


Heterogeneous photocatalytic deperoxidation with UV and visible light

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Abstract

A physical-organic study is described on the photodecomposition of dicumyl peroxide co-adsorbed with the sensitizers 4,4'-dimethylbenzil or chlorin *e*₆ on fumed (nonporous) silica. Dicumyl peroxide was decomposed by the heterogeneous photosensitization and monitored by the desorption of products acetophenone, 2-phenylpropan-2-ol, and α -methylstyrene using proton nuclear magnetic resonance and gas chromatography-mass spectrometry. Dicumyl peroxide and sensitizer were co-adsorbed on silica in 1:4 up to 200:1 ratios, with high peroxide destabilization occurring in ratios of about 10:1. This increased photodecomposition corresponded to sensitizer-peroxide distances of 6 to 9 Å. A Dexter triplet energy transfer mechanism is proposed that explains the short sensitizer and peroxide separation distances for higher peroxide O—O bond homolysis efficiencies on silica. This biphasic (gas/solid) system can thus serve both to destabilize and stabilize a peroxide, which may be of practical use for the delivery of alkoxy radicals for bacterial disinfection.

1 | INTRODUCTION

The photosensitized decomposition of organic peroxides at the gas/solid interface is a potentially useful reaction (Figure 1). Peroxides can be irradiated to reduce their stability—for example, peroxides can be photosensitized^[1–16] to become less stable—and homolyze to alkoxy radicals.^[17,18] Alkoxy radicals can be used for applications as initiators of polymerizations.^[19–30] In homogeneous solution, alkoxy radicals were shown^[11] to form by triplet energy transfer from a sensitizer to a repulsive excited state in di-*tert*-butyl peroxide, thereby homolyzing the O—O bond. Understanding photosensitization is valuable for examining peroxide stability, and we thought the field could be expanded on through the use of heterogeneous reactions.

One challenge in photosensitizing peroxides is control of the distance between the sensitizer and peroxide. The sensitizer can be dispersed in the solution,^[31–34] but solid media and supramolecular systems have been shown to enable some control of photoreactions, including

stereochemical control.^[35–53] Silica and zeolites have yielded important information on proximity control of molecules in photoreactions.^[35] De Mayo et al showed evidence for translational motion on silica of an acenaphthalene monomer and dimer on the timescale of the triplet lifetime.^[52,53] Triplet 9-cyanophenanthrene has a sufficiently long lifetime to diffuse on the surface where dimerization occurs in a facially selective manner. Oxygen quenching of triplet *meso*-tetra(*N*-methyl-4-pyridyl)porphine on porous Vycor glass was reported to be primarily a dynamic quenching process.^[39] Adsorbed ozone has also been reported^[54] for selective hydroxylation of saturated compounds on silica.

In this paper, we report on a biphasic gas/solid photoreactor system by adsorbing sensitizers 4,4'-dimethylbenzil or chlorin *e*₆ and dicumyl peroxide to fumed silica. The fumed silica is nonporous for dispersing compounds in 2D to enable some control of the peroxide photosensitized dissociation. The effect of surface sensitizer and peroxide loadings was studied by varying their ratios and analyzing the peroxide photocleavage efficiency due

