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FRONTIER ORBITAL SYMMETRY CONTROL OF INTERMOLECULAR ELECTRON TRANSFER

FINAL REPORT

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by

Brian Stevens

University of South Florida
Department of Chemistry
4202 E. Fowler Avenue, FAO-126
Tampa, Florida 33620

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This report discusses the following topics: -

1. The Recovery of Intermolecular Electron Transfer Parameters from Fluoresence Quenching in Liquids.

Analysis of the simple electron transfer fluoresence quenching sequence 1 in terms of

$$D^* + A \underset{k_D}{\overset{\upsilon_D}{\leftrightharpoons}} (DA)^* \xrightarrow{\upsilon_{et}} D^+ + A^- \qquad 1.$$

the Finite Sink Modification (FSM)[1] of the Smoluchowski-Collins-Kimball (SCK) treatment of the bimolecular processes in liquids (equ 2) provides unambiguous

$$1/k_Q = 1/k^0 + (1 - [2\pi C]^{1/3})\rho/k_D \qquad 2.$$

criteria for reaction-limited ($\upsilon_{et} \ll \upsilon_0$) and diffusion-influenced behavior from measurements of the time-independent quenching rate constant k_Q as a function of quencher concentration C. In the latter case the linear dependence of k_Q on $C^{1/3}$ affords access to the intrinsic quenching rate constant at k^0 at the encounter distance ρ and the relative fluor (D^*) quencher (A) diffusion coefficient D related to $k_D = 4\pi D\rho$ which is varied by temperature induced changes in solvent viscosity ξ.

In this way it has been demonstrated[2] that the effective electron transfer distance ρ for electron transfer from 9,10 - dicyanoanthracene to a series of aromatic amines (in acetonitrile) increases with driving force ($-\Delta G^0$) of the quenching process from a value expected for a contact (D^*A) pair (~ 400 nm) to one which exceeds that associated with a solvent (S) separated pair ($D^*[S]\ A$) or ~ 1000 pm. This in turn leads to an increase in solvent reorganization energy λ_s and reduction in overall activation free energy ($\Delta G^{\pm}$) consistent with the observed absence of a Marcus inverted region in intermolecular electron transfer.

For the same systems under the same conditions it is also noted that the intrinsic quenching rate constant

$k^0 = k_D \upsilon_{et} / \upsilon_D$ 3.

is independent of temperature over the range 0-50°C, with the implication that insofar as

$k_D/\upsilon_D = 2\pi\rho\sigma^2/3$

(with $D = \upsilon_D\sigma^2/6$ where σ is a root mean square solute displacement), the electron transfer frequency υ_{et} is also temperature independent in the region $\Delta G^{\pm} \sim 0$ where $\lambda \sim \Delta G^0$.

An examination of the same D^*/A systems in solvent mixtures of different viscosity (and the same dielectric constant) at the same T provides essentially similar (± 20%) values of both k^0 and ρ confirming this conclusion.

The recovery of electron transfer frequencies υ_{et} from equation 3 rearranged to

$\upsilon_{et} = k^0\upsilon_D/4\pi D\rho$

requires estimates of the relative solute displacement frequency υ_D assumed to be of the form

$\upsilon_D = (kT/h) \exp(-E_D/RT)$

where the activation energy E_D is obtained from the viscosity dependence on temperature. For 9, 10 - dicyanoanthracene fluoresence quenching by various donors in acetonitrile .

υ_{et} is on the order of the reciprocal longitudinal relaxation time of the solvent ($\tau_L^{-1} = 2 \times 10^{12}$ s^{-1}) but appears to vary inversely as the effective electron transfer quenching distance R[4].

On the other hand reaction limited quenching in the "normal" region, where experimental values of $k_Q \neq f(c)$ provide direct access to $k^0 = k_Q$ which exhibit an exponential dependence on T^{-1} to provide values of the activation free energy $\Delta G^{\pm}$. This permits estimation of the nuclear reorganization energy λ_v from the computational sequence:

$$k^0 \rightarrow \Delta G^{\pm} \xrightarrow{\Delta G^0} \lambda = \lambda_s + \lambda_v \xrightarrow{\lambda s} \lambda_v$$

if the solvent reorganization energy λ_s is obtained as the Marcus continuum value. However this approach is oversimplified since values of λ_v obtained for the same donor/acceptor system exhibit an unacceptable solvent dependence[5].

