its progenitors was further confirmed by thin layer chromatography and by the appearance of a blue color with Ehrlich's reagent within a few minutes of dissolution of the adduct.[11] It was possible to obtain uv and ir data for **6** and these support the Diels–Alder structure.

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(11) In contrast, isoindole **2** reacts at once with Ehrlich's reagent. (Compound **2** also gives an immediate deep violet color in the pine splint test.)

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Received June 20, 1969

The Catalytic Fixation of Molecular Nitrogen by Electrolytic and Chemical Reduction

Sir:

For some years this laboratory has been investigating the chemical modification of molecular nitrogen under mild conditions, by means of experiments based on the concept of titanium(II) as the fixing species.[1-5] We now wish to report the innovation of an electrochemical system in which titanium *catalytically* effects reduction of nitrogen to the ammonia level.

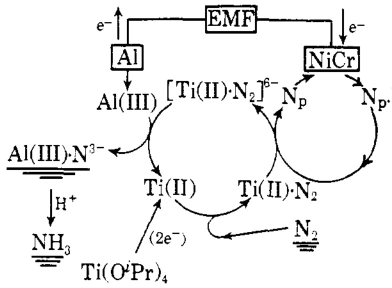
In the most successful experimental variation,[6] the electrolysis cell was fitted with an aluminum anode and a nichrome cathode, and contained a 60-ml 1,2-dimethoxyethane (glyme) solution of 1.68 mmol of titanium tetraisopropoxide, 7.6 mmol of naphthalene, 8.6 mmol of tetrabutylammonium chloride, and 42 mmol of aluminum isopropoxide. The solution, while being stirred under a slow stream of pure nitrogen, was electrolyzed at 40 V until the conductance of the cell had greatly diminished (11 days); during this time 0.155 faradays had passed through the cell and 15.1 mmol of aluminum had been lost from the anode. When the solution was treated with 40 ml of 8 *M* aqueous sodium hydroxide solution and heated in a water bath, the product ammonia (10.2 mmol, 610% yield, based on NH_3:Ti molar ratio) could be blown into an aqueous hydrochloric acid trap by a stream of gas.

When titanium tetraisopropoxide was omitted or when argon was substituted for nitrogen, no ammonia could be detected. In the absence of naphthalene, ammonia was formed, but in decreased yield. Apparently, the naphthalene functions primarily as an electron carrier, being reduced to naphthalide by the cathode and oxidized back to naphthalene by titanium–nitrogen species. Indications of the presence of naphthalide are: (1) attack of the Teflon-coated stirring bar (a property of sodium naphthalide and some other strong reducing agents) only when naphthalene is included, and (2) when the titanium tetraisopropoxide is omitted, generation of a dark greenish brown substance (sodium naphthalide in glyme is an intense brownish green) at the cathode.[7] It should be noted that naphthalide does not react with aluminum isopropoxide in glyme, as determined in a separate series of experiments.

We conjecture that the aluminum isopropoxide, in addition to serving as an electrolyte, frees the lower valent titanium compound of reduced nitrogen so that it can fix more molecular nitrogen.[8] In keeping with this hypothesis is the observation that, in a single cycle, the chemical fixation–reduction of nitrogen becomes catalytic with respect to titanium (275% NH_3) when aluminum isopropoxide is included in the previously reported[2,3] reaction of sodium metal with a glyme solution of naphthalene and titanium tetraisopropoxide.

Our observations to date are consistent with the reaction sequences diagrammed in Chart I. The electrolytic reduction of nitrogen and aspects of related titanium–aluminum systems are under continuing investigation at this time.

Chart I[a]



[a] Lower valent titanium may be monomeric or polymeric.

Acknowledgment. Financial support was provided by the National Institutes of Health (Grant GM 13797).

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(1) E. E. van Tamelen and M. A. Schwartz, *J. Am. Chem. Soc.*, **87**, 3277 (1965).

(2) E. E. van Tamelen, G. Boche, S. W. Ela, and R. B. Fechter, *ibid.*, **89**, 5707 (1967).

(3) E. E. van Tamelen, G. Boche, and R. Greeley, *ibid.*, **90**, 1677 (1968).

(4) E. E. van Tamelen and B. Åkermark, *ibid.*, **90**, 4492 (1968).

(5) E. E. van Tamelen, R. B. Fechter, S. W. Schneller, G. Boche, R. H. Greeley, and B. Åkermark, *ibid.*, **91**, 1551 (1969).

(6) Yields varied between 257 and 610%.

