A Strongly Chemiluminescent Dioxetanimine Dianion Fragmentation: Reaction of the Dicyanoanthracene Radical Anion with Superoxide Ion

**David T. Breslin and Marye Anne Fox***

Contribution from the Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, Texas 78712

Abstract: Efficient chemiluminescence accompanies the oxygenation of 9,10-dicyanoanthracene (DCA) with potassium superoxide and that of the DCA radical anion by O_2 in several polar aprotic solvents ($\phi_{cl} \sim 0.1\%$). The reaction quantitatively affords potassium cyanate and potassium 10-cyanoanthrolate, the emitting species. The observed kinetics of chemiluminescence are consistent with two competitive consecutive second-order reaction steps. The first step is reduction of DCA to its radical anion by superoxide ion, which, in a second slower step, reacts with a second equivalent of superoxide, leading to the observed products and luminescence. A dioxetanimine dianion is postulated as the intermediate whose decomposition accesses the lowest excited singlet state of potassium 10-cyanoanthrolate. AM-1 semiempirical calculations confirm that fragmentation of the proposed dioxetanimine dianion intermediate has a low activation energy barrier and is stepwise. Chemiluminescence is solvent-sensitive, correlating with the free energy of electron transfer for the reduction of DCA by superoxide. A strong dependence of ϕ_{cl} on dissolved O_2 concentration is exhibited, and three O_2-dependent non-chemiluminescent pathways are identified.

Introduction

Thermolysis of high-energy starting materials like strained 1,2-dioxetanes is often accompanied by the generation of products in electronically excited states, and chemiluminescence of such systems has been extensively investigated.[1–5] Structural variation of the strained four-membered ring strongly influences the thermal stability and chemiluminescence of dioxetanes. For example, in
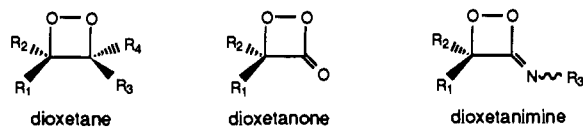
simple dioxetanes electron-donating substituents (such as amines) usually raise the ratio of excited-state singlet to excited-state triplet products.[6] The physiochemical and chemiluminescent properties of dioxetanones, such as peroxylactone intermediates postulated in luciferin bioluminescence,[7,8] are drastically altered by incorporating an exocyclic carbonyl functionality as compared with their simple dioxetane counterparts. Luminescence arising from dioxetanone decomposition is catalyzed by the presence of aromatic sensitizers with low ionization potentials, although no parallel effect takes place with simple dioxetanes. Enhanced chemiluminescence for dioxetanones under these conditions originates from chemically initiated electron-exchange luminescence (CIEEL).[9–11]

Previous investigations of other dioxetane-related compounds have focused primarily on the chemiluminescence of dioxetanones,[10,12–16] and the closely related isoelectronic dioxetanimines[17–21] have received little attention. The intermediacy of dioxetanimines has long been postulated in both chemiluminescent and non-chemiluminescent reactions, e.g., in the base-catalyzed decomposition of α-cyanohydroperoxides first studied by Aurich[22] and by Dulog.[23] Isolation of the corresponding carbonyl-containing compound (eq 1) and detection of cyanate
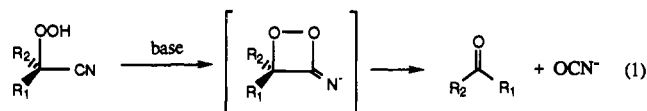
by a colorimetric test were offered as evidence for a dioxetanimine anion intermediate. Chemiluminescence via a potential dioxetanimine intermediate was also proposed in the hydrogen peroxide and base-catalyzed decomposition of 10-methyl-9-cyanoacridinium,[17] the luminescent species being identified as *N*-methylacridone. Dioxetanimines prepared by the reaction of ketenimines and singlet oxygen are stable at low temperatures and are weakly chemiluminescent upon heating, with decomposition proceeding via a biradical.[19,21]
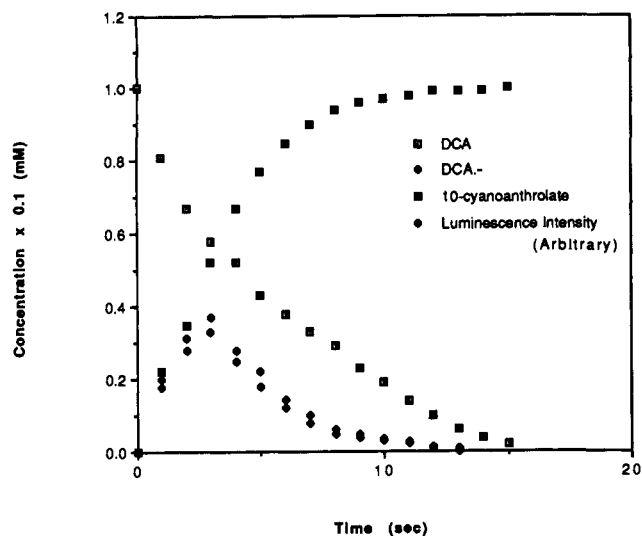
This paper describes chemiluminescence initially observed in the oxygenation of the DCA radical anion, which we suggest proceeds through a dioxetanimine derivative. Chemiluminescence

