= Ph), *tert*-butylperoxylactone (**2c,** $R_1 = t\text{-}C_4H_9$; R_2 = H), methylpropylperoxylactone (**2d,** $R_1 = CH_3$; $R_2 = CH_3CH_2CH_2$), phenylbutylperoxylactone (**2e,** R_1 = Ph; $R_2 = CH_3CH_2CH_2CH_2$), and bis(trifluoromethyl)peroxylactone (**2f,** $R_1 = R_2 = CF_3$) were prepared. Although the formation of these α-peroxylactones by photooxygenation[9] at ~ -78 °C could be established by spectroscopy (characteristic IR absorption ~ 1880 cm^{-1}), the yields were generally much lower[10] than those listed in Table I.

In addition to the spectral evidence for the assigned structures, the chemistry of the compounds listed in Table I is also consistent with the α-peroxylactone structure. For example, warming of solution of dimethylperoxylactone results in the quantitative formation of CO_2 and acetone. Furthermore, the thermolyzed solutions exhibit an intense chemiluminescence which was established as acetone phosphorescence.[11]

Given the structural assignments, let us now turn to the mechanism of reaction of ketenes with TPPO. Is there a direct, bimolecular reaction[12] between a ketene and TPPO, or does the latter first decompose to release a reactive form of oxygen (or its equivalent) which then reacts with the ketene?

To test whether or not ketenes enter into a direct, bimolecular reaction with the ozonide, the kinetics of decomposition of TPPO were determined. At −24 °C, the disappearance of TPPO is strictly first order and occurs at the same rate in the presence and absence of diphenylketene (first-order rate constants of $4.1 \pm 0.4 \times 10^{-4}$ s^{-1} and $4.5 \pm 0.1 \times 10^{-4}$ s^{-1}, respectively).[13] Thus, a direct bimolecular reaction between TPPO and diphenylketene does not occur. The ozonide instead undergoes a unimolecular decomposition which produces an oxidizing agent. That this active species is singlet oxygen is required by the following observations: (a) reaction between TPPO and ketenes occurs at a significant rate only at or above temperatures ($\sim \geq -30$ °C) for which TPPO is known to undergo decomposition to yield $^1O_2$; (b) the α-peroxylactones listed in Table I are also produced at −78 °C by photooxygenation; (c) the formation of 9,10-dimethylanthracene *endo*-peroxide (by reaction of 9,10-dimethylanthracene with TPPO) is strongly quenched by diphenylketene;[14] (d) the yields of α-peroxylactones parallel the order based on singlet oxygen lifetimes;[15] (e) reaction of ketenes with $^3O_2$ is negligible under our reaction conditions.[16]

The reaction of singlet oxygen and ethylenes to form dioxetanes is often viewed as proceeding via a perepoxide and/or zwitterion precursor.[17] In an attempt to establish whether reaction 1 (where O_2 is now understood to imply $^1O_2$) proceeds via trappable intermediates, the reactions of dimethylketene and of diphenylketene with TPPO in the presence of CH_3OH were studied. Indeed, when CH_3OH is present, α-peroxylactone formation is completely suppressed[18] and α-methoxyperacetic acids (eq 3) are produced. The same situation obtains for photooxygenation of dimethyl- or diphenylketenes at −78 °C. Since it was found that the α-peroxylactones (and the peresters formed from autoxidation) are stable to methanol under the reaction conditions, we conclude that methanol has intercepted a precursor to the α-peroxylactone (e.g., the perepoxide **4** or zwitterion **5** in eq 4).

In conclusion, the reaction of ketenes and TPPO represents a novel and direct synthesis of α-peroxylactones which may be conveniently purified by distillation and studied in inert solvents systems. The reaction mechanism involves generation of $^1O_2$ from TPPO followed by attack of $^1O_2$ on the ketene to produce a perepoxide **4** (and/or zwitterion **5**) intermediate that collapses to α-peroxylactone in inert solvents or may be trapped by methanol to yield α-methoxyperacetic acid derivatives.

