BENZYLIDENE FLUORENE OZONOLYSIS UNDER CHEMILUMINESCENCE MIMETIC CONDITIONS IN HOMOGENEOUS AND MICELLAR MEDIA
I: KINETIC LAW AS A FUNCTION OF HAMMETT'S σ CONSTANTS AND QUENCHING BY THE LEAVING MOIETY

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(Received January 2, 1987)

Summary

A series of 9-(*p*-substituted) benzylidene fluorenes (*p*-nitro, *p*-cyano, *p*-chloro, *p*-bromo, *p*-H, *p*-methyl, *p*-methoxy, *p*-methoxy-*m*-methyl and *p*-dimethylamino) was synthesized and the rates of fluorenone production on oxidation with ozone were followed fluorimetrically (apparent rates) and spectrophotometrically (true rates). The rates were plotted against Hammett's σ constants and any quenching effect of the leaving moiety on fluorenone at the moment of their production was illustrated as deviation from the plot of the apparent rates. The above effect was intensified in micellar media as a result of a more rigid confinement of the two species inside the micelle, supporting an earlier suggestion that, in chemiluminescence, even a small degree of quenching of the primary emitter by the leaving moiety can be very effective as a result of their inherent proximity at the moment of their production.

1. Introduction

Perkizas and Nikokavouras [1] have shown earlier that the chemiluminescence quantum yields of eight substituted 9-(benzylidene)-*N*-methylacridans on reaction with $^1O_2$ fit well on a plot against the Hammett's σ constants of the substituents.

The deviation of two acridans whose quantum yields were lower than expected could not be attributed to any mechanistic effect, so attention was focused on the photophysics following the chemiexcitation step and the idea was tentatively advanced that, in chemiluminescence, even a small degree of quenching of the primary emitter by the leaving moiety can be effective as a result of the inherent proximity of the two species. Indeed, unlike the usual fluorescence quenching, where energy donor and acceptor approach each other from "infinite" distances, in chemiluminescence the

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two species, simultaneously produced inside the solvent cage, are moving apart starting from "zero" distance and for a period comparable with the fluorescence lifetime of the emitter (a few nanoseconds) the two moieties can still be in relative proximity. This ought to be particularly so in the case of long-distance quenching (dipole–dipole interactions, 50 - 100 Å), where the excited moiety has a high probability of remaining, during its lifetime, inside the sphere of influence of the leaving quenching moiety. In any case on account of the inherent position of the quencher the "effective" quencher-to-emitter ratio will not be 1:1 (the two fragments are produced in this ratio) but much larger, compared with the external addition of quencher.

Evidence supporting these views was produced [2] when the constants for the quenching of the fluorescence of the primary emitter by the leaving fragments were compared with the diffusion rate constant, in connection with the above plot of chemiluminescence quantum yields against Hammett's σ constants.

In the above series of substituted acridans, the deviation of the two acridans was attributed to quenching of the fluorescence of the emitter by the leaving moiety, on the assumption that the chemiexcitation yields were uniform throughout the series, as the substituents were too far from the reaction centre. In order to avoid the uncertainty introduced by this assumption and to further strengthen the above views, the present study was undertaken under chemiluminescence mimetic conditions in which chemiexcitation efficiencies are not involved. Furthermore, as Nikokavouras and coworkers [3 - 5] have shown that carrying out a light reaction in agents resembling biological membranes affects the energy transfer in these systems, the experiments were repeated in micellar media.

2. Experimental section

2.1. Synthesis of 9-(p-substituted) benzylidene fluorenes

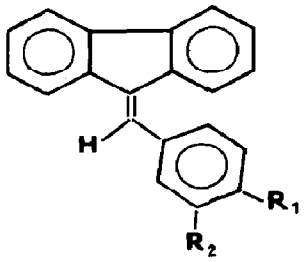
The 9-(*p*-substituted) benzylidene fluorenes of Fig. 1 (i - ix) were synthesized as described earlier [6 - 12] and were purified by recrystallization (ethanol, benzene–chloroform) and column chromatography (alumina–benzene).

