Novel Methane Activation by Sulfur Dioxide and Molecular Oxygen via Trifluoroacetylsulfuric Acid

Supporting Information

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Table of Contents

1. Experimental Results

2. NMR analysis

1. Experimental Results

1.1. Table S1. Methane sulfonation by using SO_2 and O_2.[a]

Entry	Temperature (˚C)	H_2O_2 (mol %)	MSA (yield %)[b]	Conv. (%, CH_4)
1	50	15	67.6	15.0
2	50	20	74.3	16.5
3	60	15	73.1	12.9
4	60	20	75.2	18.5

Methane sulfonation was successfully conducted with SO_2 and O_2 resulting in high yields around 75 % at low temperatures. [a]Reaction conditions: solvent, TFAOH (0.3 mL) and TFAA (0.3 mL); H_2O_2 (15—20 mol% based on SO_2, 0.11—0.15 mmol); SO_2 (40 psi, 0.73 mmol); O_2 (30 psi, 0.12 mmol); CH_4 (200 psi, 3—3.3 mmol); time (18 h). [b]The percent yield of MSA was calculated based on SO_2.

1.2. Table S2. Time study.[a]

Entry	Time (h)	MSA (yield %)[b]	Conv. (%, CH_4)
1	2	36.6	17.0
2	4	37.9	17.7
3	6	38.7	18.0
4	8	40.0	18.6
5	18	40.1	18.7

Time study was conducted for the methane sulfonation. [a]Reaction conditions: Solvent, TFAA (0.6 mL); H_2O_2 (21 mol% based on SO_2, 0.27 mmol); SO_2 (80 psi, 1.3 mmol); O_2 (50 psi, 0.2 mmol); CH_4 (200 psi, 2.8 mmol); temperature (50 °C). [b]The percent yield of MSA was calculated based on SO_2.

1.3. Table S3. Optimal ratio between sulfur dioxide and molecular oxygen during methane sulfonation conducted with 0.27 mmol trifluoroperacetic acid.[a]

Entry	**1**	**2**	**3**
	0.73 mmol SO_2	**1.3 mmol SO_2**	**1.9 mmol SO_2**
No O_2	9.7 %	5.6 %	3.4 %
20 psi O_2 (0.07 mmol)	38 %	19 %	11 %
30 psi O_2 (0.12 mmol)	54%	27 %	18 %
50 psi O_2 (0.20 mmol)	64 %	40 %	26 %
80 psi O_2 (0.36 mmol)	31 %	46 %	46 %

Under various concentrations of SO_2 and O_2, the optimal ratio between SO_2 and O_2 exhibiting a highest MSA percent yield was determined when 0.27 mmol of TFAO—OH was employed (SO_2/O_2=3.7). MSA yield was calculated based on SO_2 added. [a]Reaction conditions: solvent, TFAOH (0.3 mL) and TFAA (0.3 mL); H_2O_2 (0.27 mmol); CH_4 (200 psi, 3 mmol); temperature (50 °C); time (18 h).

1.4. Table S4. Effects of anhydrous condition with the use of TFAA.[a]

Entry	H_2O_2 (mol %)	Reaction solution	MSA (yield %)[c]
1	20	Absence of TFAA (TFAOH only as a solvent)	32.8
2[b]	20	Application of additional 2 μL of water	6.8

The reaction was conducted 1) without TFAA in the reaction mixture after the addition of H_2O_2, and 2) with additional 2 μL of water in the absence of TFAA to figure out the effects of anhydrous condition in methane sulfonation. [a]Reaction conditions: solvent, TFAA (0.122 mL); H_2O_2 (20 mol% based on SO_2, 0.15 mmol); SO_2 (40 psi, 0.73 mmol); O_2 (30 psi, 0.12 mmol); CH_4 (200 psi, 3 mmol); temperature (50 °C); time (18 h); [b]Additional water was applied to the reaction mixture (0.002 mL, 0.11 mmol). [c]The percent yield of MSA was calculated based on SO_2.

