Surface-Radical Mobility Test by Self-Sorted Recombination: Symmetrical Product upon Recombination (SPR)

Sarah J. Belh, Goutam Ghosh, and Alexander Greer*

ABSTRACT: We describe here a study of the mobility of the alkoxy radical on a surface by detection of its recombination product. A novel method called symmetrical product recombination (SPR) uses an unsymmetrical peroxide that upon sensitized homolysis recombines to a symmetrical product \[ \text{R'OOR} \rightarrow \text{R'O}^{*} + \text{OR} \rightarrow \text{ROOR} \]. This allows for self-sorting of the radical to enhance the recombination path to a symmetrical product, which has been used to deduce surface migratory aptitude. SPR also provides a new opportunity for mechanistic studies of interfacial radicals, including monitoring competition between radical recombination versus surface hydrogen abstraction. This is an approach that might work for other surface-borne radicals on natural and artificial particles.

INTRODUCTION

Nanoparticle surfaces can have advantages over homogeneous solution for the control of radical reactions. For example, surfaces may be tuned to selective reactions by controlling radical mobility. However, mechanistic studies on surface-bound radicals, such as alkoxy radicals, are still challenging. While such information is typically found with EPR trapping and \(^{31}\)P NMR spectroscopy, expanding on methods to measure the radical migratory aptitude is an area in need of research. Here, we report a symmetrical product recombination (SPR) method that allows determination of the alkoxy radical surface mobility by a symmetrical product from an unsymmetrical substrate \[ \text{R'OOR} \rightarrow \text{R'O}^{*} + \text{OR} \rightarrow \text{ROOR} \] (Figure 1). This approach is demonstrated here for alkoxy radicals but might also work for other radicals.

Radicals can form on artificial and natural surfaces. Some environmental reactions take place with particulate formation of persistent radicals. Thus, developing a trapping system that can assess surface migration is desirable.

Researchers have developed various methods for monitoring radical reactions on surfaces. One method is EPR spectroscopy, analyzing the hyperfine tensor for the interaction between the radical and the surrounding magnetic nuclei. A second approach is theoretical; for example, a \( \text{H}_2\text{Si}^{*} \) diffusion activation barrier on silicon was found to be 3.7 kcal/mol by DFT and MD simulations. A third approach is the use of \(^{31}\)P NMR spectroscopy with phosphite traps due to their oxophilicity to trap alkoxy radicals. In the third approach, alkoxy radicals on silica nanoparticles were trapped by phosphites to form phosphates. In the present article, the SPR method can help to advance the field to deduce the migratory aptitude of radicals on a particle surface.

Figure 1. Schematic of alkoxy radical migration on a nanoparticle \[ \text{R} = \text{C(}\text{Me}_2\text{)}\text{Ph}; \text{R'} = \text{Et} \]. Radical production is via cumylethyl peroxide’s photosensitized O=O homolysis, including alkoxy radical migration, and formation of a symmetrical ROOR product. Symmetrical ROOR product formation is favored, whereas chain propagation processes, for example, H-atom transfer, are disfavored.

Received: February 5, 2021
Revised: March 18, 2021
Published: April 15, 2021
A mechanism is proposed in Figure 2, in which photosensitization triggers the unsymmetrical peroxide 2 to homolyze, with the higher molecular weight PhC(Me)3O• radical of the pair remaining adsorbed and thus generating a symmetrical peroxide 3 to monitor. This supports a mechanistic hypothesis that radical recombination is detected from PhC(Me)3O• radical pairing on the nanoparticle surface. Further, it shows that the product signal is symmetry increased for 1H NMR spectroscopy and not obscured by chain propagation products, as is often seen in a homogeneous solution. The SPR method that we developed can potentially be used in combination with EPR methods for better insight into the mobility and reactions of radicals on surfaces.

