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GROUND STATE AND EXCITED STATE CHARGE TRANSFER COMPLEXES BETWEEN ELECTRON DONORS AND PYRYLIUM SALTS

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Summary

The electron acceptor behaviour of seven pyrylium salts was examined. The formation of two complexes was demonstrated in the presence of electron donor molecules. One complex occurs in the ground state and absorbs at longer wavelength ($\epsilon \approx 1800 - 2000$ M^{-1} cm^{-1}) than the starting compound and is formed with an association constant of the order of unity. The other complex is formed in the excited state with a rate constant which approaches that of diffusion when the oxidation potential of the electron donor is lower than 1.3 V.

1. Introduction

Ground state charge transfer (CT) complexes have been known for a long time [1]. In the case of heterocyclic onium ions, they involve mainly pyridinium cations and inorganic anions [2, 3]. Pyrylium salts, with their positively charged oxygen atom in the heterocycle, are strongly reactive towards nucleophiles [4]. The presence of the oxygen atom induces a non-uniform electron density distribution with a high positive charge at positions 2, 4 and 6 of the aromatic ring [5].

The absorption of pyrylium iodides is shifted to the red compared with other salts, and this has been attributed to a CT interaction between the two ions [6]. Such a red shift also occurs for pyridinium [2] and quinolinium [3] salts. This red shift is found in aprotic solvents and is believed to involve an electronic transition between the highest occupied molecular orbital of the iodide anion and the lowest unoccupied molecular orbital of the aromatic cation [7] rather than two different excited states of the iodide ions.

In a very few cases, pyrylium CT complexes have been isolated in a crystalline form with the tetracyanopropenide anion [8], the 1,2,3,4,5-pentacarbomethoxycyclopentadiene anion [9] and with a neutral electron donor, N-amino-4-(dicyanomethylene)-2,6-dimethyl-1,4-dihydropyridine [10].

Several applications have been found for the pyrylium salts in which their strong electrophilic affinity as a result of the positive charge of the aromatic pyrylium nucleus is used. Thus, in the electrophotography of poly-(N-vinylcarbazole), the addition of pyrylium dyes traps the electrons and creates, in the poly(vinylcarbazole), positive holes which migrate towards a negatively charged electrode [11]. The quantum efficiency of the sensitized reaction increases from 0.08 to 0.35 when the potential is changed [12] from 2×10^5 to 10^6 V cm^{-1}.

2. Results and discussion

Usually amines are excellent electron donors and consequently should form strong ground state CT complexes with pyrylium salts. Unfortunately, the pyrylium ions react rapidly with primary amines to form, through an addition–ring-opening–elimination reaction, a nitrogen-substituted pyridinium salt [4, 13], whereas secondary and tertiary amines give an addition–elimination reaction [14]. An intermediate CT complex can be postulated at the early stage of these reactions and a fugacious red or green colour has been claimed in several cases. A strong persistent red colour is observed, for instance, when the 2-methyl-4,6-diphenylpyrylium ion is treated with o-chloroaniline, although on precipitation only the corresponding pyrydinium salt could be isolated [15].

Consequently, great care must be taken when amines are used as electron donors and more reliable results are expected when it can be ensured that no reaction occurs between the two components of the CT complex.

A drastic inhibition in the fluorescence emission of pyrylium salts 1 - 7 (Fig. 1) is observed in the presence of traces of electron donors. This behaviour is particularly important with amino compounds but, as already
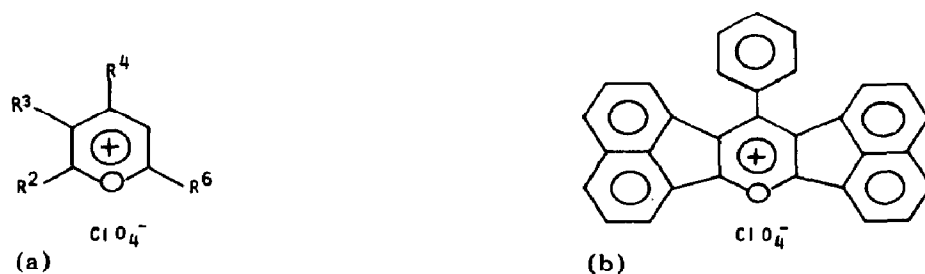

