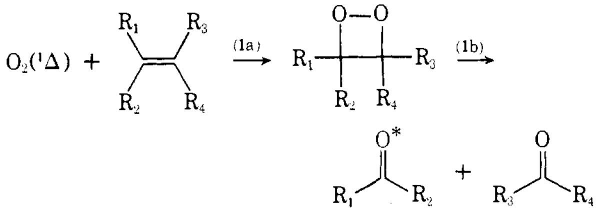
Formaldehyde (A ${}^1A_2 \rightarrow$ X ${}^1A_1$) Chemiluminescence in the Gas Phase Reaction of O_2 (a ${}^1\Delta_g$) Plus Ethyl Vinyl Ether

Sir:

Several reactive channels are known for the reactions of O_2 (${}^1\Delta_g$) with olefins.[1] Cycloaddition to produce 1,2-dioxetanes is particularly interesting since these compounds readily undergo thermally or photolytically induced decomposition to produce an electronically excited carbonyl product. Thus, reaction sequence 1 represents an efficient means to produce electronically excited products from reaction of a stable ground state molecule, olefin, with a very low lying electronically excited molecule, O_2 (${}^1\Delta$). Reaction 1a has been shown to be the sole reactive channel in solution, for those activated monoolefins which do not have allylic hydrogens.[1-4] Chemiluminescence arising from dioxetane thermal decomposition has been observed but not well characterized.[1a,b,5] We report the first gas phase study of reaction 1a and present a high resolution spectrum of a primary excited product of a dioxetane decomposition. In addition, we show via experimental and thermochemical arguments, that the adduct of O_2 (${}^1\Delta$) plus ethyl vinyl ether must pass through a *chemically activated* dioxetane configuration lying at higher energy than the transition state for thermal decomposition of ethoxy-1,2-dioxetane.[6]



(1)

We have investigated the title reaction in a discharge flow system[7a] with mass spectrometric[7b] and spectroscopic detection. Good quality visible spectra have been observed and assigned showing: formaldehyde (A ${}^1A_2 \rightarrow X^1A_1$) chemiluminescence (Figure 1), the oxygen "dimol" emission (attributed to the energy pooling process ${}^1\Delta_g + {}^1\Delta_g \rightarrow {}^3\Sigma_g^- + {}^3\Sigma_g^- + h\nu$),[8] and O_2 (b ${}^1\Sigma_g^+ \rightarrow$ X ${}^3\Sigma_g^-$) emission.[9] In general, the (A → X) emissions of carbonyl compounds are relatively structureless and difficult to recognize. The notable exception is formaldehyde which has a very characteristic spectrum in the region 350-500 nm (thus ethyl vinyl ether is an ideal substrate molecule for the study of reactions 1 because it offers the possibility of observing a significant amount of formaldehyde chemiluminescence).

The experiments reported in Table I were performed at a total pressure of 4.3 Torr, a temperature of 620 K, and a flow velocity of 1.5 m sec^{-1}. Oxygen or a 3% oxygen in helium mixture was discharged with 100 W of microwave power, and oxygen atoms were removed by the procedure of Herron and Huie.[10] This consisted of passage of the discharged gas over a freshly deposited HgO surface followed by addition of a small amount of NO_2. Spectroscopic data were obtained with a Jarrell-Ash f/8.6, 0.5-m Ebert spectrometer with grating blazed at 400 nm using a cooled EMI 9558QB photomultiplier and SSR digital photon counting equipment. The reported photon counts (Table I) are the means of several 10-sec counting periods.

Inspection of Table I shows significant amounts of formaldehyde chemiluminescence when O_2* was treated with ethyl vinyl ether.[11] The H_2CO* chemiluminescence was found to be first order in ethyl vinyl ether and strongly temperature dependent, having an activation energy of 9.8 ± 1.0 kcal mol^{-1}. The measurement of E_a was obtained by plotting the intensity of the chemiluminescence vs. $1/T$, over the temperature range 600-750 K. The large error limit, representing three times the standard deviation, was assigned after consideration of the complications introduced by probable nonradiative loss of H_2CO* (see below).[12] Comparison of our experimental E_a with the E_a values observed for decomposition of various 1,2-dioxetanes suggests that the rate limiting step in our system is reaction 1a rather than 1b. Three requirements must be met in order for this to be true. (a) Reaction 1a must have a lower E_a than 1b, (b) the adduct of O_2 (${}^1\Delta$) plus ethyl vinyl ether must be formed at an energy equal to or greater than the energy of the transition state for thermal decomposition of ethoxy dioxetane, (c) the fragmentation of this adduct must occur on a faster time scale than collisional stabilization. Kearns[1c,4] has given orbital correlation diagrams which indicate that (a) is satisfied, our thermochemical calculations (see below) show that (b) is satisfied, and (c) was directly tested by experiment.

