Structural Effects on the Intramolecular Electron Transfer Induced Decomposition of a Series of 1,2-Dioxetanes Derived from 9-Alkylidene-10-methylacridans

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Abstract: A series of 1,2-dioxetanes derived from 9-alkylidene-10-methylacridans, $Ar = CR_1R_2$, were studied: 5, $R_1 = R_2 =$ phenyl; 1, $R_1 =$ phenyl; 1, $R_1 =$ phenyl, $R_2 = H$; 6, $R_1 = R_2 = H$. Thermal decomposition of these dioxetanes in the temperature range -30 to +35 °C is accompanied by chemiluminescence (CL), *N*-methylacridone (NMA) fluorescence, with representative room temperature Φ_{CL} 's of 0.11, 0.04, and $\sim 10^{-5}$ and room temperature lifetimes of ~ 2000 , ~ 60 , and ~ 6 s, for 5, 1, and 6, respectively. The only triplet states produced in these systems is by ¹NMA* \rightsquigarrow ³NMA* as indicated by triplet counting experiments. The CL from decomposition of 1 is subject to off/on switching by successive addition of acetic acid and triethylamine. The proposed mechanism involves intramolecular electron transfer (N to peroxide bond) induced decomposition, via a boat conformation, to a dipolar intermediate that partitions between chemiexcitation and nonchemiexcitation pathways. The related low CL levels from decomposition of 1 when prepared by triphenyl phosphite ozonide oxygenation, and the CL enhancement with added triethylamine, are explained.

Recently, chemically initiated electron exchange luminescence (CIEEL) was proposed as a general category of chemiand bioluminescent reactions¹ of 1,2-dioxetanes and related compounds. Decompositions by this mechanism are characterized by accelerated rates (compared with unassisted decompositions²) and high yields of excited singlet states. If the chemiexcited molecule is intrinsically highly fluorescent, strong chemiluminescence (CL) is observed. McCapra associated the high yields of the excited singlet state of N-methylacridone (¹NMA*) from the 10-methylacridan dioxetanes **1**, **2**, and **3**³



with an electron transfer induced decomposition mechanism^{1a} while others^{1c} similarly interpreted our earlier report of a high yield of ¹NMR* from 4.⁴

In this paper, we describe the changes in decomposition rates and chemiexcitation yields of ¹NMA* with structural variation at R_1 and R_2 in the dioxetanes **1**, **5**, and **6**. A comprehensive mechanism is presented that takes into account the special stereochemical features in these systems. In addition, we discuss complications associated with using triphenyl phosphite ozonide⁵ as a singlet oxygen precursor in the low-temperature synthesis of these dioxetanes from the corresponding 9-alkylidene-10-methylacridans.

Preparation of the 9-Alkylidene-10-methylacridans. 9-Diphenylene (7) and 9-benzylidene-10-methylacridan (8) were readily prepared by addition of the appropriate Grignard or alkyllithium reagent to N-methylacridone (NMA). Spontaneous dehydration during workup provided the alkylidenes as reasonably stable, yellow solids: 7, mp 258-260 °C; 8, mp 141-142 °C.⁶ Their UV-vis absorption spectra in dichloromethane solution show two characteristic bands: 7, ϵ_{365} 10 000, ϵ_{295} 13 400; 8, ϵ_{394} 12 400, ϵ_{297} 15 600.

9-Methylene-10-methylacridan (9) is unstable in the condensed form and also undergoes facile self-sensitized photooxidation. The synthesis and handling of 9 were carried out as follows. The precursor salt 9,10-dimethylacridinium methosulfate, prepared by N-methylation of 9-methylacridine⁷ with dimethyl sulfate, was stirred with basic alumina in dichloromethane in the dark. The reaction mixture was passed rapidly through a basic alumina column to yield a solution of 9 in dichloromethane. The product was identified by its characteristic UV-vis absorption (ϵ_{383} 21 300, ϵ_{308} 27 600⁸) and NMR spectra and the apparent quantitative yield of NMA upon photooxidation.

Photosensitized Oxygenation of the 9-Alkylidene-10methylacridans. Visible-light (>530 nm) irradiation of the 9-alkylidene-10-methylacridans (5.0×10^{-5} M) in oxygensaturated dichloromethane solution at -78 °C, in the presence of methylene blue $(5.0 \times 10^{-5} \text{ M})$, results in facile photooxygenation.⁹ The resulting products appear stable at -78 °C since these samples retain their kinetic and CL integrity for at least 3 h following preparation. However, the products decompose rapidly with CL at $\gtrsim 0$ °C. NMA is quantitatively formed from decomposition of the photooxidation products from 7 and 8, and is assumed to be quantitatively formed from the decomposition of the phooxidation product from 9. The CL from all three reactions was identified as NMA fluorescence. Further, benzophenone and benzaldehyde were the only other products identified from the photooxidation reactions of 7 and 8, respectively. Accordingly, the thermally labile photooxidation products of 7, 8, and 9 are assigned the dioxetane structures 5, 1, and 6, respectively.

Rates of Chemiluminescence Decay. The CL decays showed first-order behavior to at least 3 half-lives following warmup. The calculated k_{obsd} 's, at various temperatures, appear in Table I. The dependence of the CL decay rate on triethylamine concentration, which was needed in connection with a study described below, was elucidated by adding known amounts of the amine to freshly prepared dichloromethane solutions of 1 just prior to warmup. The accelerating rate effect of added triethylamine is shown in Figure 1, lower (circles).