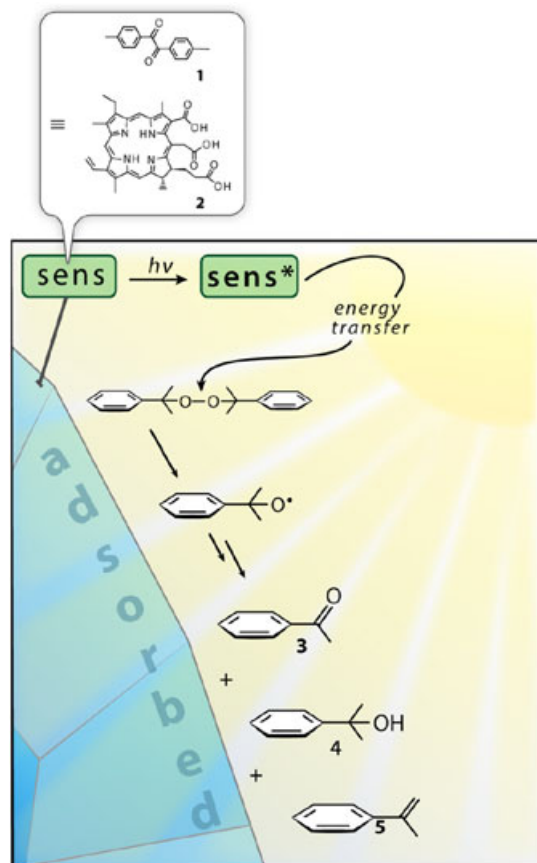


FIGURE 1 Photodecomposition of dicumyl peroxide on a silica surface in the presence of sensitizers 4,4'-dimethylbenzil **1** or chlorin e_6 **2**. Three products (**3–5**) were detected upon desorption with acetonitrile from the silica surface

to the calculated distance of available sensitizer. Our hypothesis is that peroxide photodecomposition will be maximized based on sensitizer loading of the solid support.

Studying the mechanism of photosensitized decomposition of peroxides on dry silica is a unique way to reveal information on alkoxy radical formation for potential applications. Dicumyl peroxide is fairly safe to use in low amounts based on previous reports.^[55–58] The present study uses physical-organic chemistry principles along with a gas/solid technique to add insight to topics on phase separation of reactive intermediates,^[59–64] biological peroxides, deperoxidation and safety,^[65–67] and interfacial disinfection.^[68–70] We are unaware of any previous gas/solid interfacial photosensitization study with peroxides.

2 | EXPERIMENTAL

2.1 | Reagents and instrumentation

Hydrophilic fumed silica (Sigma S5505 particles, sized: 200–300 nm; surface area: 200 ± 25 m²/g and

approximately 4 silanol groups/nm²), dicumyl peroxide (98%), 4,4'-dimethylbenzil (97%), chlorin e_6 , biphenyl, acetonitrile, acetonitrile- d_3 , dichloromethane, and methanol were purchased from commercial suppliers. Proton nuclear magnetic resonance (¹H NMR) data were collected at 400 MHz. A gas chromatography-mass spectrometry (GC/MS) instrument was used to collect chromatography and mass spectrometry data. Absorption and fluorescence spectra were also collected.

2.2 | Silica preparation

There were no special precautions to remove physisorbed water.^[71] Dicumyl peroxide and either 4,4'-dimethylbenzil **1** or chlorin e_6 **2** were co-adsorbed onto fumed silica particles by immersing the native silica particles in dichloromethane containing the dissolved reagents and with stirring for 1 hour. The dichloromethane was evaporated with a nitrogen gas stream leading to disordered compound adsorption on the silica. Compound adsorption was due to electrostatic and dispersion interactions, as well as H-bonding of compounds to silanol groups or to physisorbed water on the silica surface. Silica-bound chlorin derivatives were reported in our previous papers,^[72,73] which were examined by infrared and absorption spectroscopy showing a thin coat of the sensitizer on the glass. For the present fumed silica sensitizers **1** and **2**, we have sparingly little information on coverage of dyes and homogeneity of adsorbed compounds. For example, we cannot rule out the existence of chlorin e_6 dimers on the silica surface. For peroxide loading (0.33 mmol/g silica), silica (300 mg) was coated with 0.4 mmol, 0.1 mmol, 0.01 mmol, 0.0025 mmol, 0.001 mmol, and 0.0005 mmol of sensitizer **1** or **2** (accurate to $\pm 2\%$) and 0.1 mmol of dicumyl peroxide per gram silica. For peroxide loading (0.083 mmol/g silica), silica (300 mg) was coated with 0.1 mmol, 0.025 mmol, 0.0025 mmol, and 6.25×10^{-4} mmol of sensitizer **1** or **2** (accurate to $\pm 2\%$) and 0.025 mmol of dicumyl peroxide per gram silica.