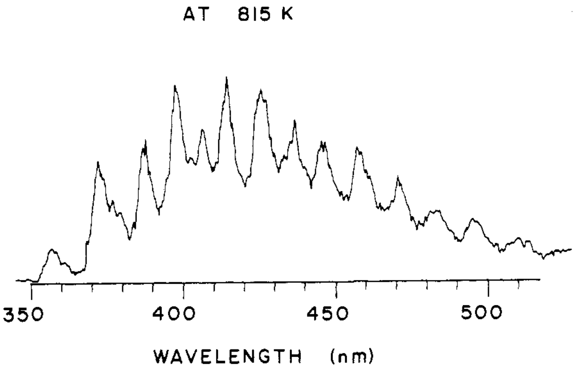


Figure 1. Chemiluminescence spectrum from the reaction of ethyl vinyl ether with O_2 (a ${}^1\Delta_g$). Spectral slit width is 1.0 nm.

Table I. Photon Counts under Various Experimental Conditions[a]

		O_2* in O_2[b]	O_2* in He–O_2[b]
With fuel[c]	HCHO (A → X) emission	1200	90
	Dimol emission	13	2
	O_2 (b → X) emission	320	8
Without fuel[c]	HCHO (A → X) emission	2	3
	Dimol emission	130	1
	O_2 (b → X) emission	6900	40

[a] Typical background is ca. 10 counts with a 10-sec counting period. [b] O_2* consists principally of O_2 (a ${}^1\Delta_g$) plus lesser amounts of O_2 (b ${}^1\Sigma_g^+$). [c] Fuel is ethyl vinyl ether.

Collisional stabilization experiments were performed in a tandem reactor apparatus consisting of a heated upstream reactor, R_I, an intermediate unheated region, and a heated downstream reactor, R_{II}. The reactants O_2 (${}^1\Delta$) and ethyl vinyl ether were allowed to mix in R_I at a total pressure of 4 Torr and temperatures ranging from 518 to 670 K, and R_{II} was maintained at 800 K. Formaldehyde chemiluminescence was observed in both reactors by axial viewing with photomultipliers and broad band filters (420 ± 40 nm). The absence of collisional stabilization was shown by introducing a large excess of 2,5-dimethylfuran in the unheated region, thus removing O_2 (${}^1\Delta$). This caused a 100-fold reduction of the emission intensity in R_{II} (the reduction was to the background level). Thus chemiluminescence in R_{II} re-

