NEAR DIFFUSION CONTROLLED PHOTOKINETICS IN AROMATIC ESTER–ALIPHATIC AMINE SYSTEMS

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Summary

The photokinetics of the interaction of aromatic esters with aliphatic amines was studied by stressing in the usual kinetic scheme a first order rate constant k_t which accounts for the formation of exciplexes and radical ion pairs via the encounter complex in situations of near diffusion controlled quenching.

In contrast with the viscosity dependence of the encounter efficiency γ the values obtained for k_t vary with the solvent polarity and with the electronic affinity of the esters in the excited state and the ionization potentials of the aliphatic amines.

1. Introduction

The formation of excited charge transfer complexes, exciplexes, in solution is generally accompanied by diffusion processes [1 - 3].

Hammond has proposed that the collision of the two partners, donor and acceptor, leads to a complex [4] and Weller [5] has suggested that the charge transfer occurs via the formation of an encounter complex in which the separation distance between the donor and acceptor was estimated to be 7 Å. In agreement with this concept, the encounter complex was introduced by Evans [6] in a kinetic scheme which has been recently modified by Buckles [7] with the introduction of the reversibility of the exciplex.

In solvents of different viscosity the overall bimolecular rate constant k_q [1] determined experimentally should contain information concerning both diffusion and charge transfer processes. Hence the establishment of a mechanism and consequently the discussion of the kinetics of exciplex formation would be easier if the contributions of diffusion and charge transfer could be separated.

We have recently reported [8] the interaction of the aromatic esters benzyl 2-naphthoate (III), benzyl 9-anthroate (IV) and benzyl 3-pyrenoate (V) with triethylamine (TEA) and diazobicyclo[2.2.2] octane (DABCO).

Although the rate constants obtained in these systems were of the order of magnitude of diffusion controlled rates, we have suggested that the process was "near diffusion controlled". From the experimental data, and in order to test this hypothesis, we have evaluated a rate constant which depends exclusively on the parameters affecting the charge transfer interaction in the case of near diffusion controlled reactions.

2. Experimental

Compounds III, IV and V have been described in the first article of this series [9] and the techniques used have been described in the second article of this series [8]. The temperature studies were carried out in an MPF-3 spectrofluorimeter using a thermostatted cell for the temperature range of 280 - 340 K and an ethanol–liquid nitrogen slush for the temperature range of 200 - 280 K. The temperatures were measured using a platinum resistance thermometer connected to a digital multimeter model 500, DANA.

3. Kinetics

The interaction of an excited molecule $^1A^*$ with a quencher Q can be explained by postulating an encounter complex $(^1A^*...Q)$. This intermediate can either dissociate to the excited monomer $^1A^*$ and Q (k_{diss}) or lead to an exciplex $(A^-Q^+)^*$ in non-polar solvents (k_1) and to a radical ion pair $(A_s^-...Q_s^+)$ in polar solvents (k_2). The exciplex can also lead to the radical ion pair (k_3) or reversibly return to the encounter complex (k_{-1}). The mechanism is best described by the following scheme:
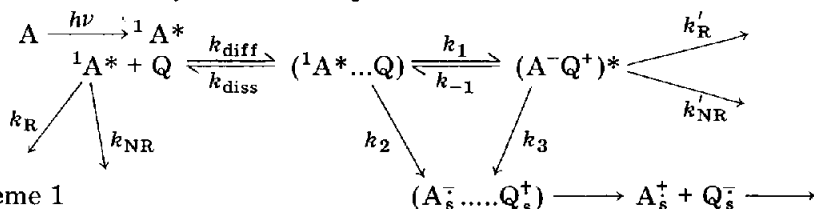
Scheme 1

where k_R, k_{NR}, k_R' and k_{NR}' are the radiative and non-radiative rate constants respectively for monomer and exciplex decay; k_{diff} is the diffusion rate constant and the remaining rate constants have been defined earlier.

