

**BENZYLIDENE FLUORENE OZONOLYSIS UNDER  
CHEMILUMINESCENCE MIMETIC CONDITIONS IN HOMOGENEOUS  
AND MICELLAR MEDIA  
II: RATE CONSTANTS OF FLUORENONE QUENCHING BY THE  
LEAVING MOIETY<sup>†</sup>**

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### Summary

The rate constants for the quenching of the fluorenone fluorescence by substituted benzaldehydes and benzoic acids (substituents: *p*-nitro, *p*-cyano, *p*-chloro, *p*-bromo, *p*-H, *p*-methyl, *p*-methoxy, *p*-methoxy-*m*-methyl, and *p*-dimethylamino) are reported in ethanolic and micellar media. These are compared with the diffusion rate constant and evidence is presented that, under chemiluminescence mimetic conditions, the quenching leaving moiety in close proximity to the emitter is responsible for most of the quenching observed. The binding constants and partition coefficients of the above compounds as well as those of the corresponding substituted 9-benzylidene fluorenes in cetyltrimethylammonium chloride are also reported together with quencher molecules per micelle. The influence of the micellar medium on the quenching rate constants is discussed and the position of the above compounds inside the micelle is reported.

### 1. Introduction

We have argued earlier [1] that if the leaving fragment in a chemiluminescent reaction is a quencher of the fluorescence of the primary emitter its quenching effect will be very pronounced as a result of the inherent proximity of the two species at the instant of their production. Indeed, on ozonolysis of nine 9-(*p*-substituted) benzylidene fluorenes (*p*-nitro (i), *p*-cyano (ii), *p*-chloro (iii), *p*-bromo (iv), *p*-H (v), *p*-methyl (vi), *p*-methoxy (vii), *p*-methoxy-*m*-methyl (viii) and *p*-dimethylamino (ix) derivatives) under chemiluminescence mimetic conditions, the reaction rates based on fluorimetric fluorenone determination did not follow the kinetic law and we attributed the negative deviation of the *p*-dimethylamino derivative (ix) to quenching by the corresponding leaving moiety. This effect was greatly enhanced in micellar media which are thermodynamically more

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stable than the solvent cage. To support this view further, we now wish to discuss the above findings in connection with the constants for the quenching of the fluorenone fluorescence by the leaving fragments and the diffusion rate constant, in ethanol and cetyltrimethylammonium chloride (CTAC) micelles.

## 2. Experimental details

### 2.1. Materials

Fluorenone and the solvents employed were purified as described in Part I. *p*-Nitrobenzaldehyde, *p*-cyanobenzaldehyde and *p*-bromobenzaldehyde were purified by sublimation. Benzaldehyde, *p*-methylbenzaldehyde and *p*-methoxybenzaldehyde were distilled under vacuum; *p*-dimethylaminobenzaldehyde and *p*-methoxy-*m*-methylbenzaldehyde were employed without further purification. The substituted benzoic acids (*p*-nitro, *p*-cyano, *p*-chloro, *p*-H, *p*-methyl, *p*-methoxy and *p*-dimethylamino) were employed without further purification. Pyrene was recrystallized from ethanol.

### 2.2. Instrumentation

The fluorescence spectra were run on an Aminco-Bowman SPF spectrofluorimeter; the absorption spectra were recorded on a Hitachi 220 spectrophotometer.

### 2.3. Preparation of samples

The fluorenone concentration in ethanol was  $1 \times 10^{-3}$  M, in CTAC it was  $1 \times 10^{-4}$  M and the results were verified at  $1 \times 10^{-3}$  M. The pyrene concentration in CTAC was  $1 \times 10^{-5}$  M. The CTAC concentrations were  $8 \times 10^{-3}$ ,  $3 \times 10^{-2}$ ,  $6 \times 10^{-2}$  and  $8 \times 10^{-2}$  M. Dissolution of fluorenone and pyrene and of the quenchers (substituted benzaldehydes and benzoic acids) in CTAC micellar aqueous solutions was performed as described in Part I. Samples for the Stern-Volmer plots were prepared by adding 2 ml ethanolic or CTAC solution of quencher to 1 ml ethanolic or CTAC solution of the same concentration. The solutions employed were not deaerated and all measurements were performed at room temperature.

