Autoxidation of Acridanyl and Benzhydryl Carbanions Adjacent to Sulfur Groups Leading to C—S Bond Cleavage with Weak Chemiluminescence

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ABSTRACT: *Autoxidation of acridanyl and benzhydryl carbanions stabilized by sulfur groups gave the corresponding ketones via radical intermediates, being accompanied by a weak light emission. While oxidation of 9-sulfenylacridanes (**1a** and **1b**) in the presence of tert-BuOK showed direct chemiluminescence (CL) due to excited 10-methylacridone, that of benzhydryl phenyl sulfide (**2**) and benzhydryldimethylsulfonium bromide (**3**) displayed CL in the presence of a fluorescer, 9,10-dibromoanthracene (DBA), due to excited benzophenone. The yields of excited species in the present oxidation are low but comparable to acyclic peroxide systems. The bimolecular energy transfer from triplet benzophenone to DBA was established in CL of the sulfonium ylide from **3**.* © 2002 Wiley Periodicals, Inc. Heteroatom Chem 13:252–257, 2002; Published online in Wiley Interscience (www.interscience.wiley.com). DOI 10.1002/hc.10025

INTRODUCTION

Autoxidation of the stabilized carbanions gives various oxidation products, depending on the source

of carbanions. The common species formed initially are the peroxy radicals and anions, which are transformed into the corresponding hydroperoxides, carbinols, or carbonyl compounds, according to the neighboring groups. For instance, while the reaction of molecular oxygen with triarylmethanides gave the hydroperoxides and/or carbinol [1], that of diphenylmethanide produced benzophenone and benzyl alcohol [2,3] probably via the Russell mechanism involving tetraoxides formed by combination of peroxy radicals [4,5]. Autoxidation of some stabilized carbanions is accompanied by a peculiar phenomenon, chemiluminescence (CL), which is ascribed to the excited carbonyl compounds formed from decomposition of peroxides [6]. Namely, CL in the above mentioned autoxidation of diphenylmethane in the presence of strong base has been observed [2], in which excited benzophenone was produced by peroxy radical disproportion. It has been sometimes suggested that tetraoxides could be the precursors for emitting species [2,7].

On the other hand, little attention has been paid to autoxidation of the sulfur-stabilized carbanions, in spite of some detailed reports on oxidation of sulfides from the mechanistic and biochemical viewpoints [8,9]. In contrast, autoxidation of the carbanions stabilized by phosphorus groups has been relatively well studied [10–12] because of its synthetic value. Previously, we found that autoxidation of some phosphonate carbanions showed weak CL

[13,14] with elimination of phosphorus groups. Our continuous interest in autoxidation of the carbanions stabilized by heteroatom groups prompted us to investigate oxidation of the sulfur-stabilized carbanions and their CL. We report here chemiluminescent autoxidation of the carbanions adjacent to sulfur groups that generates ketones via C—S bond cleavage.

RESULTS AND DISCUSSION

Autoxidation

When 9-phenylthio-10-methylacridane (**1a**) was reacted with atmospheric oxygen in the presence of *tert*-BuOK in tetrahydrofuran (THF), *N*-methylacridone (NMA) and diphenyl disulfide (PhSSPh) were obtained in 49 and 44% yield, respectively. Interestingly, this reaction at very high concentration was accompanied by a weak light emission observable by naked eyes in the dark. Although the detection of emitting light by a fluorescence spectrometer is unsuccessful because of the difficulty in measuring at such high concentration, this CL seems to be ascribed to the fluorescence of NMA, since the absorption in the UV–vis spectrum of the reaction mixture agreed with that of authentic NMA and no other absorption in the visible region was observed. As has been established in autoxidation of some stabilized carbanions [1–3], this reaction is also expected to involve a radical intermediate. Additionally, an adjacent sulfenyl group can stabilize a radical as a donor [15]. In fact, the colored reaction mixture of **1a** and *tert*-BuOK in dimethyl sulfoxide (DMSO) showed an ESR spectrum as shown in Fig. 1. This relatively sim-
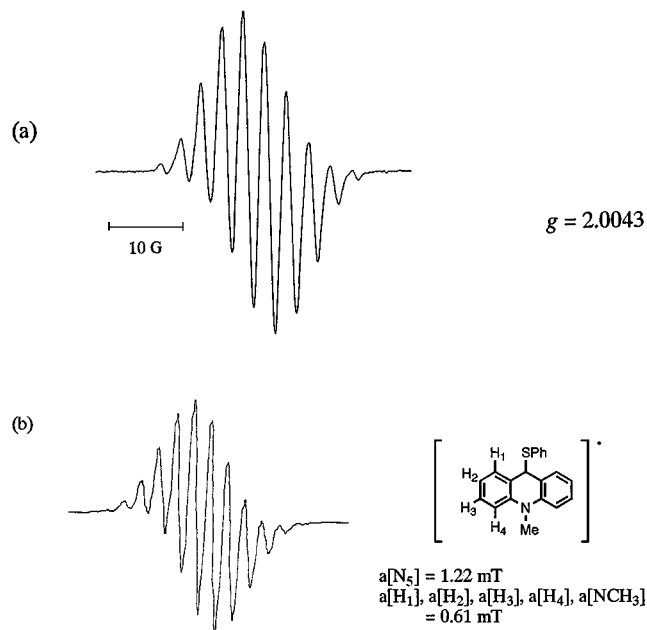

