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Mercury-Photosensitized Sulfination, Hydrosulfination, and Carbonylation of Hydrocarbons: Alkane and Alkene Conversion to Sulfonic Acids, Ketones, and Aldehydes

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Mercury-photosensitized sulfination of alkanes, RH, with SO_2 forms sulfinic acids (RSOOH) and sulfinate esters (RSOOR) in high conversion and yield; oxidation of the mixture produces RSO_2OH in high yield. Mercury-photosensitized hydrosulfination of alkenes with H_2 and SO_2 gives RSO_2OH after oxidative workup. Mercury-photosensitized carbonylation of alkanes with CO gives RCHO and R_2CO.

Introduction

Alkane activation and functionalization is an area of great current interest.[1] Most of the catalytic systems currently available suffer from two limitations: (i) the catalyst degrades rapidly, and (ii) conversions must be kept low because the functionalization product is more reactive than the starting alkane. We have been studying mercury-photosensitized reactions because both these problems are avoided. The Hg atom, having no ligands, is not degraded with time, and with "vapor-pressure selectivity"[2e] we can obtain high conversions and yields at the same time. This operates when the product is less volatile than the substrate and accumulates in the liquid phase where it is protected from attack by Hg*.

We showed that mercury-photosensitized hydrodimerizations and dehydrodimerization can be preparatively useful for the synthesis of a wide variety of organic compounds.[2] Both reactions can be carried out on a multigram scale with readily available apparatus at ordinary pressures and temperatures. The mechanisms proposed for dehydrodimerization (eqs 1–4) and hydrodimerization (eqs 5–7) involve radical intermediates. We thought it might be possible to intercept the radicals by introducing a gas that can trap R• before dimerization. In this paper, we describe our results with SO_2 and CO.

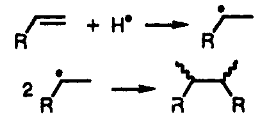
$$\mathrm{Hg + 254\ nm \rightarrow Hg^*} \tag{1}$$

$$\mathrm{RH + Hg^* \rightarrow R^\bullet + H^\bullet + Hg} \tag{2}$$

$$\mathrm{H^\bullet + RH \rightarrow R^\bullet + H_2} \tag{3}$$

$$\mathrm{2R^\bullet \rightarrow R_2 + R(-H) + RH} \tag{4}$$

$$\mathrm{Hg^* + H_2 \longrightarrow 2H^\bullet + Hg} \tag{5}$$



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(7)

We anticipated several potential problems. Radical recombination has a very low activation energy and so we could not be sure that CO or SO_2 would intercept all the R• before recombination. On the other hand, as a reactive intermediate, the radical should be present only in low concentration, whereas the concentration of trapping gas is much higher, favoring trapping over recombination. It was unclear whether the trapping gas would quench Hg* and prevent CH bond homolysis. Finally, it was uncertain what the final product would be from any RCO• and RSO_2• intermediates.

Apparatus

We have limited ourselves to ordinary pressures and temperatures and to equipment readily available in synthetic laboratories in order to facilitate the widest application of the method. Figure 1 shows the two types of reactors we used, simple modifications of the ones employed in previous Hg* reactions.[2e,j] For reactions involving alkanes (Figure 1a), the liquid substrate is placed at the bottom of the quartz reaction vessel and trapping gas is fed into the vessel by means of a long needle inserted from the top of the tube. This is termed the in situ technique (see Experimental Section). For reactions involving alkenes (Figure 1b), the substrate is placed in a separate flask, hydrogen bubbled through it, and the substrate-saturated hydrogen then passed into the bottom of the reactor, by means of a long needle inserted from the top. A flow of trapping gas is fed into the reactor separately by means of an additional needle put 5 cm below the tube neck. This is termed the "presaturation" technique (see Experimental Section).

Results

SO_2 Reactions: Saturated Substrates. The Initial Experiment. We find that SO_2 is able to largely or completely suppress dimerization by trapping[3] the radical intermediates in mercury-sensitized reactions of alkanes to give multigram quantities of SO_2-derived products. For example, with 6 mL/min of SO_2 (reflux, in situ apparatus of Figure 1a; see Experimental Section) the yield of bicyclohexyl from refluxing cyclohexane falls from 95% to 14%, and so the trapping gas almost completely suppresses dehydrodimerization. At first sight the large number of products (eq 8) is surprising. Because we still see some of the dehydrodimer 1, the trapping by SO_2 is not com-

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[1] (a) Webster, D. E. *Adv. Organomet. Chem.* 1977, *15*, 147. (b) Parshall, G. W. *Acc. Chem. Res.* 1970, *3*, 139. (c) Muetterties, E. L. *Chem. Soc. Rev.* 1983, *12*, 283. (d) Shilov, A. E. *The Activation of Saturated Hydrocarbons by Transition Metal Complexes*; D. Riedel: Dordrecht, 1984. (e) Crabtree, R. H. *Chem. Rev.* 1985, *85*, 245. (f) Gretz, E.; Oliver, T. F.; Sen, A. *J. Am. Chem. Soc.* 1987, *109*, 8109. (g) Renneke, R. F.; Hill, C. L. *J. Am. Chem. Soc.* 1986, *108*, 3528. (h) Burk, M. W.; Crabtree, R. H. *J. Chem. Soc., Chem. Commun.* 1985, 1829.

[2] (a) Brown, S. H.; Crabtree, R. H. *J. Chem. Soc., Chem. Commun.* 1987, 970. (b) Brown, S. H.; Crabtree, R. H. *Tetrahedron Lett.* 1987, *28*, 5599. (c) Brown, S. H.; Crabtree, R. H. *J. Chem. Educ.* 1988, *65*, 290. (d) Brown, S. H.; Crabtree, R. H. U.S. Patent 4,725,342, 1988. (e) Brown, S. H.; Crabtree, R. H. *J. Am. Chem. Soc.* 1989, *111*, 2935, 2946. (f) Muedas, C. A.; Ferguson, R. R.; Crabtree, R. H. *Tetrahedron Lett.* 1989, *30*, 3389. (g) Boojamra, C. G.; Crabtree, R. H.; Ferguson, R. R.; Muedas, C. A. *Tetrahedron Lett.* 1989, *30*, 5583. (h) Ferguson, R. R.; Boojamra, C. G.; Brown, S. H.; Crabtree, R. H. *Heterocycles* 1989, *28*, 121. (i) Ferguson, R. R.; Crabtree, R. H. *Nouv. J. Chem.* 1989, *13*, 647. (j) Muedas, C. M.; Ferguson, R. R.; Brown, S. H.; Crabtree, R. H. *J. Am. Chem. Soc.* 1991, *113*, 2233.

[3] (a) Block, E. *Organic Chemistry: A Series of Monographs*; Academic Press: New York, 1978; Vol. 37, p 210. (b) Farid, S. *J. Chem. Soc., Chem. Commun.* 1971, 73.

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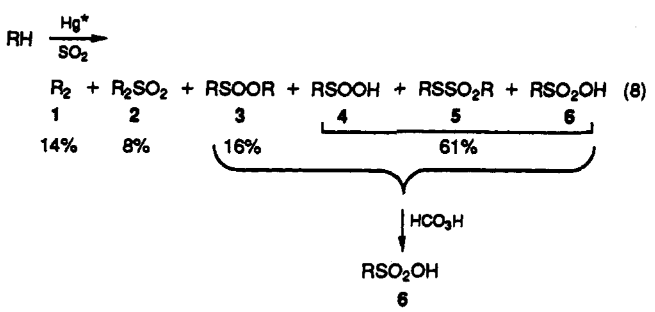

$$\mathrm{RH}\xrightarrow[\mathrm{SO_2}]{\mathrm{Hg^*}}$$

$$\underset{14\%}{\underset{\mathbf{1}}{\mathrm{R_2}}} + \underset{8\%}{\underset{\mathbf{2}}{\mathrm{R_2SO_2}}} + \underbrace{\underset{16\%}{\underset{\mathbf{3}}{\mathrm{RSOOR}}} + \underset{61\%}{\underbrace{\underset{\mathbf{4}}{\mathrm{RSOOH}} + \underset{\mathbf{5}}{\mathrm{RSSO_2R}} + \underset{\mathbf{6}}{\mathrm{RSO_2OH}}}}}_{\downarrow\ \mathrm{HCO_3H}\qquad \underset{\mathbf{6}}{\mathrm{RSO_2OH}}} \quad (8)$$

pletely effective. Sulfone **2** (8%) and sulfinate ester **3** (16%) are minor products. The major species are sulfinic acid **4** and its disproportionation products, thiosulfonate **5** and sulfonic acid **6**.[4] We report the yield of **4**–**6** taken together and refer to the mixture as "RSOOH". Under the conditions of eq 8, this fraction comprises 61% by weight of the product mixture.