### 2.4. Stern-Volmer plots

The excitation and fluorescence maxima  $\lambda_{\max}$  were 304 nm (320 nm for  $1 \times 10^{-3}$  M) and 520 nm respectively for fluorenone in both ethanolic and CTAC solutions and 338 nm and 400 nm for pyrene in both types of solution. The quencher concentrations in ethanol and CTAC (substituted benzaldehydes and benzoic acids) were  $3 \times 10^{-5}$  -  $1 \times 10^{-4}$  M for the *p*-dimethylamino (ix', ix'') derivatives,  $1 \times 10^{-4}$  -  $1 \times 10^{-3}$  M for the *p*-nitro (i', i''), *p*-methoxy (vii', vii'') and *p*-methoxy-*m*-methyl (viii', viii'') derivatives and  $5 \times 10^{-4}$  -  $8 \times 10^{-3}$  M for the *p*-cyano (ii', ii''), *p*-chloro (iii', iii''), *p*-bromo (iv', iv''), *p*-H (v', v'') and *p*-methyl (vi', vi'') derivatives. Plots of the

absorption against the concentration followed Beer's law in the concentration ranges above and therefore the peak heights of the fluorenone fluorescence were proportional to the fluorescence quantum yields in both ethanolic and CTAC solutions.

### 3. Results and discussion

#### 3.1. Fluorescence quenching in ethanol

Quenching of fluorenone by oxygen is negligible [2, 3]. The fluorescence lifetime of fluorenone in non-deaerated ethanolic solutions is  $1.8 \times 10^{-9}$  s [3]. Overlap of the fluorescence spectrum of fluorenone with the absorption spectra of quenchers i' - ix' and i'' - ix'' was not observed; the type of quenching adopted here was collisional and the quenching constants  $k_q$  were calculated from the corresponding Stern-Volmer plots [2] with at least five quencher concentrations per plot:

$$\frac{I_0}{I} = 1 + k_q \tau [Q] \quad (1)$$

A typical set of Stern-Volmer plots for quenchers ii', ii'', iii', iii'', ix' and ix'' is shown in Fig. 1. At higher quencher concentrations, an upward curvature was occasionally observed which was more pronounced with vii', vii'', viii', ix' and ix''. This effect is generally attributed to "static quenching" [4] whose influence was, however, negligible at the lower quencher concentrations employed. It should be noted here that no complex formation was detected with absorption spectroscopy at around 420 nm at high quencher concentrations. If such a complex is responsible for "static quenching" it ought to be very short lived. The quenching constants tabulated in Table 1 were calculated from the slope of the linear part of the curves [5].

Comparing the quenching constants of Table 1 with the rate constant for exit of aromatic molecules from the ethanol solvent cage which is of the order of  $10^{11} - 10^{12}$  s<sup>-1</sup> [6], we observe that quenchers ix' and ix'' have the

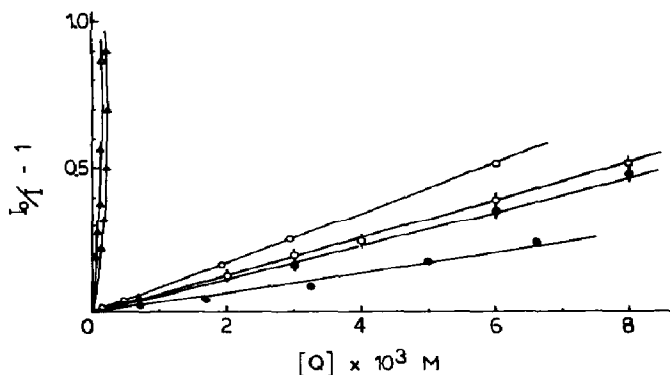


Fig. 1. Typical Stern-Volmer plots for quenchers ii' (○), ii'' (◊), iii' (●), iii'' (◆), ix' (△) and ix'' (▲).

TABLE 1

Constants for the quenching of the fluorenone fluorescence by the substituted benzaldehydes and benzoic acids