### RESULTS AND DISCUSSION

#### Products of the Reaction.

Nanoparticles coadsorbed with 4,4′-dimethylbenzil (sensitizer 1) and cumylethyl peroxide 2 were irradiated with (280 < λ < 700 nm) light in a N2-degassed glass vessel. Five products were detected in the photoreaction (Table 1). The products were dicumyl peroxide 3, cumyl alcohol 4, and acetophenone 5, as detected by HPLC upon desorbing products from the nanoparticle surface. Ethanol 6 and methane 7 can be detected by 1H NMR spectroscopy when analyzing the headspace or in a solution-phase photoreaction containing dissolved sensitizer 1 and cumylethyl peroxide 2. Diethyl peroxide 8 was not detected with our HPLC and 1H NMR spectroscopic analyses. Reversible dimerization from primary products 3 and 8 does not yield 2 in high yields, apparently because the EtO• is sufficiently volatile to disconnect from the surface. The reaction allows for a radical mobility test because it forms the bilaterally symmetrical dicumyl peroxide 3 from recombination of cumylethoxy radicals. This is somewhat reminiscent to bilaterally symmetric 1,2-di-p-tolylyl methane and 1,2-bis(4-methoxyphenyl)-ethane from the radical combination of p-xylene radical and 1-methoxy-4-methylbenzene radical, respectively, in the photolysis of silica-adsorbed 1-(4-methylphenyl)-3-(4-methoxyphenyl)-2-propanone.21

#### Radical Mobility Test.

Here, sensitizer 1 was used to homolyze 2, where we use radical recombination to symmetrical product 3 as a test for radical mobility on the nanoparticle surface. Equation 1 shows the calculated number of 1 or 2 molecules adsorbed on the particle surface using Avogadro’s number (Nₐ). Equation 2 shows the average relative yields of dicumyl peroxide 3, cumyl alcohol 4, acetophenone 5, ethanol 6, and methane 7.

#### Table 1. Product Distribution (%) for the Sensitized Homolysis of Cumylethyl Peroxide 2 That Generates Oxygen- and Carbon-Centered Radicals and Stable Products

<table>
<thead>
<tr>
<th>entry</th>
<th>peroxide 2 adsorbed (µmol/g)</th>
<th>conditions A</th>
<th>conditions B</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>dicumyl peroxide 3</td>
<td>cumyl alcohol 4</td>
</tr>
<tr>
<td>1</td>
<td>108</td>
<td>25.2 ± 0.8</td>
<td>12.7 ± 0.1</td>
</tr>
<tr>
<td>2</td>
<td>53.2</td>
<td>18.2 ± 1.0</td>
<td>14.9 ± 0.1</td>
</tr>
<tr>
<td>3</td>
<td>27.1</td>
<td>11.8 ± 0.8</td>
<td>15.9 ± 0.2</td>
</tr>
<tr>
<td>4</td>
<td>13.4</td>
<td>9.8 ± 0.6</td>
<td>14.9 ± 0.4</td>
</tr>
<tr>
<td>5</td>
<td>6.78</td>
<td>4.0 ± 2.4</td>
<td>13.2 ± 1.6</td>
</tr>
</tbody>
</table>

4,4′-dimethylbenzil (sensitizer 1) (330 µmol/g silica) with (280 < λ < 700 nm) light was carried out in the presence of cumylethyl peroxide 2 coadsorbed on particles. Relative yields determined by HPLC or 1H NMR spectroscopy and based on their integrated peak area without the use of an external standard. Relative yields of product at the air/solid interface relative to solution-phase conditions. Condition A: air/solid interface. Condition B: homogeneous photoreaction of sensitizer 1 (0.01 mM) and peroxide 2 (0.1 mM) in acetonitrile-d₃ irradiated in an NMR tube. Experimental error in condition B is ±5%. Control photoreaction of cumylethyl peroxide 2 (108 µmol/g) with (280 < λ < 700 nm) light in the absence of sensitizer 1 led to ~0.002% peroxide 3.
Further, occupation of sites by sensitizer molecules is calculated to be negligible, where the 2 to 2 distances decrease by 0.027 nm for 108 μmol 2/g nanoparticle and by <0.001 nm for 6.78 μmol 2/g nanoparticle. Equation 3 is used in conjunction with eq 2 to deduce the radical migration distance on the nanoparticles and not based on a recalculated yield of 3. Equation 4 shows the calculation for the percent particle coverage of 1 or 2. Cumuloyl radicals were generated and recombined to 3 in amounts ranging from a high of 25.2% to a low of 4.0% yield (Table 1, entries 1 and 5). This led to the calculated surface migration distance of cumuloyl radical on a nanoparticle of 0.27 nm up to a maximum of 2.9 nm (Figure 3). The selectivity is not caused by heating of the reaction. The nanoparticle photoreactions were carried out at 26 °C. During the photolysis, the particles increased in temperature by ~10 °C. This temperature rise is insufficient to cause the thermolysis of 2 or 3 based on control reactions, where thermolysis temperatures of 130 °C would have been required.22 A weaker peroxide, benzoyl peroxide, requires heating above 80 °C to split into benzoyl radicals, which in turn form phenyl radicals and CO2.23 Next, we compute the difference in the O–O bond strength of 2 relative to 3 to help rationalize the selectivity for the high yield of product 3.