Chemiluminescence and Chemiexcitation Quantum Yields. The spectrally integrated CL decays were converted into

5		1		6	
temp, °C	$k_{\rm obsd} \times 10^3$, s ⁻¹	temp, °C	$k_{\rm obsd} \times 10^2$, s ⁻¹	temp, °C	$k_{\rm obsd} \times 10^2$, s ⁻¹
36.5	1.83 ± 0.01	25.0	1.60 ± 0.01	0.0	4.25 ± 0.04
32.0	1.32 ± 0.02	20.5	1.11 ± 0.01	-10.0	2.30 ± 0.01
30.5	1.00 ± 0.01	10.0	0.40 ± 0.002	-20.0	1.20 ± 0.02
27.0	0.64 ± 0.01	0.0	0.14 ± 0.01	-30.0	0.48 ± 0.03
23.0	0.48 ± 0.01				
17.5	0.22 ± 0.01				
13.5	0.13 ± 0.01				
2.0	0.034 ± 0.002				

Table I. First-Order Rate Constants for Chemiluminescence Decays in Dichloromethane^a

^a Dioxetane concentrations typically were 10^{-5} - 10^{-4} M. The k_{obsd} 's were independent of [dioxetane] under these conditions.



Figure 1. Upper: Stern-Volmer plot of chemiluminescence quantum yields from 1, prepared by TPPO₃ route, in the presence of "excess" triethylamine in dichloromethane at 25 °C. Φ^0_{CL} is with $[Et_3N] = [TPPO_3]$ so that indicated $[Et_3N]$'s are the excess concentrations; i.e., $[Et_3N] =$ $[Et_3N]_{total} - [TPPO_3]$. Lower: effect of added triethylamine on the chemiluminescence decay from 1 in dichloromethane at 25 °C. \Box , using 1 from photosensitization experiment; O, using 1 from TPPO₃ experiment. In latter, indicated $[Et_3N]$'s are given by $[Et_3N]_{total} - [TPPO_3]$.

photon yields by comparing their curve areas with the spectrally integrated curve area of a standardized luminolhemin- H_2O_2 reaction.¹⁰ Both sample and reference were held in identical geometries relative to the photomultiplier entrance slit, and, because of the similar spectral distributions of the CLs, the photon yields were not corrected for photomultiplier spectral response.

The NMA yields from the above decompositions were determined by fluorescence assay using the method of standard additions. The CL quantum yields were calculated by

$$\Phi_{CL}$$
 = (einsteins of light produced)/
(mol of NMA produced)

The chemiexcitation yields of ¹NMA* were calculated from

$$\Phi_{\rm CE} = \Phi_{\rm CL} / \Phi_{\rm f} \tag{2}$$

(1)

where Φ_f is the fluorescence quantum yield of NMA under the experimental conditions (aerated sample at specified temperature). The needed Φ_f 's were independently measured and the results appear in Table II¹¹ along with values for Φ_{CL} and ${}^{1}\Phi_{CE}$.

Chemical Counting Experiments by Sensitized trans \rightarrow cis-Stilbene Isomerization.¹² Highly purified trans-stilbene (99.97%) was added to the photooxygenated samples at -78 °C (stilbene concentration 1.0×10^{-2} M). After the mixtures were allowed to warm to room temperature, the amount of cis-stilbene formed was measured by gas chromatography. Control experiments showed that the trans- \rightarrow cis-stilbene isomerization does not occur under the experimental conditions in the absence of the dioxetanes and also that trans-stilbene does not quench the NMA fluorescence. The NMA yields from these reactions were determined by fluorescence assay and the quantum yields for formation of cis-stilbene were calculated by

 $\Phi_{cis} = (mol of cis-stilbene)/(mol of NMA produced)$ (3)

Complications in the Oxidations with Triphenyl Phosphite Ozonide. Only very low CL levels (NMA fluorescence) were observed during warmup of mixtures of 9-benzylidene-10methylacridan (8) and triphenyl phosphite ozonide (TPPO₃ source of ${}^{1}O_{2}{}^{5}$) in dichloromethane. However, addition of triethylamine prior to, or immediately after, warmup to room temperature results in CL levels approaching those from the photosensitized reaction. The CL level increases with added triethylamine until an amount equivalent to the moles of TPPO₃ has been added. Thereafter, the CL level decreases (Figure 1, upper) while the rate of CL decay increases with added amine. The CL decays follow first-order kinetics to at least 3 half-lives.

Discussion

Properties of the 9-Alkylidene-10-methylacridans. NMR studies on 9-alkylidene-10,10-dimethyldihydroanthracenes¹³ (10) elucidated restricted boat-boat interconversion in those



systems. In general, the barrier height increases with increasing steric bulk in the R₁, R₂, X, and Y groups owing to severe steric compression in the planar conformation. For example, with $R_1 = R_2 = Cl$ and X = Y = H, the barrier is $\Delta G^{\ddagger} = 15.8$ kcal/mol, and with $R_1 = R_2 = X = Y = Cl$, $\Delta G^{\ddagger} > 24$ kcal/mol.