Quencher	$k_q\tau$ ( $M^{-1}$ )	$k_q$ ( $M^{-1} s^{-1}$ )
i'	784	$4.36 \times 10^{11}$
ii'	88	$4.90 \times 10^{10}$
iii'	28	$1.56 \times 10^{10}$
iv'	60	$3.33 \times 10^{10}$
v'	45	$2.50 \times 10^{10}$
vi'	80	$4.44 \times 10^{10}$
vii'	274	$1.52 \times 10^{11}$
viii'	135	$7.50 \times 10^{10}$
ix'	3304	$1.84 \times 10^{12}$
i''	740	$4.11 \times 10^{11}$
ii''	66	$3.67 \times 10^{10}$
iii''	47	$2.61 \times 10^{10}$
iv''	45	$2.50 \times 10^{10}$
v''	53	$2.94 \times 10^{10}$
vi''	13	$7.22 \times 10^9$
vii''	72	$4.00 \times 10^{10}$
viii''	—	—
ix''	2500	$1.38 \times 10^{12}$

possibility of quenching the fluorenone fluorescence before they escape from the solvent cage and this is in agreement with the strong negative deviation of fluorene ix in the plots of apparent reaction rates against Hammett's  $\sigma$  constants reported in Part I.

The difference in the values of  $k_q$  in Table 1 is generally in agreement with the ionization potentials of the quencher benzaldehydes and benzoic acids of the present work such as 7.51 eV for ix' and ix'', 8.60 eV and 8.43 eV for vii' and vii'' respectively and 9.33 eV and 9.35 eV for vi' and vi'' [7, 8].

Comparing the half-wave potentials of the substituted benzaldehydes and benzoic acids such as ix' and ix'' (-2.13 V), vii' and vii'' (-1.97 V), vi' and vi'' (-1.89 V) and v' and v'' (-1.79 V) [9] with the half-wave potential of fluorenone equal to -1.27 V [10] we expect that electron transfer from quencher to fluorenone will be responsible for at least part of the quenching observed; in the case of i' and i'' the opposite electron flow will be expected (-0.60 V for i' and i'' should be compared with -1.27 V for fluorenone) [10, 11].

Considering the  $k_q$  values of Table 1, it should be noted that for quenchers with a higher probability of quenching through electron transfer the quenching constants are unusually large. In fact they are larger than the diffusion rate constant equal to about  $2.1 \times 10^{10} M^{-1} s^{-1}$ . The diffusion rate constant was calculated from the modified Debye equation [12]:

$$k_d = \frac{4\pi(r_A + r_B)(d_f + d_q)N}{1000} \text{ M}^{-1} \text{ s}^{-1} \quad (2)$$

where  $r_A = r_B = 4 \times 10^{-8}$  cm,  $d_f$  is the fluorenone diffusion constant, equal to  $1.58 \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>,  $d_q$  is the diffusion constant of substituted aromatic molecules, equal to  $1.98 \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup> [13], and  $N$  is equal to  $6.023 \times 10^{23}$ .

The larger quenching constants should be attributed to the special role played by the solvent. Indeed, excited fluorenone induces a higher polarity to ethanol [14, 15], already a polar solvent, facilitating electron transfer between fluorenone and quencher, through ethanol bridges, thus increasing the rate of quenching by allowing electron transfer from larger distances. Quenching constants as high as this have been reported in the literature [16]. From the mechanism of benzylidene fluorene ozonolysis (Part I, Fig. 2) it was deduced that three products, namely *p*-phenylcarbonyloxide (Ia), *p*-phenylethoxyhydroperoxide or *p*-phenylhydroxyhydroperoxide (Ib) and substituted benzaldehyde (II), could be effective quenchers of the fluorenone fluorescence after diffusion had occurred. One of them, however, (Ia) was expected to be more effective because of its proximity to fluorenone at the instant of their production (Part I, Fig. 3).

The above three quenchers ought to have similar quenching constants for the following reasons.

(a) The quenching constants of substituted benzaldehydes and benzoic acids are similar for the same substituent (Table 1).

(b) Quenching occurs mainly through electron transfer and this is particularly so for ix' and ix''. Indeed, with any solvent effect disregarded, calculations for electron transfer from ix' and ix'' to fluorenone gave a value for  $k_q$  as high as  $1.6 \times 10^{10}$  M<sup>-1</sup> s<sup>-1</sup>; this was obtained from

$$\frac{1}{k_q} = \frac{1}{k_d} + 10^{-11} \exp\left(\frac{\Delta G^\ddagger}{RT}\right) \quad (3)$$

where  $\Delta G^\ddagger$  was calculated as described by Rehm and Weller [17] with the potential for transition to the first fluorenone singlet taken as 2.74 eV, the half-wave potential for fluorenone reduction as -1.27 V, the coulombic repulsion energy as 0.06 eV, the ionization potential for ix' and ix'' as 7.51 eV [8], the half-wave potential for ix' and ix'' as -2.13 V [11] and  $k_d = 2.1 \times 10^{10}$  M<sup>-1</sup> s<sup>-1</sup>.