$g = 2.0043$

10 G

$a[N_5] = 1.22$ mT
$a[H_1]$, $a[H_2]$, $a[H_3]$, $a[H_4]$, $a[NCH_3]$ = 0.61 mT

FIGURE 1   ESR spectrum (a) observed in DMSO and (b) computer-simulated spectrum.

ple spectrum with ten-lines led us to guess equivalence of some hyper fines [16]. Because of well agreement with a computer simulation, the observed spectrum was identified to that of 9-phenylsulfenyl-acridanyl ketyl radical.

The previously documented mechanisms concerning autoxidation help us to consider the paths of the present reaction (Scheme 1). If the Russell mechanism for self-reaction of peroxy radicals [5,17] is applied to the present reaction, the formation of
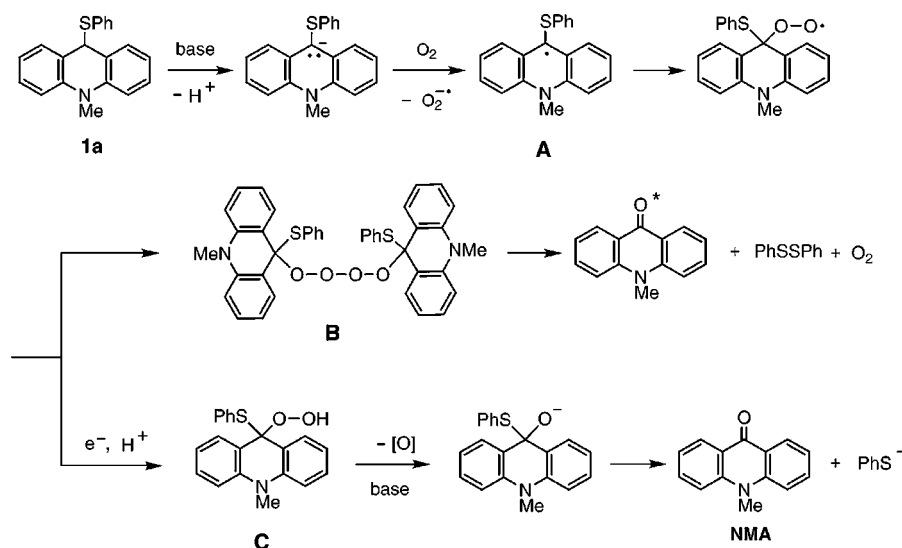
SCHEME 1

the products, NMA and PhSSPh, can be explained as follows: The initially formed carbanion is oxidized to the ketyl radical **A** by electron transfer to molecular oxygen, which reacts with oxygen to form a peroxy radical. Dimerization to the tetraoxide **B** followed by decomposition would give an excited state NMA and PhSSPh with release of oxygen. On the other hand, Ando [18,19] and Clennan [9] reported recently that oxidation of some sulfides with singlet oxygen gave the corresponding carbonyl compounds along with disulfides and others. Therefore, decomposition of the intermediary α-perhydroxy sulfide **C** into NMA and the thiol may also be involved in the present reaction. This mechanism seems not to be chemiluminescent but can be involved in the present system, because the thiolate anion could be trapped by methyl iodide to give thioanisole in 22% yield in the reaction of **1a**. We believe at present that both reaction pathways, the former being luminescent and the latter not, are competing in this oxidation, but the nonluminescent path seems to be preferable because of very low quantum efficiency of light emission, as described later.

