present and GLPC analysis (column B, 100 °C) showed a peak with retention time identical with an authentic sample of *trans*-stilbene.

Quantum Yield for the Photoinduced Disappearance of 1 in the Presence of 2. Solutions of **1** (0.1 M) and **2** (0.2 M) in dry spectral grade benzene were prepared as above and degassed 5-mL samples in sealed Pyrex ampules were irradiated in a double baffle merry-go-round apparatus with RPR 3500-Å lamps to about 10% disappearance of benzophenone. The precise quantity of **1** which had disappeared was determined by GLPC on column A. Light flux, which was found to be nearly invariant over the reaction period, was determined by 5-min exposure of an aqueous potassium ferrioxalate solution immediately before, at the midpoint, and immediately after the irradiation with analysis by standard actinometry techniques.[30] The period of the irradiation was determined on a stopwatch.

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(24) The sharp increase in rate and quantum yield with increasing initial PPh_3 concentration suggests that Scheme I may be oversimplified, at least at the relatively high initial concentrations of PPh_3 used in a typical synthetic run. These results suggest that phosphine must interact with more than one intermediate along the way to final product. The possibility that higher order kinetic dependence of the rate on initial phosphine concentration could be attributed to the photoreactions of benzophenone with diphosphines generated in a side reaction has not been excluded, although the products isolated here differ from those found in that reaction.[11]
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Solid State Photochemistry of *N,N*-Dialkyl-α-oxoamides. Type II Reactions in the Crystalline State

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Abstract: The solid state photochemistry of *N,N*-dialkyl-α-oxoamides (**1**) has been studied. The amides undergo type II cyclization giving β-lactams (**2**) selectively. The selective formation of the lactams via an unprecedented type II reaction in the crystalline state is explainable in terms of the crystal lattice restraints on the molecular motion of the biradical intermediate (**5**) formed by γ-hydrogen abstraction. The nonreactivity of *N*-alkyl-α-oxoanilides toward solid state photolysis was most reasonably explained by their unfavorable s-cis geometries for γ-hydrogen abstraction.

The Norrish type II reaction of ketones is one of the most important photochemical processes of ketones. The reaction takes place both in solution[1] and in the vapor phase.[2] However, that in the solid state has not yet been reported except for polymers such as polyacrylophenones.[3] The question of comparing photoreactivities in the solid and liquid states is an intriguing one. Solid state reactions may differ from those in solution because of the restraints on molecular motions imposed by the crystal lattice on its constituents. Recently, Scheffer and Dzakpasu reported an interesting study of solid state intramolecular hydrogen transfers.[4] Their investigation was mainly concerned with relationships between the solid state conformation of the substrates and the primary photochemical steps. In this paper, we report the first example of type II reaction of carbonyl compounds in the crystalline state, in which the behavior of the biradical formed by γ-hydrogen abstraction is apparently influenced by crystal-lattice restraints.[5]

The substrates chosen in our study are N,N-disubstituted α-oxoamides (**1**). Our previous work[6] on the solution phase photochemistry of these oxoamides showed that the primary step of the reaction was γ-hydrogen abstraction by the ketone carbonyl oxygen to give the biradical (**5**) which undergoes three

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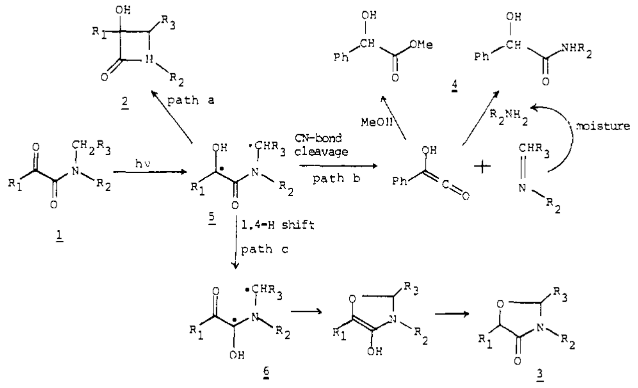
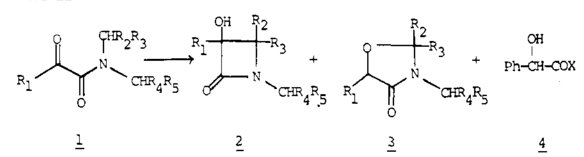
Scheme I



