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Photoionization and Electron Transfer of Biphenyl within the Channels of Al-ZSM-5 Zeolites

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There is considerable interest in the use of crystalline aluminosilicate porous materials such as zeolites to study and try to control the photophysical and photochemical properties of the occluded molecules.[1] The ability of zeolites to stabilize radical cations and trap electrons is now firmly established.[2, 3] In contrast, the reverse situation in which zeolites act as electron donors is far less documented.[4, 5] The ZSM-5 zeolites with straight (0.54 × 0.56 nm) and zigzag (0.51 × 0.55 nm) channels have been reported previously to generate radical cations spontaneously and stabilize them in the void space.[6] While the mechanism of oxidation remains unclear today, it appears that the presence of aluminum in the zeolite is a requirement for persistent radical cations. Herein we present our most striking results concerning the photolysis of biphenyl ($C_{12}H_{10}$, BP) occluded at low coverage in nonacidic ZSM-5 zeolites. The emphasis of the paper is mainly set on the photoionization of biphenyl and electron transfer. The zeolite – radical cation – electron interactions have been tuned by varying the silicon:aluminum ratio, by using charge-balancing cations, and without any additional molecules.

Weighted amounts of bisublimated BP (0.5 – 1 BP per unit cell) were mixed with freshly dehydrated $M_n[Al_nSi_{96-n}O_{192}]$ ($M = Na^+$, K^+, Cs^+; $n = 0$, 3, 6) zeolites under an inert atmosphere in a silica cell. The FT-Raman and diffuse reflectance UV/Vis absorption spectra of the mechanical powder mixtures were recorded as a function of time. All the spectroscopic data recorded after the required equilibration period of one month at a gentle temperature (50 °C) are typical of occluded BP at low coverage within the void space. The aluminum content, the extraframework cations M^+, and the cosorbed gas (argon or helium) do not induce dramatic effects upon the molecular conformation of ground state BP (BP(S_0)) as evident from similar vibrational spectroscopic characteristics to that reported previously for BP(S_0) in fluid solution and attributed to a twisted structure.[7] The ground-state absorption electronic spectra of BP occluded at low coverage in ZSM-5 are typical of isolated chromophores.[7]

Molecular mechanics calculations (MM), Monte Carlo simulations (MC), and molecular dynamics calculations (MD) provide evidence of the expected location, the structure as well as the diffusion of BP(S_0) within the void space of the $Na_4[Al_4Si_{92}O_{192}]$ zeolites.[8] The BP(S_0) molecules were found to be located preferentially in the straight channels in the vicinity of the intersection with zigzag channels (Figure 1). The expected site of BP(S_0) in ZSM-5 is in reasonable agreement with preliminary X-ray diffraction data performed at high coverage.[9]

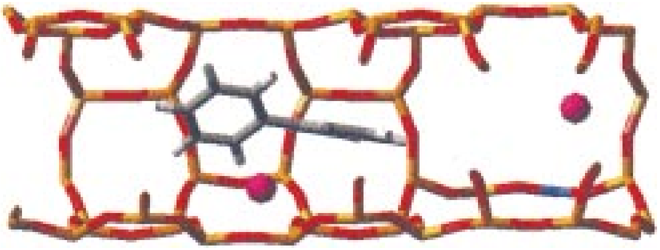

Figure 1. Cross-sectional view of biphenyl (BP, S_0) occluded in the straight channel of $Na_4Si_{92}Al_4O_{192}$ zeolite perpendicular to the b axis. The yellow Si, blue Al, and red O cylinders represent the ZSM-5 framework, the pink balls represent the extra-framework Na^+ cations, the shaded and white cylinders represent the C and H atoms of BP, respectively.

