Note

Palladium complex catalysed synthesis of sulfinic acids, sulfinic acid esters, sulfonic acids and *S*-alkyl alkanethiosulfonates

Jürgen Herwig and Wilhelm Keim

Institut für Technische Chemie und Petrolchemie der Rheinisch-Westfälischen Technischen Hochschule Aachen, Worringerweg 1, D-52074 Aachen (Germany)

(Received February 7, 1994)

Abstract

A novel reaction for the synthesis of sulfinic acids, sulfinic acids esters, sulfonic acids and *S*-alkyl alkanethiosulfonates from olefins, SO_2 and hydrogen will be described. Due to its similarity to hydroformylation, this reaction will be called hydrosulfination. Various palladium complexes $([Pd(NCCH_3)_2(R_2P(CH_2)_nPR_2)](BF_4)_2$ (R = Ph, n = 2–5; R = Me, *o*-(C_6H_4OMe), n = 3) have been applied. A strong dependency on the solvents used has been observed. For instance, sulfinic acids have only been obtained in mixtures containing water or methanol. In methylene chloride the sulfinic acids disproportionate into *S*-alkyl alkanethiosulfonates and sulfonic acids.

Key words: Catalysis; Hydrosulfination; Palladium complexes; Diphosphine complexes

Introduction

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 (eqns. (1) and (2)).

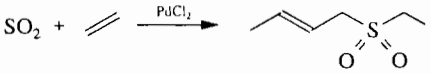
$$\text{Olefin} + CO/H_2 \longrightarrow \text{aldehydes (hydroformylation)} \quad (1)$$

$$\text{Olefin} + SO_2/H_2 \longrightarrow \text{sulfinic acids (hydrosulfination)} \quad (2)$$

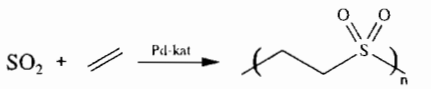
One reason is the rapid radical initiated polymerisation of alkenes with sulfur dioxide below the ceiling temperature of the resulting copolymer [1]. Moreover, the sulfinic acids formed are unstable and react further to *S*-alkyl alkanethiosulfonates and sulfonic acids (eqn. (3)).

$$R\text{–}CH{=}CH_2 + SO_2/H_2 \longrightarrow R'SO_2H \longrightarrow R'SSO_2R' + R'SO_3H + H_2O \quad (3)$$

The literature is rich with examples of stoichiometric organometallic chemistry dealing with CO and SO_2 insertion into metal–carbon bonds indicative of comparable reaction behaviour [2]. Scheme 1 exhibits: (a) insertion of CO and SO_2 into $Mn(CO)_5Me$ [3]; (b) two comparable nickel complexes of CO and SO_2 coordination. Similar palladium complexes have been described [4]. In spite of all these similarities and the large background of organometallic SO_2 chemistry, only two examples shown in eqn. (4) [5] and (5) [6] have been reported dealing with catalytic reactions of olefins and SO_2.



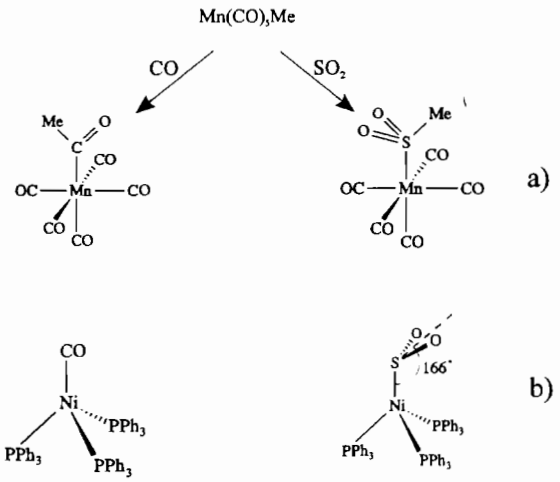
(4)



(5)