RSOOH and RSOOR can both be easily oxidized to the desired sulfonic acid **6** with performic acid (eq 8). We therefore looked for conditions that maximize the yield of the oxidizable fraction consisting of **3**–**5** relative to **1** and **2**, which are not converted to acid in this way.

Nonreflux Conditions. Several changes to the initial procedure were explored: we lowered the temperature below reflux, increased the SO_2 flow rate, and introduced a flow of H_2. As R_2 is still formed in eq 8, the R• were not completely trapped under these conditions. Our thinking was that moving to nonreflux conditions should lead to an increase in the partial pressure of SO_2, $p(SO_2)$. At the reflux temperature of cyclohexane, the mole fraction of cyclohexane in the vapor space tends toward unity, excluding any added gas from the vapor space, because $p(SO_2)$ and p(alkane) must together equal 1 atm. Reducing the temperature causes p(alkane) to fall substantially below 760 Torr, allowing $p(SO_2)$ to become much larger, favoring trapping. For example, cyclohexane at 30 °C has a vp of 120 Torr and so the partial pressure of the added gas is 640 Torr. We also found it necessary to increase the SO_2 flow rate to 20 mL/min to ensure that sufficient trapping gas was being supplied. A flow of H_2 doped into the SO_2 proved beneficial, perhaps because H atoms are formed from Hg* and H_2, and these H atoms may recombine with intermediate $RSO_2^•$. A 15 mL/min flow of H_2 gave the highest sulfonic acid yields after oxidative workup.

Under these new conditions, cyclohexane at 30 °C gave 82% by weight of RSOOH and 17% of RSOOR. Oxidation of this mixture with performic acid gave sulfonic acid (99%). No dimer was formed so the R• are now completely trapped. Curiously, only 1% of sulfone was formed.[5]

Oxidation therefore greatly simplifies the product mixture, and all reactions were treated in this way. For all the compounds studied, we find that the performic acid oxidation of both sulfinic acid and sulfinate takes place in extremely high yield (99%), and we report the percent by weight (weight %)[6] of sulfonic acid present in the involatile fraction after oxidation. The sulfonic acids were separated by solvent extraction as described in the Experimental Section.

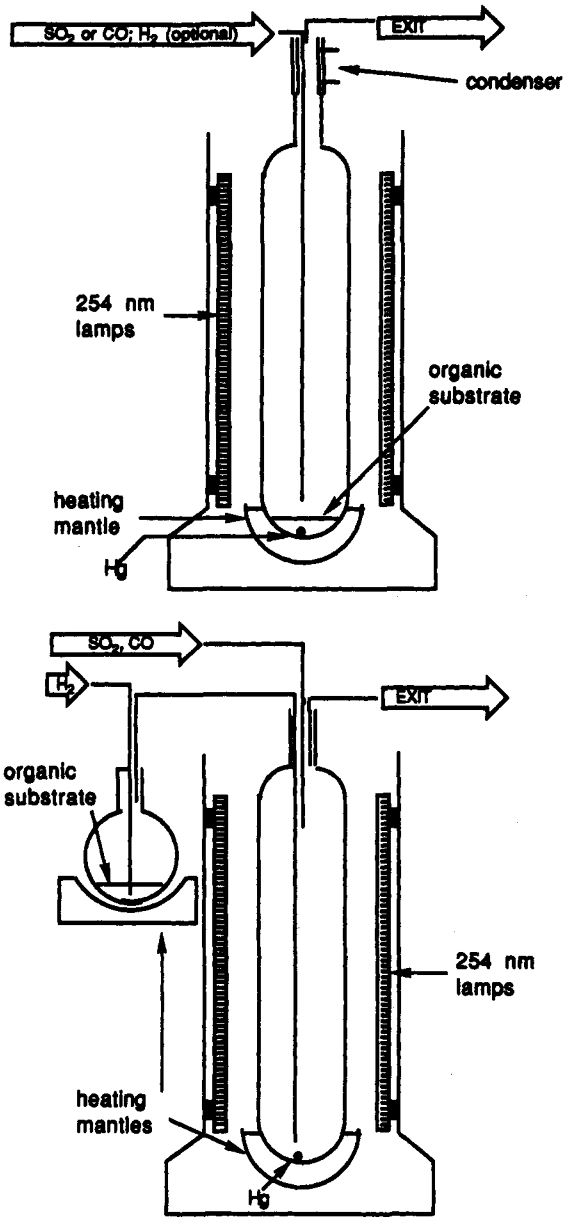

Figure 1. (a) Apparatus for in situ technique. (b) Apparatus for presaturation technique.

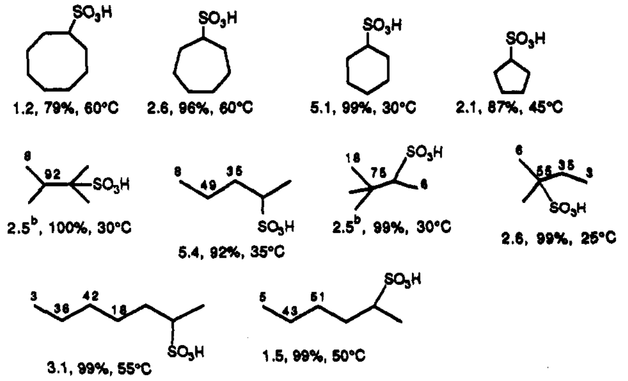

Figure 2. Some sulfonic acids from Hg-sensitized sulfination of alkanes, followed by oxidation. Numbers are as follows: production rate RSO_3H in mmol/h, weight % $RSO_3H{\cdot}3H_2O$, photolysis temperature. Reactions carried out per Experimental Section, except as indicated. Superscript b indicates no H_2 doping.

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(4) Alkane sulfinic acids are known to disproportionate, giving primarily thiosulfonate ($RSSO_2R$) and sulfonic acid (RSO_3H): (a) Kice, J. L.; Bowers, W. *J. Am. Chem. Soc.* **1962**, *84*, 605. (b) Kice, J. L.; Hampton, D. C.; Fitzgerald, A. *J. Org. Chem.* **1965**, *30*, 882. (c) Kice, J. L.; Toth, B. R.; Hampton, D. C.; Barbour, J. F. *J. Org. Chem.* **1966**, *31*, 848. (d) Kice, J. L.; Guaraldi, G.; Venier, C. G. *J. Org. Chem.* **1966**, *31*, 3561. (e) Ratcliffe, C. T.; Shreeve, J. *J. Am. Chem. Soc.* **1968**, *90*, 5403.

(5) One reason for the fall in sulfone production in changing to nonreflux conditions may be that E_{act} for recombination at the oxygen in $RSO_2^•$ may be lower than at the comparatively hindered sulfur. At the lower temperature, fewer $R^•/RSO_2^•$ interactions have sufficient energy to make the more stable sulfone.

(6) Weight % refers to sulfonic acid in the final product mixture of *involatile materials* after both photochemical and oxidation steps.

Table I. Reflux vs Nonreflux Conditions[a]

	reflux T = 50 °C			nonreflux T = 30 °C		
	RSO_3H rate of production (mmol/h)	selectivity	wt % $RSO_3H·3H_2O$	RSO_3H rate of production (mmol/h)	selectivity	wt % $RSO_3H·3H_2O$
	3.1	(3°:1°) 51:1	87	2.5	(3°:1°) 72:1	99
	5.3	(2°:1°) 15:1	98	2.5	(2°:1°) 18:1	99

[a] No H_2 doping in these short-run reactions, to eliminate selectivity enhancement when H$^{\bullet}$ becomes an important abstractor.[2e,j]

Table II. Reflux vs Nonreflux Conditions—Further Examples

	reflux conditions			nonreflux conditions		
final product	RSO_3H rate of production (mmol/h)	wt %	T (°C)	RSO_3H rate of production (mmol/h)	wt %	T (°C)
cyclohexanesulfonic acid	13	96	81	5.1	99	30
n-heptanesulfonic acid	7.5	64	98	3.1	99	55
n-hexanesulfonic acid	3.6	58	69	1.5	99	50
cyclooctanesulfonic acid	0.4	18	152	1.2	79	60

Figure 2 shows some of the compounds made by this method. In each case, the photochemical step was carried out under the nonreflux conditions mentioned above. The high selectivities achieved make this a synthetically useful procedure.

