Surface Photochemistry: Benzophenone as a Probe for the Study of Silica and Reversed Phase Silica Surfaces

In this Lifetime Distribution Analysis model, it is assumed that the lifetimes distribution of an excited probe adsorbed on a heterogeneous, porous substrate is a consequence of a distribution of ΔG^0 of activation for the probe adsorption on the substrate around a mean value $\overline{\Delta G^0}$:

$$\Delta G^0 = \overline{\Delta G^0} - \gamma x RT \qquad \textbf{(1)}$$

or, in terms of first rate constant, *k*:

$$\ln(k) = \ln(\overline{k}) - \gamma x \quad \Rightarrow \qquad k = (\overline{k})\exp(-\gamma x) \qquad \textbf{(2)}$$

where γ is a measure of the distribution width (half full width at maximum×exp(-1)). The distribution function is a sum of symmetrical or asymmetrical Voigt profiles – Gaussian-Lorentzian products – defined in Equation 3:

$$\alpha\left(\ln\left(\mathrm{k_j}\right)\right) = \sum_{\mathrm{i}} \frac{\alpha_{\max \mathrm{i}} \exp\left(-\left(1-\mathrm{m_i}\right)\left(\ln(\mathrm{k_j}) - \ln(\overline{\mathrm{k_i}})\right)^2 \ln(2)/\left(\mathrm{a_i L_i}/2\right)^2\right)}{1+\mathrm{m_i}\left(\ln(\mathrm{k_j}) - \ln(\overline{\mathrm{k_i}})\right)^2/\left(\mathrm{a_i L_i}/2\right)^2} \qquad \textbf{(3)}$$

where α (ln(k_j)) is the relative weight of k_j in the total distribution, $\overline{k}_i$ is the position of the maximum of profile *i*, $\alpha_{\max i}$ is its maximum, L_i is its full width at half maximum (fwhm), m_i is the Lorentzian weight in the profile *i* (m_i =1 corresponds to a pure lorentzian and m_i =0 corresponds to a pure gaussian), and a_i is the asymmetry factor taking the value 1 for $k_j \geq \overline{k}_i$ and a value ≥0 for $k_j < \overline{k}_i$.

The decay curve will, then, be given by:

$$\mathrm{I(t)} = \sum_{\mathrm{j}} \alpha(\ln(\mathrm{k_j}))\exp(-\mathrm{k_j t}) \qquad (4)$$

or, in terms of normalized intensity:

$$\frac{I(t)}{I(0)} = \frac{\sum_j \alpha(\ln(k_j))\exp(-k_j t)}{\sum_j \alpha(\ln(k_j))} \qquad (5)$$

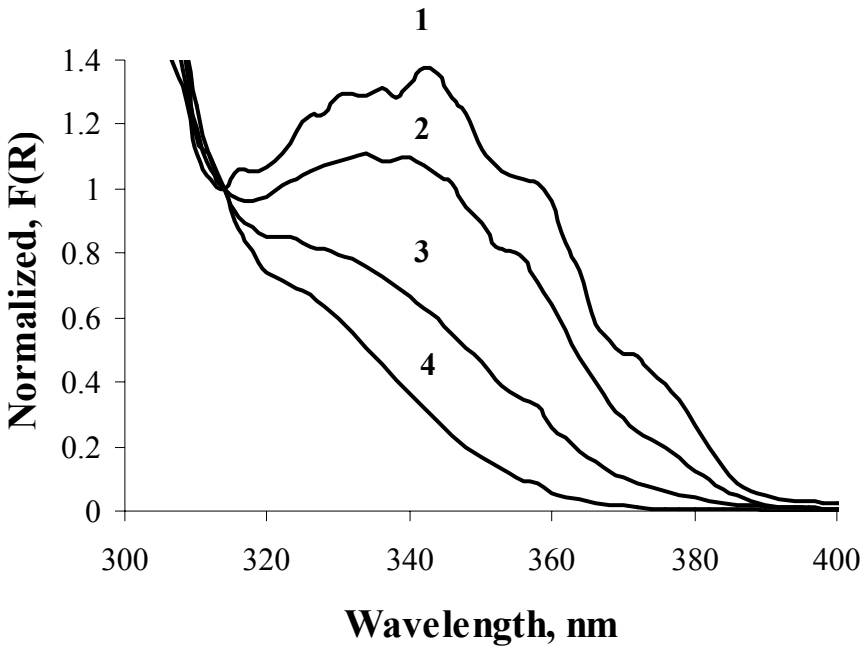

Fig. S1

Remission functions for BZP / host samples (n → π* transition only) with 250 μmol of the probe per gram of the substrate. Curve 1: Silicalite; 2: reversed-phase silica RP-18; 3: RP-8; 4: 60 Å Silica.