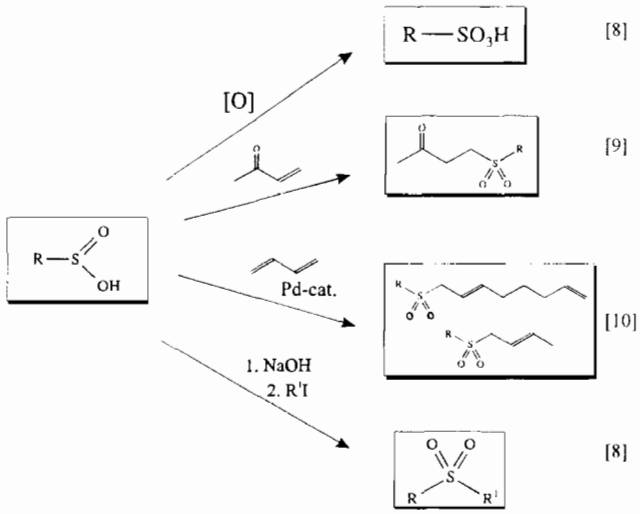
According to eqn. (2), the hydrosulfination of olefins yields sulfinic acids, as we reported in a preliminary communication [7]. Sulfinic acids, however, are rather unstable and decompose following eqn. (3).

Sulfinic acids are of industrial interest and represent potential building blocks for many organic chemicals elucidated in Scheme 2.



Scheme 1.

SSDI 0020-1693(94)03911-7



Scheme 2.

Experimental

Equipment and techniques

All experiments were carried out in a 150 ml hastelloy autoclave. NMR spectra were recorded on a Bruker 300 MHz instrument. Chemical shifts are reported relatively to TMS. IR spectra were recorded on a Nicolet 510 P FT-IR. GC-MS spectra were recorded on a Varian MAT 112 S. GC spectra were recorded on a Siemens Sichromat 1-4 (25 m OV1-HP-FS or 50 m Pona HP).

Materials

Solvents were purified, dried and saturated with argon by standard methods. SO_2, H_2 and olefins were used as purchased. All purchased ligands were used without further purification.

Metal complexes

$PdCl_2(R_2P(CH_2)_nPR_2)$ [11]

The bidentate ligands $R_2P(CH_2)_nPR_2$ (R = Ph, n = 2–5; R = Me, *o*-(C_6H_4OMe), n = 3) were mixed with an equimolar amount of $PdCl_2$ and heated up to 100 °C in a small amount of DMSO until a clear solution was obtained. After cooling down, the precipitated solid was filtered off and washed with pentane. The yields were always > 90%.

$[Pd(NCCH_3)_2(R_2P(CH_2)_nPR_2)](BF_4)_2$ [12]

0.1 mmol of $PdCl_2(R_2P(CH_2)_nPR_2)$ (R = Ph, n = 2–5; R = Me, *o*-(C_6H_4OMe), n = 3) suspended in 30 ml CH_2Cl_2 and 0.2 mmol $AgBF_4$ dissolved in 0.5 ml CH_3CN were mixed, stirred for a few minutes and the precipitated AgCl was filtered off. The resulting clear solution was directly used for catalytic experiments.

Catalytic experiments

0.1 mmol of $[Pd(NCCH_3)_2(R_2P(CH_2)_nPR_2)](BF_4)_2$ (R = Ph, n = 2–5; R = Me, *o*-(C_6H_4OMe), n = 3) dissolved in 30 ml solvent was introduced into a magnetically stirred autoclave, equipped with a gas inlet. SO_2, propene and hydrogen were introduced into the autoclave. The autoclave was placed into an oil bath, which was already heated up to reaction temperature. The reaction is stopped by lowering the temperature to room temperature and subsequently releasing the pressure. After opening the autoclave, the solvent was evaporated at room temperature, the crude product weighed and analysed by ^1H NMR and ^{13}C NMR.

