Electron Transfer Reactions in Ternary Systems on Silica Gel Surfaces: Evidence for Radical Cation Diffusion

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Electron transfer reactions have been studied between 9-anthracenecarboxylic acid co-adsorbed with perylene on silica gel surfaces employing azulene as a molecular shuttle in order to facilitate hole transfer. In this paper we present for the first time a ternary system that unambiguously demonstrates an appreciable mobility of radical cations on the silica gel surface. Rates of 10 hole transfer from the 9-anthracenecarboxylic acid radical cation to perylene via azulene have been studied using diffuse reflectance laser flash photolysis spectroscopy. Azulene has been shown to enhance the rate of electron transfer in the ternary system, demonstrating significant mobility of the azulene and its radical cation species on silica gel surfaces. The data shows that the azulene radical cation can diffuse at an appreciable rate on the silica gel surface.

Introduction

15 The photochemistry and photophysics of molecules adsorbed to oxide surfaces and contained within zeolites has been the subject of a number of studies[1-42]. The rapid mobility of molecules on oxide surfaces has been previously reported[2,6-11] 20 and studied through both energy and electron transfer reactions. The latter have also been studied on other porous materials such as clays[2,43-46]. Silica gel, which was employed in this study, is widely used in industry as a catalytic support and a greater understanding of reaction kinetics on these 25 materials is significant in optimising these applications.

Multi-photon ionisation of arenes and the subsequent electron transfer reactions of their radical cations on silica gel have been previously reported[3,4,13,14] and the influence of the nature and loading of the electron donor and electron acceptor 30 compounds on the reaction rate investigated. The kinetics of decay of radical ions on silica gel is not straightforward since the surface is heterogeneous in nature and rates rarely conform to simple exponential kinetics. We have used the model described by Albery *et al*[4,12-15,50] to characterise our 35 data sets, ensuring a comprehensive exploration of the parameter space in order to obtain a global optimum value for the rate constants[13,14].

We have previously shown that energy and electron transfer reactions in these systems are dependent upon the rate of 40 diffusion[13,14], and in the case of azulene as energy acceptor / electron donor, rates of reaction are largely determined by the rate of diffusion of this relatively more mobile species. We have demonstrated also that energetics play a role in determining electron transfer rates, and have shown a Marcus-45 type dependence of rate on the free energy for electron transfer[4,14]. In this study we also found evidence for some steric influence on reaction rates.

In previous work we studied the activation energy of back electron transfer of some derivatised anthracenes[12,15]. There 50 was a correlation between the activation energy and the size of the radical cation which suggested that movement of the radical cation and not of the electron dominated the observed kinetics. In this paper we present for the first time a ternary system that unambiguously demonstrates the mobility of 55 radical cations on the silica gel surface.

Experimental

Samples were prepared as follows: Silica gel (Davisil grade 635, 60-100 mesh, 6 nm pore size, surface area 480 m^2 g^{-1}; Aldrich Chemical Co.) was dried at a temperature of 125 $^\circ$C 60 under a vacuum of 5 x 10^{-5} mbar for 8 hours, and the vessel re-pressurised with dry nitrogen. 9-anthracenecarboxylic acid (minimum 99%, Aldrich Chemical Co.), azulene (99%, Aldrich Chemical Co.) and perylene (99%, Aldrich Chemical Co.) were dissolved in acetonitrile (spectrophotometric grade, 65 Aldrich Chemical Co.) and a known weight of the resulting solution added to the dried silica gel. The mixture was allowed to equilibrate for a period of one hour, with periodic agitation. The solvent was then removed under vacuum to a pressure of 5 x 10^{-5} mbar. The resulting sample was then 70 sealed under vacuum into a cylindrical glass cuvette (22 mm diameter x 10 mm path length). Sample loadings were determined from the mass of solution added to the silica gel. The loadings were varied between 0.1 µmol g^{-1} and 2.5 µmol g^{-1} for all three components. These concentrations correspond 75 to low surface coverages, with the highest being less than 0.1% of a homogenous 2D surface monolayer.