It should be noted that the nearest C ··· Na and C ··· Al distances are found to be 4.66 and 7.1 Å, respectively. From MD simulations data the main role of the zeolite framework appears to be to reduce the mobility of BP within the void space, and the BP(S_0) molecule performs only vibrational, internal rotation, and translational motions in the vicinity of the sorption site.[8]

An excimer laser (248 nm, 15 ns, 0.12 – 30 mJ cm^{-2}) was used as pump excitation within the $S_3 \leftarrow S_0$ ($\pi^* \leftarrow \pi$) transition of occluded BP in $M_n[Al_nSi_{96-n}O_{192}]$. This transition exhibits an intense electronic absorption around 250 nm. Decays in the UV/Vis spectra up to 300 µs were recorded after the laser photolysis of the $1BP/Si_{96}O_{192}$ and $1BP/Na_3[Al_3Si_{93}O_{192}]$ samples by the transient diffuse reflection technique.[10] It should be noted that with the pump excitation power used, no transient spectra were obtained after photolysis of the bare zeolites.

The data processing[11] of the transient spectra provides clear evidence of the pure component spectra and concentrations of the lowest triplet state BP(T_1) (355 nm) and the radical cation $BP^{+\bullet}$ (380, 660 nm) within the experimental pump energy range.[7] No spectral evidence of both the radical anion and trapped electron was found in either $1BP/Si_{96}O_{192}$ or $1BP/Na_3[Al_3Si_{93}O_{192}]$ samples under the experimental conditions used.[7, 8, 12, 13] The short lifetime of BP(T_1) is found to be shorter in $1BP/[Si_{96}O_{192}]$ (3×10^{-7} s) than in $1BP/Na_3[Al_3Si_{93}O_{192}]$ (2.4×10^{-6} s). In contrast, the lifetime of $BP^{+\bullet}$

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in 1BP/$Na_3[Al_3Si_{93}O_{192}]$ (0.8 s) was found to be markedly longer than in 1BP/$Si_{96}O_{192}$ (1.3×10^{-5} s).[12]

The transient species for the time resolved resonance Raman (TR^3) experiments were generated through photolysis at 248 nm (15 ns, 1.4–14 mJ cm^{-2}) and the resonance Raman (RR) scattering of the transient species were excited at 370 nm (8 ns, 21 mJ cm^{-2}). The time delay between the pump and probe pulses can be adjusted from 50 ns to several ms. In these experimental conditions only two transient species were detected, which were unambiguously assigned to BP(T_1) and $BP^{+\bullet}$ (Figure 2). The radical cation $BP^{+\bullet}$ is detected for the samples ($n = 0, 3, 6$; $M = Na^+$) whereas BP(T_1) is detected in high yield for $n = 0$ and only at low pump laser power.

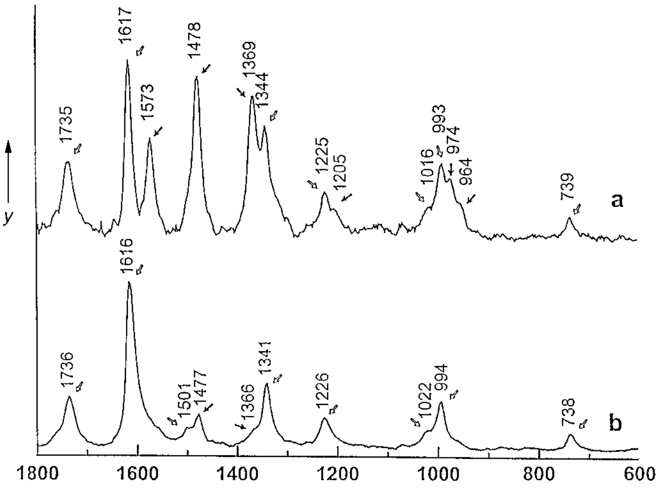

Figure 2. Time-resolved resonance Raman (TR^3) spectra of occluded photoexcited biphenyl (➡BP(T_1), ⇨$BP^{+\bullet}$; pump laser, 248 nm, 15 ns, 4 mJ cm^{-2}; probe laser, 370 nm, 8 ns, 21 mJ cm^{-2}). a) 1 BP/$Si_{96}O_{192}$: spectrum obtained after 50 ns from the photoexcitation. b) 1 BP/$Na_3Si_{93}Al_3O_{192}$: spectrum obtained after 50 ns from the photoexcitation. y = Raman intensity in arbitrary units.