Comparison of Conditions. Nonreflux conditions have some disadvantages. Colored bodies accumulate on the sides of the quartz vessel so that after a time (10–15 h) it becomes necessary to halt the reaction as light no longer penetrates the tube. Under reflux conditions, the walls consist of a liquid film of falling substrate, and so any organic material is largely washed to the bulk liquid phase where light attenuation is not important. Another advantage to refluxing is the higher sulfonic acid production rate,[7] but at the expense of final weight % of sulfonic acid and C–H bond selectivities. Table I compares results for two isomers of hexane.

With most substrates, the yield and sulfonic acid production rate are even more sensitive to exact conditions (Table II). Cyclooctane is anomalous in that the sulfonic acid production rate is higher under nonreflux conditions because of the low weight % of sulfonic acid achieved under reflux conditions.

H_2 Doping. For reactions conducted under nonreflux conditions, H_2 doping usually does not enhance weight % of RSO_2OH by more than 10%, but H_2 doping is more effective for reactions run at reflux. With cyclohexane, for example, including an H_2 flow raises the weight % of sulfonic acid from 75% to 96%, without significantly altering the alkane conversion rate.

SO_2 Reactions: Unsaturated Substrates. H atoms formed by eq 5 readily react with alkenes to give alkyl radicals, which go on to give hydrodimerization products by eqs 6 and 7. We wished to see if it would be possible to trap the radical intermediates formed in this way. The advantage of using an alkene is the high regiospecificity of radical formation.[2f,j] For example, with *n*-hexane, the secondary C–H bonds are equally reactive, giving a statistical mixture of radicals, but with 3-hexene, essentially only the hex-3-yl radical is formed; no other regioisomers were seen.

We find we can use this regiospecificity to synthesize specific sulfonic acids. From sulfination/oxidation of *n*-hexane, for example, both 2- and 3-hexane sulfonic acids are formed (43% and 51%, respectively). Hydrosulfination of 1-hexene gives the 2-substituted acid (71%) free of the 1- and 3-isomers. Hydrosulfination of 3-hexene gives the 3-substituted acid (75%), again free of the other isomers. This is successful only with olefins capable of producing secondary radical intermediates; however (Figure 3) olefins such as 2,3-dimethyl-2-butene, which can only form a tertiary radical on H atom addition, do not give a useful olefin conversion rate under our conditions.

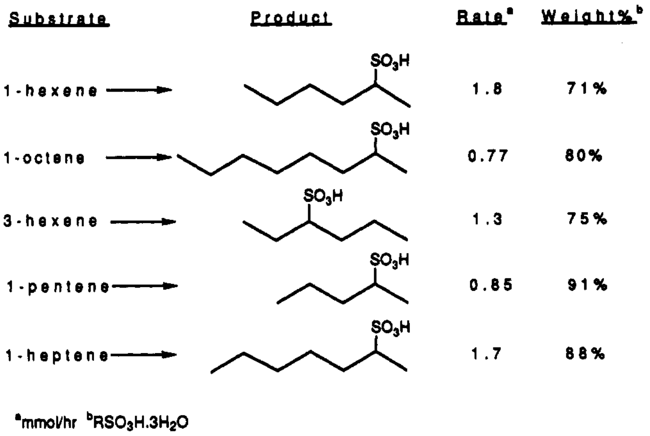

Figure 3. Some sulfonic acids from Hg-sensitized hydrosulfination of olefins and subsequent oxidation.

Discussion

Saturated Substrates. Mechanism. The insertion of photoexcited SO_2 ($SO_2^{\dagger}$)[8] into C–H bonds is known.[9]

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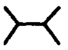
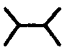
[7] Sulfonic acid production rate is based on the time of photolysis in the first step.

[8] We distinguish the symbol SO_2^{*} from $SO_2^{\dagger}$, the former denoting mercury-photosensitized SO_2 excitation, the latter denoting excitation through direct absorption of light.

[9] (a) Dainton, F. S.; Ivin, K. J. *Trans. Faraday Soc.* **1950**, *46*, 374, 382. (b) Penzhorn, R. D.; Stieglitz, W. G.; Filby, W. G.; Guenther, K. *Chemosphere* **1973**, *2*, 111. (c) Goudie, R. S.; Preston, P. N. *J. Chem. Soc. C* **1971**, 1251. (d) Ohkubo, K.; Masuda, T.; Yamasue, K.; Hayashi, K. German Patent 2,052,698, 1971. (e) Barnard, D. *J. Chem. Soc.* **1957**, 4675. (f) Kice, J. L.; Venier, G. C.; Large, G. B.; Heasley, L. *J. Am. Chem. Soc.* **1969**, *91*, 2028. (g) Durst, T.; Huang, J. C.; Sharma, N. K.; Smith, D. J. H. *Can. J. Chem.* **1978**, *56*, 512. (h) Margerum, J. D.; Lackner, A. M.; Little, M. J.; Petrusis, C. T. *J. Phys. Chem.* **1971**, *75*, 3066. (i) Masuda, T. Japan Patent 78 28, 417, 1978. (j) Timmons, R. B. *Photochem. Photobiol.* **1970**, *12*, 219. (k) Badcock, C. C.; Sidebottom, H. W.; Calvert, J. G.; Reinhardt, G. W.; Damon, E. K. *J. Am. Chem. Soc.* **1971**, *93*, 3115. (l) Sidebottom, H. W.; Badcock, C. C.; Calvert, J. G.; Rabe, B. R.; Damon, E. K. *J. Am. Chem. Soc.* **1971**, *93*, 3121. (m) Takeuchi, H.; Nagai, T.; Tokura, N. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 695.

Table III. Selectivity and Alkane Conversion Rates for the Reflux Reaction of 2,3-Dimethylbutane

	selectivity 3°:1°	ξ (mmol/h)	wt % $RSO_3H \cdot 3H_2O$
 + SO_2 + $h\nu$	17:1	0.71	98
 + SO_2 + Hg^*	51:1	3.6[b]	87
 + Hg^*	54:1	1.8[c]	97[a]

[a] Weight % dimer in involatile fraction. [b] Quantum yield (ϕ) = 0.13. [c] ϕ = 0.063.

Since a low-pressure Hg lamp is involved, we need only consider the Hg emission lines. It did not seem likely that direct absorption by SO_2 could be occurring at 254 nm, the most intense Hg line,[10a] because of the small absorption coefficient of SO_2 at that wavelength (ϵ = 1.1 atm^{-1} cm^{-1}).[10b] SO_2 does absorb more strongly at the wavelengths of the more energetic, but much less intense, Hg lines at 185 and 110 nm, for which ϵ is 50 and 130 atm^{-1} cm^{-1}, respectively.[10a,c] In the presence of Hg vapor, however, Hg itself absorbs much more strongly than SO_2 and essentially all the light should be adsorbed by the Hg. This leaves mercury photosensitization of either SO_2 (Hg^*/SO_2, eqs 10 and 11) or RH (Hg^*/RH, eq 9) as the only plausible pathways.

