

Photophysical Behavior of Diphenylpolyenes Adsorbed on Alumina by Diffuse Reflectance Laser Flash Photolysis

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Substantial transient absorptions have been detected following nanosecond laser excitation at 354 nm of diphenylpolyenes physisorbed and chemisorbed at low coverages (less than 1% of a monolayer) on high surface area γ -alumina and other metal oxide powders. For diphenylhexatriene (DPH) physisorbed on alumina, silica, and thoria, a short-lived transient that absorbs in the region 420–490 nm is assigned as the triplet state. This transient absorption of 15–30% is shown to be consistent with a quantum yield of triplet production in the adsorbed state of 3%. When excited at 354 nm, physisorbed DPH, diphenylbutadiene (DPB), and chemisorbed stilbene (DPE) give strong, long-lived transient absorptions at 590, 540, and 480 nm, respectively, which deactivate over a time scale extending over more than 6 orders of magnitude with an extremely nonexponential decay. These transients are assigned as the radical cations of the adsorbed diphenylpolyenes which decay almost exclusively by radical cation–electron recombination. The mechanism of the formation and decay of these radical cations is discussed.

Introduction

The photochemistry of species adsorbed on surfaces is a very active field of research, and one area that has received the attention of many research groups is that of an insulating oxide onto which one or more electronically active organic molecules have been adsorbed. For example, the luminescence and luminescence quenching of pyrene and similar aromatics adsorbed on silica gel have been studied in detail,^{1–7} and information concerning the mobility of adsorbates on the surface can be obtained from photochemical and photophysical investigations.^{8–10} Photochemical reactions such as the generation of benzyl radicals¹¹ or the amide photo-fries rearrangement¹² have been reported to occur on silica gel. Photoprocesses on aluminum oxide have been published,¹³ and following our work where triplet–triplet absorptions on hydrocarbons chemisorbed onto γ -alumina were detected by using diffuse reflectance laser flash photolysis,¹⁴ other researchers have now used this technique to follow photoprocesses on surfaces.¹⁵

The interaction of aromatic or polyenic π -electron systems with catalytic surfaces can be studied by optical absorption and luminescence spectroscopy. Depending on the nature of the surface, the electronic states of the adsorbates are distorted by processes

such as charge transfer to or from localized surface states or conduction bands of the adsorbents. For example, in the ground state, electron donor–acceptor (EDA) π -complexes, proton-addition complexes, σ -complexes, and radical cations have been detected by diffuse reflectance,^{16,17} luminescence,^{18,19} and ESR^{20,21} spectroscopy. Since molecular distortions are usually greater in the excited state, valuable data on the nature of adsorbent–adsorbate interactions can be obtained from excited-state spectroscopy, by using techniques as time-resolved fluorescence²² or diffuse reflectance flash photolysis.²³ The latter technique has been successfully used to determine the transient absorption spectra of organic microcrystals,²⁴ polymer-bound dyes,²⁵ doped semiconductor powders,²⁶ and, as already mentioned, adsorbed aromatic hydrocarbons.¹⁴

In this article we present the results of studies of transient absorption in diphenylpolyenes adsorbed on alumina. This class of molecules is very sensitive to environmental influences on the torsional motion of the carbon–carbon single bonds in the ground state and of carbon–carbon double bonds in the excited state. When the polyene is adsorbed, these motions may be more or less hindered and allow the occurrence of photoprocesses that would not normally be observed in solution. The triplet yield of excited diphenylpolyenes is less than 10% in solution, and therefore these molecules are good candidates to test the sensitivity of diffuse reflectance transient absorption spectroscopy by examining the intensity of triplet–triplet absorption at very low coverages of adsorbent (ca. 10^{-3} of a monolayer).

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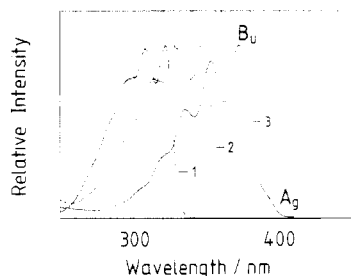


Figure 1. Fluorescence excitation spectra of (1) DPE, (2) DPB, and (3) DPH adsorbed from high vacuum on γ -alumina pretreated at $T_a = 100$ °C. The concentration is 0.1 mg of adsorbate/g of adsorbent. The A_g states of DPB and DPH can be observed as weak shoulders.