Ground state diffuse reflectance spectra were recorded using a Perkin-Elmer Lambda Bio 40 spectrophotometer equipped with a Spectralon integrating sphere using barium 80 sulphate as a reference.

The nanosecond diffuse reflectance laser flash photolysis apparatus has been described previously in references 16 and 27. In the flash photolysis experiments, excitation of the samples was with the third (355 nm, 110 mJ/pulse) harmonic 85 of a Surelite I Nd:YAG laser (Continuum). The pulse energy was attenuated using solutions of sodium nitrite in water, to ensure that transient reflectance changes were kept below 10%, where the change in reflectance is directly proportional to the concentration of transient species[47-49]. Diffusely 90 reflected analysing light from a 275 W xenon arc lamp (Oriel) was collected and focussed onto the entrance slit of an *f*/3.4

grating monochromator (Applied Photophysics) and detected with a side-on photomultiplier tube (Hamamatsu R928). Signal capture was by an LT364 Waverunner digitising oscilloscope (LeCroy), interfaced to an IBM-compatible PC.

Transient decay data has been analysed using a model which assumes a log Gaussian distribution of rate constants described previously[13,14,50] according to equation 1

$$\frac{C}{C_0} = \frac{\int_{-\infty}^{\infty} \exp\left(-t^2\right) \exp\left[-\bar{k}\, t \exp\left(\gamma t\right)\right] dt}{\int_{-\infty}^{\infty} \exp\left(-t^2\right) dt} \qquad (1)$$

which was transformed to have finite integrals as described in the appendix of reference[50]. Here C and C_0 are transient concentrations at times t = t and t = 0 after the laser pulse, γ is the width of the distribution and $\bar{k}$ is the mean rate constant. At low sample loadings and small reflectance changes (less than 10%), C and C_0 can be replaced by ΔR and ΔR_0, the reflectance changes at times t = t and t = 0 (relative to the laser pulse) respectively.

Results and Discussion

Transient absorption spectra

Transient absorption spectra were obtained using 355 nm laser excitation of the respective samples. Fig. 1 shows the transient difference spectrum obtained from photolysis of 9-anthracenecarboxylic acid co-adsorbed with perylene on silica gel following laser excitation at 355nm. Anthracene triplet (420nm) and radical cation (400 nm and 710 nm) absorption bands were assigned based upon previous measurements[3,4,13,14].
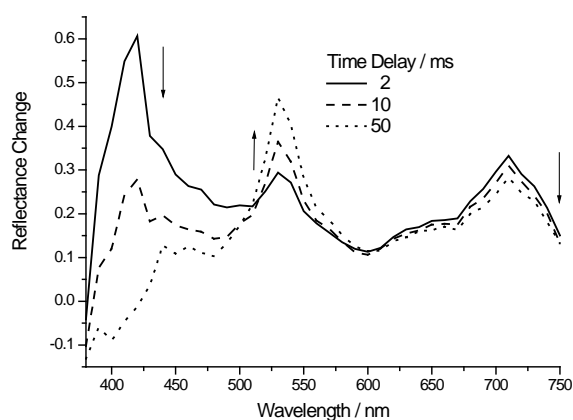

Fig. 1 Transient difference spectra of 9-anthracenecarboxylic acid (2.5 μmol g⁻¹) co-adsorbed with perylene (0.25 μmol g⁻¹) on silica gel at 2 ms (solid line), 10 ms (dashed line) and 50 ms (dotted line) following laser excitation at 355 nm.

The perylene radical cation (530 nm) absorption band was assigned by comparison to literature data of measurements

carried out on surfaces and in solution[51-54] The 9-anthracenecarboxylic acid triplet (420 nm) decays quite rapidly by both unimolecular decay and by energy transfer to perylene.