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(8) Other solvents which have been employed are $CFCl_3$ (Freon 11) and CH_2Cl_2.

(9) For a review of photooxidations, see R. W. Denny and A. Nickon, *Org. React.*, **20,** 133 (1973).

(10) For example, employing polymer-bound rose bengal as photosensitizer, ~5–10% yield of **2a** was observed, the major products being acetone and the autooxidation product of dimethylketene (a polyperester).[4] It appears that the generally lower yields obtained by photooxidation are due to competing autooxidation of the ketene and possibly by instability of α-peroxylactones to the reaction conditions.

(11) N. J. Turro, H. C. Steinmetzer, and A. Yekta, *J. Am. Chem. Soc.*, **95,** 6468 (1973), and references therein.

(12) The direct reaction of TPPO with olefins has been observed to occur at temperatures (−70 °C) below that for unimolecular decomposition (−20 °C): P. D. Bartlett and G. D. Mendenhall, *J. Am. Chem. Soc.*, **92,** 210 (1970).

(13) The initial concentrations of ketene and ozonide in CH_2Cl_2 were 4.5×10^{-2} M and 1.5×10^{-2} M, respectively. For a higher concentration of ozonide, a literature value[7] for decomposition of TPPO is $\sim 6 \times 10^{-4}$ s^{-1} at −24 °C. It appears that a direct bimolecular reaction between TPPO and ketenes is important at low temperatures (−78 °C). For example, reaction of 1a and TPPO at −78 °C yields *acetone* as the exclusive product. In the case of *tert*-butylketene, reaction at −78 °C produces α-peroxylactone in good yield.

(14) From literature rate constants and competitive quenching with 9,10-dimethylanthracene, the rate of quenching of diphenyl ketene is estimated to be $\sim 1 \times 10^7$ M^{-1} s^{-1} at −15 °C in CH_2Cl_2.

(15) P. B. Merkel and D. R. Kearns, *J. Am. Chem. Soc.*, **94,** 1029 (1972).

(16) Reaction of ketenes and TPPO are generally complete in ~1 h at −20 °C. In contrast, 90% reaction of diphenylketene, phenylbutylketene, and dimethylketene with $^3O_2$ (autoxidation) requires ~4 days, 2 days, and 10 h, respectively. Except for diphenylketene, the autoxidation products are quite different from the products produced from ketenes and TPPO.

(17) For a recent discussion, see (theory) M. J. S. Dewar, A. C. Griffin, W. Thiel, and I. J. Turchi, *J. Am. Chem. Soc.*, **97,** 4439 (1975), and S. Inagaki and K. Fukui, *ibid.*, **97,** 7480 (1975); (experimental) I. Saito, M. Imuta, Y. Takahashi, S. Matsugo, and T. Matsura, *ibid.*, **99,** 2005 (1977).

(18) Substantial amounts of methyl dimethylacetate and methyl diphenylacetate are produced in these reactions. The yields derived from reaction of molecular oxygen with the ketenes are 40% for dimethylketene and 100% for diphenylketene.

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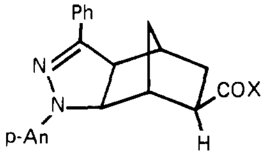
Electrochemistry of Some Surface-Bonded Pyrazoline Derivatives

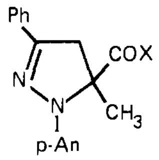
Sir:

Since the first report by Murray et al.[1] on the success of chemically modifying a metal oxide electrode by covalently attaching reagents, other laboratories,[2,3] have shown interest in this approach as a means for controlling the course of the reactions which occur at the electrode surfaces. One interesting application of this chemistry is the use of electrode surfaces with covalently attached electroactive species which can serve as electron-transfer mediators. In this regard, it is of interest to have information regarding the mode of electron transfer between the surface and the electroactive species and regarding the stability of the incipient electrode-bonded radical ions. We wish to communicate the electrochemical behavior of some electrode surface-bonded pyrazoline structures which show reversible behavior. These results provide some insight into the above concerns.

