Methane Sulfonation

A High-Yield Approach to the Sulfonation of Methane to Methanesulfonic Acid Initiated by H_2O_2 and a Metal Chloride**

*Sudip Mukhopadhyay and Alexis T. Bell**

Methane is abundant and relatively inexpensive, making it an attractive feedstock for producing bulk chemicals. However, the low reactivity of methane makes it difficult to develop commercially viable processes for methane conversion.[1] Because of favorable thermodynamics, many authors have investigated the oxidation and oxidative carbonylation of methane.[2] By contrast, the sulfonation of methane to give methanesulfonic acid has not received as much attention despite its commercial importance.[3] The current commercial process for the synthesis of methanesulfonic acid (MSA) relies on the chlorine-oxidation of thiomethane.[4] While this process is highly productive, it produces six moles of HCl per mole of MSA, resulting in a coupling of the demand for the primary product and the by-product. It has been shown[5] that $K_2S_2O_8$ can be used as a free-radical initiator to sulfonate methane with SO_3 in fuming sulfuric acid under very high methane pressure. The conversion of methane to MSA is reported to be 3–6% under 1000 psig methane pressure (1 psig = 6.895×10^3 Pa).[5] We recently have shown that metal peroxides can be used as an effective radical initiator for methane activation in sulfuric acid solvent.[6] However, once the metal peroxides have activated methane they are converted into the metal sulfate salts, which cannot be recycled back to the metal peroxide. The economics of producing and handling safely the necessary amounts of metal peroxide must also be considered if a practical process is to be developed. Thus, there is considerable incentive to look for a way to generate metal peroxo species in situ from a cheap source such as H_2O_2.

In this communication we show that methane will undergo liquid-phase sulfonation to MSA with SO_3 in sulfuric acid. A small amount of urea/H_2O_2 is used as a free-radical initiator and a small amount of a metal chloride salt, particularly $RhCl_3$, is used as a promoter [Eq. (1)].

$$CH_4 + SO_3 \xrightarrow[MCl,\ 65-75^{\circ}C,\ 3\,h]{\text{urea}/H_2O_2,\ H_2SO_4} CH_3SO_3H \qquad (1)$$

In a typical reaction[7] methane was treated with 30-wt.% SO_3 in H_2SO_4 to form MSA in the presence of small amounts of urea/H_2O_2 (Aldrich) and a metal chloride salt. Reactions were carried out in a high-pressure, glass-lined Parr autoclave. The MSA thus formed was identified and quantified by ^{1}H NMR spectroscopy.[5] Unless otherwise noted, no other sulfur-containing products were detected in either the gas or the liquid phase. Analysis of the product formed from SO_3 and $^{13}CH_4$ by ^{13}C NMR spectroscopy indicates that $^{13}CH_3SO_3H$ is formed exclusively from $^{13}CH_4$. Only a small amount of ethane was observed in the gas phase in the absence of SO_3 when 100% H_2SO_4 was used as the solvent. Since this product was absent when the autoclave was not pressurized with methane, the appearance of ethane is attributed to the coupling of methyl radicals.

Table 1 shows the effect of different promoters on the sulfonation of methane. The conversion of SO_3, the limiting reagent, is defined as the ratio of the moles of SO_3 converted into MSA to the total moles of SO_3 in to the autoclave. When urea/H_2O_2 served as the initiator, and in the absence of any promoter, the conversion of SO_3 to MSA was 23% (Table 1, entry 1). When the reaction was carried out in the presence of $CaCl_2$, $BaCl_2$, $FeCl_3$, and $NbCl_5$ there was a moderate increase in the conversion of SO_3 to MSA (entries 2–5). $TaCl_5$, $AlCl_3$, $HgCl_2$, and AgCl are even more effective as promoters (entries 6–9). The most effective promoter, though, is $RhCl_3$ (entry 10). KCl, $RuCl_3$, $[Rh(CO)_2Cl)]_2$, $NiCl_2$, $PdCl_2$, $PtCl_2$, $CuCl_2$, and $VOCl_3$ had a negative effect on MSA synthesis relative to what was observed without the addition of a promoter (entries 11–18).