Mechanism 1:

$$RH \xrightarrow{Hg^*} R^\bullet + H^\bullet \tag{9}$$

Mechanism 2:

$$SO_2 \xrightarrow{Hg^*} SO_2^* \tag{10}$$

$$RH \xrightarrow{SO_2^*} R^\bullet + H^\bullet \tag{11}$$

Subsequent steps in mechanisms 1 or 2:

$$SO_2 + R^\bullet \rightarrow RSO_2^\bullet \tag{12}$$

$$RSO_2^\bullet + (H^\bullet, R^\bullet) \rightarrow RSOO(H, R) \tag{13}$$

$$RSO_2^\bullet + R'H \rightarrow RSOOH + R^\bullet \tag{14}$$

As for the subsequent steps (eqs 12–14), SO_2 is known to trap carbon-centered radicals very rapidly.[3] Where R is $Me^\bullet$, the rate constant of eq 12 is 2×10^8 M^{-1} s^{-1}.[3a] Radical recombinations such as in eq 13 are almost always very rapid, but the concentrations of the reactive intermediates $RSO_2^\bullet$ and $H^\bullet$ are both low. Another possible route to sulfinic acid is abstraction from alkane (eq 14). The rate constant is relatively low, however. For example, where R is $MeSO_2^\bullet$ and R'H is cyclohexane, the rate constant for eq 14 is only 3×10^2 M^{-1} s^{-1},[3a] but the alkane concentration is high, and so this could still be a significant contributor.

We measured the tertiary/primary selectivity for attack at the tertiary or primary C–H bonds of 2,3-dimethylbutane and the overall alkane conversion rate in mmol/h (ξ)[11] for the three situations shown in Table III. The first entry shows the results for $SO_2/h\nu$/RH in the absence of Hg, the second for Hg^*/SO_2/RH system, and the third for Hg^*/RH in the absence of SO_2; all three reactions are conducted under reflux conditions. The selectivity and ξ values for the first entry are very different from the others, confirming that direct light absorption by SO_2 cannot account for the chemistry we see. The lower selectivity in this case probably arises from weak, but high-energy Hg lines (110, 185 nm) where SO_2 absorbs strongly. The alkane conversion rate is low because there are no *intense* Hg lines where SO_2 absorbs strongly. In support of this proposal is that we find ξ depends directly on the tube radius, r.[12] When Hg is the absorber, all the light is known to be absorbed within a few millimeters of the wall[2e] and so the reactive zone is dependent on the surface area of the reactor and therefore directly on r. When Hg lines and SO_2 are involved, the reactive zone is the whole tube and so ξ depends on r^2.

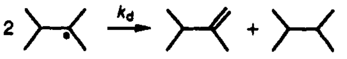
Table IV. ξ for the Reaction of Cyclohexane in Different Atmospheres[a]

atmosphere	ξ (mmol/h)	atmosphere	ξ (mmol/h)
H_2	5.9	CO	0.57
Ar	5.9	SO_2	6.3

[a] Partial pressure cyclohexane = 100 Torr, T(cyclohexane) = 25 °C.

To determine whether mechanism 1 or 2 is dominant under reflux conditions, we note that entries 2 and 3 (Table III) show similar selectivities. Entry 3 involves Hg^*/RH chemistry, suggesting that entry 2 must also do so. Under reflux conditions $p(SO_2)$ is very small, so Hg^*/RH reactive collisions (mechanism 1) must dominate the chemistry.

The ξ value found for Hg^*/RH (entry 3) is substantially less than for Hg^*/SO_2/RH (entry 2). This is consistent with the current mechanistic picture for the Hg^*/RH system. Tertiary radicals more readily disproportionate (eq 15) than recombine (eq 17). The appropriate rate ratios (k_d/k_r) are typically 1–3.[13] In the Hg^*/RH system, radical disproportionation is followed by H atom addition (eq 18) to the intermediate olefin. The net result is that not all of the radicals formed survive to give dimers. In the presence of SO_2 radicals that would disproportionate are now trapped and survive to give observable products. The selectivities and ξ values shown in entry 2 are therefore particularly significant in that they better reflect the initial radical distribution, which in previous work has always been obscured by subsequent reactions such as eqs 15 and 16. As expected on this basis, ξ does not show a large increase for cyclohexane because cyclohexyl radicals disproportionate far less, having k_d/k_r values around 0.6[13] and that on moving from Hg^*/RH to $Hg^*/RH/SO_2$ conditions ξ increases only by a factor of 1.1 for cyclohexane, rather than 2.0 as found for the tertiary radical. An alternative explanation for the increase in ξ for SO_2 reactions is that eq 14 plays a significant role by providing additional $R^\bullet$.



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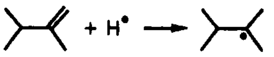

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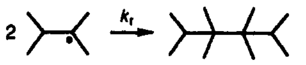

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[10] (a) *CRC Handbook of Chemistry and Physics, 66th ed.*; CRC Press: Boca Raton, FL, 1985–86. (b) Warneck, P.; Marmo, F. F.; Sullivan, J. O. *J. Chem. Phys.* **1964**, *40*, 1132. (c) Golomb, D.; Watanabe, K.; Marmo, F. F. *J. Chem. Phys.* **1962**, *36*, 958.

[11] ξ is not the same as RSO_2OH production rate, because ξ takes into account all alkane consumed by the initial photochemical step, including the "protecting" R groups of RSOOR, which are lost on oxidative workup. ξ is therefore the number of mol of R groups appearing per h in the products from the first step.

[12] For the 2,3-dimethylbutane reaction, ξ drops from 0.71 to 0.19 mmol/h when the tube radius is reduced by a factor of 2.05 (theoretical value for small tube, based on volume, ξ = 0.17 mmol/h; based on surface area, ξ = 0.35 mmol/h).

[13] Gibian, M. J.; Corley, R. C. *Chem. Rev.* **1973**, *73*, 441.

Table III and mechanism 1 apply to reflux reactions. For reactions conducted under the synthetically more useful nonreflux conditions, we still need to consider mechanism 2 (eqs 10 and 11) as a potential alternative because $p(\mathrm{SO_2})$ is much higher and the chance of quenching Hg* by SO_2 greater. We tested for SO_2*-mediated alkane activation by comparing ξ values for cyclohexane in different atmospheres (Table IV). Ar has a small quenching cross-section (QCS) for Hg* (QCS $\approx$ 0.0 Å^2)[14b] compared to cyclohexane (QCS = 14 Å^2)[14a] and is our control along with H_2 (QCS = 6.0 Å^2).[14a] In the presence of the CO (QCS = 4.1 Å^2),[14a] ξ is drastically reduced, presumably because CO competitively quenches Hg*, and CO* (from Hg* + CO) cannot subsequently activate alkane. Although SO_2 (QCS > 20 Å^2)[14c] is a highly efficient quencher like CO, ξ is slightly *higher* than with Ar. If SO_2* were unable to activate alkanes, a lower ξ, similar to that observed with CO, would be expected. This indicates that SO_2* can indeed activate C–H bonds. That $\xi(\mathrm{SO_2})$ is even greater than $\xi(\mathrm{Ar})$ shows that SO_2 is also trapping radicals before they can disproportionate.

Synthetic Aspects: Reflux vs Nonreflux Conditions. Under nonreflux conditions, selectivities and yields rise somewhat, and in general at the expense of acid production rate (Table I).[15] The enhanced selectivity may in part be due to the greater selectivity of SO_2*, but more likely to the lower temperature of the system, which would allow more efficient trapping of the more stable (and less easily trapped) secondary and tertiary radicals. We have so far been unable to distinguish between the two effects. The higher overall sulfonic acid production rate under reflux is presumably due to the enhanced p(alkane) over nonreflux conditions, causing a greater radical production rate.

Higher boiling substrates (bp >100 °C) gave much better yields of sulfonic acids at temperatures lower than reflux, probably as a result of less efficient trapping by SO_2 at the higher temperature or more radical fragmentations and rearrangements.[16] For example, the yield of cyclooctane sulfonic acid rises from 18% to 79% in moving from a reflux temperature of 152 °C to nonreflux conditions at 60 °C (Table II).