Experimental Section

The adsorbates, namely 1,2-diphenylethylene (*trans*-stilbene, DPE), 1,4-diphenyl-1,3-butadiene (DPB), and 1,6-diphenyl-1,3,5-hexatriene (DPH) were adsorbed onto alumina (active, neutral, with a specific BET surface area of approximately $100 \text{ m}^2 \text{ g}^{-1}$). Samples were also prepared by using silica (specific BET surface area $\sim 300 \text{ m}^2 \text{ g}^{-1}$) or thoria (specific BET surface area $\sim 15 \text{ m}^2 \text{ g}^{-1}$) for comparison with the behavior on alumina. Adsorption took place either under high vacuum or from liquid *n*-hexane. Prior to gas-phase adsorption the adsorbents were outgassed for 3–5 days at an elevated temperature T_a of 100 °C and at a pressure of 10^{-6} mbar to remove oxygen and physisorbed water. Partial removal of chemisorbed hydroxyl groups can be achieved at $T_a = 300$ °C. Adsorption was performed in the sealed outgassing apparatus by breaking an evacuated ampule containing 10^{-5} – 10^{-4} g of polyene/g of adsorbent, and the sample was left for 2–5 days to complete the adsorption process. For liquid-phase adsorption the adsorbents were heated for 5 h in a dry nitrogen atmosphere followed by addition of the polyene solution. The adsorption equilibrium was reached after a few minutes, with more than 99% of the polyene being adsorbed. The liquid/solid adsorption isotherms^{19b} saturate in the region of 20–30 mg of adsorbate/g of alumina, depending on the nature of the adsorbates and the pretreatment of the adsorbent. The resulting adsorbate concentrations are low, the coverage being less than 1% of a monolayer. It is believed that the distribution equilibrium of the adsorbate has been reached, since leaving the samples for several days has no effect on the results.

Ground-state diffuse reflectance spectra were recorded with two synchronously driven double monochromators (modified Spex-fluorlog II) to reject the intense fluorescence from the samples that would affect the reflectance values. The same instrument was used for recording fluorescence and excitation spectra. Fluorescence decay curves were obtained with the time-correlated single-photon counting method (Photochemical Research Associates nanosecond lamp or BESSY synchrotron radiation, and ORTEC electronics). The apparatus for diffuse reflectance laser flash photolysis has been described in detail elsewhere.^{23,24}

Results

Ground-State Absorption Spectra. The fluorescence excitation spectra and ground-state diffuse reflectance spectra of samples in which the γ -alumina has been pretreated at $T_a = 100$ °C are very similar to those of the dissolved molecules, and so it seems that the electronic systems of the diphenylpolyenes suffer no major distortion on this surface. Figure 1 shows the fluorescence excitation spectrum for DPE, DPB, and DPH adsorbed from high vacuum, while Figure 2 gives the ground-state diffuse reflectance spectrum taken in *n*-hexane for DPH/alumina adsorbed from this solvent. The position of the B_u band of the adsorbed species is red-shifted by 12 nm in the presence of liquid *n*-hexane. The same effect is observed for the other polyenes and also for a number of polycondensed aromatic hydrocarbons.^{18,19} The red-shift increases with the oscillator strength of the transitions (50 – 100 cm^{-1} for weak A_g or L_b bands and 500 – 2000 cm^{-1} for strong B_u , L_a , or B bands), and this explains why the A_g bands of DPH and DPB

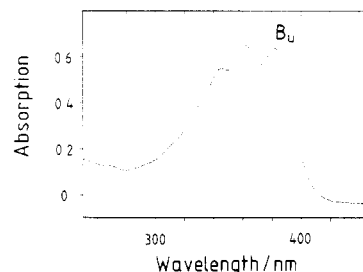


Figure 2. Diffuse reflectance ground-state absorption spectrum of DPH adsorbed on γ -alumina (0.1 mg/g) from liquid *n*-hexane. The spectrum was recorded in the presence of *n*-hexane by using two double monochromators. The A_g state cannot be observed.

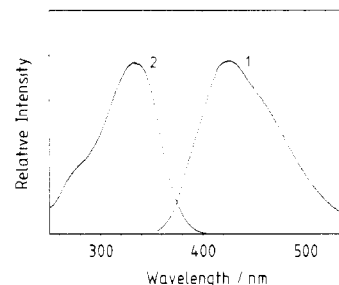


Figure 3. (1) Fluorescence and (2) fluorescence excitation spectra of the charge-transfer complex of DPE/alumina pretreated under high vacuum and $T_a = 300$ °C.