Table 2 shows the effect of different process parameters when urea/H_2O_2 and $RhCl_3$ were used as the initiator and the promoter, respectively. The conversion of SO_3 to MSA was 42% after 26 h of reaction when the initial methane pressure was 100 psig. The conversion of SO_3 to MSA increased monotonically with increasing methane pressure (Table 2, entries 1–4), reaching a level of 86% for an initial methane pressure of 650 psig. It is noted that the conversion of

[*] Prof. A. T. Bell, S. Mukhopadhyay
Department of Chemical Engineering
University of California
Berkeley, CA 94720-1462 (USA)
Fax: (+1) 510-642-4778
E-mail: bell@cchem.berkeley.edu

[**] This work was supported by Atofina Chemicals Inc., North America.

  DOI: 10.1002/ange.200350976

Table 1: Effect of different metal chloride salts on the rate of methane sulfonation with SO_3.[a]

Entry	Promoter [mmol]	MSA [mmol]	Conv. of SO_3 [%][b]	Sel. to MSA [%]
1	none, 0	4.9	23	100
2	$CaCl_2$, 0.33	7.2	34	100
3	$BaCl_2$, 0.33	6.8	32	100
4	$FeCl_3$, 0.33	6.4	30	100
5	$NbCl_5$, 0.33	6.2	29	99.8
6	$TaCl_5$, 0.33	11.5	54	99.3
7	$AlCl_3$, 0.33	11.9	56	99.3
8	$HgCl_2$, 0.33	12.5	59	99
9	AgCl, 0.33	13	61	99.6
10	$RhCl_3$, 0.33	18.3	86	99.9
11	KCl, 0.33	4.3	20	100
12	$RuCl_3$, 0.37	0.64	3	80
13	$[Rh(CO)_2Cl]_2$, 0.4	0.21	1	100
14	$NiCl_2{\cdot}6H_2O$, 0.36	0	0	0
15	$PdCl_2$, 0.33	0.06	0.27	8
16	$PtCl_2$, 0.33	0.64	3	10
17	$CuCl_2$, 0.33	0	0	0
18	$VOCl_{3,\ 0.33}$	0	0	0

[a] Reaction conditions: 650 psig (179 mmol) methane, 1.7 g (21.26 mmol) SO_3 (mol ratio methane:SO_3 = 8.4), 0.74 mmol urea/H_2O_2, 5.67 g fuming sulfuric acid (30 wt% SO_3), 3 h, 65 °C. [b] Ratio of the moles of SO_3 converted to MSA to the total moles of SO_3 taken initially in the reaction mixture.

Table 2: Effect of process parameters on the sulfonation of methane.[a]

Entry	CH_4 [psig], (mmol)	t [h]	Initiator [mmol]	$RhCl_3$ [mmol]	T [°C]	MSA [mmol]	SO_3 conv. [%],[b] (CH_4 conv. [%])[c]
1	100(31)	26	urea/H_2O_2,0.74	0.33	65	8.9	42(29)
2	200(58)	14	urea/H_2O_2,0.74	0.33	65	9.8	46(17)
3	450(125)	3	urea/H_2O_2,0.74	0.33	65	16.8	79(13)
4	650(179)	3	urea/H_2O_2,0.74	0.33	65	18.2	86(10)
5	650(179)	3	none, 0	0.33	65	0.06	0.3(–)
6	650(179)	3	urea/H_2O_2,0.16	0.33	65	14.5	68(8)
7	650(179)	3	urea/H_2O_2,0.46	0.33	65	17.6	83(10)
8	650(179)	3	urea/H_2O_2,0.96	0.33	65	13.2	62(7)
9	650(179)	3	urea/H_2O_2,0.74	0	65	4.9	23(3)
10	650(179)	3	urea/H_2O_2,0.74	0.05	65	14.7	69(8)
11	650(179)	3	urea/H_2O_2,0.74	0.14	65	20.2	95(11)
12	650(179)	3	urea/H_2O_2,0.74	0.24	65	19.1	90(10)
13	650(179)	3	urea/H_2O_2,0.74	0.33	75	19.3	91(11)
14	650(179)	3	urea/H_2O_2,0.74	0.33	85	11.5	54(6)
15	200(58)	3	urea/H_2O_2,0.74	0.33	130	4.6	22(20)
16	200(58)	3	urea/H_2O_2,0.74	0.33	160	0.5	2(24)
17	100(31)	72	urea/H_2O_2,0.65	0.30	85	11.1	52(36)
18[d]	650(179)	3	urea/H_2O_2,0.85	0.24	65	32	75(18)
19	650(179)	3	$K_2S_2O_8$, 0.74	0.33	65	3.6	17(2)
20	650(179)	3	$K_4P_2O_8$, 0.74	0.33	65	3.4	16(2)
21	650(179)	3	CaO_2, 0.74	0.33	65	13.3	63(7)
22	650(179)	3	Br_2, 0.74	0.33	65	1.9	9(2)
23	650(179)	3	Cl_2, 0.74	0.33	65	0.8	4(1)
24	650(179)	3	I_2, 0.74	0.33	65	0	0(0.5)

