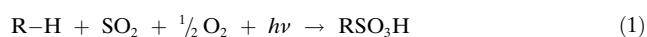


Activation of Alkanes

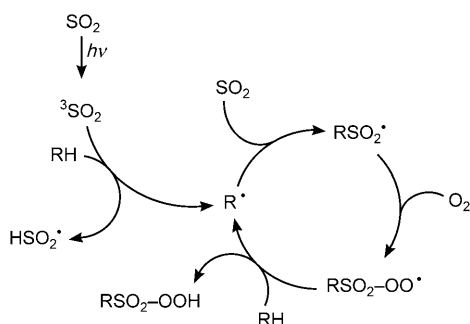
Semiconductor-Photocatalyzed Sulfoxidation of Alkanes**

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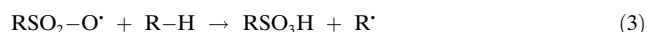
C–H bond activation and functionalization is one of the major challenges in chemistry.^[1] A rare example of an industrially applied process is the sulfoxidation of liquid alkanes by sulfur dioxide and oxygen upon UV irradiation [Eq. (1)].^[2]



In the case of the linear C_{16–20} alkanes the resulting alkanesulfonic acids are used as biodegradable surfactants. The primary reaction steps of this rare alkane functionalization consist of UV excitation of SO₂^[3] followed by hydrogen abstraction from the alkane to produce an alkyl radical (Scheme 1). Subsequent addition reactions with SO₂ and O₂ generate an alkylpersulfonyl radical, which in turn produces another alkyl starter radical and the persulfonic acid. Fragmentation and hydrogen abstraction [Eqs. (2) and (3)] afford the alkanesulfonic acid.^[4–6]



Scheme 1. Mechanism of sulfoxidation of alkanes upon UV irradiation.



According to this reaction scheme, photosulfoxidation is a photoinduced radical chain reaction and therefore proceeds without further irradiation when the substrates are short-chain alkanes (< C₁₀) devoid of impurities. In the case of long unbranched alkanes of insufficient purity, termination steps

like radical dimerization and radical–radical recombination dominate and the reaction requires permanent irradiation. However, addition of radical initiators or promoters like acetic anhydride again induces a chain reaction.^[4,5] In general regioisomeric alkyl radicals are formed in the hydrogen-abstraction step; one exception is the photosulfoxidation of adamantane in the presence of hydrogen peroxide which affords regioselectively 1-adamantanesulfonic acid.^[7] A rare example of a sensitized process is the mercury-photosensitized sulfination of alkanes with SO₂ producing initially sulfinic acids (RSOOH) and sulfinic esters, which can be further oxidized to sulfonic acids with hydrogen peroxide.^[8]

All the reactions mentioned above occur only upon excitation of sulfur dioxide or mercury with UV light. We report herein on the first catalytic photosulfoxidation of alkanes with visible light. This reaction does not require UV lamps or toxic sensitizers but only a nontoxic semiconductor powder.

When a suspension of titania in *n*-heptane was irradiated with visible light ($\lambda \geq 400$ nm) under an atmosphere of SO₂/O₂ (1:1, v/v), the formation of *n*-heptanesulfonic acid (**1**) was observed (Table 1, Figures S1 and S2 in the Supporting Information). Only traces of the sulfonic acid were observable in the absence of titania. Initial rates of product formation were 3.5 mmol L^{−1} h^{−1} and 5.0 mmol L^{−1} h^{−1} for the anatase materials Titanhydrat and Hombikat, respectively, whereas for rutile and the mixed-phase powder P25 (75% anatase/25% rutile) values of 6.0 mmol L^{−1} h^{−1} and 7.5 mmol L^{−1} h^{−1} were observed. Of the modified titania powders (entries 5–7, Table 1), which are all good photocatalysts for the complete oxidation of 4-chlorophenol with visible-light irradiation,^[9–12] only the titanium dioxide/chlororhodate complex and carbon- or nitrogen-modified titania exhibited moderate rates of 3.5 mmol L^{−1} h^{−1}.

