

## ELECTRONIC QUENCHING OF EXCITED SINGLET-STATE BENZENES IN THE VAPOUR PHASE\*

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### Summary

The quenching of the first excited singlet states of benzenes substituted with the F, CH<sub>3</sub> and CF<sub>3</sub> groups in the vapour phase by O<sub>2</sub>, NO, diolefins, and simple ketones is reported. For O<sub>2</sub> and NO, quenching is approximately gas-kinetic for aromatic molecules with ionization potentials less than 9.5 eV, but is less efficient for molecules with higher ionization potential. For quenching by diolefins a fifty-fold variation in quenching efficiency with different aromatic molecules is observed and non-fluorescent exciplex formation can be invoked to account for the observed variation in efficiency. In this case charge transfer occurs from olefin to excited aromatic, and complex formation leads to observable non-exponentiality in the fluorescence decay characteristics of one pair, *p*-fluorotoluene and *trans*-piperylene. For quenching by ketones, quenching efficiencies larger than those obtained for oxygen are observed for some molecules, and the possibility that long-range induced dipole-dipole interactions occur in the vapour phase is discussed, but the conclusion is reached that there is insufficient data to substantiate this claim.

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### Introduction

Electronic quenching of excited singlet states of benzene and simply substituted benzenes may occur by the following mechanisms: (i) electronic energy transfer; (ii) chemical interaction; (iii) enhancement of non-radiative decay; (iv) complex formation including charge transfer (exciplex) complexes.

The criterion for efficient electronic energy transfer is that the quenching molecules have a lower-lying singlet state than the aromatic donor molecule, and in principle, energy transfer could occur *via* the induced dipole-dipole interaction [1], or through the exchange mechanism [2]. Enhancement of non-radiative decay to the triplet states of the aromatic molecules would be expected to be manifested in the presence of paramagnetic species,

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and with additives containing atoms of high nuclear charge. Charge-transfer interaction giving rise to fluorescent or non-fluorescent exciplexes is a fairly recently observed phenomenon, and some form of complex formation could constitute the initial step in all quenching mechanisms, decay of the excited complex thus formed resulting in the overall observation of (i), (ii) and (iii).

Methyl-, fluoro- and trifluoromethyl-substituted benzenes provide a convenient range of aromatic molecules for experimental study of the above possible quenching interactions in the vapour phase since they are usually volatile, and differ in important parameters such as ionization potential, electron affinity, size, etc. over a considerable range, permitting testing of proposed mechanisms. We have carried out an extensive study of the quenching of the first excited singlet states of such molecules by molecular oxygen, nitric oxide, diolefins, biacetyl and 2-pentanone in an attempt to clarify the quenching mechanism in each case, and the results are reported here.

## Experimental

Full details of the experimental techniques utilized in static fluorescence quenching measurements [3], fluorescence decay time measurements [4], and fluorescence spectral measurements [5], have been given elsewhere, and will not be repeated here. Similarly, all details of the materials used and purity etc. have also been given in other reports [3, 6].

## Results

In all cases, relative quenching rate constants ( $k_Q$ ) were measured from the slopes of Stern-Volmer plots of  $\Phi_0/\Phi$  where  $\Phi_0$  is the quantum yield of fluorescence in the absence of additive,  $\Phi$  that at any pressure  $[Q]$ , and from the usual relationship:

$$\frac{\Phi_0}{\Phi} = 1 + k_Q \tau [Q] \quad (1)$$

Absolute values of  $k_Q$  were obtained from measurement of fluorescence decay times  $\tau$  under the same conditions as which  $\Phi_0$  was obtained. Values of  $k_Q$ , and the quenching cross-section derived from them using:

$$\sigma_Q^2 = k_Q \left( \frac{8\pi kT}{\mu} \right)^{-1/2} \quad (2)$$

are summarized in Table 1. Table 1 uses some data from papers previously published [3, 7] together with hitherto unpublished data. It should be noted that the addition of n-pentane in most cases resulted in curved Stern-Volmer plots, as would be expected for an additive which could only assist vibrational relaxation and not quench electronically. In such cases the initial slope of the Stern-Volmer plot is used to compute values of  $k_Q$  and  $\sigma_Q^2$ , and the values quoted thus represent maximum values of apparent electronic quenching parameters.

