b) We are indebted to Professor W. C. Gardiner for assistance in the design of these experiments.

switching from  $E_c$  to anodic potentials, but shows a double or multi-peaked 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.

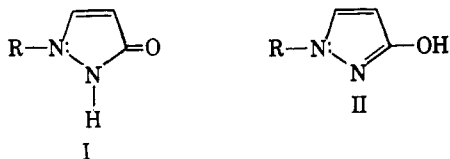
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 Received November 16, 1964

## 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.

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**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