2.2. Surfactants

The surfactant cetyltrimethylammonium chloride (CTAC) was repeatedly recrystallized from an (ethyl ether)–ethanol mixture (10:1) until the fluorescence was negligible. Dodecyltrimethylammonium chloride (DTAC) was employed without further purification.

2.3. Ozone

Ozone–air mixtures were produced with the aid of an OREC 0.3V9-A1 ozonator operating at a flow rate of 6.5 l h^{-1} and current intensity of 2.5 A.



R_1 = H	R_2 = NO_2	(i)
H	CN	(ii)
H	Cl	(iii)
H	Br	(iv)
H	H	(v)
H	CH_3	(vi)
H	OCH_3	(vii)
CH_3	OCH_3	(viii)
H	$N(CH_3)_2$	(ix)

Fig. 1. Substituted 9-benzylidene fluorenes employed.

2.4. Preparation of samples

Ethanolic solutions of the fluorenes were 1×10^{-4} M. Surfactant solutions of the fluorenes were prepared by stirring known amounts of the fluorenes (5×10^{-4} M) in DTAC (1×10^{-1} M) or CTAC (3×10^{-2} M) overnight (critical micellar concentration (CMC) for DTAC is 2.03×10^{-2} M and for CTAC is 1.3×10^{-3} M [13]).

The solutions were then centrifuged for 1 h, the clear solutions were decanted, the remaining precipitates were dissolved in ethanol and the amount of fluorene in the precipitates was determined spectrophotometrically. The fluorene concentration in the clear detergent solution was then calculated differentially and the solution was diluted with surfactant solution of the same concentration to reach 1×10^{-4} M. The measurements were repeated at concentrations of 1×10^{-5} M in both types of solution.

2.5. Experimental techniques

A fraction of the ozone–air mixture from the ozonator was passed at a flow rate of 100 ml min^{-1} in very fine bubbles through the fluorene solutions in a suitably constructed silica (Suprasil) cell of 1 cm path length.

The cell was positioned in the chamber of the measuring apparatus which, depending on the type of measurement, was an Aminco–Bowman SPF spectrophotofluorimeter, a Hitachi 220 spectrophotometer or the chemiluminescence chamber described earlier [14]. The measuring apparatus was connected to a suitable recorder, sweeping the time axis at a rate of 0.2 cm s^{-1}.

The production of fluorenone was followed at 304 nm (excitation), 520 nm (fluorescence), 248 nm (ethanol) and 250 nm (surfactant) (absorption); the reaction rates thus determined (absorption) were verified at 420 nm for compounds iii, iv, v and vi, at 426 nm for vii, at 440 nm for viii and at 248 nm for ix. Cleavage of the olefinic double bond was followed at

353 nm (i), 333 nm (ii), 328 nm (iii and iv), 325 nm (v), 330 nm (vi), 342 nm (vii), 346 nm (viii) and 397 nm (ix) in ethanol and at 363 nm (i), 341 nm (ii), 335 nm (iii), 336 nm (iv), 331 nm (v), 339 nm (vi), 350 nm (vii), 354 nm (viii) and 409 nm (ix) in CTAC. The fluorimeter slits were both 0.5 nm. The surfactant solutions were prepared and the reaction rates were measured at room temperature. To avoid excessive foaming of the surfactant and to work on the part of the curve which was a straight line, the calculations were based on the first 7 s of ozonization. The power of the lamp was 150 W.

