Direct Sulfonation of Methane to Methanesulfonic Acid with SO_2 Using Ca Salts as Promoters

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Selective catalytic functionalization of methane to value-added products is a subject of considerable contemporary interest.[1] While many authors have investigated the oxidation and oxidative carbonylation of methane,[2] 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] 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. There, therefore, is an incentive to identify a direct route for methane sulfonation with SO_3 or SO_2. Sen and co-workers[5] and more, recently, we[6] have shown that $K_2S_2O_8$ can be used as a free radical initiator to sulfonate methane with SO_3 in fuming sulfuric acid. The same approach, however, does not work if SO_2 and O_2 are used instead of SO_3. 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.[7] The question therefore arises as to whether $K_2S_2O_8$ might not be used as an effective source of oxygen for the sulfonation of methane with SO_2, since Fujiwara and co-workers have shown that $CaCl_2$ can be employed as an initiator for the carbonylation of methane in trifluoroacetic acid in the presence of $K_2S_2O_8$.[8] In this communication, we show that methane will undergo liquid-phase sulfonation to MSA with SO_2 in triflic acid, with $K_2S_2O_8$ serving as the oxidant and Ca salts as the promoter. To the best of our knowledge, this is the first example of the liquid-phase sulfonation of methane utilizing SO_2 as the sulfating agent.

In a typical reaction, CH_4 and SO_2 were reacted in triflic acid in a high-pressure, glass-lined autoclave.[9] $K_2S_2O_8$ and a catalytic amount of a Ca salt (or salts of other metals) were added to the liquid phase. Reactions were carried out for 10 h, and the MSA thus formed was identified and quantified by ^1H NMR.[6] Since SO_2 is the limiting reagent, conversions are reported on the basis of SO_2 and defined as the ratio of the moles of SO_2 converted to MSA to total moles of SO_2 taken initially. No other byproducts were detected.

Table 1 shows the effect of different promoters on the SO_2 conversion to MSA after 10 h. Almost no MSA is detected in the absence of a promoter. The chloride salts of K, Mg, Ba, and Pd are only minimally effective in promoting the formation of MSA, as compared to $CaCl_2$ (Table 1, entries 1−6). The anion associated with Ca also affects the conversion of SO_2 to MSA (Table 1, entries 7−14). CaF_2 is completely inactive, and $CaBr_2$ and CaI_2 are significantly less effective than $CaCl_2$. $Ca(OCl)_2$ and $Ca(CF_3COO)_2$ are moderately effective, but $Ca(CH_3COO)_2$ and $CaSO_4$ are completely inactive. While CaO_2 is an active promoter, only 8% of the SO_2 is converted to MSA.

The use of HCl together with CaO_2 increased the conversion of SO_2 to MSA. A maximum SO_2 conversion to MSA of 14% was achieved when the ratio of HCl to CaO_2 was increased to 2.5. When KCl was used in combination with CaO_2, only a 7% conversion of SO_2 to MSA was observed. On the other hand, addition of approximately 2.5 psig Cl_2 gas into the system together with CaO_2 resulted in a maximum 15% SO_2 conversion to MSA (Table 1, entry 19).

Table 2 shows the effects of reaction conditions on the conversion of SO_2 to MSA after 10 h of reaction time. The conversion increased from 0 to 14% when the amount of $CaCl_2$ in the reaction mixture was raised from 0 to 0.6 mmol. However, a further increase in the amount of $CaCl_2$ resulted in a decrease in the conversion to MSA. With 0.6 mmol $CaCl_2$ when the reaction was performed for 26 h, 22% SO_2 conversion to MSA was observed. On the basis of $K_2S_2O_8$, the conversion of SO_2 to MSA was 58% (Table 2, entries 1−6).