[a] Reaction conditions: SO_3 (1.7 g, 21.26 mmol), urea/H_2O_2 as radical initiator, $RhCl_3$ as promoter, solvent, fuming sulfuric acid (30 wt% SO_3, 5.67 g) as solvent. [b] Moles of SO_3 converted to MSA/total moles of SO_3 in the autoclave. [c] Moles of methane converted/moles of methane in the autoclave. [d] Amount of fuming sulfuric acid used, 11.34 g (initial SO_3 amount, 42.52 mmol).

methane, shown in parentheses, decreases with increasing methane pressure, since the number of moles of methane in the autoclave increases, whereas the number of moles of SO_3 remains constant.

The amount of free-radical initiator, urea/H_2O_2, was varied from 0 mmol to 0.96 mmol, while the amount of the promoter, $RhCl_3$, was kept constant at 0.33 mmol. It was observed that with an increase in the amount of initiator from 0 mmol to 0.16 mmol, the conversion of SO_3 to MSA increased from 0.3 to 68%. A maximum conversion of 86% was achieved with 0.74 mmol of the promoter (Table 2, entries 5–8). The reaction can also be initiated by using 50-wt% H_2O_2 solution as the initiator. An excess of SO_3 was used to remove the water ($H_2O + SO_3 \rightarrow H_2SO_4$) associated with the H_2O_2 solution. For these circumstances, the conversion of SO_3 to MSA was only 16% after 3 h of reaction in the presence of $RhCl_3$. Consequently, for all subsequent reactions, H_2O_2 was introduced as anhydrous urea/H_2O_2.

The reaction was studied with different amounts of $RhCl_3$ (Table 2, entries 9–12). With an increase in the amount of $RhCl_3$, the conversion of SO_3 to MSA increased marginally. A maximum SO_3 conversion of 95% was achieved with 0.14 mmol $RhCl_3$ for a methane pressure of 650 psig. The conversion of methane to MSA under this reaction condition was 11%.

The conversion of SO_3 to MSA increased from 86 to 91% (3 h reaction time) when the temperature was increased from 65 to 75°C. However, with a further increase in temperature to 85°C, the conversion decreased to 54% (Table 2, entries 4, 13, and 14) and a small amount of CH_3OSO_3H appeared as a product. When the reaction temperature was increased to 130°C, CH_3OSO_3H became the major product. At 160°C, the total conversion of methane was 24%, of which 0.86% was to MSA, 1.26% to CO_2, 1.2% to methanedisulfonic acid, and the balance to CH_3OSO_3H (entries 15 and 16).

The highest conversion of methane to MSA, 36% (Table 2, entry 17), was obtained after 72 h of reaction. In this case the initial methane pressure was 100 psig, the temperature was 85°C, the amount of urea/H_2O_2 was 0.65 mmol, and the amount of $RhCl_3$ was 0.3 mmol. Since the selectivity to MSA was 99.99%, the overall yield of MSA was 36% based on methane. Comparison of entries 12 and 18 in Table 2 shows that the conversion of methane to MSA can be raised by increasing the initial amount of fuming sulfuric acid. When the amount was doubled, the methane conversion increased from 10% to 18%.

The effectiveness of $K_2S_2O_8$, $K_4P_2O_8$, CaO_2, Br_2, Cl_2, and I_2 as initiators was examined in the presence of $RhCl_3$. It was found that the combination of $RhCl_3$ and urea/H_2O_2 was the most effective combination of promoter and initiator under the reaction conditions used (Table 2, entries 19–23). The order of reactivity of the initiators in the presence of $RhCl_3$ as the promoter was urea/H_2O_2 > CaO_2 > $K_2S_2O_8$ > $K_4P_2O_8$ > Br_2 > Cl_2. With iodine as the initiator, 3% of the SO_3 in the reactor was converted to CH_3OSO_3H but no MSA was detected (Table 2, entry 24), which is consistent with recent reports.[8]