TABLE 1

Quenching data for substituted benzenes, vapour, 25 °C

No.	Substituents	$\lambda_{\text{ex}}$ (nm)	$\tau_{\text{F}}$ (ns)	$k_{\text{R}} \times 10^6$ ( $\text{s}^{-1}$ )(eV)	IP (eV)	EA (eV)	Diameter (Å)	$k_{\text{Q}} \times 10^{10}$ ( $\text{l mol}^{-1} \text{s}^{-1}$ )						
								O <sub>2</sub>	NO	n-Pe	Bu	Pi	2-P	Bi
1	None	253.7	77	2.46	9.25	-1.4	5.63	10.2	8.4	0.12	0.57	2.0	14.6	12.4
2	F	265.0	9.5	23.0	9.20	-1.0	—	16.0	17.5	0.36	2.23	4.23	22.4	21.5
3	1,2 F <sub>2</sub>	264.5	5.5	29.0	9.34	-0.6	7.01	16.8	15.9	0.48	2.68	7.19	25.2	12.6
4	1,3 F <sub>2</sub>	264	6.0	27.0	9.37	-0.6	6.79	18.4	18.9	0.00	2.97	7.22	18.7	10.9
5	1,4 F <sub>2</sub>	272.5	8.0	62.5	9.17	-0.6	—	17.7	15.7	0.78	3.60	5.69	25.8	19.5
6	1,2,4 F <sub>3</sub>	270.0	3.1	116.1	9.37	—	6.14	18.8	21.2	0.58	—	—	41.9	16.5
7	1,3,5 F <sub>3</sub>	264.0	3.9	10.0	9.30	—	6.96	29.2	28.7	1.45	—	—	35.1	30.9
8	1,2,3,4 F <sub>4</sub>	264.0	1.3	146.2	9.61	—	—	9.8	15.6	0.45	—	—	27.0	16.9
9	1,2,3,5 F <sub>4</sub>	268.0	1.2	24.2	9.55	—	—	22.5	23.8	0.05	—	—	24.5	30.9
10	1,2,4,5 F <sub>4</sub>	273.0	2.0	170.0	9.39	—	—	13.7	13.1	2.13	—	—	54.4	57.5
11	F <sub>5</sub>	270.0	1.6	15.6	9.84	—	—	8.6	17.7	0.32	—	—	16.9	25.8
12	F <sub>6</sub>	270.0	1.5	6.7	9.97	—	8.61	2.9	11.9	0.85	—	—	16.3	22.0
13	1,2 F, CH <sub>3</sub>	266.5	10.5	27.0	8.92	-0.9	8.16	21.8	17.0	0.54	1.10	4.39	21.0	29.5
14	1,3 F, CH <sub>3</sub>	267.1	12.5	26.0	8.92	-0.9	6.36	23.9	18.3	—	1.35	3.14	17.4	30.1
15	1,4 F, CH <sub>3</sub>	271.2	18.4	36.0	8.79	-0.9	7.35	19.5	20.0	0.47	2.98	3.85	25.3	33.8
16	CF <sub>3</sub>	264.4	19.0	8.5	9.68	-0.4	7.02	11.6	11.5	0.73	5.57	10.5	31.5	14.8
17	1,3 (CF <sub>3</sub> ) <sub>2</sub>	265.9	20.4	8.6	10.1	0.6	8.91	8.4	10.7	0.62	10.70	21.4	31.3	23.0
18	1,4 (CF <sub>3</sub> ) <sub>2</sub>	266.8	8.6	25.0	10.1	0.6	7.56	10.5	16.0	0.54	18.3	33.7	26.6	16.9
19	1,2, F, CF <sub>3</sub>	267.4	6.5	46.0	9.63	0	8.16	14.9	18.3	1.07	6.90	17.0	32.8	27.3
20	1,3 F, CF <sub>3</sub>	267.1	6.4	47.0	9.74	0	7.46	15.1	17.8	0.70	5.60	17.6	29.8	26.6
21	1,4 F, CF <sub>3</sub>	271.2	16.2	7.8	9.77	0	—	12.3	11.4	0.34	5.38	14.2	32.6	29.3
22	CH <sub>3</sub>	267.0	56	5.36	8.82	-1.3	6.15	20.1	18.9	0.26	1.54	2.82	19.5	24.9
23	CH <sub>2</sub> F	265.0	38.6	4.15	9.51	-0.9	7.85	16.7	9.6	0.40	3.15	6.54	21.0	25.7
24	C <sub>2</sub> H <sub>5</sub>	266.9	43.4	—	8.76	—	—	22.3	23.7	—	—	—	—	—
25	t-butyl	264.0	38.8	—	8.68	—	—	25.3	17.3	—	—	—	—	—
26	1,2 (CH <sub>3</sub> ) <sub>2</sub>	269.5	52	7.31	8.56	—	7.64	23.6	22.4	0.24	—	—	36.8	33.4
27	1,3 (CH <sub>3</sub> ) <sub>2</sub>	270.5	49	7.14	8.56	—	7.76	21.0	23.0	0.17	—	—	31.1	27.2
28	1,4 (CH <sub>3</sub> ) <sub>2</sub>	272.5	44	11.8	8.45	—	6.94	23.6	29.4	0.26	—	—	36.5	33.0
29	1,2,3 (CH <sub>3</sub> ) <sub>3</sub>	268.5	70	—	8.48	—	—	19.0	20.3	—	—	—	—	—