\[
\text{molecules of 1 or 2} = (\text{moles of 1 or 2}) \times N_k
\]

\[
\text{molecule to molecule distance (nm)} = \sqrt{\frac{\text{particle surface area (nm}^2/\text{g)}}{\text{molecules of 1 or 2}}}
\]

\[
\text{radical migration distance (nm)} = \frac{2 \text{ to 2 distance (nm)}}{2} - 2 \text{ length (nm)}
\]

Figure 3. Correlation of dicumyl peroxide 3 with cumuloyl radical migration distance on the nanoparticles that arose by the sensitized homolysis of 2.

percent particle coverage of 1 or 2

\[
= \frac{\text{moles of 1 or 2/g}}{\text{SiOH groups (moles)/g}}
\]

Radical “Self-Sorting”. Unrestricted M06-2X/6-31G(d,p) calculations are used to help explain the selective formation of the O–O bond in dicumyl peroxide 3. The DFT method employed here is found to reproduce the experimental O–O bond dissociation energies of the organic peroxides.24 Our DFT study was designed to assess the geometries and bonding based on the influence the PhC(Me)2 and Et groups impart on peroxides 2, 3, and 8 and radicals PhC(Me)2O* and EndO* and also rationalize possible interfacial effects. While calculations of the surface energies were not carried out, our experimental results of preferred H transfer to PhC(Me)2O* and H-atom loss from EtO* provide a degree of justification for our use of DFT gas-phase calculations in modeling the surface process, as we will see.

Peroxides 2, 3, and 8 and their corresponding alkoxy radicals PhC(Me)2O* and EndO* were optimized to minima. The calculated torsion angle \(\theta\) (C–O–O–C) of 3 is increased (178.0°) when compared to that of 2 (124.8°) and 8 (109.9°). As the size of the substituent of the peroxide increases (8 < 2 < 3), rotation about this torsion \(\theta\) energy is increased, as we will see. To explore the energy associated with rotation around the \(\theta\) torsion angle, minima and transition structures (TS) were located on the potential energy surface. Rotation around the \(\theta\) torsion angle among the gauche and anti geometries changed the energy by 3.5 kcal/mol (for 3 though 28.0 kcal/mol for 8). The larger PhC(Me)2 substituent at the O–O bond increases the activation barrier that yields full rotation. The energy for rotating the \(\theta\) torsion angle where it adopts a syn geometry was large, 28.0 kcal/mol for 3 (due to destabilizing PhC(Me)2/PhC(Me)2 interactions), whereas the TS is 19.3 kcal/mol for 2 (due to modestly destabilizing PhC(Me)2/Et interactions) and even less at 11.2 kcal/mol for the TS of 8 (due to less destabilizing Et/Et interactions). The substituent effects that influence the structures can also influence the bond energies.

Thus, next we investigated the energetics for O–O bond homolysis. The O–O bond in peroxides is weak due in part to electronic repulsion of the lone pairs on the adjacent oxygen atoms. The \(\pi\) MO is strong between the two oxygen atoms, and the antibonding \(\pi^*\) is destabilizing. Endothermocities increases for 3 (due to a stronger O–O) than in 2 and 8. The endothermicity of 3 relative to 2 PhC(Me)2O* (39.2 kcal/mol) is greater than that of PhC(Me)2OOEt relative to PhC(Me)2O* and EndO* (37.4 kcal/mol) and EtOOEt 8 relative to 2 EndO* (37.6 kcal/mol). The presence of electron delocalization of 3 may explain its greater stability than peroxides 2 and 8 with one or two ethyl groups. It has been noted in the literature that substituting the R group Et for Ph (a slightly electron-withdrawing group)25 in Me3CO–OC(Me)2R leads to a 0.1 kcal/mol stabilization of the peroxide bond.26 Similarly, substituting the R group Et for CF3 (the latter is a strong EWG) in RO–OR leads to a 15.9 kcal/mol stabilization of the peroxide bond.26,27 Also, substituting the p-X-substituent (X = MeO for NO2) in p-X–C6H4–C(Me)2O–OEt leads to a 0.4 kcal/mol stabilization of the peroxide bond.26 Further details underlying the stabilities of peroxides have been recently rationalized in detail.28
Table 2. Radical Ionization Potential (IP), Electron Affinity (EA), and H Abstraction