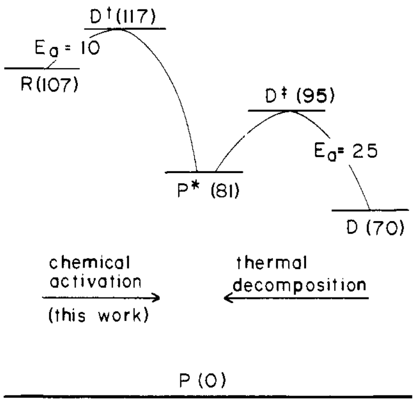


Figure 2. Enthalpy diagram comparing the chemical activation and thermal decomposition systems. (Absolute enthalpies are in kilocalories per mole and their sources are: $\Delta H_f°$ (O_2 a $^1\Delta_g$) = 22.6, L. Herzberg and G. Herzberg, *Astrophys. J.*, **108**, 163 (1947); $\Delta H_f°$ (H_2CO) = −27.7, ref 12; T_e (H_2CO^* $^1A_2$) = 80.5, G. Herzberg, "Electronic Structure and Electronic Spectra of Polyatomic Molecules", Van Nostrand, New York, N.Y., 1966. Values estimated from group additivity (ref 12) are: $\Delta H_f°$ ($H_2CCHOEt$) = −35.0; $\Delta H_f°$ (ethoxy-1,2-dioxetane) = −50.28 (using E (ring strain) = 26). Group additivity was combined with $\Delta H_f°$ (HCOOMe) = −83.6, Stull et al., "The Chemical Thermodynamics of Organic Compounds", Wiley, New York, N.Y., 1969, to obtain $\Delta H_f°$ (HCOOEt) = −92.10.) The symbols are: R = O_2 ($^1\Delta$) plus ethyl vinyl ether, P* = H_2CO^* plus HCOOEt, D = ground state ethoxy dioxetane, D‡ = transition state for thermal decomposition of ethoxy dioxetane, D† = chemically activated ethoxy dioxetane, P = ground state H_2CO plus HCOOEt. The figures in parentheses are enthalpies relative to P taken as zero.

quires the simultaneous presence of O_2 ($^1\Delta$) and ethyl vinyl ether and is rate limited by reaction 1a and *not by thermal decomposition of ethoxy dioxetane formed in R_I*. This result proves that requirement c was satisfied and establishes, via comparison with the gas kinetic collision frequency, that the lifetime of the adduct formed by reaction 1a is less than 10^{-7} sec.[13]

Our emission spectrum of the 350-500-nm region (Figure 1) is in good qualitative agreement with cool flame emission spectra reported by Sheinson and Williams.[14a] These authors established that their cool flame spectra were free of both underlying continua and emission from excited species other than H_2CO^*.[14] Close comparison of their results with Figure 1 suggests that electronically excited ethyl formate or other species can contribute only a minor component to our chemiluminescence spectrum. This raises questions concerning energy partitioning in dioxetane fragmentation.

The enthalpy diagram shown in Figure 2 was constructed using known thermochemical data,[15] group additivity rules,[15,16] and activation parameters for thermal decomposition of various dioxetanes.[17] From this we estimate that the adduct of O_2 ($^1\Delta$) plus ethyl vinyl ether is initially formed with ca. 22 kcal/mol more energy than is needed for thermal decomposition of ethoxy dioxetane. Furthermore, the adduct lies ca. 47 kcal/mol above the ground state of ethoxy dioxetane. We have shown that this adduct is not collisionally stabilized at the pressures of this work, hence we envision a rapid passage of the system to a pseudo continuum of vibronically excited product states (either $HCOOEt^*$ + H_2CO or H_2CO^* + HCOOEt). At the available energy the density of vibronic states of $HCOOEt^*$ must be much greater than that of H_2CO^* and if the energy is partitioned statistically, the product pair, H_2CO + $HCOOEt^*$, would be formed preferentially.[18] However, this argument is complicated by the fact that dioxetanes exhibit a preference for formation of *triplet* carbonyl fragments,[1a] and (a → X) phosphorescence is too weak to be observed in our apparatus. A further difficulty is that vibronically excited H_2CO^* is known to have a very short lifetime with respect to predissociation as well as nonradiative transition to the vibrationally excited ground state.[19] In addition, ethyl formate decomposes to ethylene plus formic acid with E_a = 48 kcal/mol. Thus, most, if not all, $HCOOEt^*$ will decompose via this radiationless path.[20]

In summary we believe that the elucidation and comparison of energy partitioning in thermally and chemically activated 1,2-dioxetane fragmentations is a very interesting problem and further work is needed. Additional investigations are currently in progress in our laboratory.

Acknowledgments. One of the authors (D. J. Bogan) thanks Professors N. J. Turro and K. R. Kopecky for helpful discussions. He also thanks the Naval Research Laboratory for generously providing facilities during his tenure as a National Research Council Resident Research Associate.

References and Notes

(1) For discussion see the following reviews, and references contained therein: (a) N. J. Turro and P. Lechtken, *Pure Appl. Chem.*, **33**, 363 (1973); (b) D. C. S. Lee and T. Wilson, "Chemiluminescence and Bioluminescence", J. Lee, D. M. Hercules, and M. J. Cormier, Ed., Plenum Press, New York, N.Y., 1973; (c) D. R. Kearns, *Chem. Rev.*, 71, 395 (1971); (d) R. P. Wayne, *Adv. Photochem.*, **7**, 311 (1969).