® Abstract published in *Advance ACS Abstracts*, November 1, 1993.
(1) Turro, N. J.; Lechtken, P.; Yekta, A. *Acc. Chem. Res.* **1974**, *7*, 97.
(2) Wilson, T. *Int. Rev. Sci.: Phys. Chem., Ser. Two* **1976**, *9*, 265.
(3) Adam, W. *Adv. Heterocycl. Chem.* **1977**, *21*, 437.
(4) Horn, K. A.; Koo, J.; Schmidt, S. P. *Mol. Photochem.* **1978**, *9*, 1.
(5) Adam, W.; Baader, W. J. *Bull. Soc. Chim. Belg.* **1984**, *93*, 496.
(6) Winberg, H. F.; Carnahan, J. F.; Coffman, D. D.; Brown, M. J. *J. Am. Chem. Soc.* **1965**, *87*, 2055.
(7) Hopkins, T. A.; Seliger, H. H.; White, E. H.; Cass, M. W. *J. Am. Chem. Soc.* **1967**, *89*, 7148.
(8) McCapra, F.; Chang, Y. C.; Francois, V. P. *J. Chem. Soc., Chem. Commun.* **1968**, 22.
(9) Schuster, G. B. *Acc. Chem. Res.* **1979**, *12*, 366.
(10) Schuster, G. B.; Horn, K. A.; Zupancic, J. *J. Am. Chem. Soc.* **1980**, *102*, 5279.
(11) Porter, J. E.; Schuster, G. B. *J. Org. Chem.* **1985**, *50*, 4068.

(12) Adam, W.; Yany, F. *Photochem. Photobiol.* **1980**, *31*, 267.
(13) Turro, N. J.; Chow, M.-F. *J. Am. Chem. Soc.* **1980**, *102*, 5058.
(14) Schmidt, S. P.; Vincent, M. A.; Dykstra, C. E.; Schuster, G. B. *J. Am. Chem. Soc.* **1981**, *103*, 1292.
(15) Schuster, G. B.; Schimdt, S. P. *Adv. Phys. Org. Chem.* **1982**, *18*, 187.
(16) Jaroszewski, J. W.; Ettlinger, M. G. *J. Org. Chem.* **1988**, *53*, 4637.
(17) McCapra, F.; Richardson, D. G. *Tetrahedron Lett.* **1964**, *43*, 3167.
(18) Sawaki, Y.; Ogata, Y. *J. Am. Chem. Soc.* **1977**, *99*, 6313.
(19) Ito, Y.; Matsuura, T.; Kondo, H. *J. Am. Chem. Soc.* **1979**, *101*, 7105.
(20) Ito, Y.; Yokoya, H.; Kyono, K.; Yamamura, S.; Yamada, Y.; Matsuura, T. *J. Chem. Soc., Chem. Commun.* **1980**, 898.
(21) Adam, W.; Lucchi, O. D.; Quast, H.; Recktenwald, R.; Yany, F. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 788.
(22) Aurich, H. G. *Tetrahedron Lett.* **1964**, *12*, 657.
(23) Dulog, L.; Vogt, W. *Tetrahedron Lett.* **1966**, *42*, 5169.

A Chemiluminescent Dioxetanimine Dianion Fragmentation

J. Am. Chem. Soc., Vol. 115, No. 25, 1993 11717

from the electrochemical reduction of DCA in the presence of oxygen has been reported previously,[24] but the exact nature and efficiency of the reaction were ambiguous because mechanistic and product studies were incomplete. We describe herein this chemiluminescent reaction in greater mechanistic detail, with complete product identification and with determination of the emission quantum yield. We also present mechanistic evidence and AM-1 semiempirical molecular orbital calculations that show this reaction probably takes place through a novel dioxetanimine dianion intermediate.

Experimental Section

Reagents. Potassium superoxide (Aldrich), tetrabutylammonium hexafluorophosphate (TBAPF$_6$, Southwestern Analytical), and semicarbazide hydrochloride (Matheson) were used without further purification. Dimethylformamide (Baker) was dried over molecular sieves. DMSO (Mallinckrodt) was vacuum distilled from calcium hydride. Tetrahydrofuran (Aldrich spectrograde) was dried by distilling from sodium metal. Acetonitrile was distilled from calcium hydride. DCA (Kodak) was recrystallized twice from nitromethane.

Electrochemical Measurements. A Bioanalytical Systems 100 potentiostat equipped with a Houston Instruments DMP-40 plotter was used to record cyclic voltammetry data and conduct bulk electrolyses. A three-electrode configuration consisting of a platinum working, a Ag/AgCl quasi-reference, and a platinum auxiliary electrode was used. The electrolyte was 0.1 M TBAPF$_6$ in one of several solvents, and oxygen was removed by a N$_2$ purge.