The mechanism by which H_2O_2 either alone or in combination with $RhCl_3$ promotes the sulfonation of methane is not understood. In previous studies[5,6] of methane sulfonation utilizing inorganic peroxide initiators, e.g., $K_2S_2O_8$, K_4P_2O8, CaO_2, it was suggested that decomposition of the initiator produces methyl radicals, which then react with SO_3 to form $CH_3SO_3^{\bullet}$ radicals and then CH_3SO_3H. Inhibition of the reaction by O_2 together with the appearance of small amounts of ethane in the gas phase suggest that a free-radical mechanism may be operative in the systems investigated in this study. The initiating species in the present case could be $OH^{\bullet}$ radicals formed by decomposition of H_2O_2, or $RhClO_2$ or $RhCl_2OOH$ formed from the reaction of H_2O_2 with $RhCl_3$.

The increase in the conversion of SO_3 from 23% to 86% (after 3 h reaction time) when a small amount of $RhCl_3$ is added to the synthesis mixture together with urea/H_2O_2 strongly suggests that the activation of methane is initiated not only by H_2O_2 but also by a metal–peroxo or metal–hydroperoxo species[9] produced in situ by the reversible reaction between urea/H_2O_2 and $RhCl_3$. Consistent with this logic, Table 2 shows that the maximum conversion of SO_3 to MSA (86–95%) is obtained when the molar ratio of urea/H_2O_2 to $RhCl_3$ is between 2.24 and 5.28. Furthermore, when a fresh amount of urea/H_2O_2, methane, and SO_3 was added to the reaction mixture after 3 h, the reaction proceeded in the same way as the initial reaction with fresh reaction mixture. This strongly suggests that the promoter, $RhCl_3$, is recycled in situ in the acidic solution. The importance of $RhCl_3$ is further supported by an experiment in which a fresh batch of urea/H_2O_2, methane, and SO_3 was added to a reaction mixture after 3 h, but one to which $RhCl_3$ had not been added. In this case, no additional reaction was observed.

When the reaction mixture is cooled to 0°C, most of the Rh salt can be separated from the reaction mixture by precipitation. The separation of MSA from the reaction mixture is straightforward, as MSA can be used as a solvent instead of H_2SO_4.

In conclusion, we have developed a highly effective, low-temperature reaction protocol for sulfonating methane to give methanesulfonic acid at low methane pressures. For a methane pressure of 100 psig, the conversion of methane to MSA is 29–36% and the selectivity to MSA is 99.9%. $RhCl_3$ enhances the initiation of the reaction by urea/H_2O_2, presumably through the formation of a metal–peroxo or metal–hydroperoxo species in situ. Most of the $RhCl_3$ can be recovered from the reaction mixture by precipitation at 0°C. The separation of MSA from the reaction mixture is straightforward as MSA can be used as a solvent instead of H_2SO_4. At higher temperatures (160–170°C) the same reaction scheme can be extended to synthesize CH_3OSO_3H, which can be easily hydrolyzed to methanol.

Received: January 20, 2003 [Z50976]

Keywords: C–H activation · homogeneous catalysis · methane · sulfonation

[1] a) C. L. Hill, *Activation and Functionalization of Alkanes*, Wiley, New York, **1989**; b) M. G. Axelrod, A. M. Gaffney, R. Pitchai, J. A. Sofranko, *Natural Gas Conversion II*, Elsevier, Amsterdam, **1994**, p. 93; c) C. Starr, M. F. Searl, S. Alpert, *Science* **1992**, *256*, 981; d) A. E. Shilov, G. B. Shul'pin, *Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes,* Kluwer Academic Publishers, Dordrecht, **2000**; e) G. A. Olah, A. Molnar, *Hydrocarbon Chemistry*, Wiley, New York, **1995**; f) B. A. Arndtsen, R. G. Bergman, *Science* **1995**, *270*, 1970; g) S. E. Bromberg, H. Yang, M. C. Asplund, T. Lian, B. K. McNamara, K. T. Kotz, J. S. Yeston, M. Wilkens, H. Frei, R. G. Bergman, C. B. Harris, *Science* **1997**, *278*, 260; h) M. Lin, A. Sen, *Nature* **1994**, *368*, 613; i) A. Sen, *Acc. Chem. Res.* **1998**, *31*, 550; j) J. A. Labinger, *Fuel Process. Technol.* **1995**, *42*, 325; k) R. H. Crabtree, *Chem. Rev.* **1995**, *95*, 987; l) A. E. Shilov, G. B. Shul'pin, *Chem. Rev.* **1997**, *97,* 2879; m) G. Dyker, *Angew. Chem.* **1999**, *111,* 1808; *Angew. Chem. Int. Ed.* **1999**, *38,* 1698; n) H. D. Gesser, N. R. Hunter, *Catal. Today* **1998**, *42*, 183; o) J. H. Lunsford, *Catal. Today* **2000**, *63*, 165; p) J. T. Golden, R. A. Andersen, R. G. Bergman, *J. Am. Chem. Soc.* **2001**, *123*, 5837; q) J. A. Labinger, J. E. Bercaw, *Nature* **2002**, *417*, 507; r) M. Muehlhofer, T. Strassner, W. A. Herrmann, *Angew. Chem.* **2002**, *114,* 1817; *Angew. Chem. Int. Ed.* **2002**, *41,* 1745.

