

Direct catalytic sulfonation of methane with SO₂ to methanesulfonic acid (MSA) in the presence of molecular O₂

Sudip Mukhopadhyay and Alexis T. Bell*

Department of Chemical Engineering, University of California, Berkeley, CA 94720, USA.

E-mail: bell@cchem.berkeley.edu; Fax: 1 510 642 4778; Tel: 1 510 642 1536

Received (in Cambridge, UK) 2nd April 2003, Accepted 12th May 2003

First published as an Advance Article on the web 3rd June 2003

Methane is transformed selectively to methanesulfonic acid at low temperature by liquid-phase sulfonation of methane with SO₂ and O₂ in the presence of Pd- and Cu-salts as the catalysts.

The selective catalytic functionalization of methane to value added products is a subject of considerable contemporary interest. Because of favorable thermodynamics, many authors have investigated the oxidation and oxidative carbonylation of methane.¹ By contrast, the sulfonation of methane has not received as much attention despite its commercial importance.² It has been shown^{3a-f} that in the presence of a free radical initiator methane can be sulfonated with SO₃ in fuming sulfuric acid to methanesulfonic acid (MSA) under very high methane pressure. Most recently we have shown that methane can be sulfonated to MSA by SO₂ in the presence of an excess amount of K₂S₂O₈.^{3g} The same approach, however, does not work if O₂ is used instead of K₂S₂O₈ as the oxidant. Thus, there is incentive to identify a catalytic system that would enable the use of molecular O₂. While Ishii and coworkers have reported success in the vanadium-catalyzed sulfonation of adamantane to the corresponding sulfonic acids using SO₂ and O₂, methane did not undergo sulfonation to methanesulfonic acid.^{3h} The question therefore arises whether SO₂ and O₂ can be used for methane sulfonation. In this communication, we show that methane will undergo liquid-phase sulfonation to MSA with SO₂ and O₂ in acid solvents, with catalytic amounts of Pd- and Cu-salts (Scheme 1).

In a typical reaction⁴ (Scheme 1) methane was reacted with SO₂ in CF₃SO₃H to form MSA in presence of Pd- and Cu-salts in a high-pressure, glass-lined, Parr autoclave. Reactions were carried out for 12 h at 85 °C and the MSA thus formed was identified and quantified by ¹H NMR.^{3b,c} Use of ¹³C enriched methane and ¹H, ¹³C NMR of the reaction mixture confirmed that MSA is the only liquid-phase product generated from methane in presence of SO₂. The conversions are reported on the basis of the limiting reagent, SO₂, and defined as the ratio of the moles of SO₂ converted to MSA to the moles of SO₂ fed initially to the reactor.

Table 1 shows the effect of different catalyst combinations on the rate of methane sulfonation. In the absence of any catalyst or co-catalyst, no conversion of SO₂ to MSA was achieved (Table 1, entry 1). The use of PdCl₂ in the absence of CuCl₂ gives only 6% conversion of SO₂ to MSA, whereas use of CuCl₂ in the absence of PdCl₂ gives only 1% conversion of SO₂ to MSA (Table 1, entries 2, 3). SO₂ conversions of 12–20% to MSA were obtained when PdCl₂ and CuCl₂ were used together (Table 1, entries 4, 5). A nearly identical conversion was obtained after 12 h of reaction when CuCl₂ was replaced by Cu₂Cl₂ (Table 1, entry 6). Similar levels of SO₂ conversion to MSA were achieved with acetate, trifluoroacetate, or triflate salts of Pd(II)

and CuCl₂ or with PdCl₂ and acetate, trifluoroacetate, or triflate salts of Cu(II) (Table 1, entries 7–12). Chloride salts of Rh(III), Hg(II), Co(II), Pt(II), Ru(III), Al(III), Ag(I), Ca(II), Fe(III), together with CuCl₂ showed very little or no activity, as did VOCl₃ and VO(acac)₂ with CuCl₂ (Table 1, entries 13–23). Pd(acac)₂ and Cu(acac)₂ also gave very little product (Table 1, entry 24).

