

spin density is concentrated on the four sulfur atoms. The second example is for the radical derived by the loss of a hydrogen atom from thiodyglycolic acid.^{7a} In this case B has been estimated to be 22.5 G, but since the spin density on the sulfur atom was calculated indirectly from the β -proton anisotropy, the value is probably subject to an error of at least 10%. Thus it can be

concluded that a $\cos^2 \theta$ relation is indeed applicable to sulfur-centered π radicals such that B is approximately 25 G, *i.e.*, about 60% of the corresponding value for carbon-centered π radicals.

Acknowledgment. Earlier studies on γ -irradiated crystalline dimethyl sulfoxide were carried out in this laboratory by Dr. Y. J. Chung.

Quenching of the First Excited Singlet State of Substituted Benzenes by Diolefins in the Vapor Phase

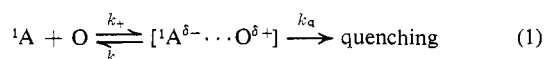
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Abstract: Rate constant data for the quenching of the first excited singlet states of a series of aromatic compounds by *trans*-1,3-pentadiene and 1,3-butadiene are presented. A strong correlation between the quenching rate constant and the estimated electron affinity of the aromatic is found, as would be expected on the basis of formation of an encounter complex stabilized by charge transfer from diolefin to excited aromatic.

The effect of additives on the fluorescence quantum yield of benzene and substituted benzenes in the gas phase has been of interest for some time and has recently been reviewed.¹ The additives chosen usually contain π electrons, although a report has been published in which saturated halogenated compounds were used to quench the $^1B_{2u}$ excited state of benzene.² Until recently, however, there has been little attempt to correlate quenching parameters with properties of quenchers relating to a particular quenching mechanism.

Breuer and Lee³ have investigated the relative contributions of the dipole-dipole and exchange mechanisms of electronic energy transfer to the quenching of the fluorescence of various substituted benzenes by cyclopentanone and 1-pyrazoline, but these electronic energy transfer mechanisms are thought not to be operative for quenching moieties such as olefins, diolefins, and molecular oxygen.⁴ Instead, the formation of a charge-transfer complex is postulated.^{4,5} This has been investigated for the quenching of singlet states of substituted benzenes by molecular oxygen^{6,7} in which case the encounter complex is stabilized by donation of charge from the aromatic compound to the oxygen.⁵ In the case of quenching by olefins,⁴ the charge transfer is proposed to be in the opposite direction as shown in eq 1, where 1A is the aromatic in its



first excited singlet state, O is the olefin and $[^1A^{\delta-} \cdots$

$O^{\delta+}]$ represents an encounter complex between excited-aromatic and olefin which is stabilized by charge transfer from the olefin to the aromatic.

On the basis of this scheme, measured quenching rate constants (k_Q) are given by the expression

$$k_Q = k_+k_q/(k_- + k_q) \quad (2)$$

The stability of the complex, and hence the quenching rate constant, will be determined by the free energy changes associated with complex formation. In solution, strong correlations between the reduction potentials of a series of excited molecules and rate constants for quenching by a variety of additives have been found.⁸⁻¹⁰ To date, such phenomena have not been investigated in the vapor phase, and the present research was directed toward this end.

Experimental Section

The apparatus, experimental technique, and purity of all the aromatic compounds used have been described elsewhere.¹ The *trans*-1,3-pentadiene was obtained from Fluka chemicals with a stated purity of greater than 99%. This was confirmed by vapor phase chromatography on a silver nitrate/ethylene glycol column and the compound was used without any attempt at further purification. The *n*-pentane was obtained from May and Baker Ltd. and vapor phase chromatography on a 5% OV1 column showed it to have 5% isopentane as an impurity. It was considered that isopentane would have a virtually identical effect on the fluorescence quantum yields of the aromatic molecules and hence no attempt was made to remove it.