Isolation of the propane sulfinic acids [13]

Sulfinic acids were only obtained in a solvent mixture containing water or methanol (5–10%) and a reaction temperature of 80 °C. The pure sulfinic acids were obtained by repeated water extraction of a CH_2Cl_2 solution of the crude product. The isomer distribution was determined by ^1H NMR. $^nPrSO_2H$, ^1H 300 MHz ($CDCl_3$): 1.06 (3H, t, J = 7.5), 1.75 (2H, sextet, J = 7.5), 2.79 (2H, t, J = 7.5); $^{13}C\{^1H\}$ 75 MHz ($CDCl_3$): 59.89, 15.29, 13.25. $^iPrSO_2H$, ^1H 300 MHz ($CDCl_3$): 1.25 (6H, d, J = 6.8), 2.8 (1H, m); $^{13}C\{^1H\}$ 75 MHz ($CDCl_3$): 55.19, 13.76.

Isolation of the propane sulfinic acid esters

Sulfinic acid esters were isolated in a solvent mixture containing CH_2Cl_2 and methanol (> 10%) and a reaction temperature of 100 °C. The sulfinic acids were removed by water extraction and the remaining sulfinic acid esters purified by distillation ($b.p._{30}$: 60–70 °C propane sulfinic acid methylester). The sulfinic acid esters were characterised by ^1H NMR and ^{13}C NMR. $^nPrSO_2Me$, ^1H 300 MHz ($CDCl_3$): 3.78 (3H, s), 2.68 (1H, d, t, J = 7.47, 5.43), 2.77 (1H, d, t, J = 7.47, 5.43), 1.75 (2H, sextet, J = 7.5), 1.06 (3H, t, J = 7.5); $^{13}C\{^1H\}$ 75 MHz ($CDCl_3$): 58.16, 54.48, 15.06, 13.37. $^iPrSO_2Me$, ^1H 300 MHz ($CDCl_3$): 3.80 (3H, s), ~2.7 (1H, m), 1.24 (3H, d, J = 7.1), 1.23 (3H, d, J = 7.1); $^{13}C\{^1H\}$ 75 MHz ($CDCl_3$): 55.25, 55.03, 13.88, 13.73.

Isolation of the S-propyl propanethiosulfononates and propane sulfonic acids [14]

S-Alkyl alkanethiosulfononates and sulfonic acids were isolated from a CH_2Cl_2 solution. The sulfonic acids were isolated by repeated water extraction of a CH_2Cl_2 solution from the crude product and characterised by ^1H NMR and ^{13}C NMR. $^nPrSO_3H$, ^1H 300 MHz ($CDCl_3$): 2.95 (2H, t), 1.86 (2H, m), 1.04 (3H, t); $^{13}C\{^1H\}$ 75 MHz ($CDCl_3$): 53.45, 17.56, 12.87. The pure *S*-alkane thiosulfonates were obtained by evaporating the CH_2Cl_2 of the remaining solution and distillation of the crude *S*-alkyl alkanethiosulfononates

(b.p.$_{1\text{-}2}$: 112 °C for *S*-propyl propanethiosulfonates). The isomer distribution was determined by GC. NMR data: $^{n}PrSO_2S^{n}Pr$, ^1H 300 MHz ($CDCl_3$): 1.04 (3H, t, $J=7.1$), 1.09 (3H, t, $J=7.1$), 1.78 (2H, sextet, $J=7.1$), 1.98 (2H, sextet, $J=7.1$), 3.12 (2H, t, $J=7.1$), 3.29 (2H, t, $J=7.1$); $^{13}C\{^1H\}$ 75 MHz ($CDCl_3$): 64.33, 38.28, 23.20, 17.38, 13.15, 12.67.

