

Free-Radical Reactions under Diffusional Constraints: Orientation Does Matter in Hydrogen Transfer

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Chemical interactions and transformations on surfaces and at interfaces are important to many research areas such as catalysis, separations, solid-phase synthesis, sensor design, geochemistry, fuel chemistry, etc. Moreover, confinement of molecules to surfaces often leads to unpredicted chemical or spectroscopic behavior arising from unusual molecular alignments or constraints on diffusion.¹ We have been exploring the effects of surface confinement, and its attendant restrictions on lateral diffusion, on high-temperature free-radical reactions through the use of chemically modified, fumed silica nanoparticles.² Organic molecules have been attached to the silica surface employing a Si–O–C_{aryl} linkage, which is thermally robust up to ca. 550 °C but is readily hydrolyzed for recovery of surface-attached products. Employing two-component systems where the second “spacer” molecule is thermally stable, we recently discovered a novel hydrogen-transfer, radical relay mechanism that is unique to the surface and can mitigate the effects of diffusional constraints (Scheme 1).^{2a}

Organic radical chemistry on surfaces continues to be widely investigated,^{1a,b,e,3} and a current emphasis is surface-initiated radical polymerization for the formation of polymer brushes and other nanostructured materials.⁴ Recently, a radical relay mechanism conceptually similar to the one shown in Scheme 1 was proposed by Fukuda and co-workers in the radical addition–fragmentation chain transfer polymerization of styrene on a related silica surface.^{4a} In our current work, we now report that even subtle changes in molecular orientation can significantly impact the rate of the hydrogen transfer, radical relay process that has much broader implications for bimolecular reactions occurring on surfaces under restricted diffusion.

The two-component surfaces investigated are shown in Chart 1.⁵ Pyrolysis of silica-immobilized 1,3-diphenylpropane (denoted as ≈DPP) was used as the probe reaction, since the kinetics of the free-radical chain decomposition are well-understood.^{2a,6} We reasoned that orientation effects, if present, would be most evident in cases where the active benzylic hydrogens are locked in a hydroaromatic ring. Hence, isomeric (by point of attachment) fluorene (FL), tetralin (TET), and dihydrophenanthrene (DHP) spacers were investigated.

Pyrolyses were conducted at 375 °C under vacuum.⁷ Gas-phase and surface-attached toluene and styrene were produced in equal amounts at low ≈DPP conversions, as found previously for ≈DPP in other two-component surfaces.^{2a} The free-radical chain mechanism for the decomposition of DPP on silica is the same as in fluid phases and has been discussed in detail elsewhere.^{2a} The chain propagation steps involve gas-phase and surface-attached benzyl radicals abstracting hydrogen at the two regiochemically distinct benzylic carbons of ≈DPP to form the corresponding toluene products, followed by β-scission of the resulting radicals to produce the surface-attached and gas-phase styrene products while regenerating the two benzyl radicals. The overall rate of decomposition of ≈DPP is controlled by the rates of the hydrogen transfer steps,

Scheme 1

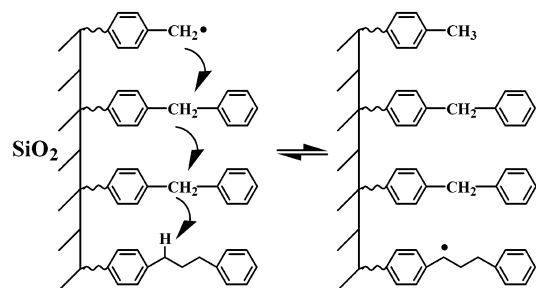
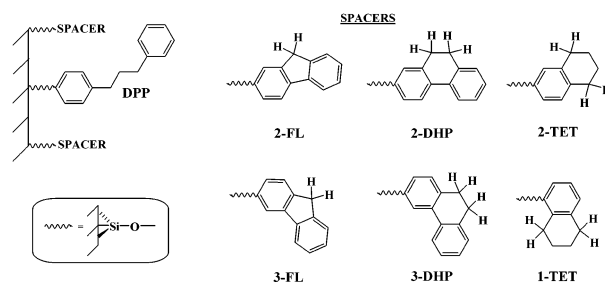


