

# Catalyzed sulfonation of methane to methanesulfonic acid

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## Abstract

Direct sulfonation of methane with  $\text{SO}_3$  to methanesulfonic acid (MSA) and methylbisulfate was investigated in sulfuric acid using Hg(I), Hg(II), and Rh(III)-salts as catalysts.  $\text{O}_2$  was found to be an important component for the regeneration of the catalyst. The effects of  $\text{O}_2$  pressure, temperature,  $\text{SO}_3$  concentration, methane pressure, and catalyst concentration were examined on the rates of  $\text{SO}_3$  conversion to MSA and methylbisulfate. The results of this investigation show that after 5 h at 148 °C using fuming sulfuric acid as the solvent, 360 psig  $\text{CH}_4$  reacts with 21 mmol of  $\text{SO}_3$  to give a 44% conversion of  $\text{SO}_3$  to MSA in the presence of 40 psig  $\text{O}_2$  and 0.075 mmol of  $\text{Hg}(\text{CF}_3\text{SO}_3)_2$  as the catalyst. The corresponding MSA selectivity is 87%. Conducting the reaction at higher temperature, higher  $\text{O}_2$  pressure and higher initial concentration of  $\text{SO}_3$ , leads to a reduction of the selectivity to MSA and an increase in the selectivity to  $\text{CH}_3\text{OSO}_3\text{H}$ . A mechanism for the formation of MSA and  $\text{CH}_3\text{OSO}_3\text{H}$  is proposed in the light of the experimental results.

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## 1. Introduction

Selective functionalization of methane to value-added products is a subject of ongoing scientific and technological interest [1]. Because of favorable thermodynamics, considerable effort has been devoted to the oxidation and oxidative carbonylation of methane [2]. By contrast, the sulfonation of methane has not received as much attention despite its commercial importance [3]. The current commercial process for the synthesis of methanesulfonic acid (MSA) occurs via the chlorine oxidation of methylmercaptan [4,5]. While this process is highly productive, it produces 6 mol 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  $\text{SO}_3$  or  $\text{SO}_2$  and  $\text{O}_2$  as the sulfonating agent. Sen and co-workers [6], and more recently we [7], have shown that free radical initiators [8] such as  $\text{K}_2\text{S}_2\text{O}_8$ ,  $\text{K}_4\text{P}_2\text{O}_8$ ,  $\text{CaO}_2$ , and Urea- $\text{H}_2\text{O}_2$  can be used to sulfonate methane with  $\text{SO}_3$  and  $\text{SO}_2$  in acid solvents, namely, fuming sulfuric acid. The problem with using an initiator is that it is consumed and cannot be recycled. Consequently, it would be preferable to identify catalytic processes that could be used to effect the

sulfonation of methane. We have recently reported success in the Pd-Cu-catalyzed sulfonation of methane with  $\text{SO}_2$  in presence of molecular  $\text{O}_2$  [9]. However, the need to use triflic acid as the solvent, which is expensive and highly corrosive is a disadvantage. Hg-based catalysts have been used at elevated temperature (200–450 °C) for methane sulfonation; however, this process has a low yield and produces MSA together with a mixture of byproducts, mainly esters and disulfonic acids, which are difficult to separate [10]. In this paper, we show that methane will undergo liquid-phase sulfonation with  $\text{SO}_3$  at moderate temperatures in sulfuric acid to form MSA selectively using a metal catalyst and molecular oxygen as the catalyst regenerator.

## 2. Experimental

Reactions were carried out in a 100 cm<sup>3</sup> high-pressure autoclave (Parr Instruments, 3000 psig maximum) constructed of Hastelloy B. Unless otherwise stated, the following procedure was used for all experiments. 0.075 mmol of  $\text{Hg}(\text{CF}_3\text{SO}_3)_2$  (Aldrich, 99.9%), and 5.67 g fuming sulfuric acid (Aldrich, 27–33%  $\text{SO}_3$ ) were added to a glass liner containing a Teflon-encased stirring bar. For some experiments, additional  $\text{SO}_3$  (Aldrich, 99%) was added to the liquid in the liner. The glass liner was then transferred to

