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Synthesis of methanesulfonyl chloride (MSC) from methane and sulfuryl chloride

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Received (in Cambridge, UK) 5th November 2003, Accepted 18th December 2003

First published as an Advance Article on the web 27th January 2004

Methane is transformed selectively to methanesulfonyl chloride at low temperature by liquid-phase reaction of methane with SO_2Cl_2 in the presence of a free radical initiator and a promoter using 100% H_2SO_4 as the solvent.

Methanesulfonyl chloride (MSC)[1] is a versatile reagent that can be used to introduce mesyl groups ($CH_3SO_2^-$) *via* substitution of hydroxyl and amino groups, and active α-hydrogens. MSC is widely used as an intermediate in the synthesis of photographic chemicals, agrochemicals, and pharmaceutical intermediates, as well as a stabilizer and catalyst. It is also widely known as a curing and chlorinating agent and as a precursor to methanesulfonic acid (MSA).[2] The commercial process for the production of MSC involves the oxidative chlorination of methylmercaptan or dimethyldisulfide in concentrated HCl.[3] Since these starting materials are expensive and toxic, there is an incentive to look for an alternative process. The use of methane, the main component of natural gas, as a starting material is particularly attractive, since methane is an abundant, low-cost carbon feed stock.

In this communication, we show that MSC can be synthesized in high yield by the reaction of methane and sulfuryl chloride, SO_2Cl_2[4] at low temperature (Scheme 1).

In a typical reaction[5] (Scheme 1) methane was reacted with SO_2Cl_2 in 100% H_2SO_4[6] to form MSC in the presence of an initiator in a high-pressure, glass-lined, Parr autoclave. Reactions were carried out for 12 h at 60 °C. ^1H and ^{13}C NMR were used to confirm that MSC is the only liquid-phase product generated from methane in the presence of SO_2Cl_2. No reaction occurred in the absence of methane, indicating that the source of the methyl group in the product is methane. Analysis of the gas phase shows that CH_3Cl was formed as the primary by-product. The other by-products were traces of polychlorinated hydrocarbons.

Fig. 1 shows ^1H and ^{13}C NMR spectra of the reaction product. The ^1H NMR peak at 3.65 ppm and the ^{13}C NMR peak at 52.78 ppm are characteristic of the methyl group in CH_3SO_2Cl. Absence of any other peaks both in the ^1H and ^{13}C NMR indicates that there were no other products formed in the liquid phase.

Conversions are reported on the basis of the limiting reagent, SO_2Cl_2, and defined as the ratio of the moles of SO_2Cl_2 converted to MSC to the moles of SO_2Cl_2 fed initially to the reactor.

$$CH_4 + SO_2Cl_2 \xrightarrow[\substack{60^{o}C,\ 12\ h \\ H_2SO_4}]{\text{Urea-}H_2O_2,\ RhCl_3} CH_3SO_2Cl + HCl$$

Scheme 1 Direct reaction of methane with SO_2Cl_2.

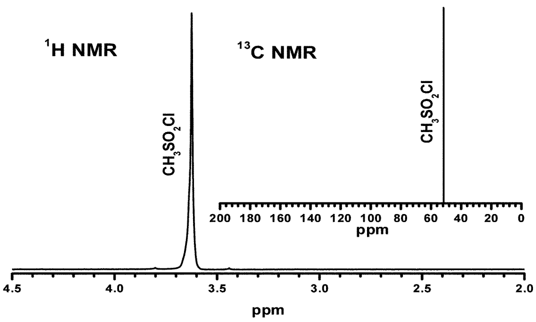

Fig. 1 ^1H and ^{13}C NMR of the reaction mixture.

Table 1 shows the effect of different initiators on the conversion of SO_2Cl_2 to MSC. In the absence of an initiator, no MSC was formed. Each of the initiators used activated methane; however, the highest activity obtained using urea–H_2O_2 in combination with $RhCl_3$. Almost 26% of the SO_2Cl_2 was converted to MSC in this case. The least active initiator was $K_4P_2O_8$. Using this material, only 12% of the SO_2Cl_2 were converted to MSC.

Table 2 shows the effect of different process parameters on the rate of methane sulfonation using urea–H_2O_2 as the initiator and $RhCl_3$ as the promoter. Increasing the CH_4 pressure from 300 to 700 psig increased the conversion of SO_2Cl_2 to MSC from 4 to 26%. However, increasing the amount of SO_2Cl_2 did not affect the conversion of SO_2Cl_2 to MSC. The conversion of SO_2Cl_2 to MSC increased from 14 to 26% when the temperature was raised from 50 to 60 °C. However, at 75 °C, only 18% of SO_2Cl_2 was converted to MSC. The low conversion at this temperature may be due to the evaporation of SO_2Cl_2 from the glass liner and its condensation between the liner and the autoclave walls during the course of the reaction. Consistent with this interpretation, a large quantity of SO_2Cl_2 (bp 68–70 °C) was observed at the bottom of the autoclave after 12 h of reaction.

The reaction requires a highly acidic solvent (see Table 2). When the reaction was carried out in H_2SO_4, the conversion of SO_2 to

Table 1 Effect of different initiators on the MSC synthesis[a]

No.	Initiator	Amount/ mmol	Promoter	MSC/mmol	Conv. of SO_2Cl_2 to MSC (%)
1	$K_4P_2O_8$	0.4	None	0.9	12
2	$K_2S_2O_8$	0.4	None	1.2	16
3	Urea–H_2O_2	0.4	None	1.3	18
4[b]	Urea–H_2O_2	0.4	$RhCl_3$	1.9	26

[a] *Reaction conditions*: methane, 700 psig (193 mmol); SO_2Cl_2, 1 g (7.4 mmol); initiator, 0.4 mmol; molar ratio of methane to SO_2Cl_2, 26; solvent, 100% H_2SO_4, 3 mL; temperature, 60 °C; time, 12 h. [b] $RhCl_3$, 0.1 mmol.