All plates containing surface-bonded electroactive species were prepared in the following manner. Plates (10 mm by 30 mm) of commercially available antimony doped SnO_2 on glass backing were washed with water, acetone, and hexane and then dried at 200 °C before use. For the preparation of the silylated surface $SnO_2/SiCH_2CH_2CH_2NHCH_2CH_2NH_2$ (SnO_2/Si3N2N), the plates were immersed in anhydrous benzene solution containing ~2% 3-(2-aminoethylamino)pyropyltrimethoxysilane for 10 min and then washed with fresh benzene several times. The plates were next immersed in 10 mL of methylene chloride solution containing 10 mg of Ia plus 15 mg of dicyclohexylcarbodimide. After the solution was heated at 50 °C for 2 h, the plates containing the bonded pyrazoline derivative were removed and rinsed with fresh methylene chloride. Synthesis of Ia makes use of the addition reaction of diarylnitrile imine to 2-carbomethoxy-5-norbornene to produce Ib.[4] Saponification of Ib in aqueous methanol produces Ia in good yields.[5] Compound IIb was similarly prepared employing methyl methacrylate.[4]



I



II

a, X=OH; b, X=OCH_3; c, X=SnO_2/Si3N2N

The electrochemical measurements were carried out in acetonitrile containing 0.1 M tetraethylammonium tetrafluoroborate and a Ag/Ag^+ (CH_3CN) reference electrode. Figure 1 shows the cyclic voltammogram for the surface bonded *N*-*p*-anisylpyrazoline derivative Ic measured with no *iR* compensation.[6] The reversible peak observed has E_{pa} equal to 0.32 V (200 mV/s) and i_c/i_a equal to unity. The ΔE_P values increase with sweep rate from 30 to 70 mV for the range shown in the figure. The surface coverage is estimated at 2×10^{14} molecules/cm^2 based on the area under the *i*–*V* curve without applying any correction. For comparison, the *i*–*V* curve for Ib using a platinum button shows peaks with E_{pa} values (200 mV/s) equal to 0.32 V (reversible, $i_c/i_a = 1$) and 1.00 V (irreversible). Each peak is a one-electron-transfer process. The first peak has $i/CV^{1/2}$ equal to $0.207A/M(V/s)^{1/2}$ at 0.2 V/s and chronocoulometry provides $nD^{1/2}$ equal to 3.4×10^{-3} cm/$s^{1/2}$.

In contrast to these results, when an electrochemical irreversible pyrazoline is bonded to the surface, thus the *N*-phenylpyrazoline analogue to Ic, the *i*–*V* curve shows a peak with E_{pa} equal to 0.46V (200 mV/s) which disappears completely after the first voltage scan. The *i*–*V* plot for *N*-phenyl-Ib shows an irreversible peak with E_{pa} equal to 0.54 V ($n = 2$) and $i/CV^{1/2}$ equal to $0.336A/M(V/s)^{1/2}$ at 0.2 V/s. Chronocoulometry provides $nD^{1/2}$ equal to 7.23×10^{-3} cm/$s^{1/2}$.