Employing the usual steady state treatment we obtain

$$\frac{I_{0f}}{I_f} = 1 + K_{SV}[Q] \tag{1}$$

The Stern–Volmer constant K_{SV} is given by

$$K_{SV} = k_q \tau_{0f} \tag{2}$$

with $\tau_{0f} = (k_R + k_{NR})^{-1}$. For low quencher concentrations [2], the bimole-cular quenching rate constant is given by

$$k_q = 4\pi N' r'_{AQ} D_{AQ} \left\{ 1 + \frac{r'_{AQ}}{(\tau_0 D_{AQ})^{1/2}} \right\} \tag{3}$$

Where r'_{AQ} is the effective encounter distance and D_{AQ} is the sum of the diffusion coefficients relative to the acceptor and donor.

For strong quenchers, eqn. (3) is reduced to the Sveshnikoff equation modified by Umberger and LaMer [10]:

$$k_q = 4\pi N' r_{AQ} D_{AQ} \gamma \left\{ 1 + \frac{r_{AQ}}{(D_{AQ}\tau_0)^{1/2}} \right\} = k_{diff} \gamma \tag{4}$$

with

$$k_{diff} = 4\pi N' r_{AQ} D_{AQ} \left\{ 1 + \frac{r_{AQ}}{(D_{AQ}\tau_0)^{1/2}} \right\} \tag{4'}$$

In eqn. (4') the term which accounts for the transient effects associated with diffusion can be neglected for solvents of low viscosity so that eqn. (4') is reduced to

$$k_{diff} = 4\pi N' r_{AQ} D_{AQ} \tag{4''}$$

The encounter distance r_{AQ} represents the sum of the van der Waals radii for both acceptor and donor [11]. The encounter efficiency γ is related to the rate constants defined in Scheme 1 by

$$\gamma = \frac{k_2 + k_1 \tau'/\tau''}{k_2 + k_1 \tau'/\tau'' + k_{diss}} \tag{5}$$

with

$$\tau' = (k_{-1} + k_3 + k'_R + k'_{NR})^{-1} \qquad \tau'' = (k_3 + k'_R + k'_{NR})^{-1}$$

The rate constant for dissociation of the encounter complex is related to the diffusion coefficient and to the binding enthalpy of this species by the equation

$$k_{diss} = \frac{3D_{AQ}}{r_{AQ}^2} \exp\left(-\frac{\Delta H_b}{RT} \right) \tag{6}$$

Equation (6) is derived on the assumption that the encounter ceases when the distance between A and Q is larger than $1.7 r_{AQ}$ [12]. The exciplex reversibility can be investigated by following the temperature dependence of the monomer to exciplex fluorescence intensity ratio I_E/I_M [13]. According to Scheme 1, ϕ_E/ϕ_M is given by

$$\frac{\phi_E}{\phi_M} = \frac{k'_R}{k_R} \frac{k_1 k_{diff} \tau''[Q]}{k_1 + (k_2 + k_{diss})(1 + k_{-1}\tau'')} \tag{7}$$

Equation (7) can be simplified within two limits.

(a) Low temperature range

If the charge transfer is an efficient process $k_1 \gg k_{diss}$ at low temperatures and, if it is assumed that in non-polar solvents $k_1 \gg k_2$, eqn. (7) is transformed into

$$\frac{\phi_E}{\phi_M} = \frac{k'_R}{k_R} k_{diff} \tau''[Q] = K \exp\left(-\frac{E_d}{RT}\right) \tag{8}$$

The activation energy E_d for the diffusion process can be evaluated from the slope of $\ln \phi_E/\phi_M$ *versus* $1/T$ if τ'' is temperature independent.

