Fluorescence Quenching of Some Aromatic Amines by Ethylene Trithiocarbonate in Solution

Reba Ray and Samaresh Mukherjee *
Department of Physical Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta, 700 032, India

The interaction of some aromatic amines such as *o*-aminobenzoic acid, methyl anthranilate, and *o*-*m*-*p*-toluidines with very dilute solutions of ethylene trithiocarbonate (ETTC) have been studied employing steady-state fluorescence quenching measurements and time-correlated single-photon counting spectroscopy. Electronic excitation transfer and static quenching is assumed to describe the higher bimolecular rate constants for the toluidine–ETTC systems. In addition, the possible interpretation of the quenching mechanism is discussed in relation to the electron-transfer between colliding species.

Electron-transfer is the most extensively studied process in fluorescence quenching reactions.[1–4] From such studies the nature of the quenching mechanism[5] and the type of quencher association[6] have become apparent. The first quenching mechanism involves fluorescence/quencher diffusion-controlled collisonal interaction and results in linear Stern–Volmer plots. The second quenching mechanism has been termed 'static' and can occur as the result of a non-fluorescence ground-state complex between the reactants.[7] In this case linear Stern–Volmer plots are also expected. The most significant advances in the study of donor–acceptor interaction have been achieved through the case of time-resolved spectroscopy. However, at low quencher concentration steady-state quenching measurements are also quite considerable to describe the fluorescer/quencher interaction.[8]

In the present work, we have investigated both steady-state and transient fluorescence quenching of some aromatic amines (D), such as *o*-aminobenzoic acid (ABA), methyl anthranilate (MA), *o*-toluidine (OT), *m*-toluidine (MT), and *p*-toluidine (PT) by ethylene trithiocarbonate (ETTC). Studies have been extended to different solvents such as ethanol, acetonitrile, dioxane, and cyclohexane at 300 K. Since the end absorption of ETTC are in the general area of D excitation, inner-filter effect is avoided by using lifetime data and rate constants for some cases are obtained by varying the excitation wavelength. In a previous publication[9] it has been suggested that a number of facts may be responsible for a high value of the quenching rate constant in the fluorescence quenching of carbazole and indole. The present paper extends our earlier studies to a number of different organic compounds in different solvents.

Experimental

Chemically pure samples of *o*-aminobenzoic acid and *o*-*m*-*p*-toluidines obtained from BDH (England) and Fluka AG (Switzerland) were either repeatedly sublimed or distilled under reduced pressure before use. Methyl anthranilate (Aldrich) was twice distilled before use. ETTC, Fluka AG, was used as such. Solvent ethanol (ET), dioxane (DO), and cyclohexane (CH) (E. Merck, spectroscopic grade) were dried and distilled before use. Acetonitrile (AN, E. Merck) was refluxed over KOH and fractionally distilled before use.

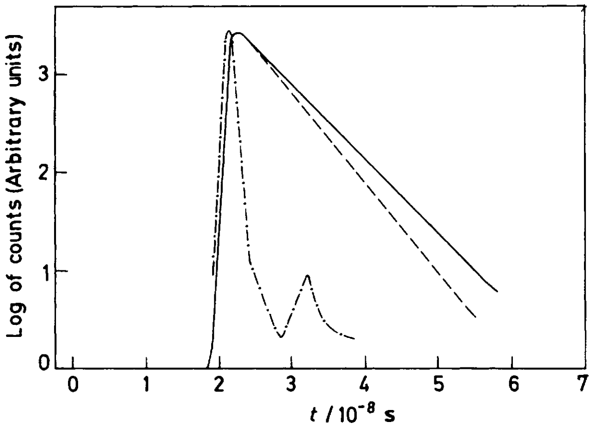

Figure 1. Fluorescence decay curves for *o*-aminobenzoic acid (1.13 × 10^{-4} mol dm^{-3}) – ETTC system measured at 385 nm ($\lambda_{exc.}$ = 345 nm): (——) [ETTC] = 0.0, (– – –) [ETTC] = 3.1 × 10^{-3} mol dm^{-3}, (–·–·–) pump profile, in cyclohexane

