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Surface catalyzed electron transfer from polycyclic aromatic hydrocarbons (PAH) to methyl viologen dication: evidence for ground-state charge transfer complex formation on silica gel[1]

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Abstract

Porous silica surfaces are shown to slowly catalyze the oxidation of adsorbed polycyclic aromatic hydrocarbons (PAH) to the corresponding radical cation via Lewis acid sites present on the surface. When a good electron acceptor such as methyl viologen dication (MV^{++}) is co-adsorbed on silica surface, a red-shifted structureless absorption band characteristic of a ground-state charge transfer (CT) complex formed between the PAH and MV^{++} is observed. Oxygen efficiently competes with MV^{++} for the trapped electrons on the active sites of silica surface causing a significant decrease in the concentration of ground-state CT complex. The rate of this electron transfer process is enhanced dramatically at the solid/liquid interface when solution of PAH in a non-polar solvent is added to dry silica containing adsorbed MV^{++}. Room temperature electron paramagnetic resonance (EPR) spectra of PAHs adsorbed on silica show a broad unresolved signal (g=2.0031–2.0045) due to PAH$^{\cdot+}$ radical cation which disappears in the presence of air but can be restored upon evacuation of the sample. The EPR measurements of mixed samples containing PAH and MV^{++} co-adsorbed on silica show a composite signal with hyperfine structure that may be due to presence of two paramagnetic species corresponding to MV$^{\cdot+}$ and possibly PAH radical cation. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Polycyclic aromatic hydrocarbons; Methyl viologen dication; Electron transfer

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1. Introduction

The formation of radical cations of certain polycyclic aromatic hydrocarbons adsorbed on silica–alumina cracking catalyst was first reported by Rooney [1,2] and Brouwer [3]. Both investigators employed EPR spectroscopy to detect radical cation formation on the catalyst surface. Radical cation formation on silica–alumina catalyst is believed to result from the interaction of hydrocarbon with Lewis acid sites present on the surface. Although Fogo [4] has suggested that the formation of radical cation could be due to a reaction involving electron transfer from a hydrocarbon–proton complex [5] (formed from the interaction of hydrocarbon with a protonic acid site on the catalyst) to molecular oxygen, Rooney and Pink [2] have questioned the validity of such notion based on the finding that oxygen exerts a marked decrease in the intensity and resolution of the EPR spectrum of PAH radical cation. Leftin and Hall [6,7] employed optical spectroscopy in addition to EPR to obtain the absorption spectra of radical cations formed by several polycyclic aromatic hydrocarbons (PAHs), phenylated amines, and olefins on a silica–alumina catalyst. Muha [8] has also reported the electron paramagnetic resonance (EPR) spectra of several PAHs adsorbed on silica–alumina catalyst. Using substrates that can form radical cation in acidic media, Hall was able to show that adsorption of alternate PAHs such as anthracene, perylene, or a phenylated amine on silica–alumina catalyst was accompanied by the formation of their corresponding radical cation [9]. Furthermore, it was found that the radical cation concentration was diminished by removing oxygen from the catalyst [9]. This observation implied that oxygen was acting as an electron acceptor in this process by removing trapped electrons from the surface active sites. It was thus reasoned that the same electrophilic centers (Lewis acid sites) responsible for the abstraction of hydrogen as hydride ions from saturated hydrocarbons could also be involved in removing an electron from unsaturated molecules of low ionization potential provided this process is energetically more favorable.

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[1] Dedicated to Prof. Jack Saltiel on the occasion of his 60th birthday.

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Dimethylviologen (MV^{++}), commonly known as methylviologen, is an efficient electron acceptor that can be reduced to its corresponding mono-cation radical ($MV^{\cdot +}$) by chemical [10–13], electrochemical [14], and photochemical [15–24] methods. The $MV^{\cdot +}$ radicals produced are unstable at room temperature due to back electron transfer or other reactions. However, recent work has shown that photoproduced $MV^{\cdot +}$ radicals on silica [23,24] or entrapped in a sol–gel matrix with pyrene as an electron donor [25] have longer lifetime than the corresponding lifetime in solution at room temperature.

In this paper, we present spectral evidence for the formation of ground-state charge transfer (CT) complex between several PAHs and MV^{++} on silica surface. The formation of this CT complex that results from electron transfer from PAH to MV^{++} via surface active sites is accompanied by a change in the color of silica surface with time. The rate of this electron transfer process is dependent on the one electron oxidation potential of the PAH in question. In the presence of air, a sharp decrease in the concentration of this CT complex is observed. When air-saturated solution of PAHs in non-polar solvents is added to MV^{++} adsorbed on silica, the silica surface immediately develops a color (due to CT complex formation) characteristic of the PAH in question. This fast electron transfer process at the solid/liquid interface is disrupted in polar solvents

2. Experimental details

Acenaphthene (Aldrich Chemicals, Milwaukee, WI, purity 99%), anthracene (Matheson Coleman & Bell, Norwood, OH, purity >99%), bibenzyl (Aldrich, purity 99%), biphenyl (Aldrich, purity 99%), chrysene (Aldrich, purity 98%), naphthalene (Matheson Coleman & Bell, Norwood, OH, purity 99%), perylene (Aldrich, purity 99%), phenanthrene (Aldrich, purity 98%), pyrene (Aldrich, purity 99%), and tetracene (2,3-benzanthracene, Aldrich, purity 99%) were all recrystallized twice from toluene before use. Methyl viologen dichloride (MV^{++}), 1,1′-dimethyl-4,4′-bipyridinium dichloride (Aldrich, purity 98%) was recrystallized from methanol before use. Cyclohexane (HPLC grade, Baker analyzed, Phillipsburg, PA) was dried over anhydrous $MgSO_4$ before use. Toluene (HPLC grade, Burdick & Jackson Laboratories, Muskegon, MI) and methanol (HPLC grade, Baker analyzed, Phillipsburg, PA) were used as received.

The physical characteristics of the silica (J.T. Baker, Phillipsburg, PA; reagent grade, 60–200 mesh) used in this work are identical to those previously reported [26]. The N_2 BET surface area for the silica was determined to be 274 $m^2\ g^{-1}$ with an average pore radius of 60 Å. The silica was used both unactivated and activated by heating at 200°C in air for a minimum of 24 h. The activated silica was cooled to room temperature in a desiccator charged with anhydrous $CaSO_4$ prior to sorbing the PAHs. Aldrich silica (Merck, grade 60/234, 100 mesh, 60 Å, Aldrich Chemicals) and Davison silica (silica gel catalyst, grade 56, Davison Specialty Chemicals, Baltimore, MD) were used as received. Cab-o-sil (Cabot Corporation, Tuscola, IL), an amorphous fumed silica with a BET surface area of 200 $m^2\ g^{-1}$ was activated at 200°C before use. Bio-Beads S-X8 (Bio-Rad Laboratories, Richmond, CA, 200–400 mesh), a spherical porous styrene-divinylbenzene copolymer with 8% crosslinking, was used as received.