2.3 | Surface coverage calculations

The distances between adsorbed sensitizer and peroxide molecules on fumed silica were calculated (Equations 1–11). Error bounds of 12% are estimated from these calculations of molecule-to-molecule distances. Equation 1 gives the number of molecules adsorbed per gram of silica, where Avogadro's number 6.0221367×10^{23} mol⁻¹ is represented by N_A . Equation 2 shows an area of 4 adsorbed molecules at a given loading amount in mmol/g silica. Equation 3 gives the calculation for sensitizer-to-sensitizer and peroxide-to-peroxide sites. Sens-peroxide distances were estimated by Equation 4 to 11.

$$\text{Number of adsorbed molecules/g SiO}_2 = (\text{mols dicumyl peroxide or mols sensitizer/g SiO}_2) \times (N_A), \quad (1)$$

$$\text{area between 4 molecules} = \frac{\text{surface area of silica } \text{\AA}^2/\text{g}}{(\text{mols peroxide or mols sensitizer/g}) \times (N_A)} \times 4, \quad (2)$$

$$\begin{aligned} & \text{peroxide-to-peroxide or sens-to-sens distance} \\ & = \sqrt{\frac{\text{surface area of silica } \text{\AA}^2/\text{g}}{(\text{mols peroxides or sensitizers/g}) \times (N_A)}} \times 4, \quad (3) \end{aligned}$$

$$\begin{aligned} & \text{average area of single sensitizer molecule (A)} \\ & = \frac{\text{surface area of silica } \text{\AA}^2/\text{g}}{\text{mols sensitizers/g} \times N_A}, \quad (4) \end{aligned}$$

$$\begin{aligned} & \text{number of peroxide molecules in surface area A} \\ & = \frac{\text{mols peroxide/g} \times N_A}{\text{surface area of silica } \text{\AA}^2/\text{g}} \times A, \quad (5) \end{aligned}$$

$$\begin{aligned} \text{length of the diagonal} & = \sqrt{(\sqrt{A})^2 + (\sqrt{A})^2} \\ & = (\sqrt{2A}), \quad (6) \end{aligned}$$

$$\begin{aligned} & \text{longest possible sensitizer-peroxide distance} \\ & = \text{eq.6}/2, \quad (7) \end{aligned}$$

$$\begin{aligned} & \text{average sensitizer-peroxide distance} = \text{eq.7}/2 \\ & (\text{average of shortest possible and longest possible distance}), \\ & \text{when peroxide mols} = \text{sensitizer mols}, \quad (8) \end{aligned}$$

$$\text{average sensitizer-peroxide distance} = (\sqrt{2A})/2, \quad (9)$$

$$\begin{aligned} & \text{when peroxide mols} < \text{sensitizer mols area of the} \\ & \text{location of single peroxide molecule (B)} \\ & = \frac{\text{surface area of silica } \text{\AA}^2/\text{g}}{\text{mols peroxides/g} \times N_A}, \quad (10) \end{aligned}$$

$$\begin{aligned} & \text{number of adsorbed molecules/g SiO}_2 \\ & = (\text{mols dicumyl peroxide or mols sensitizer/g SiO}_2) \times (N_A). \quad (11) \end{aligned}$$

2.4 | Biphasic system and photoreactor

The setup was a 20-cm³ vessel containing 100-mg silica particles adsorbed with dicumyl peroxide and sensitizer **1** or **2**, which was N₂-degassed (Figure 2). Samples were irradiated with a UV lamp ($\lambda = 254$ nm), two 400-W metal halide lamps ($\lambda = 280$ -750 nm), a Rayonet lamp ($\lambda = 350 \pm 20$ nm), a blue CW laser ($\lambda = 460 \pm 30$ nm), or a red CW diode laser ($\lambda = 669$ nm). The vial was rotated around a metal bar so the silica particles tumbled during the irradiation for 1 hour (different rates of tumbling were not investigated in the present work). Experiments were conducted at 26°C (room temperature). Temperature increases of the silica particles were not observed over the course of the experiment. We also did not find evidence for intergranule transfer of sensitizer molecules under the tumbling conditions. The absorption spectra of sensitizers **1** and **2**, but not dicumyl peroxide, overlapped with the output of the light from metal halide lamps (see Supporting Information). At the location