The electronic absorption spectra were recorded with a Cary 17D spectrophotometer. Steady-state fluorescence quenching studies were performed in a Perkin-Elmer MPF 44A fluorimeter. Steady-state fluorescence lifetime (τ_0) of amines were calculated as described earlier.[10] Fluorescence lifetime (τ'_0 and τ') were measured with sp-70 nanosecond spectrometer (Applied Photophysics Ltd, England) and 199 fluorimeter system (Edinburgh Instruments, U.K.) based on time-correlated single-photon counting spectroscopy. The nitrogen flash was operated at 28 and 30 kHz with 1 atm and 0.80 bar pressure, respectively. The full-width half-maximum of the pump function was 1.8 ns. The decay curves from multichannel analyser were transferred to Serius 1 computer and PDP11 computer, respectively. The data were analysed by the DECON program supplied by Applied Photophysics Ltd. England and Edinburgh Instruments, U.K.

Results and Discussion

It is observed that the emission intensity decreases considerably with increasing concentration of ETTC as a consequence of amine fluorescence quenching. Typical fluorescence decay profiles are shown in Figure 1 for the ABA–ETTC system. No noticeable evidence of ground-state complex formation could be detected in the absorption spectra up to the ETTC concentration used in this study (Table 1). Therefore, results of both steady-state and transient fluorescence quenching may be interpreted by the Stern–Volmer equation (1) and (2) where I_0, I, τ'_0, and τ' are the fluorescence intensities and lifetimes in the

Table 1. Fluorescence shifts ($\Delta\nu_F$ in cm^{-1}) and rate constants in different solvents

System	$\Delta\nu_F$	τ_0/ns	k_q/dm^3 mol^{-1} s^{-1}	k'_q/dm^3 mol^{-1} s^{-1}	$\lambda_{exc.}$/ nm	Range of [ETTC] mol dm^{-3} × 10^4
ABA + CH	0		7.9×10^{11}		335	
			1.3×10^{11}		340	
		12.3	9.1×10^{10}	2.8×10^{10}	345	
			2.6×10^{10}		350	
ABH + DO	0	11.2	5.5×10^{11}		340	1.2—25.5
			1.7×10^{11}		345	
			7.1×10^{10}		350	
ABA + ET	0	10.7	3.1×10^{11}		340	
			1.5×10^{11}		345	
			9.3×10^{10}		350	
ABA + AN	0	11.5	1.9×10^{11}		345	
			5.1×10^{10}		350	
MA + CH	347	7.5	1.2×10^{11}	2.2×10^{10}	345	
			3.4×10^{10}		350	
MA + DO	347	13.1	1.7×10^{11}		345	
			6.4×10^{10}		350	1.3—35.2
MA + ET	525	10.1	1.3×10^{11}		350	
			1.0×10^{11}		355	
MA + AN	347	11.2	1.9×10^{11}		345	
			5.1×10^{10}		350	
OT + CH	1 931	8.6	7.9×10^{12}	9.7×10^{11}	280	0.1—1.5
			7.0×10^{12}		270	
MT + CH	1 966	9.4	7.0×10^{12}	8.0×10^{11}	280	
			5.3×10^{12}		270	0.1—1.5
PT + CH	2 167	4.9	4.6×10^{12}	5.6×10^{11}	280	0.1—7.5
			3.9×10^{12}		270	
			2.0×10^{12}		260	

Table 2. Rate constants, $k_t = k_{sv}/\tau_0$ [from equation (3)] and W values; $\lambda_{exc.}$/280 nm in cyclohexane