3. Results and discussion

3.1. Chemiluminescence mimetic conditions

Ozone oxidation of the fluorenes shown in Fig. 1 was carried out under chemiluminescence mimetic conditions, *i.e.* in the spectrofluorimeter compartment where fluorenone, the expected primary emitter if the reaction was chemiluminescent, was excited with 304 nm light, the moment (10^{-15} s) it was produced; in this way, chemiexcitation yields were not involved, while the photophysics of the simulated chemiluminescent reaction was not different from that of a real light reaction. The reaction was not chemiluminescent and the same was true for the $^1O_2$ ($NaOCl + H_2O_2$) oxidation, probably as a result of predominant triplet [15 - 17] fluorenone formation; in fact, the reaction with $^1O_2$ gave very small fluorenone yields. The complete lack of chemiluminescence was, however, an asset in this study.

The reaction rates k_{app} determined fluorimetrically were characterized as apparent, because they were based on the fluorenone produced which was not in any way quenched, in contrast with the rates determined spectrophotometrically (true rates k_{tr}) which were based on the total fluorenone actually produced; k_{app} was used in this work because it could be affected by quenching effects. Although it does not substitute the quantum yields of our earlier work [1, 2] it is a measure of the effect under study.

3.2. Ozonolysis mechanism in ethanol and micellar media: interpretation of k_{tr} and k_{app}

The ozonolysis mechanism adopted here was that of Fliszar and Renard [18] shown in Fig. 2. Here, the primary ozonide breaks down to fluorenone and zwitterion **Ia** (path A) and substituted benzaldehyde **II** plus **III** (path B) [19].

Zwitterion **Ia** in polar solvents undergoes fast reaction to hydroperoxide **Ib** (ethanol) or **Ib** (water) [20, 21] and this fast reaction, plus the fact that ketones are less susceptive to nucleophilic addition [22, 23], prevents the recombination to normal final Griegee ozonides [18]. This, together with the planarity of the fluorenes and the small size of the ozone molecule [24], prevents steric inhibitions and a simple correlation between reaction rates and the electron content of the double bond can be expressed by Hammett's σ constants for the substituents. Thus a linear relationship

