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Unique solvent properties of straight-chain carboxylic acids for electron-transfer photoreactions

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Abstract

We have studied the electron-transfer fluorescence quenching of pyrene by diphenyliodonium cation in a series of straight-chain carboxylic acid solvents. Use of the Py-scale of solvent polarity suggests specific solvation of the pyrene by the polar head groups of the acid solvents. We hypothesize involvement of hydrogen bonding between the carboxyl functions and the π-electron cloud of pyrene. Electron-transfer quenching of pyrene fluorescence by diphenyliodonium cation is, surprisingly, not diffusion controlled. From experimental data we have estimated values for the bimolecular reaction rate constant, k_r, in each solvent over the temperature range 20–60°C, and calculated, therefrom, reorganization energies. We find that λ is more-or-less independent of acid chain length. We, therefore, infer that the head groups or the carboxylic acids are principally involved in solvent relaxation, and propose that a relaxation mechanism involving rupture (or formation) of hydrogen bonds is most likely. ©2000 Elsevier Science S.A. All rights reserved.

Keywords: Py-scale; Straight-chain carboxylic acid; Electron-transfer

1. Introduction

The properties of straight-chain carboxylic acids as reactions solvents have been little explored. Their macroscopic physical properties are, however, well-known [1–3], although most of the interest in their characterization has not been recent. In the present study we examine the behavior of a series of straight chain acids, $CH_3(CH_2)_mCO_2H$ where $0 < m < 8$, with respect to a model photoinduced electron-transfer reaction, namely electron-transfer quenching of pyrene fluorescence by diphenyliodonium cation.

$$Py^* + Ph_2I^+ \rightarrow Py^{\bullet +} + Ph_2I^\bullet \tag{1}$$

This reaction system has been the subject of an ongoing series of studies in our laboratory [4]. In solution we have found that the rate of this highly exergonic process is usually diffusion limited, and that the kinetics are not complicated by significant back electron-transfer. The choice of pyrene as a reporter fluorophore also enables characterization of the microscopic solvation environment, using the so-called Py scale [5,6].

The reaction described by Eq. (1), with pyrene or other aromatic hydrocarbon sensitizer, is often used as the basis for radiation curing technologies [4]. In this instance, the reaction occurs in media comprising mixtures of monomers, often including acrylic acid and its derivatives. Understanding the effect of protic acid reaction media on the dynamics of Eq. (1) is thus also of technological interest.

2. Experimental details

2.1. Materials

Carboxylic acids (Aldrich Chemical, best available grade) were all glass distilled, where necessary from potassium permanganate [3], in order to remove fluorescence quenching impurities. Our samples of hexanoic acid ($m = 4$) and nonanoic acid ($m = 7$) could not be rendered demonstrably free of such impurities by this procedure; hence no data obtained in these solvents are included in the present report. Pyrene (Aldrich Chemical, 99+%) and diphenyliodonium hexafluorophosphate (Avocado Chemicals, Ltd.) were used as received.

2.2. Methods

Fluorescence emission and excitation spectra were recorded on a Perkin–Elmer MPF44B spectrofluorimeter

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using 2.5 nm slits. In a typical fluorescence quenching experiment, pyrene was dissolved 2.5×10^{-3} M in spectrograde toluene; an aliquot of this solution was diluted 1 : 1000 with the desired acid. Diphenyliodonium hexafluorophosphate was dissolved 0.10 M in spectrograde acetonitrile; this solution was then diluted 1 : 10 with the appropriate carboxylic acid. Two aliquots (2.5 ml) of the organic acid solution of pyrene, representing test solution and control, were placed in 1 cm quartz cuvettes in the cavity of the spectrofluorimeter, which was thermostated to ±0.1°C, and allowed to come to thermal equilibrium. Fluorescence, excited at 365 nm, was monitored at 400 nm. Aliquots (50 μl) of the quencher solution and of the organic acid solvent system (without the diphenyliodonium salt) were then added alternately to the appropriate cuvettes, and changes in fluorescence intensity, I and I_o, respectively, were monitored. (Use of a separate control solution to which only solvent was added obviated complications of non-linear dilution effects on fluorescence intensity). Up to 10 incremental additions were performed, and values of I_o/I, estimated after each pair of additions, were used to construct a Stern–Volmer plot of the fluorescence quenching data.

Fluorescence intensity signals, obtained under controlled conditions, were of comparable amplitude in all solvents studied. This observations provided additional support for the assumptions underlying data analysis, namely that the fluorescence lifetime, τ, of pyrene was solvent independent, and that the solvents, themselves, were free of quenching impurities.