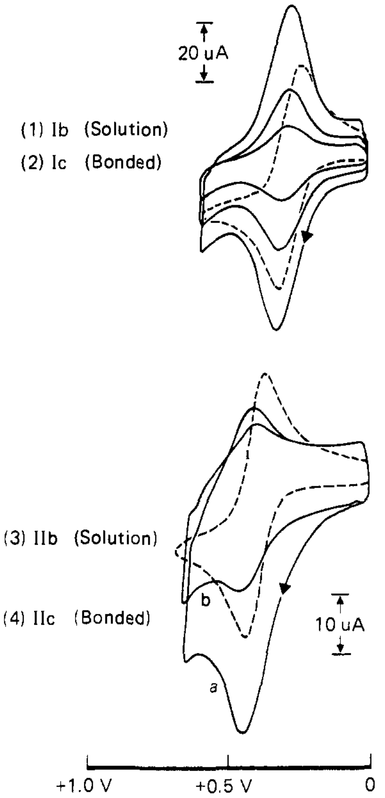


Figure 1. Cyclic voltammograms measured in CH_3CN: (1) Ib (dotted line), Pt electrode, 200 mV/s, 50 μA scale; (2) Ic, scans at 50, 100, and 200 mV/s; (3) IIb (dotted line), Pt electrode, 200 mV/s, 20 μA scale; (4) IIc, 200 mV/s (a, first scan; b, second scan).

Of particular interest is the varying electrochemical behavior of II when anchored vs. in solution. Surface bonded IIc does not display the expected *i*–*V* curve for a reversible reaction. Instead, as seen in Figure 1, the oxidation peak with E_{pa} equal to 0.43 V shows only a small i_c signal in the reverse sweeps. After the first scan, the oxidation peak is greatly reduced and barely detectable in the third scan. The surface coverage based on the first scans is 7×10^{13} molecules/cm^2, uncorrected. The *i*–*V* curve for IIb using a platinum button electrode shows two peaks with E_{pa} values (200 mV/s) equal to 0.44 V (reversible, $i_c/i_a = 1$) and 1.09 V (irreversible). Each peak is a one-electron-transfer process. The first peak has $i/CV^{1/2}$ equal to $0.196A/M(V/s)^{1/2}$ and chronocoulometry provides $nD^{1/2}$ equal to 3.01×10^{-3} cm/$s^{1/2}$. The same reversible behavior is observed using a tin oxide electrode untreated, SnO_2/Si3N2N and acylated SnO_2/3N2N. As in the I series, the *N*-phenyl analogue of IIc shows one irreversible peak with E_{pa} equal to 0.63 V which disappears with the first voltage scan.

The striking result is the different electrochemical behavior displayed by the diarylpyrazoline derivatives I and II when bonded to the surface vs. when dissolved in solution. The results are understandable in terms of the reactions available to the pyrazoline radical cations.

While the *N*-anisylpyrazoline derivatives in solution show the same high electrochemical reversibility under cyclic voltammetry conditions, the monocyclic radical cations show some decomposition on a much longer time scale to produce the corresponding pyrazole. The reaction occurs even when the pyrazoline is disubstituted in the 5 position as in II to produce the 4,5-disubstituted pyrazole.[7,8] Since an array of bonded radical cations is a less stable situation than when they can diffuse into the solution resulting from changes in solvating structure and coulombic interactions, the relative destabilization suffered by IIc radical when bonded must enhance the pyrazole-forming reaction producing an irreversible *i*–*V* curve.

Also contributing to the noted change in the electrochemical reversibility of IIc is the limited amount of electroactive material available which makes more noticeable any amount of oxidized intermediate which decomposes.

On the other hand, since pyrazole formation is a significantly more difficult process for the tricylic I derivatives,[4,5] even the surface-bonded Ic radical cation remains sufficiently stable to display a reversible *i–V* curve. The *N*-phenylpyrazolines are known to be electrochemically irreversible where the radical cations dimerize via the phenyl para position.[9]

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Book Reviews[*]

Advances in Radiation Research in Biology and Medicine. Volumes I and II. Edited by J. F. DUPLAN and A. CHAPIRO. Gordon & Breach, New York, N.Y. 1974. Vol. I: xxiv + 465 pp. $36.00. Vol. II: ix + 530 pp. $42.00.

These volumes contain the papers presented at an international symposium held at Evian in 1970. Ultraviolet, γ, and neutron radiation are included. A large proportion of Vol. I is devoted to radiation biochemistry, with particular concern for effects on DNA; Vol. II is somewhat more biological in emphasis. The papers are mostly accounts of original research, although there is some review material. It is a pity that there is no index.