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the reactor, after which the reactor was sealed and attached to a gas handling system. The reactor was pressurized with 40 psig O<sub>2</sub> (Matheson, 99.99%) and then with 360 psig CH<sub>4</sub> (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 5 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 Carusorb to remove sulfur (II) compounds. The system was then purged with N<sub>2</sub> purified by passage through oxysorb, ascarite, and molecular sieve traps. The liquid product was removed from the glass liner and added slowly to 0.5 g of H<sub>2</sub>O to convert any unconverted SO<sub>3</sub> to H<sub>2</sub>SO<sub>4</sub>. Reaction products were characterized by <sup>1</sup>H NMR.

All spectra were acquired using a Bruker AMX-400 MHz FT-NMR spectrometer. A capillary containing D<sub>2</sub>O, immersed within the NMR tube containing the sample, was used as a lock reference, and integration standard. All other chemicals were purchased from Aldrich and used without further purification. Products were identified by comparison of their <sup>1</sup>H NMR chemical shifts to standard samples. The corresponding chemical shifts for MSA was 2.93 to 3.09 ppm, depending on the concentration of MSA in the reaction mixture.

### 3. Results and discussion

In a typical experiment (see Section 2), CH<sub>4</sub> and SO<sub>3</sub> were reacted in fuming sulfuric acid in a high-pressure, glass-lined autoclave in the presence of a metal catalyst and O<sub>2</sub>. Reactions were carried out for 5 h at 130 °C and the MSA thus formed was identified and quantified by <sup>1</sup>H NMR [7].

Table 1 shows the effect of catalyst composition on the extent of SO<sub>3</sub> (the limiting reagent) conversion to MSA and CH<sub>3</sub>OSO<sub>3</sub>H. MgCl<sub>2</sub>, CaCl<sub>2</sub>, RuCl<sub>3</sub>, Co(II)phthalocyanine, TiCl<sub>4</sub>, PtCl<sub>4</sub>, FeCl<sub>3</sub>, AgCl, In(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>, Pd(CF<sub>3</sub>COO)<sub>2</sub>, Ga<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, Zn(CH<sub>3</sub>COO)<sub>2</sub>, Tl(CF<sub>3</sub>COO)<sub>2</sub>, Sn(SO<sub>4</sub>)<sub>2</sub>, and VOSO<sub>4</sub> show little or no catalytic activity. RhCl<sub>3</sub> is moderately active and exhibits a selectivity of 75% to MSA. However, the most active catalyst was Hg(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>, which produced MSA with a selectivity of 92%.

Table 2 shows the effects of anion composition on the effectiveness of Hg-based catalysts. For the Hg(I) salt, Hg<sub>2</sub>SO<sub>4</sub> was the most active, giving a 34% conversion to MSA in 5 h at 130 °C. Among the Hg(II) salts investigated, HgTe was the most active catalyst; however, the highest selectivity to MSA was achieved using Hg(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>. Turnover numbers for the Hg-based catalysts ranged from 35 to 104.

A set of reactions was performed in which the O<sub>2</sub> pressure was varied (Fig. 1a). In absence of O<sub>2</sub> and with Hg(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> as the catalyst, the conversions of SO<sub>3</sub> to products were 14% for MSA and 10% for CH<sub>3</sub>OSO<sub>3</sub>H after 5 h of reaction at 130 °C. Introducing an O<sub>2</sub> pressure of 20 psig lowered the overall rate but increased the selectivity to MSA noticeably. The SO<sub>3</sub> conversion to MSA reached a maximum for an O<sub>2</sub> pressure of 60 psig. Increasing the O<sub>2</sub> partial pressure above 60 psig decreased the selectivity to MSA (Fig. 1b).

Fig. 2 shows the effect of temperature on the conversion of SO<sub>3</sub> and the selectivity to MSA. With an increase in temperature from 95 to 130 °C, the conversion of SO<sub>3</sub> to MSA increased from 2 to 21%, while the conversion of SO<sub>3</sub> to CH<sub>3</sub>OSO<sub>3</sub>H increased from 2 to 3%. With a further increase in temperature, the conversion of SO<sub>3</sub> to MSA passed through a maximum at 148 °C, as the conversion of SO<sub>3</sub> to CH<sub>3</sub>OSO<sub>3</sub>H increased rapidly. At 160 °C, CH<sub>3</sub>OSO<sub>3</sub>H was the major product.