1.5. Table S5. Effects of higher pressure in methane sulfonation.[a]

Entry	H_2O_2 (mol %)	Final pressure (psi)	MSA (yield %)[b]	Conv. (%, CH_4)
1	15	58 psi with CH_4	33.0	45.2
2	20	59 psi with CH_4	33.1	46.2
3	15	400 psi with N_2	48.7	56.0
4	20	420 psi with N_2	47.3	54.5

By adding N_2 gas after charging with SO_2, O_2, and CH_4, the sulfonation of methane was conducted under higher pressure. [a]Reaction conditions: solvent, TFAOH (0.3 mL) and TFAA (0.3 mL); H_2O_2 (15—20 mol% based on SO_2, 0.11—0.15 mmol); SO_2 (40 psi, 0.73 mmol); O_2 (30 psi, 0.1 mmol for entry 1—2; 0.04 mmol for entry 3—4); CH_4 (0.5—0.6 mmol); N_2 (~ 400 psi); temperature (50 °C); time (18 h). [b]The percent yield of MSA was calculated based on SO_2.

1.6. Table S6. High methane conversion yields.[a]

Entry	H_2O_2 (mol %)	N_2 (psi)	MSA (yield %)[b]	Conv. (%, CH_4)
1	15	230	23.2	93.6
2	20	210	24.5	94.6

With the help of additional N_2, methane conversion yields increased up to 95% when CH_4 was employed as a limiting reagent. [a]Reaction conditions: solvent, TFAOH (0.3 mL) and TFAA (0.3 mL); H_2O_2 (20 mol% based on SO_2, 0.15 mmol); SO_2 (40 psi, 0.73mmol); O_2 (30 psi, 0.04mmol); CH_4 (0.18—0.19mmol); N_2 (~ 230 psi); temperature (50 °C); time (18 h). [b]The percent yield of MSA was calculated based on SO_2.

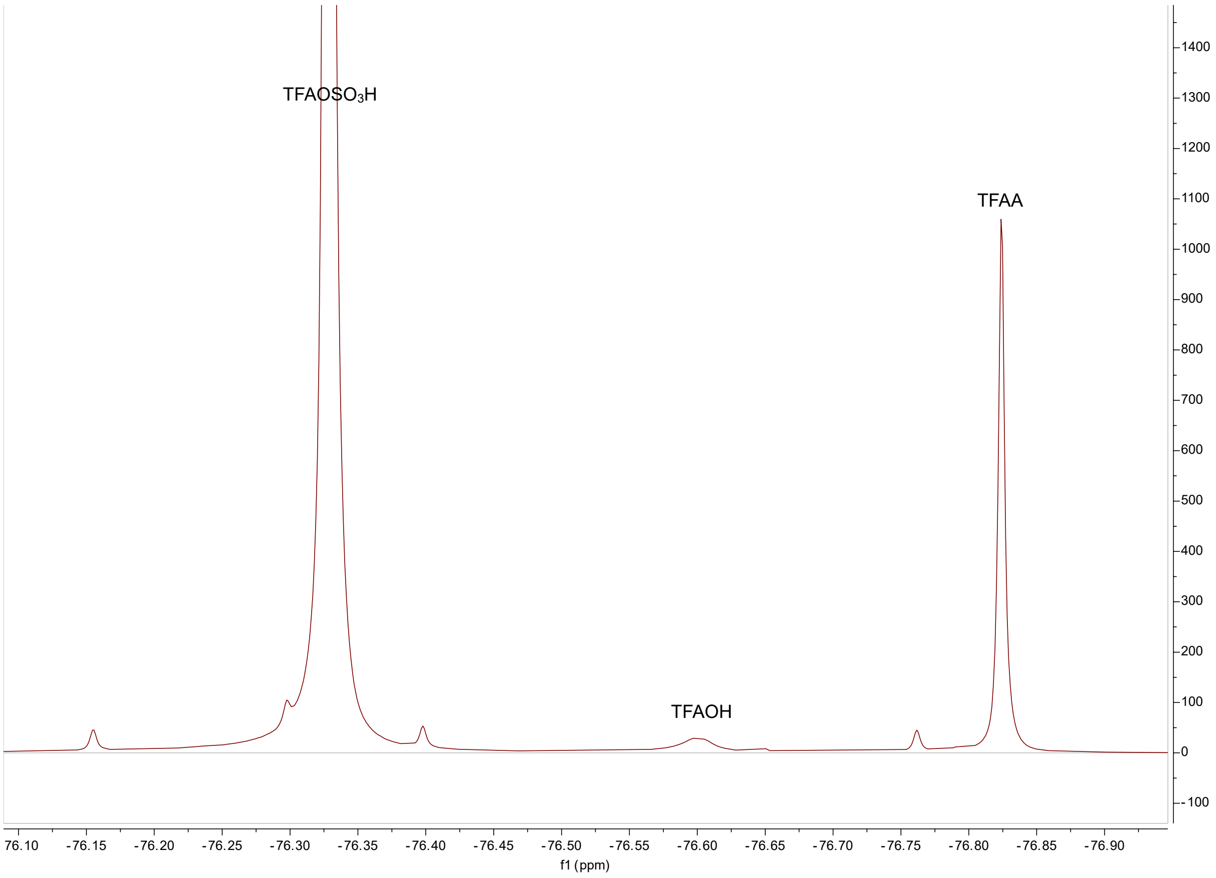
1.7. Table S7. Confirmation of free radical mechanism of the methane sulfonation using radical scavenger.[a]