The silica was loaded with PAH by adsorption from cyclohexane solution as described before [27–30]. Methyl viologen dichloride was loaded onto silica from a methanol solution. After removal of the solvent from silica surface by rotary evaporation, equal weighed amounts of silica with adsorbed PAH and MV^{++} were physically mixed for sample preparation. Except where noted, solid mixtures contained a 1:1 molar ratio of PAH:MV^{++}. Samples to be degassed were prepared by transferring a portion of the solid mixture into a glass tube equipped with a 1 cm quartz side arm cell. The tube was then placed under high vacuum (<5E-3 mm Hg pressure) for at least 48 h prior to flame sealing. For EPR studies, degassed samples were prepared in quartz NMR tubes and flame sealed.

Diffuse reflectance spectra were recorded on a cary 4E UV-Visible spectrophotometer (Varian) equipped with an integrating sphere. Baseline correction was applied with the spectrum recorded from a sample of silica that had not been loaded with PAH. Diffuse reflectance IR spectra were recorded on a Bio-Rad FTS-60 (Bio-Rad Laboratories, Digilab Division, Cambridge, MA) Fourier transform spectrophotometer. The spectrophotometer was calibrated and the baseline was recorded from a finely divided, oven dried, KBr powder (Aldrich Chemicals).

EPR measurements were performed on a Varian E-Line Century Series EPR spectrometer operating at 9.4 GHz with a modulation frequency of 100 kHz and equipped with a TM_{110} cavity. Samples consisting of PAH and/or MV^{++} adsorbed on SiO_2 were placed in quartz NMR tubes and degassed to a pressure of <5E-3 mm Hg and flame sealed. The g-values were determined versus that of Fremy's salt employed as a standard (g=2.0055). The magnetic field calibration was carried out using the same Fremy's salt solution (ca. 0.1 mM in 0.5 M Na_2CO_3 in a capillary attached to an experimental tube) and taking the distance between the low field and the central components equals 13.118 G.

3. Results and discussion

3.1. Diffuse reflectance spectroscopy

3.1.1. Radical cation and ground-state CT complex formation at solid/gas interface

During the course of our photochemical studies of PAHs adsorbed on silica we noticed that occasionally the air-saturated samples changed color with time in the dark prior to irradiation. The rate of this dark reaction depended on the nature of PAH adsorbed and correlated well with one electron oxidation potential of the PAH in question. For example, tetracene, which has an oxidation potential of 0.77 V (vs SCE) [31], was oxidized more readily than perylene (0.85 V) [31], anthracene (1.09 V) [31], pyrene (1.16 V) [31], chrysene (1.35 V) [31], acenaphthene (1.36 V) [32], phenanthrene (1.50 V) [31], naphthalene (1.54 V) [31], or biphenyl (1.91 V) [32]. When air was excluded from these solids, no color change was observed suggesting that oxygen played an important role in this process. Furthermore, no change in the color of sample was observed when air-saturated PAHs adsorbed on cab-o-sil (a highly pure form of silica) or bio-bead S-X8 (a styrene-divinylbenzene copolymer) were left in the dark for several months. These findings clearly demonstrated that the observed dark reaction in the presence of air was catalytic in nature.

Analysis of the extracted materials from these colored silica surfaces revealed that the major product was often the corresponding PAH quinone with hydroxylated PAHs accounting for the remaining minor products [33,34]. The fact that removal of oxygen from the surface resulted in no color change (or product formation) implied possible involvement of PAH radical cation as the intermediate in the observed dark reaction in good agreement with the earlier report of Hall et al. [9] who found no evidence of any PAH cation radical in the absence of oxygen. Fig. 1 shows the change in absorption profile of a freshly prepared anthracene/silica sample before (curve A) and after (curve B) 80 days in the dark. The weak absorbance around 720 nm (curve A) is due to formation of radical cation which slowly disappears with time to form other oxidation products [34]. The inset of Fig. 1 highlights the expanded region of the spectrum between 500–800 nm (where anthracene radical cation absorbs) for fresh (curve A) and 80 days old (curve B) sample. The broad red-shifted absorption band above 400 nm could be attributed to a CT complex formed between anthracene and silica active sites similar to that reported by Mao and Thomas [35] for pyrene on activated γ-alumina and silica–alumina. Absence of anthracene finger print spectrum