Table 1  
Effect of different catalysts on the sulfonation of methane to MSA<sup>a</sup>

Entry	Catalyst	<i>t</i> (h)	SO <sub>3</sub> conversion to CH <sub>3</sub> SO <sub>3</sub> H (%)	SO <sub>3</sub> conversion to CH <sub>3</sub> OSO <sub>3</sub> H (%)	Selectivity to CH <sub>3</sub> SO <sub>3</sub> H (%)
1	MgCl <sub>2</sub>	5	0	0.02	0
2	CaCl <sub>2</sub>	5	0	0	–
3	RuCl <sub>3</sub>	5	0	1	0
4	Co(II)phthalocyanine	5	0	1	0
5	TiCl <sub>4</sub>	5	0.01	0.03	25
6	PtCl <sub>4</sub>	5	0.04	10	0.4
7	FeCl <sub>3</sub>	5	0.07	0.06	54
8	AgCl	5	0.12	0	100
9	In(CF <sub>3</sub> SO <sub>3</sub> ) <sub>3</sub>	5	0.25	0.05	83
10	Pd(CF <sub>3</sub> COO) <sub>2</sub>	5	0.3	5	6
11	Ga <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	5	0.3	1	23
12	Zn(CH <sub>3</sub> COO) <sub>2</sub>	5	0.3	0	100
13	Tl(CF <sub>3</sub> CO <sub>2</sub> ) <sub>3</sub>	5	0.6	0.6	50
14	Sn(SO <sub>4</sub> ) <sub>2</sub>	5	1	1	50
15	VOSO <sub>4</sub>	5	1.2	1	55
16	RhCl <sub>3</sub>	5	6	2	75
17	Hg(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub>	5	21	1.9	92

<sup>a</sup> Reaction conditions: solvent, fuming sulfuric acid, 5.67 g; methane, 360 psig; O<sub>2</sub>, 40 psig; catalyst, 0.075 mmol; SO<sub>3</sub>, 30 wt.%; temperature, 130 °C.