Spectral Measurements. Fluorescence and chemiluminescence spectra were recorded on an SLM Aminco SPF-500 spectrofluorometer equipped with an IBM PC and IBM 6180 plotter. Absorption spectra were recorded on a Hewlett-Packard 8451-A diode array spectrophotometer equipped with a Hewlett-Packard 7470 plotter.

Product Studies. The identity of the emitting species, potassium 10-cyanoanthrolate,[24] was confirmed by comparison with absorption and emission spectra of an authentic sample. The concentration of 10-cyanoanthrolate anion was determined by absorption spectroscopy at 516 nm, ϵ = 9200 M^{-1} cm^{-1}. Cyanate was determined by preparing the hydrazodicarbamide derivative as described by Ault.[25] A suspension of 0.25 g (1.1 mmol) of DCA and 0.15 g (2.0 mmol) of KO$_2$ in 50 mL of DMF was stirred under a N$_2$ atmosphere at room temperature for 2 h. At that time, the chemiluminescence had ceased, and 50 mL of a saturated semicarbazide hydrochloride solution in water was added. The resulting white precipitate was collected by filtration. The crude yield was 0.12 g (1.0 mmol, 100%) of a white crystalline material. Recrystallization from ethanol afforded pure hydrazodicarbamide (H$_2$-NCONHNHCONH$_2$) a white solid, 0.11 g, mp 254–255 °C.[25]

Kinetics. A 1 mL aliquot of a solution of 1–10 × 10^{-5} M DCA in DMSO and a 1-mL aliquot of 1–10 × 10^{-5} M KO$_2$ in DMSO were simultaneously syringed into a 1-cm quartz cuvette equipped with a magnetic stirrer. The kinetics were followed by monitoring the luminescence or changes in the visible absorption spectra. Quantum yields for chemiluminescence were determined against a luminol standard in DMSO.[26]

Theoretical Calculation for Decomposition of the Dioxetanimine Dianion Intermediate. Heats of formation and optimized bonding geometries for the dioxetanimine dianion intermediate, 10-cyanoanthrolate anion and radical, and cyanate anion and radical were obtained using AMPAC,[27] a semiempirical molecular orbital program. Excited-state heats of formation for the dioxetanimine dianion in the reaction coordinate calculations were determined by inputting the ground-state geometry without additional optimization.

Results and Discussion

Product Studies of DCA with KO$_2$ in DMSO. In a stoichiometry of 1 DCA to 2 KO$_2$, at concentrations of approximately 10^{-4} M in DMSO, a chemiluminescent reaction proceeds with complete consumption of DCA, as evidenced by loss of its distinctive visible

Figure 1. Absorption spectra of 1 × 10^{-4} M DCA, potassium 10-cyanoanthrolate, and the DCA radical anion in DMSO.

absorption band, in approximately 15 s. Simultaneously, new absorption bands with overlapping vibrational maxima appearing at 428, 455, and 516 nm are ascribed to potassium 10-cyanoanthrolate, as previously reported by Janzen.[24] Yields of potassium 10-cyanoanthrolate can be readily ascertained by absorption spectroscopy, since there is no overlapping absorption in this region by DCA (Figure 1). Quantitative conversion to 10-cyanoanthrolate is found (eq 2). An exactly parallel reaction course is followed when O$_2$ is allowed to react with a large excess of electrochemically generated DCA radical anion.

After 4 h in aerated solution the absorption spectra of 10-cyanoanthrolate disappears, as a new structureless absorption band appears at 330 nm. This secondary product is anthraquinone, as determined by its UV absorption spectrum and by product isolation, arising from further oxidation of the 10-cyanoanthrolate anion by molecular oxygen. The 10-cyanoanthrolate anion was stable in deaerated DMSO for days; however, introduction of oxygen resulted in complete conversion to anthraquinone within 4 h. The chemical route to anthraquinone, also isolated by Janzen,[24] is firmly established and must be uninvolved in the chemiluminescent step, since it is produced after chemiluminescence ceased.

A more challenging problem was the identification and quantification of the inorganic coproduct. A colorimetric test based on formation of a copper cyanate complex has been employed previously to detect cyanate in the base-catalyzed decomposition of 2-cyanoisopropylhydroperoxide (R$_1$ = isopropyl, R$_2$ = H)[23] (eq 1), and the formation of the cyanate ion was inferred as a reasonable accompanying product from other potential dioxetanimine decompositions in later investigations.[18–20,28] Several attempts to detect cyanate directly by this route were unsuccessful: apparently an unknown species chemically interferes with the formation of the copper cyanate complex. A more reliable and definitive method for quantitative detection of cyanate is the preparation of a hydrazodicarbamide derivative by the reaction of cyanate with semicarbazide hydrochloride,[25] (eq 3). Quantitative isolation of the hydrazodicarbamide de-

(24) Janzen, E. G.; Rudy, B. C.; Lopp, I. G.; Happ, J. W. *J. Chem. Soc., Chem. Commun.* **1970**, 491.
(25) Ault, R. G.; Haworth, W. N.; Hirst, E. L. *J. Chem. Soc.* **1934**, 1722.
(26) Lee, J.; Seliger, H. H. *Photochem. Photobiol.* **1965**, *4*, 1015.
(27) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(28) Hirayama, S.; Ohmoto, T. *Kyoto Kogei Sen'i Daigaku Sen'igkubu Gakujustu Hokoku* **1979**, *9*, 275.