The reaction rate also depends on the amount of $K_2S_2O_8$ in the reaction mixture (Table 2, entries 7−10). Increasing the amount of $K_2S_2O_8$ from 0 to 5 mmol, increased the conversion of SO_2 to MSA from 0 to 14%, but increasing the amount of oxidant further

Table 1. Effect of different promoters on the rate of sulfonation of methane[a]

entry	promoter	promoter, mmol	MSA, mmol	% conv. of SO_2 to MSA	entry	promoter	promoter, mmol	MSA, mmol	% conv. of SO_2 to MSA
1	None	0	tr	tr.	10	$Ca(CF_3COO)_2$	0.6	0.26	2
2	KCl	0.6	0.13	1	11	CaI_2	0.6	0.4	3
3	$MgCl_2$	0.7	0.4	3	12	$CaBr_2$	0.6	0.66	5
4	$BaCl_2$	0.7	0.26	2	13	$CaSO_4$	0.7	0	0
5	$PdCl_2$	0.5	0.26	2	14	CaO_2	0.6	1.05	8
6	$CaCl_2$	0.6	1.84	14	15	CaO_2/HCl[b]	0.6	1.44	11
7	$Ca(OCl)_2$	0.6	0.52	4	16	CaO_2/HCl[c]	0.6	1.71	13
8	$Ca(CH_3COO)_2$	0.7	0	0	17	CaO_2/HCl[d]	0.6	1.84	14
9	CaF_2	0.6	0	0	18	CaO_2/KCl[e]	0.6	0.72	7
					19	CaO_2/Cl_2	0.6	1.97	15

[a] Reaction conditions: methane, 1000 psig (268 mmol); SO_2, 35 psig (13.14 mmol); molar ratio of methane to SO_2, 20.4; $K_2S_2O_8$, 5 mmol; triflic acid, 5 mL; time, 10 h; temperature, 65 °C. [b] Molar ratio of HCl to CaO_2, 1. [c] Molar ratio of HCl to CaO_2, 2. [d] Molar ratio of HCl to CaO_2, 2.5. [e] Molar ratio of KCl to CaO_2, 1. [f] Molar ratio of Cl_2 to CaO_2, 3.

Table 2. Effect of Reaction Conditions on the Sulfonation of Methane to MSA[a]

entry	CH₄ psig	SO₂ psig	K₂S₂O₈ mmol	CaCl₂ mmol	T °C	MSA mmol	% conv. of SO₂ to MSA	entry	CH₄ psig	SO₂ psig	K₂S₂O₈ mmol	CaCl₂ mmol	T °C	MSA mmol	% conv. of SO₂ to MSA
1	1000	35	5	0	65	tr	tr.	13	1000	35	5	0.6	75	1.57	12
2	1000	35	5	0.4	65	0.79	6	14	1000	35	5	0.6	85	1.18	9
3	1000	35	5	0.6	65	1.84	14	15[c]	200	35	5	0.6	65	0.92	7
4[b]	1000	35	5	0.6	65	2.89	22	16	600	35	5	0.6	65	0.26	2
5	1000	35	5	0.9	65	1.57	12	17	800	35	5	0.6	65	0.78	6
6	1000	35	5	1.8	65	1.18	9	18	1200	35	5	0.6	65	2.1	16
7	1000	35	0	0.6	65	0	0	19	1200	0	5	0.6	65	0	0
8	1000	35	1.9	0.6	65	0.39	3	20	1000	10	5	0.6	65	0.53	4
9	1000	35	3.7	0.6	65	1.314	10	21	1000	20	5	0.6	65	1.18	9
10	1000	35	6.3	0.6	65	0.91	7	22	1000	25	5	0.6	65	1.57	12
11	1000	35	5	0.6	45	tr	tr.	23	1000	30	5	0.6	65	1.84	14
12	1000	35	5	0.6	55	0.79	6								

[a] Reaction conditions: time, 10 h; solvent, triflic acid, 5 mL. [b] Time, 26 h. [c] Time, 72 h.

resulted in a decrease in MSA formation and the detection of a small amount of methytriflate. The observed decrease in the yield of MSA above an initial K₂S₂O₈ loading of 5 mmol is possibly due to the release of O₂, which, as discussed below, would inhibit the reaction.

The extent of SO₂ conversion observed in 10 h increased with increasing temperature up to 65 °C. However, a decrease in the conversion to MSA was observed for temperatures above 65 °C (Table 2, entries 11−14).