3. Results and discussion

3.1. Solvent polarity estimation

The ratio of the intensities of the first, I_1 (372 nm), and third, I_3 (383 nm), peaks in the vibronic progression of fluorescence bands of pyrene recorded in the pyrene emission spectrum excited at 365 nm provides the basis of the Py-scale of solvent polarity [4,5]

$$\mathrm{Py} = \frac{I_1}{I_3} \qquad (2)$$

These data are shown in Fig. 1 as a function of (1/m). Our Py values for propanoic and butyric acids are slightly lower than those reported by Dong and Winnick [5]. This difference may be attributed in part to the different slit widths used by ourselves and by the previous authors. In our experience, the absolute value of Py can be very sensitive to the experimental configuration. Extrapolation to infinite m yields an intercept value of Py = (0.93 ± 0.02). A priori we might expect this limiting value to correspond to Py obtained in aliphatic hydrocarbon media, ca. 0.58, as reported by Dong and Winnick [5]. Under our conditions, a Py value of 0.67 was obtained for n-heptane. The significantly more positive extrapolated value, corresponding to a more polar environment, suggests selective solvation of the pyrene probe by the polar carboxylic acid head groups.

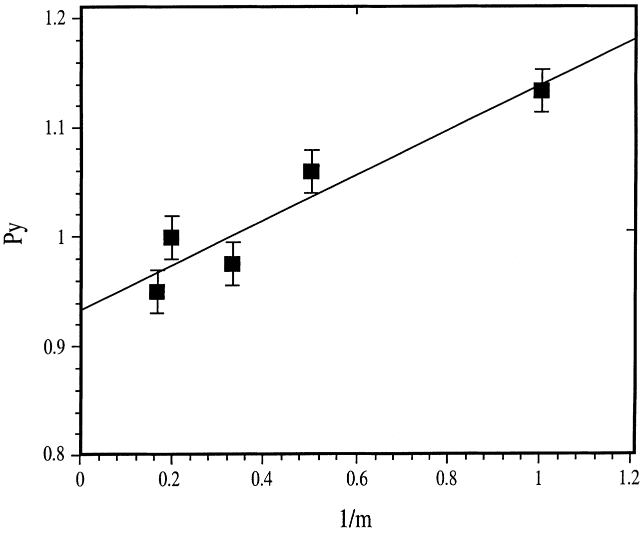

Fig. 1. Plot of Py-values of effective solvent polarity vs. reciprocal of m, the number of methylene groups in the straight-chain carboxylic acid solvents.

Hydrogen bonding to the aromatic π-cloud of the pyrene may be involved [7], although Dong and Winnick [5] claim that pyrene is not a hydrogen bond donor. Other authors [8] have expressed the position that the primary solvent–solute interaction should be the van der Waals interaction between the highly polarizable π-electron system of the aromatic hydrocarbon and the aliphatic residues of the solvent molecules. The inference of Bohon and Claussen [7], however, has been supported by recent gas-phase studies [9] of benzene-acetic acid clusters.

3.2. Fluorescence quenching experiments

Fluorescence quenching of pyrene by the diphenyliodonium cation was analyzed according to the usual Stern–Volmer relationship

$$\frac{I}{I_o} = 1 + K_{SV}[\mathrm{Q}] \qquad (3)$$

where $K_{SV} = k_{obs}\tau$ and τ is the emissive lifetime of pyrene, taken to be 114 ns [10]. We estimate that values of k_{obs} obtained in this manner are good to ±10%. A representative Stern–Volmer plot of data according to Eq. (2) is shown in Fig. 2.

Insofar as we expected the reaction to be diffusion controlled, we expected $k_{obs} = k_d$, estimated according to the Einstein–Smoluchowski relationship [11] which, in turn, reflects the macroscopic viscosity, η, of the carboxylic acid solvent. Estimates of η for organic acid solvents can be obtained from the empirical Andrade equation [2].