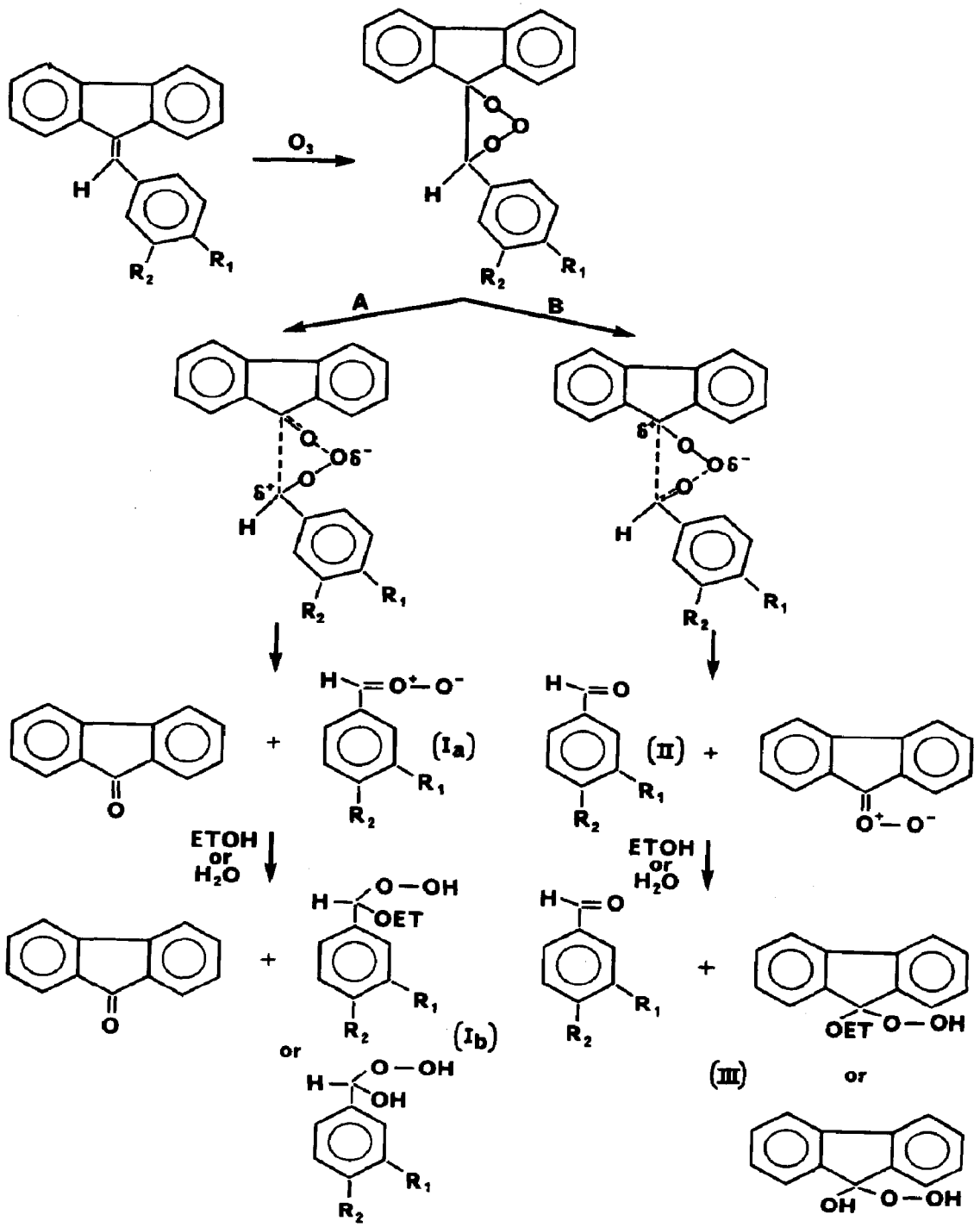


Fig. 2. Mechanism of 9-benzylidene fluorene ozonolysis.

between the reaction rates and Hammett's σ constants is to be expected. Indeed, substituents which are electron donors will stabilize the transition state of path A, increasing the rate of fluorenone production [18]; this will hold for true reaction rates as defined above. If, however, the rates of fluorenone production are measured fluorimetrically, the linear relationship between the reaction rates and Hammett's σ constants could be destroyed as a result of the additional factor of fluorescence quenching by other species, introduced by the method of measurement. This additional factor is illustrated in Fig. 3. Ozonolysis of the substituted fluorene gives fluorenone (F) and Ia encapsulated in the solvent cage, with a rate constant k_{tr}. Fluorenone is then excited (10^{-15} s) still inside the solvent cage together with Ia. It should be noted here that as absorption takes place in 10^{-15} s the time that the species F* and Ia remain in the solvent cage is of the order of 10^{-11} s, the lamp power is as high as 150 W and the concentration of F* in the bulk by the end of the first 7 s would be rather small; the concentration of molecules reacting or still enclosed in the solvent cage at any time will not be small compared with the bulk fluorenone concentration. If Ia is a quencher of F*, encapsulation of the two species in the solvent cage will cause strong quenching with a rate k_q'. The two species will then diffuse away from each other with a rate constant k_d, but, under the experimental conditions (continuous illumination), there will still be excitation of F followed by fluorescence and quenching by the species Ib, II and III, already present, with a rate constant k_q, where $k_q < k_q'$. Although Ib is derived from Ia, it should be noted that Ib, II and III cannot be found in the initial solvent cage together with F as, by the time that Ia has been transformed to Ib, the two species have escaped, while II and III are produced via another path. In any case, for the fluorenes where quenching is observed, Ia, Ib and II have