Table 2 shows the effect of different process parameters on the rate of methane sulfonation using PdCl₂ salts as the catalyst and CuCl₂ as the co-catalyst. Reactions were performed to study the effect of methane pressure on the rate of MSA formation. Increasing the CH₄ pressure from 200 to 1200 psig increased the conversion of SO₂ to MSA from a barely detectable level to 12% (Table 2, entries 1–5).

The rate of sulfonation reaction depends on the SO₂ pressure. No MSA was detected in the absence of SO₂; however, approximately 0.1 mmol of CF₃SO₃CH₃ was formed. With an increase in SO₂ pressure from 0 to 30 psig, the conversion of SO₂ to MSA increased from 0 to 12% (Table 2, entries 5–8).

No MSA was formed in the absence of O₂. With an increase in O₂ pressure from 0 to 30 psig, the conversion of SO₂ to MSA increased from 0 to 12%. However, a further increase had no effect on MSA production (Table 2, entries 9–12).

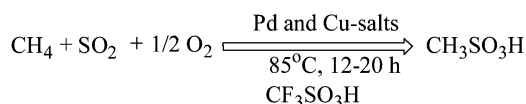
Increasing the amount of PdCl₂ from 0.05 to 0.2 mmol, the conversion of SO₂ to MSA increased from 3 to 12%. A further

Table 1 Effect of different metal chlorides on the sulfonation^a

Entry	Catalyst	Co-catalyst	t/h	MSA/ mmol	% SO ₂ to MSA ^b
1	None	None	16	0	0
2	PdCl ₂	None	12	0.71	6
3	None	CuCl ₂	14	0.12	1
4	PdCl ₂	CuCl ₂	12	1.42	12
5	PdCl ₂	CuCl ₂	40	2.36	20
6	PdCl ₂	Cu ₂ Cl ₂	12	1.18	10
7	Pd(CH ₃ COO) ₂	CuCl ₂	12	1.42	12
8	Pd(CF ₃ COO) ₂	CuCl ₂	12	1.18	10
9	Pd(CF ₃ SO ₃) ₂	CuCl ₂	12	1.3	11
10	PdCl ₂	Cu(CH ₃ COO) ₂	18	1.18	10
11	PdCl ₂	Cu(CF ₃ COO) ₂	17	1.3	11
12	PdCl ₂	Cu(CF ₃ SO ₃) ₂	16	1.42	12
13	RhCl ₃	CuCl ₂	12	0.35	3
14	HgCl ₂	CuCl ₂	12	0.24	2
15	CoCl ₂	CuCl ₂	12	0.12	1
16	PtCl ₂	CuCl ₂	12	0	0
17	RuCl ₃	CuCl ₂	12	0	0
18	AlCl ₃	CuCl ₂	12	0	0
19	AgCl	CuCl ₂	16	0	0
20	CaCl ₂	CuCl ₂	12	0	0
21	FeCl ₃	CuCl ₂	14	0	0
22	VOCl ₃	CuCl ₂	12	0	0
23	VO(acac) ₂	CuCl ₂	12	0	0
24	Pd(acac) ₂	Cu(acac) ₂	12	0.35	3

^a Reaction conditions: methane, 1200 psig (321 mmol); SO₂, 30 psig (11.82 mmol); molar ratio of methane to SO₂, 27; O₂, 30 psig (11.82 mmol); PdCl₂, 0.2 mmol; CuCl₂, 0.3 mmol; solvent, CF₃SO₃H, 5 ml; temperature, 85 °C.

^b This is the ratio of the moles of SO₂ converted to MSA to total moles of SO₂ taken initially in this reaction.



Scheme 1 Direct sulfonation of methane to methanesulfonic acid.