Entry	H_2O_2 (mol %)	Radical Scavenger	MSA (yield %)[b]	Conv. (%, CH_4)
1	20	-	74.3	16.5
2	-	-	0	0
3	20	20 mol% TEMPO	3.3	0.7
4	20	20 mol% BHT	0	0

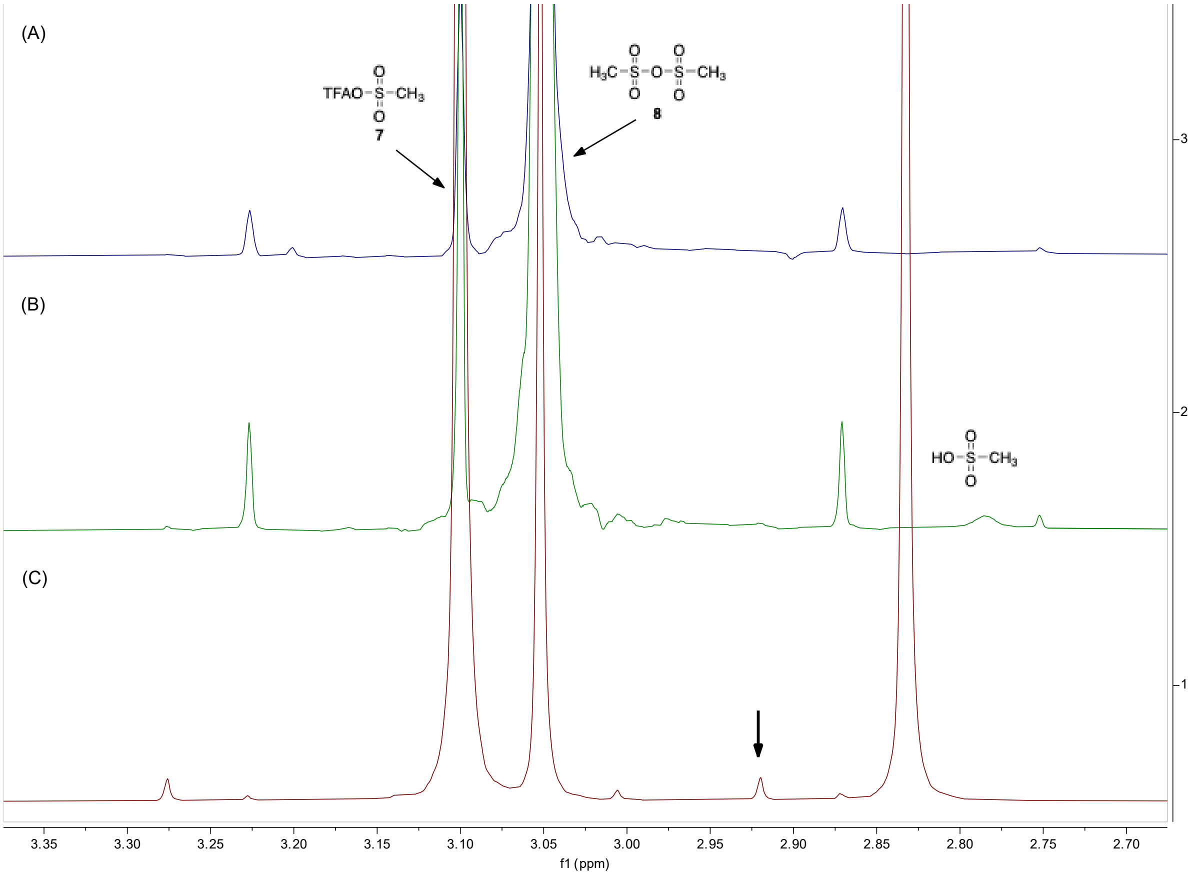
[a]Reaction conditions: solvent, TFAOH (0.3 mL) and TFAA (0.3 mL); H_2O_2 (20 mol% based on SO_2, 0.15 mmol); SO_2 (40 psi, 0.73 mmol); O_2 (30 psi, 0.12 mmol); CH_4 (200 psi, 3—3.3 mmol); time (18 h). [b]The percent yield of MSA was calculated based on SO_2.