Fig. 1. Structural formulae of (a) pyrylium salts 1 - 6 (1, $R^2 \equiv R^6 \equiv C_6H_5$; 2, $R^2 \equiv R^4 \equiv R^6 \equiv C_6H_5$; 3, $R^2 \equiv R^3 \equiv R^4 \equiv R^6 \equiv C_6H_5$; 4, $R^2 \equiv R^6 \equiv C_6H_5$, $R^4 \equiv COOC_2H_5$; 5, $R^2 \equiv R^4 \equiv C_6H_5$, $R^6 \equiv CH_3$; 6, $R^2 \equiv R^4 \equiv C_6H_5$, $R^6 \equiv CH=CH—C_6H_5$) and (b) pyrylium salt 7.

mentioned, a chemical reaction is known to occur in the ground state between pyrylium cations and amines. No new emission at higher wavelengths appeared when the fluorescence of the pyrylium salts 1 - 7 was quenched by electron donors.

A more precise study was undertaken with compounds 1 and 2 and a series of electron donors. In each case, the fluorescence quenching process followed the Stern–Volmer equation [16]

$$\frac{I_0}{I} = 1 + k_q \tau_s [Q] \qquad (1)$$

where I and I_0 are respectively the relative fluorescence intensities with and without added quencher of concentration $[Q]$, k_q is the bimolecular quenching rate constant and τ_s is the excited singlet lifetime of the fluorescer in the absence of quencher. To observe the influence of the solvent on the quenching process, the experiments were carried out in a strongly polar solvent (CH_3CN) and in a less polar solvent (CH_2Cl_2). In both cases (Table 1) the

TABLE 1

Electron transfer fluorescence quenching results for compounds 1 (in CH_2Cl_2 solution) and 2 (in CH_3CN solution) at room temperature

Donor	E_{ox}^{D} [a] (V)	Data for compound 1		Data for compound 2	
		ΔG^b (kcal mol^{-1})	log k_q [c]	ΔG^b (kcal mol^{-1})	log k_q [c]
N,N-diphenyl-p-phenylenediamine	0.35	−48.4	10.80		
Phenothiazine	0.53	−44.3	10.46		
N,N-diethylaniline	0.76	−39.0	10.43		
Triphenylamine	0.86	−36.7	10.35		
Anthracene	1.09	−31.4	10.49		
Pyrene	1.20	−28.8	10.47		
1,4-dimethoxybenzene	1.34	−25.6	10.39	−25.4	10.44
1,2-dimethoxybenzene	1.45	−23.1	10.35		
1,3-dimethoxybenzene	1.49			−21.9	10.39
Naphthalene	1.60	−19.6	10.44		
Anisole	1.76	−15.9	10.26	−15.7	10.36
p-xylene	1.77			−15.5	10.29
Mesitylene	1.80			−14.8	10.26
o-xylene	1.89			−12.7	10.21
m-xylene	1.91			−12.2	10.25
Thiophene	1.91	−12.4	10.10	−10.6	10.18
Toluene	1.98	−10.8	9.87		
Benzene	2.30	−3.5	8.02	−3.2	8.97

[a] The half-wave oxidation potentials were measured with respect to a saturated calomel electrode in CH_3CN solution [17].
[b] Free-energy change (eqn. (2)).
[c] Deduced from the slope of the Stern–Volmer plots (eqn. (1)).

quenching rate constant increases with decreasing oxidation potential of the donor until it reaches a value comparable with that of a diffusion-controlled process (2.5×10^{10} M^{-1} s^{-1} in CH$_2$Cl$_2$ and 2.7×10^{10} M^{-1} s^{-1} in CH$_3$CN at the same temperature).

The free-energy change ΔG for an electron transfer process is given by [18]

$$\Delta G \text{ (kcal mol}^{-1}) = 23.06(E_{ox}^D - E_{red}^A - \Delta E_s) \tag{2}$$

where E_{ox}^D is the oxidation potential of the donor, E_{red}^A is the reduction potential of the acceptor (-0.34 V measured with respect to a saturated calomel electrode (SCE) for 1 in CH$_2$Cl$_2$ solution and -0.39 V (SCE) for 2 in CH$_3$CN solution) and ΔE_s is the singlet excited state energy of the fluorescer (2.79 eV for 1 and 2.83 eV for 2).