The similar reaction of 9-methylthio-10-methylacridane (**1b**) also gave NMA and showed weak CL. Oxidation of 10-methylacridanylsulfonium ylide is of interest also because of the higher ability of the sulfonium cation as the leaving group. However, the preparation of the sulfonium salt from **1b** and methyl iodide was unsuccessful because of the lability of the salt that readily afforded 10-methylacridinium iodide by elimination of dimethyl sulfide.

Next, we examined autoxidation of benzhydryl phenyl sulfide (**2**) and benzhydryldimethylsulfonium bromide (**3**) in the presence of *tert*-BuOK. Oxidation of both **2** and **3** gave benzophenone as a major product in 87 and 46% yield, respectively (Scheme 2). While the detection of the ketyl radical derived from **2** by ESR measurement was unsuccessful, the radical from **3** could be detectable on the nitroxide radical, formed by the trapping with phenyl-*N*-

tert-butylnitrone, giving a typical feature of signals scattering three doublets. To our knowledge, there has been no document for the nature of the radical adjacent to a sulfonium group so far. It should be noted that the sulfur ylide derived from **3** is known to undergo the Stevens rearrangement to give (2-methylthiomethylphenyl)phenylmethane in the absence of oxygen [20,21]. However, since the rearranged product could not be detected, the interaction of oxygen with the carbanion formed by the abstraction of a proton by the base seemed to be faster than the rearrangement. Such a high reactivity of the carbanion toward oxygen was reported by Russell in the reaction of triphenyl methanide [1]. In these reactions weak CL was observed in the presence of 9,10-dibromoanthracene (DBA). As shown in Scheme 2, the observed CL is expected to occur from the dioxirane formed from the peroxy radical [22–24]. However, all attempts to detect the products expected from dioxirane were unsuccessful.

Chemiluminescence

In autoxidation of the carbanions of **1a** and **1b**, excited NMA that emits blue light was directly formed (direct CL). The singlet excited yield is defined as

$$\Phi_{CL}^* = \Phi_r \Phi_S^* \Phi_F$$

where Φ_{CL}^*, Φ_r, Φ_S^*, and Φ_F are the total CL yield, chemical yield of NMA, the singlet excited yield, and the fluorescence efficiency of NMA, respectively [25]. The values of Φ_{CL}^* were estimated by the photocounting method using luminol CL as a standard [26], and Φ_r was determined by the UV spectrum of the reaction mixtures. The total CL yields (Φ_{CL}^*) were 8.8×10^{-8} einstein/mol for **1a** and 2.9×10^{-8} einstein/mol for **1b**, respectively. According to the above equation, each Φ_S^* is calculated to be 1.8×10^{-7} einstein/mol for **1a** and 4.9×10^{-8} einstein/mol for **1b**, respectively, using $\Phi_r = 0.49$ for **1a**, $\Phi_r = 0.6$ for **1b**, and $\Phi_F = 0.98$. The values for Φ_S^* are much less than those for 1,2-dioxetane decomposition

2 X = SPh
3 X = $^+$SMe$_2$ Br$^-$

for 3 | O$_2$

e$^-$
‖
- Me$_2$S
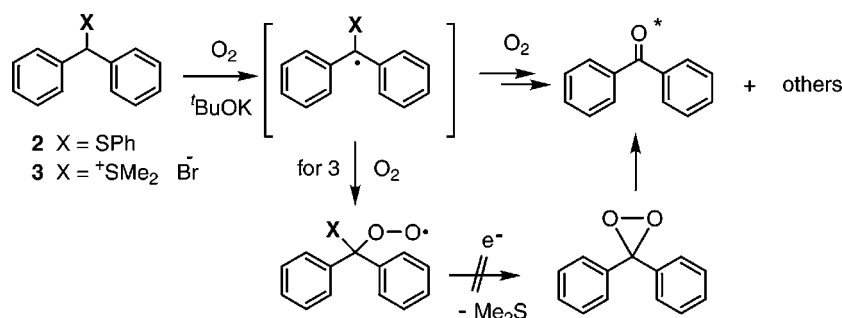
SCHEME 2

of the acridane systems **4** [27] but almost equal to the reported values for acridanylperoxyester **5** formed from the oxidation of 9-arylmethylene-10-methylacridane with *m*-chloroperbenzoic acid [28].