(b) High temperature range

At high temperatures k_{diss} increases, so that $k_{diss} \gg k_1/(1 + k_{-1}\tau'')$ and $k_{diss} \gg k_2$. Hence eqn. (7) reduces to

$$\frac{\phi_E}{\phi_M} = \frac{k'_R}{k_R} \frac{k_{diff}}{k_{diss}} \frac{k_1\tau''[Q]}{1 + k_{-1}\tau''}$$

$$= \frac{k'_R}{k_R} V_A \frac{k_1\tau''[Q]}{1 + k_1\tau''} \tag{9}$$

with $V_A = (4/3)\pi r_{AQ}^3 N'$. In reversible systems, $k_{-1} \gg k_3 + k'_R + k'_{NR} (k_{-1}\tau'' \gg 1)$ and eqn. (9) reduces to

$$\frac{\phi_E}{\phi_M} = \frac{k'_R}{k_R} V_A \exp\left(-\frac{\Delta H_b}{RT}\right)\frac{k_1}{k_{-1}}[Q]$$

$$= K' \exp\left(-\frac{\Delta H + \Delta H_b}{RT}\right) \tag{10}$$

As the enthalphy ΔH of formation of the exciplex has a negative value ($\Delta H = \Delta H_1 - \Delta H_{-1} < 0$) and $|\Delta H| \gg |\Delta H_b|$, the slope of $\ln (\phi_E/\phi_M)$ *versus* $1/T$ in the high temperature region must be positive, the whole curve presenting an inflection point.

By contrast, in irreversible systems, $k_{-1}\tau'' < 1$ and eqn. (9) becomes

$$\frac{\phi_E}{\phi_M} = \frac{k'_R}{k_R} V_A \exp\left(-\frac{\Delta H_b}{RT}\right)\tau''[Q] k_1$$

$$= K'' \exp\left(-\frac{\Delta H_1 + \Delta H_b}{RT}\right) \tag{11}$$

In this case $\ln (\phi_E/\phi_M)$ *versus* $1/T$ has a negative slope throughout the whole temperature range. At high temperatures the slope may vary while still remaining negative, but in this case it cannot be related to the enthalpy ΔH of formation of the exciplex.

The introduction of the irreversibility condition in eqn. (5) leads to

$$\gamma = \frac{k_1 + k_2}{k_1 + k_2 + k_{diss}} \tag{12}$$

The introduction of a quenching rate constant k_t associated with the charge transfer processes, such that $k_t = k_1 + k_2$, allows the overall rate constant k_q to be expressed by the equation

$$k_q = k_{diff} \frac{k_t}{k_t + k_{diss}} \tag{13}$$

A more general expression of k_t for reversible systems will be

$$k_t = k_1(1 - k_{-1}\tau') + k_2 = \frac{\gamma}{1 - \gamma} k_{diss} \tag{14}$$

which can be easily deduced from eqn. (5).

4. Results and discussion

The quenching of excited states of III, IV and V with TEA and DABCO is of a charge transfer nature [8]. The detection of exciplexes in non-polar solvents and of radical ions in polar solvents is consistent with the mechanism of Scheme 1.

The kinetic treatment described earlier was applied to these systems. To evaluate the reversibility of exciplex formation, the dependence of ratio I_E/I_M on the temperature was investigated for the systems III–TEA and V–TEA in hexane; the Stevens–Ban plots [13] obtained are shown in Fig. 1.

The linear dependence observed without an inflection point throughout the whole temperature range allows the conclusion that the reversibility of the exciplex in these systems is negligible. The values of the activation energies E_d for the diffusion of A* and Q are 1.1 kcal mol^{-1} for the system III–TEA and 2.0 kcal mol^{-1} for the system V–TEA, in good agreement with the diffusion activation energy E_d of 1.6 kcal mol^{-1} found for this solvent.

The diffusion coefficients have been estimated [1] employing the usual equation

$$D_x = \frac{kT}{6\pi\eta r_x f_t} \tag{15}$$

where

$$f_t = \left\{ 1.5 \frac{r_s}{r_x} + \left(1 + \frac{r_s}{r_x}\right)^{-1} \right\}^{-1} \tag{16}$$

and r_s and r_x are the radii of solvent and solute respectively.