<table>
<thead>
<tr>
<th>radical</th>
<th>electronegativity (IP + EA)/2 (eV)</th>
<th>H abstraction</th>
<th>comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhC(Me)₂O⁺</td>
<td>4.49</td>
<td>only H loss observed</td>
<td>observed</td>
</tr>
<tr>
<td>EtO⁺</td>
<td>5.72</td>
<td>only H loss observed</td>
<td>not observed</td>
</tr>
<tr>
<td>Me⁺</td>
<td>5.65</td>
<td>more H abstraction than EtO⁺ but less than PhC(Me)₂O⁺</td>
<td>observed</td>
</tr>
<tr>
<td>(HO)₃SiO⁺</td>
<td>5.08</td>
<td>predicted greater than Et⁺ and less than PhC(Me)₂O⁺</td>
<td></td>
</tr>
</tbody>
</table>

“Model for surface siloxy radical.

The above computed data suggest the self-sorting capacity with a higher thermal O–O bond energy in 3 than that in 2 or 8 is complementary to volatility in terms of binding affinity and selective binding, namely, dicycium peroxide 3 is adsorbed more tightly to the particle surface than 2 and 8 due to its two phenyl rings. Our computed results show that formation of a OH···π bond between (HO)₃SiOH and benzene in the gas phase is 6.0 kcal/mol and has a perpendicular orientation to the plane of the aromatic ring, at the point of plane interaction by a lengthened O–H bond. The DFT prediction is that the phenyls of PhC(Me)₂O⁺, 2, and 3 are bonded in a π-hydrogen bond to the surface SiOH groups, which has been confirmed experimentally for naphthalene.29 This is known to be stabilizing with a decreased HOMO–LUMO energy gap and an increased dipole moment. These π-hydrogen bonds are often comparable in strength to conventional H bonding.30–32

Our DFT results indicate that the EtO⁺ is weakly bonded to the SiOH group. We suggest that the SiOH···π (aromatic ring) hydrogen bonding will increase the adsorption energy, which along with the increased molecular weight underlie the lower volatilization of PhC(Me)₂O⁺ compared to EtO⁺, thereby facilitating self-sorting to reach 3. The RO⁺ OR binding process was shown to be barrierless, while the desorptive volatility process has a barrier of ∼2 kcal/mol for low molecular weight compounds. However, what about the competition with H abstraction?

Radical H-Atom Abstraction. The radicals can abstract H atoms from the SiOH groups or the adsorbed water on the nanoparticle surface. Here, we draw on a relationship between the electronegativity of radicals and whether they abstract H or dimerize, a concept borrowed in a different vein to the context of H abstraction versus alkene addition.33–36 Table 2 shows that the electronegativity can be used to assess the paths of radicals as measured by calculation of (IP + EA)/2. PhC(Me)₂O⁺ and (MeO)₃SiO⁺ are relatively electropositive radicals that are expected to abstract H. On the other hand, as the electronegativity of EtO⁺ and Me⁺ increases, the H-abstraction ability is predicted to increase, whereas their higher volatility must still play a major role in their fate.

The electronegativity of PhC(Me)₂O⁺ relative to EtO⁺ is greater, where H abstraction is observed experimentally in the former but not latter. This can be compared to the literature,37 where more electronegative t-BuO⁺ favors H abstraction compared to MeO⁺. In our series, the less electronegative radical, EtO⁺, does not give recombination or abstraction but instead only loss of Me⁺. Demethylation can be accomplished by alkoxyl radical structures bearing flanking methyl groups. A previous report with UM06-2X calculations also showed that methyl radical elimination is the main dissociation mechanism for peroxides after O−O bond cleavage.38 The Me⁺ proceeds by H abstraction to form CH₄. We find that PhC(Me)₂O⁺ abstracts a hydrogen from SiOH on the particle surface.