(c) Substituted benzaldehydes, benzoic acids, esters of benzoic acids and benzene have similar ionization potentials for the same substituent [18, 19]. It follows, therefore, that electron transfer occurs from the substituted benzene ring, irrespectively of the functional group present (carbonyl etc.). The quenching constants of the three products above will, therefore, be expected to be similar, depending only on the substituent.

It was shown in Part I that the reaction rates  $k_{app}$  measured fluorimetrically were a linear function of Hammett's  $\sigma$  constants with the exception of benzylidene fluorene ix whose negative deviation was attributed to quenching of fluorenone by the leaving moieties Ia, Ib and II. In order to

emphasize the proximity effect of Ia, we now wish to compare  $k_q'$ , the sum of the  $k_q$  values of all quenchers present, with  $k_q''$  calculated from the initial reaction rates, apparent and true (Part I). This  $k_q''$  will be the rate of fluorenone quenching from all quenchers produced as the reaction proceeds under chemiluminescence mimetic conditions. The stoichiometry of the reaction is as follows: 1 mol of benzylidene fluorene gives 1 mol of fluorenone, 1 mol of Ia, which is quickly transformed into Ib, and a maximum, in the case of benzylidene fluorene ix, of 1 mol of II. As all three have similar quenching constants, it is expected that the rate constant for total quenching will be twice that reported in Table 1, *i.e.* for benzylidene fluorene ix, a maximum total  $k_q'$  equal to about  $3.6 \times 10^{12} \text{ M}^{-1} \text{ s}^{-1}$  is expected.  $k_q''$  can be calculated from the initial true and apparent reaction rates of Tables 1 and 2 of Part I. Indeed, for a finite time period (*e.g.* the first 5 s), the true fluorenone concentration  $C_{\text{tr}}$  from ozonolysis of ix will be  $1.94 \times 10^{-5} \text{ M}$  and the apparent concentration  $C_{\text{app}}$  will be  $7.55 \times 10^{-6} \text{ M}$ ; the ratio  $C_{\text{tr}}/C_{\text{app}}$  will then express the ratio  $I_0/I$  of the Stern-Volmer equation (eqn. (1)), where  $C_{\text{tr}}$  and  $C_{\text{app}}$  are the initial rates calculated with a continuous flow of ozone. From the reaction stoichiometry, it follows that the total quencher concentration will be  $2 \times 1.94 \times 10^{-5}$  or about  $4 \times 10^{-5} \text{ M}$ . The total  $k_q''$  calculated from the Stern-Volmer equation will then be equal to  $2.17 \times 10^{13} \text{ M}^{-1} \text{ s}^{-1}$ . Employing  $(dc/dt)''$ ,  $k_q''$  will be equal to  $2.98 \times 10^{13} \text{ M}^{-1} \text{ s}^{-1}$ . Hence, although the phenomenon is more spectacular, the method of interrupted ozone additions could not be employed as chemiluminescence mimetic conditions would have, in this case, ceased to exist.

Comparing the values of  $k_q'$  and  $k_q''$  above, it is observed that  $k_q''$  calculated from the initial reaction rates is one order of magnitude larger than  $k_q'$  calculated by adding the  $k_q$  values of the individual quenchers ( $2.17 \times 10^{13} \text{ M}^{-1} \text{ s}^{-1}$  compared with  $3.6 \times 10^{12} \text{ M}^{-1} \text{ s}^{-1}$ ). The difference is attributed to the proximity of fluorenone and quencher Ia at the instant of their production, involved in the method of calculation from true and apparent reaction rates.

Regarding Fig. 2 of Part I, one of the products (III), structurally very similar to fluorenone, was not considered as a potential quencher and was not studied as such. In the extreme case, however, that this species does quench the fluorenone fluorescence, its  $k_q$  will not be larger than  $k_d$  which has a value of  $2.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ . Addition of this to  $k_q'$  raises its value by about 0.5%, which is negligible and does not affect the above reasoning.

