

that the exchange can be slowed down at such a high temperature suggests that structure **5** is of somewhat higher energy than **4**. In the pheophorbide series, where ring V is closed, the distortions⁹ introduced into the system prevent intramolecular hydrogen bonding and two distinct N-H absorptions are always observed.¹⁰

Webb and Fleischer¹¹ suggested recently that the best description of the aromatic ring current in a porphyrin is one having a 16-membered inner ring, with the four β -pyrrole positions equivalent isolated double bonds. The electronic structure is usually represented as an 18-membered cyclic polyene with two of the β -pyrrole positions isolated from the aromatic system. Our results support the older structure having two distinct types of β -pyrrole positions. The lower field of these at δ 8.90 is the one normally assigned to the aromatic system..

Acknowledgments. We thank E. Sokoloski of the National Institutes of Health for the 100-MHz pmr spectra and the Petroleum Research Fund, administered by the American Chemical Society, and the National Institute of General Medical Sciences for financial support.

(9) R. C. Petersen, *Acta Crystallogr., Sect. B*, **25**, 2527 (1969).

(10) J. J. Katz, R. C. Dougherty, and L. J. Boucher in "The Chlorophylls," L. P. Vernon and G. R. Seely, Ed., Academic Press, New York, N. Y., 1966, p 224.

(11) L. E. Webb and E. B. Fleischer, *J. Amer. Chem. Soc.*, **87**, 667 (1965).

C. B. Storm,* Y. Teklu

Department of Chemistry, Howard University
Washington, D. C. 20001

Received November 1, 1971

Is the Concerted "Ene" Mechanism of the $^1\Delta_g$ Excited Oxygen Molecule Reactions with Olefins Really Eliminated? Photooxygenation and Electrolysis in the Presence of Azide Ions¹

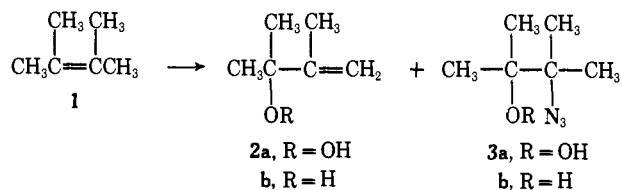
Sir:

Agreement exists that the mechanism of $^1\Delta_g$ O₂ reactions with cyclic 1,3-dienes is a concerted 1,4 addition of singlet oxygen to give endoperoxides.²

(1) Results presented in part at the EUCHEM Conference on Radiationless Processes in Photochemistry, Fortmeirion, N. Wales, United Kingdom, April 15-22, 1971.

However, no such agreement exists with regard to the mechanism of $^1\Delta_g$ O₂ reactions with olefins that lead to allylic hydroperoxides. A cyclic cis process was established by stereochemical studies³ and a large body of evidence has led to the suggestion that the cyclic process is concerted.^{2a,c,4-9} In contrast, a two-step mechanism that involves formation of a dioxetane or perepoxide intermediate was postulated by Kearns, *et al.*,^{10,11} from the fact that photooxygenation of olefins in the presence of azide ions gave the saturated azido hydroperoxides along with allylic hydroperoxides. They concluded that "these results completely rule out the concerted "ene" mechanism as a route to allylic hydroperoxides."^{10,11} We have studied dye-sensitized photooxygenations of 2,3-dimethyl-2-butene (**1**) and α -terpinene (**6**) in the presence of sodium azide, as well as the electrolysis of NaN₃ in oxygen-saturated methanolic and aqueous methanolic solutions in the presence of **1** and **6**. Our results show that the interpretation by Kearns, *et al.*,^{10,11} is not warranted.

Irradiation of 1.43 g of **1** in 170 ml of oxygen-saturated methanol, aqueous methanol, or water in the presence of Rose Bengal as described earlier^{2b,5,6} gives the allylic hydroperoxide **2a** at rates (r_{O_2}) that decrease with increasing water content of the solvent. In the presence of N₃⁻, the rates of oxygen consumption (r_{O_2}) decrease with increasing N₃⁻ concentration up to about 0.1 M N₃⁻ (Figure 1). The irradiated solutions were reduced with aqueous sodium sulfite and the alcohols **2b** and **3b** were assayed and isolated by



gas chromatography.¹² The production of the azido compound in methanol and in aqueous methanol begins at relatively high N₃⁻ concentrations where quenching of the oxygen uptake rate is already very appreciable (Figure 1). These results indicate that at least two different intermediates are involved that react with N₃⁻. Furthermore, with increasing water content of the solvent, the amount of the azido alcohol **3b** that

(2) (a) K. Gollnick, *Advan. Photochem.*, **6**, 1 (1968); (b) K. Gollnick and G. O. Schenck in "1,4-Cycloaddition Reactions; The Diels-Alder Reaction in Heterocyclic Syntheses," J. Hamer, Ed., Academic Press, New York, N. Y., 1967, Chapter 10, p 255; (c) C. S. Foote, *Accounts Chem. Res.*, **1**, 104 (1968); (d) A. U. Khan and D. R. Kearns, *Advan. Chem. Ser.*, No. 77, 143 (1968).