The similarity in wavenumbers as well as in the relative intensities of the signals between the corresponding RR features of BP(T_1) and $BP^{+\bullet}$ in solution and occluded in ZSM-5 zeolites indicates analogous molecular structures in fluid and porous media.[7, 8, 13–16] The BP(T_1) and $BP^{+\bullet}$ populations arise from two independent and parallel processes upon photolysis of BP(S_0) at 248 nm. The dependence of the BP(T_1) and $BP^{+\bullet}$ yields upon pump power indicates that BP(T_1) is the major species at very low power, which suggests that BP(T_1) is produced by a monophotonic process through $S_1 \leftarrow S_3$ internal conversion, followed by $T_1 \leftarrow S_1$ intersystem crossing.[7, 13] The large BP$\cdots$BP intermolecular distance and the slow BP diffusion in the void space are in accurate agreement with the first-order rate of the decays and energy transfer through the lattice. The radical cation $BP^{+\bullet}$ is probably generated through a biphotonic process.

The lifetime of $BP^{+\bullet}$ appears to be dramatically dependent upon a narrow range of aluminum content of the ZSM-5 zeolites. A persistent green color can be seen after laser photolysis at room temperature of 1BP/$M_6[Al_6Si_{90}O_{192}]$ ($M = Na^+, K^+$), namely of zeolites with higher aluminum content. The long lifetimes of $BP^{+\bullet}$ in $M_6[Al_6Si_{90}O_{192}]$ permit the use of conventional spectroscopic techniques with better resolution and sensitivity to monitor the restoration of the BP(S_0) state after photolysis.

The data processing[10] of the diffuse reflectance results (Figure 3) provides evidence of the generation of two species by the photolysis of 1BP/$M_6[Al_6Si_{90}O_{192}]$: $BP^{+\bullet}$ and a trapped electron. The absorption bands around 460 nm were straightforwardly assigned to the trapped electron, while the bands at 370 and 670 nm correspond to $BP^{+\bullet}$.[7, 12] The lifetimes of $BP^{+\bullet}$ and the trapped electron in 1BP/$Na_6[Al_6Si_{90}O_{192}]$ (450, 480 nm) were found to be 17 and 155 min, respectively, while their lifetimes in 1BP/$K_6[Al_6Si_{90}O_{192}]$ (448, 462 nm) were found to be 4 and 44 min, respectively. The UV/Vis spectra recorded two minutes after the photolysis of 1BP/$Cs_6[Al_6Si_{90}O_{192}]$ exhibits only the absorption bands at 470 and 510 nm, which correspond to the trapped electron. The lifetime of $BP^{+\bullet}$, which is assumed to be less than 2 min, appears markedly shorter than the trapped electron in 1BP/$Cs_6[Al_6Si_{90}O_{192}]$-(131 min).[12] Positive holes in the zeolite framework are assumed to counterbalance the negative charge of the trapped electron. The cosorption of O_2 in the 1BP/$Na_6[Al_6Si_{90}O_{192}]$ sample does not change the lifetimes of either $BP^{+\bullet}$ or the trapped electron significantly. So, the expected formation of O_2^- does not occur and the electron trapping site is probably not accessible to O_2.

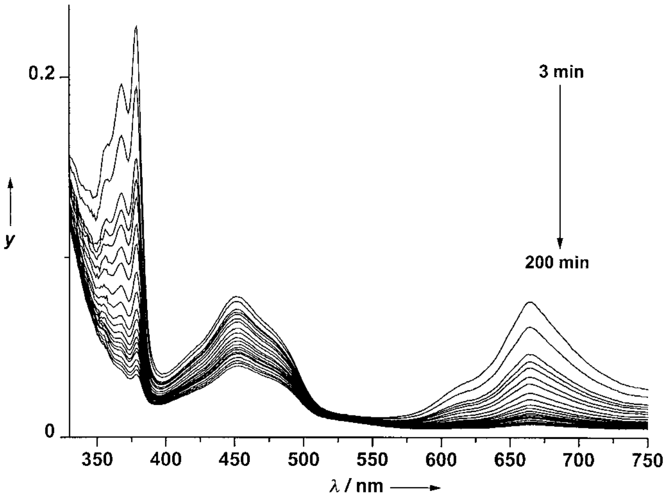

Figure 3. Diffuse reflectance UV/Vis absorption spectra of occluded photoexcited biphenyl: 1 BP/$Na_6Si_{90}Al_6O_{192}$ (photolysis 248 nm, 5 s, 30 mJ cm^{-2}). The spectra were recorded at room temperature from 3 to 200 min after the photolysis. y = reflectance in Kubelka-Munk units.