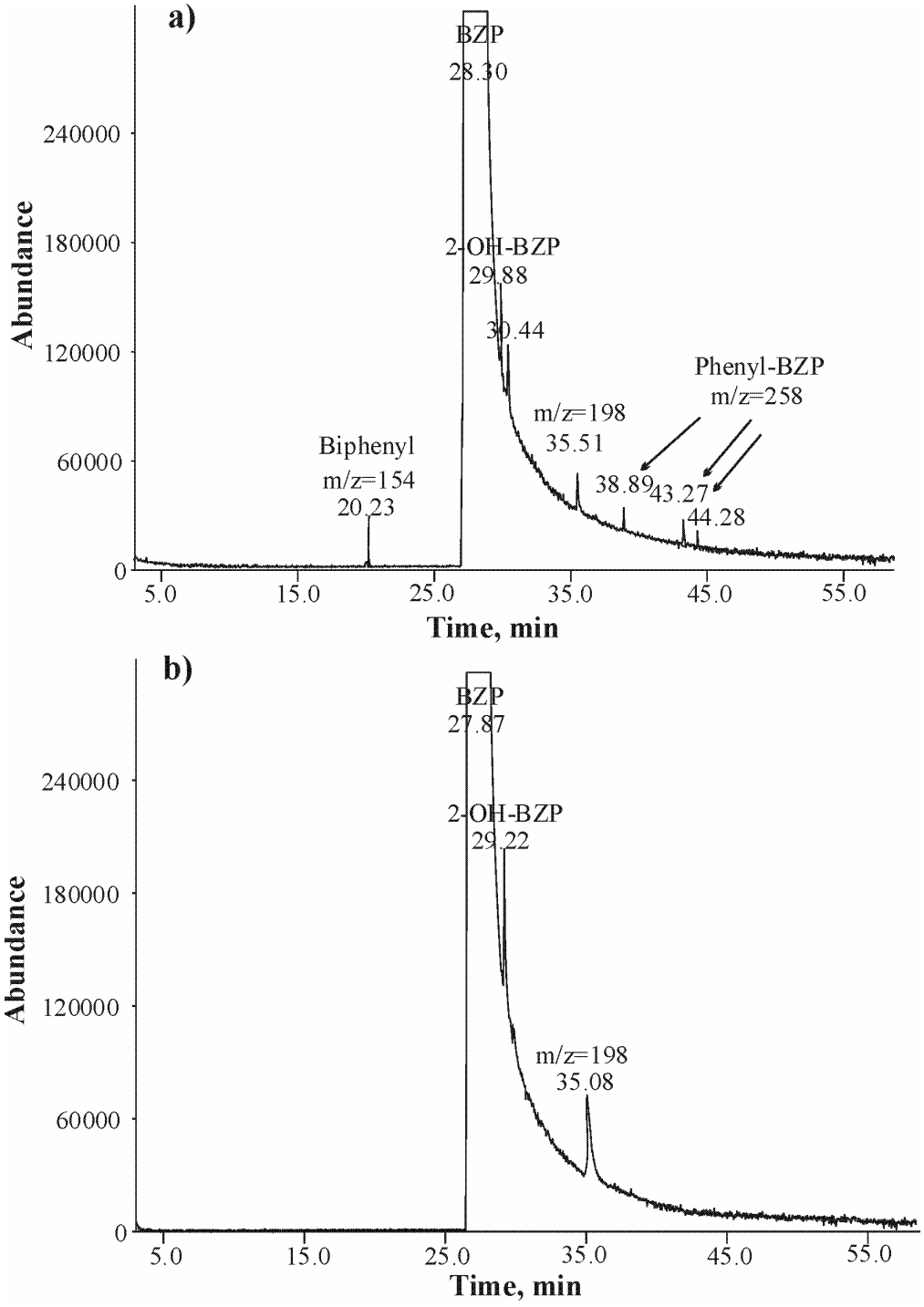

Fig. S2 – Chromatographic results (GC-MS) of the extracts of benzophenone adsorbed onto 60 Å pore silica, with: a) 266 nm excitation and b) 355 nm excitation.