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A Novel Method for the Direct Sulfonation of CH_4 with SO_3 in the Presence of KO_2 and a Promoter

Sudip Mukhopadhyay and Alexis T. Bell*

Department of Chemical Engineering, University of California, Berkeley, California 94720, U.S.A.

Abstract:

Direct sulfonation of methane with SO_3 to methanesulfonic acid (MSA) is accomplished in sulfuric acid in the presence of a small amount of KO_2 as the free radical initiator and a metal chloride. Of the several metal chlorides examined, $RhCl_3$ was found to be the most effective promoter. While KO_2 alone can activate methane, the conversion of SO_3 to MSA increases 2.3-fold when KO_2 and $RhCl_3$ are both present in the reaction mixture. The effects of different process parameters such as temperature, SO_3 concentration, methane pressure, KO_2 concentration, and $RhCl_3$ concentration have been examined on the rate of reaction. The reaction is optimized at a KO_2-to-$RhCl_3$ molar ratio of 3.16. Strongly acidic solvents such as H_2SO_4 or CF_3SO_3H are necessary for the reaction. No MSA was formed when the reaction was carried out in DMSO. A mechanism is proposed to explain the activation of CH_4 to form MSA. A critical part of the sequence is in situ formation of a metal−peroxo species via the reaction of KO_2, acid solvent, and $RhCl_3$.

Introduction

Selective functionalization of methane to value-added products is a subject of considerable contemporary interest.[1,2] Because of favorable thermodynamics, considerable effort has been devoted to the oxidation and oxidative carbonylation of methane.[3] By contrast, the sulfonation of methane has not received as much attention despite its commercial importance.[4] The current commercial process for the synthesis of methanesulfonic acid (MSA) occurs via the chlorine oxidation of methylmercaptan.[5,6] 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. As an alternative it is interesting to consider the direct sulfonation of methane using SO_3 or SO_2 and O_2 as the sulfonating agent.[7] It has been shown[8] that methane can be sulfonated with SO_3[9] in strong acids using a free radical initiator.[10] The free radical initiators used in this reaction are often highly expensive potassium persulfate or phosphate salts or highly reactive metal peroxides which are difficult to handle in case of a bulk production scale. Since aqueous H_2O_2 is only minimally active, it is worth considering alkali superoxides. In this communication, we show that methane will undergo liquid-phase sulfonation with SO_3 in sulfuric acid to form MSA, using KO_2 as free radical initiators in conjunction with $RhCl_3$. To the best of our knowledge, this is the first example of using potassium superoxide in the liquid phase to activate methane.

Results and Discussion

In a typical reaction (see Experimental Section), CH_4 and SO_3 were reacted in fuming sulfuric acid in a high-pressure autoclave. Small amounts of KO_2 and a metal chloride were added to the liquid phase. Reactions were carried out for 18 h at 95 °C, and the MSA thus formed was identified and quantified by ^1H NMR.[8a]

Table 1 shows the effect of different promoters on the rate of methane sulfonation. Notably, using KO_2 as the free radical initiator in the absence of any promoters leads to a 6% conversion of SO_3 to MSA. The presence of promoters such as $PtCl_2$, $PdCl_2$, and $RuCl_3$ has a negative effect on MSA synthesis. On the other hand, $CaCl_2$, $FeCl_3$, and $HgCl_2$ are moderately active as promoters, and $RhCl_3$ is particularly effective under the reaction conditions investigated.

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* Author for correspondence. E-mail: bell@cchem.berkeley.edu. Fax: (510) 642-4778.