Sulfinic acid is usually the major product from the photochemical step, while sulfinate ester is the principal minor one. One reason for this order may be the high rate constant of radical trapping by SO_2,[3] reducing the chance of forming sulfinate by $RSO_2^\bullet/R^\bullet$ combination. In addition, the large gas-kinetic velocity of H_2 and $H^\bullet$ in the vapor phase, compared to $R^\bullet$ or $RSO_2^\bullet$, should lead to $H^\bullet/RSO_2^\bullet$ collisions predominating over $R^\bullet/RSO_2^\bullet$ collisions; a similar effect has previously been described in connection with our earlier work.[2j] Conducting a reaction with an additional flow of H_2 usually results in a higher proportion of sulfinic acid because there are more H atoms available (by eq 5) for recombination with intermediate $RSO_2^\bullet$. In this respect, we found that it was more important to employ H_2 doping in the reflux reactions than under nonreflux conditions. The reason is that the concentration of H atoms under reflux conditions is much less than under nonreflux conditions; H_2 doping provides an important way of enhancing to the ambient H atom population, and hence the yield of sulfinic acid in the first step. As an example, for the reflux reaction of cyclohexane, yield of sulfonic acid (after oxidative workup) increases from 75% to 96% with the additional flow of H_2. In the nonreflux case, on the other hand, essentially no change is seen, and the yield increases from 98% to 99%. A minor third factor is the availability of forming RSOOH by H atom abstraction reaction from alkane by $RSO_2^\bullet$, a slow process.[3a]

Polysulfination. Charring, known[9a] to be a result of polysulfination, is not significant in our system, and we attribute this to vapor pressure selectivity.[2e] Once the comparatively involatile SO_2-derived product forms, it condenses and returns to the bulk liquid phase where it is protected from further reaction. This is because the Hg* reactions occur at a much lower rate (<10^4) in the liquid phase than the gas phase.[2e]

Unsaturated Substrates. Mechanism. In the hydrosulfination reactions (Figure 3), the mechanism is presumed to be H atom addition to olefin (eq 6) followed by trapping and recombination (eqs 12 and 13). Careful control of the relative ratios of olefin, SO_2, and H_2 was required for success. The highest yields were achieved when the H_2 stream was presaturated with olefin outside the photoreactor (Figure 1b), as opposed to reacting olefin being supplied from within the photoreactor (in situ technique, Figure 1a); this presaturation of the H_2 stream minimizes undesirable thermal and photochemistry between olefin and SO_2.

For example, in the reaction of 1-octene, the yield of sulfonic acid drops from 80% to 45% when the reaction is conducted in situ. Known photochemistry between liquid alkene and SO_2*, resulting in polysulfone formation,[9a,l] reduces the yield of sulfonic acid precursors to such a degree that we never react unsaturated substrates by the in situ method. The absorption spectrum of Hg in hydrocarbon solution is broadened to the point that little light is adsorbed by Hg,[2e] allowing the light through to excite SO_2 to SO_2*, which adds to olefin to start a chain process resulting in polysulfone.[9a,l]

Alkenes, such as 2,3-dimethylbutene, which can only give tertiary radicals, were ineffective substrates under our conditions. It is not clear why this should be, since tertiary radicals from saturated substrate C–H bond homolysis are trapped (e.g., 2,3-dimethylbutane). It may be that the added stability of the ground-state tertiary radical, the excess energy (~40 kcal/mol) the radical is born with,[2f,j] *and* the typically high k_d/k_r values for tertiary radicals[13] (which would tend to keep them in a highly energetic state by eqs 15 and 16) work together to keep SO_2 trapping inefficient.

Little charring occurs in hydrosulfination, and we once again attribute this to vapor pressure selectivity.[2e]

CO Reactions. Trapping of alkyl radicals by CO to give the corresponding acyl radicals[17] (eq 18) is reversible. The first synthetically useful example of free-radical trapping by CO was reported only in 1990 by Ryu et al.[18] In contrast to the situation for SO_2, we find that CO does not entirely suppress alkane dehydrodimerizations at the partial CO pressures we have used (<1 atm). Significant quantities of dialkyl ketone and aldehyde are formed along with the homodimer, however. Trapping is therefore ef-

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(14) (a) Cvetanovic, R. J. *Prog. React. Kinet.* **1963**, *2*, 39. (b) Zemansky, M. W. *Phys. Rev.* **1930**, *36*, 919. (c) Estimated from data in ref 14a.

(15) Cyclooctane is the notable exception.

(16) (a) Paneth, F.; Lautsch, W. *Ber.* **1931**, *64*, 2708. (b) Paneth, F.; Hofeditz, W. *Ber.* **1929**, *62*, 1335. (c) Paneth, F.; Loleit, H. *J. Chem. Soc.* **1935**, 366. (d) Paneth, F.; Lautsch, W. *J. Chem. Soc.* **1935**, 380. (d) Rice, F. O. *Trans. Faraday Soc.* **1934**, *30*, 152.

(17) (a) Abell, P. I. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 2, Chapter 13, p 94. (b) Coffman, D. D.; Pinkney, P. S.; Wall, F. T.; Wood, W. H.; Young, H. S. *J. Am. Chem. Soc.* **1952**, *74*, 3391. (c) Brubaker, M. M.; Coffman, D. D.; Hoehn, H. H. *Ibid.* **1952**, *74*, 1509. (d) Foster, R. E.; Larchar, A. W.; Lipscomb, R. D.; McKusick, B. C. *Ibid.* **1956**, *78*, 5606. (e) Sauer, J. C. *Ibid.* **1957**, *79*, 5314.

(18) Ryu, I.; Kusano, K.; Ogawa, A.; Kambe, N.; Sonoda, N. *J. Am. Chem. Soc.* **1990**, *112*, 1295.

Table V. Cyclohexane Carbonylation Reaction

p_{alkane} (Torr)	p_{CO} (Torr)	product ratio dimer:aldehyde:ketone	ξ (mmol/h)	CO products (mmol/h)	mole fraction CO compds
400	360	15.3:1.2:1[a]	8.6	0.56	0.13
180	580	4.0:1.5:1	2.2	0.47	0.38
100	660	4.2:7.7:1	0.57	0.27	0.67

[a] In addition, a complex mixture of minor products is also formed in 5–8% yield.

ficient enough to give acyl products despite the facile back-reaction to R$^\bullet$ and CO.[19] In contrast to the SO_2 chemistry, these reactions are only useful below reflux temperatures because of the thermal instability of the acyl radical and the low p(CO) under reflux conditions.

The relative amounts of carbonyl compounds and homodimer (R_2) found depend on the particular substrate and conditions. For cyclohexane, with secondary C–H bonds, significant amounts (10–70%) of aldehyde and dialkyl ketone are found. In the case of n-alkanes with more than one type of secondary C–H bond, various carbonyl compounds are formed. Primary C–H bonds are not efficiently homolyzed by Hg*, limiting the utility of this method to produce CO-derived material from primary C–H bonds. Substrates with only tertiary and primary C–H bonds, such as 2,3-dimethylbutane, yield little (<10%) CO-derived material, but mainly alkane homodimers.

The proposed pathway for the CO reactions is shown in eqs 18–21. Table V shows results for cyclohexane. The

$$\mathrm{Hg^* + RH \rightarrow R^\bullet + H^\bullet} \tag{18}$$

$$\mathrm{R^\bullet + CO \rightleftarrows RCO^\bullet} \tag{19}$$

$$\mathrm{RCO^\bullet + R^\bullet, H^\bullet \rightarrow RCO(R, H)} \tag{20}$$

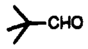
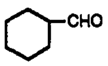
$$\mathrm{2R^\bullet \rightarrow R_2} \tag{21}$$

conversion of alkane drops off quickly as the partial pressure of CO increases probably because CO quenches Hg* without leading to product. For comprison, at 100 Torr of cyclohexane, the ξ for cyclohexane in an Ar atmosphere is 5.9 mmol/h.

The QCS of CO for Hg* is significant (QCS = 4.1 Å^2)[14a] in comparison with that for cyclohexane (QCS = 14 Å^2),[14a] which means that at high CO concentrations quenching of the excited mercury by CO is important, in which case no productive chemistry takes place. The aldehyde to ketone ratio decreases as p(alkane) increases, probably because of the higher ambient concentration of alkyl radicals in the vapor. As the temperature is raised and p(alkane) increases, the mole fraction of CO compounds decreases not only because less CO is available to trap radicals but also because the equilibrium in eq 19 lies more to the left at the higher temperature. The rate of formation of carbonyl compound varies comparatively little with decreasing p(CO), however, because the greater rate of R$^\bullet$ formation compensates for less efficient trapping.

