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 (20) Taking into account bond lengths and van der Waals radii, one may expect that the X, Y, and Z atoms of the linear XYZ species should belong to the first row. NCS⁻ appears to be only weakly complexed by 1-H₆⁹⁺. Of course complex stability also depends on solvation effects.
 (21) Complexation of CO₂ and N₂O (whose size and shape are close to those of N₃⁻) and activation of CO₂ for hydration, reduction, and carboxylation represent another very interesting potential development. Of course, since these species are electrically neutral, the stability constants would probably be much weaker and ligand modification may be required.
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Substituent Effects on the Decomposition of 1,2-Dioxetanes

Sir:

1,2-Dioxetanes are of considerable interest as surprisingly stable strained peroxides, but especially because their thermolysis is accompanied by the emission of light. The mechanism leading to chemiluminescence is currently the subject of both theoretical¹ and experimental investigation.² We now report the observation of a substituent effect on dioxetane decomposition, which provides some insight into this mechanism.

An early suggestion by McCapra³ viewed the cleavage of dioxetanes as a concerted [$2_s + 2_s$] retrocycloaddition. Orbital symmetry conservation⁴ requires that one of the carbonyl scission products be formed in an electronically excited state. Subsequently, on the basis of thermochemical calculations, Richardson⁵ proposed an alternative mechanism involving rate-limiting O-O bond cleavage to give a biradical, which then rapidly yields carbonyl products. Such a mechanism is expected to show little if any response to electronic effects in the dioxetane. In contrast, the concerted mechanism could be sensitive to substitution, particularly if the excited state formed involved significant transfer of charge. Very recently cleavage of 1,2-dioxetanes by an intramolecular electron-transfer mechanism has been proposed,⁶ in which substituent effects should be manifested. Chemiexcitation by intermolecular electron transfer is established in electroluminescence⁷ and in a number of chemiluminescent peroxide reactions.⁸ The lack of a straightforward electronic effect on dioxetane decomposition⁹ has been taken as evidence, albeit only negative, for a biradical mechanism. By suitable substitution in the series of 1,6-diaryl-2,5,7,8-tetraoxabicyclo[4.2.0]octanes **2** we have obtained evidence suggesting that transfer of charge is important in the destabilization of dioxetanes, and in the efficient generation of singlet excited states from their decomposition.

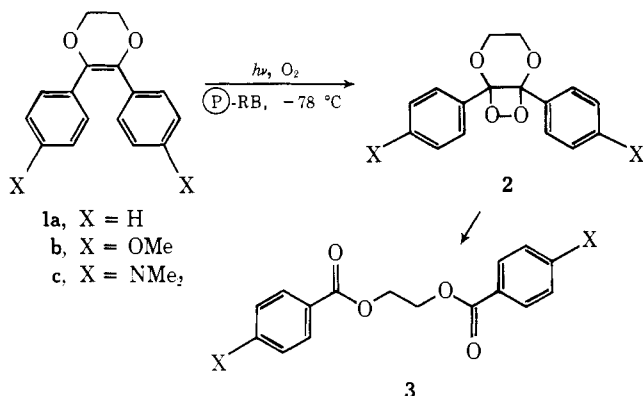


Table I. Activation Parameters and Rates of Decomposition for 1,2-Dioxetanes **2a-c**

Compd	E_a , kcal/mol	Log A	ΔH^\ddagger , kcal/mol ^a	ΔS^\ddagger , gibbs/mol ^a	Rel rate ^a
2a	24.8	12.39	24.2	-1.8	1.00 ^b
2b	24.0	12.38	23.5	-1.9	3.51
2c	19.7 ^c	11.23	19.1	-7.2	382

^a Calculated for 298.2 K. Errors ± 0.15 kcal/mol in ΔH^\ddagger and ± 0.5 gibbs/mol in ΔS^\ddagger determined by the method of Wiberg.¹⁶ ^b Corresponding to a rate constant of $1.62 \times 10^{-6} \text{ s}^{-1}$. ^c 19.7 ± 0.5 kcal/mol by the temperature drop method.¹⁷

Table II. Chemiluminescence Efficiencies of 1,2-Dioxetanes **2a-c**

Compd	$^1\phi_E$ ^a	$^3\phi_E$ ^b	$^3\phi_E/{}^1\phi_E$
2a ^c	1.9×10^{-4}	6.8×10^{-2}	350
2b ^d	2.4×10^{-4}	5.0×10^{-2}	210
2c ^e	0.22	—	<3.5 ^f

^a Chemiluminescence efficiency for the formation of singlet excited **3**. ^b Chemiluminescence efficiency for the formation of triplet excited **3**. ^c At 95.2 °C in *o*-xylene. ^d At 94.9 °C in *o*-xylene. ^e At 25.0 °C in toluene. ^f Based on a maximum value of $^3\phi_E = 1 - {}^1\phi_E$.