Note that in this study 9-carboxylic acid anthracene is used since it has been demonstrated to be immobile on the silica gel surface[13] as evidenced by the lack of delayed fluorescence following laser excitation. Hence any dynamic quenching observed is the result of the diffusional characteristics of the co-adsorbed species. The perylene radical cation (530 nm) appears concomitantly with the anthracene radical cation (710 nm) decay. Kinetic analysis of these species shows that, as expected, the rate of appearance of the perylene radical cation and dissappearance of the anthracene radical cation are the same to within experimental error (see Table 1).

Co-adsorption of azulene into the 9-anthracenecarboxylic acid / perylene system changes the observed electron transfer kinetics (*vide infra*) but does not affect the appearance of the transient difference spectra owing to both the azulene triplet and radical cation absorptions being outside the spectral range studied.

Electron Transfer Kinetics

The kinetics of electron transfer for 9-anthracenecarboxylic acid / perylene systems in both the presence and absence of varying loadings of azulene on silica gel have been measured following laser excitation at 355 nm. The kinetic data was analysed as in previous publications[13,14] using the dispersive kinetic model of Albery et al[50] which provides analytical parameters with which to characterise the decay or (in the case of perylene) rise rate constant as a function of concentration.

The extracted parameters are then analysed to yield a bimolecular rate constant characteristic of the process according to equation 2:

$$\bar{k} = \bar{k}_0 + k_q\,[quencher] \qquad (2)$$

where $\bar{k}_0$ is the unquenched decay rate constant, and k_q is the bimolecular quenching constant. Fig. 2 shows a plot of fitted $\bar{k}$ versus quencher concentration for electron transfer in the 9-anthracenecarboxylic acid / azulene / perylene system. The addition of azulene to the system decouples the decay of the anthracene radical cation and the rise of the perylene radical cation. The rate of electron transfer from the azulene to the 9-anthracene carboxylic acid radical is very rapid due to the large diffusion coefficient for the azulene on silica gel. As we have shown in a previous publication[14], molecular size plays a role in determining diffusion coefficients on silica gel, and hence the rate of diffusion of the azulene is significantly faster than that of the perylene. Given the 9-anthracenecarboxylic acid is, as previously demonstrated, hydrogen bonded and therefore fixed to the silica gel surface, the rate of electron transfer is governed in part by how quickly the azulene diffuses across the silica gel surface, and as shown previously[14] there are also energetic considerations (*vide infra*).

In the absence of azulene the bimolecular rate constant for both perylene radical cation formation and 9-anthracenecarboxylic acid radical cation decay are the same to within experimental error, and the electron transfer rate in this
5 case is governed by the rate of diffusion of the perylene. The introduction of azulene to the system causes the bimolecular rate constants for both the formation of perylene radical cation and the decay of the anthracene radical cation species to increase, but not to the same extent as would be the case if the
10 mobility of the azulene radical were the same as for free azulene and this alone was the determining factor in the
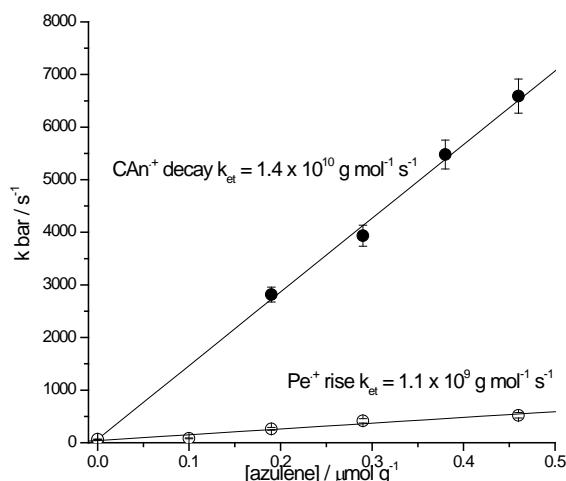