$$\eta = \exp\left\{\left[\frac{E(m)}{k_b T}\right] - 5.57\right\} \qquad (4)$$

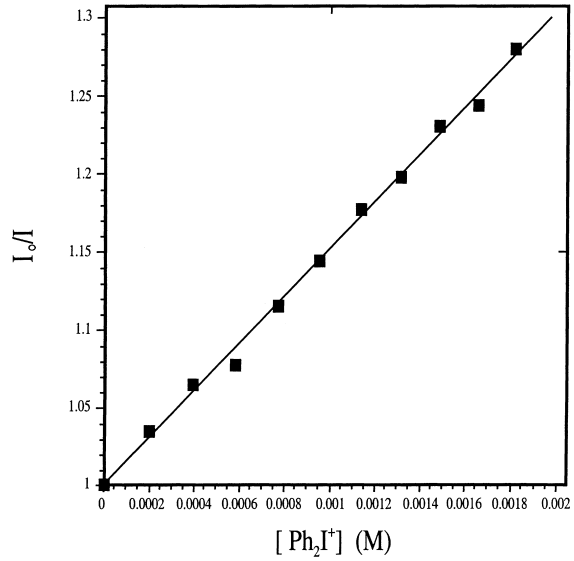

Fig. 2. Representative Stern–Volmer plot for quenching of pyrene fluorescence by diphenyliodonium cation in propanoic acid at 20°C.

where $E(m) = 0.16 + 0.0042(m + 2)$ eV. Experimental values of k_{obs} and estimates of k_d are given in Table 1. It is clear that in the carboxylic acid solvents the expectation that $k_{obs} = k_d$ is not realized.

Instead we analyze the data as follows [11]. Let

$$k_{obs} = (k_r^{-1} + k_d^{-1})^{-1} \tag{5}$$

where k_r is the bimolecular rate constant for the reaction described by Eq. (1). Estimates of k_r derived from the data of Table 1 are given in Table 2. As in the case of k_{obs} from which these data derive, their precision is expected to be +10%.

Table 1

Experimental rate constants for electron transfer quenching of pyrene fluorescence in carboxylic acid solvents, k_{obs} ($\times 10^{-9}$, $M^{-1}\,s^{-1}$), and estimates of diffusion controlled rate constants, k_d ($\times 10^{-9}$, $M^{-1}\,s^{-1}$)

m	k_{obs} at temperatures				
	20°C	30°C	40°C	50°C	60°C
0	0.9	0.9	0.8	1.1	–
1	1.3	1.6	1.8	1.6	–
2	1.0	1.2	1.2	1.6	1.3
3	1.0	1.1	1.4	1.6	1.5
5	0.7	1.4	1.5	1.8	1.6
6	1.1	1.2	1.4	1.6	1.6
8	–[a]	–[a]	1.7	2.0	2.2
	k_d at temperatures				
	20°C	30°C	40°C	50°C	60°C
0	8.2	10.6	14.6	15.8	19.5
1	5.0	6.5	8.3	10.5	12.6
2	4.2	5.5	7.0	9.0	11.0
3	3.6	4.7	6.0	7.8	9.5
5	2.6	3.5	4.5	5.8	7.2
6	2.1	2.9	3.8	4.9	6.2
8	–[a]	–[a]	2.8	3.7	4.6

[a] Decanoic acid is solid at this temperature.

The k_r data exhibit only a small temperature dependence, within the range of experimental uncertainty, but show a generally upward trend with carboxylic acid chain length.

According to the Marcus model of electron-transfer reactions [12], k_r is defined by a free energy of activation, ΔG^*, where $k_r = k_o \exp(-\Delta G^*/k_b T)$ and k_o is a frequency factor. The frequency factor may reflect the longitudinal relaxation time of the solvent [13,14], which, in turn, tends to reflect its macroscopic viscosity. Accordingly we should expect decreasing k_r with increasing m, when, in fact, we observe the opposite. The free energy of activation for an electron-transfer reaction is given by [12]

$$\Delta G^* = \left(\frac{\lambda}{4}\right)\left(1 + \frac{\Delta G}{\lambda}\right)^2 \tag{6}$$

where the free energy change in the reaction, ΔG, can be obtained from the Weller equation [15]

$$\Delta G = -E(0,0) - E_{red}(A) + E_{ox}(D) \tag{7}$$

where, for pyrene $E(0,0) = 3.12$ eV and $E_{ox}(D) = +1.06$ V (*vs.* SCE) [16], and for diphenyliodonium cation in solution, E_{red} (A) = −0.6 V (*vs.* SCE) [3]. Thus $\Delta G = -1.46$ eV for the reaction of Eq. (1). Using a value of $10^{12}\,s^{-1}$ for k_o [17,18], temperature-averaged values for k_r as a function of m, and Eq. (6), we can estimate λ for each of the carboxylic acid solvents, as given in Table 3. For the estimated level of experimental uncertainty in k_r, we expect the precision in the λ values given in Table 3 to be +0.01 eV. We find that increasing k_r with increasing m is reflected in increasing estimates of λ, insofar as the photoreaction occurs in the Marcus inverted regime.