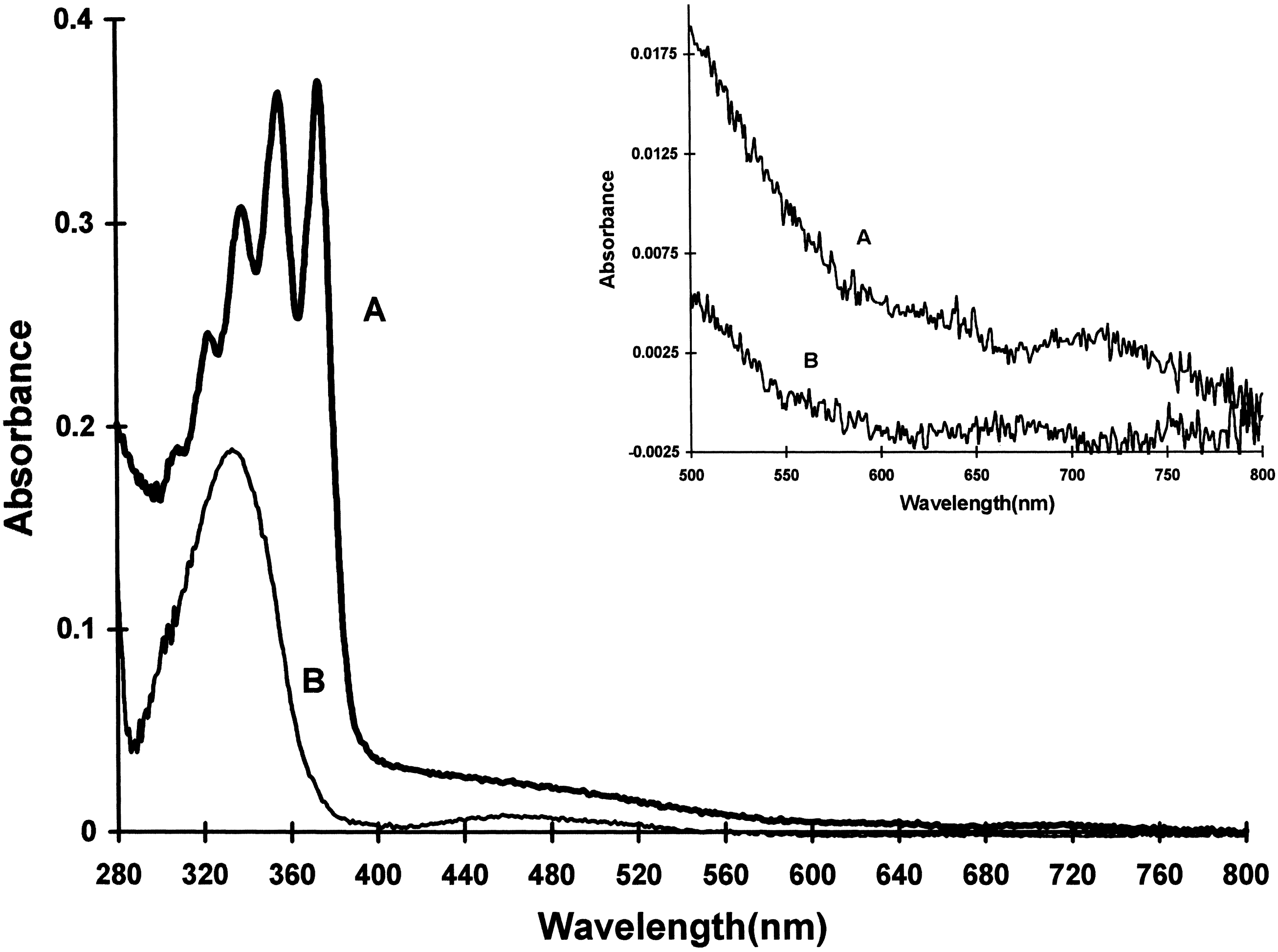

Fig. 1. Absorption profile of 1×10^{-6} mol/g anthracene adsorbed on dry silica for a freshly prepared air-saturated sample (curve A) and after 80 days in the dark (curve B). The inset shows expanded region of the spectra for curves A and B between 500–800 nm.

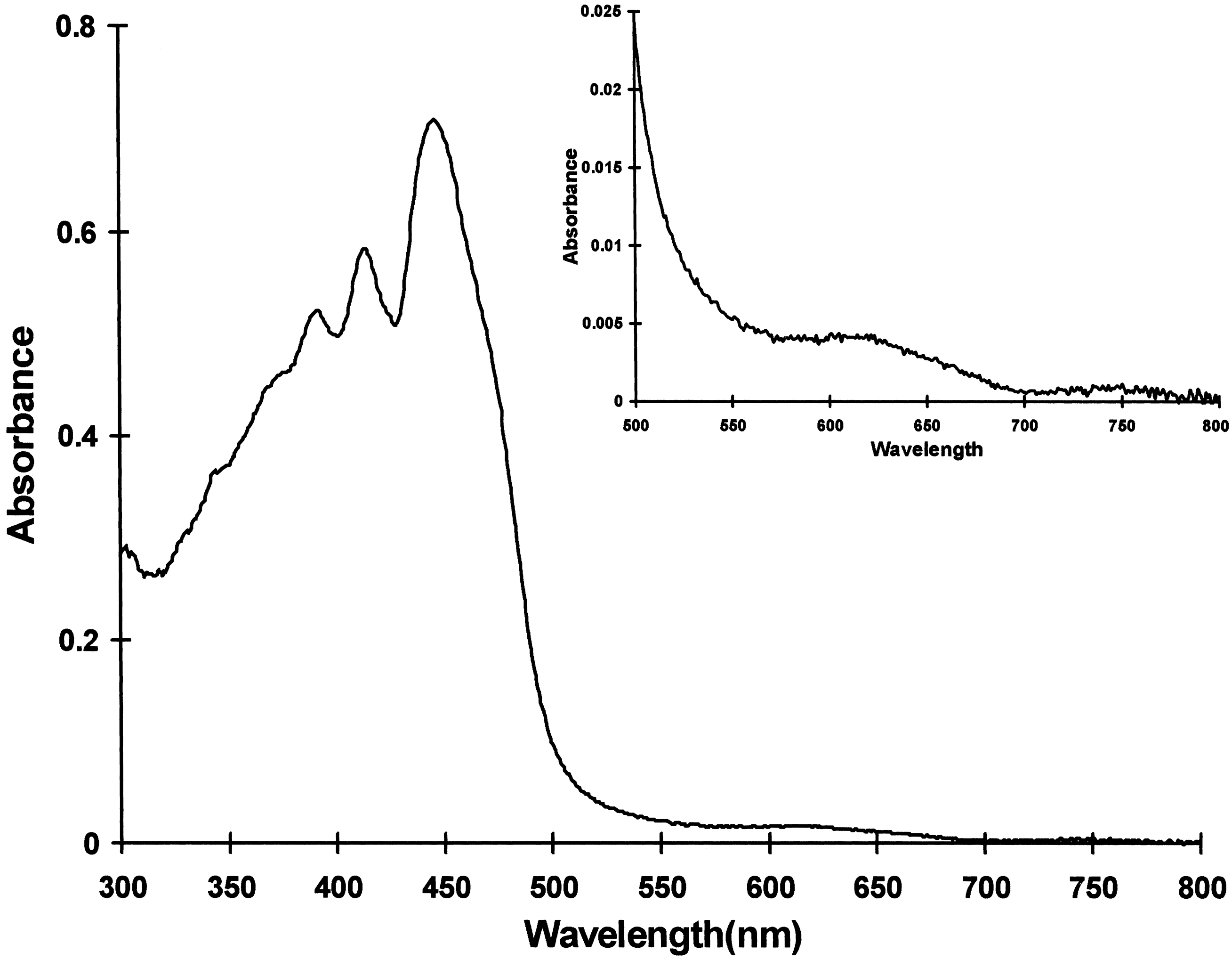

Fig. 2. Absorption profile of 5×10^{-5} mol/g perylene adsorbed on dry silica for freshly prepared air-saturated sample. The inset shows expanded region of the spectra between 500–800 nm.

in curve B indicates its total conversion to the oxidized products (e.g. 9,10-anthraquinone and hydroxylated products) [34].

Fig. 2 shows the absorption spectrum of a freshly prepared perylene on silica in air. The weak bands at 540 and 700 nm shown in the inset of Fig. 2 are attributable to the radical cation of perylene in good agreement with the reported spectrum of perylene on silica–alumina catalyst [9] and in frozen matrix [36]. These results clearly show that the initial adsorption of anthracene and perylene on silica is accompanied by the formation of a small amount of their corresponding radical cation at the active sites. Similar observations have been made for several other PAHs (not shown). Our EPR results further substantiate the formation of cation radicals of anthracene and perylene as well as several other PAHs on silica surface (vide infra). We noticed this catalytic activity of silica because most of our photochemical studies of the PAHs on dry silica were carried out at very low surface coverages (<5% of a monolayer). However, since a limited number of these active sites are available that can participate in this process, the contribution from this catalytic path to the overall chemistry of PAHs on silica surface may not be as noticeable at high surface coverages. Diffuse reflectance IR of our oven dried silica (activated at 200°C in air) revealed the presence of residual physisorbed water on the surface that can act as a nucleophile to attack the radical cation. Reaction of radical cations with water leading to hydroxylated products has been well documented for several PAHs [35,37–41]. Therefore, we attribute the formation of colored products to the reaction of PAH radical cation with physisorbed water on silica surface [33,34]. Formation of pyrene radical cation on activated silica–alumina and γ-alumina has been claimed [35] to be due to presence of active sites (generated by heat treatment) that can act as electron acceptor centers.