### 3.2. Fluorescence quenching in cetyltrimethylammonium chloride micelles

Before we could proceed to the quenching of fluorenone by quenchers  $i' - ix'$  and  $i'' - ix''$ , the binding constant of fluorenone in CTAC micelles had to be determined. This was done by employing fluorenone as the quencher of the fluorescence of pyrene, a completely micellized probe [20, 21]. Calculations were based on the equations of Encinas and Lissi [22]:



$$K_b = \frac{Q_{\text{Mic}}}{Q_w[\text{Mic}]} \quad (5)$$

$$Q_T = \frac{\bar{n}}{K_b} + \bar{n}[\text{Mic}] \quad (6)$$

where  $Q_w$  is the concentration of quencher in the aqueous phase,  $[\text{Mic}]$  is the concentration of micelles,  $Q_{\text{Mic}}$  is the quencher concentration in the micellar pseudophase,  $k_f$  is the rate constant for quencher entry in the micelle,  $k_e$  is the rate constant for quencher exit from the micelle,  $K_b$  is the binding constant,  $Q_T$  is the total quencher concentration and  $\bar{n}$  is the mean number of quencher molecules per micelle.

Figure 2 shows a set of Stern-Volmer plots for the quenching of pyrene by fluorenone at various surfactant concentrations. Plots of  $Q_T$  against  $[\text{Mic}]$  for four values of  $I_0/I$  are given in Fig. 3. From the mean slope of the plots of Fig. 3,  $\bar{n}$  was calculated and was found to be equal to 0.72, while  $K_b$  was calculated from the intercept at the  $y$  axis ( $\bar{n}/K_b$ ) and was found to be equal to  $1.08 \times 10^4 \text{ M}^{-1}$ . Comparing this value with values reported for completely micellized arenes [23] we conclude that fluorenone can be employed as a completely micellized fluorescent probe.

With fluorenone as a completely micellized fluorescent probe, the average number  $\bar{n}_Q$  of quencher molecules per micelle was calculated for quenchers  $i' - ix'$  and  $i'' - ix''$  at surfactant concentrations  $8 \times 10^{-3}$ ,  $3 \times 10^{-2}$ ,  $6 \times 10^{-2}$  and  $8 \times 10^{-2} \text{ M}$  following the above method. The partition coefficients and per cent micellization of the quencher in the micellar pseudophase at a CTAC concentration of  $3 \times 10^{-2} \text{ M}$  were calculated from  $K_b$  with a volume of CTAC micelles of 19 l for 1 mol of micelles, calculated from Tanford's equations [24, 25]. These are shown in Table 2.

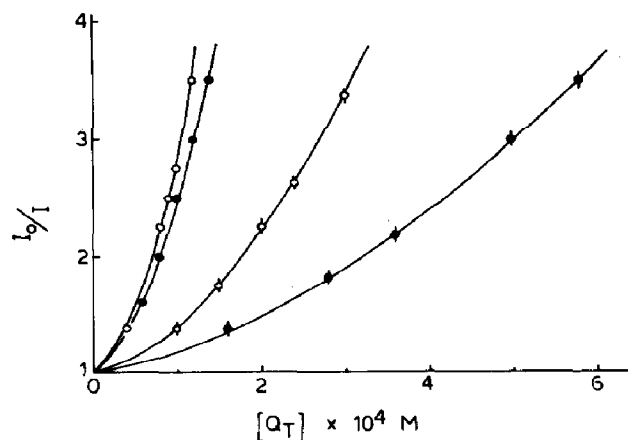


Fig. 2. Stern-Volmer plots for the quenching of pyrene by fluorenone at CTAC concentrations of  $8 \times 10^{-3} \text{ M}$  ( $\circ$ ),  $1 \times 10^{-2} \text{ M}$  ( $\bullet$ ),  $3 \times 10^{-2} \text{ M}$  ( $\diamond$ ) and  $6 \times 10^{-2} \text{ M}$  ( $\blacklozenge$ ).

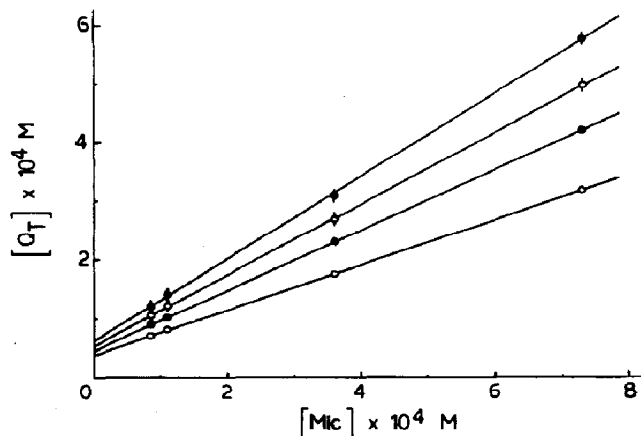


Fig. 3. Quenching of pyrene by fluorenone in CTAC plotted according to eqn. (6) for various  $I_0/I$  values:  $\circ$ , 2.0;  $\bullet$ , 2.5;  $\diamond$ , 3;  $\blacklozenge$ , 3.5.

