EFFECTS OF HETERATOM SUBSTITUENTS ON THE PROPERTIES OF DIOXANE
EFFECTS OF HETEROATOM SUBSTITUENTS ON THE PROPERTIES OF 1,2-DIOXETANES

by

R. S. Handley, A. J. Stern, and A. P. Schaap

Prepared for Publication in

Tetrahedron Letters

Department of Chemistry
Wayne State University
Detroit, MI 48202

December 4, 1984

Reproduction in whole or in part is permitted for any purpose of the United States Government

This document has been approved for public release and sale; its distribution is unlimited
**Title**: Effects of Heteroatom Substituents on the Properties of 1,2-Dioxetanes

**Authors**: R. L. Handley, A. J. Stern, and A. P. Schaap

**Performing Organization**: Department of Chemistry, Wayne State University, Detroit, MI 48202

**Contract or Grant Number**: N00014-82-K-0696

**Report Date**: December 4, 1984

**Summary**

This document has been approved for public release and sale; its distribution is unlimited.

**Key Words**: Chemiluminescence, activation energies, 1,2-dioxetanes, photooxygenation, exciplex emission

**Abstract**

Nitrogen and sulfur-substituted dioxetanes exhibit dramatically lower activation energies for decomposition compared to the corresponding oxygen-bearing dioxetane. A mechanism involving intramolecular electron-transfer processes is proposed for the cleavage of these unstable dioxetanes.
EFFECTS OF HETERATOM SUBSTITUENTS ON THE PROPERTIES OF 1,2-DIOXETANES

Richard S. Handley, Alan J. Stern, and A. Paul Schaap

Department of Chemistry, Wayne State University
Detroit, MI 48202

Abstract: Nitrogen and sulfur-substituted dioxetanes exhibit dramatically lower activation energies for decomposition compared to the corresponding oxygen-bearing dioxetane. A mechanism involving intramolecular electron-transfer processes is proposed for the cleavage of these unstable dioxetanes.

1,2-Dioxetanes of various structural types have been prepared by the cyclization of β-bromohydroperoxides and by the addition of singlet oxygen to activated alkenes. Alkyl- or phenyl-substituted dioxetanes are relatively stable and decompose at elevated temperatures to give predominantly triplet excited states. In contrast, dioxetanes bearing aryl moieties with low oxidation potentials are significantly less stable and decompose with enhanced singlet chemiexcitation efficiencies.

Photooxygenation of vinyl ethers affords alkoxy-substituted dioxetanes that exhibit properties similar to those of alkyl-substituted dioxetanes. For example, cis-3,4-diethoxy-1,2-dioxetane and cis-3,4-diethyl-1,2-dioxetane both have half-lives of several hours at 25°C and thermolyze with Arrhenius activation energies of 24.4 and 24.5 kcal/mol, respectively. However, dioxetanes derived from enamines and vinyl sulfides have been reported to be qualitatively much less stable, undergoing rapid decomposition below 0°C. No mechanistic explanation has been offered for the striking differences in the thermal stability of these dioxetanes. In order to systematically evaluate the effects of heteroatom substituents, a series of structurally related dioxetanes has been prepared. We provide herein the first report of activation parameters and rates of decomposition for nitrogen- and sulfur-substituted dioxetanes. An intramolecular electron-transfer mechanism is proposed for the cleavage of these unstable peroxides.

\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{1} & \quad \text{Ph} \quad \text{Ph} \\
\text{2} & \quad \text{Ph} \quad \text{Ph} \\
\text{3} & \quad \text{Ph} \quad \text{Ph}
\end{align*}
\]

\( \text{Ph} \quad \text{Ph} \quad \text{Ph} \quad \text{Ph} \)

\( \text{a. } X=Y=O \quad \text{b. } X=Y=S \quad \text{c. } X=O; Y=O \quad \text{d. } X=O; Y=\text{Me} \)
Alkenes 1a-d were synthesized by acid-catalyzed condensation of benzoin with 1,2-ethanediol, 1,2-ethanedithiol, 2-hydroxyethanethiol, and N,N'-dimethyl-1,2-ethanediamine. Solutions of dioxetanes 2a-d were prepared in CH$_2$Cl$_2$ by photooxygenation of 1a-d at -78°C with polystyrene-immobilized Rose Bengal and a 400-W high pressure sodium lamp. All four dioxetanes produce indirect chemiluminescence upon thermolysis in o-xylene in the presence of 9,10-dibromoanthracene (DBA). Dioxetanes 2a, 2c, and 2d were further identified by $^1$H NMR at -78°C and by their cleavage to 3a, 3c, and 3d which were fully characterized. Photooxygenation of 1b at -78°C in CH$_2$Cl$_2$ followed by warming to ambient temperature afforded not only 3b (44%) but also benzil (31%). Product yields in this latter case were determined by HPLC.