It is expected that similar conformational features apply to the 9-alkylidene-10-methylacridan systems. However, we might speculate that a planar conformation is somewhat more energetically favored in an acridan system relative to the analogous dihydroanthracene system because of additional π -electron delocalization associated with the nitrogen lone pair. Nonetheless, we anticipate that increasing bulk in R₁ and R₂ should destabilize a planar conformation in the acridans. Thus, the biphenylene system (7) should assume a more "boat-like" conformation than the methylene system (9). We suggest that the trend in the electronic absorption spectra of 7–9 reflects this change in ground-state conformation. Further, the much faster rate of reaction of 9 toward ${}^{1}O_{2}{}^{9}$ may also be associated with a more planar structure that leads to greater electron density (via nitrogen lone pair delocalization) in the alkene linkage.

Chemiexcitation Pathways in the Decomposition of the Photosensitized Oxygenation Products. There is ample precedent for 1,2-dioxetane formation from [2 + 2] cycloaddition of ${}^{1}O_{2}$ to alkenes lacking allylic hydrogens. 14 Also, the apparent quantitative formation of NMA and benzophenone, of NMA and benzaldehyde, and of NMA from the photosensitized oxygenations of 7, 8, and 9, respectively, supports the dioxetane structural assignments 5, 1, and 6, respectively.

The chemiexcitation pathways available to the acridan dioxetanes are (i) dioxetane $\rightarrow R_1R_2CO + {}^nNMA^*(\pi,\pi^*,\pi^*)$ $E_{\rm S} \approx 69, E_{\rm T} \approx 50-55 \, \rm kcal/mol^{15})$ and (ii) dioxetane $\rightarrow NMA$ + ${}^{n}R_{1}R_{2}CO^{*}$ (n, π^{*} , E_{S} and $E_{T} \gtrsim 70$ kcal/mol). The formation of ¹NMA* in these systems is readily determined through the CL which has been identified as NMA fluorescence. However, ¹NMA* may arise by direct chemiexcitation (path i, n = 1) or indirectly by path ii followed by singlet energy transfer ${}^{1}R_{1}R_{2}CO^{*} + NMA \rightarrow R_{1}R_{2}CO + {}^{1}NMA^{*}$. The second possibility could arise, despite the unfavorable energetics, if formation of n, π^* states is favored over π, π^* states in chemiexcitation reactions.¹⁶ Because of the extraordinarily fast rates of intersystem crossing in benzophenone and benzaldehyde,¹⁷ we would expect that ${}^{1}R_{1}R_{2}CO^{*} \rightarrow {}^{3}R_{1}R_{2}CO^{*}$ would be an important path leading to additional triplet state production in those systems.

Significantly, the amount of *cis*-stilbene actually measured in the chemical counting experiments agrees reasonably well with the yield *predicted* by Scheme I.

Scheme I

- (a) $^{1}NMA^{*} \xrightarrow{k_{f}} NMA$
- (b) $^{1}NMA^{*} \xrightarrow{k_{isc}} ^{3}NMA^{*}$
- (c) ${}^{3}NMA^{*} + trans$ -stilbene $\xrightarrow{k_{et}} NMA + {}^{3}stilbene^{*}$
- (d) ${}^{3}NMA* \xrightarrow{k_{d}} NMA$
- (e) ³stilbene* $\stackrel{k_c}{\rightarrow}$ cis-stilbene
- (f) ³stilbene* $\stackrel{k_t}{\rightarrow}$ trans-stilbene

The predicted quantum yield of *cis*-stilbene formation is given by

$$\Phi_{\rm cis}^{\rm pred} = ({}^{1}\Phi_{\rm CE})(\Phi_{\rm isc})(\Phi_{\rm t \rightarrow c}) \tag{4}$$

where ${}^{1}\Phi_{CE}$ is the chemiexcitation yield of ${}^{1}NMA^{*}$, Φ_{isc} is the intersystem crossing efficiency for ${}^{1}NMA^{*}$, and $\Phi_{t\rightarrow c}$ is the ${}^{3}NMA^{*}$ -sensitized trans \rightarrow cis isomerization quantum yield under the experimental conditions (aerated sample, identical stilbene concentration) independently measured as 0.58 ± 0.02 . Using this latter value, the ${}^{1}\Phi_{CE}$'s from Table I, and $\Phi_{isc} = (1 - \Phi_{f}) = 0.66$, we obtain $\Phi_{cis}^{pred} = 0.16$ for 5 at 23 °C and $\Phi_{cis}^{pred} = 0.046$ for 1 at 21 °C. The result for 1 is in reasonable agreement with the experimental result. The somewhat low experimental value of $\Phi_{cis} = 0.06$ for 5 may be an experimental artifact. ¹⁸ Finally, the $\Phi_{cis}^{pred} \approx 7 \times 10^{-6}$ for 6 is at least consistent with the result in Table I.

From the above analysis, we conclude that decomposition of these dioxetanes leads to triplet state yields in accord with the above scheme so that the only significant direct chemiexcitation pathway is dioxetane $\rightarrow {}^{1}NMA^{*} + R_{1}R_{2}CO$.

Mechanism of Decomposition of the Acridan Dioxetanes. Qualitatively, the 10-methylacridan dioxetanes decompose rapidly at room temperature relative to 1,2-dioxetanes substituted only by H, alkyl, or phenyl.² An apparent exception is 3 with a lifetime of ~10⁷ s at 25 °C in toluene compared with these lifetimes at 25 °C in dichloromethane: 1, ~60 s; 2, ~800 s;³ 4, ~2 s;⁴ 5, ~2000 s; 6, ~6 s. The dramatic rate-retarding effect of the adamantyl group in 3 has been attributed, as in the adamantylidenadamantane-1,2-dioxetane (11),¹⁹ to steric compression of the O-O bond. When the reactivity of 11 is used as a reference ($\tau \approx 10^{12}$ s at 25 °C), 3 also is classified as a highly reactive system.