n-Pe = n-pentane; Bu = 1,3 butadiene; Pi = *trans*-1,3-pentadiene; 2-p = 2-pentanone; Bi = biacetyl.

## Discussion

### *Vibrational relaxation*

Since the possibility exists in the case of the vapour-phase studies reported here that vibrational relaxation can be caused by the additive in addition to electronic quenching, it is necessary to consider the extent of such effects, and how vibrational effects can be separated from purely electronic interactions. There is no doubt that for excitation of low pressures of aromatic molecules, exemplified by results for 0.125 Torr of *p*-fluorotoluene (PFT) collision with an inert gas such as cyclohexane drastically alters the distribution of the vibronic levels emitting fluorescence, since the fluorescence spectra are markedly altered (Fig. 1). The effect is also manifested in pressure dependent quantum yields, and non-exponential fluorescence decay characteristics [5]. However, it can be seen in Fig. 1 that the spectra arising when a pressure of 2 Torr PFT is excited at 271.2 nm and that resulting from excitation at the same wavelength of 0.125 Torr PFT in the presence of a large pressure of cyclohexane are very similar, suggesting that the distribution of emitting levels is similar in these cases. It would therefore be expected that vibrational relaxation effects should be minimal if a comparatively high pressure of aromatic molecule is excited in each case, and this is borne out by the apparent quenching parameters listed in Table 1 for the *n*-pentane (*n*-Pe) additive. In all cases, the apparent quenching rate constant is an order of magnitude smaller than corresponding parameters for electronic quenching. In the subsequent discussion therefore, it has been assumed for simplicity that effects of vibrational relaxation in the present experiments are in all cases negligible.

### *Quenching by O<sub>2</sub> and NO*

It is evident from Table 1 that quenching by molecular oxygen of the excited singlet states of most of the aromatic molecules studied here is a highly efficient process. The possible products of the encounter are denoted in eqns. (3) - (6). Those arising from reaction (6) are rigorously spin-forbidden by the Wigner spin conservation laws, and thus eqn. (6) can be discounted.



Stevens [8, 9] has shown that in the case of aromatic molecules in solution eqn. (3) is the exclusive interaction between singlet states and ground state oxygen, despite the fact that eqn. (4) is permissible energetically. However, since only one molecule of  ${}^1\text{O}_2$  is produced in the total quenching of singlet aromatics to their ground states [10], and the interaction of triplet aromatics with triplet oxygen produces  ${}^1\text{O}_2$  on every encounter, eqns. (4) and (5) must be discounted. By analogy, the overall reaction occurring upon the