(2) P. D. Bartlett, G. D. Mandenhall, and A. P. Schaap, *Ann. N.Y. Acad. Sci.*, **171**, 79 (1970).

(3) (a) By "activated" we mean that one or more of the groups R_1–R_4 is a good electron donor. Ethoxy and phenyl groups fit this definition.[2] Kearns[1c,4] has predicted that substituted ethylenes having a low Π ionization potential will react by path 1a. (b) A referee has pointed out that 1,2-cycloaddition of O_2 ($^1\Delta$) to some unactivated olefins has been observed. See J. H. Wieringa, J. Strating, H. Wynberg, and W. Adam, *Tetrahedron Lett.*, 169 (1972); P. D. Bartlett and M. S. Ho, *J. Am. Chem. Soc.*, **96**, 627 (1974).

(4) D. R. Kearns, *J. Am. Chem. Soc.*, **91**, 6554 (1969).

(5) E. H. White, P. D. Wildes, J. Wiecko, H. Doshan, and C. C. Wei, *J. Am. Chem. Soc.*, **95**, 7050 (1973).

(6) A concise discussion of the basic ideas of chemically activated unimolecular decomposition and of collisional stabilization of chemically activated species has been given by P. J. Robinson and K. A. Holbrook, "Unimolecular Reactions", Wiley-Interscience, New York, N.Y., 1972, pp 268–275.

(7) (a) T. C. Frankiewicz, F. W. Williams, and R. G. Gann, *J. Chem. Phys.*, **61**, 402 (1974); (b) R. G. Gann, D. J. Bogan, T. C. Frankiewicz, and R. S. Sheinson, in preparation.

(8) S. J. Arnold, E. A. Ogryzlo, and H. Witzke, *J. Chem. Phys.*, **40**, 1769 (1964).

(9) We observed the O_2 (b → X) emission at 760 nm with a 2-nm spectral slit width. The above wavelength falls in the R branch of the transition and gives good intensity under these conditions. The structureless dimol emission was observed at 634 nm, formaldehyde at 424 nm.

(10) (a) J. T. Herron and R. E. Huie, *Ann. N.Y. Acad. Sci.*, **171**, 229 (1970); (b) R. E. Huie and J. T. Herron, *Int. J. Chem. Kinet.*, **5**, 197 (1973).

(11) Whenever O_2 ($^1\Delta$) is present there exists a small steady state concentration of O_2 ($^1\Sigma$) formed by energy pooling (O_2 ($^1\Delta_g$) + O_2 ($^1\Delta_g$) → O_2 ($^1\Sigma_g^+$) + O_2 ($^3\Sigma_g^-$)) and lost by heterogeneous and homogeneous quenching. Kearns[1c] has given a Walsh-type correlation diagram showing that O_2 ($^1\Sigma$) plus substituted olefin correlates endothermically with an electronically excited dioxetane, hence the concerted reaction forming ground state dioxetane cannot occur. We assume that O_2 ($^1\Sigma$) does not contribute to formaldehyde chemiluminescence in our system.

(12) If both radiative and nonradiative paths for loss of H_2CO^* exist, with probabilities of $\phi_r = 1 - x$ and $\phi_{nr} = x$, respectively, an accurate measurement of E_a requires that x be invariant over the temperature range of measurement. The quantity x is a function of the vibronic energy in excess of the threshold energy of the H_2CO^* (A $^1A_2$) state. The largest component of this energy (22 kcal/mol) is due to chemical activation (see text and Figure 2), since the difference between the thermal Boltzmann vibrational energies of H_2CO^* at 600 and 750 K is ca. 1 kcal/mol. Hence the assumption that x is nearly invariant in this temperature range should be valid.

(13) We would like to use the reduction in emission intensity upon addition of dimethylfuran to establish a ratio of decomposition to stabilization and thereby get a better estimate of the lifetime. However, in order to do this rigorously, we require the relative quantum yields and detection efficiencies for H_2CO^* (singlet and triplet) and $HCOOEt^*$ (singlet and triplet) for both chemical activation and thermal decomposition systems; these data are beyond our present capabilities.