Results

The quenching by *trans*-1,3-pentadiene of the aromatic compounds used in this study was analyzed in terms of the familiar Stern-Volmer equation

$$\Phi_0/\Phi_p = 1 + k_{QT}[Q] \quad (3)$$

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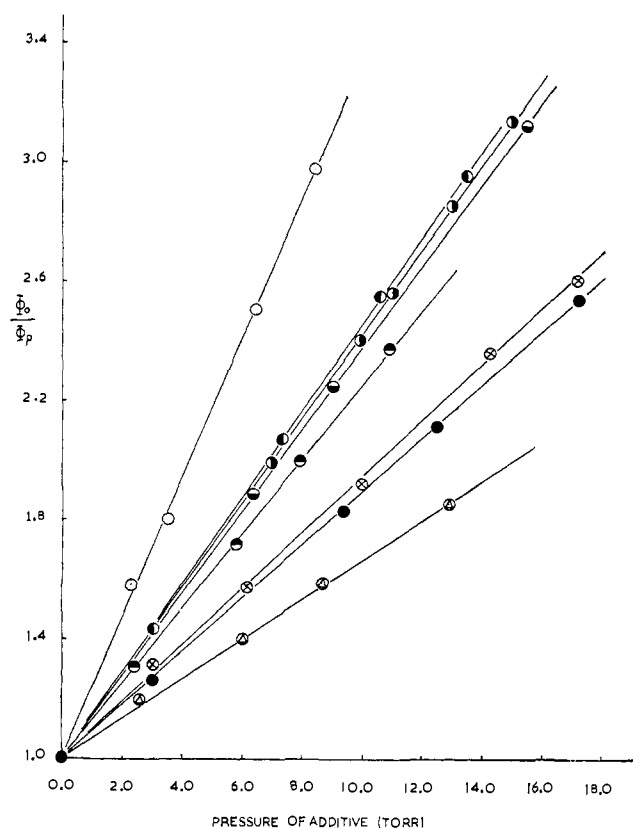
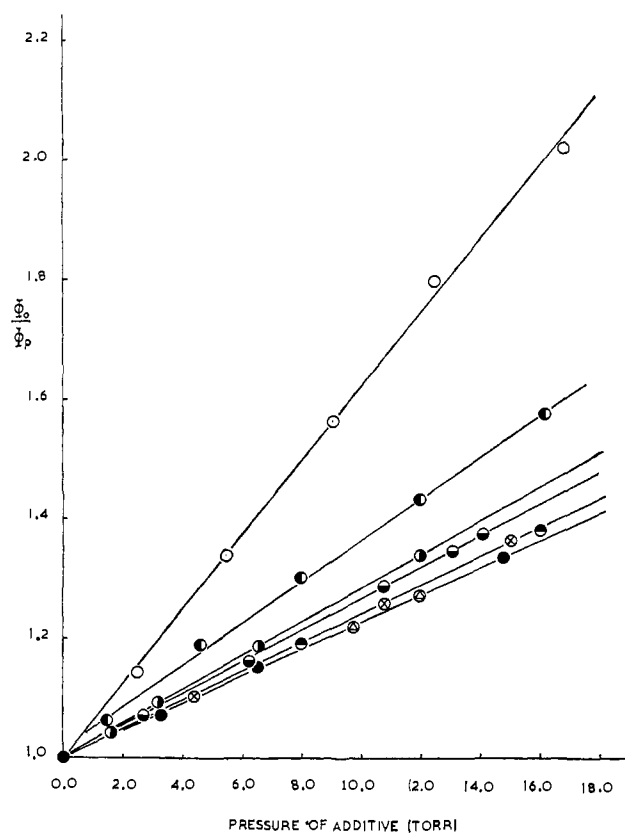
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Table I. *trans*-1,3-Pentadiene and *n*-Pentane Quenching Parameters for the Various Aromatic Compounds Listed by Substitution on the Benzene Ring