The conversion of SO₂ to MSA increased from 2 to 14% after 10 h of reaction when the methane pressure was increased from 600 to 1000 psig, but reached a plateau at 1000 psig. The reaction proceeds well even with 200-psig methane pressure. Thus, 7% conversion of SO₂ to MSA was observed after 72 h (Table 2, entries 15−18).

The reaction rate is also a function of SO₂ partial pressure. No MSA was detected in the absence of SO₂. This confirms that the source of SO₂ is neither K₂S₂O₈ nor the solvent triflic acid. At a SO₂ pressure of 10 psig, only 4% conversion to MSA was achieved. However, at 25 psig, a 12% conversion was achieved and at 30−35 psig, a 14% conversion was obtained (Table 2, entries 19−23).

Solvent composition had a marked influence on the rate of MSA formation. For the typical reaction conditions, a 2% conversion of SO₂ to MSA was found as well, using H₂SO₄ as the solvent.[9] However, in trifluoroacetic acid, 4% conversion of SO₂ to MSA was attained, and in triflic acid the conversion rose to 14%.

The mechanism of MSA formation from CH₄ and SO₂ is not known; however, it is reasonable to propose that the reaction involves free radical processes, inasmuch as it was observed that O₂ inhibits MSA formation. At least three possible initiators can be identified, each of which could react with CH₄ to produce CH₃• radicals. These include SO₄⁻• radical anions, formed via the decomposition of K₂S₂O₈, OH• radicals, produced by the decomposition of H₂O₂ produced in situ via the reaction of K₂S₂O₈ and the acid solvent, and Cl• radicals, produced via the oxidation of Cl⁻ anions. Only OH• and Cl• radicals are thought to play a significant role in the initiation process, since Table 1 shows that, in the absence of CaCl₂ or a mixture of CaO₂ and HCl, no MSA is formed. The results presented in Table 1 also suggest that Ca²⁺ cations are more effective than other divalent cations in promoting in situ formation of H₂O₂ and its subsequent decomposition to form OH• radicals. The CH₃• radicals once formed could react subsequently with SO₂, K₂S₂O₈, and methane to form MSA as suggested by Ishii and co-workers in the sulfonation of adamantane.[7]

The reason for the observed decrease in the conversion of SO₂ to MSA when more than 0.9 mmol of CaCl₂ is used in the synthesis mixture is not understood. Since the solubility of CaCl₂ in triflic acid is limited, a plateau in the conversion level should have been observed. The observed lowering in the conversion to MSA when

more than 6.3 mmol of K₂S₂O₈ is used can be attributed to the high rate of formation of O₂, which can act as a free radical scavenger,[5] thereby inhibiting the formation of MSA. This interpretation is consistent with the failure to observe any MSA when the reaction was carried out with 2-atm O₂ pressure in the autoclave.

In conclusion, we have demonstrated a synthetic approach for the direct, liquid-phase sulfonation of methane with SO₂. Under the best reaction conditions, 22% conversion of SO₂ to MSA was achieved after 26 h of reaction. For this case, 58% of the K₂S₂O₈ was consumed. Efforts are now in progress to develop a catalytic process scheme to sulfonate methane with SO₂ in which molecular O₂ is used as the oxygen source instead of K₂S₂O₈.

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(9) In a 100-mL glass-lined Parr autoclave, 5 mmol (1.4 g) K₂S₂O₈, 0.6 mmol (0.07 g) CaCl₂, and 5 mL of triflic acid were charged together with a small Teflon coated magnetic stir bar. The reactor was then purged with N₂ to expel the air out of the system. It was then pressurized first with 35 psig SO₂ (13.14 mmol) and then finally with 1000 psig methane (268 mmol) from the adjacent connecting cylinders. The reactor was then heated to 65 °C under stirring and kept at that temperature for 10 h. After the stipulated period of time, the reactor was quenched with ice and opened to collect the reaction mixture. The mixture then added slowly to 0.6 g of water and then taken for ¹H NMR analysis. D₂O and methanol was used in a capillary as the lock references. The corresponding chemical shifts for MSA were 2.78−3.02 ppm, depending on the concentration of MSA in the mixture.

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