[2] a) T. Nishiguchi, K. Nakata, K. Takaki, Y. Fujiwara, *Chem. Lett.* **1992**, *7*, 1141; b) E. G. Chepaikin, A. P. Bezruchenko, A. A. Leshcheva, G. N. Boyko, I. V. Kuzmenkov, E. H. Grigoryan, A. E. Shilov, *J. Mol. Catal. A* **2001**, *169*, 89; c) R. A. Periana, D. J. Taube, E. R. Evitt, D. G. Loffer, P. R. Wentrcek, G. Voss, T. Masuda, *Science* **1993**, *259*, 340; d) R. A. Periana, D. J. Taube, S. Gamble, H. Taube, T. Satoh, H. Fujii, *Science* **1998**, *280*, 560.

[3] a) *Ullmann's Encyclopedia of Industrial Chemistry, Vol. A25,* VCH, Weinheim, **1994**, pp. 503 – 506; b) F. M. Beringer, 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.

[4] a) J. I. Kroschwitz, M. Howe-Grant, *Kirk Othmer Encyclopedia of Chemical Technology*, Wiley, New York, **1991**; b) R. Guertin, US-A 3626004 **1971**.

[5] a) N. Basickes, T. E. Hogan, A. Sen, *J. Am. Chem. Soc.* **1996**, *118*, 13111; b) L. J. Lobree, A. T. Bell, *Ind. Eng. Chem. Res.* **2001**, *40*, 736; c) S. Mukhopadhyay, A. T. Bell, *Ind. Eng. Chem. Res.* **2002**, *41*, 5901; d) S. Mukhopadhyay, A. T. Bell, *Org. Proc. Res. Dev.* **2003**, in press; e) S. Mukhopadhyay, A. T. Bell, *J. Am. Chem. Soc.* **2003**, in press.

[6] S. Mukhopadhyay, A. T. Bell, *Angew. Chem.* **2003**, *115*, 1049; *Angew. Chem. Int. Ed.* **2003**, *42*, 1019.

[7] A 100-mL glass-lined high-pressure Parr autoclave reactor equipped with a small Teflon-coated magnetic stir bar was charged with urea/H_2O_2 (0.74 mmol), $RhCl_3$ (0.33 mmol), and fuming H_2SO_4 (5.69 g; 1.707 g of SO_3 in 3.983 g H_2SO_4). The reactor was purged with N_2 to expel the air from the system and then pressurized with methane (650 psig) from the adjacent connecting cylinders. The reaction mixture was stirred and heated to 65 °C for 3 h. After the stipulated period of time, the reactor was cooled with ice, vented, and opened. The reaction mixture was then added slowly to 0.5 g of water and then taken for ^{1}H NMR analysis. D_2O and methanol were used in a capillary as the lock references. The corresponding ^{1}H NMR chemical shifts for MSA were between 2.87 ppm and 3.02 ppm, depending on the concentration of MSA in the mixture.

[8] R. A. Periana, O. Mirinov, D. J. Taube, S. Gamble, *Chem. Commun.* **2002**, 2376.

[9] For the activation of methane with a Ca–peroxo species in the presence of a stoichiometric amount of $K_2S_2O_8$ see, a) M. Asadullah, T. Kitamura, Y. Fujiwara, *Angew. Chem.* **2000**, *112*, 2609; *Angew. Chem. Int. Ed.* **2000**, *39*, 2475; b) For the use of oxovanadium(v)peroxo complexes in methane activation, see G. V. Nizova, G. Siiss-Fank, G. B. Shul'pin, *Chem. Commun.* **1997**, 397; However, with this V – peroxo complex, no conversion of SO_3 to MSA is observed under our reaction conditions.