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Table 1. **Effect of different promoters on the sulfonation of methane to MSA**[a]

entry	promoters	*t*, h	% conversion of SO_3 to MSA
1	none	18	5
2	$PtCl_2$	20	tr
3	$PdCl_2$	19	0
4	$RuCl_3$	21	2
5	$CaCl_2$	20	8
6	$FeCl_3$	18	9
7	$HgCl_2$	18	10
8	$RhCl_3$	18	14

[a] Reaction conditions unless otherwise stated: solvent, fuming sulfuric acid, 5.67 g; SO_3, 1.7 g (21.25 mmol) methane, 300 psig (84.9 mmol); KO_2, 0.98 mmol; promoters, 0.31 mmol; time, 18 h; temperature, 95 °C

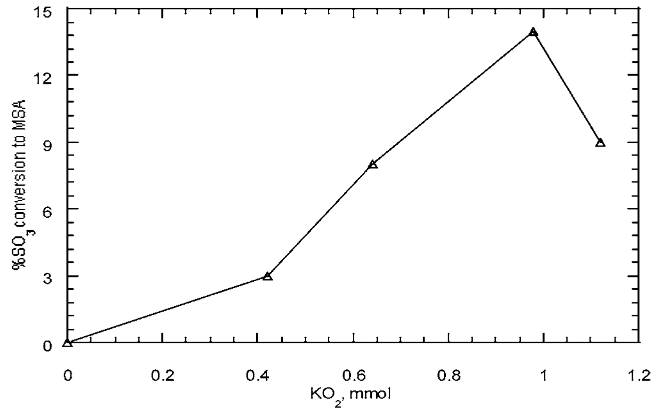

Figure 1. **Effect of KO_2 concentration on the conversion of SO_3 to MSA. *Reaction conditions:* solvent, fuming sulfuric acid, 5.67 g; SO_3, 1.7 g (21.25 mmol) methane, 300 psig (84.9 mmol); KO_2, 0.98 mmol; $RhCl_3$, 0.31 mmol; time, 18 h; temperature, 95 °C.**

The reaction was studied with different amounts of KO_2 but a fixed amount of $RhCl_3$. It is observed in Figure 1 that the conversion of SO_3 to MSA increases when the amount of KO_2 in the reaction mixture is raised from 0 to 0.98 mmol. However, a further increase in the amount of KO_2 results in a decrease in the SO_3 conversion to MSA.

The effect of the amount of $RhCl_3$ added to the reaction mixture is shown in Figure 2. For a constant amount of KO_2, the conversion of SO_3 to MSA increases from 4 to 14% after 18 h as the amount of $RhCl_3$ is increased from 0.08 to 0.31 mmol. However, a further increase in the ratio of KO_2 to $RhCl_3$ is deleterious to the MSA yield. The highest conversion of SO_3 to MSA is obtained with 0.31 mmol $RhCl_3$ in the presence of 0.98 mmol KO_2. Thus, the effective ratio of KO_2 to $RhCl_3$ is 3.16.

Figure 3 shows that the conversion of SO_3 observed after 18 h increases with increasing temperature up to 95 °C. However, a decrease in the conversion to MSA is observed for temperatures higher than 95 °C.

Figure 4 shows the effects of methane pressures on the conversion of SO_3 to MSA. The conversion of SO_3 to MSA increases from 1 to 24% when the methane pressure is increased from 50 to 1000 psig.

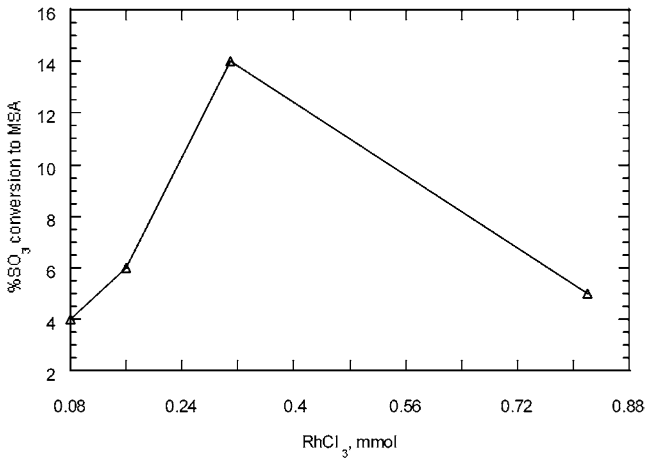

Figure 2. **Effect of $RhCl_3$ amount on the conversion of SO_3 to MSA. *Reaction conditions:* solvent, fuming sulfuric acid, 5.67 g; SO_3, 1.7 g (21.25 mmol) methane, 300 psig (84.9 mmol); KO_2, 0.98 mmol; time, 18 h; temperature, 95 °C.**