11718 *J. Am. Chem. Soc., Vol. 115, No. 25, 1993*

Breslin and Fox

Figure 2. Concentration profile for the reaction of DCA with 2 equiv of KO_2 in DMSO.

rivative (eq 3) is direct evidence for quantitative formation of cyanate in the reaction mixture obtained as in eq 2 in DMSO.


Triplet yields encountered for dioxetanimine decompositions are typically 10^{-3}.[19,20] However, detection of triplet-state products of this fragmentation reaction could not be accomplished for the following reasons. UV–visible spectroscopy is not diagnostic, since starting materials, products, or intermediates absorb across the entire spectrum (Figure 1). Phosphorescence of 10-cyanoanthrolate could also not be detected, presumably because O_2, a product of the reaction, is an extremely effective triplet quencher. Detection of triplet-state products by inducing fluorescence of 9,10-dibromoanthracene (DBA) has commonly been used.[19,20] However, this strategy cannot be employed because the 10-cyanoanthrolate T_0–S_0 energy gap is of lower energy than the DBA T_2–S_0 energy gap. If the remaining products (99.8%) of this dioxetanimine decomposition are formed as triplets, the excited triplet/singlet product ratio would be 500. Dioxetan-imine decompositions always have higher triplet/singlet product ratios,[19,20] thus indicating that spin orbit coupling is lower in this system.

Kinetics Studies of DCA with KO_2 in DMSO. The kinetics of the chemiluminescent reaction in DMSO can be followed readily by absorption spectroscopy and by monitoring luminescence intensity. The absorption spectra for DCA (starting material), potassium 10-cyanoanthrolate (product), and the DCA radical anion (intermediate) in DMSO are shown in Figure 1. The absorption bands can be easily deconvoluted to obtain quantitative data.

A representative reaction profile for the reaction of DCA with KO_2 in DMSO is shown in Figure 2. Time-dependent concentrations of DCA (408 nm), 10-cyanoanthrolate (516 nm), and the DCA radical anion (708 nm) were monitored by absorption spectroscopy. The observed growth and decay of the DCA radical anion during the reaction require competitive rates of formation and subsequent reaction for this intermediate. Scheme I illustrates a two-step mechanism accounting for this concentration profile with competitive, consecutive, second-order kinetics, assuming k_1 and k_2 to be approximately equal. Because an exact solution to the differential equations for this kinetic model is impossible, McMillan has developed a numerical approximation method.[29]

(29) McMillan, W. G. *J. Am. Chem. Soc.* **1957**, *79*, 4838.

Scheme I. Proposed Mechanism for the Chemiluminescent Reaction of DCA with KO_2.
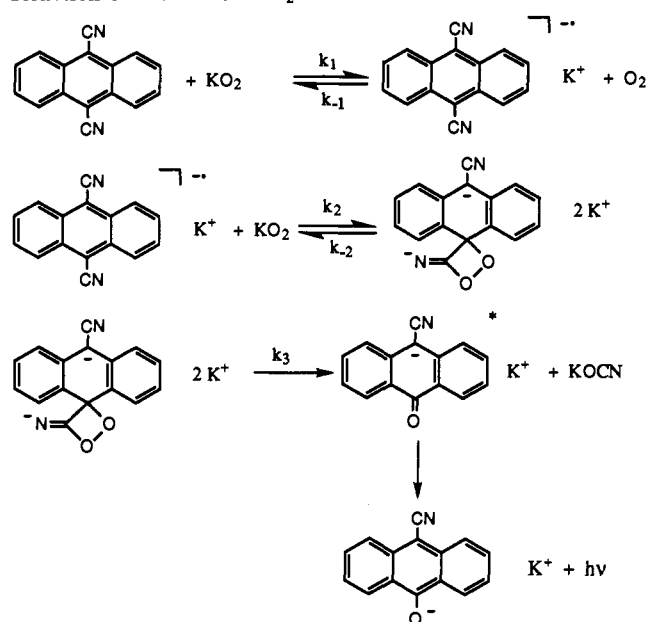
Table I. Rate Constants for the Reaction of the DCA Radical Anion with Potassium Superoxide[a]

species	wavelength (nm)	k_2 (M^{-1} s^{-1}) produced chemically[b]	produced electrochemically[c]
DCA radical anion	708	6500	6300
potassium 10-cyano-anthrolate	516	5600	5800

[a] Rate constants determined by measuring the disappearance of the DCA radical anion at 708 nm or appearance of potassium 10-cyanoanthrolate at 516 nm, error ±20%. [b] DCA radical anion produced by the reaction of DCA with KO_2. [c] DCA radical anion generated by electrochemical reduction at –1.0 V (SCE) in DMSO containing 0.1 M TBAPF$_6$ electrolyte at a platinum working electrode.

