Direct Sulfonation of Methane to Methanesulfonic Acid by Sulfur Trioxide Catalyzed by Cerium(IV) Sulfate in the Presence of Molecular Oxygen

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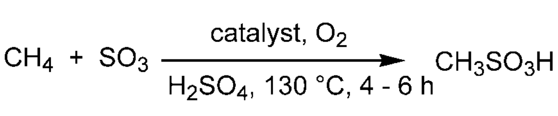
Abstract: Direct sulfonation of methane with SO_3 to methanesulfonic acid (MSA) is accomplished in sulfuric acid with almost 100% selectivity in the presence of a catalyst, namely, Ce and Rh salts and molecular oxygen as the catalyst regenerator. In the absence of O_2, the catalyst remains effective but the selectivity to MSA decreases to 53% and byproducts, principally CH_3OSO_3H, are formed. The effects of O_2 pressure, catalyst concentration, temperature, SO_3 concentration, and methane pressure have been examined on the rate of SO_3 conversion to MSA. The conversion of SO_3 to MSA was the same when CF_3SO_3H was used as the solvent instead of H_2SO_4.

Keywords: C–H activation; metal catalyst; methane; methanesulfonic acid; molecular oxygen; sulfonation; sulfur trioxide

Methanesulfonic acid (MSA, 70 wt %) is widely used in electrochemical systems and is an excellent catalyst for the esterification, alkylation, and condensation of organic compounds.[1] Lower reaction temperatures are required when using MSA rather than titanate catalysts, and purer, more colorless products can be obtained using MSA than those produced using sulfuric or *para*-toluenesulfonic acid as the catalyst. Anhydrous MSA is also particularly well suited for pharmaceutical applications and as a catalyst for aromatic alkylation. The current commercial process for the synthesis of MSA involves chlorine oxidation of methylmercaptan.[2] 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 byproduct. As an alternative it is interesting to consider a direct methane sulfonation route using SO_3 or SO_2 and O_2 as the sulfonating agent. Sen and co-workers[3a] and, more recently, we[3b, c] have shown that a compound such as $K_2S_2O_8$ can be used as a free radical initiator[3d] to sulfonate methane with SO_3 in fuming sulfuric acid.

Identification of a catalytic process for the sulfonation of methane would highly desirable, since this would eliminate the need for a free-radical initiator. While Ishii and co-workers have reported success in the vanadium-catalyzed sulfonation of adamantane to the corresponding sulfonic acids using SO_2 and O_2, methane did not undergo sulfonation to MSA.[4] Hg-based catalysts have been used at elevated temperature (300–450 °C) for methane sulfonation with SO_3 to MSA; however this process exhibits a low yield and cannot be implemented due to problems in isolating MSA from a mixture of byproducts, mainly esters and disulfonic acids formed during this reaction.[5] In subsequent studies, Periana and co-workers[6] have reported the selective sulfonation of CH_4 to MSA in fuming sulfuric acid at 180 to 220 °C using Hg salts[6a] or Pt complexes as the catalyst.[6b] In both the cases, the metal cations undergo reduction and are reoxidized by sulfuric acid.[6] We have recently shown that $Hg(CF_3SO_3H)_2$ can be used in the presence of O_2 to synthesize MSA by the reaction of methane and SO_3 in fuming sulfuric acid.[7] While Hg salts are effective catalysts, their toxicity motivates the search for alternative catalysts. This work was undertaken to assess the catalytic activity of various metal salts (Scheme 1). It is shown that salts of Ce and Rh are particularly attractive for the sulfonation of methane to MSA.

Table 1 shows the effect of different catalysts on the rate of the sulfonation reaction. In a typical reaction (see Experimental Section), CH_4 and SO_3 were reacted in fuming sulfuric acid in a high-pressure, glass-lined autoclave in the presence of a catalyst and O_2. Reactions were carried out for 4–6 h at 130 °C and the MSA thus formed was identified and quantified by ^{1}H NMR.[3b] The conversion is reported on the basis of the limiting reagent, SO_3, and is defined as the ratio of the moles



$$CH_4 + SO_3 \xrightarrow[H_2SO_4,\ 130\ °C,\ 4-6\ h]{\text{catalyst, } O_2} CH_3SO_3H$$

Scheme 1. Direct reaction of methane with SO_3 in the presence of O_2.