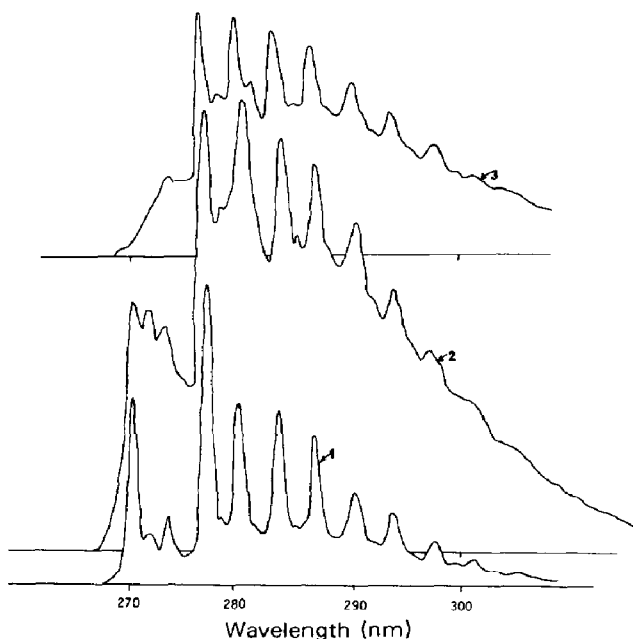
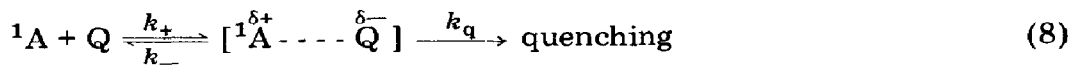


Fig. 1. Fluorescence spectra of *p*-fluorotoluene excited at 271.2 nm: (1) 0.125 Torr; (2) 0.125 Torr + saturated vapour pressure of cyclohexane; (3) 2 Torr.

addition of NO to a singlet aromatic molecule is held to be:



Since both reactions (3) and (7) have a spin statistical factor of unity *via* the exchange mechanism, they might be expected to have unit collision efficiency. Figure 2 shows that for most molecules, this is the case, the average asymptotic rate constant being  $2.2 \times 10^{11} \text{ l mol}^{-1} \text{ s}^{-1}$ , close to the gas kinetic rate constant. However, not all of the aromatic molecules are quenched with this high efficiency, and the reason can be sought in the case of oxygen in the efficiency of initial complex formation, dubbed an "oxci-plex" by Stevens, and its stability. If the complex is stabilized by charge transfer (from aromatic molecule to quencher), then the simple quenching scheme can be replaced by the more complex scheme (8)



and the measured quenching rate constant  $k_Q$  is now given by  $k_Q = k_+k_q / (k_- + k_q)$ . Provided  $k_q$  is small compared with  $k_-$ ,  $k_Q$  can then be represented by  $k_qK$ , where  $K$  is the equilibrium constant for complex formation,  $k_+/k_-$ . Since  $\log K$  is related linearly to free energy changes, it might be expected that  $\log k_Q$  might show some correlation with free energy change which can be estimated from ionization potentials of the aromatic and electron affinity of the quencher. Ground-state ionization potentials only are available, but since the  $S_0-S_1$  excitation energy does not vary significantly over the range of

