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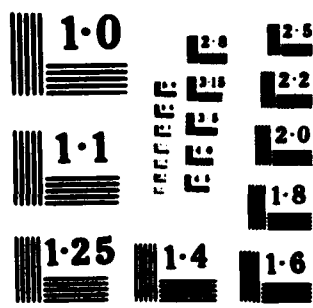
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EFFECTS OF HETEROATOM SUBSTITUENTS
ON THE PROPERTIES OF 1,2-DIOXETANES

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

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

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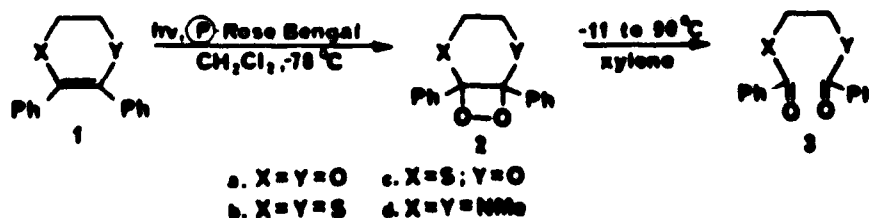
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Abstract: Nitrogen and sulfur-substituted dioxetanes exhibit dramatically lower activation energies for decomposition compared to the corresponding oxygen-bearing dioxetane. A mechanism involving intramolecular electron-transfer processes is proposed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

1,2-Dioxetanes¹ of various structural types have been prepared by the cyclization of β -bromohydroperoxides^{2a} and by the addition of singlet oxygen to activated alkenes.^{2b,c} Alkyl- or phenyl-substituted dioxetanes are relatively stable and decompose at elevated temperatures to give predominantly triplet excited states.¹ In contrast, dioxetanes bearing aryl moieties with low oxidation potentials are significantly less stable and decompose with enhanced singlet chemiexcitation efficiencies.³

Photooxygenation of vinyl ethers affords alkoxy-substituted dioxetanes that exhibit properties similar to those of alkyl-substituted dioxetanes.⁴ For example, *cis*-3,4-diethoxy-1,2-dioxetane^{4a,b} and *cis*-3,4-diethyl-1,2-dioxetane^{4c} 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 enamines⁵ and vinyl sulfides⁶ 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 **2** 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.



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.⁷ Solutions of dioxetanes 2a-d were prepared in CH₂Cl₂ by photooxygenation of 1a-d at -78°C with polystyrene-immobilized Rose Bengal⁹ 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).^{4a} Dioxetanes 2a, 2c, and 2d were further identified by ¹H NMR at -78°C and by their cleavage to 3a, 3c, and 3d which were fully characterized. Photooxygenation of 1b at -78°C in CH₂Cl₂ followed by warming to ambient temperature affords 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.^{6,10} 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.

Dioxetane (X,Y)	Temp. Range, °C	E _a , kcal/mol	Log A	k _{rel} ^a (25°C)	τ _{1/2} ^a (25°C)
2a (O,O)	70.0 to 90.3	24.8	12.4	1 ^b	115 h
2b (S,S)	-11.5 to +20.5	18.8	13.6	3.96 x 10 ⁵	1.05 s
2c (S,O)	-11.5 to +21.5	17.4 ^c	12.2	1.66 x 10 ⁵	2.49 s
2d (MeN, MeN)	- 0.7 to +29.6	16.6	11.1	5.12 x 10 ⁴	8.09 s

^aCalculated 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 (λ_{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 (λ_{max} = 533 nm) and in methylcyclohexane (λ_{max} = 561 nm). A plausible explanation for this unusual emission involves an intramolecular exciplex.¹¹ Goto has reported chemiluminescence from an exciplex generated by the thermolysis of an indole-substituted dioxetane.^{3d} However, in that case emission from the fluorescent indole group as well as the exciplex was observed.

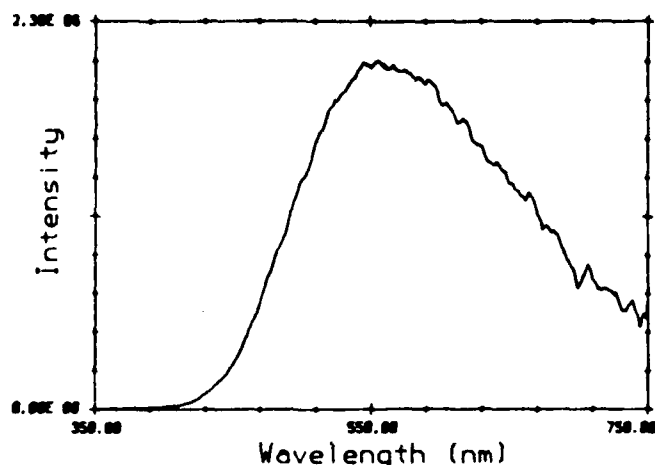
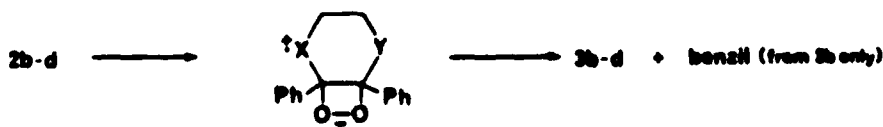


Figure 1. Chemiluminescence spectrum of dioxetane 2c in air-saturated *o*-xylene at -11°C , corrected for the decay of total light intensity during the scan.

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.^{1,3g} 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 σ^+ value (*p*-MeS, -0.16; *p*-Me, -0.31; *p*-MeO, -0.78; *p*-Me₂N, -1.7).^{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 σ^* orbital.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 ($E_{\text{ox}}^{\text{H}}: \text{Et}_3\text{N}, +0.96 \text{ V}; \text{Me}_2\text{S}, +0.88$)¹⁶ are dramatically less stable than a similar dioxetane with an alkoxy substituent possessing a much higher oxidation potential ($E_{\text{ox}}^{\text{H}} \text{ Et}_2\text{O}, > +2.5 \text{ V}$).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.

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7. 1b: mp 101-102°C (lit.⁸ 101.9-102.2°C); ¹H NMR (CDCl₃) δ 3.40 (s, 4H), 7.2 (m, 10H). 1c: 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). 1d: 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.
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13. Another indication of the greater stabilization of adjacent positive charge by oxygen vs. sulfur is the observation that ClCH₂OCH₂CH₃ hydrolyzes 1000-fold faster than ClCH₂SCH₂CH₃.^{14a} It should be noted, however, that Caserio found that this order of stabilization is reversed in the gas phase.^{14b}
14. (a) F. G. Bordwell, G. D. Cooper, and H. Morita, *J. Am. Chem. Soc.*, **79**, 376 (1957) and references therein; (b) J. K. Pau, M. B. Ruggera, J. K. Kim, and M. C. Caserio, *Ibid.*, **100**, 4242 (1978).
15. Intramolecular electron-transfer mechanisms have been proposed for the decomposition of unstable dioxetanes bearing easily oxidized aryl groups.³
16. Oxidation peak potentials determined by cyclic voltammetry in MeCN vs. SCE. Et₂O shows no oxidation at potentials less than 2.5 V.

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