(14) (a) R. S. Sheinson and F. W. Williams, *Combust. Flame*, **21**, 221 (1973). (b) These authors used the known spectroscopic constants of the H_2CO^* (A $^1A_2$) state to show that the line widths in their spectra were attributable, at all experimental gas kinetic temperatures, to the rotational temperature of H_2CO^*.

(15) S. W. Benson, "Thermochemical Kinetics", Wiley, New York, N.Y., 1968.

(16) H. E. O'Neal and W. R. Richardson, *J. Am. Chem. Soc.*, **92**, 6553 (1970); **93**, 1828 (1971). We have followed these authors in assigning a strain energy of 26 kcal/mol to the 1,2-dioxetane ring.

(17) Data cited in ref 1a.

(18) Nonstatistical energy partitioning requires a very short lived activated complex. This is consistent with the results of the collisional stabilization experiments.

(19) (a) E. S. Yeung and C. B. Moore, *J. Chem. Phys.*, **58**, 3988 (1973); (b) R. L. Jaffe, D. M. Hayes, and K. Morokuma, *J. Chem. Phys.*, **60**, 5108 (1974).

(20) (a) S. W. Benson and H. E. O'Neal, "Kinetic Data on Gas Phase Unimolecular Reactions", NSRDS-NBS 21, U. S. Department of Commerce, 1970; (b) We thank S. W. Benson for calling this to our attention.

Denis J. Bogan,* Ronald S. Sheinson
Richard G. Gann, Frederick W. Williams
Chemical Dynamics Branch, Naval Research Laboratory
Washington, D.C. 20375

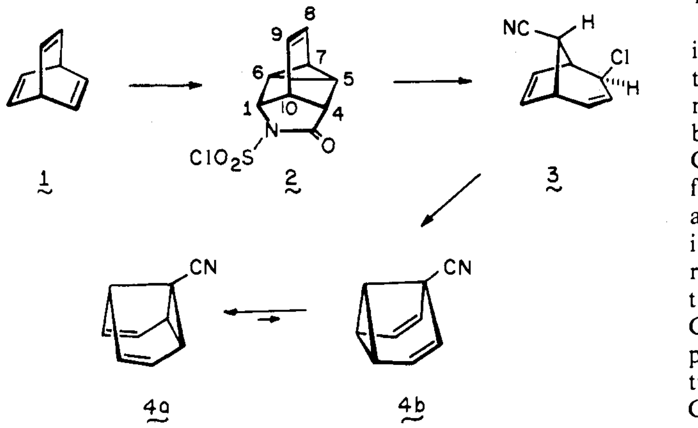
Received September 28, 1974

1(5)-Cyanosemibullvalene from Barrelene. Spectral and Crystal Structure Analysis of the Marked Equilibrium Preference Exerted by an Efficient π-Electron Acceptor Substituent

Sir:

Despite the recent development of a variety of synthetic routes to the semibullvalene nucleus,[1-6] the most versatile of these[4,5] still fails in its ability to direct the introduction of such groups as cyano and carbalkoxy. Consequently, the effect of efficient π-electron acceptor substituents on the facile Cope rearrangement process[7] remained to be assessed. In a particularly stringent test of predicted[8] strong equilibrium influences, a highly serviceable route to 1(5)-cyanosemibullvalene has been devised, and the detailed structural features of this molecule have been elucidated. In agreement with theory, the impact of the cyano functionality is to shift the Cope equilibrium toward that direction in which bonding to the cyclopropane ring is heavily preferred. Since a single 7-cyano substituent does not suffice to perturb the cycloheptatriene equilibrium in the norcaradiene direction[9] (two are necessary),[10,11] the structural features peculiar to the semibullvalene nucleus are seen to respond most dramatically to electronic imbalances.