Substituent(s)	Aromatic press., Torr	λ_{ex} , nm	Lifetime ^a τ , nsec	<i>trans</i> -1,3-Pentadiene			<i>n</i> -Pentane	
				Slope, Torr ⁻¹	$k_Q, \times 10^{10}$ l. mol ⁻¹ sec ⁻¹	$\sigma^2_Q, \times 10^{-16}$ cm ²	Slope, Torr ⁻¹	$k_Q, \times 10^9$ l. mol ⁻¹ sec ⁻¹
None	15.0	253.7	77.0	0.088	2.00	2.54	0.0052	1.18
CH ₃	2.2	266.5	56.0	0.094	2.82	3.64	0.0087	2.61
CH ₂ F	2.5	265.0	38.0	0.142	6.54	8.92	0.0087	3.99
F	2.3	265.0	9.5	0.024	4.23	5.61	0.0020	3.60
1,2-F,F	3.8	264.5	5.5	0.023	7.19	9.87	0.0015	4.75
1,3-F,F	3.5	263.5	6.0	0.023	7.22	9.91	0.0000	0.00
1,4-F,F	2.0	272.0	8.0	0.028	5.69	7.81	0.0039	7.80
1,2-F,CH ₃	2.5	266.5	10.0	0.027	4.39	5.98	0.0033	5.40
1,4-F,CH ₃	2.2	271.2	14.8	0.035	3.85	5.25	0.0043	4.74
1-CF ₃	6.0	264.4	23.7	0.135	10.50	15.04	0.0111	7.25
1,2-F,CF ₃	2.2	267.4	6.8	0.066	16.97	24.74	0.0042	10.69
1,3-F,CF ₃	2.4	267.8	6.3	0.062	17.58	25.63	0.0025	7.03
1,4-F,CF ₃	2.5	264.0	16.2	0.127	14.20	20.70	0.0031	3.41
1,3-CF ₃ ,CF ₃	3.6	265.9	19.3	0.228	21.39	32.31	0.0067	6.20
1,4-CF ₃ ,CF ₃	2.3	266.8	8.0	0.148	33.73	50.96	0.0024	5.40

^a Lifetimes taken from ref 7.**Figure 1.** Stern-Volmer plots of Φ_0/Φ_p against pressure of additive in Torr: \circ = 1,3-bis(trifluoromethyl)benzene, \odot = 1,4-bis(trifluoromethyl)benzene, \bullet = benzyl fluoride, \ominus = trifluoromethylbenzene, \oplus = *p*-fluorobenzo trifluoride, \otimes = toluene, \bullet = benzene, \otimes = *o*-fluorobenzo trifluoride.**Figure 2.** Stern-Volmer plots of Φ_0/Φ_p against pressure of additive in Torr: \circ = *m*-fluorobenzo trifluoride, \bullet = *p*-fluorotoluene, \bullet = *p*-difluorobenzene, \ominus = *o*-fluorotoluene, \oplus = *m*-fluorotoluene, \otimes = fluorobenzene, \bullet = *m*-difluorobenzene, \otimes = *o*-difluorobenzene.

where Φ_0 is the fluorescence quantum yield of the aromatic compound in the absence of quencher and Φ_p is the quantum yield in the presence of a concentration [Q] of quencher. τ is the measured fluorescence decay time and k_Q is the quenching rate constant.

Plots of Φ_0/Φ_p against [Q] for the various aromatic compounds are shown in Figures 1 and 2 and the slopes of the plots along with the values of τ used to obtain k_Q are given in Table I. The results of similar experiments in which *n*-pentane was used as the additive are

also included in Table I. Quenching cross sections obtained from the relationship

$$\sigma_Q^2 = k_Q(8\pi kT/\mu)^{-1/2} \quad (4)$$

where k is Boltzmann's constant, μ is the reduced mass of the collision pair, and σ_Q^2 is the cross section, are also included in Table I.