Chart 1



which are particularly sensitive to the surface coverage and the structure of intervening spacer molecules.^{2a}

The initial pyrolysis rates for ≈DPP at 375 °C in the presence of the hydroaromatic spacer molecules are compared in Table 1. The ≈DPP rates are all substantially larger in the presence of the hydrogen donor spacers compared with surfaces of ≈DPP at similar coverages without hydrogen donating spacers ($0.7\text{--}1.1 \times 10^{-4} \text{ \% s}^{-1}$).^{2a} However, the rate is strikingly sensitive to *both* the structure of the spacer molecule (vide infra) and its orientation on the surface. For example, the rate of ≈DPP pyrolysis with 2-FL is 2.4-times faster than that with 3-FL, 2.8-times faster for 2-TET spacer than for 1-TET, and 2.4-times faster for 2-DHP compared with 3-DHP (Table 1).⁸

The results suggest that a meta-orientation for the surface linkage (see Chart 1), with respect to the reactive benzylic hydrogens, provides the most efficient geometry for promoting the hydrogen transfer, radical relay process on the surface. In Table 2, the relative pyrolysis rates are compared with the relative rates for hydrogen transfer from the corresponding hydrocarbon in solution to the 2-allylbenzyl radical.⁹ The relative rates are normalized for the number of benzylic hydrogens, which are all assumed to be active. A remarkable linear correlation ($r^2 = 0.986$) with near unit slope (1.06) exists between the ≈DPP pyrolysis rates on the surface in the presence of the spacers containing meta-type linkages and the solution-phase hydrogen transfer rate constants, consistent with the critical role of hydrogen transfers in determining the ≈DPP pyrolysis rate. Previously for the diphenylmethane spacers,^{2a} where the benzylic hydrogens are not locked in a ring, the para-linked

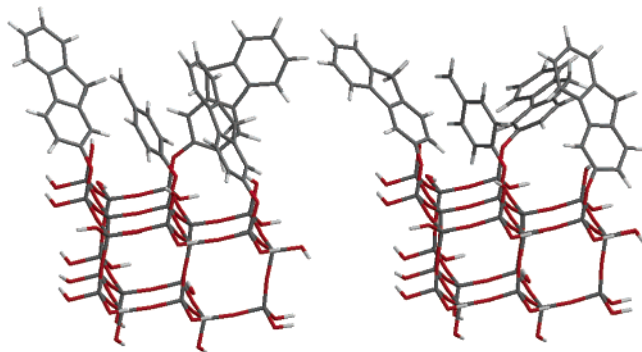


Figure 1. Molecular model of hydrogen transfer from the ≈ 2 -FL (left) and ≈ 3 -FL (right) hydroaromatic spacers to a benzyl radical on the [111] surface of β -cristobalite possessing 4.55 single SiOH nm⁻² as a model for the fumed silica. The benzyl radical is shown surrounded by three neighboring fluorene molecules with 0.50 nm separation (O–O). The fluorenes are separated by 0.87 nm (O–O) corresponding to a 1.5 molecule nm⁻² coverage, similar to that measured for saturation coverage.

Table 1. Effect of Spacers on \approx DPP Pyrolysis Rate at 375 °C

surface composition	coverage (nm ⁻²) ^a	mol ratio ^b	no. of runs	rate $\times 10^4$ (% s ⁻¹) ^c
\approx DPP/ ≈ 2 -FL	0.54/1.44	2.7	5	201 ^d
\approx DPP/ ≈ 3 -FL	0.39/1.08	2.8	5	82
\approx DPP/ ≈ 2 -TET	0.36/1.47	4.1	7	42
\approx DPP/ ≈ 1 -TET	0.27/0.89	3.3	6	15
\approx DPP/ ≈ 2 -DHP	0.47/1.59	3.4	6	21
\approx DPP/ ≈ 3 -DHP	0.71/1.21	1.7	5	8.6