Scheme II



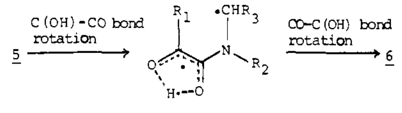
a: R_1=Ph, R_2=R_4=H, R_3=R_5=Ph
b: R_1=Me, R_2=R_4=H, R_3=R_5=Ph
C: R_1=Ph, R_2=R_3=R_4=R_5=Me
d: R_1=Ph, R_2=R_4=H, R_3,R_5= -$(CH_2)_3$-
e: R_1=R_2=R_3=R_4=R_5=Me

Table I. Photochemical Reaction of α-Oxoamides

starting materials	melting pts, °C	reaction conditions	yields, % 2	3	4
1a	97	solid state, 0 °C	82	*a*	*a*
		in benzene[b]	~100	*a*	*a*
		in methanol[b]	86	*a*	*a*
1b	39	solid state, −78 °C	89	*a*	*a*
		in benzene[b]	94	*a*	*a*
		in methanol[b]	17	78	*a*
1c	126	solid state, 0 °C	83	*c*	*a*
		in benzene[b]	*c*	62	29[d]
		in methanol[b]	22	58	16[e]
		in DMF[b]	13	31	35[d]
1d	106	solid state, 0 °C	358	20	*a*
		in benzene[b]	27	34	*a*
		in methanol[b]	4	60	*a*
		in DMF[b]	16	48	*a*
1e	*f*	solid state, −78 °C	31	29	*a*
		in benzene[b]	*a*	86	*a*
		in methanol[b]	*a*	~100	*a*
		neat liquid[b]	*c*	65	*a*
		neat liquid, −20 °C	*a*	73	*a*

[a] Not detected. [b] At room temperature, ~25 °C. [c] Trace. [d] *N*-Isopropylmandelamide. [e] Methyl mandelate. [f] Liquid at room temperature.

Scheme III



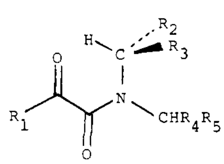


Figure 1. Most favorable excited state conformation for γ-hydrogen abstraction in the α-oxoamide.

types of reactions, i.e., type II cyclization (path a) to afford the β-lactam (**2**), type II elimination (path b) followed by addition of a nucleophile to give a mandelic acid derivative (**4**), and 1,4-hydrogen shift (path c) followed by cyclization to yield the oxazolidin-4-one (**3**) (see Scheme I). Yields of these products in the solution phase reaction are dependent on substituents and solvents.[6]

Solid State Photoreactions. The amides were crystallized from *n*-hexane or methanol-water, and irradiated as described in the Experimental Section. All five *N*,*N*-dialkyl-α-oxoamides (**1a–e**) underwent efficient photochemical reactions in the crystalline states. In the case of benzoylformamides **1a** and **1c**, the reaction proceeded gradually even when the crystals were exposed to the scattered light in the laboratory. The results of the photoreactions in the solid states and in solution are summarized in Table I. The five amides yielded the corresponding β-lactams (**2**) as main products in the solid state photolysis. The efficient type II cyclization of the oxoamides in the solid states is of interest in view of the fact that some acyclic ketones afford type II products efficiently in the liquid phase but are inert toward photolysis in the crystalline states.[7] The specific formation of **2a** and **2b** in the solid state photolysis of *N*,*N*-dibenzylamides **1a** and **1b** is not surprising since similar results were obtained in the photolysis of the amides in an aprotic solvent. On the other hand, the results of the solid state photolysis of **1c**, **1d**, and **1e** were quite different from those of the liquid phase photolysis, in which the oxazolidinones (**3**) were main products irrespective of solvents.