The values of D_{AQ} are presented in Table 1. The diffusion constants were calculated from eqn. (4') and the dissociation constants from eqn. (6), assuming a binding enthalphy ΔH_b, for the encounter complex equal to zero. These constants are listed in Table 2. The encounter efficiency γ and the rate constant k_t determined in these systems are given in Table 3.

The parameter γ is a measure of the efficiency of the encounter and has therefore been used to assess the probability of the charge transfer process
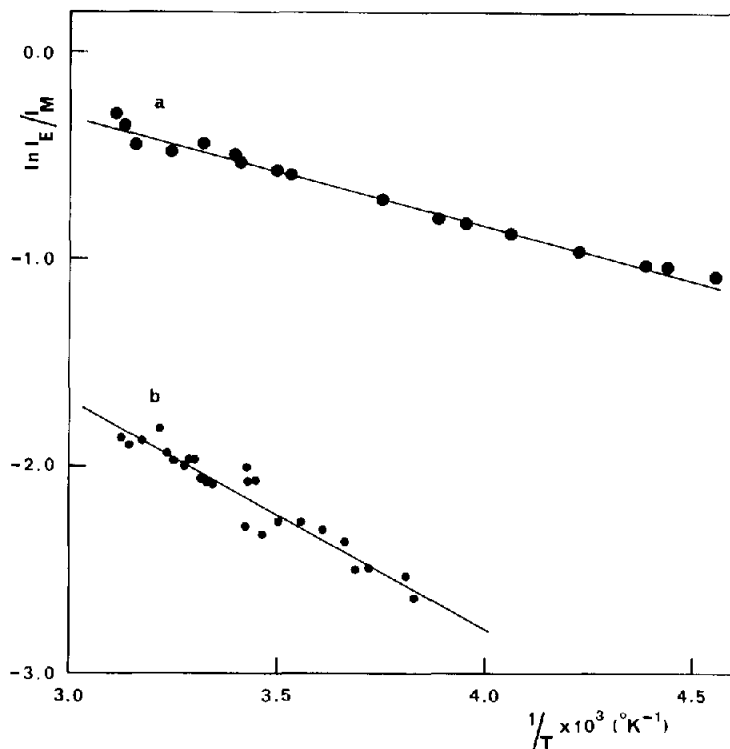
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Fig. 1. Stevens Ban plots for the systems (a) III–TEA (1 M) and (b) V–TEA (1 M) in hexane.

TABLE 1

Diffusion coefficients D_{AQ} (= D_A + D_Q) of the systems III–Q, IV–Q and V–Q

Solvent	$D_{AQ} \times 10^{5}$ [a] ($cm^2 s^{-1}$)		
	III-Q [b]	IV–Q [b]	V–Q [b]
Hexane	7.2	6.9	6.9
Cyclohexane	2.3	2.3	2.2
Acetonitrile	5.8	5.6	5.4
Dimethylformamide	2.4	2.3	2.2

[a] T = 295 K; [b] Q = TEA or DABCO.

[14]. From examination of Table 3 it can be seen that the values do not correlate with solvent polarity although they do with the viscosity. However, k_t gives the expected variation with the solvent polarity and, as shown in Fig. 2, with the difference between the half-wave reduction potentials in the excited state of the esters and the ionization potentials of the amines [14]. The deviations observed for the system IV–TEA in both polar and non-polar solvents reflect the large stabilization gained in the excited state due to

TABLE 2

Calculated diffusion rate constants and experimental quenching rate constants of the systems III–DABCO, III–TEA, IV–TEA and V–TEA

Solvent	III-Q				IV-Q		
	$k_q{}^a \times 10^{-10}$ (dm³ mol⁻¹ s⁻¹)	$k_q{}^b \times 10^{-10}$ (dm³ mol⁻¹ s⁻¹)	$k_{diff}{}^c \times 10^{-10}$ (dm³ mol⁻¹ s⁻¹)	$k_{diss} \times 10^{-10}$ (s⁻¹)	$k_q{}^b \times 10^{-10}$ (dm³ mol⁻¹ s⁻¹)	$k_{diff}{}^c \times 10^{-10}$ (dm³ mol⁻¹ s⁻¹)	$k_{diss} \times 10^{-10}$ (s⁻¹)
Hexane	2.57	1.51	3.77	4.52	1.67	3.76	4.05
Cyclohexane	1.15	1.01	1.22	1.47	0.88	1.22	1.32
Acetonitrile	2.30	1.78	3.03	3.63	1.83	3.01	3.24
Dimethylformamide	1.19	0.98	1.22	1.47	0.95	1.22	1.32