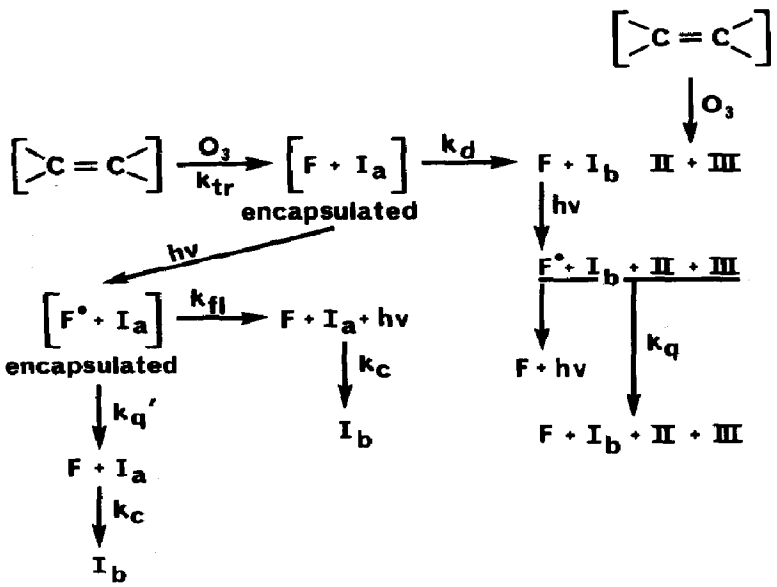


Fig. 3. Fluorescence quenching scheme of fluorenone (F) by the leaving moiety.

similar quenching efficiencies on F [25]. The reaction rates k_{app} measured fluorimetrically will therefore be smaller than the true rates k_{tr}, in the cases in which there is quenching of the fluorenone fluorescence by the leaving moiety.

It is expected that the mechanism of ozonolysis illustrated in Fig. 2 will be the same in micellar media, at least for reactions occurring in the Stern region where the polarity is similar to that of ethanol [26]. Furthermore, dipolar species such as ozone do not affect the micellar structure [27], nor do the free radicals from ozonization of water [28], in the bulk phase. The fluorenes of the present work solubilized in micellar media were enclosed in the Stern region as established by comparison of their absorption spectra, a well-accepted technique [29, 30] in hexane, ethanol, CTAC, DTAC and ethanol–water (1:1), with a dielectric constant equal to 50 [31].

The longer-wavelength bands of fluorenes vii, viii and ix are of the charge transfer type, while the longer-wavelength bands of fluorenes i - vi are of the $\pi \rightarrow \pi^*$ type [32], also sensitive to changes in solvent polarity [33]. These bands in CTAC and DTAC micellar media resembled more closely those in ethanol and ethanol–water, indicating that the fluorenes were solubilized in the Stern region; the same was found for fluorenone on observation of the $\pi \rightarrow \pi^*$ absorption at 298 nm [34].

3.3. Correlation of Hammett's σ constants with $\log k_{tr}$ *and* $\log k_{app}$

The logarithms of the true reaction rates and the initial rates in ethanol and CTAC aqueous micellar solutions are shown in Table 1, while the logarithms of the apparent rates are similarly shown in Table 2. The reaction rates were measured in the region around 250 nm and the measurements were repeated in the region 420 - 440 nm. In this region there is no overlap of the absorption spectra of fluorenone with most of the ozonolysis products. Hence we conclude that any small overlap would not affect our results especially at the low concentration of the first 7 s of reaction. In Figs. 4 and 5, the true reaction rates and apparent reaction rates respectively are plotted against Hammett's σ constants [35] for the substituents in ethanolic and micellar media. From these plots, the following conclusions can be drawn.

(a) $\log k_{tr}$ (Fig. 4(a)) is a linear function of Hammett's σ constant, as expected, since the electron-donating ability of the substituent is directly related to the stabilization of the transition state of path A (Fig. 2).

(b) $\log k_{app}$ (Fig. 5(a)) follows the same law with the exception of fluorene ix, the rate of which is much lower than that required by the law and this deviation is attributed to quenching of the fluorenone fluorescence by the corresponding fragment Ia (Fig. 2).