The selective formation of the β-lactams in the solid state photolysis is of interest in both mechanistic and synthetic view points.[8] The fact that the β-lactams become favored in the solid state reaction can be explained as follows. Formation of **3** involves considerably more molecular motion of the biradical intermediate **5** than does formation of **2** (Scheme II). The 1,4-hydrogen migration of **5** (path c) in aprotic media is constrained to the planar or nearly planar cisoid transition state[9] (Scheme III), which requires rotation of the C(OH)-CO bond of **5** because γ-hydrogen abstraction can occur only from the transoid form of **1** (see Figure 1). The resulting biradical has to rotate the CO-C(OH) bond again to undergo cyclization. Such molecular motions are possible in solution but prevented by crystal-lattice restraints in the solid state. The absence of the ketene-derived product **4** in the solid state photolysis of **1c** can be explained in terms of the lack of a suitable trapping agent in the medium. The ketene is presumed to decompose during irradiation, although a possibility that the ketene reacts with the imine to produce the starting material (a reverse reaction of path b) cannot be eliminated.

The selectivities in the solid state reactions of **1d** and **1e** were relatively low as shown in Table I. The low selectivities may be ascribable to the incomplete crystallinity of the amides under the reaction conditions. The amide **1e** is liquid at room temperature and was solidified by cooling to −78 °C before irradiation, but the solid was not completely crystalline but partially glassy. Although **1d** is a moderately high melting solid, it turned to a greasy semisolid at the end of irradiation. An attempt to avoid the partial liquefaction by lowering the reaction temperature was unsuccessful because the solid state reaction of **1d** became extremely inefficient below −30 °C. On the other hand, the selectivity was almost perfect in the case of **1c**. This seems to be due to the high melting point of the

Table II. Temperature Effects on the Photoreactions in Solution

reactant	solvent	reaction temp, °C	yields, % 2	3	4
1c	MeOH	−40 to ca. −30	16	82	*a*
		~25	22	58	16[b]
		50	19	34	47[b]
		65	18	22	54[b]
		90	18	11	62[b]
1d	MeOH	~25	4	60	*a*
		−50 to ca. −40	*c*	66	*a*
1e	AcOEt	~25	6	52	*a*
		−50 to ca. −40	*c*	55	*a*

[a] Not detected. [b] Methyl mandelate. [c] Trace.

reaction mixture (94-114 °C at 42% conversion; 93-108 °C at 88% conversion).

It may be conceivable that the solid state reactions involve reaction from micro pools of liquid caused by localized heating, and that the selective formation of the β-lactams is due to the solvent effects of the liquefied oxoamides, since the photochemical reactions of the α-oxoamides show substantial solvent effects. This possibility can, however, be eliminated because photolysis of **1e** in the liquid neat phase gave at most only a trace of **2e** both at 25 and −20 °C. Furthermore, the yields of the lactams **2c** and **2d** were poor even in the photolysis in dimethylformamide which is presumed to be a good model for liquid α-oxoamides.

All these results are consistent with the above explanation that crystallinity of the reactants plays important roles in the selective formation of the β-lactams.

Finally, stereoselectivity of the photoreaction is worth noting. Stereoisomers can exist for the lactams **2a, 2b,** and **2d.** However, in the case of **2a** and **2b,** the NMR spectra of the isolated product and the reaction mixture showed that only one stereoisomer was produced exclusively[10] both in the solid and liquid state photolyses, though the configuration was not assigned. Meanwhile, the absence (or presence) of stereoisomers was not clear in the case of **2d** because the NMR spectrum was quite complex.