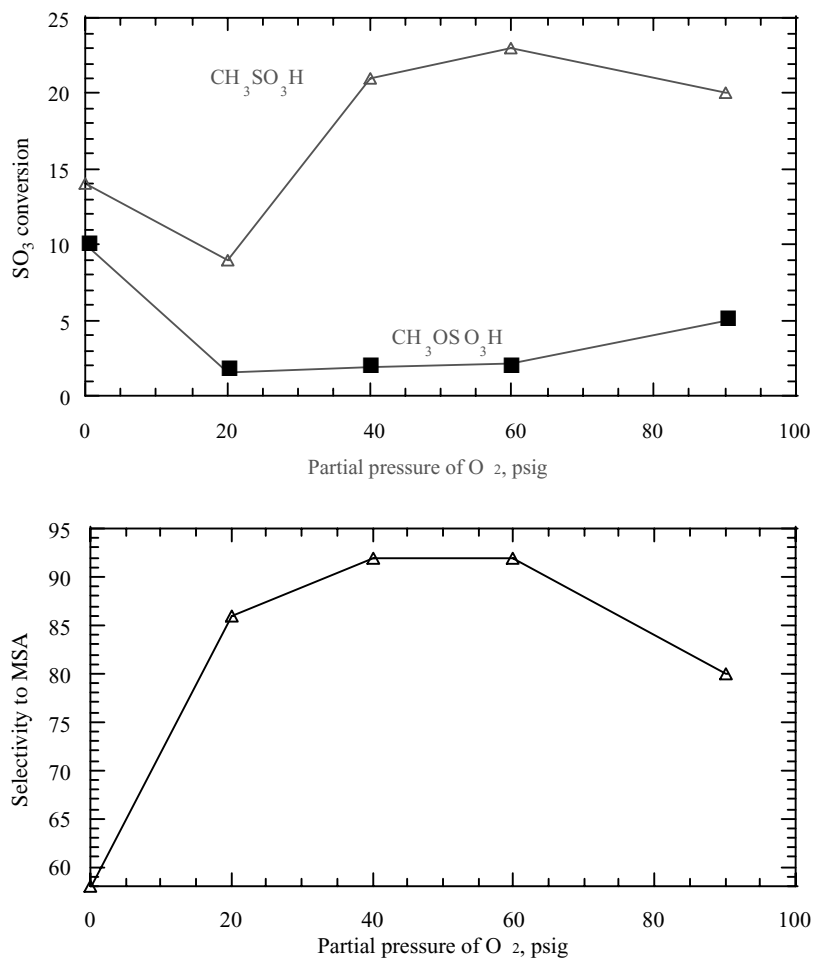


Fig. 1. Effect of O<sub>2</sub> partial pressure on (a) the conversion of SO<sub>3</sub> to CH<sub>3</sub>SO<sub>3</sub>H and CH<sub>3</sub>OSO<sub>3</sub>H and (b) on the selectivity to CH<sub>3</sub>SO<sub>3</sub>H. Reaction conditions: solvent, fuming sulfuric acid, 5.67 g; CH<sub>4</sub>, 360 psig; Hg(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>, 0.075 mmol; SO<sub>3</sub>, 30 wt.%; time, 5 h; temperature, 130 °C.

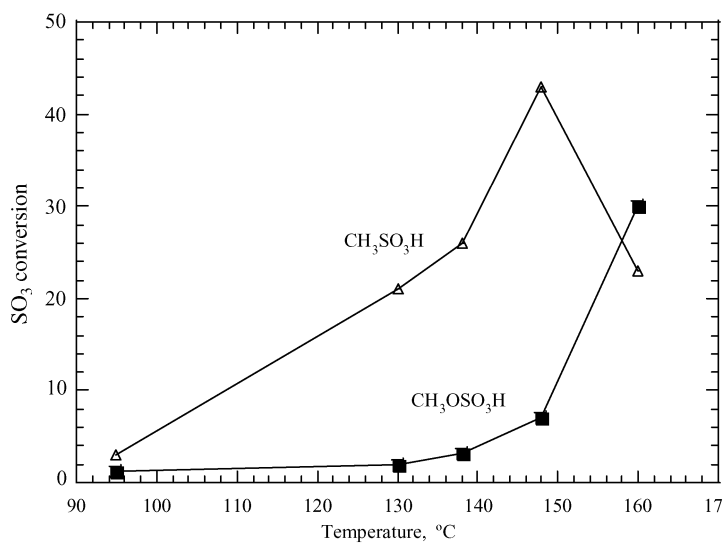


Fig. 2. Effect of temperature on the conversion of SO<sub>3</sub> to CH<sub>3</sub>SO<sub>3</sub>H and CH<sub>3</sub>OSO<sub>3</sub>H. Reaction conditions: solvent, fuming sulfuric acid, 5.67 g; CH<sub>4</sub>, 360 psig; O<sub>2</sub>, 40 psig; Hg(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>, 0.075 mmol; SO<sub>3</sub>, 30 wt.%; time, 5 h.

Table 2  
Effect of different Hg-salts on the sulfonation of methane to MSA<sup>a</sup>

Entry	Catalyst	<i>t</i> (h)	SO <sub>3</sub> conversion to CH <sub>3</sub> SO <sub>3</sub> H (%) (TON)	SO <sub>3</sub> conversion to CH <sub>3</sub> OSO <sub>3</sub> H (%)	Selectivity to CH <sub>3</sub> SO <sub>3</sub> H (%)
1	Hg <sub>2</sub> SO <sub>4</sub>	5	34 (98)	6	85
2	Hg <sub>2</sub> Cl <sub>2</sub>	5	28 (81)	5	85
3	Hg(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub>	5	21 (60)	1.9	92
4	HgSO <sub>4</sub>	5	17 (49)	3	85
5	HgCl <sub>2</sub>	5	16 (46)	2	89
6	Hg(CH <sub>3</sub> COO) <sub>2</sub>	5	12 (35)	1.5	89
7	HgTe	5	36 (104)	14	72

<sup>a</sup> Reaction conditions: solvent, fuming sulfuric acid, 5.67 g; methane, 360 psig; O<sub>2</sub>, 40 psig; Hg-salts, 0.075 mmol; SO<sub>3</sub>, 30 wt.%; temperature, 130 °C.