2. Photoinduced Intramolecular Electron Transfer in Flexible Donor/Spacer/Acceptor Systems Containing an Extended Unsaturated Spacer System

The compound 1 -nitro, 4" -amino, p-terphenyl is found to exhibit additional long-wave absorption and fluorescence bands (in dioxane) compared to those of p-terphenyl. Whereas the short-wave (SW) fluorescence band is excited only by absorption in the SW absorption band, the long-wave (LW) fluorescence is excited by absorption in both SW and LW absorption bands and is selectively quenched by polar additives. The large fluorescence Stokes Shifts ($\sim 10^4 cm^{-1}$ peak to peak) indicates that the emitting states are not those excited directly.

It is proposed[6] that the short-wave mono exponential fluorescence originates in the partially-relaxed excited state designated $(A\phi_3)^*D$ in which the excited electron is delocalised over the coplanar groups enclosed parenthetically, whereas the biexponential long-wave component originates in the completely delocalised state $(A\phi_3D)^*$ which is thermally coupled to the lower energy TICT state $A^-\phi_3D^+$. This electron transfer quenching of the non-emissive TICT state by both electron donors and acceptors effectively reduces the LW fluorescence component. Quenching distances are found to be 540 pm (CH_3CN), 460 pm (CH_3OH) and 410 pm (H_20).

Selective quenching of the SW component by "heavy-atom" systems (e.g. CCl_4) is found to be reaction limited.

3. Electron Transfer Sensitized Reactions

Essential to the solar energy storage aspects of photoinduced electron transfer is a resultant chemical transformation. During the course of this work it was noted[7] that rubrene endoperoxide (RO_2) quenches 9, 10- dicyanoanthracene (S^*) fluorescence in (benzonitree) with a diffusion-limited rate constant, and simultaneous production of rubene (R) in the cycloreversion process.

$$RO_2 \rightarrow R + O_2$$

In the presence of a magnetic field of 600 gauss the cycloreversion quantum yield of 0.07 ± 0.07 was found to increase by > 50%. This is consistent with the quenching sequence

$$^1S^* + RO_2 \rightarrow {}^2S^- + {}^2RO_2^+ \rightarrow S + {}^3RO_2 \rightarrow R + {}^3O_2$$

and supported by the observation that the use of chloranil (triplet state) as sensitizer increases the cycloreversion yield to 0.62 ± 0.03 in the absence of a magnetic field.

4. The Recovery of Solute and Fractal Dimensions from Electron Transfer Quenching Data

Available parameters for the system

$$A^* + B \rightarrow A^+ + B^-$$

are the encounter diameter

$\rho_{AB} = r_A + r_B$

and the coefficient of relative diffusive approach

$D_{AB} = D_A + D_B$

If similar data are available for the related systems

$A^* + C \rightarrow A^+ + C^-$

$B^* + C \rightarrow B^+ + C^-$

then in principle it is possible to recover individual encounter radii r_A, r_B and r_C together with individual diffusion coefficients D_A, D_B and D_C.

This has been accomplished for the triad

A= anthracene

B= 9, 10-dicyanoanthracene

C= diazabicycloctane

with dioxane as solvent. The recovered parameters tabulated below:

System	ρ (pm)	$10^{10}D_i(m^2/s)$ (298K)
AC	520	12.0
BC	760	13.7
AB	890	9.2

provide the individual values

	r_i (pm)	$10^{10}D_i(m^2/s)$	σ_i(pm)
A	320	3.7	380
B	560	5.4	260

C	200	8.3	170

where the diffusive displacements σ_i are obtained as

$$\sigma_i = kT/6\pi\xi D_i$$

where ξ denotes solvent viscosity. Clearly the inequality $r_B \neq \sigma_B$ is indicative of a quenching orientation requirement, although for the approximately spherical species C the encounter radius r is close to the fractal dimension σ.

