

Substituent Effect on the Chemiluminescence Quantum Efficiency of Some Acridan Derivatives Chemiluminescence Quenching

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Reaction of eight 9-benzylidene-N-methylacridan derivatives with singlet oxygen results in chemiluminescence quantum yields giving a good fit if plotted versus *Hammett's* " σ " values. To account for the deviation of two derivatives, the quenching constants of the leaving moieties on the fluorescence of the primary emitter are compared with the diffusion constant in the medium, verifying an earlier suggestion that even small quenching efficiencies of the leaving moiety greatly affect chemiluminescence quantum yields.

(Keywords: Acridans; Chemiluminescence; Quenching)

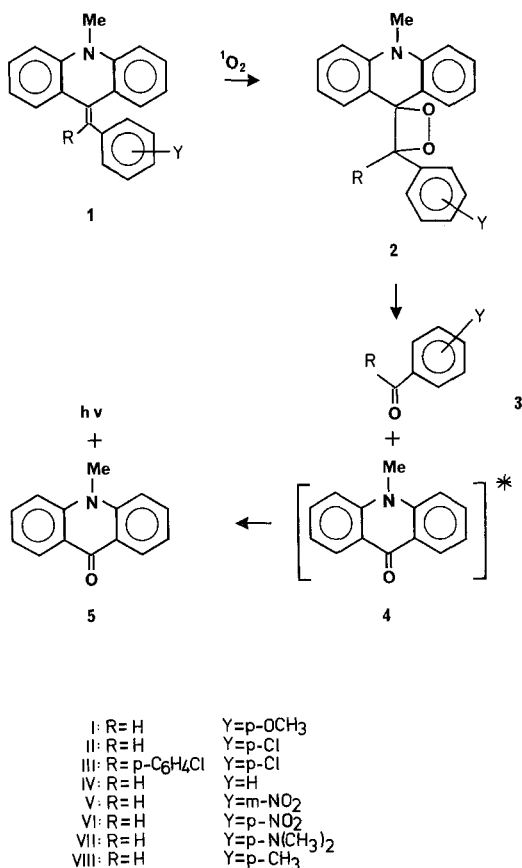
Substituenteneffekte auf die Chemilumineszenz-Quantenausbeute einiger Acridan-Derivate. Chemilumineszenz Quench-Effekte

Die Reaktion von acht 9-Benzyliden-N-methylacridanen mit Singlet-Sauerstoff ergibt Chemilumineszenz-Quantenausbeuten, die eine gute lineare Abhängigkeit gegenüber den *Hammett'schen* σ -Werten zeigen. Um die Abweichung zweier Derivate zu erklären, wurden die Quench-Konstanten für die bei der Fluoreszenz des Primär-Emitters entstehenden Moleküle in Relation zur Diffusionskonstante gesetzt. Es bestätigte sich die frühere Vermutung, daß auch eine geringer Quench-Effizienz von entstehenden Produkten einen sehr großen Effekt auf die Chemilumineszenz-Quantenausbeuten haben kann.

Introduction

In an earlier report¹ we have shown that the chemiluminescence quantum yields of the substituted 9-benzylidene-N-methylacridans (see Scheme 1) on reaction with $^1\text{O}_2$ ($\text{NaOCl} + \text{H}_2\text{O}_2$) in N,N-dimethylformamide (DMF) solutions fit well a plot versus *Hammett's* " σ "

Scheme 1



constants, the higher quantum yields being associated with negative “ σ ” values. Since two acridans [the *p*-N(CH₃)₂ and *m*-NO₂ derivatives] did not fit in the plot—their quantum yields being much lower than expected—and since there was no apparent mechanistic interpretation for this deviation, attention was focussed on the photophysics of light emission following the chemiexcitation step. Indeed, it was shown that the aldehydes **3** derived from the above two acridans are quenchers of the fluorescence of N-methylacridone (*NMA*) (**5**) which is the primary emitter in this light reaction (Scheme 1); however, this effect was not so pronounced as to account for the high deviations in chemiluminescence quantum yields [at least at a ratio (*NMA*): aldehyde equal to 1; the two moieties are produced in this ratio]. It was argued that unlike normal

fluorescence quenching (where one visualizes the energy donor and acceptor approaching each other from “infinite” distances) in this case the two species are moving apart starting from “zero” distances. The two moieties formed—even disregarding any cage effect—should not move faster than diffusion allows; therefore, for a period comparable to the fluorescence lifetime of the emitter (a few nanoseconds) the two moieties are still in relative proximity. As dipole-dipole interactions can occur at distances as large as 50–100 Å, the excited moiety in such interactions has a high probability of remaining inside the sphere of influence of the quenching moiety, in which case the “effective” quencher to emitter ratio is not 1:1 but very much larger as compared with “normal” external equimolar addition of quencher to the emitting species.

To provide further evidence supporting this view that in chemiluminescence the quenching by the leaving moiety can be very efficient, we now wish to report a comparison of the quenching rate constants (K_q) for this series of leaving moieties **3** on the primary emitter (*NMA*) (**5**), with the diffusion rate constant (K_d) in the medium, in connection with *Hammett's* “ σ ” constants of the substituents versus chemiluminescence quantum yields.