It seemed possible that some of the aldehyde initially formed did not survive to be observed as a product from our system. Since the aldehydic C–H bond is weak (~86 kcal),[20] H atoms, Hg*, and alkyl radicals present in the system can all abstract H and give back the RCO$^\bullet$ radical. The well-documented susceptibility of the aldehydic C–H bond to cleavage[21] induced us to check for potential decarbonylation in our carbonylation system by looking at the reaction of various aldehydes with H atoms, formed via eq 5. Results are shown in Table VI and our proposed scheme in eqs 22–26. The highest R_2 to R_2CO ratio was

Table VI. Ratio of Dimer to Dialkyl Ketone from Reaction of Aldehydes with Hydrogen Atoms[a]

	ratio dimer:ketone
	41.8:1
	10.5:1
	1.8:1

[a] Reactions carried out at the same temperature (T = 40 °C), to eliminate temperature-dependent differences in the equilibrium constant for eq 18.[22]

$$\mathrm{Hg^* + H_2 \rightarrow 2H^\bullet} \tag{22}$$

$$\mathrm{RCHO + H^\bullet \rightarrow RCO^\bullet + H_2} \tag{23}$$

$$\mathrm{RCO^\bullet \rightleftarrows R^\bullet + CO} \tag{24}$$

$$\mathrm{2R^\bullet \rightarrow R_2} \tag{25}$$

$$\mathrm{RCO^\bullet + R^\bullet \rightarrow R_2CO} \tag{26}$$

found for pivalaldehyde, presumably because the R group is tertiary and so loss of CO from RCO$^\bullet$ is particularly easy. The greater stability of tertiary radicals means that the equilibrium lies more to the left in eq 18 for tertiary compared to secondary radicals, which would explain the low yield of CO-derived material from alkanes having only tertiary and primary C–H bonds, such as 2,3-dimethylbutane[23] (in which the tertiary radicals do not add CO and the primary C–H bonds are not efficiently homolyzed). Cyclohexylcarboxaldehyde and 1-heptanal show lower

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(19) (a) Cadman, P.; Dodwell, C.; Trotman-Dickenson, A. F.; White, A. J. *J. Chem. Soc. A* **1970**, 2371. (b) Cadman, P.; Dodwell, C.; Trotman-Dickenson, A. F.; White, A. J. *Ibid.* **1970**, 3190. (c) Lewis, S. N.; Miller, J. J.; Winstein, S. *J. Org. Chem.* **1972**, *37*, 1478. (d) Perkins, M. J.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1974**, 297. (e) Schuh, H.; Hamilton, E. J., Jr.; Paul, H.; Fischer, H. *Helv. Chim. Acta* **1974**, *57*, 2011. (f) Lunazzi, L.; Ingold, K. U.; Scalano, J. C. *J. Phys. Chem.* **1983**, *87*, 529. (g) Turro, N. J.; Gould, I. R.; Baretz, B. H. *Ibid.* **1983**, *87*, 531. (h) Lusztyk, J.; Lusztyk, E.; Maillard, B.; Lunazzi, L.; Ingold, K. U. *J. Am. Chem. Soc.* **1983**, *105*, 4475. (i) Lusztyk, J.; Lusztyk, E.; Maillard, B.; Ingold, K. U. *Ibid.* **1984**, *106*, 2923. (j) Patel, V. F.; Pattenden, G. *Tetrahedron Lett.* **1988**, *29*, 707. (k) Murphy, J. A.; Patterson, C. W.; Wooster, N. F. *Ibid.* **1988**, *29*, 955. (l) Beckwith, A. L. J.; Bowry, V. W. *J. Org. Chem.* **1988**, *53*, 1632.

(20) McMillen, D. F.; Golden, D. M. *Ann. Rev. Phys. Chem.* **1982**, *33*, 493.

(21) (a) Kharasch, M. S.; Urry, W. H.; Kuderna, B. M. *J. Org. Chem.* **1949**, *14*, 248. (b) Harris, E. F. P.; Waters, W. A. *Nature* **1952**, *170*, 212. (c) Patric, R. M., Jr. *J. Org. Chem.* **1952**, *17*, 1009. (d) Davies, A. G.; Sutcliffe, R. *J. Chem. Soc., Chem. Commun.* **1979**, 473. (e) Davies, A. G.; Sutcliffe, R. *J. Chem. Soc., Perkin Trans. 2* **1980**, 819. (f) Chatgilialoglu, C.; Lunazzi, L.; Macciantelli, D.; Placucci, G. *J. Am. Chem. Soc.* **1984**, *106*, 5252. (g) Gottschalk, P.; Neckers, D. C. *J. Org. Chem.* **1985**, *50*, 3498. (h) Beckwith, A. L. J.; Hay, B. P. *J. Am. Chem. Soc.* **1989**, *111*, 2674.

(22) For example, changing the system temperature from 40 to 60 °C in the H atom reaction of 1-heptanal causes the R_2 to R_2CO ratio to rise from 1.8:1 to 3.8:1, presumably because eq 24 lies further to the right at the higher temperature.

(23) An additional source of instability for acyl radicals derived from tertiary radicals has its origin in the characteristically high gas-phase autodisproportionation–combination ratios (k_d/k_r) for tertiary radicals, typically k_d/k_r = 1–3, compared to k_d/k_r for secondary radicals, typically 0.6.[13] Because CO is not a good trap, approximately 100% of the intermediate teritary alkyl radicals are ~40 kcal above the ground state, having arisen from the recycling of an olefin by a hydrogen atom,[2f,j] and the equilibrium in eq 3 is shifted strongly to the left. Not surprisingly, hydrodimerizations of olefins in the presence of CO produce homodimers almost exclusively, with little or no observable CO incorporation.

product ratios. That we observe any dimer or ketone indicates that in our alkane/CO experiments some aldehyde is perhaps lost by H atom attack on its way down to the bulk liquid phase.

Conclusion

Synthetically useful quantities of alkane sulfonic acids can be made with high selectivity by mercury-photosensitized sulfination of alkanes or hydrosulfination of alkenes, followed by oxidation. Mercury-photosensitized carbonylation of alkanes produces significant quantities of dialkyl ketone and aldehyde. SO_2 is a much more efficient trap than CO and will trap tertiary radicals, in contrast to CO for which secondary species are the most stable radicals trapped. Only in the SO_2 reactions are multigram quantities of functionalized product observed, as a result of the greater trapping efficiency of SO_2 and of the fact that SO_2^* can activate C–H bonds with selectivity and efficiency comparable to Hg^*; in contrast, CO merely quenches Hg^* without leading to products.

Photochemical sulfination of alkanes has been of little preparative importance because of low bond selectivity and low alkane conversion rates.[9a] This new method represents the first synthetically useful method of photochemical sulfination of alkanes. On the other hand, overoxidation (charring) and complex mixtures are common results of alkane sulfonation,[24] but this new method avoids these problems by vapor pressure selectivity.[2e]

Experimental Section

General. The photochemical reaction assembly is shown in Figure 1. Quartz tubes of varying sizes (0.16 L, 0.675 L, 1.5 L) from Southern New England Ultraviolet Corp. were employed in a Rayonet 128 W photoreactor (16 low-pressure Hg bulbs × 8 W/bulb, circular array). All hydrocarbons were of commercial grade and from Aldrich Chemical Co. all gases of commercial grade and from Linde, 30% hydrogen peroxide from Mallinckrodt, and 98% formic acid from EM Science; all chemicals were used as received. ^{13}C NMR spectra were obtained on a Bruker 250-MHz spectrometer. GC analyses were carried out on a Varian 3400 gas chromatograph (50-m capillary column; methylsilicone, 0.25 mm i.d., 0.25-μm film thickness) with a 3100 Varian integrator. Caution: mercury vapor is toxic and appropriate precautions must be taken.

In Situ Technique. An excess of saturated hydrocarbon substrate was placed in the quartz photoreactor according to Figure 1a and a drop of Hg added. Trapping gas (SO_2 or CO) was passed into the system through a long needle. An additional flow of H_2 was employed in most of the SO_2 reactions. A condenser is required for reactions run at reflux, but is useful at lower temperatures also.

Presaturation Technique. An excess of unsaturated hydrocarbon substrate was placed in a separate vessel as depicted in Figure 1b. A drop of Hg was added to the quartz photoreactor. H_2 was bubbled through substrate contained in the external vessel. The alkene-containing H_2 stream was then passed into the quartz tube by a long needle that reached the bottom of the tube. An additional flow of SO_2 was fed directly into the tube via a long needle put 5 cm below the tube neck.