Table 2 Effect of process parameters on the sulfonation reaction[a]

No.	CH_4/psig	SO_2Cl_2/ mmol	T/°C	Solvent	MSC/ mmol	Conv. of SO_2Cl_2 to MSC (%)
1	300	7.4	60	H_2SO_4	0.3	4
2	500	7.4	60	H_2SO_4	0.8	11
3	700	7.4	60	H_2SO_4	1.9	26
4	700	6	60	H_2SO_4	1.5	25
5	700	10	60	H_2SO_4	1.9	26
6	700	7.4	50	H_2SO_4	1.0	14
7	700	7.4	75	H_2SO_4	1.3	18
8	700	7.4	60	MSA[b]	0.6	8
9	700	7.4	60	TFMSA[c]	0.9	28
10	700	7.4	60	SO_2Cl_2	0.4	5

[a] *Reaction conditions*: urea–H_2O_2, 0.4 mmol; $RhCl_3$, 0.1 mmol; time, 12 h; solvent, 3 mL. [b] MSA is methanesulfonic acid. [c] TFMSA is trifluoromethanesulfonic acid.

DOI: 10.1039/b314160h

MSC was 26%, and it was 28% when trifluorormethanesulfonic acid (TFMSA) was used as the solvent. However, only an 8% conversion of SO_2Cl_2 to MSC was achieved in MSA, and in SO_2Cl_2, a 5% conversion of SO_2Cl_2 to MSC is obtained after 12 h of reaction.

In a separate set of reactions MSC was hydrolyzed completely with water to MSA at 50 °C for 2 h.[7] The only by-product was HCl which can be separated easily by distillation. The chemical shift (using D_2O as the NMR solvent) for the methyl group of MSA was 2.97 ppm in the ^{1}H NMR and 39.5 ppm in the ^{13}C NMR.

The synthesis of MSC is believed to proceed *via* a free radical pathway[2] as written in Scheme 2. This scheme is supported by the observation that in the presence of O_2, no MSC is formed. Since O_2 is a well-known free radical scavenger, it is inferred that MSC formation involves free radicals. Further supporting this idea is the observation that in the absence of SO_2Cl_2, C_2H_6 is observed as a result of the coupling of two methyl radicals. The presence of trace amounts of polychlorinated impurities ($<0.5\%$) in the head space of the autoclave strongly suggests the radical initiated chlorination of methane and ethane. The reaction is assumed to start with the abstraction of hydrogen from methane molecules by the initiator species I·, where I· can be $SO_4^{-\cdot}$, $PO_4^{2-\cdot}$, OH·, RhO· or RhOO·. The methyl radical thus formed then reacts with SO_2Cl_2 to form CH_3SO_2Cl and Cl·. Cl· radicals can then abstract hydrogen from methane to generate CH_3· radicals and HCl. Reaction (1) is the initiation step; whereas, reactions (2) and (3) are the propagation steps. Reaction (4) is a radical termination step. Also though not written, two CH_3· radicals can couple to form C_2H_6.

In conclusion, we have developed a highly selective, low-temperature approach for the synthesis of MSC involving the reaction of methane and SO_2Cl_2. MSC is a low boiling liquid (bp 60°/21 mm Hg) that can be isolated readily by distillation from the reaction mixture. The reaction is highly selective, and as much as 26% of the SO_2Cl_2 charged is converted to MSC at 60 °C using sulfuric acid as the solvent. The MSC thus formed can be isolated and hydrolyzed with water to MSA, which is also a valuable product.

ATOFINA Chemicals, Inc., North America, funded this study.

$$CH_4 + I^\bullet \rightarrow CH_3^\bullet + IH \quad (1)$$
$$CH_3^\bullet + SO_2Cl_2 \rightarrow CH_3SO_2Cl + Cl^\bullet \quad (2)$$
$$CH_4 + Cl^\bullet \rightarrow HCl + CH_3^\bullet \quad (3)$$
$$CH_3^\bullet + Cl^\bullet \rightarrow CH_3Cl \quad (4)$$

Scheme 2 Proposed reaction mechanism.

Notes and references

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5 In a 100 mL glass-lined, Parr autoclave reactor, 0.4 mmol initiator, 7.4 mmol SO_2Cl_2 and 3 mL 100% H_2SO_4 were charged together with a small Teflon-coated magnetic stir bar. N_2 was bubbled through the reactor to remove any air from the system. The reactor was pressurized with 700 psig of methane and then heated to 60 °C under stirring for 12 h. After the stipulated period of time, the reactor was cooled to room temperature, vented, and opened to collect the reaction mixture. The mixture was analyzed by ^{1}H and ^{13}C NMR analysis. A mixture of D_2O and H_2O in a capillary was used as the lock and reference. The corresponding ^{1}H chemical shift of the methyl group in MSC was δ 3.6 to 3.75, depending on the concentration of MSC in the mixture.

6 100% H_2SO_4 was prepared in the laboratory by adding SO_3 (Aldrich) to a stock solution of concentrated H_2SO_4 (Aldrich).

7 The synthesis of MSC (bp 60°/21 mm Hg) from methane and SO_2Cl_2 and subsequent hydrolysis to MSA has an advantage over the direct free-radical initiated methane sulfonation with SO_3 in fuming sulfuric acid, since it avoids the difficult distillation of MSA from sulfuric acid. Such distillation must be performed under vacuum, since MSA (bp 167°/10 mm Hg) decomposes to a mixture of $CH_3SO_3CH_3$, SO_2 and H_2O at around 180 °C.