Compound	W	k_t/dm^3 mol^{-1} s^{-1}
OT	0.85—0.90	3.5×10^{12}
MT	0.65—0.95	3.8×10^{12}
PT	0.74—0.96	1.3×10^{12}

absence and presence of quencher (Q), respectively. The terms k_q and k'_q are the bimolecular rate constants, and τ_0 is the unquenched fluorescence lifetime. Equations (1) and (2) hold

$$I_0/I = 1 + k_q\tau_0[Q] \qquad (1)$$

$$\tau'_0/\tau' = 1 + k'_q\tau'_0[Q] \qquad (2)$$

approximately for all the systems studied here (Figures 2 and 3), from which the rate constants are readily calculated. The values of k_q and k'_q are listed in Table 1. The fact that ETTC quenches not only the fluorescence of ABA and toluidines, but also that of MA may imply that charge-transfer interaction other than hydrogen-bonding makes significant contribution to spectral changes with gradual addition of ETTC. Moreover, delocalization of an electron from the π-system of one molecule to another *via* charge-transfer, is not unlikely to describe the present non-radiative process.[11] Accordingly, from the viewpoint of the charge-transfer or electron-transfer mechanism the quenching process may be caused by a direct interaction of an n-orbital of the amine with the π-electron system of ETTC in the excited state.[12—14] It is noteworthy that a large red shift (Table 1) is observed in the case of the toluidines. This spectral shift is rather expected since electron density on the aromatic ring is increased by the electron-donating ability of the methyl group in addition to the effect of its amino group and the λ-electron system of the benzene ring. It can be seen from Table 1 that the bimolecular rate constants of the quenching process are affected to a certain extent by the wavelength of the excitation light used. Moreover both k_q and k'_q values are approaching or similar to diffusion-controlled rate constant values, indicating dynamic quenching of ABA and MA flourescence by ETTC.

A point to note here is that some of the k_q values are quite high $\sim 10^{12}$ dm^3 mol^{-1} s^{-1}. Such a value is unrealistic. Moreover, the fact that values of k_q and k'_q differ significantly and this difference increases with fluorescence shift (Table 1), implies stronger interaction and, hence, greater probability of ground-state complex formation between isomeric toluidine–ETTC systems.[15] This leads to the following modified form of the Stern–Volmer equation (3)[16] where the terms have their usual meanings as described earlier.[9] From equation (3) rate

$$\frac{1 - (I/I_0)}{[Q]} = k_t\tau_0(I/I_0) + \frac{1 - W}{[Q]} \qquad (3)$$

constants (k_t) and W values are readily calculated as described earlier.[17] Figure 4 shows the plots of $1 - (I/I_0)/[\text{ETTC}]$ *vs.* I/I_0 for the *o-m-p*-toluidines–ETTC systems. As can readily be seen from Figure 4 the intercept is quite large and becomes strictly zero if the linear condition *i.e.* W = 1 is satisfied. The range of W and k_t values is given in Table 2. One must note that k_t values (Table 2) are still quite high. Moreover, no appreciable deviation from Stern–Volmer plots can be detected in any of the systems studied here. Furthermore, W values are very close to unity. These observations clearly lead to the suggestion that quenching here occurs by some other mechanism. The lowest excited electronic state of ETTC lies well below the corresponding singlet in the toluidines. Furthermore, it is noteworthy that the overlap between the emission spectrum of the toluidines (290—340 nm) and the absorption spectrum of ETTC (270—340 nm) is significant[9] and the greater the spectral overlap the more efficient is the energy transfer. Hence, quenching in this case must be occurring mainly by energy transfer.[17—19] In