Discussion

The fluorescence quenching observed may be due to the following processes. (a) Vibrational relaxation to

Table II. *trans*-1,3-Pentadiene and 1,3-Butadiene Quenching and Free-Energy Parameters for the Various Aromatic Compounds Listed by Substitution on the Benzene Ring

No.	Substituent(s)	EA, eV	<i>trans</i> -1,3-Pentadiene			1,3-Butadiene		
			$k_Q, \times 10^{10} \text{ l. mol}^{-1} \text{ sec}^{-1}$	$\log k_Q$	$-G,^a \text{ eV}$	$k_Q,^b \times 10^{10} \text{ l. mn}^{-1} \text{ sec}^{-1}$	$\log k_Q$	$-G,^a \text{ eV}$
1	None	-1.4	2.00	10.30	-5.07	0.57	9.76	-5.58
2	CH ₃	-1.3	2.82	10.45	-5.21	1.54	10.19	-5.48
3	CH ₂ F	-0.9	6.54	10.82	-4.78	3.15	10.50	-5.29
4	F	-1.0	4.23	10.63	-4.88	2.23	10.35	-5.40
5	1,2-F,F	-0.6	7.19	10.86	-4.47	2.68	10.43	-5.00
6	1,3-F,F	-0.6	7.22	10.86	-4.45	2.97	10.48	-5.00
7	1,4-F,F	-0.6	5.69	10.76	-4.60	3.60	10.56	-5.00
8	1,2-F,CH ₃	-0.9	4.39	10.64	-4.81	1.10	10.04	-5.30
9	1,3-F,CH ₃	-0.9	3.14	10.50	-4.82	1.35	10.13	-5.30
10	1,4-F,CH ₃	-0.9	3.85	10.59	-4.89	2.98	10.48	-5.30
11	CF ₃	-0.4	10.50	11.02	-4.27	5.57	10.75	-4.80
12	1,2-F,CF ₃	0.0	16.97	11.23	-3.92	6.90	10.83	-4.43
13	1,3-F,CF ₃	0.0	17.58	11.25	-3.93	5.60	10.75	-4.44
14	1,4-F,CF ₃	0.0	14.20	11.15	-3.86	5.38	10.73	-4.37
15	1,3-CF ₃ ,CF ₃	0.6	21.39	11.33	-3.30	10.67	11.03	-3.80
16	1,4-CF ₃ ,CF ₃	0.6	33.73	11.53	-3.31	18.30	11.26	-3.82

^a Calculated using values of 8.56 and 9.07 eV for the ionization potentials of *trans*-1,3-pentadiene and 1,3-butadiene from M. J. S. Dewar and S. D. Worley, *J. Chem. Phys.*, **49**, 2454 (1968). ^b Taken from ref 4.

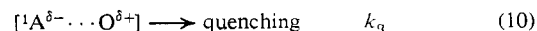
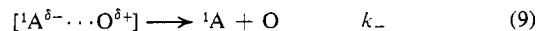
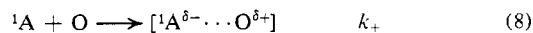
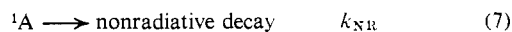
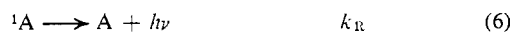
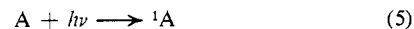
give a set of emitting levels different from that initially populated. (b) Formation of an encounter complex from which the following electronic quenching processes might occur: (i) electronic energy transfer by the Dexter exchange mechanism, (ii) chemical interaction, (iii) enhancement of nonradiative decay to the ground or triplet state of the aromatic molecule. (c) Long-range energy transfer.