The dioxetanes **2a-c** were prepared by low temperature photooxygenation of the corresponding olefins **1a-c**¹⁰ using polymer-bound Rose Bengal (P-RB)¹² and methods previously described.^{13,14} Yields were typically $\sim 80\%$. The dioxetanes **2a-c** were insufficiently stable for combustion analysis, but all gave a centrosymmetric AA'BB' multiplet in the ¹H NMR spectrum, as has been observed for 2,5,7,8-tetraoxabicyclo[4.2.0]octane itself.¹⁵ The ¹³C NMR spectrum of **2a** showed quaternary carbons at 109 ppm corresponding to those in the dioxetane ring. Thermolysis of **2a-c** in *o*-xylene or toluene afforded quantitatively the expected diesters **3a-c**, which were fully characterized. Rates of decomposition of **2a-c** were studied by decay of chemiluminescence and were identical with those derived by ¹H NMR.

The rate constants obtained from chemiluminescence measurements were reproducible (variation $< \pm 3\%$) and gave excellent Arrhenius plots. The relevant activation parameters and rates are summarized in Table I. Controls showed that the marked differences observed for **2c** were not due to a change of solvent from *o*-xylene to toluene. The rates of decomposition of **2c** were further independent of concentration and presence of radical inhibitor or triplet quencher. Normal decomposition rates for trimethyl-1,2-dioxetane in our sample of toluene and the identical activation energy for **2c** obtained by the temperature drop method¹⁷ in this solvent indicate that the enhanced rates observed for **2c** (Table I) are not the results of impurity catalysis. Instead, a real substituent effect is involved.

The substituent effect on rates extends also to chemiluminescence efficiencies. Esters **3a** and **3b** are not detectably fluorescent, so excited singlet and triplet yields from **2a** and **2b** were determined from Stern-Volmer plots using 9,10-diphenylanthracene (DPA) and 9,10-dibromoanthracene (DBA) as energy acceptors.^{9,17} Ester **3c** is fluorescent¹⁸ and the chemiluminescence of **2c** matches this fluorescence, allowing direct evaluation of the singlet chemiluminescence efficiency in this case. The results are presented in Table II.¹⁹ Not only is the total yield of excited states higher for **2c**, but the singlet yield is increased more than three orders of magnitude compared with **2a**.

Examination of Table I shows that, no matter what the choice of substituent constant, a linear Hammett plot is not possible using the observed activation parameters, nor can a satisfactory isokinetic relationship be obtained. These observations, taken together with the chemiluminescence efficiencies