Under the given experimental conditions, formation of **1** stopped after 6 h of irradiation time (Figure S3 in the Supporting Information). However, separating the catalyst powder and washing with methanol restored the activity.

Table 1: Initial rate *r_i* for the formation of heptanesulfonic acid (**1**) in the presence of various titania photocatalysts (see the Experimental Section).

Entry	Photocatalyst ^[a]	<i>r_i</i> [mmol L ^{−1} h ^{−1}]
1	Titanhydrat(A)	3.5
2	TiO ₂ (Hombikat, A)	5.0
3	TiO ₂ (B)	6.0
4	TiO ₂ (P25, A + B)	7.5
5	[TiO ₂]OPtCl ₄ (A)	0.0
6	[TiO ₂]ORhCl ₃ (A)	3.5
7	TiO ₂ -C, TiO ₂ -N (A)	3.5

[a] A and B designate anatase and rutile modifications, respectively.

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Even after this procedure had been repeated three times, the photocatalyst still retained its original activity (Figure 1). This observation suggested that the reaction is inhibited by strong product adsorption and that washing desorbs the sulfonic acid. Accordingly, no product formed when **1** was added to the suspension prior to irradiation. A similar deactivation and

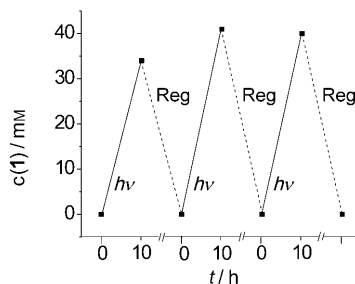


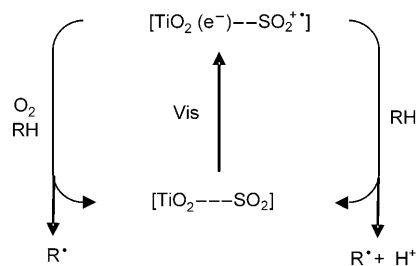
Figure 1. Sequential photosulfoxidation of *n*-heptane. $\lambda_{\text{irr}} \geq 400$ nm. Reg = regeneration of catalyst.

activation was observed during photooxidation of sulfur dioxide in the presence of gaseous *n*-heptane at UV-irradiated titania.^[13] Product formation was also inhibited when small amounts of water (0.3 vol %) were present in the suspension. This may be because the reactive surface centers for heptane oxidation are blocked by preferential adsorption.

When the reaction was stopped after 2 h of irradiation—this corresponds to the formation of **1** in 15 mM concentration—and the reaction mixture was left for three days in the dark at room temperature, product formation continued affording 50 mM of **1**. However, when the radical scavenger hydroquinone^[14] was present during the dark phase, the production of sulfonic acid did not continue.

These findings suggest that this novel photosulfoxidation is also a radical chain reaction. However, in this case the alkyl starter radical is generated not by UV excitation of sulfur dioxide but through absorption of visible light by the TiO_2 /*n*-heptane/ SO_2 / O_2 system. Since only the modified titania powders (entries 5–7, Table 1) are able to absorb visible light, it seems likely that the unmodified materials (entries 1–4, Table 1) form a charge-transfer complex with sulfur dioxide. In fact, exposure of P25 to sulfur dioxide resulted in a yellowish coloration of the powder, which corresponds to a broad absorption maximum in the diffuse reflectance spectrum at 410–420 nm (see Figure S4 in the Supporting Information).