The effect of initial SO<sub>3</sub> concentration on the conversion of SO<sub>3</sub> to MSA observed after 5 h is shown in Fig. 3. The conversion of SO<sub>3</sub> to MSA increased rapidly initially with increasing initial concentration of SO<sub>3</sub>. However, this increase reached a maximum at ~40% SO<sub>3</sub> in the initial reaction mixture. Above this concentration, the conversion of SO<sub>3</sub> to MSA decreased as the conversion to CH<sub>3</sub>OSO<sub>3</sub>H increased at an accelerating rate.

Fig. 4 shows the effects of methane pressure on the conversion of SO<sub>3</sub> to MSA. The conversion of SO<sub>3</sub> to MSA increased from 0 to 34% as the methane pressure was increased from 0 to 600 psig. By contrast, the conversion of SO<sub>3</sub> to CH<sub>3</sub>OSO<sub>3</sub>H began building up above a methane pressure of 360 psig.

The reaction rate depends, as well, on the catalyst loading as shown in Fig. 5. With an increase in the amount of Hg(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> from 0 to 0.075 mmol, the conversion of SO<sub>3</sub> to MSA increased from 0 to 21%. However, at higher catalyst concentrations, the increase in MSA formation became slower and more CH<sub>3</sub>OSO<sub>3</sub>H was formed.

Two mechanisms can be proposed for the sulfonation of methane that are consistent with the experimental observa-

tions. In the absence of O<sub>2</sub>, the work of Sen and co-workers [6] and that presented here demonstrate that HgSO<sub>4</sub> will initiate the formation of MSA. Sen and co-workers proposed that HgSO<sub>4</sub> and other metal salts may serve as a free-radical initiator (I<sup>•</sup>) and that MSA is formed via a free-radical process, such as that shown in Scheme 1. CH<sub>3</sub>OSO<sub>3</sub>H could then be envisioned to form via Hg(II) catalyzed oxidation of MSA by SO<sub>3</sub> [11]. When O<sub>2</sub> is present in the gas phase, the free radical mechanism involved in the MSA formation is suppressed, as a consequence of the reaction of O<sub>2</sub> with the methyl radicals. Under such circumstances, it is possible to propose a catalyzed reaction mechanism for the formation of MSA and CH<sub>3</sub>OSO<sub>3</sub>H, such as that shown in Scheme 2. This scheme consists of three basic steps (i) activation of methane, (ii) methane functionalization, and (iii) catalyst regeneration. In the activation step, methane reacts with Hg(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> to form a methyl-mercury species [11], CH<sub>3</sub>HgOSO<sub>2</sub>CF<sub>3</sub>, which then may react either with SO<sub>3</sub> to form MSA or with H<sub>2</sub>SO<sub>4</sub> to form CH<sub>3</sub>OSO<sub>3</sub>H. During the functionalization step, Hg(II) is reduced to Hg(I) and, hence, during the catalyst regeneration step, Hg(I) is reoxidized to Hg(II) via reaction with O<sub>2</sub>.