Results and Discussion

The diffusion rate constant (K_d) was calculated from the modified *Debye* equation²

$$K_d = \frac{1}{4} \left(2 + \frac{d_1}{d_2} + \frac{d_2}{d_1} \right) \frac{8 RT}{3 \cdot 10^3 n} \quad (1)$$

where n is the viscosity of the solvent and d_1 , d_2 are the molecular diameters of the fragments moving apart. Substituting $8.31 \cdot 10^7$ erg/mol · deg K for R , $0.84 \cdot 10^{-2}$ g s⁻¹ cm⁻¹ for n (the viscosity of N,N-dimethylformamide at 293° K) and assuming $d_1 = d_2$, the rate constant for the moving apart of the fragments becomes $k_d = 7.73 \cdot 10^9$ l mol⁻¹ s⁻¹.

Regarding the quenching of *NMA* by the substituted aldehydes (and ketone) produced on decomposition of the intermediate dioxetan, it should be noted that there is very little overlap between the fluorescence spectrum of *NMA* and the absorption spectra of the substituted aldehydes, indicating that resonance energy transfer to the aldehydes is unlikely. The alternative left is quenching through molecular “contact” in general inside the solvent cage in which the two moieties are simultaneously produced. In this case, the quenching constants K_d can be calculated from the relationship

$$K_q = K_{SV}/\tau_d \quad (2)$$

where K_{SV} is the *Stern-Volmer* constant and τ_d is the energy donor's fluorescence lifetime, equal to $7.6 \cdot 10^{-9}$ s (the fluorescence lifetime of *NMA* in *N,N*-dimethylformamide³). The *Stern-Volmer* constants were calculated from the *Stern-Volmer* plots

$$\frac{I_0}{I} = 1 + K_{SV}[Q] \quad (3)$$

($[Q]$ is the concentration of the added quencher), with at least four quencher concentrations per plot.

The quenching constants for the quenching of *NMA** by the substituted aldehydes (which represent the second moiety from the decomposition of the acridan derivatives) are shown in Table 1 together with the chemiluminescence quantum yields of the reactions and *Hammett's* " σ " constants of the substituents.

Table 1

Substituent	" σ " Constant ⁴	Chemiluminescence Quantum Yield ¹ (Einstein mol ⁻¹)	K_d (l mol ⁻¹ s ⁻¹)
<i>p</i> -OCH ₃	-0.268	$1.31 \cdot 10^{-2}$	$1.15 \cdot 10^9$
<i>p</i> -CH ₃	-0.170	$8.77 \cdot 10^{-3}$	$3 \cdot 10^9$
<i>p</i> -H	0	$4.4 \cdot 10^{-3}$	$3.9 \cdot 10^9$
<i>p</i> -Cl	+0.277	$1.3 \cdot 10^{-3}$	$8.3 \cdot 10^{10}$
di- <i>p</i> -Cl	+0.454	$2.73 \cdot 10^{-4}$	$4.6 \cdot 10^{10}$
<i>p</i> -N(CH ₃) ₂	-0.830	$1.4 \cdot 10^{-4}$	$1.64 \cdot 10^{11}$
<i>p</i> -NO ₂	+0.778	$8.18 \cdot 10^{-5}$	$7.2 \cdot 10^{10}$
<i>m</i> -NO ₂	+0.710	$6 \cdot 10^{-6}$	$2.64 \cdot 10^{10}$

Comparing the values of K_d with the value of K_d —which was found equal to $7.73 \cdot 10^9$ l mol⁻¹ s⁻¹—the following three cases may be distinguished.

(a) $K_d > k_q$, good fit

To this group belong the *p*-OCH₃, *p*-CH₃, and *p*-H derivatives, which fit well on the plot of chemiluminescence quantum yields versus *Hammett's* " σ " values¹ and are associated with negative or zero " σ " values as required by the electrophilicity of the singlet oxygen attacking the double bond to form the critical dioxetan intermediate. In this case, the chemiluminescence quantum yield is a direct result of the reaction mechanism and is not altered by any quenching of the excited product by the leaving moiety.

(b) $K_d < k_q$, *bad fit*

This group includes the *p*-N(CH₃)₂ and *m*-NO₂ derivatives. The chemiluminescence quantum yields deviate from the plot¹ versus Hammett's "σ" values, being much lower than expected. This deviation illustrates the dramatic effect of the leaving group's quenching efficiency on the quantum yield of the light reaction. Particularly in the case of the *p*-N(CH₃)₂ derivative with its highly negative "σ" value coupled with the presence of a lone pair of electrons on the aliphatic amine nitrogen which according to the CIEEL mechanism of chemiexcitation⁵ could give rise to even higher chemiexcitation yields, the difference between predicted and measured quantum yields is even more striking. It is, however, easily attributable to the inequality $K_d \ll K_q$.