FIGURE 2 Illustration of the photoreactor with silica particles tumbling inside the vial

where the sample was placed, the fluence rate for the 280- to 750-nm light source was measured using a custom dosimetry system and found to be 22 ± 2 mW/cm² as was previously measured with a power meter.^[74] After the irradiation, the sensitizer **1** or **2**, dicumyl peroxide and products were desorbed with a polar solvent, such as acetonitrile. The solution was then filtered with a 25 mm syringe through a 0.25 μ m propylene membrane and analyzed by ¹H NMR and GC/MS. For the latter, biphenyl was added as an internal standard. The surface was not recharged with peroxide after the photolysis. We would generate new silica samples for each measurement. We report the results that are the average of 3 experiments for each measurement. The biphasic reactor using the 280- to 750-nm light source and fumed silica adsorbed to sensitizers 4,4'-dimethylbenzil **1** or chlorin e₆ **2** for photodecomposition of dicumyl peroxide is described next.

3 | RESULTS AND DISCUSSION

3.1 | Effect of conditions on dicumyl peroxide stability

We examined the stability of dicumyl peroxide with a series of experiments. The experiments show that in our 2-phase system, dicumyl peroxide is stable (ie, no decomposition) in the presence or absence of 280- to 750-nm light when adsorbed on fumed silica. In contrast, the photolysis

of dicumyl peroxide and sensitizer **1** or **2** co-absorbed on silica led to its decomposition. Using ¹H NMR and GC/MS, the homogeneous and heterogeneous photosensitized decomposition of dicumyl peroxide led to acetophenone (**3**), 2-phenylpropan-2-ol (**4**), and α -methylstyrene (**5**). The ratios of products of 4,4'-dimethylbenzil photosensitized decomposition of dicumyl peroxide on silica or in homogeneous acetonitrile differ. Thus, the dissociation of dicumyl peroxide to cumyloxy radicals can lead to subsequent reactions and even volatile products. The detection of ethane and other volatile by-products was not investigated. Products that resulted from reactions of radicals with the sensitizers **1** and **2** themselves were not readily detectable. A mass balance of the reaction was found to be approximately 70% to 80%. Higher total yields of 2-phenylpropan-2-ol **4** were observed in the heterogeneous reaction as would be expected due to the surface silanols acting as hydrogen donors. This finding is analogous to solution-phase studies,^[75] where higher yields of 2-phenylpropan-2-ol **4** were seen in hydrogen donor solvents; otherwise, the main product was acetophenone **3**.

3.2 | Effect of sensitizer loading on peroxide photodecomposition

The loading of sensitizer and dicumyl peroxide was investigated on silica to evaluate their influence on the photodecomposition of dicumyl peroxide. Table 1 shows the

TABLE 1 Photodecomposition of dicumyl peroxide on dry silica in the presence of adsorbed sensitizer 4,4'-dimethylbenzil **1** or chlorin e₆ **2**^a

Entry	Sens	Peroxide/ Sens Ratio	Peroxide/ Peroxide Distance, Å	Sens/Sens Distance, Å	Peroxide/ Sens Distance, Å	Peroxide Photodecomp, % ^b	Surface Concentration of Peroxide, μ mol/m ²	Surface Concentration of Sensitizer, μ mol/m ²
1	1 ^c	1:4	20 \pm 1	10 \pm 0.6	~0	6.6 \pm 1.1	1.65	6.60
2	1 ^c	1:1	20 \pm 1	20 \pm 1	2.0 \pm 0.1	11.3 \pm 2.4	1.65	1.65
3	1 ^c	10:1	20 \pm 1	63 \pm 4	6.0 \pm 0.4	21.8 \pm 4.8	1.65	0.16
4	1 ^c	40:1	20 \pm 1	127 \pm 7	17 \pm 1	8.2 \pm 1.5	1.65	0.04
5	1 ^c	100:1	20 \pm 1	201 \pm 12	30 \pm 2	5.4 \pm 3.4	1.65	0.02
6	1 ^c	200:1	20 \pm 1	284 \pm 23	45 \pm 3	3.7 \pm 1.1	1.65	0.01
7	1 ^d	1:4	40 \pm 2	20 \pm 1	2.0 \pm 0.1	5.1 \pm 2.6	0.41	1.65
8	1 ^d	1:1	40 \pm 2	40 \pm 2	9.0 \pm 0.5	12.8 \pm 2.1	0.41	0.41
9	1 ^d	10:1	40 \pm 2	127 \pm 7	17 \pm 1	6.3 \pm 1.3	0.41	0.04
10	1 ^d	40:1	40 \pm 2	257 \pm 12	39 \pm 2	1.1 \pm 3.1	0.41	0.01
11	2 ^e	10:1	20 \pm 1	63 \pm 4	4.0 \pm 0.2	9.9 \pm 1	1.65	0.16
12	2 ^e	100:1	20 \pm 1	201 \pm 12	23 \pm 1	4.9 \pm 1.4	1.65	0.02

^aAverage of 3 experiments. Biphenyl was added after the photolysis as the internal standard.