Several groups have previously noted that the decomposition of sulfur-substituted dioxetanes can yield mixtures of products derived from C-C and C-S bond cleavage. It should be emphasized that benzil is not formed from the decomposition of 2c.

Rate constants for the decomposition of 2a-d were determined from measurements of the decay of chemiluminescence intensity of 10$^{-4}$-10$^{-5}$ M solutions in o-xylene in the presence of 10$^{-5}$ M DBA. The isothermal decompositions were monitored for at least three half-lives and were first order in all cases. Rates were found to be independent of DBA and dioxetane concentration. Activation parameters were calculated from Arrhenius plots.

Table 1. Activation Parameters and Rates of Decomposition for 1,2-Dioxetanes 2a-d.

<table>
<thead>
<tr>
<th>Dioxetane (X,Y)</th>
<th>Temp. Range, °C</th>
<th>$E_a$, kcal/mol</th>
<th>Log A</th>
<th>$k_{rel}$ (25°C)</th>
<th>$\tau^{1/2}$ (25°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a (0,0)</td>
<td>70.0 to 90.3</td>
<td>24.8</td>
<td>12.4</td>
<td>1b</td>
<td>115 h</td>
</tr>
<tr>
<td>2b (S,S)</td>
<td>-11.5 to +20.5</td>
<td>18.8</td>
<td>13.6</td>
<td>3.96 x 10$^5$</td>
<td>1.05 s</td>
</tr>
<tr>
<td>2c (S,0)</td>
<td>-11.5 to +21.5</td>
<td>17.4</td>
<td>12.2</td>
<td>1.66 x 10$^5$</td>
<td>2.49 s</td>
</tr>
<tr>
<td>2d (MeN, MeN)</td>
<td>-0.7 to +29.6</td>
<td>16.6</td>
<td>11.1</td>
<td>5.12 x 10$^4$</td>
<td>8.09 s</td>
</tr>
</tbody>
</table>

*Calculated from the Arrhenius plots. bCorresponding to a rate constant of 1.67 x 10$^{-6}$ s$^{-1}$ in o-xylene at 25°C. cRates of decomposition for 2c were the same if the direct emission was monitored in the absence of DBA.

In addition to the indirect "blue" chemiluminescence that can be observed visually from 1a-d in the presence of DBA, we have also found that injection of a cold solution of the mixed oxygen-sulfur dioxetane 2c into o-xylene at ambient temperature results in an intense "yellow" chemiluminescence ($\lambda_{max} = 553$ nm). This direct emission is of particular interest because cleavage product 3c is not detectably fluorescent. Figure 1 shows a chemiluminescence spectrum of 2c in o-xylene obtained at -11°C with a Spex Fluorolog spectrofluorometer. Correction was made for the decay of total light intensity during the scan by use of a second detector in a ratio mode. This luminescence is also observed in acetonitrile ($\lambda_{max} = 533$ nm) and in methycyclohexane ($\lambda_{max} = 561$ nm). A plausible explanation for this unusual emission involves an intramolecular exciplex. Goto has reported chemiluminescence from an exciplex generated by the thermolysis of an indole-substituted dioxetane. However, in that case emission from the fluorescent indole group as well as the exciplex was observed.
Several lines of evidence indicate that "stable" dioxetanes such as 2a decompose by a stepwise process involving homolysis of the peroxide bond to form a diradical with subsequent C-C bond cleavage.\textsuperscript{1,3} Clearly, an alternate mechanistic explanation is required to account for the distinct properties of nitrogen- and sulfur-substituted dioxetanes 2b-d. It might be proposed that these dioxetanes decompose via a concerted pathway. Heteroatom substituents would be expected to stabilize a transition state in which unsaturated carbonyl carbons bearing a partial positive charge are developed. One measure of the electron-donating ability of a substituent is the $\sigma^+$ value ($p$-MeS, -0.16; $p$-Me, -0.31; $p$-MeO, -0.78; $p$-Me$_2$N, -1.7).\textsuperscript{12,13} On this basis, however, one would have predicted oxygen-substituted dioxetanes to be less stable than sulfur-bearing dioxetanes. Also arguing against a concerted mechanism involving both ring carbon atoms is the observation that a single sulfur atom destabilizes the dioxetane to the same degree as two sulfur moieties.