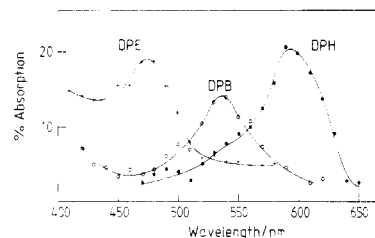


Figure 4. Transient absorption spectra of (1) DPE on alumina pretreated at 300 °C, (2) DPB on alumina pretreated at 100 °C, and (3) DPH on alumina pretreated at 100 °C. The spectra were recorded 1 ms after the laser pulse.

can be observed as weak shoulders in the absence of *n*-hexane but are completely hidden under the B_u bands when *n*-hexane is present. The cause of the red-shift is not fully understood, but it may arise from differences in adsorption geometries or in polarizing effects caused by the presence of *n*-hexane.

When the alumina substrate is pretreated at a higher T_a , different fluorescence and absorption bands are observed, which are structureless and occur at slightly longer wavelengths than for samples of lower T_a . Figure 3 depicts these spectra for DPE/alumina where $T_a = 300$ °C. By comparison with the behavior of condensed aromatic molecules, the spectra are assigned as EDA complexes formed between the polyenes acting as π -donors and Lewis acid acceptor sites of the oxide surface.¹⁹ A stronger interaction between adsorbate and adsorbent therefore exists in samples where the substrate has been treated at higher T_a , i.e., under conditions where a larger proportion of dehydroxylated sites are produced.

Transient Absorption Spectra and Their Assignment. All samples exhibit transient absorption following pulsed nanosecond excitation at 354 nm, except for DPE physisorbed on alumina, which does not absorb at this wavelength (see Figure 1). Figure 4 illustrates that each transient absorption spectrum (recorded 1 ms after excitation) consists of a single broad maximum with poorly resolved sidebands. The spectrum for DPE was obtained from the EDA complex on alumina formed at higher T_a , which does absorb at 354 nm (see Figure 3). The λ_{max} of the transient absorptions is red-shifted as the number of double bonds in the compound increases. Attention is drawn to the fact that all the spectra in Figure 4 are recorded 1 ms after the exciting pulse; in

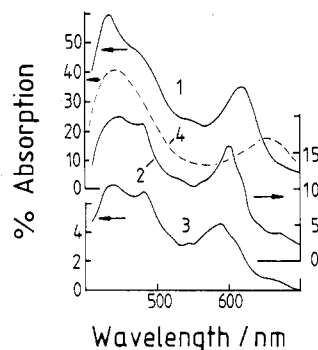


Figure 5. Transient absorption spectra of (1) DPH/alumina, *n*-hexane, $T_a = 100\text{ }^\circ\text{C}$, (2) DPH/alumina, high vacuum, $T_a = 100\text{ }^\circ\text{C}$, (3) DPH/silica, high vacuum, $T_a = 100\text{ }^\circ\text{C}$, and (4) DPH/thoria, high vacuum, $T_a = 100\text{ }^\circ\text{C}$. The spectra were recorded immediately after the laser pulse.

TABLE I: Transient Absorption Maxima of Adsorbed Stilbene (DPE), Diphenylbutadiene (DPB), and Diphenylhexatriene (DPH)

adsorbate	adsorbent	adsorption technique; T_a , $^\circ\text{C}$	main absorption bands/nm	
			long-lived radical cation	short-lived triplet
DPE	alumina	HV; ^a 300 $^\circ\text{C}$	475	
DPE	thoria	HV; 100 $^\circ\text{C}$	480	
DPB	alumina	HV; 100 $^\circ\text{C}$	535	
DPH	silica	HV; 100 $^\circ\text{C}$	585	440
DPH	alumina	HV; 100 $^\circ\text{C}$	595	440
DPH	alumina	<i>n</i> -hexane; 100 $^\circ\text{C}$	620	435
DPH	thoria	HV; 100 $^\circ\text{C}$	650	440

^a High vacuum.

the case of adsorbed DPH an additional feature can be observed when monitoring at much shorter times after the laser flash. This feature comprises a peak at 440 nm and a shoulder at 490 nm and has almost entirely disappeared after 0.75 ms. Figure 5 shows how the λ_{max} of the longer lived transient located near 600 nm is sensitive to both the adsorbent and the adsorption technique, whereas the position of the 440- and 490-nm features belonging to the shorter lived species is essentially independent of these factors, although their relative sizes are influenced by the adsorbent and the adsorption technique. A summary of the transient spectral data is given in Table I.