TABLE 2

Binding constants  $K_b$ , mean binding constants  $\bar{K}_b$ , range of mean occupation number per micelle, mean occupation number  $\bar{n}_Q$ , range of quencher concentrations  $Q_M$  per micelle calculated from the mean occupation numbers per micelle, mean partition coefficient  $\bar{K}_D$  and per cent micellization for substituted benzaldehydes and benzoic acids in  $3 \times 10^{-2}$  M cetyltrimethylammonium chloride solutions

Quencher	$K_b$ ( $M^{-1}$ )	$\bar{K}_b$ ( $M^{-1}$ )	Range of $\bar{n}_Q$	$\bar{n}_Q$	Range of $Q_M$ ( $\times 10 M l^{-1}$ )	$\bar{K}_D$	Micellization (%)
i'	$1545 \pm 50$	1545	0.10 - 0.20	0.14	0.05 - 0.10	75	36
i''	$1976 \pm 300$	1976	0.30 - 0.70	0.53	0.17 - 0.37	104	43
ii'	$1634 \pm 86$	1634	1.11 - 2.04	1.43	0.52 - 1.07	80	37
ii''	$1600 \pm 100$	1600	1.20 - 3.40	2.20	0.63 - 1.77	75	35
iii'	$4184 \pm 370$	4184	2.01 - 4.95	3.60	1.07 - 2.56	219	60
iii''	$4170 \pm 466$	4170	3.97 - 13.4	8.74	2.07 - 7.00	217	50
iv'	$3948 \pm 760$	3948	2.01 - 4.95	3.59	1.05 - 2.57	224	59
iv''	$3900 \pm 200$	3900	2.70 - 5.05	3.45	1.41 - 2.63	218	57
v'	$1506 \pm 286$	1506	1.87 - 5.89	3.82	0.97 - 3.08	96	35
v''	$2334 \pm 424$	2334	4.06 - 21.3	12.60	2.12 - 11.14	121	54
vi'	$4457 \pm 143$	4457	2.42 - 3.72	3.07	0.49 - 1.94	279	61
vi''	$4500 \pm 200$	4500	2.10 - 3.20	2.98	1.09 - 1.67	270	58
vii'	$566 \pm 50$	566	0.80 - 1.40	1.00	0.42 - 0.73	30	17
vii''	$551 \pm 68$	551	0.77 - 1.92	1.23	0.40 - 1.01	28	17
viii'	$509 \pm 60$	509	0.74 - 1.30	1.06	0.39 - 0.68	27	15
viii''	—	—	—	—	—	—	—
ix'	$566 \pm 99$	566	0.06 - 0.07	0.05	0.03 - 0.04	30	17
ix''	$840 \pm 222$	840	0.09 - 0.14	0.12	0.07 - 0.08	44	23

The quenching constants in the CTAC micellar system were calculated from the equation of Infelta [26] (eqn. (7)).

$$\frac{I_0}{I} = \left( \frac{1}{k_Q \tau} \right) \exp(-\bar{n}_Q) \sum_{i=0}^{i=\infty} \frac{\bar{n}_Q^i}{\{(1/k_Q \tau) + i\} i!} \quad (7)$$



where  $\tau$  is the lifetime of the fluorenone fluorescence, equal to  $1.8 \times 10^{-9}$  s,  $k_Q$  is the pseudo-first-order quenching constant,  $i$  is the number of quencher molecules per micelle and  $\bar{n}_Q$  is as defined above. This equation describes quenching which is of both dynamic and static nature. The values of  $\bar{n}_Q$  were obtained from Table 2 above, while  $i$  was given values in the range 0 -  $\bar{n}_Q$ . The values of  $k_Q$  thus obtained for quenchers i' - ix' and i'' - ix'' are shown in Table 3.