Temperature Effects. Since the solid state photoreactions were carried out at low temperatures in order to avoid melting of the reaction mixture, it is conceivable that the reaction temperature may be more important than the crystallinity of the reactant for the selective formation of the β-lactams. Accordingly, the temperature effects on the liquid and solid phase reactions were examined. The yields of the products in the photolysis of **1c** in methanol were apparently temperature dependent as Table II shows. The oxazolidin-4-one (**3c**) was a main product at low temperatures, while the type II cleavage product, methyl mandelate (**4**), was produced predominantly at high temperatures. A possibility of thermal conversion of **3c** to methyl mandelate in the high temperature reaction was eliminated because **3c** in methanol was quite stable even at 100 °C. Meanwhile, the yield the lactam **2c** did not increase at low temperatures but was almost independent of the reaction temperature. Also in the case of **1d** and **1e,** lowering the reaction temperature did not increase the yield of the lactam.

On the other hand, the selectivity in the solid state photolysis of **1c** was high not only at 0 °C but also at 25 °C. The yield of **2c** was still moderately high even at 60 °C, but became very low at 95 °C where the reaction mixture gradually liquefied as the reaction proceeded (Table III). On the basis of these results, we can conclude that the selective formation of the β-lactams in the solid state photolysis is due to the crystallinity of the reactants rather than the low reaction temperature.

The remarkable temperature effect in the photolysis of **1c** in methanol could be explained on the assumption that the activation energies (E) and the frequency factors (A) for the three biradical reactions (1,4-hydrogen shift, type II cyclization and elimination) are as follows: $E_{\text{elim}} > E_{\text{cycl}} > E_{\text{Hshift}}$ and $A_{\text{elim}} > A_{\text{cycl}} > A_{\text{Hshift}}$, although no data in support of this assumption are available at present.[11]

Table III. Temperature Effects of the Solid State Photoreactions

reactant	reaction temp, °C	yields, % 2	3	4
1c	0	83	*a*	*b*
	~25	82	*a*	*b*
	60	65	5	6[c]
	92	27	6	41[c]

[a] Trace. [b] Not detected. [c] *N*-Isopropylmandelamide.

Table IV. Effects of Conversion Percent in the Solid State Photolysis of **1d**

conversion, %	yields, % 2d	3d
100	58	20
44	61	13
18	64	10

Table V. Effects of Crystallization Methods

reactant	crystallization method	crystal forms	melting pts, °C	yields, % 2	3
1a	from *n*-hexane	prisms	96-97	82	*a*
	from MeOH-H_2O	needles	96-97.5	80	*a*
1c	from *n*-hexane	prisms	124-126	83	*b*
	from MeOH-H_2O	prisms	124-125.5	82	*b*
	by evaporation of CH_2Cl_2 soln		121-124	61	15

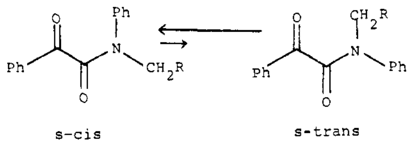
[a] Not detected. [b] Trace.

Effects of Conversion Percent. The relatively low selectivity in the photolysis of **1d** was ascribable to the partial liquefaction of the reaction mixture during irradiation as described above. Therefore, lowering the conversion percent of the reaction was expected to improve the selectivity. In fact, the β-lactam **1d** was formed more selectively at low conversion (Table IV). This result also indicates that the crystallinity of the reactant plays important roles in the selective formation of the lactam. The selectivity in the solid state photolysis of **1d** was not so high even in the case of low conversion. This result is, however, not unreasonable because the conversion percent at the crystal surfaces may be much higher in spite of the low total conversion percent.

Methods of Crystallization. Although the crystal forms of the amides **1a** and **1c** varied with crystallization solvents (*n*-hexane or methanol-water), the melting points were independent of the solvents. The efficiency and the selectivity (in case of **1c**) of the solid state reactions were also not affected by the crystallization solvents (Table V). On the other hand, when the crystals of **1c** were deposited on a glass plate by evaporating the methylene chloride solution of **1c,** the selectivity became low and 15% of the oxazolidin-4-one (**3c**) was produced. This result is presumed to be ascribable to the incomplete crystallinity.