We, therefore, propose a mechanism for the decomposition of 2b-d involving initial intramolecular electron-transfer from the heteroatom to the peroxide $\sigma^*$ orbital.\textsuperscript{15} This mechanism requires that the stability of the dioxetane be related to the oxidation potential of the heteroatom substituent. Consistent with this suggestion are the present results which show that dioxetanes bearing easily oxidized groups such as amines or sulfides ($E^\circ_X$: Et$_3$N, +0.96 V; Me$_2$S, +0.88)\textsuperscript{16} are dramatically less stable than a similar dioxetane with an alkoxy substituent possessing a much higher oxidation potential ($E^\circ_X$ Et$_2$O, > +2.5 V).\textsuperscript{16}

Additional experiments in this area are in progress. Of particular interest are the mechanistic details of the chemiexcitation process, exciplex emission, and dual decomposition modes of 2b.
Acknowledgments. Support from the Office of Naval Research is gratefully acknowledged. We also thank Dr. Manfred Steinfatt for initial experiments with dioxetane 2d.

References and Notes


7. Ib: mp 101-102°C (lit.8 101.9-102.2°C); 1H NMR (CDCl3) δ 3.40 (s, 4H), 7.2 (m, 10H). lcf: mp 64-65°C; 1H NMR (CDCl3) δ 3.22 (t, 2H, 4.5 Hz), 4.51 (t, 2H, 4.5 Hz), 7.1 (m, 10H). ldd: mp 180-182°C; 1H NMR (CDCl3) δ 2.38 (s, 6H), 2.97 (s, 4H), 7.2 (m, 10H). Satisfactory analysis of all alkenes.


11. No direct emission is observed from 2d and only very weak emission from 2b.


13. Another indication of the greater stabilization of adjacent positive charge by oxygen vs. sulfur is the observation that CI CH2OCH2CH3 hydrolyzes 1000-fold faster than CICH2SCH2CH3.14a It should be noted, however, that Caserio found that this order of stabilization is reversed in the gas phase.14b


15. Intramolecular electron-transfer mechanisms have been proposed for the decomposition of unstable dioxetanes bearing easily oxidized ary groups.

16. Oxidation peak potentials determined by cyclic voltammetry in MeCN vs. SCE. EtOH shows no oxidation at potentials less than 2.5 V.
ABSTRACTS DISTRIBUTION LIST, OSIA

Dr. M. A. El-Sayed  
Department of Chemistry  
University of California  
Los Angeles, California 90024

Dr. E. R. Bernstein  
Department of Chemistry  
Colorado State University  
Fort Collins, Colorado 80521

Dr. J. R. MacDonald  
Chemistry Division  
Naval Research Laboratory  
Code 6110  
Washington, D.C. 20375

Dr. G. B. Schuster  
Chemistry Department  
University of Illinois  
Urbana, Illinois 61801

Dr. W. M. Jackson  
Department of Chemistry  
Howard University  
Washington, D.C. 20059

Dr. M. S. Wrighton  
Department of Chemistry  
Massachusetts Institute of Technology  
Cambridge, Massachusetts 02139

Dr. A. Paul Schaap  
Department of Chemistry  
Wayne State University  
Detroit, Michigan 48202

Dr. Gary Bjorklund  
IBM  
5600 Cottle Road  
San Jose, California 95143

Dr. G. A. Crosby  
Chemistry Department  
Washington State University  
Pullman, Washington 99164

Dr. W. E. Moerner  
I.B.M. Corporation  
5600 Cottle Road  
San Jose, California 95193

Dr. Theodore Pavlopoulos  
NOSC  
Code 5132  
San Diego, California 91232

Dr. D. M. Burland  
IBM  
San Jose Research Center  
5600 Cottle Road  
San Jose, California 95143