Formation of PAH radical cations reported in this work is not heat related based on the fact that we observe a similar activity for unactivated silica. The catalytic activity of silica used in our work arises from small amounts of aluminum impurity (141 PPM) [42] present in the silica. This notion is further supported by the observation that PAHs adsorbed on cab-o-sil (a highly pure form of silica with no aluminum impurity present) show no sign of any thermal degradation (oxidation) for times exceeding several months. These findings are in good agreement with the reports on the catalytic activity of silica–alumina catalyst where Lewis acid sites have been implicated as the surface active sites responsible for the formation of radical cations of several aromatic hydrocarbons [1–3,6–9,24,35].

In order to examine the involvement of these sites in facilitating electron transfer from PAH to a good electron acceptor, we employed MV^{++} in conjunction with diffuse reflectance and EPR spectroscopy to obtain experimental evidence for the role of silica surface in facilitating this process. In general, equal amounts of silica with adsorbed PAH and MV^{++} were physically mixed to obtain a 1:1 molar ratio solid mixtures. Two samples were then prepared in glass tubes equipped with a 0.1 cm quartz side arm cell. One sample was degassed to <5E-3 mm Hg pressure and flame sealed under vacuum while the other was left under an atmosphere of air. Changes in the absorption profile of both samples were recorded with time using diffuse reflectance spectroscopy. Fig. 3 shows the observed changes in the absorption profile of degassed anthracene:MV^{++}/silica with time. The solid sample slowly turned purple becoming more intense in color with time. Accordingly, its spectra showed growth of new peaks in the red region of the spectrum with time. These red-shifted broad and structureless bands are assigned to the CT complex formed between anthracene and MV^{++}. A similar spectral change was also observed for degassed perylene:MV^{++}/silica sample (not shown). Charge transfer complex formation between the π system of aromatic hydrocarbons and silanol groups of silica (via H-bonding) has been proposed by Pohle [43] to explain the observed wavenumber shifts ($\Delta\nu^{-}_{OH}$) in the infrared spectra of adsorbed benzene and its methyl and fluoro derivatives. Mao and Thomas [35] have also proposed CT complex formation between pyrene and the activated sites of γ-alumina and silica–alumina as a mean to explain the newly formed red-shifted bands in the absorption spectra of pyrene on these surfaces. The net change in the absorption spectrum of anthracene:MV^{++}/silica mixture with time is shown in Fig. 4. These spectra were obtained by subtracting the spectrum at different time intervals, *t*, from the spectrum at time zero (initial). A similar observation was also made for perylene:MV^{++}/silica (not shown). Although the evolved structured spectra shown in Fig. 4 resemble the absorption spectrum of $MV^{\bullet +}$ radical cation reported on silica [24], sol–gel [23,25,44] and zeolite [45], any contribution from the corresponding anthracene radical cation (λ_{max}=720 nm) [36] will be masked by $MV^{\bullet +}$ due to its strong absorption in this region of the spectrum (see curve A in the inset of Fig. 1). This change in the absorption spectrum with time suggests that the initially formed CT complex slowly dissociates to the corresponding $PAH^{\bullet +}$ and $MV^{\bullet +}$ radical cations. The above notion is further supported by our EPR data (vide infra).

Air-saturated samples of perylene:MV^{++}/silica and anthracene:MV^{++}/silica developed red-shifted structureless bands with time indicative of charge transfer complex formation. However, the rise in intensity of this band was much smaller than the corresponding increase in the intensity of the bands for degassed samples during the same reaction time indicating that oxygen exerted a pronounced

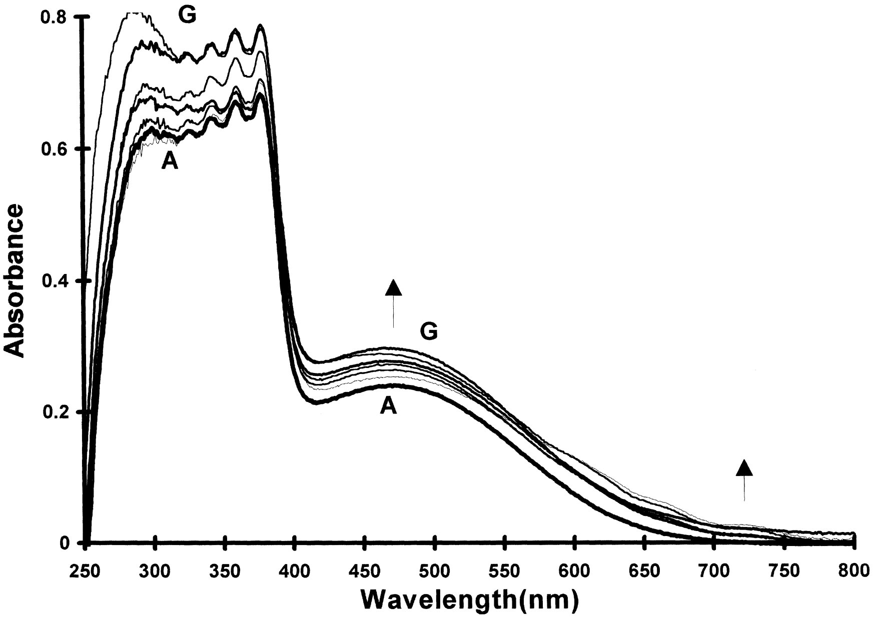

Fig. 3. Changes in the absorption spectra of a degassed anthracene/methyl viologen/silica sample (5×10^{-5} mol/g anthracene, 2.5×10^{-5} mol/g MV^{++}) with time in the dark. Curves A through G were obtained: 2 h, 2 days, 5 days, 19 days, 37 days, 84 days, and 145 days after preparation, respectively.