	V-Q		
	$k_q{}^b \times 10^{-10}$ (dm³ mol⁻¹ s⁻¹)	$k_{diff}{}^c \times 10^{-10}$ (dm³ mol⁻¹ s⁻¹)	$k_{diss} \times 10^{-10}$ (s⁻¹)
Hexane	1.13	3.70	3.93
Cyclohexane	0.73	1.19	1.25
Acetonitrile	1.22	2.97	3.06
Dimethylformamide	0.77	1.21	1.25

[a] Q = DABCO; [b] Q = TEA; [c] calculated from eqn. (4″).

TABLE 3

Encounter efficiencies γ and charge transfer rate constants k_t for the systems III–DABCO, III–TEA, IV–TEA and V–TEA

Solvent	$\eta_{20}°C$ (cP)	ϵ	III–DABCO		III–TEA		IV–TEA		V–TEA	
			γ	$k_t \times 10^{-10}$ (s^{-1})	γ	$k_t \times 10^{-10}$ (s^{-1})	γ	$k_t \times 10^{-10}$ (s^{-1})	γ	$k_t \times 10^{-10}$ (s^{-1})
Hexane	0.32	1.9	0.68 (0.62)	9.6 (7.4)	0.40 (0.36)	3.0 (2.5)	0.44 (0.39)	3.2 (2.9)	0.31 (0.28)	2.0 (1.8)
Cyclohexane	0.96	2.0	0.94 (0.82)	23.0 (6.7)	0.83 (0.61)	3.4 (2.3)	0.71 (0.59)	3.2 (2.1)	0.62 (0.54)	1.8 (1.7)
Acetonitrile	0.36	37.0	0.76 (0.69)	11.5 (8.3)	0.59 (0.46)	5.2 (3.1)	0.61 (0.54)	5.1 (4.9)	0.42 (0.38)	2.2 (2.2)
Dimethylformamide	0.93	36.7	0.97 (0.85)	47.7 (8.3)	0.80 (0.70)	5.9 (3.4)	0.79 (0.67)	5.0 (3.0)	0.64 (0.54)	2.2 (1.7)

The values in brackets are calculated using eqn. (4') for k_{diff}. The rate constant k_t for the system III–TEA in CCl_4 is 3.0×10^{10} s^{-1} (2.1×10^{10} s^{-1} calculated using eqn. (4')).
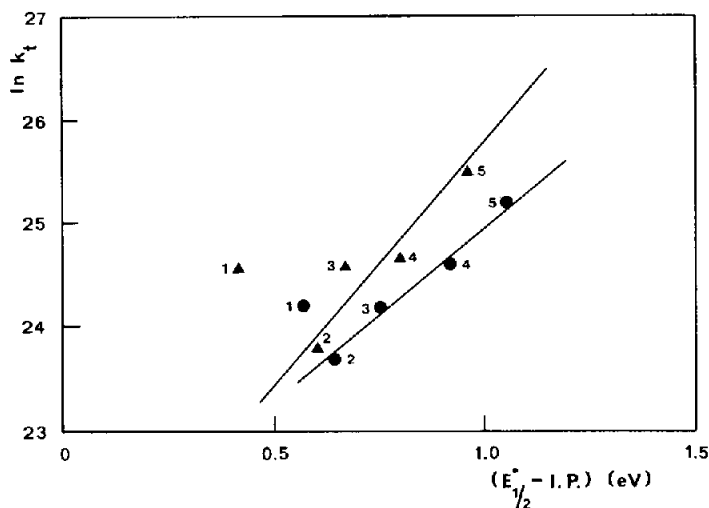
Fig. 2. Plots of the logarithm of the charge transfer rate constants of the systems IV–TEA (1), V–TEA (2), III TEA (3), benzyl-1-naphthoate–TEA (4) and III–DABCO (5) $vs.$ the difference between the half-wave potential of the excited ester and the amine ionization potential. Solvents: •, hexane; ▲, acetonitrile.