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Table 1. Effect of different catalysts on the rate of sulfonation of methane to MSA.[a]

Entry	Catalyst	*t* [h]	% SO_3 to MSA	MSA [mmol]	% SO_3 to CH_3OSO_3H	% Selectivity to MSA
1	$VOSO_4$	5	1.2	0.26	1	55
2	$Sn(SO_4)_2$	5	1	0.21	1	50
3	$RhCl_3$	6	7	1.49	1.5	82
4	$Ce(SO_4)_2$	6	11	2.34	0.01	99.9
5	$Ce_2(SO_4)_3$	6	10	2.13	0.09	99
6	$CaCl_2$	5	0	0	0	–
7	$TiCl_4$	5	0.01	–	0.03	25
8	$FeCl_3$	5	0.07	0.015	0.06	54
9	$RuCl_3$	5	0	0	1	0
10	Co(II)phthalocyanine	4	0	0	1	0
11	AgCl	5	0.12	0.026	0	100
12	$Zn(CH_3COO)_2$	5	0.3	0.06	0	100
13	$Ga_2(SO_4)_3$	4	0.3	0.06	1	23
14	$In(CF_3SO_3)_3$	5	0.25	0.053	0.05	83
15	$Tl(CF_3CO_2)_3$	5	0.6	0.13	0.6	50
16	$Pd(CF_3COO)_2$	5	0.3	0.06	5	6
17	$PtCl_4$	5	0.04	0.008	10	0.4

[a] Reaction conditions unless otherwise stated: CH_4, 360 psig (101 mmol); SO_3, 1.7 g (21.26 mmol); molar ratio of CH_4 to SO_3, 4.75; O_2, 40 psig (14.8 mmol); catalyst, 0.09 mmol; solvent, fuming sulfuric acid, 5.67 g; temperature, 130 °C.

of SO_3 converted to MSA to the moles of SO_3 taken initially in to the reactor.

$VOSO_4$ and $Sn(SO_4)_2$ exhibited limited activity and $RhCl_3$ was moderately active; however, all three catalysts showed high selectivity to MSA (Table 1, entries 1–3). Ce(IV) or Ce(III) sulfates showed activities superior to $RhCl_3$ and, more importantly MSA selectivities > 99% (Table 1, entries 4 and 5). Notably, almost no MSA formation was detected when $CaCl_2$, $TiCl_4$, $FeCl_3$, $RuCl_3$, Co(II) phthalocyanine, AgCl, $Zn(CH_3COO)_2$, $Ga_2(SO_4)_3$, $In(CF_3SO_3)_3$, or $Tl(CF_3COO)_3$ were used as the catalyst (Table 1, entries 6–15). $Pd(CF_3COO)_2$ and $PtCl_4$ exhibited modest activity and high selectivity to CH_3OSO_3H (Table 1, entries 16 and 17).

Given the high activity of $Ce(SO_4)_2$, the effects of the reaction conditions on the conversion of SO_3 and the selectivity to MSA were investigated. The results of these experiments are presented in Table 2. The O_2 partial pressure (Table 2, entries 1–5) affects both the catalyst activity and selectivity. In the absence of O_2, 8% of the initial SO_3 is converted to MSA and 7% of the SO_3 is converted to CH_3OSO_3H after 6 h of reaction at 130 °C. Raising the O_2 partial pressure to 40 psig lowered the overall sulfonation rate; however, the selectivity to MSA increased from 53 to 99.9%. Further increasing the O_2 partial pressure to 60 psig decreased the MSA selectivity to 88%. The major byproduct detected in this case was CH_3OSO_3H. Thus, with 40 psig O_2, a 23% conversion of SO_3 to MSA was achieved in 42 h with 99.9% selectivity. The reaction rate depends on the catalyst loading (Table 2, entries 6–10). Increasing the amount of $Ce(SO_4)_2$ from 0 to 0.09 mmol increased the conversion of SO_3 to MSA from 0 to 11% without affecting the MSA selectivity, which remained at *ca.* 100%. Raising the temperature from 95 to 130 °C increased the conversion of SO_3 to MSA from 4 to 11% (Table 2, entries 11–14). However, the conversion of SO_3 to CH_3OSO_3H remained constant at 0–0.01%. The conversion to MSA reached a maximum of 16% at 150 °C; however, the conversion of SO_3 to CH_3OSO_3H at this temperature also rose to 9%, and 1% methanedisulfonic acid was detected as well.

The conversion of SO_3 to MSA observed after 6 h of reaction increased with increasing initial SO_3 concentration up to a concentration of 30 wt %, at which point the conversion of SO_3 to MSA was 11%. However, raising the SO_3 concentration to 56 wt % decreased the amount of MSA formed and increased the amounts of CH_3OSO_3H (7%) and methanedisulfonic acid $[CH_2(SO_3H)_2]$ (1%) formed (Table 2, entries 15 and 16). For a given set of reaction conditions, replacing H_2SO_4 by trifluoromethanesulfonic acid resulted in an identical conversion of SO_3 to MSA.