Excited State Geometries in the Crystalline States. The fact that the α-oxoamides **1a–1e** undergo γ-hydrogen abstraction efficiently even in the crystalline states indicates that the geometries of the amides in the crystalline states are favorable for γ-hydrogen abstraction at least in the excited states. It is well-known that the favorable geometry for γ-hydrogen ab-

Scheme IV



1f: R=H
1g: R=Me
1h: R=Ph

straction is one in which the hydrogen being abstracted is coplanar with the carbonyl group.[12] Since amide groups are planar,[13] the α-oxoamides can achieve such a geometry only when they possess coplanar or nearly coplanar transoid dicarbonyl geometries (Figure 1). Although it is quite difficult to know the excited state geometries of the amides in the crystalline states, those of related compounds in solvent glasses have been investigated. The excited states of α-dicarbonyl compounds such as dialkyl, diaryl, and alkyl aryl α-diketones,[14,15] α-oxoacids,[16] or α-oxoesters[16] have been presumed to possess coplanar or nearly coplanar dicarbonyl geometries. Therefore, it is highly probable that the most stable excited state geometry of α-oxoamides is also planar about the CO-CO bond and favorable for γ-hydrogen transfer (Figure 1). The very rapid γ-hydrogen abstraction of the α-oxoamides in solution[6] is also consistent with the favorable excited state geometry for the intramolecular hydrogen abstraction.[17]

On the other hand, it is well-known that α-dicarbonyl compounds can possess coplanar dicarbonyl geometries in the ground states only when there are no large steric hindrances in the geometries.[14-16] Examination of molecular models showed that the ground state geometries of *N,N*-dialkyl-α-oxoamides could not be planar because of the steric repulsion between the alkyl groups on nitrogen and the ketone carbonyl oxygen as in the case of *N,N'*-tetraalkyloxamides.[18] Therefore, the CO-CO bond of the α-oxoamides is presumed to rotate to some extent on excitation even in the crystalline states so as to make γ-hydrogen abstraction possible. However, such rotation may not be necessary for the hydrogen abstraction if the ketone carbonyl group becomes pyramidal on excitation.[19]

α-Oxoanilides. *N*-Alkyl-α-oxoanilides (**1f-1h**) were completely inert toward photolysis in the crystalline states in distinction from the photoreactions in solution.[6] The unexpected nonreactivity of the anilides may be attributable to the infavorable geometry for γ-hydrogen transfer in the crystalline states. Two rotational isomers, s-cis and s-trans, can exist for *N*-alkylanilides (Scheme IV). In fact, the NMR spectrum of **1f** showed the presence of a major isomer (~95%) and a minor isomer (~5%). The ratio was almost independent of solvents (C_6D_6, $CDCl_3$, or CD_3OD). The major isomer was assigned to be a s-cis isomer as follows. The NMR study on a number of unsymmetrically N-substituted α-oxoamides[20] using lanthanide shift reagents revealed that europium binded to the amide carbonyl oxygen rather than the ketone carbonyl oxygen and the substituent syn to the amide oxygen showed considerably larger lanthanide induced shift (LIS) than that anti to the oxygen. Since the methyl group of the major isomer of **1f** showed much larger LIS than that of the minor isomer,[21] the major isomer was assigned to be the s-cis isomer. The assignment was further supported by the fact that in *N*-alkylarylamides the s-cis isomer is more stable than the s-trans isomer unless bulky substituents are present at the ortho position of the aryl group.[22]

Although solid state and solution configuration do not necessarily correspond, it appears to be quite unlikely that only one isomer would exist in the crystalline state and the other isomer would be observed in overwhelming preponderance by NMR in solvents of varying polarity.[23] Therefore, it is highly probable that the anilides exist in the s-cis geometry also in the crystalline states, and γ-hydrogen abstraction cannot occur from the geometry because the alkyl group bearing γ-hydrogen is remote from the ketone carbonyl group. In conclusion, the inertness of the α-oxoanilides is most reasonably explained by the unfavorable geometry for γ-hydrogen transfer, although other possibilities such as rapid deactivation of the excited amides or efficient reversion of the biradical[24] **5** to **1** in the solid states cannot be excluded at present.