changes in its geometry [9, 15] which increase its electron affinity E_a^* in the excited state to a value greater than $E_a + \Delta E_{0,0}$.

The increase of k_t in polar solvents relative to non-polar solvents is certainly associated with a larger decrease of the free energy of the radical ion pair than of the free energy of the exciplex in polar solvents, electron transfer being a more favourable route than charge transfer. However, the variation is not large, particularly in the system V–TEA. This suggests that the free energies of the exciplex and radical ions may have similar values in polar solvents thus enabling the formation of the radical ion pair via the exciplex in these systems as indicated in Scheme 1.

In order to test this treatment we applied it to the system perylene–dimethylaniline which has been studied by Ware [16] and Stevens [17]. The results are presented in Table 4 and show that the rate constants k_t do not depend on the viscosity.

It should be pointed out that this treatment is not applicable to systems in which the encounter efficiency γ approaches unity since in this case large errors will be introduced, as happens in the system III–DABCO where a correlation with viscosity is obtained. In such cases, it is necessary to determine experimentally the effective encounter distance r'_{AQ} [2]. Indeed, for partly diffusion controlled reactions it has recently been shown [18] that r'_{AQ} can be larger than the calculated value r_{AQ} which we used in this work. This confirms that the treatment described will not be suitable in such situations.

The calculation of k_{diff} was made with no correction for the transient effects since on the one hand there was no experimental evidence for them

TABLE 4

Calculated charge transfer rate constants k_t in the system perylene–dimethylaniline

Solvents	$\eta_{25\,°C}$ (cP)	ϵ	γ [a]	γ [b]	$k_t \times 10^{-10}$ (s^{-1})
Acetone	0.30	20.1	0.57	0.36	2.3
Acetonitrile	0.34	37.0	0.72	0.43	2.8
Methanol	0.54	32.6	0.85	0.55	2.8
Pyridine	0.88	12.0	0.64	0.43	1.1
Dimethylacetamide	0.92	37.8	0.75	0.48	1.3
Ethanol	1.08	24.3	1.06	0.68	2.5
n-Propanol	2.00	20.1	1.4	0.82	2.8

[a] Calculated from $k_{diff} = 8RT/3000\,\eta$; [b] calculated from eqn. (4″).

(the fluorescence decays were exponentials and no difference was found between ϕ_0/ϕ and τ_0/τ) and on the other hand the solvents used were not very viscous. However, owing to the short lifetimes of the esters used in this work, transient effects should be present and indeed when a correction is introduced (see Table 2) the viscosity dependence of k_t is eliminated in the system III–DABCO for which small errors in k_{diff} are reflected in large errors in the magnitude of k_t.

The importance of these effects can be illustrated for the interaction of benzyl 1-naphthoate [9] with TEA in which case the introduction of the corrective term

$$1 + r_{AQ}(D_{AQ}\tau_0)^{-1/2} = 1.23$$

changes the encounter efficiency γ from 0.73 to 0.59 in acetonitrile. This points to the need for this correction even in a solvent of low viscosity when lifetimes are very short.

In conclusion, whilst the validity of the treatment used is limited by the approximations made in the calculation of k_{diss} and in the estimation of encounter distances, we believe that in situations near the diffusion controlled limit it seems adequate to emphasize the relevance of k_t in assessing the magnitude of the charge transfer interaction rather than the overall bimolecular rate constant k_q or the encounter efficiency γ.

A similar treatment which has been successfully applied to energy transfer processes [19, 20] gives good support to our conclusions.

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