Values of the solvation shell's contribution to reorganization energy are often estimated by the dielectric continuum approximation [12,18], whereby

$$\lambda = e^2[(2r_D)^{-1} + (2R_A)^{-1} + (r_{DA})^{-1}](n^{-2} - \varepsilon^{-1}) \tag{8}$$

Using literature values for the dielectric constants, ε, and indices of refraction, n, for the carboxylic acids [19], and assuming $2r_D = 2r_A = r_{DA} = 8$ Å, we obtain the dielectric continuum approximations for λ, as also given in Table 3. These values decrease monotonically with m. Only for the case of acetic acid, $m = 0$, is there reasonable agreement between calculated and experimental values of λ. Disagreement in the other cases is, however, unsurprising. It is now generally accepted that for hydrogen bonding solvents use of the dielectric continuum approximation can be problematical ([20] references cited therein) [21]. Further consideration of the derivation of this approximation, which ignores the possibility that solvent relaxation may be activated, suggests that it ought to be inapplicable to any system involving 'strong' solvents, according to Kivelson's classification [22].

The small degree of variation in the experimentally based estimates of λ with carbon acid chain length, suggests that the same relaxation mechanism is coupled to the

Table 2
Bimolecular rate constants, k_r ($\times 10^{-9}$, $M^{-1}\,s^{-1}$), for pyrene fluorescence quenching from Eq. (5) and data of Table 1

m	k_r at temperatures					
	20°C	30°C	40°C	50°C	60°C	Avg.
0	1.0	1.0	0.8	1.2	–	(1.00 ± 0.14)
1	1.8	2.2	2.3	1.9	–	(2.05 ± 0.20)
2	1.4	1.5	1.5	1.9	1.5	(1.56 ± 0.17)
3	1.5	1.4	1.9	2.0	1.7	(1.70 ± 0.23)
5	0.9	2.4	2.3	2.6	2.1	(2.06 ± 0.60)
6	2.4	2.1	2.2	2.3	2.2	(2.24 ± 0.10)
8	–	–	4.1	4.2	4.0	(4.10 ± 0.08)
Avg.[a]	(1.50 ± 0.50)	(1.76 ± 0.50)	(1.83 ± 0.54)	(1.98 ± 0.43)	(1.88 ± 0.28)	–

[a] Excluding data for decanoic acid.

Table 3
Estimated reorganization energy parameters for various carboxylic acid solvents

m	λ^a (eV)	λ^b (eV)
0	(0.74 ± 0.01)	0.69
1	0.76	0.43
2	0.75	0.33
3	0.76	0.24
5	0.77	0.13
6	0.77	0.09
8	0.80	0.09
Avg.	(0.76 ± 0.02)	–

[a] From experimental k_r and Eq. (6).
[b] From Eq. (8).

electron-transfer event in all the solvents studied. We inferred, above, that solvation of pyrene in these solvents may involve hydrogen bonding between the carboxyl functional group and the aromatic π-electron cloud of the pyrene. It is, therefore, reasonable to view the relaxation process in these solvents as involving the breaking (or forming) of hydrogen bonds, either between solvent and pyrene, or among molecules in the solvent cage. Somewhat analogously, relaxation of photoexcited perylene in *n*-alcohol solutions has been shown to be coupled to reorganization of the hydrogen bonded solvent network around the fluorophore [8]. Similarly, Germanenko and El-Shall [9] infered a structural change from π-hydrogen bonding to ion–dipole interaction in the gas phase benzene–acetic acid complex on photoionization. For purposes of comparison, we note that the enthalpy of formation of hydrogen bonds in acetic acid dimer is 0.33 eV [23].

4. Conclusions

We have studied the electron-transfer fluorescence quenching of pyrene by diphenyliodonium cation in a series of straight-chain carboxylic acid solvents. Use of the Py-scale of solvent polarity suggests specific solvation of the pyrene by the polar head groups of the acid solvents. We hypothesize involvement of hydrogen bonding between the carboxyl functions and the π-electron cloud of pyrene. The electron-transfer quenching reaction is, surprisingly, not diffusion controlled. We have estimated values for the bimolecular reaction rate constant, k_r, in each solvent over the temperature range 20–60°C, and calculated, therefrom, reorganization energies. We find that λ is more-or-less independent of acid chain length. We, therefore, infer that the head groups of the carboxylic acids are principally involved in solvent relaxation, and propose that a relaxation mechanism involving rupture (or formation) of hydrogen bonds is most likely.

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