Scheme I

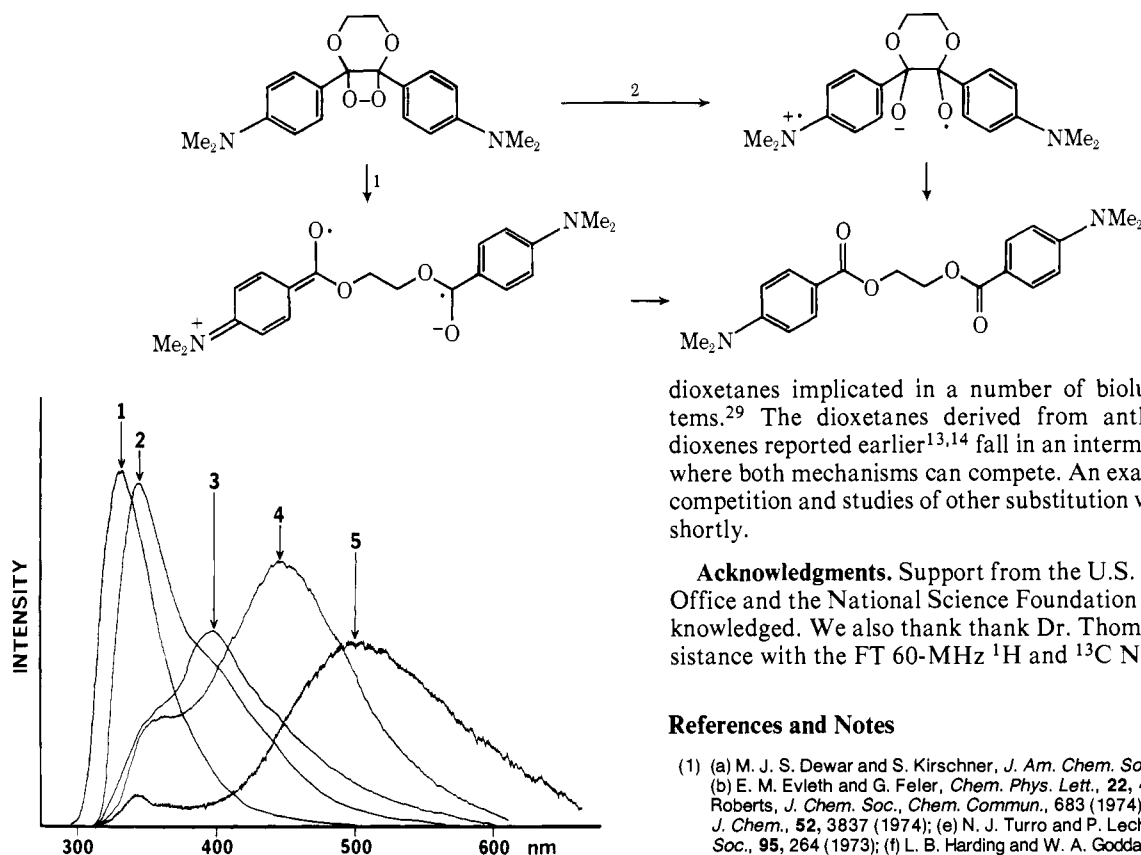


Figure 1. Fluorescence of diester **3c** in various solvents at 25 °C using 310-nm excitation: (1) methylocyclohexane, (2) toluene, (3) 1,4-dioxane, (4) 1,2-dichloroethane, (5) *N,N'*-dimethylformamide.

in Table II, suggest that **2c** decomposes by a mechanism different from that obtaining for **2a** and **2b**. Diester **3c** is distinct from **3a** and **3b** by virtue of its fluorescence, and the nature of this fluorescence may relate to the special properties of **2c**.

The fluorescence spectra of diester **3c** in a number of solvents are shown in Figure 1. In methylocyclohexane an uncomplicated emission from a π, π^* excited state is seen. In toluene, however, there is a feature on the long wavelength side of the emission. With increasing solvent polarity, this shoulder shifts and becomes much more pronounced at the expense of the short wavelength emission. This fact, together with the temperature dependence of the fluorescence spectrum, implicates an emission which has been suggested to arise from a twisted internal charge-transfer state.²²⁻²⁴

Present results are insufficient to allow firm conclusions about the mechanism of cleavage of **2c**. Nevertheless, several factors are suggestive of electron transfer mechanisms such as **16b** and **225** outlined in Scheme I. One electron oxidation of *N,N'*-dimethylaniline requires some 15 kcal/mol less energy than that of anisole,²⁶ and the facility with which charge can be transferred from the anilino moiety is illustrated by the spectroscopic properties of **3c**. Moreover, dioxetanes should be particularly readily reduced in view of the broad correlation between the ease of reduction of peroxides and their activation energies for thermolysis.^{27,28} The development of charged intermediates implies that cleavage of **2c** should be accelerated by polar solvents. There is indeed a marked effect of solvent polarity on the stability of **2c**, which is absent for **2a**, in accord with expectation.

The cleavage of **2a** and **2b** is consistent with a biradical mechanism, though a concerted mechanism can not be entirely excluded. Thus there appear to be two distinct mechanisms of dioxetane cleavage, with **3c** providing a clear analogy for the

dioxetanes implicated in a number of bioluminescent systems.²⁹ The dioxetanes derived from anthryl-substituted dioxenes reported earlier^{13,14} fall in an intermediate category, where both mechanisms can compete. An examination of this competition and studies of other substitution will be published shortly.

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- (30) Alfred P. Sloan Research Fellow, 1974-1978.

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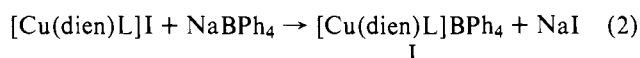
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Interaction of an Aliphatic C-H Bond with Copper in a Norbornene(diethylenetriamine)copper(I) Cation Complex

Sir:

As would be predicted by all structural models, a diethylenetriamine (H₂NCH₂CH₂N(H)CH₂CH₂NH₂ or dien) complex of copper(I) has an open coordination site through which another ligand can be bound. In addition, the use of a polydentate ligand, such as dien, should prevent both the lability toward substitution and the tendency to disproportionation of copper(I).^{1,2} For example, the complex [Cu(dien)-CO]BPh₄ is known as a thermally stable species.² We have now studied the binding of olefins to [Cu(dien)]⁺ and in one case have identified an expected and potentially significant Cu⁺-H-C bond.