^bIn the absence of sensitizer, less than 1% photocleavage of the peroxide was observed.

^cSensitizer was 4,4'-dimethylbenzil; the quantity of dicumyl peroxide was 0.33 mmol/g silica.

^dSensitizer was 4,4'-dimethylbenzil; the quantity of dicumyl peroxide was 0.083 mmol/g silica.

^eSensitizer was chlorin e₆; the quantity of dicumyl peroxide was 0.33 mmol/g silica.

results of dicumyl peroxide photosensitized decomposition with peroxide-to-sensitizer ratios ranging from 1:4 to 200:1. These surfaces contained 0.33 mmol dicumyl peroxide per gram silica and the peroxide photodecomposition yield increased from 3.5% to 22% when the loading was increased from 1:4 to 10:1. At 10:1, the maximum was reached (entry 3). The percent decomposition of dicumyl peroxide decreased from 22% to 3.7% with the loading increased from 40:1 to 200:1. For surfaces containing 0.083 mmol dicumyl peroxide per gram silica, the photodecomposition of dicumyl peroxide reached a maximum at a 1:1 ratio (entry 8). This higher decomposition yield is similar for surfaces containing 0.33 mmol dicumyl peroxide per gram silica, where the decomposition of dicumyl peroxide was increased at a 10:1 ratio compared to a 100:1 ratio (entries 11 and 12). The high absorption coefficient led to opaque silica and prevented us from a wider study of high loading ratios of **2**. Enhanced peroxide decomposition has been found for **1** in about 10:1 ratios in Table 1, which led us to calculate the average distances separating peroxide and sensitizer that is also of interest.

3.3 | Spatial control in the sensitized peroxide photodecomposition

Table 1 shows the calculated average distances separating peroxide and sensitizer. Here, we thought that it is appropriate to calculate the nearest edge rather than the geometric center of the sensitizer to compute distances to the O—O bond, acknowledging these compounds have internal rotors that will cause the distance and angle between them to vary. The error in the silica surface area and the error in weighing compounds also account for the variations. Figure 3 shows that the sensitized peroxide decomposition was higher with sensitizer/peroxide distances of 6 to 9 Å on silica. The distance effect decreases, for less than 6 Å or greater than 9 Å. The finding of this spatial separation of the sensitizer and peroxide was useful for explaining the origins of the peroxide photodecomposition as is discussed following the next section. Next, we focus on the influence of excitation wavelength on the sensitized decomposition of the peroxide.

3.4 | Effect of excitation wavelength on peroxide decomposition

To examine the effect of excitation wavelength on peroxide decomposition, experiments were conducted in the presence and absence of sensitizer. In this way, the relative effectiveness of light source and sensitizer could be evaluated. In the absence of sensitizer, Table 2 shows that peroxide decomposition was more effective with the 254-nm light source (entry 1) as compared with the other