(7) Apparently the naphthalide is oxidized by tetrabutylammonium ion in the absence of titanium tetraisopropoxide and not by the anode since the dissolution of aluminum accounts for 99% of the electrons recovered from the anode. Tributylamine can be recovered from the reaction mixture after work-up (82%). However, it is clear that the tetrabutylammonium chloride is being slowly consumed in some way, since the conductivity of an electrolysis solution after prolonged electrolysis is a fraction of its initial value and can be restored by addition of more tetrabutylammonium chloride. When sodium naphthalide is allowed to react with tetrabutylammonium chloride under a stream of nitrogen, tributylamine is found in the reaction flask and 1,2-dibromobutane is found in a dilute bromine solution through which the effluent gas is passed.

(8) *Cf.* M. E. Vol'pin, M. A. Ilatovskaya, L. V. Kosyakova, and V. B. Shur, *Chem. Commun.*, 1074 (1968).

(9) National Institutes of Health Postdoctoral Fellow, 1969–.

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Received July 19, 1969

Photochemistry without Light

Sir:

We wish to report a general method for achieving "photochemistry without light."[1] The principle in-

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(1) This expression has been used previously in a specific case where it was suggested that a common intermediate might have been involved in a photochemical and a nonphotochemical reaction: H. E. Zimmerman, D. S. Crumrine, D. Döpp, and P. S. Huyffer, *J. Amer. Chem. Soc.*, **91**, 434 (1969).

volved is the use of singlet and triplet excited states generated in chemical reactions.

Chemiluminescence is a phenomenon in which chemical energy is converted into electronic excitation energy.[2] Normally, the excited intermediate or prod-

$$B + C \longrightarrow D^*$$

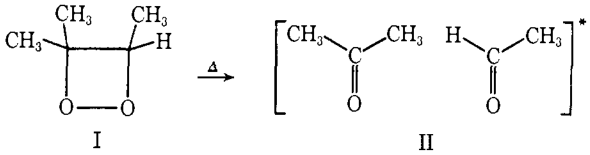
uct molecule D^* is fluorescent, and light emission occurs as an end result of the chemical reaction. The excitation energy can also be transferred either intermolecularly, $D^* + A \rightarrow A^* + D$, or intramolecularly[3]

$$\begin{tikzcd} A\text{–}C \arrow[r] & A\text{–}D^* \arrow[d] \\ & A^*\text{–}D \end{tikzcd}$$

These processes have been detected in the past by light emission from the A molecule or moiety. We now report that the electronic excitation energy that resides in D^* can be used to do work.

In principle, any chemiluminescent reaction can be used as an "energy generator."[2] In the present communication, we have used a phthalic hydrazide[4] and trimethyl-2-oxaoxetane (I)[5] as the energy sources.

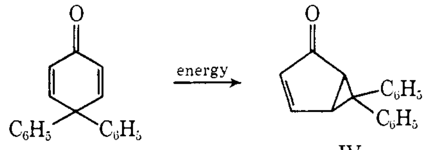
Oxaoxetanes[6] appear to be critical intermediates in most known organic chemiluminescent reactions in solution. Recently, a member of this class, I, has been isolated and shown to generate electronically excited states on thermal decomposition.[5]



I II

Intermolecular energy transfer from II was demonstrated by the fluorescence of added anthracene and the phosphorescence of added biacetyl.[5,7] We now find that the excitation energy of the products (II) can be transferred to acceptors, which subsequently undergo a "photochemical" change. For example, a degassed solution of 0.35 *M* I and 0.006 *M trans*-stilbene in benzene heated to *ca.* 100° for 7 min yields 20% of *cis*-stilbene.[8] The *cis*-stilbene was isolated by chromatography on silica gel, and its identity was confirmed by ultraviolet spectra and R_f values.[9,10] Blank runs on *trans*-stilbene and thermally decomposed oxaoxetane solutions were negative.

The principle of "photochemistry without light" was then applied to the photoisomerism of 4,4-diphenylcyclohexadienone (III). This reaction has been studied



III IV

extensively by Zimmerman, *et al.*,[11] who showed that the photoproduct IV was formed from the triplet state of III with a quantum yield of 0.85. Using the new method, a benzene solution of I (0.5 *M*) and III (0.01 *M*) was heated on a steam bath for 10 min. Chromatography of the product on a cellulose tlc plate, by a modification of the method of Zimmerman, *et al.*, yielded compound IV (*ca.* 25% yield), with ultraviolet and infrared spectra identical with those reported.[11] It would appear, therefore, that the new method, with the proper energy source,[12] can achieve results normally obtainable in photosensitized reactions energized by light (triplet intermediates).[14]

Isomerism was also noted in a reaction using the oxidation of a diacyl hydrazide[4] as the energy source. Thus, the *trans*-hydrazide V was oxidized to give a mixture of styrylphthalic acids that contained 3% of the *cis* isomer (determined by glpc of the methyl esters). Provided higher yields can be obtained, one can conceive of extensions of this approach: intramolecular energy transfer from any of the energy generators (EG) used in chemiluminescence to an acceptor molecule (A)

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(2) K. D. Gundermann, "Chemilumineszenz Organischer Verbindungen," Springer-Verlag, New York, N. Y., 1968.