We agree with the previous suggestion that the (i) increased reactivity and (ii) apparently exclusive operation of the chemiexcitation pathway to ¹NMA* in the acridan dioxetanes are consistent with an *electron transfer induced decomposition* mechanism.^{1c} Further support for this mechanism and the importance of the nitrogen lone pair is the reversible quenching of the CL by acetic acid. We observe that addition of excess acetic acid (0.1 M) to a dichloromethane solution of 1 prior to, or immediately after, warmup to room temperature results in complete quenching of the CL. However, the CL can be almost completely recovered if triethylamine is immediately added. This off-on switching function of acids and bases in Figure 2 is ascribed to reversible protonation of the nitrogen lone pair.²⁰

The discussion that follows focuses on the dioxetanes 5 ($R_1 = R_2 = phenyl$), 1 ($R_1 = phenyl$; $R_2 = H$), and 6 ($R_1 = R_2 = H$) which were studied under identical experimental conditions and represent a systematic change in structure. It is our intention to draw attention to several apparently important features of these systems via the proposed mechanism.

A Proposed Scheme for Electron-Induced Decomposition. The dihydroacridan ring system is conformationally flexible via a boat \rightleftharpoons planar \rightleftharpoons boat' equilibrium. For discussion purposes, we need only consider the equilibrium shown below as the α boat $\rightleftharpoons \beta$ boat. Further, we expect the two diastereomers of each boat to rapidly equilibrate by inversion at nitrogen so that only the more stable diastereomer is shown for each boat conformation below.



In the β boat, the distance between the nitrogen and the nearer oxygen is ~3 Å. We suggest that a rate-determining electron transfer from nitrogen into the LUMO $\sigma^*_{O-O^{21}}$ results in concerted, or subsequent, O-O bond cleavage to 12. This dipolar intermediate then partitions between CE and non-CE paths.

According to Scheme II, the measured first-order rate constant for CL decay is given by $k_{obsd} = k_1 K$ where K is the equilibrium constant for α boat $\rightleftharpoons \beta$ boat. Molecular models indicate severe steric interactions between the R groups and the ortho H in the acridan ring in the β boat, which would mean that the α boat (or planar conformation) is the favored ground-state stereoisomer. As the steric bulk in the R groups increases, K becomes smaller, leading to a smaller k_{obsd} (as-



Time, Sec

Figure 2. Effect of added acetic acid and triethylamine on the chemiluminescence from 1 in dichloromethane at 25 °C.

Scheme II



suming no change in k_1). We suggest that the structure-reactivity pattern in Table I reflects this shift in ground-state equilibrium.

The kinetic data in Table I give rather good Arrhenius plots that lead to E_a 's for the CL decays of 9.3 ± 0.1 , 15.5 ± 0.3 , and 20.0 ± 0.2 kcal/mol for 6 ($R_1 = R_2 = H$), 1 ($R_1 =$ phenyl; $R_2 = H$), and 5 ($R_1 = R_2 =$ phenyl), respectively. If the rate of the intrinsic electron transfer step (k_1) is unchanged through the dioxetane series, the variations in the E_a 's indicate the effect of increasing steric strain in the β -boat conformation and imply that the E_a for k_1 is ≤ 10 kcal/mol.²²

Chemiluminescence and Chemiexcitation Quantum Yields. From the scheme, the yield of ¹NMA* is determined by the partitioning of **12** between the competing C-C bond homolysis (k_C) and back electron transfer (k_T) steps. We suggest that bond homolysis in **12** directly leads to a charge-transfer state
 Table II. Chemiluminescence, Chemiexcitation, and NMA

 Fluorescence Quantum Yields at Various Temperatures in

 Dichloromethane

starting dioxetane	temp, °C	$\Phi_{\rm CL}{}^a$	$\Phi_{\mathrm{f}}{}^{b}$	$\Phi_{\rm CE}{}^c$	Φ_{cis}
	36.0	0.11	0.23	0.48	0.060 ± 0.007
	23.0	0.14	0.33	0.42	
5	14.5	0.16	0.40	0.40	
	8.0	0.18	0.48	0.37	
	21.0	0.042	0.34	0.12 ^d	0.030 ± 0.004
	17.0	0.043	0.38	0.11	
1	10.0	0.044	0.43	0.10	
	0.0	0.044	0.51	0.086	
	23.0	6.4×10^{-6}	0.33	19 × 10 ⁻⁶	$<(7.6 \pm 0.6) \ 10^{-6} \ e$
	8.0	5.5×10^{-6}	0.48	11×10^{-6}	· · ·
6	0.0	5.4×10^{-6}	0.51	11×10^{-6}	
	-7.7	4.3×10^{-6}	0.58	7.4×10^{-6}	

^a Measured relative to luminol-hemin-H₂O₂ as a standard, ref 10. ^b Independently measured relative to quinine sulfate as a standard. ^c Chemiexcitation yield of ¹NMA^{*}. ^d Compared with $\Phi_{CE} = 0.25$ in toluene at 25 °C as reported in ref 3. ^e No *cis*-stilbene observed beyond amount in original purified *trans*-stilbene sample. Value in table is estimated detection limit.

of NMA which relaxes efficiently to the fluorescent $S_1(\pi,\pi^*)$ state. The competing back electron transfer yields biradical 13, which gives ground-state products after rapid C-C bond homolysis (k_C') . The dependence of k_C/k_T on R_1 and R_2 (5 > 1 \gg 6) results from an increase in the magnitude of k_C with phenyl substitution.