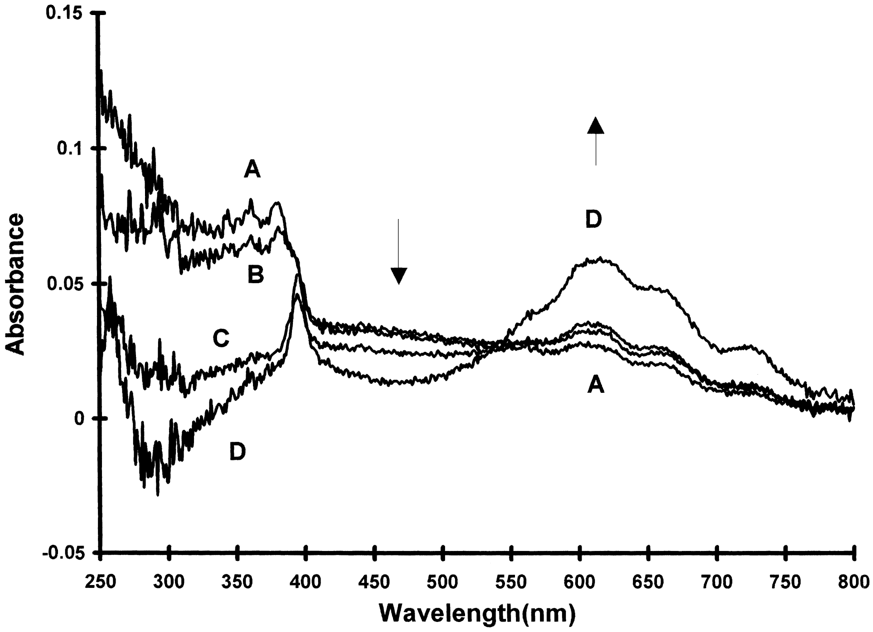

Fig. 4. Net changes in the spectra of degassed anthracene/methyl viologen/silica sample shown in Fig. 3 with time. These spectra were obtained by subtracting the absorption spectrum of the sample at different time intervals, *t*, from the initial spectrum at time zero (curve A in Fig. 3). Curve A (after 2 days), B (after 5 days), C (after 19 days), and D (after 145 days).

effect on the yield of ground-state CT complex. Such behavior suggests that oxygen serves as a low potential 'trap' for electrons precluding the formation of reduced MV^{++} (causing a decrease in the concentration of CT complex). This is not too surprising in view of the fact that gaseous oxygen physisorbed on the surface of silica can be in intimate contact with the PAH molecules residing on the active sites to intercept the electrons before they can diffuse towards MV^{++}. When air was admitted into the degassed samples of anthracene:MV^{++}/SiO_2 and perylene:MV^{++}/SiO_2, no significant change in the color of samples was visibly noticed over a period of several hours. However, the absorption peaks due to $MV^{\bullet +}$ (shown in Fig. 4) disappeared, consistent with oxygen quenching of this species, leaving a residual absorption at 720 nm (similar to the inset of Fig. 1) corresponding to PAH radical cation which is not quenched by oxygen. The insensitivity of these colored species to oxygen coupled with the small changes in the absorption profile supports our assignment that (a) the newly formed red-shifted bands are due to charge transfer complexes of PAH and MV^{++} and (b) only a small amount of CT complex molecules dissociate into the corresponding $PAH^{\bullet +}$ and $MV^{\bullet +}$ radical cations in good accord with the slow molecular diffusion of adsorbed species on silica surface [46].

3.1.2. Ground-state CT complex formation at solid/liquid interface

When solutions of PAHs (1E–3 M) in a non-polar solvent such as cyclohexane were added to solid silica containing adsorbed MV^{++} (2.5E–5 mol/g), the white silica became colored immediately upon contact with solution. The liquid phase remained clear indicating that the observed chemistry took place at silica surface. Rooney and Pink [2] have also reported a change in the color of silica–alumina catalyst upon addition of a dilute solution of anthracene in benzene, carbon disulfide or carbon tetrachloride. The observed color was characteristic of the PAH under investigation and its intensity appeared to depend on the oxidation potential of PAH in question. For example, addition of biphenyl (1.91 V) [31] or bibenzyl (2.35 V) [31] solution to silica containing adsorbed MV^{++} did not impart any color change. This was consistent with the higher oxidation potential of both biphenyl and bibenzyl compared to other PAHs studied in this work. A similar behavior was observed when Aldrich silica and Davison silica with adsorbed MV^{++} were employed. Table 1 summarizes the results of CT complex formation between several PAHs and MV^{++} at the solid/liquid interface of silica/cyclohexane. No spectral evidence for the formation of any ground-state CT complex was observed when equimolar solutions of PAH and MV^{++} in organic solvents were mixed in the absence of silica. Similarly, when solution of PAHs in polar solvents was added to silica containing adsorbed MV^{++}, no color was developed. This phenomenon, the immediate formation of a CT complex with MV^{++}, implies that electron transfer from PAH to MV^{++} is facilitated at the solid/non-polar liquid interface. One plausible explanation for this observation involves rapid adsorption of dissolved PAH onto the active sites (Lewis acid sites) of more polar silica followed by electron transfer to MV^{++} molecules in the close proximity of adsorbed PAH to form a CT complex. Lack of any CT complex formation in

Table 1
Color development at silica/cyclohexane interface upon charge transfer complex formation between different PAHs and methyl viologen dication (MV^{++})[a]

Adsorbate[b]	PAH in cyclohexane	Silica color before the addition of PAH solution	Silica color after the addition of PAH solution
MV^{++}	Acenaphthene	White	Orange
MV^{++}	Anthracene	White	Purple
MV^{++}	Naphthalene	White	Light yellow
MV^{++}	Phenanthrene	White	Red-purple
MV^{++}	Pyrene	White	Red-purple
MV^{++}	Chrysene	White	Yellow-orange
MV^{++}	Perylene	Yellow	Greenish-yellow
MV^{++}	Bibenzyl	White	White

[a] 1–2 ml air saturated solution of PAH in cyclohexane (1E–3 M) was added to a vial containing ~0.2 g 2.5E–5 mol/g MV^{++} adsorbed on silica at room temperature.

[b] Aldrich silica activated (at 200°C for at least 24 h) or non-activated was used for the adsorption of MV^{++}.

polar solvents could be attributed to the ability of these solvents to retain the PAH thereby disabling the less polar silica surface from absorbing these molecules. As a result, no significant amount of PAH can adsorb onto the silica surface rendering electron transfer process highly unlikely. Alternatively, polar solvents can desorb MV^{++} from the silica surface and disrupt electron transfer process. Fig. 5 shows the absorption spectra of the solid phase (silica) immediately after the addition of cyclohexane solution of PAH followed by removal of cyclohexane by filtration. The observed red-shifted bands are assigned to the CT complex of the corresponding PAHs and MV^{++}.