(3) A. Nickon and J. F. Bagli, *J. Amer. Chem. Soc.*, **81**, 6330 (1959); **83**, 1498 (1961).

(4) K. Gollnick, *Advan. Chem. Ser.*, No. 77, 78 (1968).

(5) K. Gollnick and G. O. Schenck, *Pure Appl. Chem.*, **9**, 507 (1964), and references cited therein.

(6) K. Gollnick, T. Franken, G. Schade, and G. Dörhöfer, *Ann. N. Y. Acad. Sci.*, **171**, 89 (1970).

(7) R. Higgins, C. S. Foote, and H. Cheng, *Advan. Chem. Ser.*, No. 77, 102 (1968).

(8) C. S. Foote, R. W. Denny, L. Weaver, Y. Chang, and J. Peters, *Ann. N. Y. Acad. Sci.*, **171**, 139 (1970).

(9) F. A. Litt and A. Nickon, *Advan. Chem. Ser.*, No. 77, 118 (1968).

(10) W. Fenical, D. R. Kearns, and P. Radlick, *J. Amer. Chem. Soc.*, **91**, 3396, 7771 (1969).

(11) D. R. Kearns, W. Fenical, and P. Radlick, *Ann. N. Y. Acad. Sci.*, **171**, 34 (1970).

(12) Physical data and spectra of **2b** and **3b** agree very well with those reported.^{10,13}

(13) G. O. Schenck and K. H. Schulte-Elte, *Justus Liebig's Ann. Chem.*, **618**, 185 (1958).

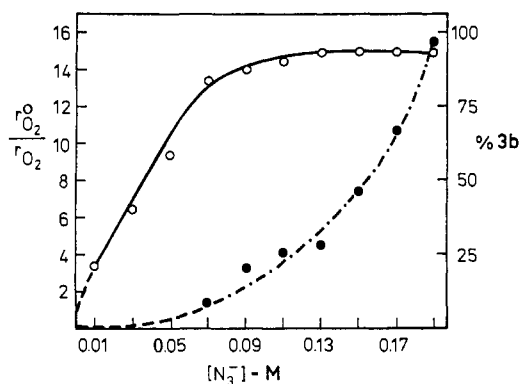
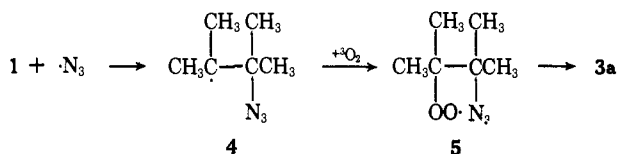


Figure 1. Ratio of rates of oxygen consumption by 1 in the absence ($r_{O_2}^0$) and presence of N_3^- (r_{O_2}) as a function of $[N_3^-]$, and percentage of azido alcohol 3b formation as a function of $[N_3^-]$ in 40% aqueous methanol: \circ — \circ , $r_{O_2}^0/r_{O_2}$ as $f([N_3^-])$; \bullet — \bullet , % 3b as $f([N_3^-])$.

could be isolated without reduction with sodium sulfite increased. Reaction of hydroperoxide 2a with 1 to give 2b and the epoxide of 1, which subsequently reacts with N_3^- to 3b, is excluded since no 2b was found at high N_3^- concentrations. In control experiments 3a and 3b were not formed from 2a or 2b, respectively, when treated with N_3^- .

Electrolysis (2.6 V, 50 mA) of 2 g of NaN_3 for 17 hr in 200 ml of oxygen-saturated methanol or aqueous methanol in the presence of 7 g of 1 yielded about 500 mg of 3b and some polymeric material. So far, we have not isolated the azido hydroperoxide 3a. However, that the oxygen in the azido alcohol stems from O_2 rather than from the solvent is concluded from the fact that in nitrogen-saturated solutions only 2,3-diazido-2,3-dimethylbutane¹⁴ and some unidentified compounds were formed, but no 3b.¹⁵

Thus, formation of 3b occurs by addition of N_3 radicals to 1 to give 4, which adds 3O_2 to give 5, which



in turn abstracts hydrogen to form 3a. By some unknown reduction reaction, 3a is transformed to 3b, as is the case in the photooxygenation reaction.¹⁶