Fig. 2 Electron transfer plots for azulene to 9-anthracenecarboxylic acid (CAn) radical cation (●) and perylene (Pe) to azulene radical
15 cation (○) following laser excitation at 355 nm as a function of azulene concentration.

electron transfer rate. However, were the azulene radical to be immobile on the surface there may be expected to be no
20 enhancement to the perylene rise kinetics on addition of azulene based on purely diffusional arguments. As previously mentioned, energetic factors have been shown to influence electron transfer rates and a Marcus dependence was shown for a range of electron donors[4,14]. In this instance the
25 oxidation potential of the perylene (0.92 V vs Ag/AgCl [55], relative to 1.26 V for anthracene and 1.04 V for azulene versus the same reference electrode[14]) is such that the free energy for electron transfer between the azulene radical cation and perylene is lower than that between the anthracene radical
30 cation and perylene, which would suggest that on energetic grounds electron transfer between the former two should be slower than between the latter (see figure 8 in reference 14).

Additionally the similarity in free energy for electron transfer in the 9-anthracenecarboxylic acid / azulene and 9-
35 anthracenecarboxylic acid / perylene couples shows that the slow rate of electron transfer in the anthracene / perylene system is a result of slow diffusion by the perylene rather than being dominated by energetic considerations. Therefore the observed *increased* rate of electron transfer to perylene
40 observed in the presence of azulene must be ascribable to

considerable mobility of the azulene radical cation, where diffusion of the azulene radical to the perylene is faster than diffusion of the perylene to the azulene radical. Even allowing for energetic effects, however, the rate of diffusion of the
45 azulene radical is less than that of the free azulene, since an order of magnitude reduction in the electron transfer rate would not be expected on energetic grounds alone. However, it clearly has a larger diffusion coefficient than perylene demonstrating the complex interaction of parameters which
50 determine difusion rates on silica gel. A summary of the measured bimolecular rate constants are given in Table 1.

The table shows that the introduction of azulene in the perylene / 9-anthracenecarboxylic acid system greatly increases the rates of electron transfer in this ternary system,
55 demonstrating the effectiveness of a small molecule as a shuttle of, in this instance, a hole between two relatively immobile species seperated by a relatively large distance. This constitutes to our knowledge the first unambiguous demonstration of the mobility of radical cations on the silica
60 gel surface, and also the first demonstration of a molecular shuttle of this type in an amorphous system.

Table 1 Bimolecular rate constants for electron transfer between azulene (Az) and the 9-anthracenecarboxylic acid (An-9-CA) radical
65 cation and perylene (Pe) and the azulene radical cation, where x denotes the fact that the concentration of that species is changing.

System	k_{et} / g mol^{-1} s^{-1}	
	Perylene$^{•+}$ rise 530 nm	Anthracene$^{•+}$ decay 710 nm
1 An-9-CA : x Pe	$8.3 \pm 0.8 \times 10^7$	$6.5 \pm 0.8 \times 10^7$
1 An-9-CA : x Az : 1 Pe	$1.1 \pm 0.2 \times 10^9$	$1.4 \pm 0.3 \times 10^{10}$

Conclusions

We have demonstrated electron transfer in this ternary system
70 using azulene for hole transfer between 9-anthracenecarboxylic acid radical cation as an electron acceptor and perylene as an electron donor. The radical cation species of both perylene and 9-anthracenecarboxylic acid can be seen in the transient absorption spectra. The absorption
75 bands are well separated from one another as well as that of the triplet excited states of the parent species and hence their kinetics can be independently measured.

The presence of an azulene molecular hole shuttle has been shown to substantially enhance the rate of electron transfer.
80 From comparison of bimolecular rate constants and consideration of possible energetic influences, mobility of the azulene radical cation is clearly demonstrated, with its rate of diffusion being still rapid relative to perylene even though it is shown to be slower than for the neutral azulene species.
85 This study shows the potential of such shuttles as electron transfer catalysts and offers a means of controlling charge separation times in these systems.

Notes and references

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