A secondary reaction between SiO⁺ and PhC(Me)₂O⁺ to form SiOOC(Me)₂Ph is possible but was not discerned. EtO⁺ and Me⁺ are noted, as our trapping does not address the problem of direct detection that follows the radicals themselves on and off the surface. We assumed a facile volatility and transit off of the surface, whereas CH₄ increases in the surrounding medium over time. Adsorption of EtO⁺ is lower than adsorption PhC(Me)₂O⁺; otherwise, there would have been dimerization to reach 8, which is not observed.

A comparison of the DFT-calculated energy difference between the alkoxy radicals and the corresponding siloxy radical species is instructive. A comparison of the calculated energy difference between the H bonding of the alkoxy radical and the alcohol systems is shown in Figure 4. Notice that the

Figure 4. Calculated energy difference between H-bonded isomers.

RO⁺···HOSi(OH)₃ hydrogen bonding is stronger by 13.7–13.9 kcal/mol compared to the ROH⁺···OSi(OH)₃ hydrogen bonding (cf. I and III with II and IV). There are also similar stabilizing effects for H-bonding arrangements of EtO⁺···HOSi(OH)₃ (−8.4 kcal/mol) and PhC(Me)₂O⁺···HOSi(OH)₃ (−10.3 kcal/mol) compared to their separated species, respectively, although the PhC(Me)₂O⁺ forms a slightly more stable H bond than EtO⁺ with HOSi(OH)₃. The related H-atom transfer of surface SiOH groups is similarly not expected to proceed at any significant rate.

From a hydrogen-bonding point of view, cumyloxy radical is a candidate for both SiOH···(p)PhC(Me)₂O⁺ and PhC-(Me)₂O⁺···HOSi(OH)₃ hydrogen bonding. As has been reported, the silanol groups or silanols occupied with water can bind to naphthalene by p···HOSi bonding.29 Similarly, alkoxyl radicals can form a weak RO⁺···HOR hydrogen bond to alcohols, although the activation energy for H-atom transfer is high,39–41 which is consistent with our DFT results.

Similar to the H-abstraction analysis in Figure 4 and Table 2, the reactions were analyzed with mathematical deductions on the particle surface. What we deduce next is a facet inhibiting
radical recombination to form the symmetrical product 3, where radicals can abstract an H atom from the SiOH group (or adsorbed water) on the particle surface. Equation 5 shows the calculated number of silanol groups per gram using the known surface area (200 m²/g) and the known 4 SiOH/nm² of silica. Equation 6 uses Avogadro’s number (Nₐ) in the conversion of the number of silanol groups per gram of silica found using eq 4 to moles of silanol per gram. The presence of SiOH groups attenuates cumyloxy radical migration due to H-abstraction reactivity, as we will see next.

\[
\text{SiOH groups per gram particle} = \frac{\text{surface area} (\text{m}^2/\text{g}) \times (\text{silanol groups present}/\text{m}^3)}{N_a} \tag{5}
\]

\[
\text{SiOH groups (moles)/grams of particle} = \frac{\text{number of SiOH groups/grams of particle}}{N_a} \tag{6}
\]

Figure 5 shows that the cumyloxy radical can bypass 2–3 SiOH groups before H abstraction becomes competitive. After

\[
\frac{\text{max. SiOH groups bypassed by the cumyloxy radical}}{\text{max. SiOH groups bypassed by the cumyloxy radical}} = \frac{\text{radical migration distance} \times \text{radical length} \times 4}{\text{SiOH per nm}^2} \tag{7}
\]

at high loadings of 2. Surface SiOH groups to propagate silicate-type SiO* radicals are minimal; otherwise, the diffusion distances would have been 0.5 nm given the distance between the SiOH groups on the surface. A lower loading of 2 was used in the photoreaction, where it seems possible that the SiOH position is sterically hindered by the surface of the nanoparticle itself. Polymer studies have provided information on the cumyloxy radical H-atom abstraction limited by steric hindrance imposed from the methyl substituents on the secondary positions within poly(propylene) and poly(isobutylene).47

We find a relationship between the migration distance of the cumyloxy radical and its tendency to dimerize or abstract a hydrogen atom from the surface. Cumyloxy radical gives recombination in a 2:1 preference to abstraction at a high loading of 2 (entry 1). On the other hand, when the loading of 2 decreases (entry 5), H abstraction is observed in an elevated 3:3:1 preference over recombination. These ratios are measured by the relative yields of 3 and 4. The acetophenone 5 product is also observed by cumyloxy radical’s loss of Me*.