^a Surface coverages in molecules per nm² surface area (200 m² g⁻¹ for the fumed silica used). ^b Spacer hydroaromatic-to-diphenylpropane ratio. Rates are not very sensitive-to-this ratio.⁸ ^c Initial rates determined from the slopes of linear regressions of \approx DPP conversion (typically 3–15%) versus reaction time. Correlation coefficients for the regression analyses were in the range of 0.986–0.998. Error in rates is $\pm 10\%$. ^d Rate has been reexamined with several batches and is ca. 2-fold faster than previously reported.^{2a}

Table 2. Correlation of Pyrolysis and Hydrogen Transfer Rates^a

surface composition	rel. pyrol. rate 375 °C, per H	rel. H-transfer rate 375 °C, per H ^b
\approx DPP/ $\approx 3,5$ -DMB ^c	1.0	1.0
\approx DPP/ $\approx m$ -DPM ^c	11.4	7.3
\approx DPP/ $\approx p$ -DPM ^c	16.0	
\approx DPP/ ≈ 2 -TET	8.9	7.5
\approx DPP/ ≈ 1 -TET	3.0	
\approx DPP/ ≈ 2 -DHP	4.2	11.5
\approx DPP/ ≈ 3 -DHP	1.9	
\approx DPP/ ≈ 2 -FL	89.0	80.5
\approx DPP/ ≈ 3 -FL	39.0	

^a Rates are normalized for the number of benzylic hydrogens. ^b Relative rates for hydrogen transfer from the hydrogen donor to the 2-allylbenzyl radical in solution extrapolated from 160 °C using Arrhenius parameters for DMB, DPM, and FL cases; DHP and TET are extrapolated relative to DPM. ^c DMB is dimethylbenzene and DPM is diphenylmethane. The \approx DPP pyrolysis rates for 3,5-DMB, *m*-DPM, and *p*-DPM spacers are 7.1, 27, and 38×10^{-4} % s⁻¹, respectively, from ref 2a.

isomer was in fact faster due to the stabilizing effect of the *p*-silyloxy linkage on the diphenylmethyl radical intermediate.¹⁰ However, in the case of the related fluorene isomers, the resulting geometric constraints result in a much slower pyrolysis rate for the para-isomer.¹¹

The origin of this effect can be visualized from the simple molecular models shown in Figure 1, where H-transfer to the benzyl radical from the ≈ 2 -FL and ≈ 3 -FL isomers is compared on a small portion of a model silica surface.¹² Rotations about the Si–O and

O–C_{aryl} bonds clearly show that the meta-linkage associated with the ≈ 2 -FL spacer affords the most favorable separation and geometry for the hydrogen transfer without requiring serious steric interference. Similar conclusions are drawn from examination of the other isomeric spacer pairs.

These pyrolysis studies clearly show that geometric constraints can play a large role in the rates of hydrogen transfer steps for free-radical reactions under restricted diffusion. These new insights suggest that similar orientation effects may be involved in other chemical transformations between molecules on surfaces even at high temperatures, and could be important in the synthesis of nanostructured polymer films on surfaces.

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- (7) The pyrolysis apparatus and procedure have been described.² In brief, a weighed amount of sample was placed in a T-shaped Pyrex tube, evacuated and sealed at ca. 2×10^{-6} Torr. The sample was pyrolyzed in a preheated calibrated three-zone tube furnace, and the gas-phase products were trapped in the tube arm placed in a liquid nitrogen bath. The volatile products collected in the trap were dissolved in acetone (100 μ L) containing cumene as an internal standard, and the solution was analyzed by GC and GC–MS. Surface-attached pyrolysis products were hydrolyzed from the silica with 1 N NaOH, and the internal standards, 2,5-dimethylphenol and *p*-phenylphenol were added to the solution. The solution was acidified and extracted with CH₂Cl₂, evaporated, dried, silylated with ca. 300 μ L of *N,O*-bis(trimethylsilyl)-trifluoroacetamide (BSTFA) in pyridine (1:2 v/v) and analyzed by GC and GC–MS.
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