It is unlikely that the transient spectra of DPE and DPB corresponding to the triplet-triplet absorption since the published^{27,28} spectra in a fluid solution have values for λ_{max} of 360 and 380 nm and 390 nm, respectively, which lie below the short-wavelength limit of our apparatus. However, the triplet-triplet absorption spectrum of DPH in the dissolved state²⁸⁻³⁰ is very similar to that shown in Figure 5 for adsorbed DPH (centered around 430–440 nm). We could also observe the same transient by adding alumina to act as a scatterer in a solution of DPH in ethanol, a solvent from which DPH is not adsorbed. We therefore assign the short-lived transient of adsorbed DPH as the triplet-triplet absorption of the physisorbed species. There is good evidence that the long-lived transient in DPH (see Figure 4) and the transient absorptions in DPE and DPB are due to radical cations. For many aromatic hydrocarbons these species are known as stable adsorbates on substrates such as $\text{Al}_2\text{O}_3/\text{SiO}_2$ mixed-oxide cracking catalysts¹⁷ and on highly active alumina precipitated from aluminum sulfate.¹⁹ The radicals were identified by optical and ESR spectroscopy^{20,21} and by quantum mechanical calculations,³¹ and the stable radical cation of the asymmetric 1,1-diphenylethene

TABLE II: Mean Fluorescence Decay Time, τ_f , and the Initial Rate of Decay of the Triplet State of DPH, k_T^{in} , for Adsorbed Polyenes

sample	τ_f/ns	$k_T^{\text{in}}/\text{s}^{-1}$
DPE/alumina, HV, ^a $T_a = 100\text{ }^\circ\text{C}$	1.1	
DPE/alumina, HV, $T_a = 300\text{ }^\circ\text{C}$	3.6	
DPB/alumina, HV	0.65	
DPH/alumina, HV	8.1	3×10^5
DPH/alumina, <i>n</i> -hexane	2.8	5×10^5
DPH/thoria, HV	2.5	1.7×10^5

^a High vacuum.

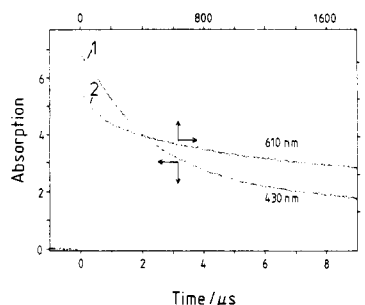


Figure 6. Decay curves of the two transient absorptions of DPH on alumina, adsorbed from *n*-hexane, $T_a = 100\text{ }^\circ\text{C}$.

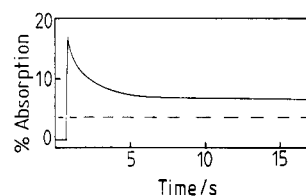


Figure 7. Long-lived decay of the transient absorption at 610 nm of DPH on alumina, *n*-hexane, $T_a = 100\text{ }^\circ\text{C}$. The dashed line was recorded 5 min after the laser flash.

on $\text{Al}_2\text{O}_3/\text{SiO}_2$ was assigned by resonance Raman spectroscopy.³² For DPE adsorbed on $\text{Al}_2\text{O}_3/\text{SiO}_2$ the radical cation is known to have its stronger absorption band at 480 nm, while for DPB and DPH adsorbed on this catalyst the strongest ground-state absorption bands occur at 542 and 602 nm, respectively.¹⁷ In solution a short-lived transient ($\tau < 100\text{ ns}$, $\lambda_{\text{max}} = 478\text{ nm}$) is reported after flashing charge-transfer complexes of DPE in the presence of an electron acceptor such as fumaronitrile,³³ this transient is assigned as the radical cation. We therefore assign the transients in DPE and DPB and the long-lived transient of DPH as radical cations. The generation of these species after excitation will be considered in the Discussion.

Decay Kinetics. Triplet-State Decay. Owing to experimental limitations, the triplet state can be detected only for adsorbed DPH (see Figure 5). The shoulder/peak at 490 nm is almost absent when the adsorbent is thoria, and the sensitivity to environment suggests some symmetry-forbidden vibronic structure. However, whatever the reason for the shoulder, it is important to note that the decay in this region is identical with that of the main band at 430 nm. The triplet state of DPH adsorbed on thoria decays by quite a good first-order process. For the other adsorbents the triplet decays are nonexponential, but a reasonable fit to a first-order process is possible over the initial part of the decay. For this reason the rate constants given in Table II are labeled k_T^{in} to indicate the initial triplet decay constant. k_T^{in} is similar to the rate constants for the triplet decay in a fluid solution, where k_T is 10^4 – 10^5 s^{-1} at room temperature.²⁸ Curve 1 of Figure 6 shows the decay of the triplet of DPH/alumina adsorbed from *n*-hexane; this decay is quite a good exponential. No phosphorescence of adsorbed DPH was seen, although it would be expected to occur at 830 nm, on the basis of the triplet energy of 143 kJ mol^{-1} obtained from quenching experiments.³⁰ The heavy-atom effect