(c) In micellar media (Fig. 4(b)) the kinetic law for true rates is still valid. Here, however, positive deviations for fluorenes i, ii and ix are observed. This is due to a more efficient penetration of the three fluorenes in the micellar Stern region, resulting in rate increases as the reactants of the bimolecular reaction are confined in closer proximity. Indeed it has been

TABLE 1

Logarithm of the true reaction rates and initial rates[a] in ethanolic and cetyltrimethylammonium chloride[b] micellar solutions

Fluorene	*Ethanol*				*CTAC*			
	$\log k_{tr}$	$(dc/dt)_{tr}$ (M s^{-1})	$\log k_{tr}''$	$(dc/dt)_{tr}''$ (M s^{-1})	$\log k_{tr}$	$(dc/dt)_{tr}$ (M s^{-1})	$\log k_{tr}''$	$(dc/dt)_{tr}''$ (M s^{-1})
i	−2.23	5.81×10^{-7}	−1.83	1.46×10^{-6}	−1.80	1.59×10^{-6}	−1.18	6.22×10^{-6}
ii	−2.11	7.56×10^{-7}	−1.70	1.95×10^{-6}	−1.82	1.51×10^{-6}	−1.24	5.38×10^{-6}
iii	−1.77	1.59×10^{-6}	−1.41	3.75×10^{-6}	−1.81	1.48×10^{-6}	−1.31	2.37×10^{-6}
iv	−1.80	1.52×10^{-6}	−1.41	3.75×10^{-6}	−1.81	1.48×10^{-6}	−1.31	2.37×10^{-6}
v	−1.65	2.02×10^{-6}	−1.28	5.00×10^{-6}	−1.71	1.82×10^{-6}	−1.25	4.47×10^{-6}
vi	−1.58	2.39×10^{-6}	−1.21	5.74×10^{-6}	−1.64	2.13×10^{-6}	−1.18	6.18×10^{-6}
vii	−1.50	2.59×10^{-6}	−1.18	6.18×10^{-6}	−1.62	2.25×10^{-6}	−1.15	6.53×10^{-6}
viii	−1.47	3.03×10^{-6}	−1.17	6.36×10^{-6}	−1.59	2.39×10^{-6}	−1.14	6.70×10^{-6}
ix	−1.36	3.87×10^{-6}	−1.08	7.73×10^{-6}	−1.39	3.96×10^{-6}	−0.94	1.03×10^{-5}

[a]The absorption or fluorescence values and the corresponding fluorenone concentration were fed to a programmed computer and were compatible for pseudo-first-order with a correlation coefficient of over 0.99.
[b]Similar results were obtained in DTAC micellar solutions.
[c]k_{tr}'' are the reaction rates that have been measured with interrupted flows of ozone.

TABLE 2

Logarithm of the apparent reaction rates and initial rates in ethanolic and cetyltrimethylammonium chloride micellar solutions[a]

Fluorene	*Ethanol*		*CTAC*	
	$\log k_{app}$	$(dc/dt)_{app}$ (M s^{-1})	$\log k_{app}$	$(dc/dt)_{app}$ (M s^{-1})
i	−1.83	1.43×10^{-6}	−1.18	5.50×10^{-6}
ii	−1.70	1.90×10^{-6}	−1.26	4.70×10^{-6}
iii	−1.41	3.53×10^{-6}	−1.32	4.22×10^{-6}
iv	−1.42	3.42×10^{-6}	−1.32	4.16×10^{-6}
v	−1.30	4.39×10^{-6}	−1.26	4.68×10^{-6}
vi	−1.23	5.00×10^{-6}	−1.23	5.00×10^{-6}
vii	−1.20	5.33×10^{-6}	−1.20	5.33×10^{-6}
viii	−1.16	5.71×10^{-6}	−1.15	5.77×10^{-6}
ix	−1.80	1.50×10^{-6}	−2.97	3.33×10^{-7}

[a]Similar results were obtained in DTAC micellar solutions.