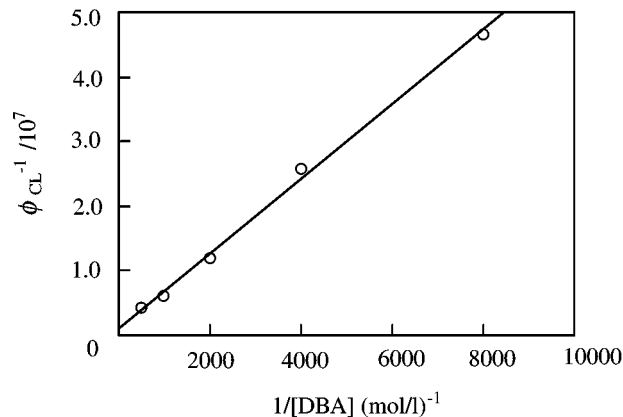FIGURE 2   Reciprocal plot of CL quantum yield (Φ_{CL}) against concentration of DBA for **3**.
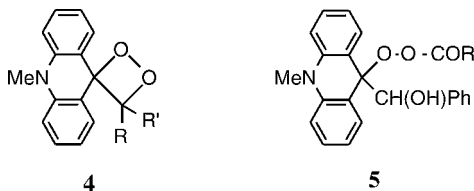
On the other hand, CL from the reaction of **2** or **3** is the result of energy transfer from excited benzophenone to DBA. Generally, the CL quantum yield ($\Phi_{CL}^{Flu.}$) in the presence of the fluorescers is estimated from a linear relationship between a double reciprocal plot of emission intensity versus fluorescer concentration [25]. Such a linear relationship means that light emission is ascribed to a bimolecular interaction between the excited species and the fluorescer. Therefore, emission intensity in the oxidation of **2** and **3** was measured in the presence of DBA as a triplet energy acceptor [25]. While a linear relationship for the CL of **3** and DBA could be obtained, plotting for **2** displayed a random fashion in our several attempts. This would be due to the interaction between the peroxide anion and DBA [29] as well as the unsettled concentration of the semistabilized carbanion of **2**, depending on the circumstances. Nevertheless, DBA showed higher emission intensity than DPA (a singlet energy acceptor) in both CL of **2** and **3** at each concentration of the fluorescers, in agreement with the favored formation of benzophenone in a triplet excited state.

The linear relationship in the reaction of **3** in the presence of DBA is shown in Fig. 2, which permits us to estimate $\Phi_{CL}^{Flu.(\infty)}$ as well as the yield of triplet benzophenone in this reaction. The value of $\Phi_{CL}^{DBA(\infty)}$ at the infinite concentration of DBA could be calculated from the intercept as 8.5×10^{-7} einstein/mol. The total CL quantum yield is represented as

$$\Phi_{CL}^{DBA(\infty)} = \Phi_r \Phi_T^* \Phi_{TS} \Phi_F^{DBA}$$

where $\Phi_r, \Phi_T^*, \Phi_{TS}$, and Φ_F^{DBA} are the chemical yields of formed benzophenone, the yield of triplet benzophenone, the limiting triplet–singlet energy transfer efficiency, and the fluorescence quantum yield of DBA (0.1), respectively [25]. On the assumption that Φ_{TS} is relatively insensitive to triplet ketone structure and generally constant (ca. 0.3) [30] and use of $\Phi_r = 0.46$ allowed us to calculate Φ_T^* as $6.2 \times$

10^{-5} einstein/mol. This value is very small compared to CL from thermal dioxetane decomposition, but comparable to CL from the similar base promoted autoxidation of diphenylmethane generating triplet benzophenone [3].

In conclusion, we have investigated autoxidation of the sulfur-stabilized carbanions, which resulted in carbon–sulfur bond cleavage to give the corresponding ketones accompanied by weak chemiluminescence. The reactions involved the radical intermediates formed by the electron transfer from the carbanions to oxygen. The resulting radical reacted with oxygen to form the peroxy radical, which further underwent elimination of the sulfur group to afford the excited ketone, though the yields of which were low.