Table II. Reversible Reduction Potentials of DCA and O_2 in Various Polar Aprotic Solvents

solvent	$E^{1/2}$(DCA)[a] (V vs SCE)	$E^{1/2}$(O^2)[a] (V vs SCE)	chemiluminescence yield ($\phi \times 10^3$)[b]
THF	–0.83	–0.95	2.0
DMF	–0.81	–0.87	1.0
DMSO	–0.75	–0.77	1.0
acetonitrile	–0.89	–0.82	>0.001

[a] Mean value between the oxidative and reductive peak potentials obtained by cyclic voltammetry on a Pt electrode at room temperature in anhydrous solvent containing 0.1 M TBAPF$_6$; scan rate 100 mV/s; ±30 mV. [b] Measured versus a luminol standard, ±10%, for the reaction of DCA with 2 equiv of KO_2.

with which a ratio of 5 for k_1/k_2 is obtained. After 4 s, the first step (k_1) is essentially complete, and the rate of change of the DCA radical anion and 10-cyanoanthrolate concentrations is due primarily to k_2. The second-order rate constant k_2, as measured by the nearly simultaneous DCA radical anion disappearance and potassium 10-cyanoanthrolate appearance, is in accord with this conclusion (Table I). An estimate of 3×10^4 M^{-1} s^{-1} for k_1 is obtained from the experimentally determined value of k_2 (6100 M^{-1} s^{-1}, which is the average value as measured by DCA disappearance and anthrolate appearance), with the ratio k_1/k_2 = 5 obtained as above.

Solvent Effects on Chemiluminescence Efficiency. The chemi-luminescence efficiency of this reaction depends strongly on the solvent as shown in Table II. The observation of luminescence correlates with the exothermicity of electron transfer from

Scheme II. Proposed Mechanism for the Solvent-Sensitive Non-Chemiluminescent Reaction of DCA with KO_2.

Scheme III. Proposed Mechanism for the Non-Chemiluminescent Reaction of the DCA Radical Anion with O_2.
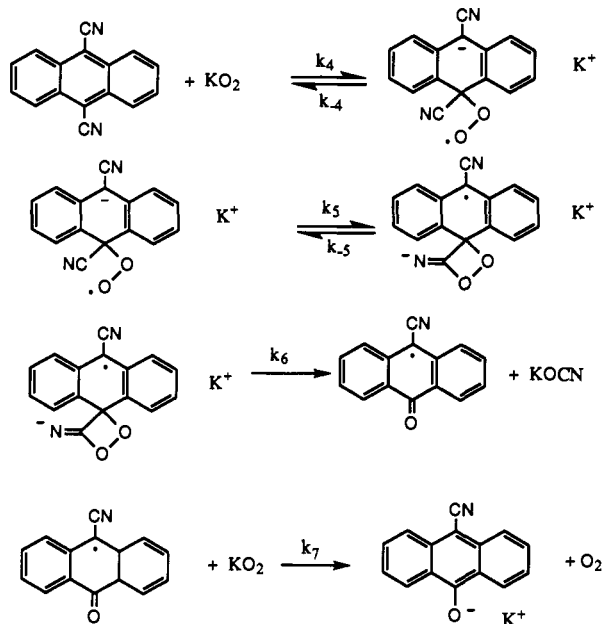
superoxide to DCA, which is solvent-dependent. In acetonitrile, where no chemiluminescence is observed, the reduction of DCA by KO_2 is endergonic. Although the same products are isolated from acetonitrile as in the chemiluminescent reaction, these appear to have been formed by an alternative non-chemiluminescent pathway. Scheme II illustrates a proposed non-chemiluminescent pathway to products in acetonitrile. In acetonitrile KO_2 does not act as a reductant toward DCA, but instead acts as a nucleophile. Subsequent cyclization of the resulting radical anion forms a four-member dioxetanimine radical anion, and fragmentation parallel to that shown in Scheme I leads to the 10-cyanoanthronyl radical, which is further reduced, ultimately to the anionic species. However, because cleavage produces the 10-cyanoanthrol radical instead of the anion, potassium 10-cyanoanthrolate anion luminescence is not observed. Radicals and radical ions typically do not luminesce or do so inefficiently, because of the low energy gap between the lowest excited doublet and ground state as evidenced by their near-IR absorption spectra.

Chemiluminescence might be expected from the route in Scheme II if a vibrationally excited 10-cyanoanthrol radical were efficiently reduced by a DCA radical anion before it could relax. However, this route is thermodynamically infeasible, since the difference of the reduction potential in acetonitrile of 10-cyanoanthrol (+0.2 V vs SCE) and the oxidation potential for the DCA radical anion (–0.75 V vs SCE) is less than the energy of excited state 10-cyanoanthrolate (2.3 V).

In contrast, luminescence and transient formation of the DCA radical anion are observed in DMSO, DMF, and THF, since reduction of DCA by KO_2 is exergonic in these solvents. Apparently the key step in the chemiluminescent route is formation of the dioxetanimine dianion, which is the product of a rapid reaction of the DCA radical anion with superoxide.