Dr. John Cooper  
Code 6170  
Naval Research Laboratory  
Washington, D.C. 20375

Dr. George E. Walrafen  
Department of Chemistry  
Howard University  
Washington, D.C. 20059

Dr. Joe Brandelik  
AFWAL/AADO-1  
Wright Patterson AFB  
Fairborn, Ohio 45433

Dr. Carmen Ortiz  
Consejo Superior de Investigaciones Cientificas  
Serrano 117  
Madrid 6, SPAIN

Dr. John J. Wright  
Physics Department  
University of New Hampshire  
Durham, New Hampshire 03824

Dr. Kent R. Wilson  
Chemistry Department  
University of California  
La Jolla, California 92039
<table>
<thead>
<tr>
<th>Office of Naval Research</th>
<th>2</th>
<th>Dr. David Young</th>
</tr>
</thead>
<tbody>
<tr>
<td>Attn: Code 413</td>
<td></td>
<td>Code 334</td>
</tr>
<tr>
<td>800 N. Quincy Street</td>
<td></td>
<td>NORDA</td>
</tr>
<tr>
<td>Arlington, Virginia 22217</td>
<td></td>
<td>NSTL, Mississippi 39529</td>
</tr>
<tr>
<td>Dr. Bernard Douada</td>
<td>1</td>
<td>Naval Weapons Center</td>
</tr>
<tr>
<td>Naval Weapons Support Center</td>
<td></td>
<td>Attn: Dr. A. B. Amster</td>
</tr>
<tr>
<td>Code 5042</td>
<td></td>
<td>Chemistry Division</td>
</tr>
<tr>
<td>Crane, Indiana 47522</td>
<td></td>
<td>China Lake, California 93555</td>
</tr>
<tr>
<td>Commander, Naval Air Systems</td>
<td>1</td>
<td>Scientific Advisor</td>
</tr>
<tr>
<td>Command</td>
<td></td>
<td>Commandant of the Marine Corps</td>
</tr>
<tr>
<td>Attn: Code 310C (H. Rosenwasser)</td>
<td></td>
<td>Code RD-1</td>
</tr>
<tr>
<td>Washington, D.C. 20360</td>
<td></td>
<td>Washington, D.C. 20380</td>
</tr>
<tr>
<td>Naval Civil Engineering Laboratory</td>
<td>1</td>
<td>U.S. Army Research Office</td>
</tr>
<tr>
<td>Attn: Dr. R. W. Orisko</td>
<td></td>
<td>Attn: CRD-AA-IP</td>
</tr>
<tr>
<td>Port Hueneme, California 93401</td>
<td></td>
<td>P.O. Box 12211</td>
</tr>
<tr>
<td>Defense Technical Information Center</td>
<td>12</td>
<td>Research Triangle Park, NC 27709</td>
</tr>
<tr>
<td>Building 5, Cameron Station</td>
<td></td>
<td>Mr. John Boyle</td>
</tr>
<tr>
<td>Alexandria, Virginia 22314</td>
<td></td>
<td>Materials Branch</td>
</tr>
<tr>
<td>DTNSRDC</td>
<td>1</td>
<td>Naval Ship Engineering Center</td>
</tr>
<tr>
<td>Attn: Dr. G. Bosmajian</td>
<td></td>
<td>Philadelphia, Pennsylvania 19112</td>
</tr>
<tr>
<td>Applied Chemistry Division</td>
<td></td>
<td>Naval Ocean Systems Center</td>
</tr>
<tr>
<td>Annapolis, Maryland 21401</td>
<td></td>
<td>Attn: Dr. S. Yamamoto</td>
</tr>
<tr>
<td>Dr. William Tolles</td>
<td>1</td>
<td>Marine Sciences Division</td>
</tr>
<tr>
<td>Superintendent</td>
<td></td>
<td>San Diego, California 91232</td>
</tr>
<tr>
<td>Chemistry Division, Code 6100</td>
<td></td>
<td>Naval Research Laboratory</td>
</tr>
<tr>
<td>Naval Research Laboratory</td>
<td></td>
<td>Washington, D.C. 20375</td>
</tr>
</tbody>
</table>
DATE
ILMED
-8