EXPERIMENTAL

Preparation of 9-Phenylthio-10-methylacridane (**1a**)

To a solution of sodium ethoxide prepared from sodium (0.7 g, 30.4 mmol) in ethanol (100 ml) was added thiophenol (0.32 ml, 3.09 mmol). After 10 min, 10-methylacridinium iodide (1.0 g, 3.11 mmol) was added and a red color of the acridinium salt disappeared immediately. After the mixture had been stirred for 1 h and water added, the product was extracted with chloroform and the extract was dried over Na_2SO_4. After evaporation of the solvent, the residue was chromatographed using silica gel and chloroform as an eluant to give **1a**, which was recrystalized from hexane–chloroform to give white needles (0.29 g, 31%). mp 139–141°C. ^{1}H NMR (60 MHz, CDCl$_3$) δ 3.10 (s, 3H, SMe), 5.45 (s, 1H, 9-H), 6.70–7.28 (m, 8H, aromatic H), *m/z* 303 (M$^+$). Anal. Calcd.

for $C_{20}H_{17}NS$: C, 79.17; H, 5.65; N, 4.62%. Found: 79.30; H, 5.43; N, 4.56%.

Preparation of 9-Methylthio-10-methylacridane (1b)

To a solution of 10-methylacridinium iodide (5 g, 15.6 mmol) in DMSO (60 ml) was added an aqueous solution of sodium methylthiolate (5%, 50 ml), and the reaction mixture was stirred for 1 h. The product was extracted with chloroform and the extract was dried over Na_2SO_4. The similar procedure for purification as described above gave pure **1b** as pale yellow needles (1.96 g, 49%). mp 114–115°C. ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.87 (s, 3H, SMe), 3.35 (s, 3H, NMe), 5.03 (s, 1H, 9-H), 6.68–7.33 (m, 8H, aromatic H), m/z 241 (M$^+$). Anal. Calcd. for $C_{15}H_{15}NS$: C, 74.65; H, 6.26; N, 5.80%. Found: C, 74.64; H, 6.21; N, 5.77%.

Benzhydryl phenyl sulfide (**2**) [31] and benzhydryldimethylsulfomium bromide (**3**) [19] are known compounds.

Autoxidation of 1a, 1b, 2, and 3

A solution of **1a** (0.5 g, 2.07 mmol) and *tert*-BuOK (0.4 g, 3.0 mmol) in DMSO (50 ml) was bubbled with oxygen for 2 h at room temperature. After addition of water (30 ml), the product was extracted with chloroform and the extract was dried over Na_2SO_4. After evaporation of the solvent, the residue was chromatographed on silica gel, using chloroform as an eluant to give NMA (0.25 g, 59%), which showed the same chemical and physical properties as those of an authentic sample. When excess methyl iodide was added to the reaction mixture, thioanisole was detected in 22% yield by gas chromatography.

Autoxidation of **1b**, **2**, and **3** was carried out in a similar manner. Analysis of benzophenone and diphenyl sulfide was done by gas chromatography.

Measurement of CL Quantum Yield

The CL quantum yields were measured by a photocounting method using a photomultiplier (R464 Hamamatsu Photonics K.K.) connected with a photocounting unit (C3866), photocounting board (M3949), and handling software (U3997). The calibration was made by a standard method with luminol chemiluminescence in the presence of *tert*-BuOK in dry DMSO [12]. The quantum efficiency of the photomultiplier in the range of 450–500 nm was almost equal within 4%. The emission maximum wave numbers of luminol (485 nm) and NMA (455 nm) was in this region. For other fluorophores,

DPA and DBA, the emission efficiency was calibrated based on the characteristic curve of the photomultiplier. All measurements were done under the same conditions.

A solution (1 ml) of *tert*-BuOK (2.0×10^{-2} mol/l in DMSO) was added to each solution (2 ml) of acridanes **1a** and **1b** (1.00×10^{-3} mol/l in DMSO) in a quartz cell, and photons produced during 204 s were counted, which led to estimation of the collected photons by comparison with the above described luminol luminescence. The resulting solution was diluted at once with a mixed solution of DMSO (18 ml) and *t*-BuOH (9 ml) for the UV measurement. The yield of NMA was calculated by comparison of the absorption at 401 nm with the standard solution of NMA (1×10^{-4} mol/l) in the same solvent. The CL quantum yield was calculated as a quotient of photons per produced NMA. The quantum yields of CL in the presence of DBA were measured for the solutions (2 ml) of **2** and **3** (1×10^{-4} mol/l in DMSO) containing various concentrations of DBA and *tert*-BuOK (2.0×10^{-2} mol/l in DMSO). The reciprocal of each quantum yield against the reciprocal of each concentration of DBA was plotted.

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