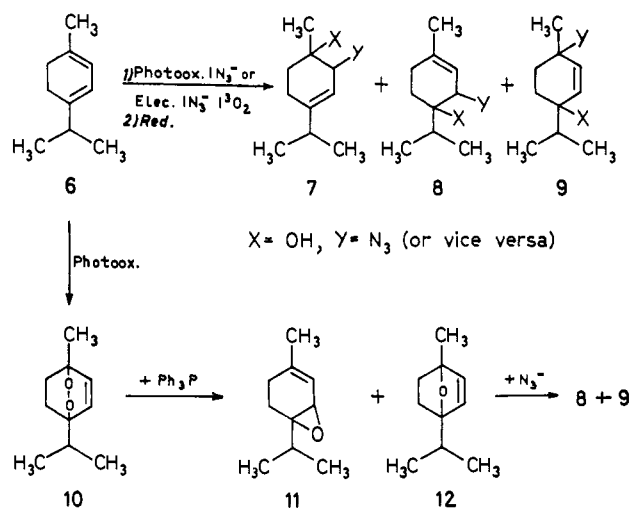
These results support our view that in photooxygenation reactions in the presence of azide ions, azido radicals are formed that can produce azido hydroperoxides. To check this assumption further, α -terpinene (6) was photooxygenated as well as subjected to electrolytic treatment under similar conditions.

In the absence of NaN_3 , 6 was photooxygenated to ascaridole (10).^{2b} In the presence of NaN_3 , however, a mixture was obtained that contained azido alcohols 7, 8, and 9. According to gas chromatography,

(14) Satisfactory elemental analysis for the diazide was obtained: nmr one sharp singlet at τ 8.72 ($CDCl_3$).

(15) For studies on the electrolytic formation of N_3 radicals and on their reactions with olefins, see: H. Schäfer, *Angew. Chem.*, **81**, 940 (1969); **82**, 134 (1970), and references cited therein.

(16) In the meantime, using 2a as a model compound, we found that organic hydroperoxides slowly react with N_3^- in aqueous methanolic solutions to give the corresponding alcohols and some molecular nitrogen.



elemental analysis, and ir and nmr spectra, the same mixture was formed during electrolysis of N_3^- in the presence of 6 and 3O_2 .¹⁷ Ascaridole (10) did not react with NaN_3 under the experimental conditions.¹⁸

From these results it seems unlikely that in photooxygenation of monoolefins in the presence of N_3^- azido products are formed by interception of dioxetane or peroxide intermediates.^{10,11} In our opinion, the results are compatible with the assumption that in photooxygenation reactions, interaction between N_3^- and one intermediate (presumably the triplet excited sensitizer) gives rise to a decrease of the oxygen uptake rate, whereas the interaction between N_3^- with another intermediate (presumably singlet oxygen) results in electron transfer producing N_3 radicals that ultimately yield the azido compounds. The proposed refutation of the "ene" mechanism as a route to allylic hydroperoxides in $^1\Delta_g O_2$ reactions with olefins is thus rendered doubtful.

Acknowledgments. We are grateful to the Deutsche Forschungsgemeinschaft and to the Fonds der deutschen Industrie who supported our work done at Munich.

(17) Satisfactory elemental analysis ($C_{10}H_{17}N_3O$) for the isomeric mixture was obtained, although we have not yet separated the components. Analysis of the nmr spectra of the mixtures, aided by europium shift reagents, showed that 7, 8, and 9 are present in a ratio of about 38:17:25.

(18) By reduction of 10 with triphenylphosphine to a mixture of oxides 11 and 12 (identified by elemental analysis and nmr spectra) followed by treatment with N_3^- , we were able to obtain 8 and 9 in a ratio of about 1:1.

(19) University of Munich.

(20) Max-Planck-Institut at Mülheim-Ruhr.

Klaus Gollnick,^{*19,20} Dieter Haisch,¹⁹ Gerhard Schade²⁰

Organisch-Chemisches Institut der Universität München
Munich 2, Germany

Max-Planck-Institut für Kohlenforschung
Abteilung Strahlenchemie
Mülheim-Ruhr, Germany

Received August 30, 1971

Fractional Three-Center Bonds in Carboranes

Sir:

The objective Edmiston-Ruedenberg procedure^{1,2} for obtaining localized orbitals from accurate self-consis-

(1) C. Edmiston and K. Ruedenberg, *Rev. Mod. Phys.*, **35**, 467 (1963).

(2) E. Switkes, R. M. Stevens, W. N. Lipscomb, and M. D. Newton, *J. Chem. Phys.*, **51**, 2085 (1969).