The EPR spectrum (77 K, Figure 4 a) recorded immediately after irradiation of the 1BP/$Na_6[Al_6Si_{90}O_{192}]$ sample at room temperature under argon consists of a complicated pattern containing the signals of three paramagnetic species: $BP^{+\bullet}$, which corresponds to the seven resolved lines,[17] a trapped electron, and a positive hole. After annealing the sample at room temperature the well resolved lines evolve to the broader remaining signals (77 K) that correspond to both the remaining trapped electron and the positive hole (Figure 4b). The seven resolved lines evolve faster for the irradiated 1BP/$K_6[Al_6Si_{90}O_{192}]$ sample, whereas they are practically absent in

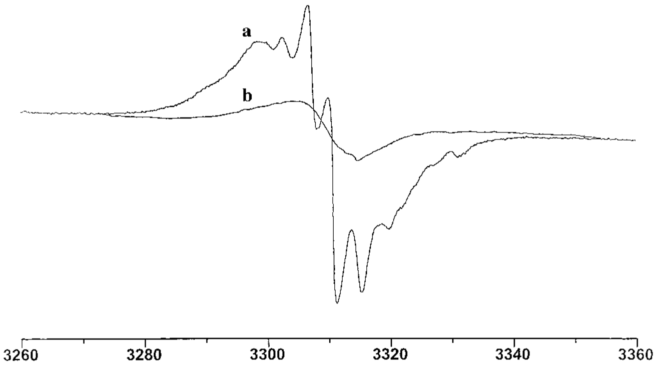

Figure 4. EPR spectra of occluded photoexcited biphenyl : 1BP/$Na_6Si_{90}Al_6O_{192}$ (photolysis 248 nm, 5 s, 30 mJ). a) spectrum obtained at 77 K, 1 min after the photolysis at room temperature; b) Spectrum obtained at 77 K, 1000 min after the photolysis.

the EPR spectra of the $1BP/Cs_6[Al_6Si_{90}O_{192}]$ sample recorded immediately after photolysis at room temperature. None of the EPR spectra exhibit any fine structure that corresponds to electrons trapped as $M_n^{(n-1)+}$ ($M = Na^+, K^+, Cs^+$) metallic clusters.[2, 4]

The presence of 6 Al atoms for 90 Si atoms in the framework and the tight fit of the channels of the ZSM-5 zeolites appears essential to trap the electron and to hinder the recombination with either $BP^{+\bullet}$ or a positive hole. Through the photoionization $BP \rightarrow BP^{+\bullet} + e$, the ejected electron e is trapped by the framework according to Equation (1). The $BP(S_0)$ ground state is then restored through Equation (2), and finally the trapped electron and the positive hole recombine to restore the neutral zeolite [Eq. (3)].

$$BP^{+\bullet}/M_6[Al_6Si_{90}O_{192}] + e \rightarrow BP^{+\bullet}/M_6[Al_6Si_{90}O_{192}]^{-\bullet} \quad (1)$$

$$BP^{+\bullet}/M_6[Al_6Si_{90}O_{192}]^{-\bullet} \rightarrow BP/M_6[Al_6Si_{90}O_{192}]^{-\bullet+\bullet} \quad (2)$$

$$BP/M_6[Al_6Si_{90}O_{192}]^{-\bullet+\bullet} \rightarrow BP/M_6[Al_6Si_{90}O_{192}] \quad (3)$$