(3) E. H. White and D. F. Roswell, *J. Amer. Chem. Soc.*, **89**, 3944 (1967); E. H. White, D. R. Roberts, and D. F. Roswell, "Molecular Luminescence," E. C. Lim, Ed., W. A. Benjamin, Inc., New York, N. Y. 1969, p 479; D. R. Roberts, V. Paul, D. F. Roswell, and E. H. White, in preparation.

(4) E. H. White, "Light and Life," W. D. McElroy and B. Glass, Ed., The Johns Hopkins Press, Baltimore, Md., 1961; E. H. White, O. C. Zafiriou, H. M. Kagi, and J. H. M. Hill, *J. Amer. Chem. Soc.*, **86**, 940 (1964); E. H. White and M. M. Bursey, *ibid.*, **86**, 941 (1964); E. H. White and M. M. Bursey, *J. Org. Chem.*, 31, 1912 (1966); E. H. White and K. Matsuo, *ibid.*, **32**, 1921 (1967); E. H. White, O. C. Zafiriou, D. R. Roberts, and E. G. Nash, *J. Amer. Chem. Soc.*, **90**, 5932 (1968); E. H. White, D. F. Roswell, and O. C. Zafiriou, *J. Org. Chem.*, **34**, 2462 (1969).

(5) K. R. Kopecky, J. H. Van De Sande, and C. Mumford, *Can. J. Chem.*, **46**, 25 (1968); K. R. Kopecky and C. Mumford, Abstracts, 51st Annual Conferences of the Chemical Institute of Canada, Vancouver, B. C., June 1968, p 41; K. R. Kopecky and C. Mumford, *Can. J. Chem.*, **47**, 709 (1969). Dr. Kopecky kindly furnished us with a preprint of the latter article.

(6) E. H. White and M. J. C. Harding, *J. Amer. Chem. Soc.*, **86**, 5686 (1964); E. H. White and M. J. C. Harding, *Photochem. Photobiol.*, **4**, 1129 (1965); T. A. Hopkins, H. H. Seliger, E. H. White, and M. W. Cass, *J. Amer. Chem. Soc.*, 89, 7148 (1967); E. H. White, E. Rapaport, T. A. Hopkins, and H. H. Seliger, *ibid.*, **91**, 2178 (1969); F. McCapra, *Quart. Rev.* (London), **20**, 485 (1966).

(7) We have noted that 9,10-dibromoanthracene chemiluminesces in this system far more brightly than anthracene. This result also indicates that the triplet states of the carbonyl compounds in II can be intercepted (as well as the singlet states): V. A. Belyakov and R. F. Vasil'ev, *Dokl. Phys. Chem.*, **176**, 731 (1967).

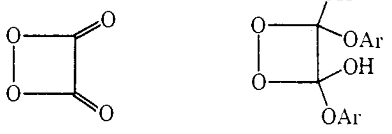
(8) The quantum yield for the photochemical isomerization of *trans*-stilbene to the *cis* isomer has been reported to be 0.67 at 333 nm in methylpentane: H. Stegemeyer, *J. Phys. Chem.*, **66**, 2555 (1962). Values of 0.24 to 0.41 have been reported for the sensitized isomerization: G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Amer. Chem. Soc.*, **86**, 3197 (1964).

(9) Tlc on silica gel and glpc analyses on 5% QF-1 on 80–100 Chromosorb Q (Applied Science Labs) at 110 and 130°, and 2% Apiezon L on 80–100 Chromosorb Q (Applied Science Labs) at 140°.

(10) The oxaoxetane (I) can be by-passed by using the precursor of I, 3-bromo-2-methyl-2-butyl hydroperoxide,[5] a base, and the substrate.

(11) H. E. Zimmerman and D. I. Schuster, *J. Amer. Chem. Soc.*, **84**, 4527 (1962); H. E. Zimmerman, R. Keese, J. Nasielski, and J. S. Swenton, *ibid.*, **88**, 4895 (1966); H. E. Zimmerman and J. S. Swenton, *ibid.*, **89**, 906 (1967).