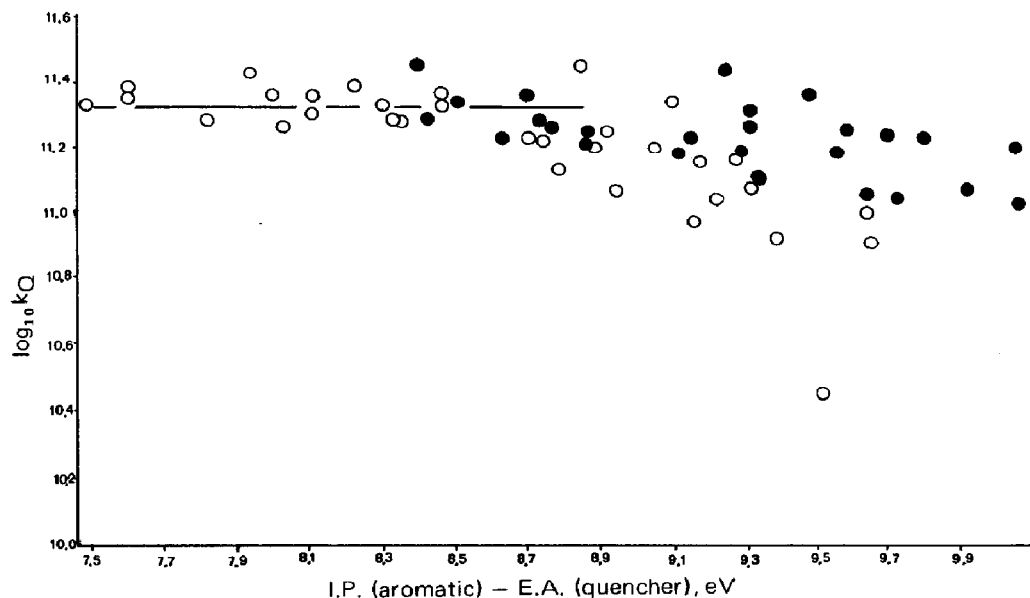


Fig. 2. Variations of  $\log_{10} k_Q$  with IP (Aromatic)–EA (quencher) for oxygen ( $\circ$ ) and nitric oxide ( $\bullet$ ) quenching. Numbers refer to Table 1. See footnote\*.

compounds studied, this approximation is valid. Figure 2 shows that despite considerable scatter, due in part to the variation in molecular size of the aromatic donor molecule and consequent variation in gas-kinetic collision cross-section which has not been taken into account, for aromatic molecules of high ionization potential, quenching by oxygen does become less than collision controlled, lending some credence to the mechanism proposed. The shape of the curve in Fig. 2 is reminiscent of that obtained for the fluorescence quenching of compounds such as acetonitrile which are quenched by electron transfer [11], although in the range of free energy changes and quenching efficiencies is more limited in the present case. Despite the admittedly limited evidence here in support of the formation of an encounter complex stabilized by charge transfer, a cautionary note should be sounded in that it is possible to correlate other molecular parameters, such as polarizability, with ionization potential, and thus it cannot be stated categorically that charge-transfer is necessarily involved in complex formation. In solution such effects can be tested by change in polarity of solvent, but such tests cannot, of course, be applied to the vapour phase experiments.

The data for NO quenching do not show such a pronounced fall-off of  $\log_{10} k_Q$  with IP (aromatic) and the mechanism of quenching by this additive is uncertain, despite earlier views that the  $O_2$  and NO quenching was similar [7].

\*Values of electron affinities for NO and  $O_2$  are taken from Phys. Rev., A6 (1974) 607 and 631 and have values of 0.024 and 0.44 eV respectively. These values differ from those used in ref. 7, but are more accurate. We wish to thank Dr. R. J. Donovan for pointing out the recent values of electron affinities to us.

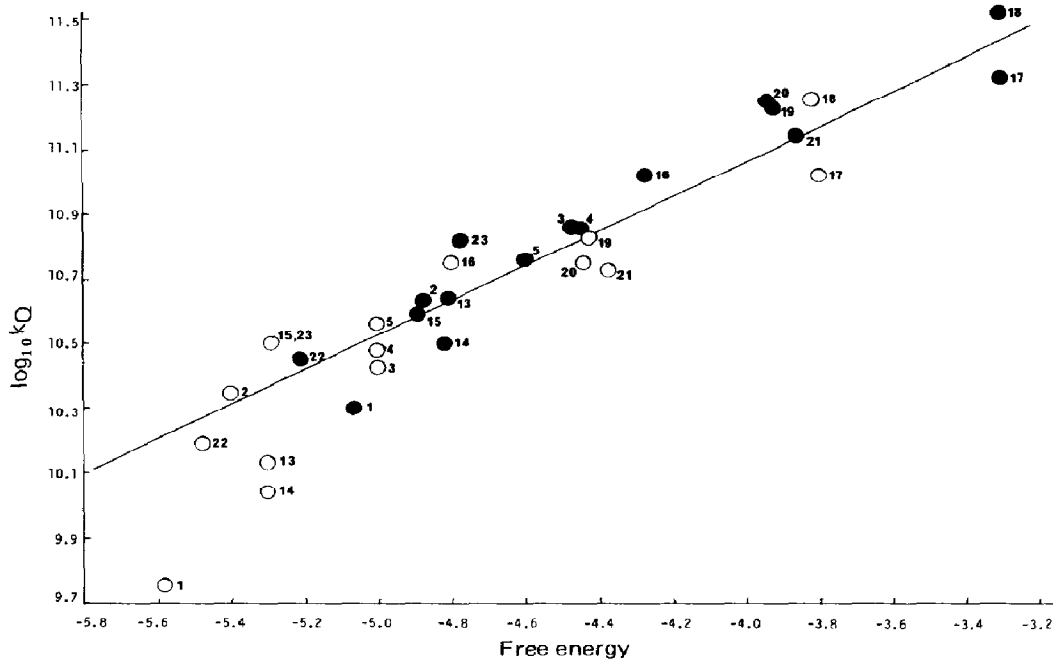
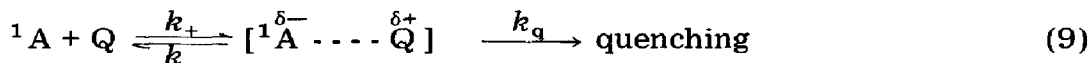