The products from volatile radicals Me* and EtO* were difficult to quantitate. Me* can abstract a H atom and be detected as CH₃CHO. Despite their volatility, detection in a solution-phase reaction (condition B) was more accessible than in the headspace of an air/particle reaction (condition A), as seen in Table 1.

The cumyloxy radical migration on a silica surface is rationalized because of the relatively low H-bonding strength to the surface. For example, the experimental diffusional activation energy was reported to be 1.9 kcal/mol for 2,2,6,6-tetramethylpiperidine-1-oxyl radical from hydrogen bonding to the surface SiOH.42 In passing, we also mention a report on longitudinal-field muon spin relaxation showing the diffusion activation energy to be 2.6 kcal/mol for the *CCl₂CH₃ radical due to association to the surface SiOH.33

**Mechanism.** Upon excitation, nanoparticle-adsorbed 1 transfers energy to the O=O bond of 2 resulting in its homolysis. Our previous work suggested this to be a Dexter (triplet) energy transfer process. In the present work, we found the following. (i) The higher the percent the nanoparticle was loaded with 2, a greater amount of 3 was formed selectively by radical recombination. (ii) The cumyloxy radical migration distance extended as far as 2.9 nm as measured by its recombination. (iii) HPLC and ¹H NMR spectroscopy enable the SPR approach, with the latter detection improved due to association to the surface SiOH.

Figure 5. Maximum number of SiOH bypassed by the cumyloxy radical as it migrates linearly on the particle surface as deduced by the formation of recombination (3) and abstraction (4) products. Y axis represents a measure of recombination (3 formation) vs H abstraction (4 formation).

### Table 1. Cumyloxy Radical H-atom Abstraction in Photocatalytic Reactions of 1

<table>
<thead>
<tr>
<th>Condition</th>
<th>Peroxide Compound</th>
<th>Cumyl Alcohol</th>
<th>Me* Formation</th>
<th>Detection Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>CS₂O</td>
<td>0.25</td>
<td>0.15</td>
<td>0.12 mM</td>
</tr>
<tr>
<td>B</td>
<td>CS₂O</td>
<td>0.25</td>
<td>0.15</td>
<td>0.12 mM</td>
</tr>
<tr>
<td>C</td>
<td>CS₂O</td>
<td>0.25</td>
<td>0.15</td>
<td>0.12 mM</td>
</tr>
</tbody>
</table>

References:
42. J. Phys. Chem. B 2021, 125, 4212–4220
O−O bond energy in symmetrical 3 is increased by 1.8 kcal/mol upon exchange with unsymmetrical 2, which contributes to enriching to dimerize PhC(Me)2O∗ to 3 on the particle surface. (v) The reaction disfavors the formation of SiO∗ surface radicals due to an endothermicity of 17.0–18.2 kcal/mol based on DFT calculations. Yet under higher energy conditions, SiO∗ has been detected by 60Co γ irradiation of SiOH49,50 and by “OH reactions.51 In our case, H-atom loss of EtO∗ to reach 6 and H-atom gain of Me∗ to reach 4 may occur on the surface or in the gas phase. (vi) The cumyloxy radical recombination increased relative to cumyl alcohol formation by surface H-atom transfer when bypassing <3 SiOH groups; otherwise, cumyl alcohol formation is competitive. Reduction of radical migration would be expected on a surface with a greater concentration of silanol groups, e.g., on zeolit silica.49

In summary, the SPR strategy is simple; it capitalizes on the retention of the heavier cumyloxy radical than the lighter volatile radicals to facilitate self-sorting and thus formation of the symmetrical product 3. The SPR method described here is appropriate for the detection of a radical migration up to 2.9 nm in the present case. There is increased migration of cumyloxy radical at lower loadings of 2 compared to higher loadings. However, there are competitive paths due to the higher loading of 2: one is SiOH H abstraction to form cumyl alcohol 4. With a higher O−O bond energy and lower volatility, product 3 enriches itself since reagent 2 generates the more labile EtO∗ and Me∗ upon sensitized decomposition. Over extended photolysis times Me∗ formation increases by PhC(Me)2O∗ demethylation, which attenuates the SPR assessment, as there is less of the alkyl radical to dimerize to symmetrical product 3.