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of thorium did not induce phosphorescence in a sample of DPH adsorbed on thoria, and only for DPE/thoria could weak low-temperature phosphorescence be seen at 585 nm, the transition energy being exactly the same as in solution³⁴ or in the pure crystal.³⁵

Radical Cation Decay. The transient absorptions arising from radical cations (see Figure 4) decay by a complex mechanism extending over time scales that vary from milliseconds to minutes. Curve 2 of Figure 6 depicts the early part of the decay, and Figure 7 shows the decay over several seconds. Even after 5 s there is a residual transient absorption of 7%, and this drops to 4% after 5 min and then proceeds to decay even further. By repetitive excitation of the same area of the sample we could show from the ground-state diffuse reflectance spectrum that the intermediates deactivate mainly back to the ground state and that no permanent products are formed.

Fluorescence Decay. Fluorescence is one of the main deactivation channels in all three adsorbates. As a guide to the temporal behavior, the mean first-order decay times over the first two decades are given in Table II, but the decays are nonexponential, which is believed to be a result of radiative and nonradiative decay processes that are site-dependent. For DPH, the initial and final slopes of the semilogarithmic decay curve differ by a factor of 6. This can be explained by the fact that a small change in the energy gap, ΔE , between $^1B_u(S_2)$ and $^1A_g(S_1)$ produces a very large effect on the radiative lifetime of the forbidden $^1A_g(S_1) \rightarrow ^1A_g(S_0)$ fluorescence,³⁶ even though the value of ΔE itself may be extremely small. This is clearly illustrated by the effect of adding *n*-hexane to DPH/alumina, which reduced ΔE and τ_f (see Figures 1 and 2 and Table II) without altering the fluorescence yield. For DPE the fluorescence lifetime is determined largely by the nonradiative torsional deactivation in S_1 from the trans to perpendicular configuration. This process is strongly hindered in the adsorbed state, and it is probable that both steric hindrance and the height of the torsional barrier are site-dependent, which explains why the fluorescence decay is nonexponential. For adsorbed DPB the initial and final slopes of the semilogarithmic decay curve differ by a factor of only 2, and the first three decades can be fitted as two exponentials. However, the two decay constants may have no real significance because James and Ware shown³⁷ that a Gaussian distribution of rate constants can often be fitted as a biexponential decay.

Intensity of Transient Absorption Signals. Experimental Measurements. Despite the low intensity of exciting radiation (5–30 mJ cm⁻² pulse⁻¹) and the extremely low coverages of adsorbent, large transient absorptions are obtained. This is because the transients are generated close to the front surface of the sample, and therefore only a very small amount of absorbing transient is sufficient to give the whole sample the appearance of being colored. The DPH/alumina/*n*-hexane system shows the strongest absorption of about 60%, recorded immediately after excitation with 30 mJ cm⁻², which is comparable to that observed in the ground state (cf. Figures 2 and 6). Absorptions of around 30% were recorded for the other alumina samples. The higher percentage absorption in the DPH/alumina/*n*-hexane system is probably due to the scattering coefficient of the sample being lower in a liquid environment. On silica the maximum absorptions are in the region of 5–10%.

Model Calculations. It is assumed that the species that exhibits transient absorption is formed via a short-lived intermediate according to the following simple reaction scheme:



where A is the ground-state absorber, A* is a short-lived intermediate (e.g., a singlet), and T is longer lived (e.g., a triplet). This

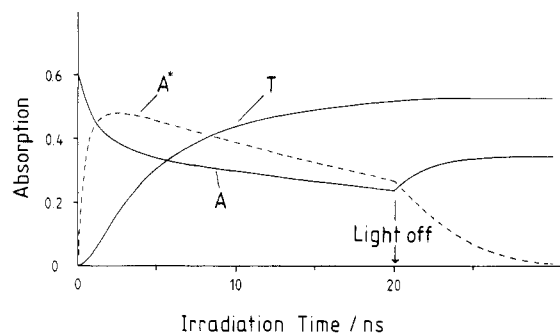


Figure 8. Computer calculations of changes in the absorption of the ground-state A, a short-lived intermediate A*, and a long-lived transient T as a function of time during the excitation pulse. Calculations are performed by assuming $k_{SG} = 3 \times 10^8$ s⁻¹, $k_{ST} = 10^8$ s⁻¹, and $k_{TG} < 10^6$ s⁻¹, and a constant laser intensity of 1.5 mJ s⁻¹ cm⁻² over a 20-ns pulse.