Experimental Section

General Procedure for the Solid State Photoreactions. The recrystallized α-oxoamide (**1**) (100-300 mg) was sandwiched between a pair of Pyrex plates (thickness 2 mm) and put into a polyethylene envelope. The envelope was sealed and placed in a cold medium (water, ice-water, or dry ice-methanol) and irradiated with a high-pressure mercury lamp (100 W) for 1-10 h. The lamp was used with a vessel for immersion type irradiation which contained dry air. The products were isolated by column chromatography on silica gel. The structures of **2a**, **2b**, **2c**, **3b**, **3c**, and **3e** were confirmed by direct comparison with samples obtained in the photoreaction of the corresponding starting materials in solution,[6] while **2d**,[8a] **3d**,[8a] and *N*-isopropylmandelamide (**4c**)[25] were identified on the basis of the melting points and the spectral data. The products, **2a-e**, **3b**, **3e**, and **4c** were stable under the irradiation and workup conditions, while **3c** and **3d** decomposed slowly on standing in the presence of air.

3,4,4-Trimethyl-3-hydroxy-1-isopropylazetidin-2-one (**2e**): mp 122-124 °C; IR (KBr) 3250 and 1720 cm^{-1}; NMR ($CDCl_3$) δ 1.17-1.47 (15 H, 5 Me), 3.58 (m, 1 H, N-CH).

Anal. Calcd for $C_9H_{17}O_2N$: C, 63.13; H, 10.01; N, 8.18. Found: C, 63.15; H, 10.04; N, 7.89.

General Procedure for the Photoreactions in Solution. A solution of the oxoamide **1** (1%) was irradiated in a Pyrex vessel under argon with a high-pressure mercury lamp for 3-5 h. When the reaction temperature was higher than the boiling point of the solvent, the solution was sealed in a Pyrex tube. The photolysis of **1e** in the liquid neat phase was carried out as in the case of solid state photolysis.

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Chemiluminescent Reactions of Lucigenin. 1. Reactions of Lucigenin with Hydrogen Peroxide

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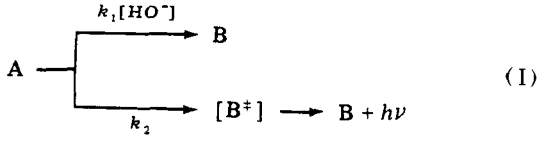
Abstract: The chemiluminescent reaction of lucigenin (*N,N'*-dimethyl-9,9'-biacridine, **1**) at various pH values (solvent H$_2$O, 30 °C, $\mu = 1.0$) with hydrogen peroxide in excess is first order to 6 half-lives. At constant pH the reaction rate was determined to be dependent upon the first power of the concentration of hydrogen peroxide and to be independent of concentrations of **1** and buffers. From the pH dependence of the pseudo-first-order rate constant (k_{obsd}, $[\text{H}_2\text{O}_2]_\text{T} \gg [\mathbf{1}]$) the rate of disappearance of **1** follows the general expression $d[\mathbf{1}]/dt = [\mathbf{1}]\{k_1[\text{HO}_2^-] + k_2[\text{HO}_2^-][\text{HO}^-]\}$. Diminution in light emission with time was shown to follow the same rate law and the quantum yield was established to be independent of [**1**], total hydrogen peroxide concentration ($[\text{H}_2\text{O}_2]_\text{T}$), and pH. These results establish that the chemiluminescent reaction of **1** with hydrogen peroxide follows the same rate law as does the overall disappearance of **1** from solution in the presence of varying concentrations of H$_2$O$_2$ and at all pH values. Replacement of H$_2$O with *t*-BuO$_2$H provides less light than obtained in the absence of any peroxide agent. Lucigenin reacts with H$_2$O$_2$ and *t*-BuO$_2$H at various pH values to produce *N*-methylacridone (**2**) as the major fluorescent product. The chemiluminescent spectrum at any time could be shown to result from emission by excited **2** and subsequent absorption by **1.** Competing dioxetane and linear peroxide mechanisms (with H$_2$O$_2$ and *t*-BuO$_2$H) are proposed and discussed. Evidence is presented which suggests that the 9,9'-dioxetane of **1** provides **2** + **2*** by the two competing pathways of spontaneous fragmentation and 1e$^-$ transfer.