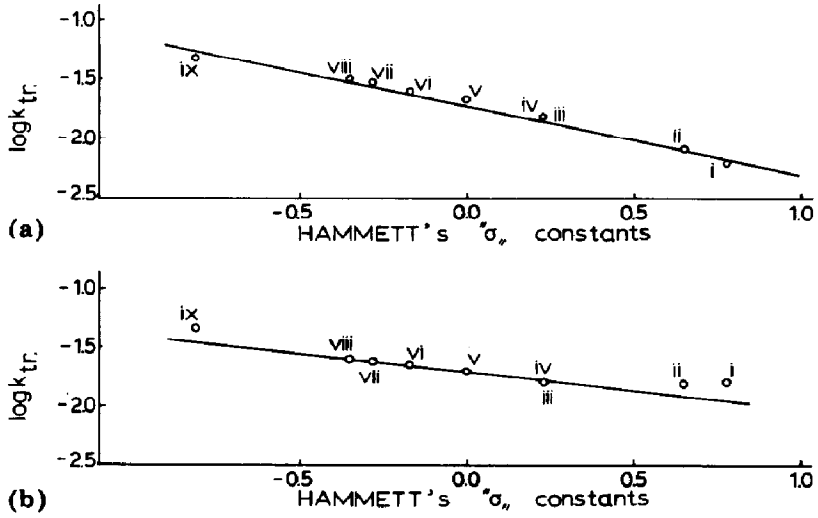


Fig. 4. Logarithm of the true reaction rates as a function of Hammett's σ constants for the substituents shown in Fig. 1: (a) in ethanol; (b) in CTAC micelles.

shown [25] with pyrene and fluorenone fluorescence probes that these three fluorenes are more efficiently micellized than the rest of the fluorenes employed here (the binding constant, partition coefficient and per cent micellization are 2.77×10^4 M^{-1}, 1.3×10^3 and 91% respectively for fluorene i, in contrast to 3.52×10^3 M^{-1}, $(1 - 8) \times 10^2$ and 56% for fluorene iii).

(d) In micellar media the kinetic law for plots of $\log k_{app}$ against Hammett's σ constants (Fig. 5(b)) is still valid, with the exception of fluorene ix, characterized by a negative deviation as in Fig. 5(a); here, however, the effect is more pronounced as a result, we believe, of a more efficient quenching of the fluorenone fluorescence by the corresponding Ia species of Fig. 2. Indeed, here, the fluorescer and quencher are enclosed in a

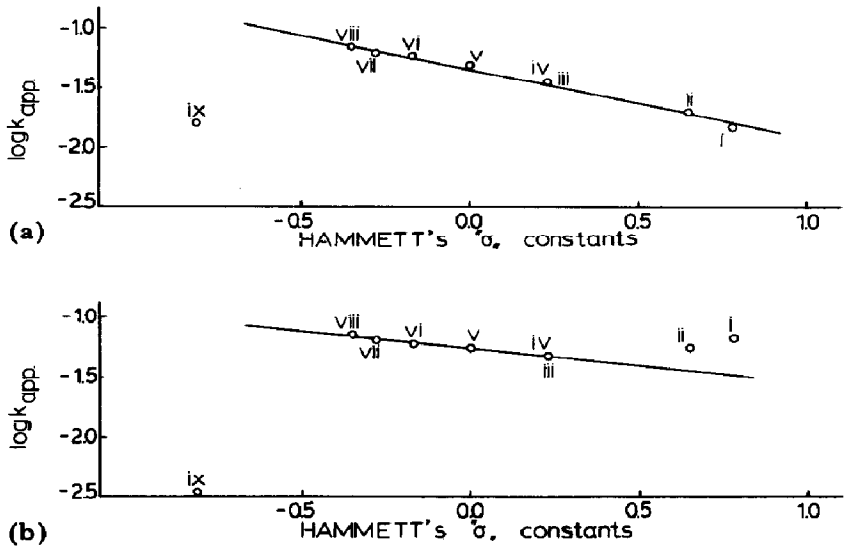


Fig. 5. Logarithm of the apparent reaction rates as a function of Hammett's σ constants for the substituents shown in Fig. 1: (a) in ethanol; (b) in CTAC micelles.