The rate constants k_q (eqn. (1) and Table 1) and ΔG (eqn. (2) and Table 1) were used to construct a Weller plot [18] (Fig. 2). The observed fluorescence quenching profile is typical of an electron transfer mechanism [18, 19].

However, when the concentration of the donor is increased, a new absorption band is observed which can be attributed to a ground state CT complex between the pyrylium salt and the electron donor. In several cases, an important overlap of this new band with the absorption band of the electron acceptor occurs which prevents accurate measurements from being made. Nevertheless, well-separated new absorption bands could be recorded for pyrylium salts 4 and 5 when they were brought together with the
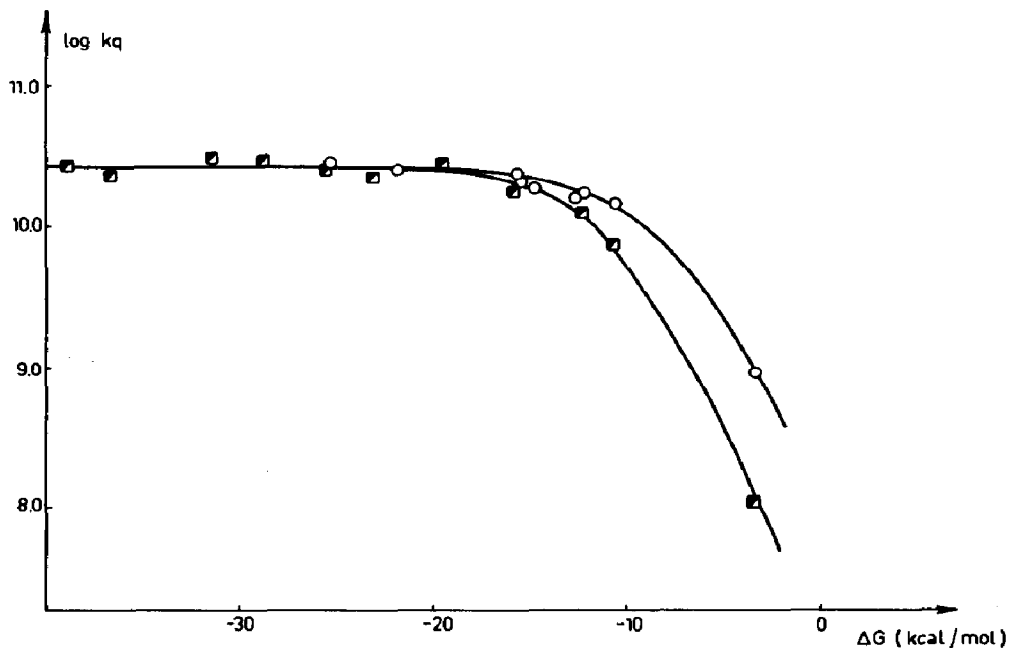

Fig. 2. Plot of k_q vs. ΔG for fluorescence quenching of 1 in CH$_2$Cl$_2$ (■) and 2 in CH$_3$CN (○) (see Table 1).