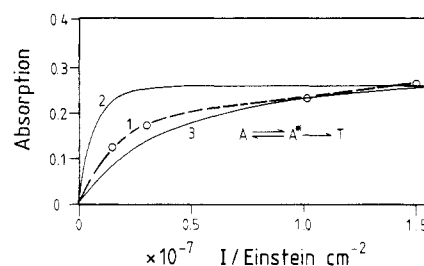


Figure 9. Plot of transient absorption versus photon fluence (H) for DPH adsorbed on thoria ($T_a = 100$ °C): (1) experimental curve, where the ground-state concentration = 5×10^{-4} mol dm⁻³, the extinction coefficient at the exciting wavelength is 5×10^{-4} dm³ mol⁻¹ cm⁻¹, $\lambda_{exc} = 354$ nm (pulse duration 20 ns), $\lambda_{mon} = 40$ nm, and H is varied by neutral density filters; (2) calculated curve, assuming $\Phi_T = 0.17$ and $\tau_{A^*} \gg t_{pulse}$; (3) calculated curve, assuming $\Phi_T = 0.03$ and $\tau_{A^*} \ll t_{pulse}$. Computer calculations are based on scheme 1.

scheme is oversimplified because different adsorption sites will affect the rate constants, but if the assumptions $\tau_f \ll t_{pulse}$, $\tau_f \ll k_{ST}$, and $k_{SG} \ll k_{TG}$ are made, variations in the rate constants are insignificant, and the model allows reasonable estimation of transient absorption intensities. The absorptions of the three species can be calculated by using methods we have developed and described previously.^{38,39} Figure 8 shows how these absorptions vary over the width of the laser pulse by using a set of rate constants and absorption cross sections that are appropriate for DPE on alumina. It can be seen that the absorption of the long-lived transient T and depletion of the ground state A tend to saturate toward the end of the laser pulse, i.e., within 20 ns. The absorption of A* has maximized within the first 3 ns, corresponding to rapid formation of A* from A, and simultaneously the ground state has been completely depopulated in the region near the front surface of the sample. The concentration of A* drops slowly after 3 ns, on account of its return to the ground state and formation of T, which grows quite slowly during the laser pulse. Immediately after the end of excitation, absorption by T continues to grow only slightly because it has almost reached its saturation value.

The role played by the short-lived intermediate A* in determining the yield of the long-lived transient as a function of the exciting photon fluence can be elucidated with the help of Figure 9. The dashed line, curve 1, shows the experimentally observed relationship between the size of the transient absorption of DPH on thoria and the photon fluence of the exciting pulse. Assuming that the decay of A* is slow relative to the width of the laser pulse, curve 2 can be constructed, which shows the predicted variation with laser fluence when $\Phi_T = 0.17$. The absorption is expected to saturate at very low exciting photon fluences, which is contrary

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to the experiment. However, the observed mean lifetime of the fluorescence of DPH is 2.5 ns, which is well within the width of the laser pulse. Curve 3, calculated with $\tau_A = 2.5$ ns and $\Phi_T = 0.03$, gives a reasonably good fit to the observed curve and shows that the experimental results can be explained theoretically. An increase in absorption during the excitation pulse is to be expected due to decay of A^* back to A and subsequent reexcitation to increase the overall yield of T . The calculations clearly demonstrate that when τ_{A^*} is very much smaller than the pulse duration, substantial absorption by transients may be observed since the ground-state molecules are likely to undergo excitation many times.

Discussion

The photophysical and photochemical properties of *trans*-stilbene have been exhaustively investigated in dilute fluid solution.⁴⁰ The rate of *cis* \leftrightarrow *trans* isomerization shows both temperature and viscosity dependence. For reactions originating in the first excited state S_1 it has been established that there is an energy barrier in going from the *trans* to the perpendicular configuration of S_1 , which explains the temperature dependence of the rate constant $k_{tp}(S_1)$ for this process. *trans*-Stilbene was one of the first molecules to be investigated in the adsorbed state, and we have recently demonstrated that less photoisomerization occurs in the adsorbed state.⁴¹ We showed that the activation energy is slightly lower in the adsorbed state, and a smaller Arrhenius preexponential factor causes $k_{tp}(S_1)$ to be lower by 3 orders of magnitude for stilbene on γ -alumina. Fluorescence yields of DPE, DPB, and DPH in the adsorbed state are invariably high, i.e., in the range 0.5–0.7, which clearly demonstrates that the radiative deactivation pathway $S_1 \rightarrow S_0$ is the most important for all three adsorbed polyenes. The case of triplet deactivation is somewhat different, and, as explained earlier, Φ_T is considered to be in the region of 0.03. We could observe triplet–triplet absorption only in the case of adsorbed DPH; for the other adsorbates this absorption lies below the short-wavelength limit of our apparatus. However, the other adsorbates also have high fluorescence yields, and so the triplet formation yields are expected to be small.