# CONCLUSION

The SPR method that quantifies radical surface migration will have limitations. It requires detectable recombination product quantities by HPLC and 1H NMR spectroscopy. Despite this limitation, our findings provide a new approach important to radical migration on nanoparticles. Our conclusion is that SPR is appropriate for radical migration studies on particle surfaces, suggesting that this methodology might work on other radicals, such as free radicals on airborne fine particulate matter.

While there is value for research in control over surface radical delivery and persistence, especially when radical persistence is detected in airborne particulate matter, the question is what technology can be developed to make inroads. Current EPR methods detect surface radicals, where differentiating between radical propagation versus migration presents challenges. Furthermore, mechanistic understanding of radicals at the air/solid interface lags well behind that of radical reactions in homogeneous solution.

Future mechanistic efforts are needed for analyzing the properties of radicals at interfaces. Particle designs could include the following. (i) Use of a particle system with variable tumbling rates to enhance surface radical diffusion and facilitate transiting off of volatile radicals, in particular given the importance of volatile alkyl radicals as reactive intermediates in atmospheric chemistry.12–36 (ii) An alkyl radical surface migration system can be studied experimentally based on surface silanols with increasing water content to assess the effects on the radical migration distance.57–60 Simulations of alkyl radical surface migration can also be studied by silica cluster models with quantum mechanics/molecular mechanics methods.61 (iii) A complementary SPR/EPR method can be developed for product distribution by radical recombination and assist in distinguishing between stationary and migratory surface radicals. (iv) Radical migration on surfaces by mass spectrometry can be investigated to homolyze R18O18OR and R16O16OR for recombination to R18O16OR peroxides (Figure 6), which is reminiscent of isotope-sorting recombination that has been achieved.62,63

Figure 6. Schematic of our air/solid heterogeneous system with a dispersion of R18O18OR and R16O16OR peroxides on a nanoparticle. Upon irradiation, the resulting mixed peroxides R14O16OR will provide indirect evidence of surface alkoxy radical migration.

# EXPERIMENTAL SECTION

**General.** Acetophenone, cumene hydroperoxide, cumyl alcohol, 4,4′-dimethylbenzil 1, and dicumyl peroxide 3 were purchased from Sigma-Aldrich and used as received. Acetonitrile, acetonitrile-d3, chloroform-d3, dichloromethane, methanol, and HPLC-grade water were purchased from VWR Technology instrument (column: ZORBAX Eclipse XDB-C18).

**Sample Preparation.** Unfunctionalized hydrophilic fumed silica nanoparticles (200–300 nm diameter, 200 ± 25 m2/g surface area) were purchased from Sigma-Aldrich and washed in a Soxhlet extractor with dichloromethane and methanol prior to use. The nanoparticles were then dried in a furnace at 110 °C for 24 h. 4,4′-Dimethylbenzil 1 and cumylethyl peroxide 2 were coadsorbed onto the nanoparticles in a manner similar to that described previously.64 The 4,4′-dimethylbenzil 1 (330 μmol) and cumylethyl peroxide 2 (amounts ranging from a high of 108 μmol to a low of 6.8 μmol) were dissolved in 5 mL of dichloromethane and stirred with 1.0 g of nanoparticles for 30 min in a 25 mL Teflon bottle. The dichloromethane was then evaporated by use of a vacuum, leaving the reagents adsorbed, assumed to be uniformly distributed on the nanoparticles. This equated to percent loading of adsorbed sensitizer 1 and peroxide 2 in amounts of 25% and 0.87–13.8%, respectively. Notice that the surface was loaded with high sensitizer to low peroxide ratios, that is, sensitizer to peroxide loading ratios ranging from 3:1 to 49:1. We previously reported sensitizer to peroxide loading ratios of up to 4:1,64 and there have been reports of high dye polymer loadings.65 These ratios of sensitizer to substrate were high for the photosensitized homolysis of 2 and purposely dissimilar to most of the literature on sensitization reactions that use very low sensitizer quantities.66 This permitted us to maintain an optimal sensitizer–peroxide distance of 7 Å for the triplet sensitized homolysis, as we previously established.64 Close
intermolecular distances afford high yields of triplet-sensitized O–O homolysis of peroxides. Another paper has been published on such a reaction.67