To determine the role of process a, quenching experiments were also carried out using a molecule of similar size and complexity to the *trans*-1,3-pentadiene used, *i.e.*, *n*-pentane. As can be seen from Table I, with the exception of the quenching of *m*-fluorotoluene, rate constants for apparent quenching by *n*-pentane which can be attributed to vibrational relaxation are at the greatest of the order of 10% of those for *trans*-1,3-pentadiene and in most cases substantially less. We may therefore conclude that the greatest contribution to quenching of the singlet states of the aromatic molecules must arise through one of the mechanisms b or c. There is further support for this conclusion in that rate constants for quenching by the olefin obtained from relative quantum yield measurements and those obtained by measurement of fluorescence lifetimes as a function of pressure of quencher agree within 10%. Since the quantum yield measurement is a ratio of rate constants, $k_R/(k_R + k_{NR} + k_Q[Q])$, and the lifetime is the inverse of the sum of a set of rate constants $(k_R + k_{NR} + k_Q[Q])^{-1}$, the two sets of measurements would not be expected to yield the same result unless the distribution of emitting levels remained substantially the same, *i.e.*, both $k_R/(k_R + k_{NR})$ and $(k_R + k_{NR})^{-1}$ remain constant, observed changes being due almost exclusively to the term in $k_Q[Q]$. Finally, there is good spectroscopic evidence, to be presented elsewhere,¹¹ that for most of the molecules studied here at the pressures and excitation wavelengths used in this study the system is close to the Boltzmann distribution of emitting levels. These results can be contrasted with those obtained by Wettack, *et al.*,¹² who studied the quenching of single vibronic levels of benzene at very low

pressures by acetone. In this case, a comparative study revealed that a substantial contribution to the overall quenching efficiency arose from vibrational relaxation-redistribution rather than electronic quenching, but such large effects are not to be expected in the present situation in which an initial distribution of emitting levels is at or near thermal equilibrium.

In the work of Wettack, accurate estimation of the purely electronic quenching efficiency was possible by subtraction of the cross sections for acetone and propane, since only fluorescence originating in a unique vibronic level was monitored. In the present case total fluorescence was monitored, and simple subtraction of the *n*-pentane result from that for *trans*-1,3-pentadiene is invalid. Nevertheless, the fact that the vibrational relaxation effects are small in these experiments permits the use of the olefin data without correction, to investigate the electronic quenching mechanism.

Long-range quenching effects (process c) may be discounted in the present case, since quenching efficiencies are in all cases less than those calculated on the basis of gas-kinetic hard sphere collision theory. Without identifying the mode of electronic quenching, therefore, we may on the basis of previous observations propose the following simple kinetic scheme



Here A is the aromatic molecule with superscripts showing the multiplicity and the other symbols are the same as used previously

It has already been noted that the overall quenching rate constant (k_Q) is given by $k_+k_q/(k_- + k_q)$, so that if k_+ is the hard-sphere gas-kinetic collision frequency, k_Q is governed by $k_q/(k_- + k_q)$, or the equilibrium constant for formation K_{eq} of the complex. The stability of the encounter complex, given by the logarithm of the equilibrium constant, will be linearly related to the