In design, the synthetic scheme is founded upon skeletal reorganization and concomitant suitable functionalization of barrelene (**1**)[12] and proceeds initially by uniparticulate electrophilic addition[13] of chlorosulfonyl isocyanate in dichloromethane solution. Mixing of equimolar quantities of the two reagents at −78° followed by gradual warming during 1 hr to room temperature led in 74% yield to an oily product consisting chiefly of *N*-chlorosulfonyl lactam **2**.[14,15] This material was not purified but treated directly with dimethylformamide at 75-95° for 40 hr.[16] Isolation of the resulting product by preparative VPC at 130° (10% SE-30) afforded *exo*-4-chloro-*anti*-8-cyanobicyclo[3.2.1]octa-2,6-diene (**3**) as a colorless solid, mp 70-71° (31%). Structural assignment to **3** follows from its elemental composition, an intense infrared band (in CH_2Cl_2) at 2245 cm^{-1}, and the ^1H NMR spectrum.[17] As with many dibenzobicyclo[3.2.1]octadienes,[18] the low level of spin interaction between H_4 and H_5 (3 Hz) as well as between the pair of bridgehead protons (H_1,H_5) and H_8 (<1 Hz) uniquely defines the stereochemical features. Treatment of **3** with potassium *tert*-butoxide in DMSO-THF gave **4** in 56% isolated (VPC) yield as colorless white needles, mp 50.5-51°. Quantitative assessment of the **4a** ⇄ **4b** equilibrium constant was not possible on the basis of its ^1H NMR behavior. Although **4a** was clearly indicated to be the predominant isomer, the absence of spectral alteration from 0 to −115° (in CD_2Cl_2-CF_2Cl_2) and the small changes witnessed in the 0 to +99° range ($Cl_2C{=}CCl_2$ solution) were not conducive to measurement of K_{eq}.[5] An estimate was possible by ^{13}C NMR spectroscopy,[19] given the assumption that Anet's value for the chemical shift of C_4 and C_6 (131.8 ppm) in "frozen" semibullvalene recorded at −160° [7c] is relatable to the same carbon atoms in **4a** (130.0 ppm).[20] Using these data, a $K_{eq}{}^{25°}$ of 1.05×10^{-2} results, which translates into an energy difference of 2.8 kcal/mol or 0.12 eV favoring **4a**.



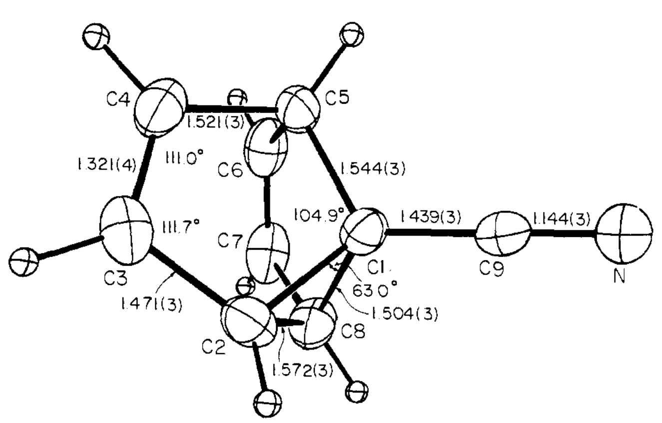


Figure 1.

Full characterization of **4** in the solid state at −45° has been achieved by three-dimensional X-ray crystallographic techniques. As a consequence of the relative stabilities of **4a** and **4b**, the crystals consist wholly of tautomer **4a**. The substance crystallizes with the orthorhombic space group $P2_12_12_1$, with four molecules per cell. The cell constants are: a = 6.693 (2), b = 8.301 (3), and c = 12.393 (4) Å. The phase problem was solved by direct methods using the program MULTAN[21] and the structure refined by the usual methods. After refinement of all the atomic parameters including those of the hydrogen atoms, the R factor is 0.056 for 1192 independent reflections.[22]

The molecule, with bond distances and angles of interest, is illustrated in Figure 1. As shown in Figure 2, the structure possesses nearly exact noncrystallographic mirror symmetry, with the mirror containing C(9), C(1), and C(5) and bisecting the cyclopropane ring. Bonds C(3)-C(4) and C(6)-C(7) are highly localized and characteristically olefinic. The distances between C(4) and C(6) [2.352 (3) Å] and C(3) and C(7) [3.072 (3) Å] are too long for bonding interaction and quite possibly can be no shorter because of repulsive interactions between the opposed π orbitals. The two five-membered rings are significantly nonplanar, with C(3)-C(4) and C(6)-C(7) being forced outward from the planes of the other three atoms in each ring. The angle between the two planes formed by C(2)-C(3)-C(4)-C(5) and C(5)-C(6)-C(7)-C(8) is 98.1°, placing the p-π lobes of