Fig. 3. Variation of  $\log_{10} k_Q$  with free energy change for quenching by butadiene (○) and *trans*-pentadiene (●). Numbers refer to Table 1.

### Quenching by olefins

A twenty-five fold variation in rate constant was obtained (Table 1) for the quenching of fluorescence of substituted benzenes by 1,3-butadiene (Bu) and *trans*-piperylene (Pi) and again, it is possible to invoke a mechanism involving the formation of a charge-transfer complex or exciplex [6]. In this case, however, it is evident that the aromatic molecules of highest ionization potential are quenched most efficiently, and evidently charge-transfer occurs in the opposite sense to that in the case of oxygen quenching:



It is possible to estimate free energy changes for complex formation from a variety of experimental data, and the correlation between  $\log k_Q$  and estimated free energy change is illustrated in Fig. 3. It should be stressed that the expectation of such correlation depends upon the attainment of equilibrium between the exciplex and starting materials, and the fact that  $k_q$  is necessarily small compared with  $k_-$ , and is relatively unchanged from aromatic molecule to aromatic molecule. In such cases

$$k_Q = Kk_q, \text{ where } K = k_+/k_-$$

and thus

$$\log k_Q = \frac{-\Delta G}{RT} + \log k_q \quad (10)$$

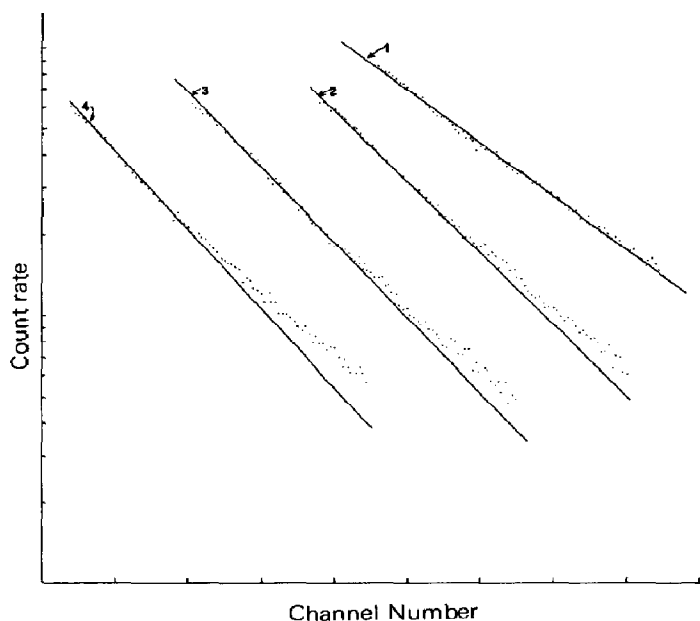


Fig. 4. Fluorescence decay curves of 2.0 Torr *p*-fluorotoluene excited at 271.2 nm: (1) alone; (2) with 7.9 Torr *trans*-pentadiene; (3) with 16.1 Torr *trans*-pentadiene; (4) with 23.4 Torr *trans*-pentadiene.