The results in Table II indicate that the Φ_{CL} 's for all three systems increase with decreasing temperature. However, because of the strong *inverse dependence* of Φ_f on temperature, the chemiexcitation yields of ¹NMA* actually show a modest *positive dependence* on temperature. For the proposed scheme, the partitioning factors for the CE and non-CE paths are $\Phi_{CE} = k_C/(k_C + k_T)$ and $\Phi_{non-CE} = k_T/(k_C + k_T)$ so that $\Phi_{CE}/\Phi_{non-CE} = k_C/k_T$ and

$$\ln \left[\Phi_{\rm CE} / (1 - \Phi_{\rm CE}) \right] = \ln \left(A_{\rm C} / A_{\rm T} \right) - \left(E_{\rm a}^{\rm C} - E_{\rm a}^{\rm T} \right) / RT$$
(5)

These Arrhenius plots, shown in Figure 3, lead to estimates of $E_a^{C} - E_a^{T}$ of 2.4 ± 0.1 , 2.9 ± 0.1 , and 4.5 ± 0.3 kcal/mol for 5 (R₁ = R₂ = phenyl), 1 (R₁ = phenyl; R₂ = H), and 6 (R₁ = R₂ = H), respectively, in accord with the above proposed scheme, assuming that E_a^{T} is the same in all three systems.

The above partitioning scheme is somewhat analogous to one proposed recently by Richardson and co-workers²³ to explain structural effects on chemiexcitation yields in the unassisted dioxetane decompositions. In that scheme, the initially formed singlet biradical partitions between C-C bond homolysis (with mostly ground-state products formed) and intersystem crossing to the triplet biradical which necessarily yields one triplet-state product upon C-C bond homolysis. Substituents that accelerate the C-C bond homolysis lead to lower total chemiexcitation yields (with ³ Φ_{CE} dominant) in contrast to higher chemiexcitation yields (with ¹ Φ_{CE} dominant) by the proposed induced decomposition mechanism.

Complications in the TPPO₃ Oxygenation Reaction. The observation of (i) very low CL levels and (ii) CL enhancement with triethylamine in the decomposition of 1 prepared by TPPO₃⁵ is attributed to Scheme III.

Actually, the added triethylamine has both positive and negative effects on the CL level. The CL level increases with added amine until apparently all of the triphenyl phosphate (byproduct from the TPPO₃ decomposition) is scavenged as Et_3N ·(C₆H₅O)₃PO, thereby freeing 1 for the electron transfer

Scheme III

$$TPPO_3 \longrightarrow (C_6H_5O)_2PO + {}^{1}O_2$$

$$8 + {}^{1}O_{2} \longrightarrow 1$$

$$1 + (C_{6}H_{5}O)_{3}PO \implies 1 \cdot (C_{6}H_{5}O)_{3}PO \xrightarrow{Et_{3}N} 1 + Et_{3}N \cdot (C_{6}H_{5}O)_{3}PO$$
excess • complex complex complex by Scheme I with CL by Scheme I with CL

induced decomposition. Triethylamine added beyond the stoichiometric amount of triethyl phosphate (calculated on the basis of triethyl phosphite) decreases the CL level as shown in Figure 1, upper. This decrease in CL arises from (i) induced decomposition of 1^{24} (Figure 1, lower) and (ii) quenching of ¹NMA* by triethylamine. An independent photoexcitation study of the latter reaction indicates a Stern-Volmer slope of $k_q \tau_f = 9.4 \pm 1.0 \text{ M}^{-1}$. A scheme for the decomposition of 1 in the presence of triethylamine follows.

Scheme IV

_ .

(a')
$$1 \xrightarrow{\phi_{CEk_1}} 1NMA^* + C_6H_5CHO$$
 first-order
decomposition along
CE and non-CE paths
(b') $1 \xrightarrow{\phi_{non-CEk_1}} NMA + C_6H_5CHO$
(c') $1 + Et_3N \xrightarrow{k_D} NMA + C_6H_5CHO$ amine-induced
decomposition
(d') $1NMA^* \xrightarrow{k_T} NMA$ radiative decay
(e') $1NMA^* \xrightarrow{k_T} NMA$ all nonradiative decays



The Stern-Volmer equation for quenching of the chemiexcitation yield of ¹NMA* is

$$\Phi^{0}_{CE}/\Phi_{CE} = \{1 + k_{Q}\tau_{f}[Et_{3}N]\}\{1 + k_{D}\tau[Et_{3}N]\}$$
(6)

where Φ^0_{CE} and Φ_{CE} are the chemiexcitation yields in the absence and presence of triethylamine, τ_f is the fluorescence lifetime of ¹NMA* in the absence of triethylamine, and τ is the lifetime of 1 in the absence of triethylamine ($\tau = 66$ s at 25 °C in dichloromethane).