Table 2 Effect of process parameters on the sulfonation reaction^a

Entry	CH ₄ /psig	SO ₂ /psig	O ₂ /psig	PdCl ₂ /mmol	CuCl ₂ /mmol	T/°C	% SO ₂ to MSA
1	200	30	30	0.2	0.3	85	tr
2	400	30	30	0.2	0.3	85	1
3	650	30	30	0.2	0.3	85	2
4	1000	30	30	0.2	0.3	85	8
5	1200	30	30	0.2	0.3	85	12
6	1200	0	30	0.2	0.3	85	0
7	1200	10	30	0.2	0.3	85	3
8	1200	20	30	0.2	0.3	85	7
9	1200	30	0	0.2	0.3	85	0
10	1200	30	10	0.2	0.3	85	6
11	1200	30	20	0.2	0.3	85	9
12	1200	30	40	0.2	0.3	85	10
13	1200	30	30	0.05	0.3	85	3
14	1200	30	30	0.1	0.3	85	7
15	1200	30	30	0.3	0.3	85	12
16	1200	30	30	0.2	0.05	85	7
17	1200	30	30	0.2	0.1	85	8
18	1200	30	30	0.2	0.2	85	10
19	1200	30	30	0.2	0.3	65	2
20	1200	30	30	0.2	0.3	75	8
21	1200	30	30	0.2	0.3	100	13

^a Reaction conditions: time, 12 h; solvent, CF₃SO₃H, 5 ml.

increase in the amount of PdCl₂ had no effect on the MSA conversion (Table 2, entries 13–15).

When the amount of CuCl₂ was increased from 0.05 to 0.3 mmol, the SO₂ conversion to MSA increased from 7 to 12% (Table 2, entries 16–18). In the absence of CuCl₂, Pd-black particles were observed in the reaction mixture after 4 h of reaction, whereas in presence of CuCl₂ the appearance of Pd-black particles was not so prominent. This suggests that CuCl₂ enhances the rate of oxidation of Pd(0) to Pd(II) species.

The conversion of SO₂ to MSA increased from 2 to 12% when the temperature was raised from 65 to 85 °C. At 100 °C, a 13% conversion of SO₂ to MSA was achieved and a trace amount of CF₃SO₃CH₃ was also detected (Table 2, entries 19–21).

The reaction requires a highly acidic solvent. When performed in H₂SO₄, 5% conversion of SO₂ to MSA was observed; however, no reaction was observed using acetic acid as the solvent. A 12% conversion of SO₂ to MSA was achieved using CF₃SO₃H as the solvent. To verify that the solvent CF₃SO₃H does not react with CH₄ to give CH₃SO₃H and CHF₃ (CH₄ + CF₃SO₃H → CH₃SO₃H + CHF₃), a controlled reaction was performed in presence of O₂ and catalysts in CF₃SO₃H. No SO₂ was added. Under these conditions, MSA was not detected after 12 h of reaction. Likewise, no CHF₃ was detected by ¹⁹F NMR. A small amount of CF₃SO₃CH₃ was observed as the sole product.

The mechanism by which Pd(II) and Cu(II) promote the sulfonation of CH₄ to MSA is not understood. It seems plausible to suggest, though, that the reaction proceeds *via* an electrophilic substitution of high valent Pd-species with CH₄^{1h-j,5,6} and subsequent SO₂ insertion and oxidation^{3h} to form MSA and Pd(0). Cu(II) then promotes the reoxidation of Pd(0) to Pd(II) in presence of O₂.⁷

In conclusion, we have developed a highly selective low-temperature reaction protocol to sulfonate methane to methane-

sulfonic acid using SO₂ as the sulfonating agent and O₂ as the oxidant in the presence of a redox catalyst system comprising Pd(II) and Cu(II) salts. The reaction is highly selective, and as much as 20% of the SO₂ charged is converted to MSA with only 30 psig SO₂, the maximum available pressure. The product MSA can be isolated from the reaction mixture by distillation under reduced pressure.

ATOFINA Chemicals, Inc., North America, funded this study.