Introduction

Lophine (1877),[1] luminol (1928),[2] and lucigenin (1935)[3] stand as the classic organic chemiluminescent agents. Of these three compounds, the chemiluminescent (CL) reactions of *N,N'*-dimethyl-9,9'-biacridine (lucigenin, **1**) are possibly the least understood. Indeed, chemiluminescence has been reported to occur on the addition of numerous nucleophiles and reducing agents to solutions of **1.** However, none of these studies included a systematic approach to the mechanism of the CL reactions; few workers have even bothered to maintain constant pH. The application of kinetic methods to the elucidation of the mechanism of CL reactions may, by itself, be of limited use for the simple reason that light production may represent a minor reaction path. However, it is well appreciated[4] that the rate laws for both of two parallel reactions may be determined from the overall kinetic expression for disappearance of the common substrate and the fractional yield of product arising from the minor reaction. Light is a product of the minor CL reaction and the chemiluminescent quantum yield (Φ_CL) is a measure of the fractional yield of the minor reaction. As a pertinent example, consider the reactions of eq I where the major reaction is not light producing. At constant pH the rate of disappearance of A and appearance of B will be pseudo first order and the pseudo-first-order rate constant (k_ψ) will be equal to $k_1[\text{HO}^-] + k_2$. Since $k_1[\text{HO}^-] \gg k_2$, $k_\psi = k_1[\text{HO}^-]$, so that the rates of disappearance of A and (appearance of B) will be under the kinetic control of the major reaction path. For this reason a plot of log k_ψ vs. pH will be of slope +1. A plot of the logarithm of the first-order rate constants for decay of photon emission vs. pH will necessarily also be linear and of slope +1. If α is defined as the mole fraction of A that passes through the CL pathway (i.e., $\alpha = k_2/k_1[\text{HO}^-]$), then α is equivalent to Φ_ex, the overall efficiency of producing the excited state B‡, and directly proportional to the quantum yield (Φ_CL). It follows from eq I that a plot of log Φ_CL ($=\Phi_\text{fl}k_2/k_1[\text{HO}^-]$ where Φ_fl is the fluorescence quantum yield equating Φ_fl to α) vs. pH would be linear but of slope −1. Such a relationship would establish that the very minor CL reaction is independent of [HO$^-$]. If both the major reaction and the minor CL reaction were of the same order in HO$^-$, H$_3$O$^+$, X, etc., then a change in the concentrations of these reagents would not alter Φ_CL. This approach has been employed herein to establish the composition of the transition state for the CL reaction of **1** with hydrogen peroxide.



(I)

Experimental Section

Materials. *N,N'*-Dimethyl-9,9'-biacridinium nitrate (1) (Aldrich Chemical Co.) was repeatedly recrystallized from ethanol-water (5/95 v/v) to give orange crystals that were dried at 100 °C (0.1 mmHg) for 24 h, mp 250 °C dec (lit.[5] 250 °C). UV-vis (water, pH 3.72): 453 nm (log ϵ 3.93), 430 (4.03), 420 (3.95), 369 (4.55), 354 (4.24), 260 (5.22). *N*-Methylacridone (**2**) was prepared by a literature procedure[6] and recrystallized (three times) from absolute ethanol to give yellow crystals (needles) that melted at 210–211 °C (lit.[6] 209–210

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