Rearrangement of (6) and substitution of the value of $k_Q \tau_f$ gives

$$(\Phi^{0}_{CE}/\Phi_{CE})/\{1+9.4 \text{ M}^{-1}[\text{Et}_{3}\text{N}]\} = 1 + k_{D}\tau[\text{Et}_{3}\text{N}]$$
(7)

This modified plot in Figure 4 provides $k_D \tau = 15.8 \pm 1.5 \text{ M}^{-1}$ and leads to $k_D = 0.24 \text{ M}^{-1} \text{ s}^{-1}$.

An independent estimate of k_D is provided by the kinetic data in Figure 1, lower, which measures the accelerating effect of added triethylamine on the decomposition of 1 (prepared by either the TPPO₃ or photosensitization route). This data follows the kinetic equation

$$k_{\text{obsd}} = k_1 + k_D[\text{Et}_3\text{N}] =$$

0.015 ± 0.002 s⁻¹ + 0.27 ± 0.03 M⁻¹ s⁻¹ [Et₃N] (8)

Thus, excellent agreement on the magnitude of k_D , the bimolecular rate constant for triethylamine-induced decomposition of 1, is obtained from two independent measurements.

We assume that the *bimolecular* amine induced decomposition of 1 is mechanistically similar to the *intramolecular*



Figure 3. Arrhenius plots based on partitioning between CE and non-CE paths in Scheme II: upper, 5; middle, 1; lower, 6.



Figure 4. Modified Stern-Volmer plot of chemiexcitation quantum yields from 1, prepared by TPPO₃ route, in presence of "excess" triethylamine in dichloromethane at 25 °C. Φ^0_{CE} is with [Et₃N] = [TPPO₃] so that indicated [Et₃N]'s are excess concentrations; i.e., [Et₃N] = [Et₃N]_{total} - [TPPO₃].

electron transfer induced decomposition of 1. Thus, it may be expected that a CE branching pathway operates along k_D as it does along k_1 . However, the above analysis is consistent with CE only via k_1 .

This dilemma can be mollified by the following analysis. A modification of the proposed scheme where (c') is replaced by

$$1 + Et_3N \xrightarrow{\Phi_{CE}k_D} 1_{NMA^*} + C_6H_5CHO \qquad (c'')$$

and

$$1 + \text{Et}_3 \text{N} \xrightarrow{\Phi'_{\text{non-CE}kD}} \text{NMA} + \text{C}_6\text{H}_5\text{CHO} \qquad (c''')$$

leads to

$$\begin{aligned} & \{\Phi^{0}_{CE}/\Phi_{CE}\}/\{1+9.4 \ M^{-1}[Et_{3}N]\} = \\ & \{1+k_{D}\tau[Et_{3}N]\}/\{1+(\Phi'_{CE}k_{D}/\Phi_{CE}k_{1})[Et_{3}N]\} = \\ & \{1+15.8 \ M^{-1}[Et_{3}N]\}/\{1+110 \ M^{-1}\Phi'_{CE}[Et_{3}N]\} \end{aligned}$$
(9)

It follows from (9) that, over the concentration range of triethylamine used in this experiment, the CE contribution from path c'' would be imperceptible if $\Phi'_{CE} \leq 0.01$. More specifically, the intrinsically large CE from the intramolecular electron transfer induced decomposition would mask a sig-

nificant, but small, CE contribution from the triethylamineinduced decomposition.

Experimental Section

Materials. Dichloromethane (Matheson Coleman and Bell, reagent grade) was purified by filtering through a silica gel column followed by fractional distillation. Triethylamine (Matheson Coleman and Bell, reagent grade) was fractionally distilled. *trans*-Stilbene (Matheson, scintillation grade, 99.8%) was further purified by preparative gas chromatography to provide a sample containing $\leq 0.03\%$ cis-stilbene. Methylene blue was recrystallized twice from chloroform-ether. Luminol (Matheson Coleman and Bell) and quinine sulfate (Aldrich Chemical Co.) were recrystallized three times from 95% ethanol. Hemin chloride (Calbiochem), benzaldehyde (Mallinckrodt, analytical reagent grade), and benzophenone (Princeton Organics, Prinz quality) were used as received.

Syntheses. 9-Diphenylene-10-methylacridan (7). Into a 200-mL, three-necked, round-bottom flask containing 7.2 g (0.1010 mol) of *n*-butyllithium (90% in ether) and 60 mL of dry THF and equipped with an efficient magnetic stirrer, a cooling condenser, and a pressure-equalized addition funnel was added dropwise under nitrogen 17.1 g (0.1018 mol) of diphenylmethane over a period of 20 min at room temperature. After all the diphenylmethane was added, the mixture was stirred continuously for 24 h under nitrogen atmosphere at room temperature, and then 3 g (0.0114 mol) of NMA was added to the diphenylmethyllithium solution. The mixture was stirred for 2 h at room temperature and then poured into a beaker which contained 200 ml of 10% hydrochloric acid. The solution was neutralized with 1 M sodium hydroxide solution until pH 10. The reaction mixture was extracted three times with 50-mL portions of dichloromethane solution and dried over anhydrous magnesium sulfate. The organic phase was filtered and concentrated in vacuo, yielding 9-diphenylene-10-methylacridan as a light yellow colored solid. Recrystallization of the crude product from 95% alcohol gave 1.8 g (35% yield) of pure product: mp 258-260 °C; mass spectrum m/e 359; NMR (CDCl₃) δ 3.43 (3 H, singlet) and 7.10 (18 H, broad). Anal. Calcd for C₂₁H₂₇N: C, 90.21; H, 5.89; N, 3.90. Found: C, 89.13; H, 6.31; N, 3.84.

