Sulfonation of Methane

Direct Liquid-Phase Sulfonation of Methane to Methanesulfonic Acid by SO_3 in the Presence of a Metal Peroxide**

*Sudip Mukhopadhyay and Alexis T. Bell**

Selective functionalization of methane to value-added products is a significant contemporary challenge.[1] Methane is a very unreactive molecule, as demonstrated by its high C–H bond strength ($438.8\,kJ\,mol^{-1}$), high ionization potential (12.5 eV), low proton affinity (4.4 eV), and low acidity ($pK_a = 48$). 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] Sen and co-workers,[4] and more recently we,[5] 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.[6] However, even with a methane pressure of 1000 psig (6.89 MPa), methane conversions to methanesulfonic acid (MSA) of only 3 to 6 % could be achieved.[4,5] This together with difficulties associated with the separation of the highly soluble potassium salts from the reaction mixture have motivated the search for a more efficient process. 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 how to sulfonate methane under low to moderate methane pressure. Herein, we show that methane will undergo liquid-phase sulfonation with 30 wt % SO_3 in sulfuric acid to form MSA, using metal peroxides as free-radical initiators. To the best of our knowledge, this is the first example of using metal peroxides in the liquid-phase at slightly above atmospheric pressure and room temperature to activate methane.

In a typical reaction CH_4 and SO_3 were allowed to react in fuming sulfuric acid in a high-pressure, glass-lined autoclave.[8] A small amount of metal peroxide was added to the liquid phase. Reactions were carried out for 5 h, and the resulting MSA was identified and quantified by ^1H NMR spectroscopy.[5]

Calcium peroxide is the best initiator for the reaction conditions used (Table 1, entry 7). The peroxides of strontium and lead are only minimally effective in promoting the sulfonation of methane (Table 1, entries 1 and 2), as compared to calcium peroxide. On the other hand, peroxides of Na, Li, Ba, and Mg are moderately effective (entries 3–6).

Table 1: Effect of different metal peroxides on the conversion of SO_3 to MSA.[a]

Entry	Metal peroxide	Amount [mmol]	% Conv. of SO_3 to MSA
1	strontium peroxide	0.212	8
2	lead peroxide	0.212	16
3	sodium peroxide	0.212	24
4	lithium peroxide	0.212	29
5	barium peroxide	0.212	30
6	magnesium peroxide	0.25	34
7	calcium peroxide	0.2	43

[a] Reaction conditions unless otherwise stated: methane: 650 psig; SO_3: 30 wt%, 1.7 g; molar ratio of methane to SO_3: 8.4:1; fuming sulfuric acid: 5.67 g; time: 5 h; temperature: 65 °C.

Table 2 shows the effects of varying the reaction conditions on the conversion of SO_3 to MSA. By using BaO_2 as the initiator, the conversion of SO_3 to MSA increased from 2 to 48 % when the methane pressure was increased from 50 to 1000 psig (Table 2, entries 1–5). The reaction rate also depends on the initial SO_3 concentration. With an increase in SO_3 concentration the MSA conversion increased initially; however, above an initial concentration of 42 %, the conversion of SO_3 to MSA decreased due to the formation of methanedisulfonic acid and methane bisulfate (Table 2, entries 6–8). The conversion increased when the amount of barium peroxides in the reaction mixture was raised from 0 to 0.6 mmol. However, a further increase in the amount of metal peroxide resulted in a decrease in the SO_3 conversion (Table 2, entries 9–13).

The conversion of SO_3 to MSA observed after 5 h increased with increasing temperature up to 70 °C. However, a decrease in the conversion to MSA was observed for temperatures greater than 70 °C (Table 2, entries 14–18).

Table 2: Effect of reaction conditions on the conversion of SO_3 to MSA.[a]

Entry	CH_4 [psig]	SO_3 [wt %]	Metal peroxide M	Metal peroxide amount [mmol]	*t* [h]	*T* [°C]	Conv. of SO_3 to MSA [%]
1	50	30	Ba	0.212	5	65	2
2	200	30	Ba	0.212	5	65	11
3	300	30	Ba	0.212	5	65	24
4	650	30	Ba	0.212	5	65	30
5	1000	30	Ba	0.212	5	65	48
6	650	21	Ba	0.212	5	65	40
7	650	42	Ba	0.212	5	65	42
8	650	56	Ba	0.212	5	65	22
9	650	30	Ba	0.0	5	65	0
10	650	30	Ba	0.118	5	65	25
11	650	30	Ba	0.414	5	65	70
12	650	30	Ba	0.6	5	65	74
13	650	30	Ba	0.8	5	65	61
14	650	30	Ba	0.212	5	35	2
15	650	30	Ba	0.212	5	45	12
16	650	30	Ba	0.212	5	70	34
17	650	30	Ba	0.212	5	85	29
18	650	30	Ba	0.212	5	100	14
19	650	30	Ca	0.41	5	65	89
20	650	30	Ca	0.6	5	65	91
21	30	46	Ca	0.42	36	70	10