(c) $K_d < K_q$, *good fit*

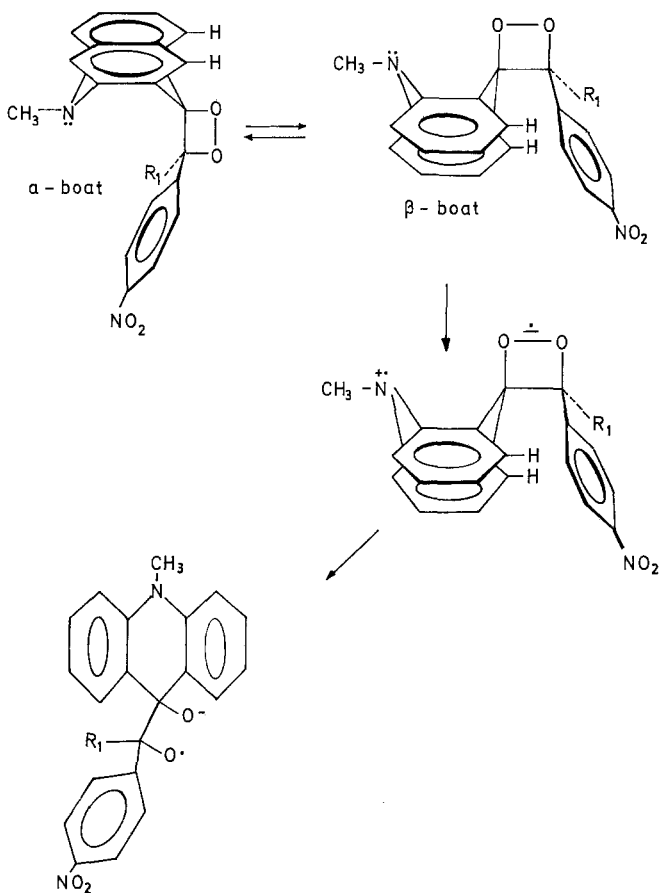
This group includes the *p*-Cl, *p*-NO₂ and di-*p*-Cl derivatives, the quantum yields of which fit the plot versus Hammett's "σ" constants, although according to the above arguments they ought to be lower. An explanation of this discrepancy would require the presence of another factor raising the chemiexcitation efficiency of the light reactions of these three derivatives, yet not affecting, or little affecting the light reactions of the other derivatives. Such a factor is apparent when the chemiexcitation step is considered in the light of the CIEEL (Chemically Induced Electron Exchange Luminescence) mechanism⁵ as applied in the case of acridan chemiluminescence⁶.

Indeed, the acridan dioxetan **2** shown in Scheme 1 equilibrates between α- and β-boat conformations as shown in a simplified way in Scheme 2.

In the β-boat conformation the critical electron transfer from the heterocyclic nitrogen atom to the O—O bond of the dioxetan (required by the CIEEL mechanism) is facilitated by proximity (~ 3 Å), in contrast to the α-boat conformation. Any effect tending to stabilize the β-boat conformation should increase the chemiexcitation efficiency. The *p*-NO₂, *p*-Cl and di-*p*-Cl groups are associated with a strong electron withdrawing effect as compared with the other substituents employed here [*m*-NO₂ is not as strong and indeed the *m*-NO₂ derivative belongs to case (b)]; so, apart from the initial electrophilic attack of singlet oxygen on the double bond, the step leading to cleavage of the O—O bond will be facilitated by the three substituents of case (c): lowering of the electronic content of the O—O bond (apart from through space stabilization of the β-boat conformation) will render easier the electron transfer from the heterocyclic nitrogen to the peroxide, increasing eventually the chemiexcitation efficiency and explaining the apparent discrepancy.

Encouraged by the above results we extend now this study to other

Scheme 2



chemiluminescent systems to find out if these assumptions find further support. Since mechanistic interpretations are usually based on chemiexcitation yields, which are in turn calculated from chemiluminescence quantum yields, the latter need a correction taking into account the quenching efficiency of the leaving moiety on the primary emitter.

Experimental

NMA was prepared by the method of Decker⁷ and was employed chromatographically pure. *DMF* was spectroscopy grade and benzaldehyde, *p*-nitrobenzaldehyde, *m*-nitrobenzaldehyde, 4,4'-dichlorobenzophenone, *p*-dimethylaminobenzaldehyde, *p*-chlorobenzaldehyde, *p*-methylbenzaldehyde and

p-methoxybenzaldehyde were analytical grade. The acridan derivatives **1** were synthesized as described earlier¹.

NMA fluorescence spectra were run on an Amico-Bowman SPF spectrofluorimeter with excitation λ_{max} 365 nm, and were corrected for self-absorption if the added aldehydes absorbed in this region. The *Stern-Volmer* constants (K_{SV}) were calculated from the slopes of the straight lines obtained when the ratios $(I_0/I) - 1$ (I_0 is the fluorescence intensity of *NMA* and I is the fluorescence intensity of *NMA* in the presence of each aldehyde) were plotted versus aldehyde concentration for at least four aldehyde concentrations at emission λ_{max} ca. 420 nm.

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