electron donors (Fig. 3). For a given acceptor, the energy of the CT complex is directly related to the ionization potential of the donor, or to the energy of its highest occupied molecular orbital. This can also be expressed in terms of the oxidation half-wave potential E_{ox}^{D} of the donor. The variation in the energy E_{CT} of the CT band with E_{ox}^{D} is given in Table 2 for compounds 4 and 5.
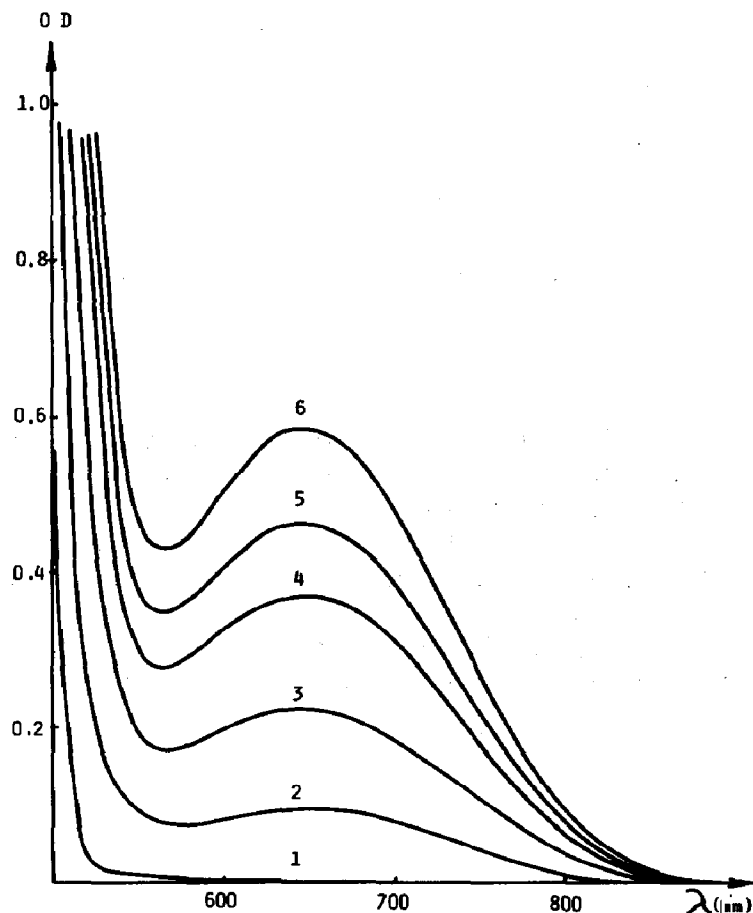

Fig. 3. Change in the absorbance of the CT band of 4 (concentration, 1.3×10^{-3} M) with increasing concentration of pyrene (OD, optical density): curve 1, 0.00 M; curve 2, 0.014 M; curve 3, 0.034 M; curve 4, 0.063 M; curve 5, 0.083 M; curve 6, 0.125 M.

When E_{CT} is plotted against E_{ox}^{D} of the donor, the points corresponding to perylene and 9-methylanthracene do not lie on the straight line which passes through the four other points. An analogous observation was made some time ago with the triphenyl-, tetraphenyl- and pentaphenyl-substituted pyrylium cations [21], when attempts were made to correlate the maxima of the first CT bands with the lowest unoccupied molecular orbital energies of the acceptors; a possible overlap of the longer wavelength absorption of these salts with the CT bands as well as non-coplanarity of the substituents was suggested to explain this divergence. Another explanation could be the

TABLE 2

Position of the maximum of the charge transfer absorption band given by **4** and **5** with various donors (in CH_2Cl_2 solution)

Donor	E_{ox}^{D} [a] (V)	Data for compound 4		Data for compound 5	
		λ_{CT} (nm)	E_{CT} (eV)	λ_{CT} (nm)	E_{CT} (eV)
Pyrene	1.2	646	1.92	530	2.34
Anthracene	1.09	656	1.89	538	2.30
9-methylanthracene	0.96	708	1.75	[b]	[b]
Perylene	0.85	814	1.52	638	1.94
Phenothiazine	0.53	685	1.81	676	1.83
N,N-diphenyl-p-phenylenediamine	0.35	712	1.74	694	1.79

[a] The half-wave oxidation potentials in CH_3CN solutions were measured with respect to an SCE (taken from ref. 20).
[b] Not investigated.

inhomogeneous structure of the electron donors used, although such an argument can hardly explain the difference in behaviour between anthracene and 9-methylanthracene towards the pyrylium salt **4**.