If  $k_q$  is not small compared with  $k_-$ , it is not permissible to use the thermodynamic function for  $K$ , and thus the relationship becomes invalid. It should be noted that for compounds 17 and 18, quenching occurs with gas kinetic efficiency, whereas for 1, the quenching is quite inefficient. For the efficient quenching, the mechanism implies long-lived exciplex formation, and the possibility exists that these may be fluorescent. However, for all pairs studied to date, no luminescence other than the normal fluorescence spectrum of the aromatic molecule has been observed in the vapour phase, indicating non-fluorescent exciplex formation in each case. Ware [2] has shown that non-fluorescent exciplex formation, and subsequent reverse dissociation of the exciplex, will cause the fluorescence decay characteristics of the excited state to be non-exponential, and we have tested this in a particular case. For very efficient or very inefficient interactions it would not be expected that the degree of non-exponentiality introduced into the fluorescence decay would be observable, but for intermediate cases, non-exponential decay should be observed. In Fig. 4 we show typical fluorescence decay characteristics for fluorescence from *p*-fluorotoluene vapour alone, and in the presence of varying concentrations of *trans*-piperylene. Non-exponential decay is clearly observable, and this has been analysed according to the method of Ware *et al.* [12], permitting values for the individual rate constants,  $k_q$  and  $k_-$  to be evaluated, assuming the value of  $k_+$  to be the gas kinetic rate constant. Values of  $k_q$  and  $k_-$  obtained were  $5 \times 10^{-6} \text{ s}^{-1}$  and  $4 \times 10^7 \text{ s}^{-1}$  respectively. It can thus be seen that  $k_q$  is indeed smaller than  $k_-$ , showing that the assumptions involved in the



correlation of overall quenching efficiency with free-energy changes are valid. The lifetime of the non-fluorescent exciplex formed between PFT and *trans*-1,3-pentadiene is thus observed to be 22.2 ns, and so it may be possible to observe the species in absorption by a suitable laser-flash photolysis experiment. Investigations into the non-exponential decay characteristics of other aromatic-olefin pairs in the vapour-phase are currently being carried out, and since quenching by such mechanisms should have negative temperature coefficients, work is in progress to study the temperature dependence of quenching.

Care must be taken in vapour-phase experiments that effects ascribed to complex formation, and in particular, the observation of non-exponential fluorescence decay curves, are not due to other effects, especially vibrational relaxation. Collisional vibrational relaxation has been shown to lead to non-exponentiality in the fluorescence decay characteristics of PFT at low pressures [5], but can be discounted in the present case, since addition of n-pentane did not cause non-exponential decay. Moreover, for excitation of PFT alone at 265.4 nm at low pressures, results show that collisional effects are minimal, the initially populated levels behaving very similarly to the Boltzmann distribution of emitting levels [6]. Nevertheless, addition of diolefin to PFT excited at this wavelength does lead to non-exponential decay, indicating a cause other than vibrational relaxation.

#### *Quenching by ketones*

In contrast to quenching by olefins which have high singlet energy levels, quenching by the ketones biacetyl and 2-pentanone can involve singlet-singlet energy transfer, since in all cases the excited singlet energy levels of the ketones lie lower than the corresponding singlet energy levels of the aromatic molecules. Table 1 shows that rate constants for quenching by the ketones are very large, never less than the corresponding rate constant for quenching by O<sub>2</sub>, and in most cases considerably larger. As stated earlier, the possible mechanisms of electronic energy transfer are the short-range exchange interaction [2], with efficiency given by:

$$P_{D^* - A}^* = \frac{2\pi}{h} K_e^2 \exp^2(-2R/L) \int_0^\infty f_D(\nu) F_A(\nu) d\nu \quad (11)$$

and the long-range induced dipole-dipole interaction [1] with efficiency given by:

$$P_{D^* - A}^* = \frac{9000 K_r^2 \ln 10}{128\pi^6 N n^2 \tau_D R^6} \int_0^\infty f_D(\nu) \epsilon(\nu) \frac{d\nu}{\nu^4} \quad (12)$$

where  $\nu$  is the frequency in wavenumbers,  $\epsilon(\nu)$  is the molar decadic extinction coefficient of A;  $F_A(\nu)$  is the acceptor absorption coefficient also normalized to unity;  $f_D(\nu)$  is the spectral distribution of the fluorescence of D\* normalized to unity;  $R$  is the intermolecular separation,  $L$  is the effective Bohr radius,  $K_e^2$  is a constant with dimensions of energy squared,  $K_r$  is an orienta-