Effect of O_2 on Chemiluminescence in DMSO. The efficiency of luminescence is also strongly dependent on the concentration of dissolved oxygen. In O_2-saturated DMSO only 2% of the chemiluminescence observed in the deaerated solution could be detected. Oxygen saturation of N_2-purged DMSO solutions of potassium 10-cyanoanthrolate produces only a 33% fluorescence decrease. Since the observed chemiluminescence quenching is significantly greater than that anticipated from simple interception of the potassium 10-cyanoanthrolate excited state by O_2, as shown by fluorescence quenching, oxygen must provide an alternative non-chemiluminescent route(s). The effect of oxygen is primarily
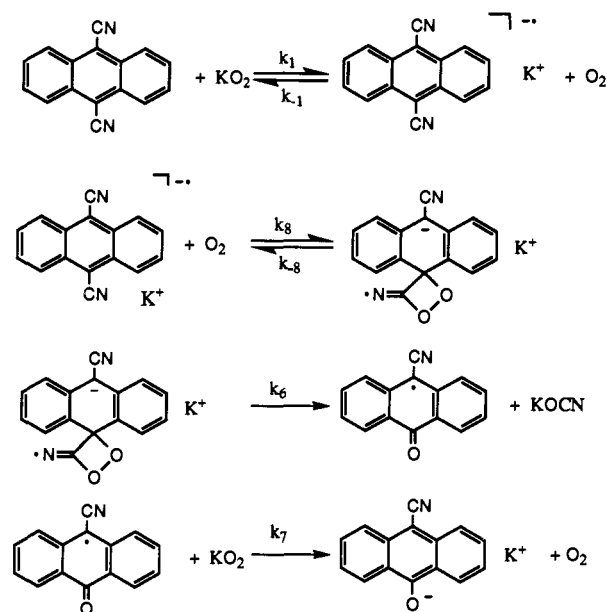
from trapping of the DCA radical anion by molecular oxygen, favoring the non-chemiluminescent pathway shown in Scheme III. The partitioning of the DCA radical anion into the chemiluminescent (Scheme I, k_2) and non-chemiluminescent (Scheme III, k_8) pathways can be solved, since k_2 is known (Table I), and the rate constant for the reaction of the DCA radical anion with oxygen (k_7) has been estimated as 120 M^{-1} s^{-1}.[28] From this route a 91% decrease of chemiluminescence efficiency in O_2-saturated solution from that observed in deaerated solution is expected. Additional chemiluminescence quenching is presumably also due to a shift in equilibrium concentration of O_2 in Scheme I, since O_2 is produced locally in the first step. Introduction of additional oxygen beyond that required from dioxetanimine dianion formation, shifts the electron-transfer equilibrium away from reduction of DCA, thereby favoring nucleophilic attack by superoxide on neutral DCA, a non-chemiluminescent pathway (k_4, Scheme II). The extent of participation of this chemiluminescence-quenching route cannot be estimated directly, since the rate constant k_4 in DMSO is unknown. However, nucleophilic addition of hydroxide ion to DCA in DMSO has a rate constant of 33 M^{-1} s^{-1}.[28] Assuming that the rate constant for nucleophilic attack by superoxide ion is similar to that of hydroxide leads to an additional quenching through k_4 of 10%. Combining both oxygen promoted-product quenching and non-chemiluminescence pathways accounts for an overall quenching of 95%, which is very close to the observed 98% quenching.
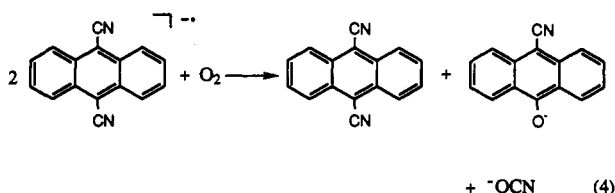
Reduction of the dioxetanimine radical anion generated in steps k_4 (Scheme II) or k_8 (Scheme III) by superoxide is conceivable. Such reduction regenerates the dioxetanimine dianion, allowing entry into the chemiluminescence manifold. The rates of cyclization and fragmentation of the dioxetanimine radical anion intermediate or its reduction by superoxide are unknown, and any estimation of these values is highly speculative. We contend that cyclization and fragmentation of the dioxetanimine radical anion occurs at a comparable or faster rate than reduction by superoxide.

Although chemiluminescence is observed when an electrochemically generated DCA radical anion reacts with molecular oxygen, discussed below, this would be a minor route to electronically excited products here, because trapping of the DCA radical anion by KO_2 (6000 M^{-1} s^{-1}) is much faster than trapping by O_2 (120 M^{-1} s^{-1}). Furthermore, the lower O_2 (than KO_2)

concentrations in these experiments makes trapping by O_2 even less favorable, so that chemiluminescence by this route is unimportant.

Reaction of the Electrochemically Generated DCA Radical Anion with KO_2. The initial reduction of DCA by superoxide as shown in Scheme I (k_1) can be circumvented by starting with the DCA radical anion and reacting with KO_2. Mixing solutions of the electrochemically generated DCA radical anion with KO_2 yielded a similar second-order rate constant for k_2, Table I, as that obtained with DCA and 2 equiv of KO_2 in DMSO. The agreement in the value of k_2 by these two separate preparative methods lends further support to the proposed chemiluminescent mechanism in Scheme I. Monitoring time-dependent luminescence intensity cannot yield quantitative rate constants, since the luminescence intensity scale is arbitrary. However, qualitatively the decay of luminescence intensity versus time followed second order kinetics as expected from Scheme I.