It should be noted that the fast direct recombination $BP^{+\bullet} + e \rightarrow BP$ probably occurs in $[Si_{96}O_{192}]$ and $M_3[Al_3Si_{90}O_{192}]$ with lower aluminum content, since no clear evidence of the electronic absorption of the trapped electron was found. The ability of the $M_6[Al_6Si_{90}O_{192}]^{-\bullet}$ zeolite to provide one electron to $BP^{+\bullet}$ appears to increase from Na^+ to Cs^+ and is in relation with the basic character of the oxygen atoms of the framework. Unfortunately, no definitive evidence of the electron trapping site as well as the positive hole site in the zeolite is provided in the present work. However, it is clear that the electron is captured by the ZSM-5 framework by using the Lewis acid character of the aluminum atoms. In spite of the fact that the zeolite has captured an electron, the $M_6[Al_6Si_{90}O_{192}]^{-\bullet}$ framework can provide another electron to occluded $BP^{+\bullet}$ to restore BP in $M_6[Al_6Si_{90}O_{192}]^{-\bullet+\bullet}$ and the coexistence of both trapped electrons and positive holes remain for a long time in the ZSM-5 framework at room temperature. Radiolysis or electron irradiation of bare ZSM-5 with low aluminum content do not provide stable electron-hole pairs,[18] whereas intense and energetic irradiation of bare faujasitic zeolites such as $Na_{56}[Si_{136}Al_{56}O_{384}]$ generates relatively stable positive holes and trapped electrons as extra-framework $Na_n^{(n-1)+}$ clusters.[19]

Experimental Section

The sodium-exchanged ZSM5 samples (Si/Al = 13, 25) were obtained from VAW aluminium (Schwandorf, Germany) and the silicalite-1 sample was a gift from Dr J. Patarin (ESA-CNRS 7015, Mulhouse, France). The unit cell compositions of the calcined and dehydrated M_nZSM-5 were found to be $Si_{96}O_{192}$, $Na_3Si_{93}Al_3O_{192}$, and $Na_6Si_{90}Al_6O_{192}$ from elemental analysis. Exchanged $K_6Si_{90}Al_6O_{192}$ and $Cs_6Si_{90}Al_6O_{192}$ were obtained and characterized as previously described. The carefully calcined and deoxygenated M_nZSM-5 zeolites were transferred into a quartz cell connected to vacuum and gas lines. Weighted amounts of bisublimated BP corresponding to one BP molecule per unit cell were introduced into the cell under dry Ar and shaken. After four weeks at 50°C the samples were found to be fully equilibrated samples. A Bruker IFS 88W instrument was used as a near-IR FT-Raman spectrometer in the 3500–150 cm^{-1} wavenumber range. A Nd:YAG laser with an output at 1064 nm was applied for the excitation. The diffuse reflectance spectra were recorded between 200 and 900 nm with a Cary 3 spectrometer equipped with an integrating sphere, and with the corresponding empty dehydrated zeolite as the reference. The EPR spectra of the X-band were recorded on a Varian E109 spectrometer at both room and liquid-nitrogen temperature.

The detailed experimental set-up for time-resolved diffuse reflectance measurements has been given previously.[10] It included an excimer laser as pump source and a pulsed xenon lamp as the probe source. The time-resolved diffuse reflectance data were described by $1 - R_t$, where R_t is the ratio of reflectivity with and without laser excitation. The detailed experimental set-up for TR^3 pump-probe system has been given previously.[8] It included an excimer laser for the pump excitation and a Nd:YAG laser system for the probe pulse. The data processing were carried out with the SIMPLISMA program.[11] The SIMPLISMA approach is a tool for self-modeling mixture analysis, which means that it resolves mixture data into pure component UV/Vis spectra and concentrations, without using prior information about the mixtures. The lifetimes of the transient species are derived from the analysis of the UV/Vis decays by using the Albery function based on a small number of parameters: $\bar{k}$ the average first-order rate constant of the transient species and γ the width of the distribution.[12] The modeling results published herewith were generated with the program $Cerius^2$ developed by Molecular Simulations Incorporated. The details of the calculations are analogous to that reported previously for other aromatics occluded in zeolites.[8]

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