Accordingly, we propose the mechanism for alkyl radical generation depicted in Scheme 2. Visible light excitation of the charge-transfer complex affords a conduction band electron $[\text{TiO}_2(e^-)]$ and an adsorbed sulfur dioxide radical cation. Oxygen reduction by $[\text{TiO}_2(e^-)]$ produces superoxide, and the adsorbed sulfur radical cation may oxidize the alkane to the alkyl radical and a proton.^[15] Superoxide may also generate an alkyl radical through protonation by adsorbed water or surface OH groups to the hydroperoxyl radical^[18] and subsequent hydrogen abstraction from the alkane. The alkyl radical thus produced is expected to initiate a radical chain reaction as formulated for the stoichiometric UV



Scheme 2. Proposed mechanism for alkyl radical generation.

photosulfoxidation summarized in Scheme 1 and Equations (2) and (3).

The proposed mechanism is supported by the observation that the reaction is inhibited in the presence of only 10 vol % 2-propanol; this compound should be oxidized much more readily than the alkane, and it is also an efficient OH radical scavenger.^[19]

The general applicability of the presented C–H activation is demonstrated by the successful photosulfoxidation of cyclohexane and adamantane. Since adamantane is a solid, the reaction was conducted in glacial acetic acid (see Figures S5 and S6 in the Supporting Information). Of the anatase powders investigated, Titanhydrot led to the highest yield of 1-adamantanesulfonic acid (**2**) (Figure 2).

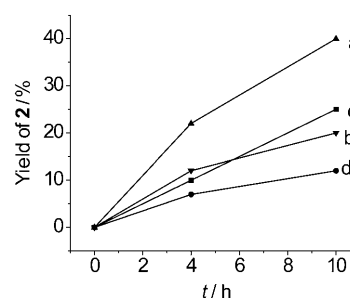


Figure 2. Yield of adamantanesulfonic acid (**2**) in the presence of the photocatalysts Titanhydrot (a), P25 (b), TiO_2 -C (c), and TiO_2 -N (d).

In summary, this novel visible-light-induced C–H activation can be classified as a semiconductor-photocatalysis type B reaction, and the previously known two-component addition^[20] is extended to a three-component system.

Experimental Section

Titanhydrot (Kerr-McGee Pigments, $300 \text{ m}^2 \text{ g}^{-1}$) and P25 (Degussa, $50 \text{ m}^2 \text{ g}^{-1}$) were used as received. We are grateful to Prof. T. Egerton for a sample of high-surface-area rutile ($140 \text{ m}^2 \text{ g}^{-1}$). $[\text{TiO}_2]\text{OPtCl}_4$,^[9] TiO_2 -C,^[10] TiO_2 -N,^[11] and $[\text{TiO}_2]\text{ORhCl}_3$,^[12] were prepared according to literature procedures and have surface areas of 260, 160, 170, and $230 \text{ m}^2 \text{ g}^{-1}$, respectively. Adamantane (Acros) and *n*-heptane (Fischer) were used as received.

Titania powder (30 mg) was suspended in *n*-heptane or cyclohexane (15 mL) in a Solidex glass cuvette and sonicated for 15 min. Thereafter, a gaseous mixture of O_2 and SO_2 (60 mL, 1:1 v/v) was added by a syringe. Irradiation was performed with an Osram XBO 150 W xenon arc lamp (I_0 (400–520 nm) = $2 \times 10^{-6} \text{ Einsteins}^{-1} \text{ cm}^{-2}$)

installed in a light condensing lamp housing (PTI A1010S) on an optical train. A cutoff filter of $\lambda \geq 400$ nm was placed in front of the cuvette. The suspension was stirred magnetically. After 5 h of irradiation, the photocatalyst was removed with a micropore filter (Whatman 0.45 μm) and the filtrate was concentrated in vacuo. The slightly yellow, oily residue was dissolved in methanol (3 mL) and analyzed by HPLC^[21,22] (see the Supporting Information). Adamantane (136.2 mg, 1 mmol) was photosulfoxidized analogously in glacial acetic acid (15 mL; see the Supporting Information). The high photocatalyst concentration of 2 g L⁻¹ ensures complete light absorption in each experiment, and therefore the initial rates (calculated from the product concentration at 5 h irradiation time) are comparable.

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