Notes and references

- (a) C. L. Hill, *Activation and functionalization of Alkanes*, Wiley, New York, 1989; (b) M. G. Axelrod, A. M. Gaffney, R. Pitchai and J. A. Sofranko, *Natural Gas Conversion II*, Elsevier, Amsterdam, 1994, p. 93; (c) G. A. Olah and A. Molnar, *Hydrocarbon Chemistry*, Wiley, New York, 1995; (d) G. J. Hutchings, M. S. Scurrell and J. R. Woodhouse, *Chem. Soc. Rev.*, 1989, **18**, 251; (e) R. M. Ormerod, *Chem. Soc. Rev.*, 2003, **32**, 17; (f) K. Otsuka and Y. Wang, *Appl. Catal.*, 2001, **222**, 145; (g) A. Ueno, *Catalysis*, 2000, **15**, 185; (h) G. Dyker, *Angew. Chem., Int. Ed.*, 1999, **38**, 1698; R. A. Periana, D. J. Taube, E. R. Evitt, D. G. Loffer, P. R. Wentreck, G. Voss and T. Masuda, *Science*, 1993, **259**, 340; (i) R. A. Periana, D. J. Taube, S. Gamble, H. Taube, T. Satoh and H. Fujii, *Science*, 1998, **280**, 560; (j) R. A. Periana, O. Mirinov, D. J. Taube and S. Gamble, *Chem. Commun.*, 2002, 2376.
- (a) *Ullmann's Encyclopedia of Industrial Chemistry*, VCH, Weinheim, 1994, Vol. A25, pp. 503–506; (b) F. M. Beringer and R. A. Falk, *J. Am. Chem. Soc.*, 1959, **81**, 2997; (c) H. A. Young, *J. Am. Chem. Soc.*, 1937, **59**, 811; (d) R. C. Murray, *J. Chem. Soc.*, 1933, 739.
- (a) N. Basicakes, T. E. Hogan and A. Sen, *J. Am. Chem. Soc.*, 1996, **118**, 13111; (b) L. J. Lobree and A. T. Bell, *Ind. Eng. Chem. Res.*, 2001, **40**, 736; (c) S. Mukhopadhyay and A. T. Bell, *Ind. Eng. Chem. Res.*, 2002, **41**, 5901; (d) S. Mukhopadhyay and A. T. Bell, *Org. Process. Res. Dev.*, 2003, **7**, 161; (e) S. Mukhopadhyay and A. T. Bell, *Angew. Chem., Int. Ed.*, 2003, **42**, 1019; (f) S. Mukhopadhyay and A. T. Bell, *Angew. Chem., Int. Ed.*, 2003, in press; (g) S. Mukhopadhyay and A. T. Bell, *J. Am. Chem. Soc.*, 2003, **125**, 4406; (h) Y. Ishii, K. Matsunaka and S. Sakaguchi, *J. Am. Chem. Soc.*, 2000, **122**, 7390.
- In a 100-ml glass lined high pressure Parr autoclave reactor, 0.2 mmol PdCl₂, 0.3 mmol CuCl₂, and 5 ml of trifluoromethanesulfonic acid were charged together with a small Teflon coated magnetic stir bar. The reactor was then pressurized with 30 psig SO₂, 30 psig O₂, and then ultimately with 1200-psig methane from the adjacent connecting cylinders. The reactor was then heated to 85 °C under stirring and kept at that temperature for 12 h. After the stipulated period of time, the reactor was cooled to room temperature and opened to collect the reaction mixture. The mixture was then added slowly to 1.0 g of water and then taken for ¹H NMR analysis. D₂O and methanol were used in a capillary as the lock references. The corresponding chemical shift for MSA was 2.78 to 2.98 ppm, depending on the concentration of MSA in the mixture.
- Pd and Cu catalyst combination is used for the carbonylation of methane to acetic acid in CF₃COOH as the solvent, see (a) T. Nishiguchi, K. Nakata, K. Takaki and Y. Fujiwara, *Chem. Lett.*, 1992, 1141; (b) A. Sen, *Platinum Met. Rev.*, 1991, **35**, 126; (c) L.-C. Kao, A. C. Hutson and A. Sen, *J. Am. Chem. Soc.*, 1991, **113**, 700; (d) Carbene based Pd-catalyst has been used recently for methane oxidation, see M. Muehlhofer, T. Strassner and W. A. Herrmann, *Angew. Chem., Int. Ed.*, 2002, **41**, 1745.
- Pt-salt based methane activation by Shilov chemistry, see (a) A. E. Shilov and G. B. Shul'pin, *Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes*, Kluwer Academic Publishers: Dordrecht, 2000; (b) For a nice mechanistic recent review see J. A. Labinger and J. E. Bercaw, *Nature*, 2002, **417**, 507.
- For the role of co-catalysts in PdCl₂ catalyzed C–H bond activation in benzene, see S. Mukhopadhyay, G. Rothenberg, G. Lando, K. Agbaria, M. Kazanci and Y. Sasson, *Adv. Synth. Catal.*, 2001, **343**, 455.