5. Frontier Orbital Symmetry Control of Back Electron Transfers

Certain electron donor/acceptor complexes exhibit dual (structureless) absorption bands in polar liquids, expected for the existence of structural isomers, predicted on the basis of frontier orbital correlation as "weak" and "strong" EDA complexes. Depending on the system, excitation of these complexes is expected to produce rapid (or slow) change separation followed by slow (or rapid) geminate radical ion recombination. Following laser excitation of various EDA complexes in each absorption band, the lifetimes of the resultant radical ions D^+ and A^- were recorded at appropriate wavelengths with the following exemplary results:

EDA System	λ_{ex}(nm)	τ_{A-}(ps)	τ_{D+}(ps)
chloranil/	355	155 ± 30	140 ± 20
naphthalene	532	140 ± 10	110 ± 20
TCHE/naph-	355	96 ± 8	93 ± 20
thalene	532	200 ± 60	210 ± 20

Thus

a) radical ion recombination rates are indeed dependent on excitation frequency for the TCNE/naphthalene system, the only example of this behavior;

b) recombination rates are independent of excitation frequency for the chloranil/ naphthalene complex contrary to expectation

c) in all other cases examined ion recombination proved too rapid to monitor with the ps time resolution available. Some systems prepared did not exhibit a second EDA complex absorption band possibly due to limited solubility of the individual components in polar solvents. Meanwhile the extension to vitronic orbital symmetry classifications to include low-frequency intermolecular vitronational symmetry components in complexes of C_s, C_{2v} and C_{3v} point groups have shown[8] that in each case a vibronic symmetry component is available to promote adiabatic as distinct from non-adiabatic forward and reverse electron transfer.

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Parameterisation of Photoinduced Intermolecular Electron Transfer in the "Normal" Region.

B. Stevens and C.J. Biver III

Department of Chemistry, University of South Florida, Tampa, FL 33620.

Abstract

Reaction-limited fluorescence quenching in the normal region provides direct access to the intrinsic quenching rate constant k° which increases with temperature for the systems examined providing values of the activation free-energy $\Delta G^{\neq}$. This in turn permits recovery of the re-organization energy λ, from estimates of the overall free-energy change ΔG°, which is resolved into solvent (λ_S) and nuclear (λ_V) components if λ_S is given by the continuum model. λ_V is found to be solvent dependent in the range 0.35-1.10 eV.

Introduction

The simple sequence I describing photo-induced intermolecular electron transfer in liquids provides the relationship II for the time -

$$F^* + Q \underset{\upsilon_D}{\overset{k_D}{\rightleftharpoons}} (FQ)^* \xrightarrow{\upsilon_t} F^{\pm} + Q^{\mp} \qquad \text{I}$$

independent quenching rate constant k_Q, available from

$$k_Q = k_D \upsilon_t / (\upsilon_D + \upsilon_t) \qquad \text{II}$$

measurements of the relative fluorescence quantum yield $I_0/I(C)$ as a function of quencher (Q) concentration C and a knowledge of the lifetime τ_0 of electronically-excited fluor F* when C=O (equ. III)

$$k_Q = (I_0/I(c) - 1)/\tau_0 C \qquad \text{III}$$

Of particular interest from the theoretical standpoint is the dependence of the electron-transfer rate constant υ_t on the overall change in free energy ΔG° to which it is related[1] by equations IV; here υ_t° defines the

$$\upsilon_t = \upsilon_t^\circ \exp(-\Delta G^{\neq} / RT) \qquad \text{IVa}$$

$$\Delta G^{\neq} = (\lambda + \Delta G^\circ)^2 / 4\lambda \qquad \text{IVb}$$

maximum activationless ($\Delta G^{\neq} = 0$) transfer frequency when $\Delta G^\circ = -\lambda$ and $\lambda = \lambda_s + \lambda_v > 0$ is a composite reorganization energy with solvent (λ_s) and nuclear (λ_v) components[2].