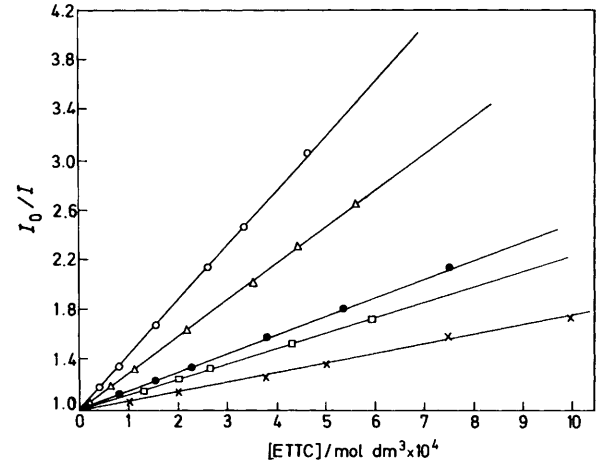

Figure 2. Stern–Volmer plots for *o*-aminobenzoic acid ($\lambda_{exc.}$ 340 nm) in: (○) dioxane, (△) ethanol, (×) cyclohexane, and for methyl anthranilate ($\lambda_{exc.}$ 345 nm) in: (●) acetonitrile, (□) dioxane

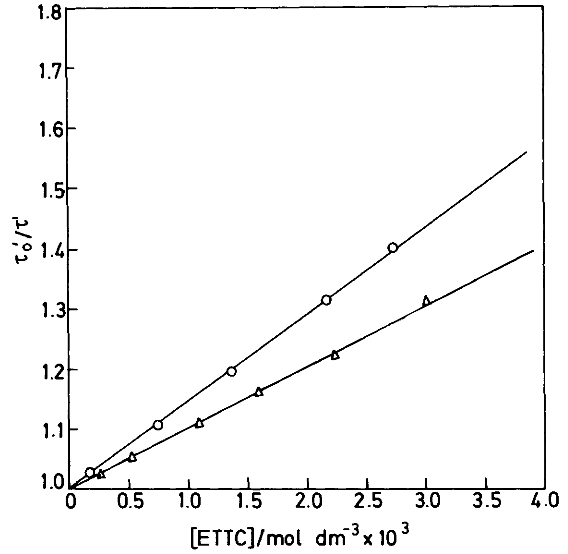

Figure 3. Stern–Volmer plots for (○) *o*-aminobenzoic acid and (△) methyl anthranilate in cyclohexane

support of the above facts it may be mentioned here that Stern–Volmer quenching analysis *via* lifetime measurements is usually unaffected by static quenching. Therefore, if the quenching rate constant from lifetime measurements still exceeds appreciably that of diffusion-controlled limits, some long-range interaction must be taking place, either *via* energy transfer or charge-transfer. A further point for consideration is that the ETTC concentrations ($\sim 10^{-5}$ mol dm^{-3}) used for toluidine (Table 1) fluorescence quenching are about an order of magnitude lower than that required for ABA and MA and we believe that quencher concentration is somehow related with a high k_q value.[8] In fact, if the quencher is efficient the quencher concentration is usually small enough to make the steady-state measurements valid.[20]

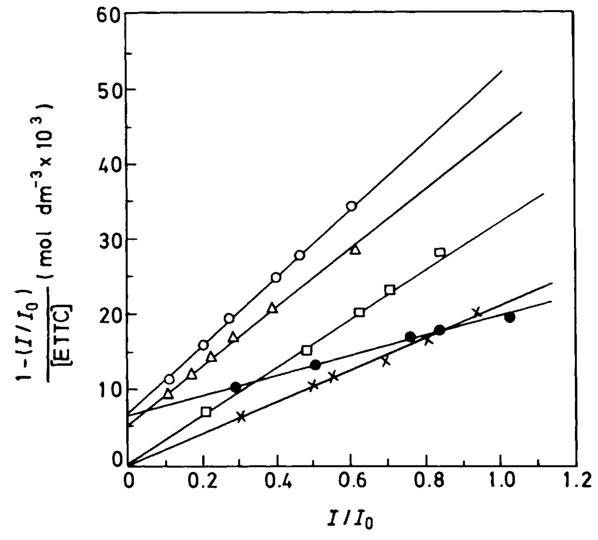

Figure 4. Plot of $1 - (I/I_0)/[\text{ETTC}]$ *vs.* I/I_0; (○) OT, (△) MT, (●) PT, (□) *o*-aminobenzoic acid and (×) methyl anthranilate in cyclohexane

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