The similarity between the decay of the triplet of DPH/alumina and that recorded in a fluid solution implies that the rotational mobility of the triplet of the adsorbed polyene is quite similar to that in the dissolved state. This suggests that the molecule is not adsorbed completely flat, and therefore rotation about the double bond in T_1 can be fast enough to allow the radiationless $T_1 \rightarrow S_0$ transition to have a high probability. It also means that hardly any torsional barrier will exist in going from the *trans* to the perpendicular state, which appears to be an important deactivation channel in T_1 ; rapid *trans* to perpendicular deactivation clearly explains both the absence of phosphorescence and the insensitivity of the decay to heavy-atom effects. These conclusions can be contrasted with those drawn from studies of the rate of fluorescence and photoisomerization of adsorbed DPE,⁴¹ where adsorption on alumina means that the torsional motion about the carbon–carbon double bond is strongly reduced in the S_1 state. However, at room temperature the rate is still comparable to the rate of fluorescence, i.e., $k_{tp}(S_1) \sim 5 \times 10^8$ s⁻¹.

The long-lived transients, the absorption spectra of which are given in Figure 4, are assigned to a radical species, either the polyene radical cation $R^{+\bullet}$ or radical ion pairs comprising $R^{+\bullet}$ and a surface center $S^{\bullet-}$. The nature of the interaction between alumina and the diphenylpolyene has a large influence on the behavior of the adsorbate. Surface defects such as Al ions with tetrahedral coordination that have one or two coordinatively unsaturated (CUS) sites can act as electron acceptors, and the energy of these unoccupied orbitals depends strongly on the distortion of the regular surface structure. The properties observed when $T_a = 100$ °C are very similar to those recorded in a dilute fluid solution and show that the adsorbate is essentially physi-

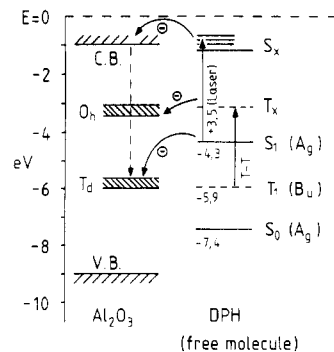


Figure 10. Energy level diagram of alumina showing the positions of the valence band (VB) and conduction band (CB) and including the approximate energies of the Al surface centers with T_d and O_h coordination. The energy levels of DPH relative to its ionization potential is also shown.

sorbed. Most of the alumina surface is still covered with hydroxyl groups, and the concentration of CUS centers is rather low. No stable charge-transfer complexes of the polyenes can be formed at this T_a even if adsorption occurs close to a CUS center; this is because the concentration of surface hydroxyl groups is so high that a large separation distance exists between donors and acceptors. At higher T_a partial removal of chemisorbed hydroxyl groups can allow direct contact between the polyene and the surface of the alumina. A greater number of adjacent dehydroxylated or CUS sites therefore exists,⁴² and so the donor–acceptor distance can be significantly reduced. This will result in a better overlap between the π -orbitals and the CUS orbitals, and stability is thereby provided to the charge-transfer complexes. Figure 10 gives an energy diagram for alumina, showing aluminum surface states that have both tetrahedral and octahedral coordination,^{43,44} and it also includes the energy levels of DPH relative to the ionization potential of the free molecule.⁴⁵ It is evident from Figure 10 that electron transfer from the S_1 state of DPH to a tetrahedral vacancy is feasible. Two-photon electron transfer is possible via a mechanism involving S_1 and T_1 , as shown in Figure 10. Electron transfer has been postulated to occur between an adsorbate and an oxide substrate; e.g., in the case of pyrene/ TiO_2 it has been reported that radical intermediates could be detected.⁴⁶

With regard to radical formation from excited physisorbed molecules, such as takes place with DPB and DPH on alumina or silica, the mechanism is not fully understood. The highly hydroxylated surface will mean that very few adsorbate molecules are directly in contact with a CUS center. However, the acceptor sites can be populated by electron tunneling, electron diffusion, or two-photon excitation (see Figure 10). It is also possible that as in the case of pyrene adsorbed on silica,⁴⁷ the electron is taken up into the bulk of the alumina itself. Thus electron transfer may occur from the excited physisorbed species to the oxide, although the quantum yield of this process is very low.