Results and discussion

Propene hydrosulfination

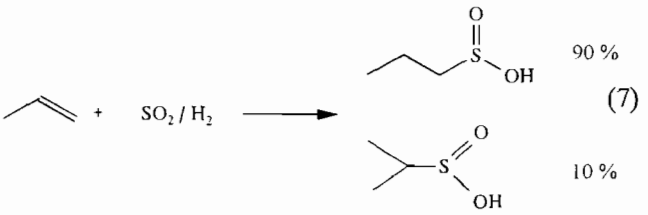
Propene, SO_2 and H_2 were reacted with catalytic amounts of the following palladium complexes: $[Pd(NCCH_3)_2(R_2P(CH_2)_nPR_2)](BF_4)_2$ (R = Ph, $n=2$–5; R = Me, *o*-(C_6H_4OMe), $n=3$). When methylene chloride is used as a solvent, only small amounts of the corresponding sulfinic acid can be isolated because the sulfinic acid formed as first product easily disproportionates into *S*-propyl propanethiosulfonates and propane sulfonic acid and water (eqn. (3)). The selectivity to the disproportionation products is always > 70 %, determined by ^1H NMR. The rest consists of sulfinic acid, dipropylsulfon and small amounts of not yet identified compounds. The *S*-propyl propanethiosulfonates comprise a mixture of four isomers listed in Table 1. No remarkable change in this distribution using different reaction conditions, such as propene, or SO_2 intake, H_2 pressure and reaction temperature, was observed.

The main product of > 70% is the primary–primary addition product. The two isomers of primary–secondary addition amount to > 20%. The secondary–secondary isomer is only present in small amounts. The isomer distribution is indicative of a Markownikow and anti-Markownikow metal hydride addition well known from hydroformylation and referred to as the 'normal–iso ratio'. In this regard hydrosulfination also parallels hydroformylation.

To isolate the propane sulfinic acid as main product, the disproportionation catalysed by acids must be prevented. As shown in eqn. (6) protonation can occur yielding an R–SO^+ moiety.

(6)

Obviously, by adding water the protonation can be depressed. Indeed, in a mixture of acetone–water (30:2) the disproportionation is less than 1% (^1H NMR) and the pure acid can be isolated and thus synthesised. The n:iso ratio amounts to 90:10 (eqn. (7)).



(7)

For synthesis of the pure sulfinic acid the yield decreases with increasing formation of the acid. In a standard experiment (80 °C, 3.7 g SO_2, 3.7 g propene, 25 bar H_2, solvent: acetone/water 30/2, 0.12 mmol $dpppPd(NCCH_3)_2[BF_4]_2$), 1.47 g pure sulfinic acid with the above isomer distribution (conversion 23% [SO_2], activity 817 g/mol h) were isolated. This behaviour is attributed to ligand poisoning by the free acid. This is circumvented when the free acid reacts further according to eqn. (3) or by the *in situ* reaction with α,β-unsaturated ketones shown in Scheme 2 [9].

Various palladium complexes have been applied. As shown in Table 2 the complexes exhibit a different activity. Best results have been obtained with dppp (1,3-bis(diphenylphosphino)propane) as ligand. Interestingly, these results are similar to the polyketone formation from ethene and CO as reported by Drent *et al.*, in which dppp is also the best ligand [15]. According to Drent this is due to the stabilisation of a square planar as well as a trigonal bipyramidal transition state with dppp as the ligand. The dependency of the chain lengths connecting the two phosphorus atoms is also

TABLE 1. Isomer distribution (%) of the *S*-propyl propanethiosulfonates at 80 °C, H_2 (25 bar), propene (8 bar, 2.5 g), SO_2 (3 bar, 2.5-3.0 g) with the system $[Pd(NCCH_3)_2dppp](BF_4)_2$