All reactions were run at atmospheric pressure. By either method, the crude mixture of products collects by condensation inside the quartz reaction vessel. Starting alkane is removed under reduced pressure, ordinarily on a rotary evaporator. Further isolation of products is described more fully below. Products were analyzed by a variety of methods, discussed below.

Procedure for a Specific Case. Synthesis of Cyclohexanesulfonic Acid. Photochemical Step. The in situ technique (Figure 1a) was employed. A 1.5-L quartz tube was charged with 25.25 g of cyclohexane and primed with SO_2/H_2 prior to turning on the lights. The SO_2 flow rate (flow meter) was 20 mL/min, and the H_2 flow rate was 15 mL/min. A two-stage trap (ice-water followed by CCl_4N_2 slush) was employed to collect cyclohexane entrained in the gas stream. Nonreflux conditions were employed, and the reactor temperature was maintained at 30 °C by air cooling of the lamp-warmed photolysis chamber. The photolysis time was 1 h 45 min. After photolysis, the reaction mixture was weighed together with the trapped material (26.03 g) and transferred to a round-bottom flask, the photolysis tube was washed with chloroform, and the washings were added to the flask. The alkane and chloroform were removed on a rotary evaporator to give 1.95 g of a yellow oil. The volatiles comprised only cyclohexane and chloroform; (25.25 g - 26.03 g + 1.95 g) or 1.17 g of cyclohexane was converted. **Oxidation Step.**[25] To calculate the maximum amount of oxidant that could be required, it was assumed that the entire product mass was sulfinic acid; this is (mass of involatile product)/(MW of sulfinic acid) or in this case 0.013 equiv of H_2O_2. To a well-stirred solution of the crude product mixture and 11 mL of 98% HCOOH was added one-half of the oxidant, or 0.75 g of 30% H_2O_2, in one shot. An exotherm was noted after 2 min, and the temperature was maintained at ~40 °C. The rest of the oxidant was added in 20% aliquots, withdrawing a drop and checking for peroxides by the KI test 10 min after every new addition and halting new additions on the first positive result.[26] HCOOH, H_2O, etc. were then largely removed by rotary evaporation to give the crude sulfonic acid (1.89 g). **Purification of $RSO_2OH{\cdot}3H_2O$.** The product was shaken with 100 mL of H_2O and 25 mL of diethyl ether in a separatory funnel. After 20 min the whitish, somewhat opaque water layer was separated and transferred to a round-bottom flask, and the water was removed on a rotary evaporator at 100 °C. The product was formed as crystals: 1.85 g, 61% yield (based on alkane conversion), 98 wt %.[6] No reproducible mp was found as a result of the hydroscopic character of the compound, but the ^{13}C NMR spectrum (see Spectroscopic Data) matched the spectrum of the independently[28] synthesized material and no extraneous resonances were observed. In addition, the IR spectrum showed the expected bands for the sulfonic acid group.

Figure 2. Photochemical Step. The in situ technique was employed. A 1.5-L quartz tube was charged with excess starting alkane (≥0.1 mol of alkane per h of reaction) and primed with SO_2/H_2 prior to turning on the lights. The SO_2 flow rate was 20 mL/min and the H_2 flow rate was 15 mL/min, except as indicated. For more volatile alkanes, a condenser with recycled ice-water was employed. The reactor temperature was controlled by providing more or less cooling air to the lamp-warmed photolysis chamber. The photolysis time was 1–15 h. After photolysis, the reaction mixture was transferred to a round-bottom flask and the photolysis tube washed with chloroform, and the washings were added to the flask. The alkane and chloroform were removed on a rotary evaporator to give a yellow to dark brown oil. **Oxidation Step.**[25] To calculate ceiling level of oxidant required, it was assumed that the entire product mass was sulfinic acid; let this be Z mol. To a well-stirred solution of the crude product mixture and $846Z$ mL of 98% HCOOH was added half of the oxidant ($0.5(Z(34/0.30))$g of 30% H_2O_2) in one shot. An exotherm was noted after 2 min, and the temperature was maintained at ~40 °C. The rest of the oxidant was added in 20% aliquots, withdrawing a drop and checking for peroxides by the KI test

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[24] (a) Quaedvlieg, M. In *Methoden der Organischen Chemie* (*Houben-Weyl*), 4th ed.; Müller, E., Ed.; Thieme Verlag: Stuttgart, 1955; Vol. IX, Chapter 14. (b) Gilbert, E. E. *Sulfonation and Related Reactions*; Interscience: New York, 1965.

[25] Adapted from: Swern, D.; Billen, G. N.; Findley, T. W.; Scanlan, J. T. *J. Am. Chem. Soc.* **1945**, 1786.

[26] In some cases we used up the entire theoretical amount of oxidant when from NMR study of crude we knew that there was significant sulfinate ester present. We believe this is due either to the use of partially decomposed 30% H_2O_2 or to metal ion (formic acid impurities) or Hg (solvated) catalyzed peroxide decomposition.

[27] (a) Coates, R. M.; Chen, J. P. *Tetrahedron Lett.* **1969**, 2705. (b) Muth, F. In *Methoden der Organischen Chemie* (*Houben-Weyl*), 4th ed.; Müller, E., Ed.; Thieme Verlag: Stuttgart, 1955; Vol. IX, Chapter 20.

[28] (a) Borsche, W.; Lange, W. *Chem. Ber.* **1905**, 2766 (b) Davies, W.; Dick, J. H. *J. Chem. Soc.* **1932**, 483. (c) Borsche, W.; Lange, W. *Chem. Ber.* **1907**, *40*, 2221. (d) Turkieqicz, N.; Pilat, St. *Chem. Ber.* **1938**, *71*, 284. (e) Toptschiew, A. V. *Dokl. Akad. Nauk SSSR* **1957**, *113*, 1302. (f) Wagner, F. C.; Reid, E. *J. Am. Chem. Soc.* **1931**, *53*, 3410. (g) Miron, S.; Richter, G. H. *J. Am. Chem. Soc.* **1949**, *71*, 453.

10 min after every new addition and halting new additions on the first positive result.[26] (RSO_2OR from the oxidation of RSOOR spontaneously hydrolyzes to RSO_2OH under these conditions.[24a,27]) HCOOH, H_2O, etc. were then largely removed by rotary evaporation. **Purification of $RSO_2OH{\cdot}3H_2O$.** The product was shaken with 100 mL of H_2O and 25 mL of diethyl ether in a separatory funnel. After 20 min (or when the H_2O layer was clear, except in the case of the cyclohexane reaction), the water layer was separated and most of the water was removed on a rotary evaporator at 100 °C. Further water removal (optional) was done by azeotropic distillation with benzene in a Dean-Stark apparatus, followed by rotary evaporation to remove the benzene (Caution: benzene is toxic).

Figure 3. Photochemical Step. The presaturation technique was employed with a 1.5-L quartz tube. The tube was primed with H_2 prior to energizing the lights, and the external vessel was charged with excess olefin. The SO_2 and H_2 flow rates were 7 and 21 mL/min, respectively. The temperature of the quartz tube was kept at 45 °C. The temperature of the olefin was chosen so that p(olefin) was ~100 Torr, or ~20 mol % of the H_2 stream. The photolysis time was 1–10 h. The oxidation and purification steps were the same as for Figure 2.