system thermodynamically more stable than the solvent cage (the rate of exit from the ethanol solvent cage is 10^{11} - 10^{12} s^{-1} [23] compared with the rate of exit of aromatic molecules from micelles of 10^6 s^{-1} [36]).

The difference between the true and the apparent reaction rates, which is a measure of the quenching of the fluorenone fluorescence by the leaving moiety, especially in the case of fluorene ix, is more clearly illustrated when the ratios of the true to apparent rates are considered. This is shown in Table 3, where the ratios $\log k_{tr}/\log k_{app}$ in ethanolic and micellar media are presented.

From the ratios above, it becomes strikingly obvious that fluorene ix deviates from the rest of the fluorenes and the reason can be no other than quenching of the emitter. This is dramatically more pronounced in micelles where the emitter and the quencher are more closely confined; in this case, more effective quenching gives rise to a lower apparent rate and therefore to a lower ratio $\log k_{tr}/\log k_{app}$ or higher ratio k_{tr}/k_{app}. An intriguing aspect of Table 3 was that the ratios $\log k_{tr}/\log k_{app}$ were predominantly higher than unity while lower ratios, or at least ratios equal to unity, would be expected in the absence of quenching. Although academically interesting, this does not affect the results reported here, as the experiments were performed under precisely identical conditions. Eventually it was found that this was due to the method of measurement. The stream of ozone bubbles following the longitudinal axis of the spectrophotometer cell reduced the "effective" path length, lowering the measured fluorenone concentration. Indeed, when the absorption measurements were obtained on interruptions of the ozone passage, the optical densities were increased, resulting in k_{tr}'' higher than k_{tr} (Table 1) and the ratios of Table 3 were closer to unity for most fluorenes; the fluorescence measurements were far less influenced by this effect. The

TABLE 3

Ratios of true-to-apparent reaction rates and initial rates in ethanolic and cetyltrimethylammonium chloride micellar solutions

Fluorene	$\log k_{tr}/\log k_{app}$	
	Ethanol	*CTAC*
i	1.22	1.53
ii	1.24	1.44
iii	1.26	1.37
iv	1.27	1.37
v	1.27	1.36
vi	1.28	1.33
vii	1.25	1.35
viii	1.27	1.38
ix	0.76	0.72

method of interrupted ozone additions could not, however, be employed as chemiluminescence mimetic conditions would, in this case, cease to exist.

In conclusion, it has been shown in this work that, under chemiluminescence mimetic conditions where excitation yields are not involved, quenching by the leaving moiety can be very effective. Hence, although all nine fluorenes employed here follow the same kinetic law ($\log k_{tr}$ against Hammett's σ constants), when the same law is established fluorimetrically ($\log k_{app}$ against Hammett's σ constants) deviations appear which we can attribute to no other than the quenching by the leaving moiety of the emitting species. This effect is more pronounced when the two moieties are produced inside micelles, where the emitter and the quencher are more rigidly held together, and this further supports the above assumption. Unanswered questions, however, still remain. The quenching constants of the leaving moieties on the fluorenone fluorescence ought to be determined and discussed in connection with the diffusion rate constant and the plots of the present work. Furthermore, proof that it is the quencher in close proximity to the emitter, at the moment of their production, that is responsible for most of the quenching observed and not the quencher already diffused away (this is most important in chemiluminescence) should also be presented, but these are subjects of a second article [25].

Acknowledgment

One of us (L.P.) is indebted to the Greek Atomic Energy Commission for a maintenance grant.

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