The Beilstein Guide. By O. WEISSBACK. Springer-Verlag, New York and Heidelberg. 1976. 95 pp. $4.90.

This soft-bound booklet describes with great precision and succinctness the organization of Beilstein's "Handbuch der Organischen Chemie", and the principles on which it is based. Proper attention to what is stated should allow a searcher to find a desired item of information efficiently, but attentiveness is essential, for the presentation is concentrated and in no way repetitive. The emphasis is primarily on what the organization is and somewhat less on how to use it. There are many helpful examples, however. Nearly half of the work is a German-English-French glossary, which includes a great majority of the terms used in Beilstein. It should enable the reader who knows little or no German to make effective use of Beilstein nevertheless.

Chromium: Its Physicochemical Behavior and Petrologic Significance. Edited by T. N. IRVINE. Pergamon Press, New York, N.Y. 1975. 296 pp. $30.00.

This book is offered as an issue of *Geochimica et Cosmochimica Acta* and contains 24 papers presented at the Carnegie Institution Conference held in January 1974. The papers are concerned with thermochemistry, crystallography, phase equilibria, etc., largely in a mineralogical context. They are partly review papers and partly reports of original research. There is no index.

Colloid and Interface Science. Volumes II–V. Edited by M. KERKER. Academic Press, New York, N.Y. 1976. Vol. II: xx + 481 pp. $21.00. Vol. III: xx + 548 pp. $22.50. Vol. IV: xviii + 587 pp. $22.00; Vol. V: xvi + 507 pp. $22.00.

These volumes contain the 221 contributed papers presented at the International Conference on Colloids and Surfaces, held in June 1976. Some are reviews, but most are accounts of original research. Many are given as abstracts only; in others, the description of experimental procedures varies from general indications to precise details. The papers have been reproduced from the authors' typescripts, in a variety of type faces, but the method of reproduction is superior to that usually encountered and makes an impression more like that of a typeset book.

Volume II contains the papers on "Aerosols, Emulsions, and Surfactants". Volume III is devoted to "Adsorption, Catalysis, Solid Surfaces, Wetting, Surface Tension, and Water". In Volume IV, we find papers on "Hydrosols and Rheology", and in Volume V, "Biocolloids, Polymers, Monolayers, Membranes and General Papers". There are no indexes.

Crystal Growth and Characterization. Edited by R. UEDA and J. B. MULLIN. American Elsevier, New York, and North-Holland Publishing Co., Amsterdam. 1975. vii + 419 pp. $33.95.

This book contains the proceedings of the Second International Spring School on Crystal Growth, held in Japan in 1974. There are 27 papers, reproduced from typescript that appears to have been photoreduced to about half size, and accompanied by abundant photographs, drawings, and graphs. The emphasis is on crystal growth from melts and on surface and structural properties. The subject matter is generally discussed from the standpoint of the materials scientist interested in semiconductors, optical materials, and other technological applications.

Encyclopedia of Antibiotics. By JOHN S. GLASBY. Wiley/Interscience, New York, N.Y. 1977. 372 pp. $42.50.

If one knows the name of an antibiotic, this book allows one to find out quickly its formula, structure if known, its source and isolation procedure, physical properties, and its biological and medicinal action, together with a few key references. The patent literature has been given due attention. The scope of the work is broad, since the author has followed the definition of Benedict and Langlyke for the term antibiotic: a substance derived from or produced by a living organism, capable of inhibiting microorganisms in low concentration. The book is well produced and convenient to use.

Mathematical Models of Metabolic Regulation. Edited by T. KELETI and S. LAKATOS. Akademia Kiadó, Budapest. 1976. 260 pp. $15.00.

This work is Volume 18 of Symposia Biologica Hungarica and contains the papers delivered at the FEBS Advanced Course No. 27,

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[*] Unsigned book reviews are by the Book Reviews Editor.