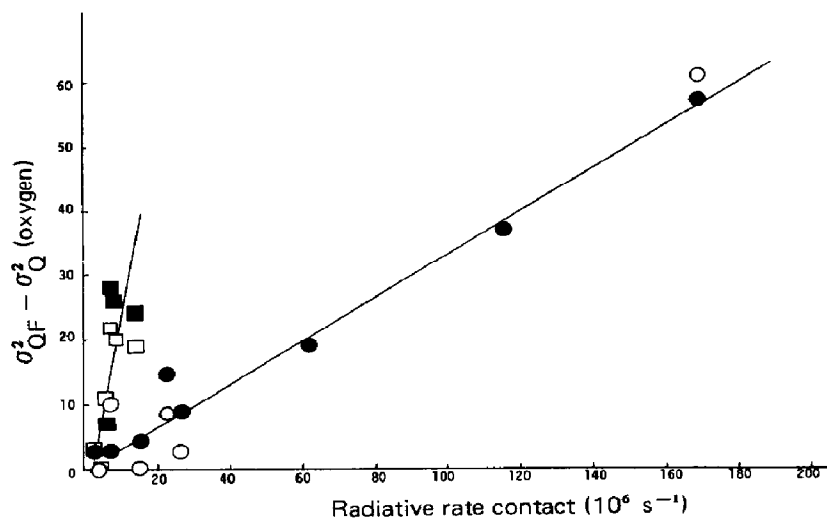


Fig. 5. Variation of  $\sigma_{QF}^2 - \sigma_Q^2$  (oxygen) with radiative rate constant for fluoro- (circles) and methyl- (squares) benzenes quenched by biacetyl (open symbols) and 2-pentanone (solid symbols).

tion factor, of value  $2/3$  for a random distribution;  $N$  is Avagadro's number;  $n$  is the refractive index of the solvent and  $\tau_D$  is the radiative lifetime of the donor molecule. In vapour-phase experiments it is difficult to distinguish between these two mechanisms, but Breuer and Lee [3] have proposed that the cross-section for quenching by oxygen should be taken as representing the magnitude of the exchange interaction, and that any efficiency in excess of this may be due to the induced dipole-dipole interaction. For the latter case, after correction for spectral overlap variations correlation of quenching efficiency with inverse of the radiative lifetime of the donor molecule ( $k_R$ ) would be expected, all other terms being taken as constant, and this correlation has been demonstrated for a range of substituted benzenes quenched by pyrazoline [13]. In the present case there is a wide variation in size of the aromatic donor molecule, which makes direct comparison difficult. Taking results for the two series of compounds available, the methyl- and fluoro-benzenes, plots of "excess" cross-section (that for quenching by the ketones minus that for quenching by oxygen) against radiative rate constant for the donor are given in Fig. 5. There is some evidence of a correlation, but it is evident that results for the two series do not lie on the same line, and there is nothing in the Forster equation which could explain this fact. Moreover, the errors in radiative rate constant are considerable, and for many of the fluorinated benzenes, the quenching efficiency of oxygen is less than the collision controlled rate, necessitating the use of the averaged value of  $21.7 \text{ \AA}^2$  for the cross-section for quenching by  $O_2$  to derive the "excess" cross-section plotted in Fig. 5. It may well be that there are other explanations to account for the variation in efficiency of quenching by the ketones with aromatic donor molecule, although there seem to be no theoretical reasons why long-range effects should not occur in the vapour

phase. The fact that some of the larger fluoro-benzenes have smallest quenching efficiencies, which argues against size being the sole rate-determining factor, may be an indication that there is a contribution to the total electronic energy transfer efficiency of the induced-dipole type in these systems but more precise data will be required, however, before this can be fully substantiated.

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