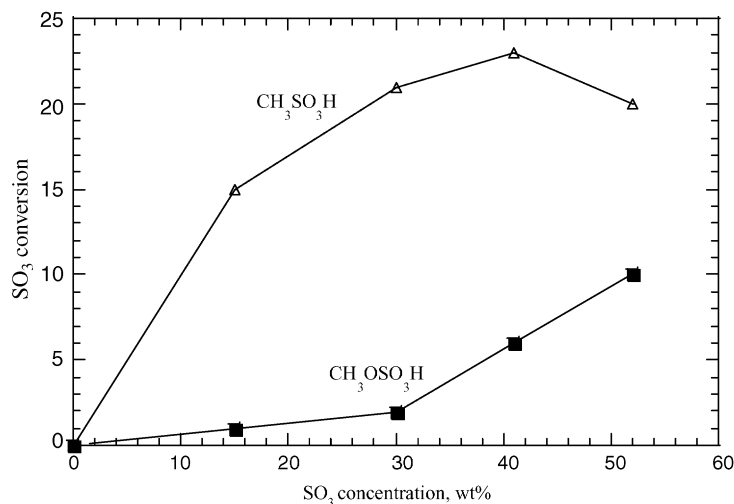


Fig. 3. Effect of SO<sub>3</sub> concentration on the conversion of SO<sub>3</sub> to CH<sub>3</sub>SO<sub>3</sub>H and CH<sub>3</sub>OSO<sub>3</sub>H. Reaction conditions: solvent, fuming sulfuric acid, 5.67 g; CH<sub>4</sub>, 360 psig; O<sub>2</sub>, 40 psig; Hg(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>, 0.075 mmol; time, 5 h; temperature, 130 °C.

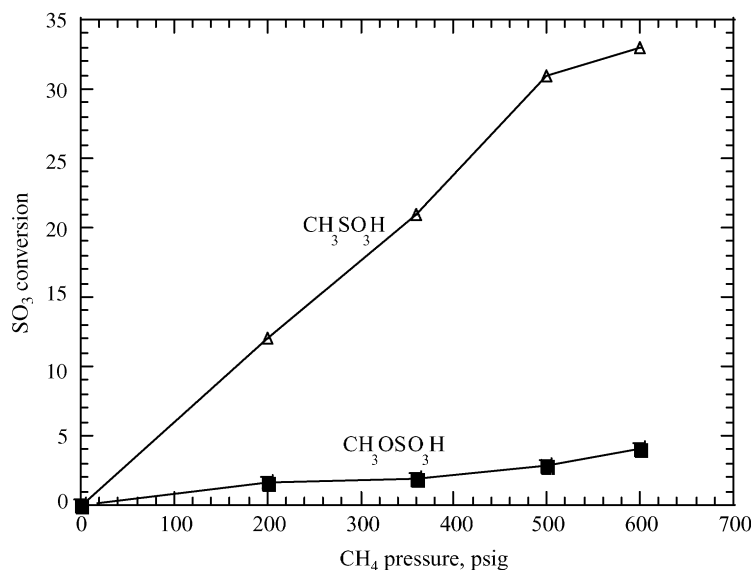


Fig. 4. Effect of CH<sub>4</sub> partial pressure on the conversion of SO<sub>3</sub> to CH<sub>3</sub>SO<sub>3</sub>H and CH<sub>3</sub>OSO<sub>3</sub>H. Reaction conditions: solvent, fuming sulfuric acid, 5.67 g; O<sub>2</sub>, 40 psig; Hg(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>, 0.075 mmol; SO<sub>3</sub>, 30 wt.%; time, 5 h; temperature, 130 °C.

The proposed reaction mechanisms presented in Schemes 1 and 2 can be used to interpret the effects of reaction conditions on the conversion of SO<sub>3</sub> to MSA and CH<sub>3</sub>OSO<sub>3</sub>H presented in Figs. 1–5. The formation of MSA in the absence of O<sub>2</sub> shown in Fig. 1a is assumed to occur via the free-radical mechanism of Scheme 1. CH<sub>3</sub>OSO<sub>3</sub>H is then formed by SO<sub>3</sub> oxidation of MSA. As the O<sub>2</sub> pressure is increased, this mechanism is suppressed and the catalyzed mechanism (Scheme 2) takes over. In support of this conclusion, we have reported that the sulfonation of methane by SO<sub>3</sub> is suppressed by the addition of O<sub>2</sub> to the gas phase in systems where the sulfonation occurs solely via free radical mechanism [7]. The increase in the conversion of SO<sub>3</sub> to MSA with increasing O<sub>2</sub> partial pressure is attributed

