Palladium-catalysed Hydrosulfination: Synthesis of Sulfonic Acids and *S*-Alkyl Alkanethiosulfonates from Alkenes, Sulfur Dioxide and Hydrogen

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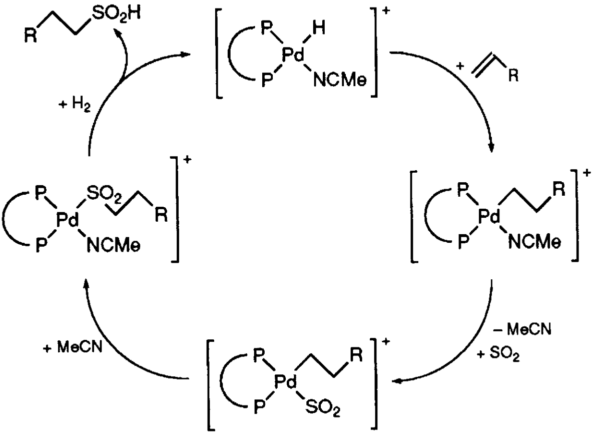
S-Alkyl alkanethiosulfonates and sulfonic acids can easily be synthesized from sulfur dioxide, alkenes, hydrogen and a cationic palladium(II)-diphosphine complex like $[Pd(dppp)(MeCN)_2][X]_2$ **1** [X = non or weakly coordinating anion; dppp = 1,3-bis(diphenylphosphino)propane], at temperatures above the ceiling temperature of the SO_2–alkene copolymer.

Although the hydroformylation reaction has been known for more than 50 years, up to now no comparable reaction with sulfur dioxide instead of carbon monoxide has been reported. One reason is the rapid, radical-initiated polymerization of alkenes with sulfur dioxide below the ceiling temperature of the resulting copolymer.[1] Moreover, the sulfinic acids formed are unstable and react further to give *S*-alkyl alkanethiosulfonates and sulfonic acids [eqn. (1)].[2]

$$R{-}CH{=}CH_2 + SO_2/H_2 \rightarrow R'SO_2H \rightarrow R'SO_2SR' + R'SO_3H + H_2O \quad (1)$$

We describe here the facile synthesis of *S*-alkyl alkanethiosulfonates and sulfonic acids in a 1 : 1 ratio from SO_2, aliphatic alkenes and hydrogen with the catalytic systems $[Pd(Ph_2P(CH_2)_nPPh_2)(MeCN)_2][BF_4]_2$ (n = 2,3,4,5) generated from diphosphine palladium(II) chlorides and silver tetrafluoroborate in $CH_2Cl_2/MeCN$.[3] ^1H NMR was used to quantify the products. For the generation of *S*-alkyl alkanethiosulfonates and sulfonic acids, it is necessary to apply a temperature above the ceiling temperature of the SO_2–alkene copolymer, otherwise only alternating copolymers are obtained.[4] Owing to the high ceiling temperature of the ethene–SO_2 copolymer (140 °C),[5] the above reaction is not suitable for ethene, the selectivity is low and a variety of products is formed. It is noteworthy, that with ethene/SO_2/hydrogen at 80 °C the alternating polymer is formed at rates of 8800 g mol^{-1} h^{-1}, which is 100 times faster than without hydrogen under otherwise identical conditions. For propene and other alk-1-enes, the ceiling temperature is lower than 80 °C. At this temperature propene, but-1-ene, hex-1-ene and isobutene have been reacted with SO_2, H_2 and the catalyst system **1** giving conversions of >90% and selectivities of *ca.* 70% for *S*-alkyl alkanethiosulfonates and sulfonic acids. As side reactions, formation of the corresponding sulfone RSO_2R and the sulfide RSR are observed.



Scheme 1

Table 1 Isomer distribution (%) of the *S*-propyl propanethiosulfonates at 80 °C H_2 (25 bar), propene (8 bar)

S-Propylthiosulfonate	Isomer	Isomer distribution (%)
$PrSO_2SPr$	Primary-Primary	77.4
$PrSO_2SPr^i$ Pr^iSO_2SPr	Primary-Secondary Secondary-Primary	20.3
$Pr^iSO_2SPr^i$	Secondary-Secondary	2.3

Analogous to hydroformylation, the SO_2 addition can occur in the primary or secondary position, thus yielding four isomers as shown for the *S*-alkyl alkanethiosulfonates of propene in Table 1. The rate of the reaction of propene, SO_2 and H_2 is 6050 g mol^{-1} h^{-1} at 80 °C, rises up to 10950 g mol^{-1} h^{-1} at 100 °C and decreases to 9350 g mol^{-1} h^{-1} at 120 °C with only small changes in selectivity at all three temperatures. Among the tested phosphorus ligands the reaction rate for dppp [1,3-bis(diphenylphosphino)propane] appears to be optimal. Dppe [1,2-bis(diphenylphosphino)ethane], dppb [1,4-bis(diphenylphosphino)butane] and dpppent [1,5-bis(diphenylphosphino)pentane] give lower rates, namely 3500, 5450 and 310 g mol^{-1} h^{-1}, respectively. These results parallel those from the copolymerization of ethene and carbon monoxide.[6]

It can be postulated that the reaction proceeds through the corresponding sulfinic acid as an intermediate (Scheme 1). Mechanistically a catalysis *via* a Pd-hydride species is invoked. The following results support this assumption: when propene and SO_2 are reacted below the ceiling temperature and hydrogen is omitted no products are formed. When propene, SO_2 and D_2 are reacted, the product obtained is free of deuterium in the methyl groups. This is consistent with a rapid reversible insertion of propene into the Pd-D bond.

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