Reaction of O_2 with the Electrochemically Generated DCA Radical Anion. Alternatively, trapping the DCA radical anion with molecular oxygen rather than KO_2 also led to chemiluminescence. Preparation of the DCA radical anion by bulk electrolysis of 1×10^{-4} M DCA in DMF or THF containing 0.1 M $TBAPF_6$ electrolyte at -1.0 V (SCE) produced an intensely purple colored solution after passing 1 equiv of electrons. Bubbling oxygen through this DCA radical anion solution resulted in bright yellow luminescence, which lasted for approximately 15 s, depending on the oxygen flow rate. An absorption spectra of the resulting deep yellow solution showed a 1:1 ratio of DCA and potassium 10-cyanoanthrolate, which is quantitative for the stoichiometry shown in eq 4. Cyanate formation is quantitative

$$2 \quad \text{[anthracene-CN structure]}^{-\cdot} + O_2 \longrightarrow \text{[anthracene-CN]} + \text{[anthracene-CN-O}^-\text{]}$$

$$+ {}^-OCN \qquad (4)$$

by the hydrazodicarbamide derivative method described earlier. Kinetics measurements were not attempted under these conditions because controlling dissolved oxygen concentration for quantitative measurements in heterogeneous reactions such as this is extremely difficult.

In acetonitrile, the electrochemically produced DCA radical anion reacted with O_2 to yield the products shown in eq 4, but without chemiluminescence. Apparently, nucleophilic attack on DCA by superoxide in acetonitrile is operative, as discussed above.

Theoretical Study of the Dioxetanimine Dianion Decomposition. Insight into the mechanism of the chemiluminescent step is provided by AM-1 semiempirical molecular orbital calculations. The dioxetanimine dianion heat of formation is calculated to be 127.3 kcal/mol higher than the sum of the 10-cyanoanthrolate and cyanate ground-state heats of formation. The first excited singlet and triplet states of 10-cyanoanthrolate are also calculated to lie 64.4 and 42.0 kcal/mol above its ground state, respectively, clearly demonstrating that the dioxetanimine dianion has sufficient energy content that its ground-state decomposition can populate either the first excited singlet or triplet product energy surfaces.

The timing of the bond breaking events of this formal retro [2 + 2] cycloaddition reaction, thermally forbidden in a concerted cleavage, was also investigated by performing a reaction pathway calculation. Heats of formation are calculated for the dioxetanimine dianion along a reaction coordinate where the C–C and O–O bonds, illustrated below as dotted bonds, were separately stretched. A 12.7 kcal/mol activation energy barrier for cleavage of the dioxetanimine dianion calculated for C–C bond stretching is considerably less than the 52.1 kcal/mol barrier calculated for cleavage corresponding to O–O bond stretching.
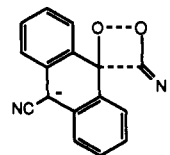
Apparently the C–C bond is further stretched in the transition state compared with the weak O–O bond, because the incipient p-orbital developed at the 9-anthracenyl carbon restores anthracene aromaticity. Presumably the high yield of observed excited singlet state product (0.2%), compared with previously investigated dioxetanimine decompositions where singlet excited state yields are 10^{-5}–10^{-6},[19,20] arises because spin orbital coupling is minimized, since this requires preferential O–O bond breaking.

The C–C (dotted) bond, which must be broken in the chemiluminescent step, is calculated as 1.59 Å in the minimum-energy conformation of the dioxetanimine dianion intermediate. Calculations show that this bond is elongated at the transition state to 2.38 Å. Stretching of this bond simultaneously causes distinct structural reorganization elsewhere in the molecule, specifically with the atoms comprising the cyanate fragment. The calculated O–O bond distance is only 0.03 Å longer in the transition state than at the energy minimum, suggestive that fragmentation is stepwise. Considerable reorganization indicative of the hybridization changes of the imine nitrogen along the C–C reaction coordinate is also calculated. A 0.05-Å calculated decrease in the C–N imine bond distance and an increased OCN bond angle (123° at the minimum energy conformation and 146° at the transition state) upon approaching the transition state suggest the development of significant triple bond character between these atoms. Furthermore, electron density localized on the imine nitrogen at the energy minimum is transferred to the 9-anthracenyl carbon in the transition state.

When the dotted C–C bond is ultimately stretched to 2.4 Å along this reaction coordinate, the O–O bond finally ruptures and a precipitous drop in heat of formation is calculated, Figure 3. The intended crossing of the ground state with the first excited singlet energy surface can take place, since little nuclear reorganization is required. The avoided crossing onto the triplet energy surface is also energetically possible; however, this requires an electron spin flip which, as previously discussed, is unlikely.