9-Benzylidene-10-methylacridan (8). Into a 250-mL, three-necked, round-bottom flask containing 0.019 mol of freshly prepared benzylmagnesium chloride in 30 mL of dry ether and equipped with a condenser, mechanical stirrer, and dropping funnel was added 1.0 g (0.0048 mol) of N-methylacridone dissolved in 150 mL of dry tetrahydrofuran over a period of 10-15 min at room temperature. The reaction mixture was refluxed for 30 min, cooled to room temperature. and poured into 200 mL of 10% hydrochloric acid. The pH of the mixture was adjusted to 10 by addition of 1 M sodium hydroxide. The aqueous phase was extracted three times with 50-mL portions of dichloromethane. The combined organic extractions were dried over anhydrous magnesium sulfate, filtered, and concentrated in vacuo to give a yellow solid. Recrystallization from 95% ethanol gave 0.85 g (63%) of a yellow solid: mp 141-142 °C (lit. mp 140-142 °C⁶); mass spectrum m/e 283; NMR (CDCl₃) δ 3.40 (3 H, singlet), 6.57 (1 H, singlet), and 7.13 (13 H, broad).

9,10-Dimethylacridinium Methosulfate. A solution of 6.0 g (0.031 mol) of 9-methylacridine⁷ and 6 mL of dimethyl sulfate in 120 mL of toluene was refluxed for 1 h. The resulting yellow-green crystals were collected by filtration and then recrystallized from 95% ethanol to give 7.0 g (71%) of the product, mp 233 °C dec.

9-Methylene-10-methylacridan (9). To a stirred mixture of 0.032 g (0.10 mmol) of 9,10-dimethylacridinium methosulfate in 50 mL of dichloromethane in an aluminum-foiled flask was added 1.0 g of basic alumina (Ventron) in small portions over 15 min at room temperature. The mixture was stirred for 5 h and checked periodically by UV-vis spectroscopy for product formation. The mixture was passed quickly through a column of basic alumina and the resulting dichloromethane solution was stored in the dark at 0 °C. The concentration of **9** in the dichloromethane solution was determined by exhaustive photooxidation of a sample, followed by assay of the formed NMA by UV-vis spectroscopy. This photooxidation/NMA assay method gave reproducible results indicating quantitative conversion of the starting salt to **9**. These standard solutions of **9** in dichloromethane were diluted as needed for the following experiments.

Triphenyl Phosphite Ozonide (TPPO₃) Oxygenations. TPPO₃ was prepared by passing a stream of ozone (generated by a Welsbach ozonator, Model T-408) into a 0.10 M solution of freshly distilled triphenyl phosphite in dichloromethane at -78 °C until the development of a blue color. The excess ozone (blue color) was purged from the cold solution by a stream of dry nitrogen. The reactants were then added to the cold solution in amounts to achieve the desired concentrations. For chemiluminescence decay rate and quantum yield measurements, the samples were transferred into cylindrical tubes reproducibly positioned in a clear Pyrex Dewar under constant-temperature conditions. The measurements were carried out as described below.

Photooxygenation Procedure. The photooxygenations were carried out by irradiating air-saturated solutions of **7**, **8**, or **9** in dichloromethane through a 530-nm short-wavelength cutoff filter with a Sylvania DWY tungsten-iodine lamp (650 W) in the presence of methylene blue $(5.0 \times 10^{-5} \text{ M})$ at $-78 \, ^{\circ}\text{C}$. Typical irradiation times required for nearly complete oxygenation of solutions containing 5.0 $\times 10^{-5} \text{ M}$ alkene: **7**, 3 h; **8**, 30 min; **9**, 15 min.

Chemiluminescence Spectra. Chemiluminescence spectra were recorded on an American Instrument Co. spectrofluorimeter equipped with a Hamamatsu R446 photomultiplier tube. A clear Pyrex Dewar was put in place of the usual sample holder. A 1-cm square cuvette containing the TPPO₃ or photooxygenated samples at -78 °C was placed in the Dewar maintained at 25 °C and the chemiluminescence spectrum was recorded during warmup of the sample using 0.25-mm entrance and exit slits on the scanning monochromator. The recorded spectrum was identical with NMA fluorescence in all systems studied.

Chemiluminescence Decay Rates. The total chemiluminescence decays from the TPPO₃ or photooxygenated samples were monitored using cyclindrical cells reproducibly positioned in a temperature-controlled clear Pyrex Dewar immediately in front of the entrance slit to the photomultiplier housing. The decays were followed to at least 3 half-lives following thermal equilibrium.

Chemiluminescence Quantum Yields. The TPPO₃ or photooxygenation samples were positioned as described above under "Chemiluminescence Decay Rates." The total light vs. time decay curves were recorded. Photon yields of emission were determined by comparing the areas under the CL decays with similar curves obtained from the standardized luminol-hemin- H_2O_2 reaction¹⁰ run in exactly the same geometry. Because of the similarity of the two CL spectra, no correction was made for photomultiplier spectral response.