For DPE/alumina the ground-state species is an EDA complex from which radicals can be formed quite easily in the excited state, exactly as occurs for stilbene–fumarionitrile in fluid solution.³³ In this case, three different types of transient species were suggested, namely the contact radical ion pair, the solvent-shared radical ion pair, and the free radical ion. Coulombic interaction will be a major factor in determining the lifetime of the radical pair, and the more separated that the charges are, the longer the radicals will live. The decay of the long-lived transient has several components in different time ranges, which suggests that there is quite a wide range in the distances between radical ion pairs. In the adsorbed state, the principal species is expected to be the contact

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ion pair, although the very long-lived component is more likely to arise from well-separated radical ion pairs, and this implies that there must be some diffusion of the contact radical pairs to give isolated radical ions that live for much longer periods of time.

Conclusions

Radical cations are responsible for the long-lived transient in adsorbed DPH, DPB, and DPH.

The triplet state could be detected for adsorbed DPH and is a much shorter lived transient species.

Despite the low surface coverage and the low triplet or radical formation yields, large transient absorption signals are detected.

This is because the short-lived precursor of the observed transient can decay back to the ground state during the laser pulse and therefore be available for reexcitation to increase the concentration of the longer lived transient species.

The rotational mobility of the triplet state of adsorbed DPH is similar to that in the dissolved state.

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Registry No. DPE, 588-59-0; DPB, 3817-93-4; DPH, 1720-32-7; alumina, 1344-28-1; silica, 7631-86-9; thoria, 1314-20-1.

Temperature-Programmed Reactions with Anomalous Diffusion

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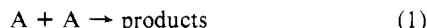
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Temperature-programmed reactions (TPR) of particles exhibiting anomalous diffusion are simulated by the Monte Carlo procedure. The reaction order of the reaction $A + A \rightarrow \text{products}$ in 1D is found to be $X = 3$, in agreement with previous results for the same reaction at constant temperature. The reaction order for fully directed walkers in 1D is also found to be $X = 3$ for both TPR and constant-temperature reactions. It is shown that the TPR procedure also allows the determination of the activation energy of diffusion in a single experimental run.

1. Introduction

Particle diffusion on or inside fractal media exhibits anomalous long-time behavior (ref 1-3 and references cited therein). Consequently, diffusion-controlled heterogeneous chemical reactions that occur in or on such media are also anomalous in the low-concentration limit, i.e., the so-called fractal chemical kinetics.³⁻⁹ For example, it has been demonstrated experimentally^{5,9} and by Monte Carlo simulations^{3,7,8} that the long-time behavior (i.e., the low-concentration regime) of the elementary reaction between A particles given by



may be described by the following rate equation:

$$-dq/dt = C_0 q^X \quad X \geq 2 \quad (2)$$

where q is the density (concentration) of A particles, C_0 is a constant, and the reaction order (exponent X) for fractal chemical kinetics may be much larger than 2 (note that eq 2 is the classical textbook second-order reaction).

These recent findings are relevant for many aspects of physical chemistry, such as surface science, chemical and electrochemical reactions on rough samples and fractal surfaces (ref 9-11 and

references cited therein), catalysis (fractal catalysts: powders and porous materials^{10,11} (for recent results on the fractal topology of the Pt/ γ -Al₂O₃ system see ref 12 and references cited therein), exciton fusion on clusters,⁵ biochemical reactions,⁹ etc. Also, fractallike behavior for electronic excitation migration and trapping has recently been reported.⁴

It should be noted that the experiments and simulations that support eq 2 with $X > 2$ have been carried out at fixed temperature. Nevertheless, the experiments are frequently performed by raising uniformly the temperature of the reactants, starting from a certain preset low temperature where the reaction rate is negligible. This procedure, called temperature-programmed reaction (TPR), has become a widely employed tool for the study of the interaction of adsorbates with surfaces¹³ (for a recent review see, for example, ref 14). In this respect, recently a new technique for the study of the temperature-programmed desorption from high surface area solids has been developed.¹⁵ Hopefully, this new technique would give valuable information on TPRs by using large area fractal catalysts. Therefore, we have considered it useful to investigate how anomalous diffusion could influence the information that is obtained by using the TPR procedure. The aim of the present work can be summarized as follow: (1) to analyze

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