3.2. EPR spectroscopy

To confirm the formation of PAH-derived radicals from PAHs adsorbed on silica we performed EPR measurements on degassed and aerated samples. All the degassed samples showed strong signals consisting of a single line with g values in the range of 2.0032–2.0041 characteristic of free radicals (Fig. 6). The aerated samples on the other hand showed none or an extremely weak EPR signal. An increase in the concentration of PAH on the surface was always accompanied by a rise in the intensity of the EPR signal suggesting that the corresponding radicals were derived from PAH. We assign the observed signals to radical cations ($PAH^{\bullet +}$) of the respective PAHs. Since the samples were protected from light prior to and during the EPR measurements, formation of these radicals seem to be thermally induced in good agreement with previous reports on thermal formation of several PAH radical cations on silica–alumina catalyst [1–9,35]. Recording the spectra at low modulation amplitude (0.33 G) and low (1 mW) and high (up to 20 mW) microwave power, or at low temperature (77 K) did not improve the spectral resolution. Multi-line EPR spectra from several PAHs adsorbed on silica–alumina catalyst have been reported [2,8,35]. In contrast, irradiation (λ_{ex}>350 nm) of MV^{++} adsorbed on silica in vacuo produced a multi-line spectrum with 16 well resolved hyperfine components separated by 1.76–1.95 G and with g=2.0035 (Fig. 7). This

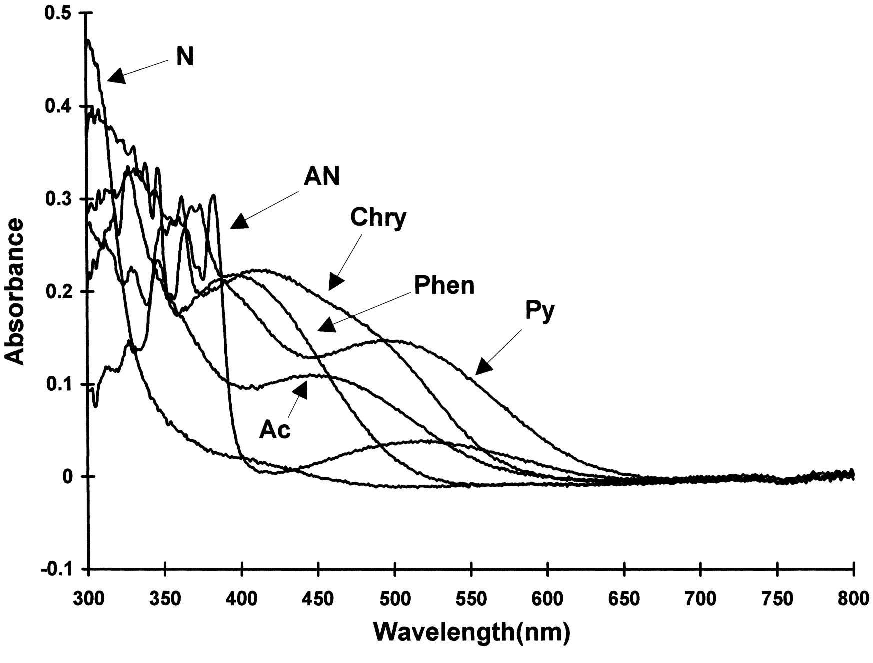

Fig. 5. Absorption spectra of air-saturated acenaphthene/methyl viologen/silica (curve Ac), anthracene/methyl viologen/silica (curve AN), chrysene/methyl viologen/silica (curve Chry), naphthalene/methyl viologen/silica (curve N), phenanthrene/methyl viologen/silica (curve Phen), and pyrene/methyl viologen/silica (curve Py).

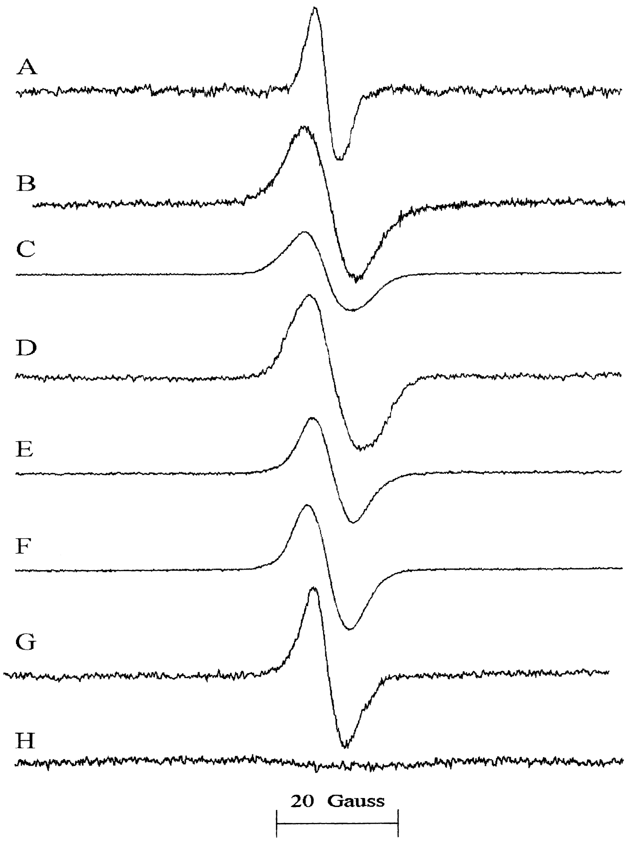

Fig. 6. Room temperature EPR signals from PAHs adsorbed on silica under vacuum. (A) Tetracene (5.5×10^{-6} mol/g), (B) perylene (5×10^{-6} mol/g), (C) anthracene (10^{-5} mol/g), (D) 2-*tert*-butylanthracene (1.1×10^{-6} mol/g), (E) pyrene (2.5×10^{-5} mol/g), (F) chrysene (8.4×10^{-6} mol/g), (G) naphthalene (2.7×10^{-5} mol/g), (H) plain silica. Instrumental settings: microwave power 2 mW, modulation amplitude 1.32 G, receiver gain 2×10^4 (A, D, H), 2.5×10^4 (B), 2×10^3 (C), 5×10^3 (E), 2×10^3 (F), 1.6×10^4 (G). Note: the total amount (in gram) of PAHs/SiO_2 used in this experiment varied from sample to sample.

spectrum is similar to that reported by Thomas et al. [24] for photoinduced reaction of MV^{++} on silica gel surface which was interpreted as a composite of two superimposed signals. One signal with the hyperfine structure was attributed to the methyl viologen radical cation $MV^{\bullet+}$ based on its similarity to the reported spectrum in ethanol [47]. The other, a broad structureless signal with the peak-to-peak line width of ca. 10 G (in our case), was assigned to paramagnetic species derived from holes on silica gel surface or their derivatives [24].