Equations IV predict the existence of a (Marcus) "inverted region" ($\Delta G^\circ < -\lambda$) in which an increase in driving force ($-\Delta G^\circ$) is accompanied by an increase in activation free energy $\Delta G^{\neq}$ and concomitant reduction in υ_t (IVa) and k_Q. Despite considerable effort[3] since the seminal work of Rehm and Weller[4], the existence of an inverted region has yet to be established for intermolecular electron transfer in liquids, where $k_Q(\upsilon_t >> \upsilon_D) = k_D$ assumes a diffusion - limited value k_D as $-\Delta G^\circ \rightarrow \infty$. The examination of electron-transfer quenching in the "normal" region ($\Delta G^{\neq} > 0 < \Delta G^\circ + \lambda$) where the process is expected to be reaction - limited with k_Q ($\upsilon_t \ll \upsilon_D$) $= k_D\upsilon_t/\upsilon_D$ (equ. II) is less well-documented[5]. However, under these conditions the computational sequence V

$$k_Q(T) \rightarrow \Delta G^{\neq} \xrightarrow{\Delta G^\circ} \lambda \xrightarrow{\lambda s} \lambda v \qquad \text{V}$$

provides access to the nuclear reorganization energy λ_v (usually treated as an adjustable parameter) insofar as ΔG° is available from redox potentials (equ. VI) λ_s (equ. VII) is related[6] to

$$\Delta G^\circ = E_{ox} - E_{red} - E_F^* + e^2/\varepsilon\rho \qquad \text{VI}$$

$$\lambda s = e^2 \left\{ \frac{2}{r_F^\pm} + \frac{2}{r_Q^\pm} - \frac{1}{\rho} \right\} \left\{ \frac{1}{n^2} - \frac{1}{\varepsilon} \right\} \qquad \text{VII}$$

the encounter diameter ρ, ionic radii $r^\pm$, and solvent refractive index n and dielectric constant ε; e denotes the electronic charge.

Here we present an analysis of "reaction-limited" electron-transfer quenching data $k_Q(T)$ in the normal region where, in terms of the Finite Sink Modification VIII[7] of the Smoluchowski-Collins-Kimball expression[8], k_Q is independent of quencher concentration C and reduces to (cf. equ. IVa)

$$k_Q\,(C) = k_D\upsilon_t/(\upsilon_D + \upsilon_t[1 - (2\pi C)^{1/3}\rho] \qquad \text{VIII}$$

$$k_Q = k^\circ = k_D\upsilon_t/\upsilon_D = K\upsilon_t^\circ \exp\left(-\Delta G^{\neq}/RT\right) \qquad \text{IX}$$

where $K = k_D/\upsilon_D$ may be regarded as an equilibrium constant for encounter pair formation, and $\Delta G^{\neq}$ (ΔG°) provides access to the reorganization energy via sequence V.

Experimental

Relative fluorescence quantum yields $I_0/I(C)$ and fluor lifetimes $\tau_0(T)$ in the absence of quenchers were determined as previously described[9]. 9,10-dicyanoanthracene (DCNA) (Kodak 99%) was used as received. Benzylamine (Aldrich 99%), n-butylamine (Aldrich 99+%) and diethylamine (Aldrich 98%) were fractionally distilled before use. Acetonitrile (Aldrich 99.9%) was treated with alumina (MCB 8-14 mesh), and fractionally distilled; methanol (99.9%), ethanol (HPLC), 1-butanol (99.9%) and ethylene glycol (99+%) from Aldrich were used without further purification.

Results and Discussion

Quenching data shown in Figure 1 illustrate (linear) Stern-Volmer behaviour and the Finite Sink representation typical of reaction-limited quenching exhibited by the systems examined at the indicated temperatures. The corresponding rate constants $k_Q = k^\circ$ are collected in Table 1 together with recovered values of the activation free energy $\Delta G^{\neq}$ and pre-exponential terms $K\upsilon_t^\circ$ (equ. IX). In each case the fluor optical density at the excitation frequency and the fluorescence spectrum were unchanged by the addition of quencher, confirming the absence of both exciplex and ground-state complex formation.