For the calculation of  $k_Q$  ( $M^{-1} s^{-1}$ ), a modification of the Stern-Volmer equation was employed [27]:

$$\frac{I_0}{I} = 1 + k_q \tau [Q_M] \quad (8)$$

where  $\tau$  is equal to  $1.8 \times 10^{-9}$  s and the effective quencher concentration [28], the number of moles of quencher

$$[Q_M] = \frac{\bar{n}_Q}{V} \quad (9)$$

bound in the micellar pseudophase, is given in Table 2, while  $V$ , the micellar volume per mole of micelles, equal to 19 l, has been calculated above. The values of  $k_Q$  thus calculated for quenchers i' - ix' and i'' - ix'' are given in Table 3. It should be noted here that the plots of eqn. (8) occasionally at

TABLE 3

Quenching rate constants of substituted benzaldehydes and benzoic acids on fluorenone in  $3 \times 10^{-2}$  M cetyltrimethylammonium chloride solutions

Quencher	$k_Q$ ( $s^{-1}$ )	$k_Q \tau$ ( $M^{-1}$ )	$k_Q$ ( $M^{-1} s^{-1}$ )
i'	$8.27 \times 10^8$	28.53	$1.58 \times 10^{10}$
ii'	$4.25 \times 10^8$	9.75	$5.41 \times 10^9$
iii'	$2.70 \times 10^8$	1.10	$6.13 \times 10^8$
iv'	$2.50 \times 10^8$	1.11	$6.15 \times 10^8$
v'	$3.00 \times 10^8$	4.84	$2.69 \times 10^9$
vi'	$3.00 \times 10^8$	4.79	$2.66 \times 10^9$
vii'	$5.50 \times 10^8$	9.57	$4.44 \times 10^9$
viii'	$5.50 \times 10^8$	10.35	$5.75 \times 10^9$
ix'	$1.12 \times 10^{10}$	388.33	$2.15 \times 10^{11}$
i''	$3.11 \times 10^8$	5.74	$3.19 \times 10^9$
ii''	$1.61 \times 10^8$	5.52	$3.06 \times 10^9$
iii''	$1.67 \times 10^7$	0.62	$3.41 \times 10^8$
iv''	$3.22 \times 10^7$	0.71	$3.93 \times 10^8$
v''	$5.19 \times 10^7$	1.64	$9.31 \times 10^8$
vi''	$7.90 \times 10^7$	2.71	$1.50 \times 10^9$
vii''	$2.83 \times 10^8$	18.82	$1.04 \times 10^{10}$
viii''	—	—	—
ix''	$2.68 \times 10^9$	83.33	$4.62 \times 10^{10}$

high concentrations showed an upward curvature; in such cases, calculations were based on the linear part of the plot.

Equation (8) can be employed only if the fluorenone fluorescence lifetime is smaller than the time required for exit of the quencher from the micellar Stern layer. The latter can be calculated [29] from

$$t_d = \frac{3\pi x^2 nr}{k_B T} \quad (10)$$

where  $t_d$  is the time required for diffusion of the quencher through the Stern layer,  $x$  is the width of the Stern layer,  $n$  is the viscosity of the Stern layer,  $r$  is the radius of the quencher,  $k_B$  is Boltzmann's constant and  $T$  is the absolute temperature. For  $x = 0.3 - 0.6$  nm [30],  $r = 0.3$  nm [29],  $n = 8$  cP and  $T = 300$  K,  $k_d$  becomes equal to  $(2 - 9) \times 10^{-9}$  s and the rate of exit is equal to  $(1.11 - 5.50) \times 10^8$  s<sup>-1</sup>. Hence the fluorenone fluorescence lifetime, equal to  $1.8 \times 10^{-9}$  s, is indeed smaller than the time of exit of the quencher.

Considering the values of  $k_q$  and  $k_a$  in the micellar medium shown in Table 3, a large difference in the effect of quenchers ix' and ix'' is observed compared with that of quenchers i' - viii' and i'' - viii''; this is as high as two orders of magnitude and is in agreement with the results reported in Part I.

### 3.3. Comparison of quenching rate constants in ethanolic and micellar solutions

From a comparison of the  $k_q$  values of Table 3 in micellar solutions with those of Table 1 in ethanolic solutions, it is observed that quenching is less efficient in micellar than in homogeneous solutions. This can be easily explained for quenchers i' - viii' and i'' - viii'' when viewed in the light of the Stokes-Einstein equation [21]:

$$k_D = \frac{8RT}{3000n} \quad (11)$$

where  $k_d$  is the diffusion rate constant and  $n$  is the viscosity of the medium; here the micellar Stern layer is equal to 8 cP for CTAC [31]. The high viscosity of the Stern layer gives rise to low rates of diffusion, negatively affecting the dynamics of quenching. This, however, is not enough to explain the lower (less than  $k_D$ ) values of  $k_q$  for ix' and ix'' in micellar solutions compared with those in ethanol ( $k_q > k_D$ ). Here quenching due to electron transfer from ix' and ix'' to fluorenone is adversely affected by the separation of the electron donor and acceptor in the Stern layer. Indeed, it has been shown above that fluorenone is deeply located in the Stern layer, while ix' and ix'' are closer to the aqueous interface (absorption  $\lambda_{max}$  is equal to 321 nm in hexane, 339 nm in ethanol, 348 nm in CTAC and 352 nm in water).

Furthermore, the orientation of the solvent (ethanol) around the solvent cage, which served as a bridge to facilitate the electron transfer in homogeneous media, does not exist in the micellar phase.

As with the homogeneous solutions above, the sum  $k'_{q(m)}$  of the quenching constants of all quenchers present in the micellar solution will now be compared with the quenching constant  $k''_{q(m)}$  calculated from the true and apparent initial reaction rates in micellar solutions, calculated with a continuous flow of ozone and reported in Part I. The reasoning followed for homogeneous solution is still valid in micellar media as illustrated in Table 3 and, therefore, all quenchers present are considered to have similar quenching constants. In this case  $k'_{q(m)}$  for quenchers Ia, Ib and II from fluorene ix, which is characterized by the larger deviation, has a value of  $2 \times 2.15 \times 10^{11}$  or  $4.3 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$ .

$k''_{q(m)}$  was calculated as for ethanolic solutions with the aid of the Stern-Volmer equation from the initial reaction rates calculated with a continuous flow of ozone (Part I, Tables 1 and 2) for the first 5 s of ozonolysis. Here, however, at the instant of their production all quenchers are completely micellized, as the rates of exit from the micelle are smaller than the quenching rate constants (the rate of exit is  $(1.11 - 5.50) \times 10^8 \text{ s}^{-1}$  compared with a quenching rate constant for the quenchers from ix of  $1.12 \times 10^{10} \text{ s}^{-1}$ ) and, therefore, the quencher concentration introduced in the Stern-Volmer equation is the sum required by the reaction stoichiometry. For a sum of quencher concentrations equal to  $3.96 \times 10^{-5} \text{ M}$ ,  $k''_{q(m)}$  is found to be equal to  $1.45 \times 10^{14} \text{ M}^{-1} \text{ s}^{-1}$ . (Employing  $(dc/dt)''$ ,  $k_q''$  will be equal to  $1.62 \times 10^{14} \text{ M}^{-1} \text{ s}^{-1}$ .)

Again, here, as in homogeneous solutions, the value of  $k''_{q(m)}$  is found to be larger than that of  $k'_{q(m)}$ ; this is again attributed to quenching by the leaving moiety at the instant of production of the emitter and quencher involved in the method of measurement of  $k''_{q(m)}$ . In this case, however, encapsulation of the two moieties in the micelle, a cage thermodynamically more stable than the solvent cage, results in intensification of the effect so that  $k''_{q(m)}$  is larger than  $k'_{q(m)}$  by almost three orders of magnitude, in contrast with homogeneous solutions where  $k''_{q(m)}$  is larger than  $k'_{q(m)}$  by only one order of magnitude.

#### 4. Conclusions

The negative deviation of fluorene ix in the plots of the logarithm of the apparent reaction rates against Hammett's  $\sigma$  constants under chemiluminescence mimetic conditions (Part I) has now been explained. It has been shown that, for this particular fluorene, the constant for quenching of the emitter by the leaving moiety is larger than the diffusion rate constant, in both homogeneous and micellar media, which is not the case with the rest of the fluorenes studied here. Furthermore, it has been shown that, under chemiluminescence mimetic conditions, it is the inherent proximity of the emitter and the quencher that is responsible for most of the quenching observed ( $k_q'$  should be compared with  $k_q''$  and  $k'_{q(m)}$  with  $k''_{q(m)}$ ). Apart from the negative deviation of fluorene ix in the plot of  $\log k_{app}$  against

Hammett's  $\sigma$  constants, positive deviations of fluorenes i, ii and ix were observed in the plot of  $\log k_{tr}$  against Hammett's  $\sigma$  constants in micellar media (Part I). This piece of work will not be completed until these positive deviations are quantitatively rationalized and this is the subject of Part III [32].

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