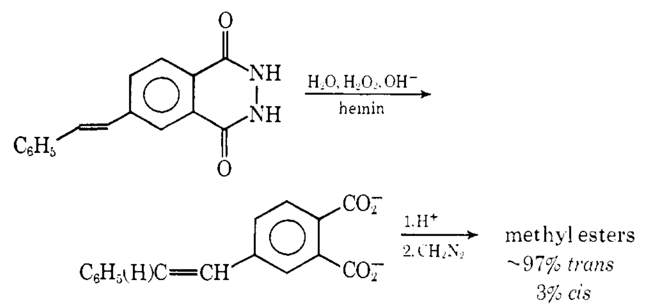
(12) We have tried to use as an energy source, without notable success, the intermediate formed in the reaction of hydrogen peroxide with various active esters of oxalic acid.[13] This intermediate successfully transfers excitation energy to fluorescent compounds.[13] An oxaoxetane structure (i) has been proposed for the intermediate, but a solvate such as ii appears more probable.



i ii

(13) M. M. Rauhut, *Accounts Chem. Res.*, **2**, 80 (1969).

(14) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1966; P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **5**, 21 (1968).



(to be acted on) attached by a labile bond to the energy generator.

$$A + EG \xrightarrow[\text{formation}]{\text{bond}} A\text{—}EG \xrightarrow{\text{oxidation}}$$

$$\underset{\text{product}}{\text{product—EG}} \xrightarrow[\text{cleavage}]{\text{bond}} \text{product} + \underset{\text{product}}{EG}$$

The yields reported in this communication have not been optimized. With development, this method of photochemistry should be useful in theoretical studies and in practical areas. Among the advantages of the new method are: (1) the localization of *all* the energy initially in the donor moiety, and (2) the requirement of only simple equipment, beakers not monochromators.[15]

Acknowledgment. We thank the Public Health Service for its financial support (Research Grant No. 5 RO1 7868 from the National Institute of Neurological Diseases and Blindness). We also thank Dr. Harold Doshan for carrying out extensive exploratory work.

[15] NOTE ADDED IN PROOF. Using the oxaoxetane, we have also been able to convert acenaphthylene into its *trans* dimer.

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Book Reviews

The Fundamentals of Theoretical Chemistry. Wave Mechanics Applied to the Study of Atoms and Molecules. By RAYMOND DAUDEL, Directeur du Centre de Mecanique, Ondulatoire Appliquee du C.N.R.S., Professor at the Sorbonne. Pergamon Press Inc., 44-01 21st St., Long Island City, N. Y. 1968. xx + 211 pp. 14 × 22 cm. $10.00.

This book is a translation from the French of a book written in 1952 and published in 1956. It originally was published as Volume VI in "Traite de Physique Theorique et de Physique Mathematique." The text is based on Professor Daudel's lectures for final year undergraduates and is intended to serve as an introduction to his other book, "Electronic Structure of Molecules."

After a very brief review of quantum mechanics and the wave function for the hydrogen atom, the book devotes a long chapter to the helium atom. The methods of Hylleraas and Pluvinage are discussed briefly, but most of the emphasis is placed on the symmetry aspects of an expansion in atomic orbitals obtained by neglecting electron repulsion effects. The method for determining which term symbols go with a particular configuration is described, but no method for systematically forming eigenfunctions of angular momentum is mentioned. A brief mention is made of several other methods, such as Hartree-Fock. This chapter, like most of the book, has the tone of a review article rather than a systematic development of the subject. Most of the discussion is presented as a description or prescription without proof.

The next chapter contains an introduction to the self-consistent field theory of many electron atoms. The concept of a loge is introduced in this chapter and used extensively in a later chapter to try to explain the geometry of molecules. Basically a loge is a region of space in which one would almost always find one electron of a given spin and almost never two electrons of the same spin. As this concept originated with Professor Daudel and was new at the time, the book lapses into some detailed proofs concerning criteria for the possibility of such divisions of space into loges and for construction of localized orbitals. This may well be the only place that many of these proofs appear in print.

The rest of the book consists of a description of the methods of calculating molecular wave functions which were in vogue in 1952. The simple calculations on H_2 are discussed; the rules for constructing spin states are presented without proof; nonempirical and semiempirical LCAO-MO methods are discussed. Calculation of rotational and vibrational wave functions is mentioned as is the calculation of dipole moments and other properties. Finally there is a long chapter on the classification of chemical bonds based on the idea of loges.

This book is a very short and superficial review of the state of quantum chemistry in 1952. As such it is probably of very limited value. The book is also a monograph explaining the concept of a loge and its use in predicting molecular geometry. This concept is still used by some people although it has never gained wide acceptance. For anyone interested in learning about loges, the book would be required reading.

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