AM-1 calculations of the decomposition resulting from fragmentation of the dioxetanimine radical anion were pursued, since this was thought to be a major pathway contributing to inefficient chemiluminescence, Scheme II. The radical anion (corresponding to one-electron oxidation of the dioxetanimine dianion) is calculated as metastable because geometry optimization yielded either the uncyclized radical anion (Scheme II, k_{-5}) or direct fragmentation (Scheme II, k_6). The energy of activation for cyclization of the dioxetanimine radical anion, ultimately leading to the observed products, is 18.9 kcal/mol by these calculations. Although the cyclization energy barrier is higher than the barrier for cleavage of the dioxetanimine dianion, it is sufficiently low to be competitive. The heat of formation for the transition state of the dioxetanimine radical anion is calculated as 87.9 kcal/mol above the sum of the heats of formation for the 10-cyanoanthronyl radical and cyanate ion products. The first excited doublet and quartet states of the 10-cyanoanthronyl radical are calculated as 31.9 and 49.8 kcal/mol, respectively, above its ground state. Although the transition state meets the energy requirements for chemiluminescence, efficient luminescence would not be expected, since the low energy gap between these states is predictive of internal conversion as an effective nonradiative deactivation pathway.

Conclusions

The reaction of the DCA radical anion and potassium superoxide produces a strong yellow luminescence ($\phi = 0.1\%$) in
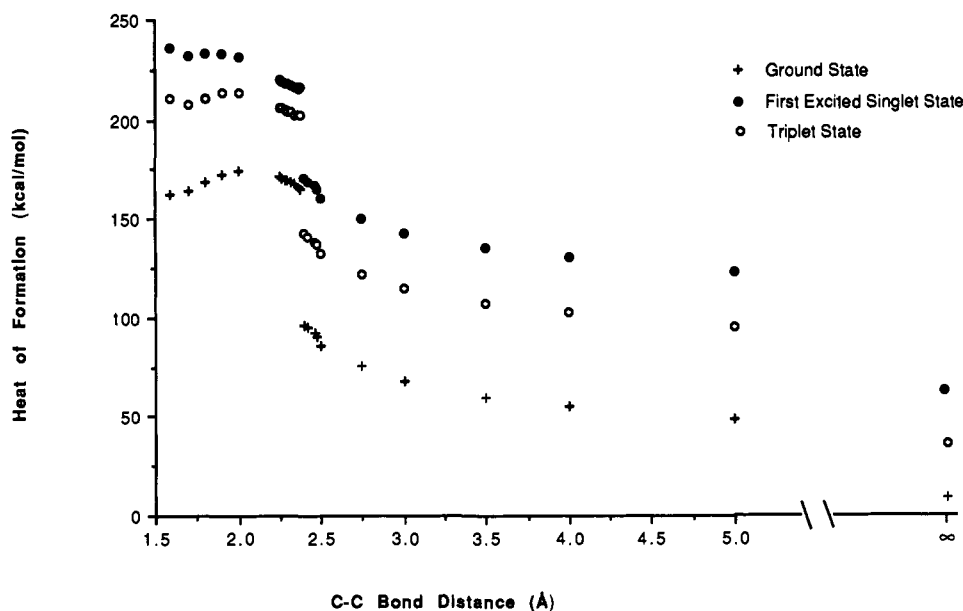
Figure 3. AMPAC-calculated C–C reaction coordinate energy diagram for the chemiluminescent fragmentation of the dioxetanimine dianion intermediate.

DMSO. Potassium 10-cyanoanthrolate and potassium cyanate are produced, clearly suggesting the intermediacy of a dioxetanimine dianion. Especially noteworthy is the relatively high quantum efficiency for excited-state formation, specifically singlet excited states, unlike the case for previously investigated dioxetanimine decompositions.[18–20,29] The corresponding radical anion decomposition is not chemiluminescent, probably because of efficient nonradiative decay modes for the 10-cyanoanthronyl radical. DCA radical anion formation and chemiluminescence are solvent-dependent, an unexpected effect deriving from a change in free energy for the electron transfer from superoxide ion to DCA in the solvents surveyed. The switch in exergonicity of electron transfer between the DCA radical anion and O_2 in different solvents has relevance to the mechanism of DCA-sensitized photooxygenation of electron-rich alkenes. Only recently has the solvent dependency on superoxide and singlet oxygen pathways been addressed.[30] AM-1 semiempirical molecular orbital calculations assisted in elucidation of the chemi-

luminescent step, which is calculated to be a stepwise process. Chemiluminescent assays of active oxygen metabolites such as superoxide have important biomedical applications, and reactions of this type may provide intriguing alternative detection systems if a lipophilic precursor can be prepared.

Supplementary Material Available: Tables listing internal coordinates for the AMPAC-calculated optimized geometries of the dioxetanimine dianion intermediate, 10-cyanoanthrolate (singlet ground, first excited singlet, and lowest triplet states), 10-cyanoanthronyl radical (doublet ground, first excited doublet, and lowest quartet states), cyanate ion, and cyanoyl radical (9 pages). Ordering information is available on any current masthead page.

(30) Sakurai, T.; Uematsu, Y.; Tanaka, O.; Inoue, H. *J. Chem. Soc., Perkin Trans. 2* **1992**, 2163.