A more homogeneous experiment would be to use the same electron donor with a series of pyrylium salts. This has been investigated with anthracene and the series of compounds 1 - 7. In the present case, a much better linear correlation is obtained (Fig. 4) when the energy of the maximum of the CT band is plotted against the reduction potential of the
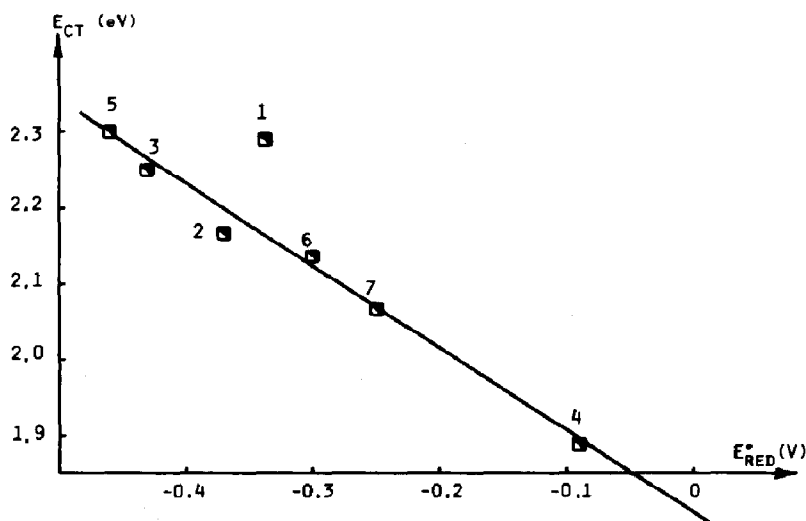

Fig. 4. Variation in the energy of the CT band with the reduction potential of pyrylium salts 1 - 7 (see Table 3).

pyrylium salts. The reduction potentials were measured by means of cyclic voltammetry (Table 3); this technique also shows that the reduction is a one-electron process.

The extinction coefficient of the complex and its association constant can be determined from the optical densities OD of the product of the interaction, as long as the reactants do not absorb at the same wavelength as the products. The formation of a ground state complex AD_n between a donor D and an acceptor A involving an equilibrium of the type

$$A + nD \rightleftharpoons AD_n$$
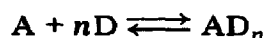
can be solved easily by using the general expression of Benesi and Hildebrand [22]:

$$Ka\epsilon - KOD = \frac{OD}{d^n}$$

where K $(= [AD_n]/[A][D]^n)$ is the association constant, a and d are the concentrations of A and D respectively, OD is the optical density of the solution at a wavelength at which the absorption of A and D are negligible and ϵ is the extinction coefficient of the complex at that wavelength.

The relation of Benesi and Hildebrand is obtained from the fact that OD/ϵ is the concentration of the complex for an optical cell 1 cm in length. When $n = 1$, the plot of OD/d versus OD is found to be linear; this indicates that the complex is a one-to-one complex. The slope is then equal to $-K$ and the intercept with the x axis is equal to $a\epsilon$. To obtain the molar extinction coefficient of the complex, OD has to be measured at the absorption maximum.

This was carried out for compound 4 with anthracene and pyrene (Fig. 5), and the following values were obtained: for compound 4 with anthracene, $K = 2$ l mol^{-1} and $\epsilon = 2050$ M^{-1} cm^{-1}; for compound 4 with pyrene, $K = 4$ l mol^{-1} and $\epsilon = 1350$ M^{-1} cm^{-1}.

TABLE 3

Position of the maximum of the charge transfer absorption band formed by pyrylium salts 1 - 7 with anthracene ($E_{ox}^D = 1.09$ eV) in CH_2Cl_2 solution

Compound	E_{red}^{A} [a] (V)	λ_{CT} (nm)	λ_{CT} (eV)
1	−0.34	540	2.30
2	−0.37	570	2.17
3	−0.43	550	2.25
4	−0.09	656	1.89
5	−0.46	540	2.30
6	−0.30	580	2.14
7	−0.25	600	2.07