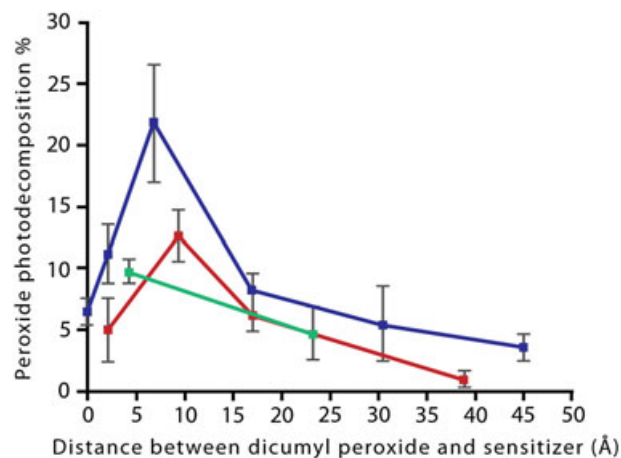


FIGURE 3 Plot of percent photocleavage of dicumyl peroxide by sensitization with 4,4'-dimethylbenzil (blue and red lines) and chlorin e_6 (green line) based on the distance between the peroxide and sensitizer (Å). The quantity of dicumyl peroxide loaded was 0.33 mmol/g silica (blue and green lines) or 0.083 mmol/g silica (red line). In the absence of sensitizer, there was no photocleavage of dicumyl peroxide

TABLE 2 Wavelength dependence in the photodecomposition of dicumyl peroxide on dry silica in the presence or absence of adsorbed sensitizer

Entry	Wavelength, nm	Sensitizer	Peroxide Photodecomposition, % ^a
1	254	...	32 ± 3 ^b
2	280-750	1	22 ± 5 ^{c,d}
3	350 ± 20	1	1.8 ± 0.2 ^{c,d}
4	350 ± 20	2	4.1 ± 0.5 ^{c,d}
5	460 ± 30	2	<1 ^{c,d}
6	669	2	7.5 ± 0.8 ^{c,d}

^aAverage of 3 experiments, samples were irradiated for 1 hour (fluence rates were not determined). Biphenyl was added after the photolysis as the internal standard.

^bThe quantity of dicumyl peroxide was 0.33 mmol/g silica. There was no sensitizer; the photocleavage of the peroxide is the result of direct irradiation.

^cSensitizer was 4,4'-dimethylbenzil **1** or chlorin e_6 **2**; the quantity of dicumyl peroxide was 0.33 mmol/g silica.

^dIn the absence of sensitizer, less than 1% photocleavage of the peroxide was observed.

light sources showing less than 1% peroxide decomposition. In the presence of sensitizer, peroxide decomposition was readily observed when the absorption band of sensitizer overlapped with the light source emission. For example, 4,4'-dimethylbenzil **1** absorption ranges from 250 to 320 nm, which explains the low peroxide decomposition with the 350-nm light source. Similarly, chlorin e_6 **2** absorption of the 320- to 430-nm Soret band (S_0 - S_2) and

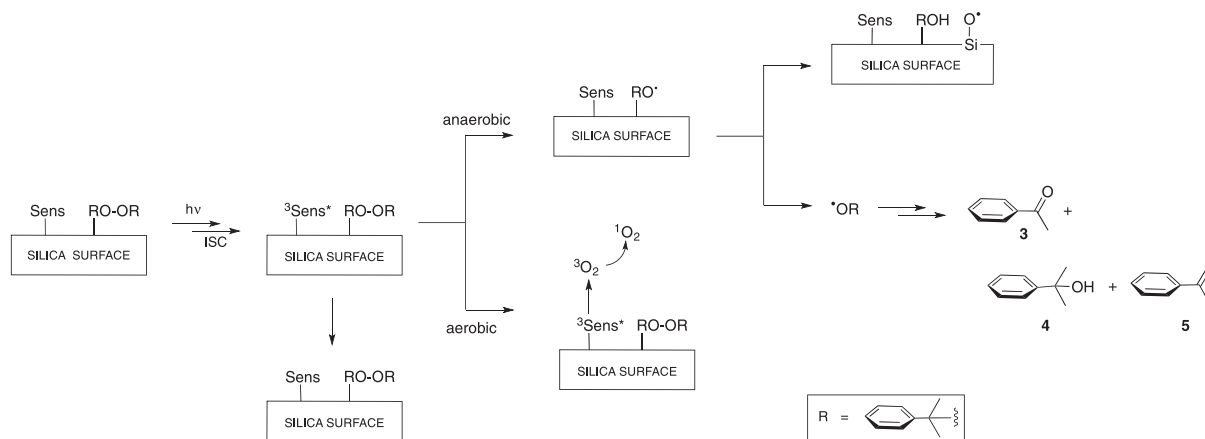


FIGURE 4 Proposed mechanism for the sensitized photodecomposition of dicumyl peroxide at the gas/solid interface and formation of products

the 660-nm Q-bands (S_0 - S_1) with the 280- to 750-nm, 350-nm, and 669-nm light sources led to higher decomposition of the peroxide (entries 2-4 and 6). Little or no decomposition of the peroxide was observed with 460-nm light source, a region where chlorin e_6 **2** absorbs poorly (entry 5). Next, we focus on mechanistic considerations in destabilizing the peroxide bond.