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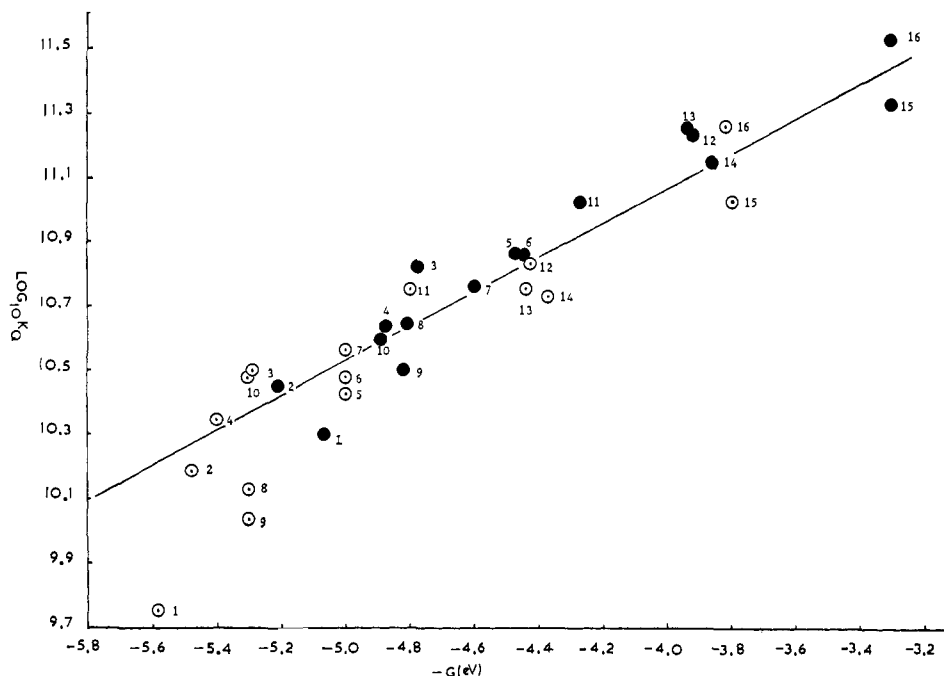


Figure 3. The variation of $\log k_Q$ with $-G$. Filled circles refer to *trans*-1,3-pentadiene and open circles to 1,3-butadiene, and the numbers are those assigned to the compounds in Table II.

free-energy changes associated with complex formation. For molecules in the vapor phase, the magnitude of such free energy changes can be related to the ionization potential of the quencher (IP), excitation energy (ΔE), and electron affinity of the excited singlet state of the aromatic molecule (EA),^{9,10} such that

$$\log K_{eq} \propto (\Delta E + EA - IP + C) \text{ or } (-G + C) \quad (11)$$

where C is a constant.

The former two parameters are readily available but little data are available concerning electron affinities of excited states. If ground state values are accepted, the data shown in Table II are obtained. It should be noted that the electron affinities have in some cases been estimated from those of benzene as a reference compound and use of the correlation noted by Naff and Cooper¹³ that the electron affinity of the molecule on substitution by fluorine, methyl and trifluoromethyl¹⁴ groups increases additively by 0.4, 0.1, and 1.0 eV, respectively, per substituent. The relation between free energy change and quenching rate constant as given by eq 11 is shown in Figure 3, for quenching by

trans-1,3-pentadiene and also by 1,3-butadiene⁴ (data also given in Table II).

The correlation noted in Figure 3 is far stronger than the uncertainties in values of electron affinity would warrant but nevertheless may be used to support the concept of an encounter complex stabilized by charge transfer. The correlation implies that the stability of the complex is the rate-determining parameter for the overall quenching and thus the electronic quenching step must have a similar rate constant k_q , since $\log k_Q$ is given by eq 12. The nature of the electronic quenching step is not revealed in these experiments, although electronic energy transfer by the exchange mechanism (i) may be ruled out since singlet energy levels of the olefins used are much higher than those of the excited benzenes. It would be of interest to test the conclusion that

$$\log k_Q = \frac{\Delta G}{2.303RT} + \log k_q \quad (12)$$

k_q varies little from molecule to molecule by direct observation of the complexes, but since these may be short lived, and are certainly nonluminescent, such observations may prove to be difficult.

Acknowledgment. We are very grateful to Dr. M. Godfrey for helpful discussions and to the Science Research Council and the Royal Society for financial support.

(13) W. T. Naff and C. P. Cooper, *J. Chem. Phys.*, **49**, 2787 (1968).

(14) The value for CF_3 was given by Dr. M. Godfrey of this department and is based upon the value which if used in semiempirical LCAO calculations results in matching of calculated electronic energy levels with experimental values for these compounds.