The mechanism by which Ce catalyzes the sulfonation of methane is not known. A free radical mechanism[9] can be ruled out since it is known that in the presence of O_2 free-radical initiated sulfonation is strongly inhibited.[3a–c] An alternative idea is that methane undergoes oxidative addition to Ce(IV) in a manner similar to that proposed for Hg(II).[6a] If this were the case, then Ce(IV) cations would be expected to be reduced to Ce(III) cations. The function of O_2 in such a scheme would be to reoxidize Ce(III) back to Ce(IV). Consistent with this hypothesis, the conversion of SO_3 to MSA is observed to increase with increasing O_2 partial pressure. Howev-

Table 2. Effect of different process parameters on the rate of sulfonation of methane to MSA.[a]

Entry	Parameter	t [h]	% SO_3 to MSA	% SO_3 to CH_3OSO_3H	MSA [mmol]	% Selectivity to MSA
1	O_2, 0 psig	6	8	7	1.7	53
2	20 psig	6	8	1.2	1.7	87
3	40 psig	6	11	0.01	2.34	99.9
4	40 psig	42	23	0.1	4.9	99.9
5	60 psig	6	12	1.6	2.55	88
6	$Ce(SO_4)_2$, 0 mmol	6	0	0	0	–
7	0.03 mmol	6	4	0	0.85	100
8	0.06 mmol	6	8	0	1.7	100
9	0.09 mmol	6	11	0.01	2.34	99.9
10	0.12 mmol	6	12	0.5	2.55	96
11	Temp, 95 °C	6	4	0	0.85	100
12	120 °C	6	7	0	1.49	100
13	130 °C	6	11	0.01	2.34	99.9
14[b]	150 °C	6	16	9	3.4	61
15	SO_3, 30 wt %	6	11	0.01	2.34	99.9
16[b]	SO_3, 56 wt %	6	9	7	1.91	53

[a] Reaction conditions unless otherwise stated : CH_4, 360 psig (101 mmol); O_2, 40 psig; catalyst, $Ce(SO_4)_2$, 0.09 mmol; solvent, fuming sulfuric acid, 5.67 g; $T = 130$ °C.

[b] Ca.0.6 to 1% methanedisulfonic acid was also formed as a byproduct.

er, when the O_2 partial pressure exceeds 40 psig, oxidation of MSA to CH_3OSO_3H occurs and the selectivity to MSA is lost. The decrease in SO_3 conversion to MSA with increasing temperature is attributable to the oxidation of MSA to CH_3OSO_3H, which occurs more rapidly with increasing temperature. While SO_3 is required for the formation of MSA, above a certain critical SO_3 concentration sulfonation of MSA to methanedisulfonic occurs.

In conclusion, we have demonstrated a catalytic process for the direct, liquid-phase sulfonation of methane with SO_3 in the presence of molecular O_2 at relatively low temperature and methane pressure. Under the best reaction conditions, 23% conversion of SO_3, 33% conversion of O_2, and 4.85% conversion of methane to MSA was achieved in fuming sulfuric acid with 99.9% product (MSA) selectivity, using $Ce(SO_4)_2$ as the catalyst. The production rate of MSA was 1.3 mole/mole catalyst-h. Besides Ce salts, $RhCl_3$ emerged as an effective catalyst in sulfonating CH_4 with SO_3 in the presence of O_2.

Experimental Section

Reactions were carried out in a 100 cm^3 high-pressure autoclave (Parr Instruments – 3000 psig maximum) constructed of Hastelloy B. Unless otherwise stated, the following procedure was used for all experiments. 0.09 mmol of $Ce(SO_4)_2$ (Aldrich Chemical Company), and 5.67 g fuming sulfuric acid (Aldrich Chemical Company, 27–33% SO_3) were added to a glass liner containing a Teflon-encased stirring bar. For some experiments, additional SO_3 (Aldrich Chemical Company, 99%) was added to the liquid in the liner. The glass liner was then transferred to the reactor, after which the reactor was sealed and attached to a gas handling system. The reactor was pressurized with 40 psig O_2 (Matheson, 99.99%) and then with 360 psig CH_4 (Matheson, ultra high purity). The reactor was heated to 130 °C, a process which took 15–20 min, and this temperature was then maintained for up to 6 h, unless stated otherwise. Following reaction, the reactor was cooled in an ice bath to room temperature (~0.35 h), and the reactor was vented. The gases exiting the reactor were passed through scrubbers containing NaOH and Carbusorb to remove sulfur(II) compounds. The system was then purged with N_2 purified by passage through oxysorb, ascarite, and molecular sieve traps. The liquid product was removed from the glass liner and added slowly to 0.6 g of H_2O to convert any unreacted SO_3 to H_2SO_4. Reaction products were characterized by ^1H NMR. All spectra were acquired using a Bruker AMX-400 MHz FT-NMR spectrometer. A capillary containing D_2O, immersed within the NMR tube containing the sample, was used as a lock reference, and integration standard. All other chemicals were purchased from Aldrich Chemical Company and used without further purification. Products were identified by comparison of their ^1H NMR chemical shifts to standard samples. The corresponding chemical shifts for MSA was 2.93 ppm to 3.18 ppm, depending on the concentration of MSA in the reaction mixture.

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