NMA yields were determined by the method of standard additions. The reaction mixture was divided into five equal parts and to each was added a different aliquot of a standardized NMA solution. The NMA fluorescence from each sample was recorded. The unknown NMA concentration was determined by plotting fluorescence yield vs. concentration of added NMA and extrapolating to zero concentration of added NMA. The Y intercept provides the fluorescence intensity of the unknown NMA and the slope gives the constant relating fluorescence intensity to concentration. The Φ_{CL} 's were calculated from eq 1 in the text.

Quantum Yields for Formation of cis-Stilbene. ³NMA*-Sensitized Reaction. An aerated solution of NMA $(1.0 \times 10^{-3} \text{ M})$ and transstilbene (99.97%) $(1.0 \times 10^{-2} \text{ M})$ in dichloromethane was irradiated at 366 nm using a 150-W Xe-Hg arc for 40 min. The cis-stilbene yield was measured to be 4.1×10^{-6} mol on a Hewlett-Packard Model 5730 gas chromatograph using a flame ionization detector (25% SE-30 on Chromosorb P column at 230 °C). The photons absorbed during the irradiation period as determined by conventional ferrioxalate actinometry,²⁵ in conjunction with a correction for the transmitted photons (0.01%), was calculated to be 1.1×10^{-5} einstein. The quantum efficiency of the ³NMA-sensitized isomerization was calculated from $\Phi_{t\rightarrow c} = \{\text{mol of } cis\text{-stilbene produced} \} / [einsteins of light ab$ $sorbed]} / \Phi_{isc}$, where Φ_{isc} is the intersystem crossing efficiency of ¹NMA* taken as $\Phi_{isc} = 1 - \Phi_{f} = 0.66$ at 23.0 °C. This procedure indicates that $\Phi_{t\rightarrow c} = 0.58$.

Chemical Counting Experiment. To photooxygenated samples of **7**, **8**, or **9** ($\sim 10^{-2}$ M in alkene) in dichloromethane was added ultrapure *trans*-stilbene (99.97%) (stilbene concentration 1.0×10^{-2} M) at -78 °C. The mixtures were allowed to warm to room temperature. The *cis*-stilbene produced was measured by gas chromatography as described above and the NMA yields were determined by fluorescence assay using the method of standard additions. The quantum yields for formation of *cis*-stilbene calculated from eq 3, after accounting for the background of *cis*-stilbene of 3.7×10^{-6} M, appear in Table II.

Product Analyses. Photooxygenations of solutions of 7 or 8 in dichloromethane $(1.0 \times 10^{-2} \text{ M})$ were carried out as described above. These samples were warmed to room temperature and allowed react for 5 h. The NMA yield in each sample was determined by fluorescence assay using the method of standard additions. The identifications and assays of benzophenone from 7 and benzaldehyde from 8 were by gas chromatography on a Hewlett-Packard Model 5730 chromatograph. Conditions were as follows: benzophenone, 25% SE-30 on Chromosorb P column at 230 °C, diphenylmethane as internal standard; benzaldehyde, 20% Carbowax 20M on Chromosorb P column at 130 °C, mesitylene as an internal standard. Yields of benzophenone and benzaldehyde, based on moles of NMA, were 100 $\pm 10\%$.

References and Notes

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Solvolysis in 2,2,2-Trifluoroethanol–Water and 2,2,2-Trifluoroethanol-Ethanol Mixtures. Selectivity of the Intermediates and N Values

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Abstract: Solvolysis of 1-adamantyl bromide (1-Br) in eight TFE-EtOH mixtures gave a Grunwald-Winstein m_{GW} value of 1.50, and the ethyl (1-OEt) and trifluoroethyl (1-OTFE) ethers. The selectivity ratios for reaction with the solvent components $k_{\text{TFE}}/k_{\text{EtOH}}$ are medium dependent, being 2.60-0.83. In TFE-H₂O, $m_{\text{GW}} = 0.56$ and the $k_{\text{TFE}}/k_{\text{H}_{2}\text{O}}$ ratios increase with X_{H_2O} from 0.49 to 2.04. Solvolysis of 1-anisyl-2-methylpropen-1-yl tosylate (2-OTs) in TFE-EtOH gives $m_{GW} = 0.89$ and an average $k_{\text{TFE}}/k_{\text{EtOH}}$ value of 0.086. Methyl tosylate was solvolyzed in several TFE-EtOH and TFE-H₂O mixtures and new values of the nucleophilic parameter N were determined. Products were derived from the free cation in the solvolysis of 2-OTs and from the solvent-separated ion pair in the solvolysis of 1-Br, and the selectivities of these species were analyzed. The nucleophilicities of TFE-H₂O and TFE-EtOH mixtures and the recent use of the comparison of TFE-H₂O and EtOH-H₂O mixtures for evaluating solvent participation in solvolysis reactions were discussed.

2,2,2-Trifluoroethanol (TFE) and aqueous TFE have been used frequently as media for solvolytic reactions during the last decade,^{1,2} owing to their high ionizing power. The analogous binary solvent mixtures TFE-EtOH were investigated much less and only recently.³⁻⁶ These two binary solvent mixtures are complementary to one another. By starting from TFE ($\epsilon = 26.14$ at 25 °C)⁷ and increasing the dielectric constant by addition of water ($\epsilon = 78.54$ at 25 °C)⁸ the ionizing power of the medium increases, as judged by the increased solvolysis rate of t-BuCl at higher mole fraction of water $(X_{\rm H_2O})^2$ Simultaneously, the nucleophilicity of the medium also increases since water is more nucleophilic than TFE.9