to the increased rate of reoxidation of Hg(I) to Hg(II). For O<sub>2</sub> pressures between 20 and 40 psig, the increase in the conversion of SO<sub>3</sub> to CH<sub>3</sub>OSO<sub>3</sub>H is roughly an order of magnitude smaller, suggesting that the reaction of Hg(II) methylene species with H<sub>2</sub>SO<sub>4</sub> is much slower than that with SO<sub>3</sub>. Above an O<sub>2</sub> pressure of 40 psig, the conversion of SO<sub>3</sub> to MSA passes through a maximum as the conversion of SO<sub>3</sub> to CH<sub>3</sub>OSO<sub>3</sub>H rises at an accelerating rate. This trend may be due to the direct O<sub>2</sub> oxidation of MSA to CH<sub>3</sub>OSO<sub>3</sub>H at higher O<sub>2</sub> pressures. This conclusion is supported by the results of a control reaction between CH<sub>3</sub>SO<sub>3</sub>H and O<sub>2</sub>, which showed that CH<sub>3</sub>SO<sub>3</sub>H is slowly oxidized to CH<sub>3</sub>OSO<sub>3</sub>H (2% conversion) at 160 °C in the presence of Hg(II).

The nearly linear increases in the conversions of SO<sub>3</sub> to MSA and CH<sub>3</sub>OSO<sub>3</sub>H with catalyst concentration and CH<sub>4</sub> pressure shown in Figs. 4 and 5 are consistent with Scheme 2, which predicts that neither variable influences the selectivity to MSA. Both sets of data indicate that the rate of MSA formation is roughly an order of magnitude higher than the rate of CH<sub>3</sub>OSO<sub>3</sub>H formation. The two-fold higher SO<sub>3</sub> conversion observed using Hg<sub>2</sub>SO<sub>4</sub> as the catalyst compared to HgSO<sub>4</sub> (Table 2) is also consistent with Scheme 2. Since Hg(I) and Hg(II) are interconverted during the reaction cycle, the two-fold higher conversion for Hg<sub>2</sub>SO<sub>4</sub> versus HgSO<sub>4</sub> when the same number of moles of

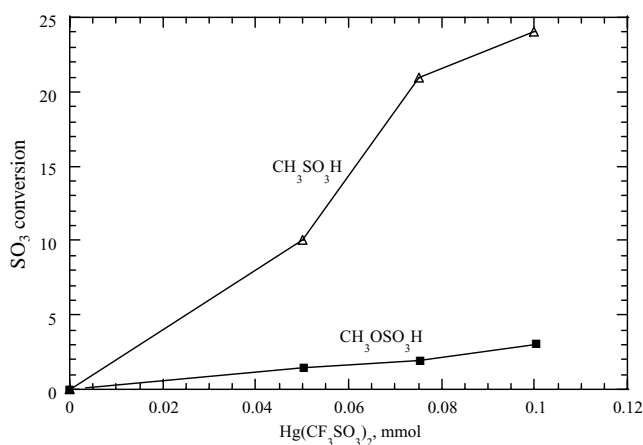
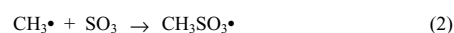
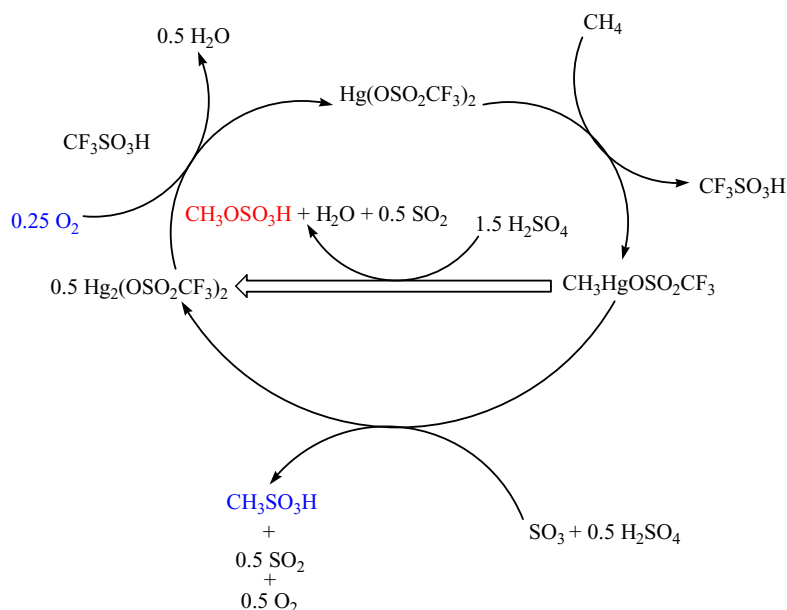