Photosensitization reactions were carried out using a 5 mL airight vial. The nanoparticles were tumbled by a stirring paddle during the irradiation, where samples were placed at a distance of ~10 cm midpoint between two 400 W metal halide lamps delivering light (280 < > 700 nm). The fluence rate at a midpoint in between the bulbs was 21.8 ± 2.4 mW/cm².68 Upon irradiation, the temperature of the particles was found to rise by ~10°C, as we detected in a similar system previously.7 This was measured by a thermos couple probe attached to an IR thermometer. After photolysis, compounds were desorbed from the nanoparticle surface by stirring with 2 mL of acetonitrile for 20 min. Particles in acetonitrile were removed passing through a syringe filter. Acetonitrile was then completely evaporated, and the residue was analyzed by HPLC (C-18 reverse-phase column, 80% MeOH–H₂O v/v mobile phase, 1 mL/min flow rate) and ³H NMR spectroscopy (with acetonitrile-d₂). Even with modest peroxide 2 surface loadings of 0.9–13.8% and ~15% conversion of the reaction, dicumyl peroxide product 3 was readily detected by HPLC and ³H NMR spectroscopy. To analyze the volatile products released off the silica surface after photolysis, head space analysis was done with 1 mL of gas was drawn up in a glass syringe and slowly bubbled into chloroform-d and analyzed by ³H NMR spectroscopy. For heterogeneous reactions, due to the apparatus design, filtering of light below 300 nm was not carried out as was done in previous work with homogenous solutions.18 Without sensitizer 1, control photoreactions showed conversion of cumylethyl peroxide 2 (108 μmol/g) with (280 < λ < 700 nm) light to dicumyl peroxide 3 in <0.002%, whereas the sensitized reaction produced >1000-fold more. For the homogeneous photoreactions, sensitizer 1 (0.01 mM) and peroxide 2 (0.1 mM) in acetonitrile-d₂ were irradiated in an NMR tube for 1 h using the 400 W metal halide lamp system.

**Theoretical Section.** DFT calculations were carried out to analyze the structural aspects and reactions of peroxides 2–4 and alkoxy radicals PhC(Me)₂O and EtO*. All calculations were conducted with the Gaussian16 program (revision C.01).69 We used UM06-2X along with Pople’s 6-31G(d,p) basis set. Thermal corrections to 298 K were used in the reported energies. The quality of the energetics with the 6-31G(d,p) basis set was reasonable in comparison to UM06-2X calculations with the use of a larger basis set [6-311+G(3df,2p)].24 Vibrational frequency calculations were conducted to analyze all stationary points. The TS structures were verified by both frequency calculations and tracing their internal reaction coordinates (IRC). To compute the O–O bond cleavage, the endothermcity of peroxides 2–4 relative to their corresponding alkoxy radicals was computed by comparing the optimized energies of the former to the latter as radical pairs separated by a distance of 3.0 Å. Simulations of R···HO and O···HO hydrogen bonding of PhC(Me)₂O*, EtO*, PhC-(Me)₂OH, EtOH or C₆H₆ were carried out with (HO)₂SiOH and (HO)₃SiO* molecules in the gas phase as an approximate model of silanol or silanxy sites at the air/solid interface.

**ASSOCIATED CONTENT**

 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcb.1c01099.

UV–vis and ¹H NMR spectra, HPLC trace, details of sensitizer 1 and peroxide 2 loading onto nanoparticles, compound detection, results of temperature studies, illustrations of grids depicting compound loading and migration on the nanoparticle surface, and descriptions of the energies and geometries of the stationary points (PDF)

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**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

We acknowledge the National Science Foundation (CHE-1856765). This work used Comet, the Extreme Science and Engineering Discovery Environment (XSEDE) cluster at the San Diego Supercomputer Center, which is supported by the NSF (ACI-1548562) through allocation CHE-200050. We thank Leda Lee for the graphic arts work.

**REFERENCES**