Spectroscopic Data: Figures 2 and 3. The ^1H NMR spectra for the sulfonic acids all had the characteristic chemical shift for the acidic proton at ~10–12 ppm. All of the sulfonic acids showed IR bands corresponding to the $-SO_3H$ group at 1200, 1050, and 650 cm^{-1}. ^{13}C NMR was particularly useful. We confirmed the identities of two literature compounds (cyclohexanesulfonic acid and 2-hexanesulfonic acid) by independently preparing them according to published methods[28] and comparing the ^{13}C NMR spectra of these compounds with ^{13}C NMR spectra of compounds made by the present method. Accurate melting points were often difficult to determine because of the hygroscopic nature of sulfonic acids. To identify an unknown, we relied on precedent for the probable identity of the compound and then on the number, chemical shifts (^{13}C NMR chemical shift calculations), and multiplicities of peaks in the ^{13}C NMR spectrum for confirmation. Microanalysis of the sulfonic acids was not meaningful because of the very hygroscopic nature of the compounds. We report ^{13}C NMR spectra for the sulfonic acid hydrates (see supplementary material), which were isolated as light yellow crystals or oils (depending on dryness). Cycloheptanesulfonic acid, $CDCl_3$: δ 61.96 (d), 28.04 (t), 27.97 (t), 25.49 (t). Cyclohexanesulfonic acid,[28a,b] $(CD_3)CO$: δ 59.46 (d), 30.46 (t), 27.38 (t), 25.19 (t). Cyclooctanesulfonic acid, $CDCl_3$: δ 61.09 (d), 26.68 (t), 26.03 (t), 25.98 (t), 24.82 (t). Cyclopentanesulfonic acid,[28c,d] $(CD_3)_2CO$: δ 60.74 (d), 28.52 (t), 26.06 (t). 2,3-Dimethyl-2-butanesulfonic acid, $CDCl_3$: δ 64.01 (s), 32.72 (d), 19.63 (q), 18.38 (q). 3,3-Dimethyl-2-butanesulfonic acid, $(CD_3)_2CO$: δ 65.68 (d), 33.07 (s), 27.90 (q), 12.11 (q). 2-Heptanesulfonic acid,[28e] $CDCl_3$: δ 56.03 (d), 31.12 (t), 30.10 (t), 25.87 (t), 22.07 (t), 21.99 (t), 13.69 (q), 13.55 (q). 2-Hexanesulfonic acid,[27f] $CDCl_3$: δ 56.20 (d), 29.77 (t), 28.23 (t), 21.95 (t), 13.66 (q), 13.35 (q). 3-Hexanesulfonic acid, $CDCl_3$: δ 61.68 (d), 30.26 (t), 21.81 (t), 19.53 (t), 13.44 (q), 10.59 (q). 2-Methyl-2-butanesulfonic acid, $CDCl_3$: δ 60.30 (s), 28.51 (t), 20.48 (q), 7.84 (q). 2-Octanesulfonic acid, $CDCl_3$: δ 56.27 (d), 31.39 (t), 30.30 (t), 28.76 (t), 26.33 (t), 22.29 (t), 13.83 (q), 13.72 (q). 2-Pentanesulfonic acid,[28g] $CDCl_3$: δ 55.80 (d), 32.28 (t), 19.46 (t), 13.79 (q), 13.40 (q). 3-Pentanesulfonic acid, $CDCl_3$: δ 63.01 (d), 21.22 (t), 10.66 (q) (determined by subtracting the spectrum of 2-pentanesulfonic acid from the spectrum of 2-pentanesulfonic acid and 3-pentanesulfonic acid together). Also, cyclohexyl cyclohexanesulfinate, $CDCl_3$: δ 70.84 (d), 49.83 (d), 33.79 (t), 26.46 (t), 25.84 (t), 25.44 (t), 24.73 (t) (microanalysis: expected H, 9.63; C, 62.57. Found: H, 9.72; C, 62.20.

Table I. Photochemical Step. The general details are the same as for Figure 2, except that a heating mantle was used for the reflux reactions. The lights were energized only after reflux was attained. No H_2 doping was used, and reaction times were less than 1.5 h (to avoid H atom build up and associated C–H bond selectivity enhancement[2e,j]). The oxidation and purification steps were the same as for Figure 2.

Table II. Photochemical Step. The general details are same as for Figure 2, except that a heating mantel was used for reflux reactions. The oxidation and purification steps were the same as for Figure 2.

Table III. Photochemical Step. The general details are the same as for Figure 2, except that a 0.675-L quartz tube equipped with a heating mantle was employed. The lights were energized only after a reflux state was attained. The SO_2 flow rate was 15 mL/min, and no H_2 doping was used. For the control reaction without Hg, all quartzware and glassware were soaked for 24 h in a concd HNO_3 bath to remove traces of Hg and fresh cannulae were used to avoid possible mercury contamination. No trapping gas was employed in dehydrodimerization. The photolysis time was 1–6 h. The oxidation and purification steps for the SO_2 reactions were the same as for Figure 2. For the dehydrodimerization, alkane removal by rotary evaporation gave the dimer.[2a–e] Products were identified by capillary GC or NMR. Quantum yields were calculated by method of ref 2e,j.

Table IV. Photochemical Step. The general details were the same as for Figure 2, except that other gases (CO, Ar, and H_2) replaced SO_2 as the reaction medium (p(quenching gas) ≈ 100 Torr). The gas flow rate was 15 mL/min, and no H_2 doping was used in any of the Ar, CO, or SO_2 cases. The tube was primed with the appropriate gas prior to energizing the lights. The photolysis time was less than 2 h. For the SO_2 reaction, alkane was removed by rotary evaporation, leaving SO_2-derived materials. For the dehydrodimerization (Ar, H_2), alkane was removed by rotary evaporation, leaving the dimer.[2a–e] For the CO reaction, alkane was removed by rotary evaporation, leaving dimer and CO-derived materials. Products were analyzed by capillary GC or NMR.

Table V. The in situ technique was employed with a 1.5-L quartz tube. The tube was charged with excess cyclohexane (~0.1 mol/h of reaction) and primed with CO prior to energizing the lights. The CO flow rate was 15 mL/min. The temperature of the quartz tube determined p(alkane) and was controlled by providing more or less cooling air to the lamp-warmed photolysis chamber. The photolysis time was 1–5 h. After photolysis, the reaction mixture was transferred to a round-bottom flask and the tube was washed with chloroform, and the tube washings were added to the flask. The alkane and chloroform were then removed on a rotary evaporator. The crude product was a clear oil and comprised dimer, dialkyl ketone, and aldehyde. The compounds were analyzed by capillary GC.

Table VI. The in situ technique was employed with a 1.5-L quartz tube. The tube was charged with excess aldehyde (~0.1 mol/h of reaction) and primed with H_2 prior to energizing lights. A low H_2 flow rate of ~10 mL/min was employed to maintain a positive pressure of H_2 in the system, but with the cannula tip above the tube neck to avoid flushing out alkane for radical disproportionation. The temperature of the system was constant for all reactions. The photolysis time was 1–5 h. The crude product comprised mainly aldehyde, dimer, and dialkyl ketone. The product mixtures were analyzed by capillary GC.

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Registry No. Mg, 7439-97-6; SO_2, 7446-09-5; CO, 630-08-0; 2,3-dimethylbutane, 79-29-8; 2,2-dimethylbutane, 75-83-2; 2,3-dimethyl-2-butanesulfonic acid, 135469-37-3; 3,3-dimethyl-2-butanesulfonic acid, 135469-38-4; cyclohexanesulfonic acid, 6922-46-9; heptanesulfonic acid, 60586-80-3; hexanesulfonic acid, 13595-73-8; cyclooctanesulfonic acid, 135469-39-5; cyclohexane, 110-82-7; heptane, 142-82-5; hexane, 110-54-3; cyclooctane, 292-64-8; bicyclohexyl, 92-51-3; cyclohexanecarboxaldehyde, 2043-61-0; bicyclohexyl ketone, 119-60-8; pivalaldehyde, 630-19-3; heptanal, 111-71-7; 2,2,3,3-tetramethylbutane, 594-82-1; 2,2,4,4-tetramethylpentan–3–one, 815-24-7; dodecane, 112-40-3; tridecan-7-one, 462-18-0; 1-hexene, 592-41-6; 1-octene, 111-66-0; 3-hexene, 592-47-2; 1-pentene, 109-67-1; 1-heptene, 592-76-7; 2-octanesulfonic acid, 135469-40-8; 3-hexanesulfonic acid, 135469-41-9; 2-pentanesulfonic acid, 7433-51-4; 2-heptanesulfonic acid, 102881-70-9; cycloheptanesulfonic acid, 135469-42-0; cyclopentanesulfonic acid, 19247-73-5; 2-hexanesulfonic acid, 23311-88-8; 2-methyl-2-butanesulfonic acid, 135469-44-2; 3-pentanesulfonic acid, 51650-30-7; cyclohexyl cyclohexanesulfinate, 135469-43-1.

Supplementary Material Available: ^{13}C NMR spectra (13 pages). Ordering information is given on any current masthead page.