[a] Reaction conditions unless otherwise stated: time: 5 h; solvent: fuming sulfuric acid (30 wt% SO_3), 5.67 g.

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Under the best reaction conditions with 650 psig methane and using 0.41 to 0.6 mmol of CaO_2 as the radical initiator, a 89 to 91 % conversion of SO_3 to MSA was observed (Table 2, entries 19 and 20). The methane conversion to MSA under these conditions was 11 %. Remarkably, 18 % of the methane, and correspondingly 10 % of the SO_3, was converted to MSA at 70 °C with a methane pressure of only 30 psig using CaO_2 as the initiator (Table 2, entry 21).

The acidity of the solvent media has a marked influence on the rate of MSA formation (Table 3). Thus, in trifluoroacetic acid, a 19 % conversion of SO_3 to MSA was attained, whereas in sulfuric acid the conversion rose to 89 %. Triflic acid was not as effective as sulfuric acid due possibly to the consumption of SO_3 to form polysulfonic acids of the general formula $CF_3(SO_3)_nH$ by the reaction of triflic acid and SO_3.

Table 3: Effect of solvent media on the conversion of SO_3 to MSA[a]

Solvent	*t* [h]	Conv. of SO_3 to MSA [%]
CF_3COOH	10	19
H_2SO_4	5	89
CF_3SO_3H	5	53

[a] Reaction conditions unless otherwise stated: methane: 650 psig; CaO_2: 0.4 mmol; SO_3: 1.7 g; molar ratio of methane to SO_3: 8.4:1; fuming sulfuric acid: 5.67 g; time: 5 h; temperature: 65 °C.

The mechanism by which CH_4 reacts with SO_3 to form MSA is not understood; however, it is reasonable to suggest that the reaction proceeds by a mechanism inovolving free radicals, since the presence of molecular oxygen inhibits the formation of MSA. It is conceivable that methane activation involves Ca^{+2} ions and H_2O_2 generated by the reaction of CaO_2 and H_2SO_4. Once $CH_3^{\bullet}$ radicals are generated they can react with SO_3 to form $CH_3SO_3^{\bullet}$ radicals, which can in turn, abstract hydrogen from methane to form MSA.[5] To assess whether H_2O_2 generated by the reaction of CaO_2 and H_2SO_4 might be solely responsible for the activation of CH_4, an experiment was conducted in which 0.6 mmol of H_2O_2 was used as the initiator.[9] A SO_3 conversion to MSA of 9 % was obtained in this experiment. If $CaCl_2$ (0.6 mmol) was added to the synthesis mixture containing H_2O_2, while keeping the amount of free SO_3 the same, the conversion of SO_3 to MSA rose to 16 %. This is considerably lower than the 72 % conversion of SO_3 to MSA observed when 0.6 mmol of CaO_2 was used in place of $CaCl_2$ and H_2O_2, which suggests that CaO_2 has a unique role in the activation of methane.

The observed lowering in the conversion of SO_3 to MSA (Table 2, entries 13 and 14) when more than 0.6 mmol of metal peroxide was used in the synthesis mixture can be attributed to the high rate of decomposition of H_2O_2 to O_2, which can act as a free radical scavenger,[4] thereby inhibiting the formation of MSA. This interpretation is consistent with the failure to observe any MSA when the reaction was carried out in the presence of 30 psig of O_2.

The observation of a maximum in the conversion of SO_3 to MSA with increasing temperature, such as that seen in entries 15–18 in Table 2, can be interpreted as follows: For temperatures lower than that for the best conversion, increasing the temperature accelerates the kinetics of MSA formation. When temperature is raised above that for the maximum conversion of SO_3 to MSA, a rapid decomposition of CaO_2 or H_2O_2 generated in situ occurs and the O_2 thus released inhibits the free-radical processes leading to MSA.