Intermolecular electron transfer is implicated as the quenching mechanism since energy transfer would be endothermic and no permanent photochemical change was detected. The overall free energy changes (ΔG°) listed in Table 2 are estimated from equation VI with common values for the reduction potential ($E_{red} = 0.91$ eV) and excitation energy ($E_F^* = 2.90$ eV) of the fluor (DCNA) and a coulombic term $C = e^2/\varepsilon\rho$ which varies slightly with solvent dielectric constant ε; a common value of $\rho =$

430 pm recovered for benzylamine under diffusion-influenced conditions[10] was used for all quenchers. Equation IVb in the form

$$\lambda = 2\,\Delta G^{\neq} - \Delta G^{\circ} \pm 2\,\Delta G^{\neq}(1 - \Delta G^{\circ}/\Delta G^{\neq})^{1/2} \qquad \text{IX}$$

provides estimated values for the reorganization energies λ listed in Table 2 together with those for the nuclear reorganization energy $\lambda_v = \lambda - \lambda_s$ from the solvent reorganization energy λ_s given by equation VIII with $r_{F^+} = 2\,r_{Q^-}$.

Under reaction-limited conditions where $k_Q = k_D k^{\circ}/(k_D + k^{\circ}) \rightarrow k^{\circ}\,(k_D >> k^{\circ}) = k_D \upsilon_t/\upsilon_D$ the effect of solvent viscosity n on the rate of diffusive reactant approach is eliminated insofar as the quotient $k_D/\upsilon_D = K = 4\pi N\rho^3/3000$ depends[11] only on the encounter diameter ρ for the formation of an unbound (contact) intermediate complex $(FQ)^*$. However, an increase in solvent viscosity reduces the encounter rate constant k_D such that reaction-limited behaviour becomes diffusion-influenced ($k_D \sim k^{\circ}$) and eventually diffusion-limited[12] ($k_D << k^{\circ}$); thus both benzylamine and diethylamine exhibit diffusion-limited quenching in ethylene glycol[13] where the intrinsic rate constant k° is not available, while more exergonic systems than those listed undergo diffusion-influenced quenching even in the most fluid media, acetonitrile and methanol. In this context it is of interest to note that k° for the DCNA/n-butylamine system in ethylene glycol is lower by a factor of 2 than in methanol and acetonitrile and appears to originate in a higher activation free-energy for the intrinsic quenching frequency υ_t (Table 1). Within the quoted uncertainty limits the pre-exponential terms $K\upsilon_t^{\circ}$ are on the order of those reported by Previtali et al[14] for nitrobenzene quenching of aromatic triplet states in acetonitrile (3.5×10^{11} M^{-1}s^{-1}) and methanol (1×10^{12} M^{-1}s^{-1}) which, insofar as K is unchanged, do not reflect the relative longitudinal solvent relaxation times $\tau_L = 3.3$ ps (methanol) and $\tau_L = 0.3$ ps (acetonitrile) expected if $\upsilon_t^{\circ} = \tau_L^{-1}$. This may be a consequence of intermediate complex stabilization (as in exciplex formation) which reduces υ_D and increases the formation constant K to an extent which depends on solvent. As previously noted reaction-limited quenching by benzylamine in methanol ($k^\circ << k_D$) becomes diffusion influenced in acetonitrile[10] ($k^\circ \sim k_D$) where the recovered value of $k^\circ \doteq 2.5 \times 10^{10}\ M^{-1}s^{-1} = K\upsilon_t^\circ$ is temperature-independent in the range 0°-50°C; insofar as these solvents have similar viscosities this indicates a significantly higher value of the term $K\upsilon_t^\circ$ in acetonitrile for this quencher.

Estimated values of λ_v (Table 2) appear to contribute significantly to the overall reorganization energy λ recovered from equ. X. This contrasts with the findings of Mou et al[16] for the fluorescence quenching of phenanthrene derivatives by aromatic amines in acetonitrile, that $\lambda \sim \lambda_s$ or $\lambda_v \sim 0$ assuming λ has a common value for all systems examined (at a single temperature); these authors use equs. IVb and IX in the form XI (for the reaction limit)

$$\ln k_Q = \ln K\upsilon_t^\circ - \lambda/4kT - \Delta G^\circ(1 + \Delta G^\circ/2\lambda)/2kT \qquad \text{XI}$$