Fig. 5. Effect of catalyst concentration on the conversion of SO<sub>3</sub> to CH<sub>3</sub>SO<sub>3</sub>H and CH<sub>3</sub>OSO<sub>3</sub>H. Reaction conditions: solvent, fuming sulfuric acid, 5.67 g; O<sub>2</sub>, 40 psig; catalyst, Hg(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>; SO<sub>3</sub>, 30 wt.%; CH<sub>4</sub> pressure, 360 psig; time, 5 h; temperature, 130 °C.



Scheme 1. Proposed reaction mechanism in the absence of O<sub>2</sub>.

Scheme 2. Proposed reaction mechanism in the presence of O<sub>2</sub>.

catalyst are used is simply a consequence of the two-fold higher number of moles of Hg that are introduced when using Hg<sub>2</sub>SO<sub>4</sub>. The effect of increasing SO<sub>3</sub> concentration is different from that of increasing CH<sub>4</sub> pressure. At initial SO<sub>3</sub> concentrations above about 20%, the conversion of SO<sub>3</sub> to MSA increases more slowly as the conversion to CH<sub>3</sub>OSO<sub>3</sub>H accelerates. This trend can be ascribed to the Hg(II)-catalyzed oxidation of MSA by SO<sub>3</sub> via the reaction CH<sub>3</sub>SO<sub>3</sub>H + SO<sub>3</sub> → CH<sub>3</sub>OSO<sub>3</sub>H + SO<sub>2</sub>. We have found that this reaction will occur at 130 °C in the absence of a catalyst (2% conversion), and is accelerated when metal salts are present (5% conversion).

Fig. 2 shows that the conversions of SO<sub>3</sub> to MSA and CH<sub>3</sub>OSO<sub>3</sub>H both increase with increasing temperature. These changes are accompanied by an increase in the selectivity to MSA for temperatures up to about 140 °C. The turn over number is approximately 118. However, above 145 °C, further increases in temperature cause a rapid decrease in the conversion of SO<sub>3</sub> to MSA and a corresponding rapid rise in to the conversion to CH<sub>3</sub>OSO<sub>3</sub>H. The observed increase in the selectivity to MSA for temperatures between 95 and 140 °C suggests that the activation energy for the reaction of the Hg(II) methylide species (see Scheme 2) with SO<sub>3</sub> is higher than that with H<sub>2</sub>SO<sub>4</sub>. The reversal in the MSA selectivity at temperatures above 140 °C may be due to the progressively more rapid oxidation of MSA to CH<sub>3</sub>OSO<sub>3</sub>H by either SO<sub>3</sub> or O<sub>2</sub>.

#### 4. Conclusion

We have demonstrated a catalytic approach for the direct, liquid-phase sulfonation of methane with SO<sub>3</sub> in the presence of molecular O<sub>2</sub>. The most effective catalysts are

Hg salts, of which Hg(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> exhibits the highest activity and selectivity with a turn over number of 118. RhCl<sub>3</sub> though less effective than Hg salts will also catalyze the reaction. It is proposed that the sulfonation of CH<sub>4</sub> is initiated by electrophilic attack of CH<sub>4</sub> by Hg(II). The methylide thus formed then reacts with SO<sub>3</sub> to form MSA and or with H<sub>2</sub>SO<sub>4</sub> to form CH<sub>3</sub>OSO<sub>3</sub>H. Both processes reduce Hg(II) to Hg(I), and the latter species is then reoxidized by O<sub>2</sub>.

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