In conclusion, we have demonstrated a synthetic approach for the direct, liquid-phase sulfonation of methane with 30 wt % SO_3 in sulfuric acid. Under the best reaction conditions, 91 % conversion of SO_3 to MSA was achieved. The respective methane conversion to MSA was 11–18 %. CaO_2 is an effective radical initiator even at low reaction temperatures and CH_4 pressures.

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[8] In a 100-mL glass-lined Parr autoclave, CaO_2 (0.6 mmol), and SO_3 (1.7 g) and H_2SO_4 (3.99 g) were charged, together with a small teflon-coated magnetic stirring bar. The reactor was purged with N_2 to expel the air out of the system and sealed. The autoclave was then pressurized with 650 psig methane and heated to 70 °C for 5 h while stirred. After the stipulated period of time, the reactor was quenched with ice and opened to collect the reaction mixture. The reaction mixture was then added slowly to water (0.5 g) and analyzed by ^1H NMR spectroscopy. D_2O and methanol, contained in a capillary placed adjacent to the NMR tube containing the sample, were used as the lock and references. The corresponding

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chemical shift for MSA was $\delta = 2.82$ ppm to 3.02 ppm, depending on the concentration of MSA in the mixture.

[9] For the H_2O_2 (0.6 mmol) initiated reaction, 50% H_2O_2 (0.04 g; Aldrich) and liquid SO_3 (0.1 g; Aldrich) were added to fuming sulfuric acid (5.67 g, 30% SO_3). For the $CaCl_2$ (0.6 mmol) and H_2O_2 (0.6 mmol) initiated reaction, $CaCl_2$ (0.067 g), 50% H_2O_2 (0.04 g; Aldrich), and liquid SO_3 (0.1 g; Aldrich) were used with fuming sulfuric acid (5.67 g). For an accurate comparison, in the CaO_2 (0.6 mmol) initiated reaction mixture, water (0.02 g) and SO_3 (0.1 g) were also added to fuming sulfuric acid (5.67 g).

Anti-Bredt-Brückenkopfolefine

P. Roach, R. Warmuth* ____ **3147 – 3150**

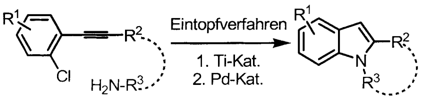
Die Raumtemperatur-Stabilisierung von Bicyclo[2.2.2]oct-1-en und Bicyclo-[3.2.1]oct-1-en

In Schutzhaft: Bemerkenswert stabil bei 60 °C ist das hochgespannte Anti-Bredt-Brückenkopfolefin Bicyclo[2.2.2]oct-1-en (**1**), wenn es photochemisch im Inneren des Hemicarceranden **2** erzeugt wird. Der Wirt verhindert nicht nur die Dimerisierung von **1**, sondern verlangsamt auch die intramolekulare Retro-Diels-Alder-Reaktion des Gastes um mehrere Größenordnungen.

Katalytische Indolsynthese

H. Siebeneicher, I. Bytschkov, S. Doye* ____ **3151 – 3153**

Ein flexibles katalytisches Eintopfverfahren zur Synthese von Indolen



Durch Kombination einer $[Cp_2TiMe_2]$-katalysierten Hydroaminierung von Alkinen mit einer bislang unbekannten Pd-katalysierten N-Arylierung von Iminen wurde eine breit anwendbare Methode zur Synthese von Indolen erhalten, bei der gleich zwei C-N-Bindungen in einem Eintopfverfahren geknüpft werden (siehe Schema).

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Entschuldigung

In der Zuschrift „Direct Liquid-Phase Sulfonation of Methane to Methanesulfonic Acid by SO_3 in the Presence of a Metal Peroxide“ von S. Mukhopadhyay und A. T. Bell (*Angew. Chem.* **2003**, *115*, 1049 – 1051; *Angew. Chem. Int. Ed.* **2003**, *42*, 1019 – 1021) haben die Autoren ihren thematisch verwandten, aber unabhängigen Beitrag „Direct Sulfonation of Methane to Methanesulfonic Acid with SO_2 Using Ca Salts as Promoters“ (S. Mukhopadhyay und A. T. Bell, *J. Am. Chem. Soc.* **2003**, *125*, 4406 – 4407) nicht zitiert (und umgekehrt). Die Autoren entschuldigen sich für dieses Versehen.