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Quenching of Rubicene Fluorescence by Amines

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In a previous paper,[1] the charge transfer (CT) interaction between an excited fluorescer and a quencher was shown to play a significant part in the mechanism of fluorescence quenching on the basis of the correlation between the quenching constants and the electron affinities of quenchers. A study was made on quenching of fluorescence of anthracene and pyrene by electron-accepting substances. With the purpose of clarifying further the inner quenching mechanism, the present work was carried out for the systems of rubicene and various amines, where excited rubicene may be considered as an electron-acceptor and amines as electron-donors. Amines have been known to be effective quenchers, and if their large quenching abilities can be attributed to their strong electron-donating powers, it will be expected that in combinations of a given fluorescer and a series of amines their effective quenching radii are related to their ionization potentials.

The advantage in dealing with these systems is that rubicene fluoresces at a relatively long wavelength (553 mμ) and the amines employed scarecely absorb the exciting light (436 mμ), so that the possibility of the trivial "quenching" caused by the inner filter effect and the waste of exciting light can be excluded to permit one to make a more reliable discussion.

Experimental

Rubicene was synthesized from fluorenone[2] and recrystallized several times from toluene. The absorption spectrum of this sample agreed with that given in literature.[3] The liquid amines were fractionally distilled in a nitrogen atmosphere under reduced pressure after being dried with potassium hydroxide, and the crystalline amines were recrystallized and sublimed in a vacuum. Such amines as are very apt to be colored were purified by repeated distillations or sublimations in a vacuum until they became colorless. Toluene was distilled once from a G. R. grade reagent and used as a solvent for the measurement of fluorescence. For the observation of CT bands, spectro-grade carbon tetrachloride was used as a solvent and purified chloranil was employed as an electron-acceptor.

The apparatus and the procedure were almost the same as described in the previous paper.[1] The excitation wavelength was selected at 4358Å Hg line with a Bausch & Lomb grating monochromator. The concentration of rubicene was 4.96×10^{-5} mol/l.

Results and Discussion

The ionization potentials of the amines were estimated by making use of the CT absorption bands of chloranil complexes with these amines. It is well known that for a given electron-acceptor the CT absorption maximum, $\boldsymbol{h}\nu_{\mathrm{CT}}$, can be related to the ionization potential of a donor, I_p, as follows:[4]

$$\boldsymbol{h}\nu_{\mathrm{CT}} = aI_p + b$$

where a and b are the constants to be determined experimentally. Since the interaction between an aliphatic amine and chloranil (n–π interaction) may be different from that between an aromatic amine and chloranil (π–π interaction), the two cases should be treated separately.[4] Using those amines whose ionization potentials had been measured directly,[5] the following relations were obtained by the method of least squares:

$$\boldsymbol{h}\nu_{\mathrm{CT}} = 0.60\, I_p - 2.58 \text{ (eV) (aliphatic)}$$

$$\boldsymbol{h}\nu_{\mathrm{CT}} = 0.45\, I_p - 1.32 \text{ (eV) (aromatic)}$$

From these the ionization potentials of the other amines were estimated.[6] The I_p-values thus obtained as well as the positions of the CT bands observed are given in Table 1.

The quenching constants were evaluated from the Stern-Volmer equation:[7]

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Table 1. The position of CT bands, the ionization potentials, the quenching constants and the effective quenching radii for the amines

No.	Compound	Position of CT-band		I_p	k	(γR)
		(mμ)	(eV)	(eV)	(l/mol)	(Å)
1	*N,N,N',N'*-Tetramethyl-*p*-phenylenediamine	890	1.39	5.97	121	82.5
2	*N,N,N',N'*-Tetramethylbenzidine	848	1.46	6.12	96	74.1
3	*N,N*-Dimethyl-*p*-phenylenediamine	868	1.42	6.04	109	69.1
4	*p*-Phenylenediamine	760	1.64	6.52	108	61.1
5	Benzidine	690	1.82	6.87	77	53.6
6	*N,N*-Dimethyl-*β*-naphthylamine	750	1.65	6.54	62	42.3
7	*o*-Phenylenediamine	620	1.99	7.29	58	32.8
8	*N,N*-Diethylaniline	725	1.71	6.67*	46.7	31.7
9	*N,N*-Dimethylaniline	641	1.93	7.14*	51	31.3
10	*α*-Naphthylamine	646	1.92	7.30*	46.8	29.1
11	*m*-Phenylenediamine	630	1.97	7.26	50	28.3
12	*N*-Methylaniline	600	2.07	7.34*	47	27.2
13	*N,N'*-Diphenylethylenediamine	608	2.03	7.38	32.2	23.6
14	*N*-Phenyl-*β*-naphthylamine	710	1.75	6.76	32.7	23.4
15	*p*-Toluidine	584	2.12	7.50*	40	23.1
16	*o*-Anisidine	584	2.12	7.57	37.2	22.0
17	*N*-Phenyl-*α*-naphthylamine	701	1.76	6.78	30.2	21.6
18	Diphenylamine	653	1.90	7.25*	13.7	9.3
19	Tri-*n*-butylamine	711	1.74	7.22	11.8	8.9
20	Triethylamine	660	1.87	7.85*	12.6	7.7
21	Aniline	570	2.18	7.70*	8.8	4.9
22	Diethylenetriamine	530	2.34	8.23	2.4	1.4
23	*N,N*-Dimethylbenzylamine	500	2.48	8.45	1.7	1.1
24	Triphenylamine	710	1.74	6.68*	0.8	0.6
	Diethylamine	558	2.22	8.01*	—	—