3.5 | Mechanistic considerations

The biphasic (gas/solid) photoreactor is useful for probing the mechanism of sensitized peroxide photodegradation, as it enables the spatial separation of the compounds, among other control features. Figure 4 shows a mechanism that is consistent with the data collected.

Formation of products **3**–**5** is consistent with dicumyl peroxide O—O bond homolysis and subsequent H atom transfer and methyl radical loss reactions. When the surface separation distance between the sensitizer and the peroxide is 6 to 9 Å, the decomposition is favored. This photodecomposition is attributed to a Dexter mechanism between the peroxide and the excited sensitizer. On the silica surface, single-digit angstrom translational migration of the triplet sensitizer and dicumyl peroxide could account for the maxima at 6–9 Å observed in Figure 3. Here, there is triplet energy transfer to the peroxide repulsive O—O orbital. The nonporous silica enables the coating of the sensitizer and peroxide molecules in 2D. Assuming no fumed silica defects, the compounds migrate up to approximately 9 Å beyond their van der Waals radii. De Mayo et al.^[51,52] have shown mobilities of approximately 5 Å of adsorbed photoexcited compounds in their silica-surface photochemical studies, although direct van der Waals contact is not a requirement of triplet-triplet energy transfer as has been noted in glasses^[75] and supramolecular systems.^[76–78]

When the excitation wavelength overlaps the sensitizer, the peroxide decomposition is increased. The sensitization process at the gas/solid interface accounts for the peroxide decomposition. Here, silica-adsorbed dicumyl peroxide free of sensitizer decomposes with 254-nm light, but not with other light sources above 280 nm, since dicumyl peroxide only weakly absorbs above 270 nm. By maintaining an anaerobic condition, the significance of the biphasic sensitized peroxide decomposition is evident. However, it may be noted that silica bound sensitizers can also produce 1O_2 under aerobic conditions.^[72,73] Our photoreactor was presently examined only under anaerobic conditions, where a dual action, 1O_2 production and peroxidation decomposition, has not yet been tested.

In summary, by studying the separation of compounds on the surface and the excitation wavelength, a heterogeneous photosensitization provides valuable insight to peroxide instability. The peroxide photodecomposition yield is a function of sensitizer and peroxide loading on silica (Table 1). The presence of the sensitizer and a close distance relative to the peroxide on the silica surface has mechanistic significance. This heterogeneous photodecomposition of dicumyl peroxide is a sensitized process, as it does not readily occur by direct irradiation of the peroxide above 280 nm in the absence of sensitizer (Table 2).

4 | CONCLUSION

A physical-organic study is described on the photosensitized decomposition of an organic peroxide. Here, mechanistic results were collected with a biphasic (gas/solid) system. This biphasic system enabled a facile decomposition route in the presence of a sensitizer. By varying the loading of sensitizer and the excitation wavelength, the system can be tuned to destabilize the

peroxide. Our observations are consistent with a short migration of reagents on the surface and a long lifetime in which the sensitizer is assumed to be in the triplet state. An excited singlet sensitizer would be too short-lived to enable energy transfer to the O—O bond.

Future research efforts could focus on (1) a solid that synthetically anchors the sensitizer to restrict mobility, (2) the detection of alkoxy radicals by EPR^[79,80] or deducing their surface persistence with mixed ROOR and R¹⁸O¹⁸OR peroxides for possible scrambled products RO¹⁸OR by mass spectrometry, and (3) alkoxy radicals to transit off of the surface into biological samples. There may be an advantage in the controlled release of alkoxy radicals and singlet oxygen in tandem or separate quantities in disinfection reactions.

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Gas chromatography-mass spectrometry data for the calibration curve of dicumyl peroxide. Absorption and emission spectra of sensitizers **1** and **2**.

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