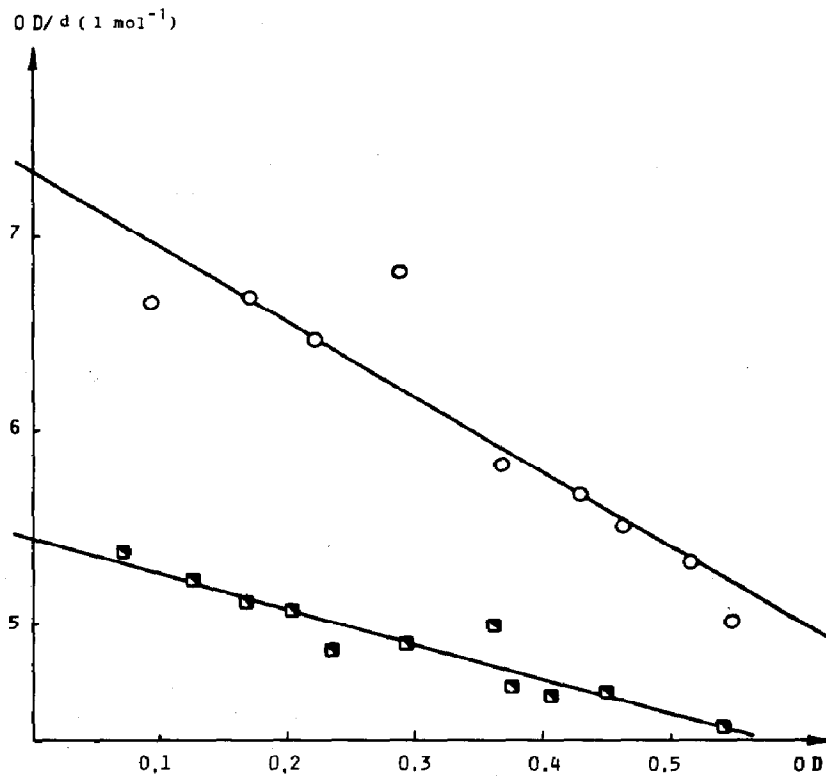[a] The reduction potentials of acceptors 1 - 7 were measured by means of cyclic voltammetry.

Fig. 5. Plot of OD/*d* *vs.* OD, where OD is the optical density at the maximum absorption of the CT complex, for product 4 in the presence of anthracene (○) and pyrene (◙).

3. Experimental section

3.1. Spectra

The absorption spectra were obtained on a Varian Cary model 219 UV–visible spectrophotometer.

The fluorescence spectra were recorded on a Perkin–Elmer MPF-44B spectrofluorometer equipped with a DCS 2U correction unit or on an Aminco SPF-500 correcting spectrofluorometer.

3.2. Materials

CH_3CN and CH_2Cl_2 were spectrograde (Merck; Uvasol) and used as received. The chemicals were generally of the highest purity available and were used as received, except for the liquids which were redistilled. The pyrylium salts were prepared as already described in ref. 23 for compound 1, ref. 24 for compounds 2, 3, 6 and 7, ref. 25 for compound 4 and ref. 26 for compound 5, and were purified by repeated crystallizations from glacial acetic acid.

3.3. Lifetimes

The fluorescence lifetimes were determined by single-photon counting (Ortec electronics and Intertechnique multichannel analyser) as described by Ware and coworkers [27].

3.4. Redox potentials

The redox potentials were obtained by means of cyclic voltammetry using a PAR model 173 potentiostat monitored with a PAR model 175 programmer coupled to a TGM x–y Sefram recorder. The electrochemical measurements were performed in CH_2Cl_2 or CH_3CN solvent using 0.1 M tetraethylammonium perchlorate as the supporting electrolyte. The reference electrode was a calomel electrode saturated with KCl and separated from the main solution by a bridge consisting of a glass tube closed by a glass frit of medium porosity and containing the supporting electrolyte. The working electrode was a platinum gauze and the counterelectrode was a platinum surface 1 cm × 1 cm.

3.5. Fluorescence quenching procedure

The electron donor of known concentration in CH_2Cl_2 or CH_3CN solution was added through a 10 μl syringe to a 3 ml solution of the pyrylium salt (the optical densities were adjusted to the range 0.05 - 0.1 at the absorption maximum).

The relative emission intensities were recorded at the wavelength of the maximum emission and the data were treated using the Stern–Volmer equation [16].

3.6. Ground state charge transfer complex formation

The pyrylium salt was dissolved in CH_2Cl_2 to a concentration of about 10^{-3} M. The absorption spectrum was recorded (with saturation at the long wavelength absorption band). The electron donor was added to the solution in such a way that its concentration increased by 5×10^{-3} M between two recordings of the spectra. The new band was observed at longer wavelengths and the optical density was measured at the absorption maximum.

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