together with values of $K = 0.86$ (from the Fuoss equation with $\rho = 700$ pm) and an assumed value of $\upsilon_t^\circ = 1.0 \times 10^{11}\ s^{-1}$ (after Weller) to obtain λ from k_Q for an interpolated value of k_Q (ΔG°) corresponding to $\Delta G^\circ = 0$. On the other hand Zhu and Rasaiah[17] find that the parameter $A = \lambda_s/\lambda$ for electron transfer in the betaine-30/triacetin system increases with temperature from ~0.02 (228 K) to 0.8(318 K) although Barbara and coworkers[18], responsible for the measurements, use a hybrid model to predict a value of A ~0.4 over this temperature range. From a non-linear least squared fitting procedure with $K\upsilon_t^\circ$ and λ as adjustable parameters for aromatic hydrocarbon quenching by electron acceptors, Previtali et al[19] find that $\lambda \sim \lambda_s \sim 1.1$ eV with $K\upsilon_t^\circ = 6.8 \times 10^{11}\ M^{-1}s^{-1}$ in acetonitrile and $K\upsilon_t^\circ = 1.8 \times 10^{12}\ M^{-1}s^{-1}$ in methanol which compare favorably with those estimated for triplet state quenching by nitrobenzenes in the same solvents (vide supra) and the values listed in Table 1.

Clearly more experimental data are required to resolve these discrepancies which may originate in

a) a temperature dependence of ΔG° and λ not accomodated in Table 2;

b) contributions from the diffusional rate constant k_D to the experimental quenching constant k_Q in the absence of an independent criterion of transfer-limited quenching;

c) the assumption of a common value of λ for different donor/acceptor systems in the same solvent.

Acknowledgments

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Table 1. Quenching of DCNA Fluorescence by Electron Donors in Solvents Indicated. Rate Constants $k_Q = k^\circ$ Frequency Factors $K\upsilon_t^\circ$ and Activation Free Energies $\Delta G^{\neq}$.

a) Benzylamine as Donor

Solvent	10^{-9} k° $(M^{-1}s^{-1})^a$				
	0°C	22°C	50°C	$K\upsilon_t^\circ(M^{-1}s^{-1})$	$\Delta G^{\neq}$ (k_{cal})
CH_3OH	1.6	2.6	4.2	8.5×10^{11}	3.4
C_2H_5OH	1.7	2.3	3.7	3.0×10^{11}	2.8
$n\text{-}C_4H_9OH$	1.5	2.4	4.2	1.3×10^{12}	3.7

b) n-Butylamine as Donor

CH_3CN	0.75	1.2	2.0	4.3×10^{11}	3.4
CH_3OH	.71	1.2	2.1	9.8×10^{11}	4.0
$(CH_2OH)_2$	.35	.65	1.1	7.5×10^{11}	4.2

c) Diethylamine as Donor

CH_3CN	4.1	5.9	8.6	5.0×10^{11}	2.6
CH_3OH	2.8	4.2	6.6	7.1×10^{11}	3.0

[a] estimated uncertainty + 7 %.

Table 2. Nuclear Reorganization Energies λ_v Recovered From Equ. IX for Systems Indicated.

Quencher	Solvent	ΔG°(ev)	ΔG≠(ev)	λ(ev)	λ_s(ev)	λ_v(ev)
	CH_3CN	-0.62	0.15	1.60	1.14	0.46
n-butylamine	CH_3OH	-0.61	0.17	1.68	1.15	0.53
	$(CH_2OH)_2$	-0.62	0.18	1.74	1.00	0.74
diethylamine	CH_3CN	-0.67	0.11	1.49	1.14	0.35
	CH_3OH	-0.68	0.13	1.59	1.15	0.44
	CH_3OH	-0.78	0.15	1.83	1.15	0.68
benzylamine	C_2H_5OH	-0.81	0.12	1.72	1.05	0.67
	n-C_4H_9OH	-0.88	0.16	2.02	0.91	1.10