* Directly measured ionization potentials taken from Ref. 5, used for determining the values of *a* and *b*.

$$I_0/I = 1 + k[\mathrm{Q}]$$

where I_0 and I are the fluorescence intensities respectively in the absence and presence of the quencher. The slopes of the plots of $(I_0-I)/I$ against [Q], the concentration of quencher, give the quenching constants, k, which are listed in Table 1.

Since the absorption spectrum of rubicene was not affected by the addition of an amine, it may be considered that a dynamical quenching process is predominant and the interaction of rubicene in the ground state with an amine is very small, but in the excited state, quite large.

For dynamical quenching, the quenching constant is approximated by the following formula:[7,8)]

$$k = 4\pi N'\tau D(\gamma R)$$

where τ is the fluorescence life-time of rubicene in the absence of a quencher, N' is the number of the fluorescent molecules per millimol, *i. e.*, 6.02×10^{20}, D is the relative diffusion constant in toluene, *i. e.*, the sum of the diffusion constants for rubicene and a quencher, and (γR) represents the effective quenching radius. τ was estimated by the relation $\tau=\tau_0\phi$,[*2] where τ_0 is the natural life-time evaluated from the absorption spectrum of rubicene, and ϕ_0 is the fluorescence quantum yield of rubicene determined by comparing it with that of perylene in a degassed benzene solution.[9)] The diffusion constants of the fluorescer and the quenchers were estimated by the method of Othmer and Thaker.[10)] The (γR)-values obtained from the above formula are also listed in Table 1.

Since the effective quenching radius of a quencher can be reasonably taken as a measure for its quenching ability, it is of great interest to plot the effective quenching radii, (γR), against the ionization potentials, I_p, which is shown in Fig. 1.

As is seen from the figure, a good correlation can be recognized between (γR) and I_p; that is, the lower the ionization potential of an amine, the larger its effective quenching radius. This fact suggests that the charge transfer or electron trans-

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[*2] Our values were: $\phi=0.18$, $\tau_0=7.05\times 10^{-9}$ sec; therefore, $\tau=1.27\times 10^{-9}$ sec.

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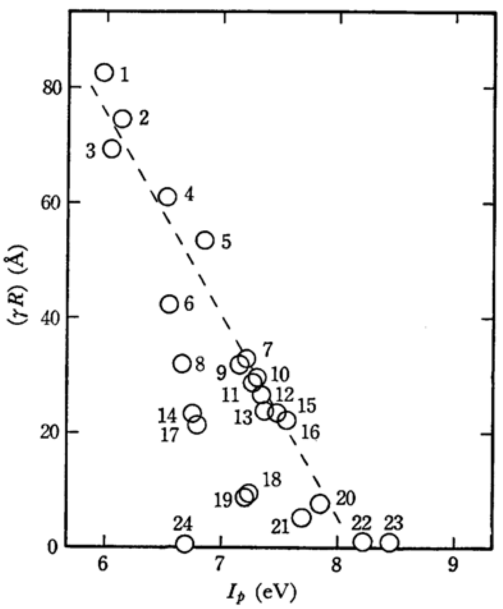

Fig. 1. Relation between the ionization potentials and the effective quenching radii of the amines. Numerals refer to the respective numbers of the compounds in Table 1. The broken curve is drawn tentatively.

fer mechanism[11] is especiallyi mportant for fluorescence quenching.

Because the absorption spectra of the amines and the fluorescence spectrum of rubicene do not overlap at all, the energy transfer mechanism,[12] in which excited rubicene is an energy-donor and amines are energy-acceptors, can be left out of account. The trend observed can not be explained by the mechanism of external heavy-atom effect, in which rubicene in the singlet excited state is converted into the triplet state.

As one can see from Fig. 1, the (γR)-values for some *N*-substituted amines[*3] are considerably smaller than those expected from their I_p-values. This may be interpreted in terms of a kind of steric effect; *e. g.*, the steric effect of the massive groups attached to the nitrogen atom. A remarkable example is found in triphenylamine, whose molecular structure may be unfavorable for an interaction.

The relationship between (γR) and I_p will be useful for estimating the ionization potential of an amine from its (γR)-value.

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12) Th. Förster, *Discussions Faraday Soc.*, **27**, 7 (1959).

[*3] Those compounds (Nos. 8, 14, 17, 18, 19, 24) that lie extraordinarily lower than the tentatively drawn curve in Fig. 1.