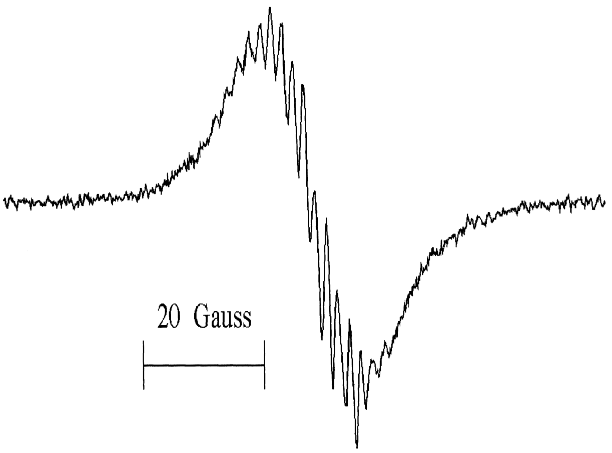

Fig. 7. EPR signal from irradiated (λ_{ex}>350 nm) sample of MV^{++} adsorbed on silica (degassed). Instrumental settings: microwave power 1 mW, modulation amplitude 0.33 G, gain level 2.5×10^4, time constant 0.25 s; scan rate 4 min/100 G.

Air has a profound effect on the intensity of the EPR signals. This is shown in Fig. 8 for perylene, anthracene, and naphthalene. While degassed samples show intense EPR signal (curves A, C, and E; Fig. 8), it is clear that upon exposure to air the signals are either markedly decreased, as in the case of perylene (curve B, Fig. 8) or almost totally diminished, as found for anthracene and naphthalene (curves D and F in Fig. 8, respectively). There are two possible mechanisms that can account for this effect. (a) Oxygen reacts with the $PAH^{\bullet+}$ radical cation (chemical quenching) forming non-paramagnetic products. In this case, the decrease of EPR amplitudes would correspond to the real decrease of radical concentration. (b) Oxygen interacts physically with the radicals causing broadening of the

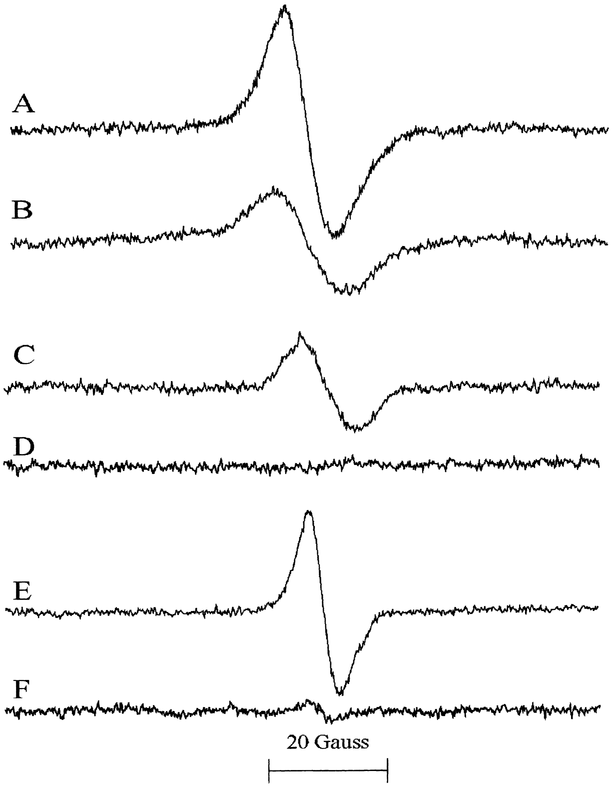

Fig. 8. Comparison of EPR signals for degassed (curves A, C, and E) and aerated (curves B, D, and F) samples of perylene/silica (5×10^{-6} mol/g), anthracene/silica (2.4×10^{-5} mol/g), and naphthalene/silica (2.7×10^{-5} mol/g). Instrumental settings: microwave power 2 mW, modulation amplitude 1.32 G, receiver gain 2.5×10^4 (A–D), 1.6×10^4 (E), and 2×10^4 (F).

EPR signal with a concomitant decrease in the amplitude. This phenomenon has been reported to occur for perylene radical cation on silica–alumina catalyst which produced a 7-line spectrum under degassed conditions [2], but the spectral resolution was gradually lost concomitant with a significant decrease in the signal intensity upon admission of 4.5 mm Hg and 18 mm Hg of oxygen [2]. Apparently, a similar oxygen effect could be responsible for the loss of signal intensity observed by us (Fig. 8). This suggestion is supported by the observation that when perylene/silica sample that had been initially degassed then exposed to air was evacuated again, its original strong EPR signal was recovered (curves A, B, and D in Fig. 9). A similar effect was observed for all the other PAHs studied (not shown).

EPR measurements of our air saturated PAH/silica samples showed no evidence for the presence of superoxide neither at room temperature nor at 77 K. For example, spectrum C in Fig. 9 shows EPR signal from air saturated perylene/silica sample recorded at 77 K. The absence of EPR signal from superoxide may be due to its reaction with PAH at room temperature, when it is initially formed. Superoxide is an extremely strong base and in aprotic environments it could abstract a proton (in this case from PAH or possibly silanols) to form an unstable $^{\bullet}O_2H$ radical which could not be seen without trapping. EPR spectra of superoxide formed by UV irradiation of naphthalene [30] and pyrene [48] on silica in air at 77 K have been reported. The reported photoinduced formation of superoxide involves electron transfer from the excited state of PAH to oxygen which is a more efficient way to produce superoxide than our thermal process that apparently does not generate an EPR detectable concentration of this species.

Fig. 10(A) shows room temperature EPR spectrum of a degassed sample of anthracene/MV^{++} adsorbed on silica (1:20 molar ratio). The good match between this multi-line spectrum and that shown in Fig. 7 for irradiated MV^{++}/SiO_2 is indicative of $MV^{\bullet +}$ radical cation and a second radical species (presumably $PAH^{\bullet +}$ radical cation, although we can not rule out the possibility of a radical species other than that of PAH based on our available data). In contrast, 2-*tert*-butylanthracene/MV^{++} (1:1 molar ratio) adsorbed on silica