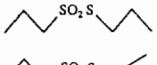
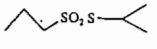
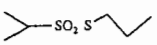
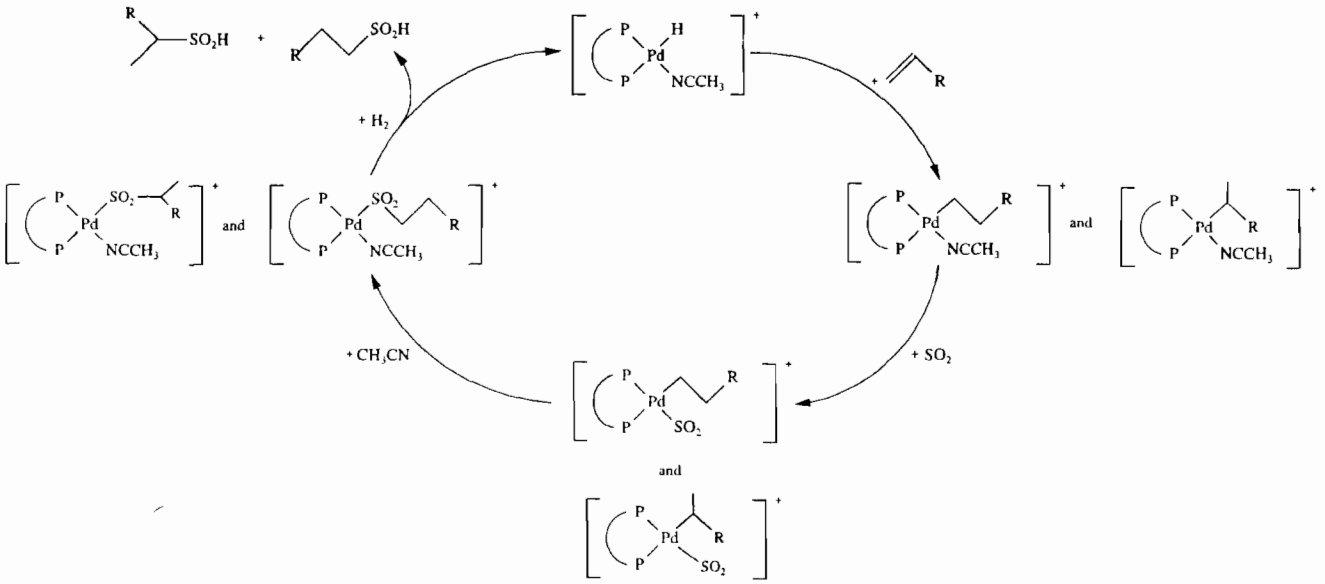
S-Propyl propanethiosulfonate	Isomer	Isomer distribution (%)
	primary–primary	77.4
	primary–secondary	20.3
	secondary–primary	
	secondary–secondary	2.3

TABLE 2. Effect of n and R on the activity of $[Pd(NCCH_3)_2(R_2P(CH_2)_nPR_2)](BF_4)_2$ at 80 °C, H_2 (25 bar), propene (8 bar) in 30 ml CH_2Cl_2

n	R	Abbreviation	Activity (g(thiosulfonic ester and sulfonic acid)/mol h)	Conversion (SO_2) (%)
2	Ph	dppe	3500	44
3	Ph	dppp	6050	12
4	Ph	dppb	5400	64
5	Ph	dpppent	310	3
3	*o*-Anisyl	dapp	230	38
3	Me	dmpp	150	4



Scheme 3.

obvious from Table 2. The basic ligand dmpp (1,3-bis(dimethylphosphino)propane) shows only modest activity, probably for electronic reasons. In contrast to the Pd-catalysed copolymerisation of ethene and CO, dapp (1,3-bis(di-{*o*-methoxy}phenylphosphino)propane) is less active in hydrosulfination than dppp. Of greatest importance is the reaction temperature chosen. Here the ceiling temperature (T_C) of the propene/SO_2 copolymer (~80 °C) is crucial. If the reaction is run below the ceiling temperature, SO_2/propene copolymer is the main product besides small amounts of sulfinic acids and its disproportionation products. The best results for sulfinic acids formation are obtained at 80 °C. The highest activity is observed at 100 °C.