2. NMR analysis

2.1. ^{19}F NMR spectrum: (470 MHz, TFAD): Generation of trifluoroacetylsulfuric acid ($TFAOSO_3H$).



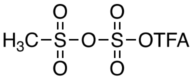
After the reaction mixture containing TFAA, TFAOH, H_2O_2, SO_2 and O_2 was stirred at 50 °C for 16 h, $TFAOSO_3H$ was extracted with DCM-d_2 for NMR analysis. TFAOH, TFAA and H_2O diluted in DCM-d_2 were added separately to distinguish the observed peaks from each other. Depending on the amount and the ratio of TFAOH and $TFAOSO_3H$, TFAOH and $TFAOSO_3H$ peaks shifted, however, the patter between $TFAOSO_3H$, TFAOH, and TFAA remained the same.



2.2. ^1H NMR spectrum (400 MHz, TFAD): Unknown peak at 2.92 ppm.

Reaction conditions: (A) When methanesulfonic anhydride (**8**) was added to the solution of 0.3 mL TFAD and 0.2 mL TFAA, the formation of **7** was detected to exhibit **7** and **8**. (B) When 3 μL H_2O_2 was added to the solution of (A), no peak was observed at around 2.92 ppm. (C) When 10 μL $TFAOSO_3H$ was added to the solution of (A), a small peak around 2.92 ppm was detected.

In Figure 4, we identified **7, 8**, and MSA, however small peaks at 3.18 and 2.82 ppm were not elucidated unambiguously. However, we conducted the experiments using unlabeled MSAA (**8**) and obtained NMR spectra as shown here. We identified **7** and **8** along with MSA in these solvent systems, and observed a minor peak at 2.92 ppm, which would correspond with the small peaks at 3.18 and 2.82 ppm in the previous experiment and its NMR spectrum. Thus we speculate the peak at 2.92 ppm as one of the methanesulfonic anhydride derivative such as

 $\mathrm{H_3C-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OTFA}$, which was hydrolyzed to provide MSA after work-up.