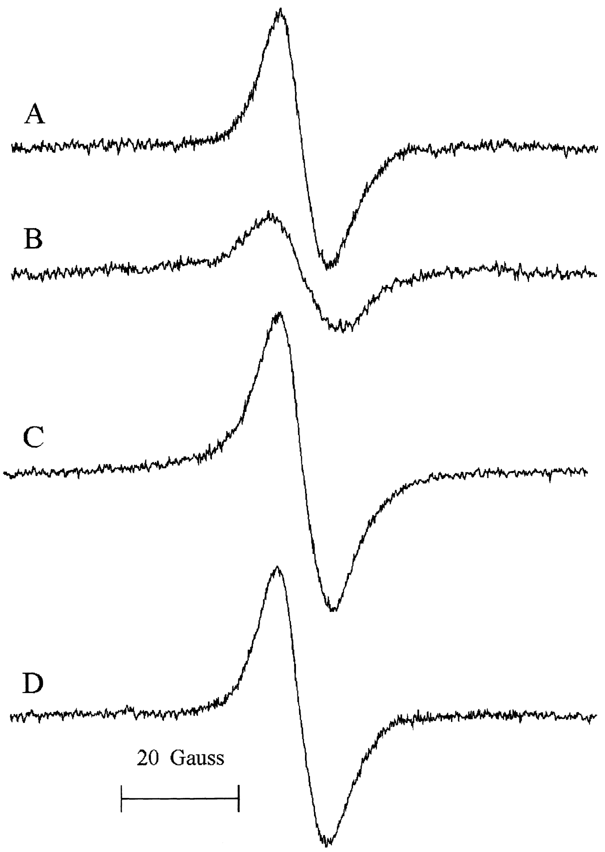

Fig. 9. EPR signals from perylene adsorbed on silica (5E–6 mol/g) for degassed (A), aerated (by admitting air into the degassed sample, curve B), and degassed (the aerated sample was evacuated again, curve D) at room temperature. Spectrum C is the same as B but recorded at 77 K. Instrumental settings: microwave power 2 mW, modulation amplitude 1.32 G (for A, B, and D), 0.165 G (C), receiver gain 2.5×10^4 (for A, B, and D) and 10×10^3 (C).

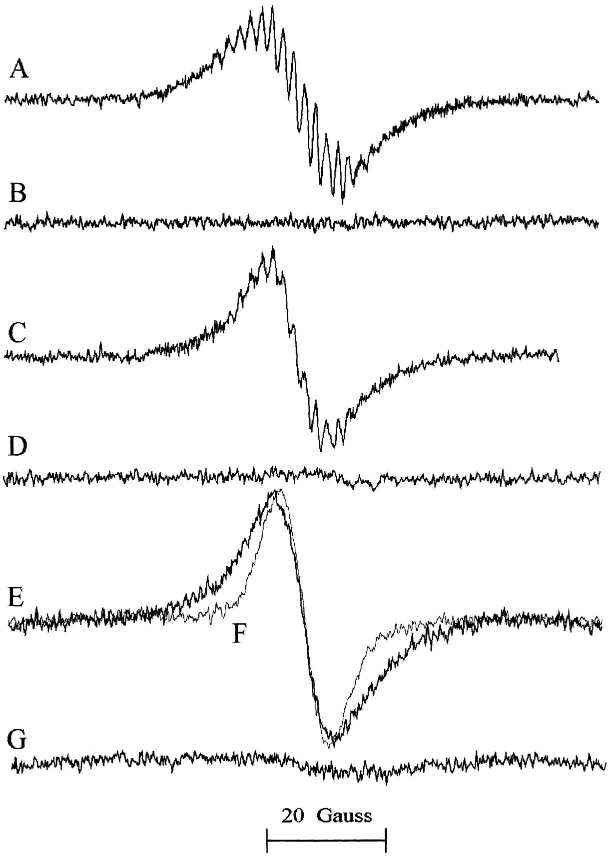

Fig. 10. EPR spectra of different PAHs and MV^{++} adsorbed on silica. (A) Anthracene/MV^{++} (1:20 mole ratio) degassed; (B) same as A after admission of air; (C) *tert*-butylanthracene/MV^{++} (1:1 mole ratio), degassed; (D) same as C after admission of air; (E) perylene/MV^{++} (1:5 mole ratio) degassed; (G) same as E after admission of air; (F) signal from degassed perylene/silica. Instrumental settings: microwave power: 2 mW (A–F), modulation amplitude 0.33 G (A–D), 1.32 G (E, F) receiver gain 2.5×10^4 (A–F), time constant 0.25 s, scan rate 8 min/100 G.

produced a multi-line EPR spectrum (curve C, Fig. 10) whose peak-to-peak line width is less than that of anthracene/MV^{++}/silica or MV^{++}/silica (Fig. 7). The difference between EPR spectra of anthracene/MV^{++}/silica and 2-*tert*-butylanthracene/MV^{++}/silica suggests that $MV^{\bullet +}$ radical cation does not reside as a 'free' molecule on silica surface but rather interacts and is sensitive to the nature of PAH. We believe presence of *tert*-butyl group which imparts asymmetry to the anthracene molecule is responsible for the observed effect [49]. Fig. 10(E) shows EPR spectrum of a degassed perylene/MV^{++} adsorbed on silica (1:5 molar ratio). Because of its low intensity, the signal was recorded at higher modulation amplitude (1.32 G) compared to that used for anthracene/MV^{++}/silica and 2-*tert*-butylanthracene/MV^{++}/silica (curves A and C in Fig. 10), which explains the lack of hyperfine structure. Recording the signal at lower modulation amplitude (0.33 G) improved the resolution but gave rise to a very weak signal (not shown). The presence of the $MV^{\bullet +}$ radical cation in this perylene/MV^{++}/silica system is additionally corroborated by the observation that the signal (curve E, Fig. 10) had different shape and its peak-to-peak line width was larger than that from perylene/silica alone (curve F, Fig. 10). When air was admitted into the samples, the signal immediately disappeared (curves B, D, and G in Fig. 10) consistent with the known fast reaction of $MV^{\bullet +}$ with oxygen. This observation also suggests that the second radical species (either PAH radical cation or another radical species of unknown origin) is sensitive to oxygen as well. Subsequent evacuation of the samples that had been exposed to air recovered the EPR signal (not shown).

4. Conclusion

Silica active sites (formed by aluminum impurity) are shown to be responsible for the formation of the cation radical of adsorbed polycyclic aromatic hydrocarbons. This surface catalyzed electron transfer process is dependent on the one electron oxidation potential of the PAH lending easily oxidizable PAHs more prone to radical cation formation. Oxygen can act as an electron acceptor to intercept the trapped electrons from the active sites. Oxygen also exerts a dramatic effect on the intensity and resolution of EPR signal observed from PAH radical cation. The EPR signal is almost completely diminished in the presence of air, but can be restored by evacuating the sample. This reversible process is consistent with the role of oxygen in signal weakening with no net reaction with the radical cation. In the absence of oxygen, good electron acceptors such as MV^{++} co-adsorbed on the surface can interact with the PAH at the active site to intercept the electron and form a ground-state CT complex. The concentration of ground-state CT complex is reduced significantly in the presence of air suggesting that physisorbed oxygen can serve as a trap for electrons. The observed oxygen effect is likely due to ease of diffusion of gaseous oxygen (compared to MV^{++}) on silica surface to access the adsorbed PAHs at the active sites. The rate of this CT complex formation between PAH and MV^{++} is enhanced dramatically at the solid/liquid interface when non-polar solvents are employed. This fast electron transfer process at the solid/liquid interface (slurry) could be attributed to rapid adsorption of PAH from the non-polar media to more polar silica surface active sites that contain adsorbed MV^{++} residing in the close proximity of these sites.

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