A general method for preparing monomeric olefinic cationic complexes of copper(I)³ can be given by the equations⁴



where L = ethylene, norbornene, dimethyl maleate (DMM), and dimethyl fumarate (DMFu). The complex I can be recovered as a white crystalline solid, the stability of which depends on the nature of the olefin.⁵ The olefin can be displaced in every case by a molecule of CO or a molecule of P(OC₂H₅)₃.^{4,5} In this paper we report the structure, as determined by x ray, for the complex in which the olefin is bicyclo[2.2.1]hepta-2-ene. This particular complex has an unusual five-coordinate geometry and contains norbornene displaying a special bonding mode. Both these characteristics may be significant in understanding copper-photoassisted valence isomerization processes.⁶

Crystal Data. C₃₅H₄₃BCuN₃; mol wt, 580; orthorhombic; *a* = 19.804 (3), *b* = 16.551 (2), *c* = 9.440 (1) Å; *Z* = 4; *d*_{calcd} = 1.245 g/cm³; *μ* (Cu Kα) = 11.6 cm⁻¹; space group *Pna*2₁ (from structural analysis). Diffraction intensities were measured in the *θ*-2*θ* scan mode using Ni-filtered Cu Kα radiation on a Siemens on-line single-crystal diffractometer; 2463 independent reflections (6° < 2*θ* < 120°) were collected from a crystal of approximate dimensions 0.10 × 0.24 × 0.48 mm, sealed in a glass capillary under nitrogen. The structure was solved by the heavy-atom method and refined by full-matrix least-squares technique⁷ with anisotropic thermal parameters for all nonhydrogen atoms⁸ to an *R* value of 4.8%, for 1525 independent data (*I* > 2*σ*(*I*)). The crystals are composed of discrete [Cu(dien)(C₇H₁₀)]⁺ cations and BPh₄⁻ anions. A sketch of the macrocation is shown in Figure 1 and pertinent bond distances and angles are given in Table I. See the paragraph at the end of the paper regarding supplementary material.

The cation has no elements of symmetry. If the C=C bond is considered as occupying a single coordination site, the polyhedron about copper may be described as a slightly distorted trigonal bipyramid with the midpoint C(11)-C(12), N(1), and N(3) in the equatorial plane, N(2) and H(17) trans to each other in the axial positions. Besides the unusual coordination geometry for copper(I),¹ other chemically interesting structural features of the cation are (i) the monomeric nature of the copper(I) complex¹⁰ and (ii) the anchoring mode of the norbornene to the metal both through the olefinic C(11)-C(12) bond and the Cu-H-C interaction. A strong Cu-H(17) interaction can be established by the direct location of the interacting hydrogen.⁸ The Cu-H distance (2.01 (15) Å) compares very well with the only very short Mo-H interactions known (2.15 and 1.93 Å),^{11,12} all the other structurally identified metal-H interactions being far weaker.¹³ It was proposed that metal induced aliphatic C-H activation on coordinated olefins occurs through a metal-olefin interacting mode^{14,15} which is exemplified by the copper-norbornene interaction in

Table I. Bond Distances (Angstroms) and Angles (Degrees) with Their Estimated Standard Deviations

Coordination sphere		
Cu-N(1) = 2.008 (6)	N(1)-Cu-N(3) = 105.6 (3)	A-Cu-N(2) = 108.2 (4)
Cu-N(2) = 2.252 (7)	N(1)-Cu-A ^a = 125.6 (4)	A-Cu-H(17) = 56 (5)
Cu-N(3) = 2.109 (8)	N(3)-Cu-A ^a = 128.4 (4)	N(2)-Cu-H(17) = 165 (5)
Cu-C(11) = 2.19 (1)	N(1)-Cu-N(2) = 83.3 (3)	C(11)-Cu-C(12) = 36.8 (5)
Cu-C(12) = 2.19 (1)	N(1)-Cu-H(17) = 106 (4)	C(17)-H(17)-Cu = 158 (17)
Cu-A ^a = 2.08 (1)	N(3)-Cu-N(2) = 81.5 (4)	
Cu-H(17) = 2.01 (15)	N(3)-Cu-H(17) = 107 (4)	
Cu-C(17) = 2.78 (1)		
Norbornene ligand		
C(11)-C(12) = 1.38 (2)	C(16)-C(17) = 1.54 (2)	C(13)-C(14)-C(15) = 105.8 (7)
C(11)-C(16) = 1.37 (2)	C(13)-C(17) = 1.56 (2)	C(14)-C(15)-C(16) = 98.9 (8)
C(12)-C(13) = 1.39 (2)	C(11)-C(12)-C(13) = 109.3 (10)	C(15)-C(16)-C(11) = 103.5 (10)
C(13)-C(14) = 1.52 (1)	C(12)-C(13)-C(14) = 107.5 (12)	C(15)-C(16)-C(17) = 103.7 (11)
C(14)-C(15) = 1.53 (1)	C(12)-C(13)-C(17) = 100.3 (10)	C(11)-C(16)-C(17) = 104.2 (12)
C(15)-C(16) = 1.57 (1)	C(14)-C(13)-C(17) = 97.9 (10)	C(16)-C(17)-C(13) = 90.5 (12)
C(17)-H(17) = 0.81 (15)		

^a A is the midpoint of C(11)-C(12).