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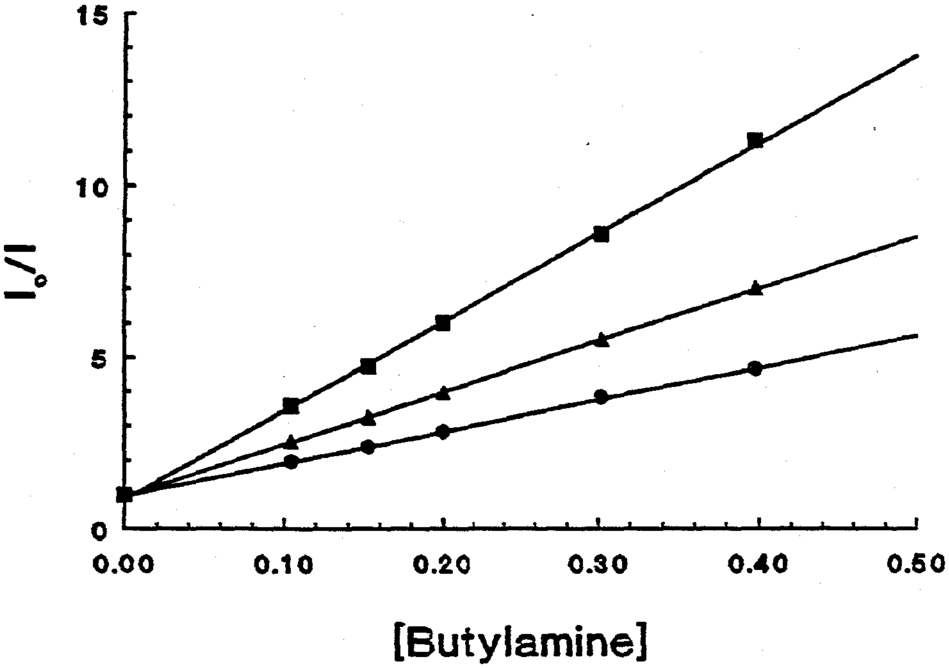
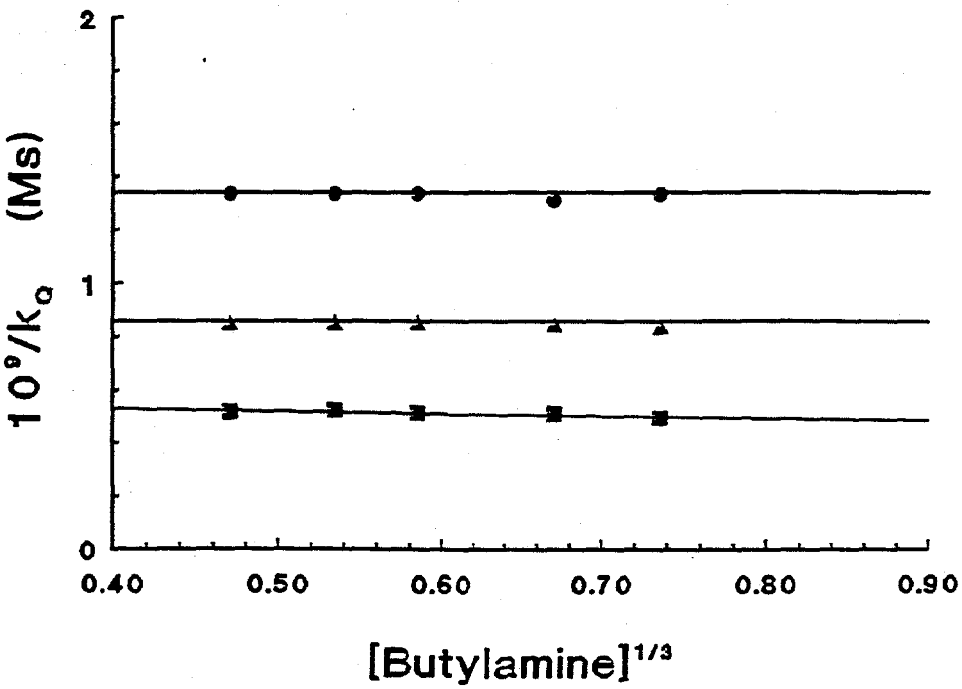
Figure 1. DCNA fluorescence quenching by n-butylamine in acetonitvile according to Stern-Volumer equ. III (above) and FSM equ. VIII (below) at 0°C (●), 22°C (▲) and 50°C (■).



15
10
5
0
I₀/I
0.00
0.10
0.20
0.30
0.40
0.50
[Butylamine]



2
1
0
10⁹/k_q (Ms)
0.40
0.50
0.60
0.70
0.80
0.90
[Butylamine]^1/3