In hydroformylation, hydrogenation of the olefin is a known side reaction. We investigated the isomerisation and hydrogenation capability of the system $dpppPd(NCCH_3)_2[BF_4]_2$ with 1-hexene (70 °C, 5 bar H_2). After 6 h, nearly all the 1-hexene was isomerised, but only 1.3% was hydrogenated after 23 h.

Hydrosulfination of various olefins

For hydrosulfination of olefins to occur one must work above the ceiling temperature of the olefin/SO_2 copolymer. Due to the high ceiling temperature of > 135 °C for the ethene/SO_2 copolymer, hydrosulfination cannot be applied to ethene, because the palladium complexes used as catalysts decompose. When the reaction is carried out below the ceiling temperature of 135 °C only ethene/SO_2 copolymers are formed, which are also known from the radically initiated copolymerisation of ethene with SO_2.

Interestingly, the copolymer of SO_2 and ethene made by palladium catalysis is perfectly alternating as could be established by solid state NMR. Copolymers made by radical initiation consist of ~90% alternating and ~10% not alternating units.

Olefins such as 1-hexene (T_C = 60 °C), 1-butene (T_C = 64 °C), cyclohexene (T_C = 24 °C) or isobutene (T_C = 4 °C) could be hydrosulfinated. The results will be reported in a forthcoming paper.

Mechanistic considerations

In analogy to hydroformylation the reaction mechanism in Scheme 3 is proposed for the hydrosulfination of propene. Pd–H adds propene yielding the two Markownikow and anti-Markownikow products. SO_2 coordination followed by insertion yields the two corresponding insertion products. The sulfinic acids are formed by H_2 addition thus closing the catalytic cycle. We did not investigate the role of acetonitrile. To support this mechanism, experiments with added deuterium were carried out expecting the formation of $CH_3CHDCH_2SO_2SCH_2CHDCH_3$. Unfortunately, H/D exchange occurred preventing an exact assertion.

Acknowledgements

We are very grateful to BP Chemicals for financial support and to DEGUSSA AG for a generous loan of palladium chloride.

References

1 N. Tokura, *Encyclopedia of Polymer Science and Technology,* Vol. 9, Wiley, New York, 1968, p. 460.
2 A. Wojcicki, *Acc. Chem. Res., 4* (1971) 344.
3 A. Wojcicki and F.A. Hartmann, *J. Am. Chem. Soc., 88* (1966) 844.
4 Th. Hoffmann, H. Hoffnann, M. Karabi, P. Zdunneck, E. Wenschuh, J. Reinhold and M. Schüler, *Z. Anorg. Allg. Chem., 565* (1988) 91.
5 H.S. Klein, *J. Chem. Soc., Chem. Commun.,* (1968) 377.
6 E. Drent, *Eur. Patent Applic. No. 220 765* (1987).
7 W. Keim and J. Herwig, *J. Chem. Soc., Chem. Commun.,* (1993) 1592.
8 R.R. Ferguson and R.H. Crabtree, *J. Org. Chem., 56* (1991) 5503.
9 K. Schank, *Houben Weyl, Methoden der organischen Chemie,* Vol. E11 (Part 2), Georg Thieme, Stuttgart, 4th edn., 1985, p. 1145.
10 U.M. Dzhemilev and R.V. Kunakova, *J. Organomet. Chem., 455* (1993) 1.
11 A. Westland, *J. Chem. Soc.,* (1965) 3060.
12 C. Pisiano, G. Consiglio, A. Sirioni and M. Moret, *J. Chem. Soc., Chem. Commun.,* (1991) 421.
13 F. Freeman and C.A. Angletakis, *Org. Magn. Reson., 21* (1983) 86.
14 F. Freeman and C.A. Angletakis, *J. Org. Chem., 47* (1982) 4194.
15 E. Drent, J.A.M. van Broekhoven and M.J. Doyle, *J. Organomet. Chem., 417* (1991) 235.