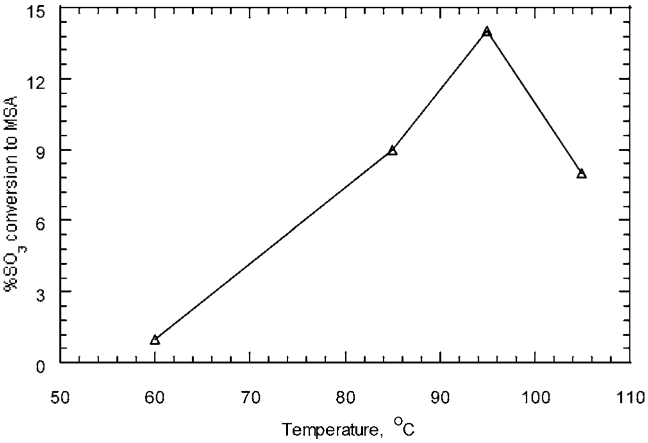

Figure 3. **Effect of temperature on the conversion of SO_3 to MSA formation. *Reaction conditions:* solvent, fuming sulfuric acid, 5.67 g; SO_3, 1.7 g (21.25 mmol) methane, 300 psig (84.9 mmol); KO_2, 0.98 mmol; $RhCl_3$, 0.31 mmol; time, 18 h.**

The reaction rate also depends on the initial concentration of SO_3. As shown in Figure 5, with increasing SO_3 concentration, the MSA conversion increases initially; however, above an initial concentration of 39%, the conversion of SO_3 to MSA decreases due to the formation of methylbisulfate as a byproduct.

The sulfonation of CH_4 requires an acidic solvent. H_2SO_4 is the most effective solvent (14% conversion in 18 h), triflic acid is moderately active (7% conversion in 18 h), and trifluoroacetic acid is the least effective (3% conversion in 20 h). No MSA was formed when DMSO was used as the solvent.

The experimental results can be interpreted in terms of a free radical mechanism. The appearance of C_2H_6 in the autoclave headspace in the absence of SO_3 and the termination of the reaction in the presence of molecular O_2 support our hypothesis of a free radical mechanism. KO_2 readily reacts with H_2SO_4 to form H_2O_2 ($2KO_2 + H_2SO_4 \rightarrow K_2SO_4 + H_2O_2 + O_2$).[11] The H_2O_2 thus formed could react with the promoter, $RhCl_3$ to generate the active radical species, I•, which may consist of a rhodium−peroxo or hydroperoxo

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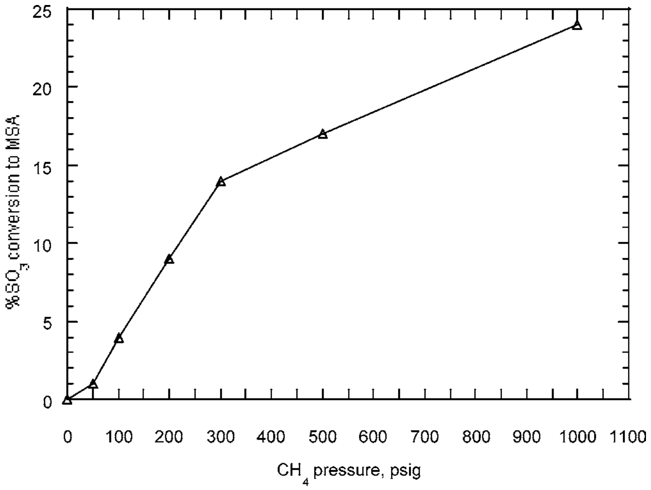

Figure 4. **Effect of CH_4 partial pressure on the conversion of SO_3 to MSA. *Reaction conditions:* solvent, fuming sulfuric acid, 5.67 g; SO_3, 1.7 g (21.25 mmol); KO_2, 0.98 mmol; $RhCl_3$, 0.31 mmol; temperature, 95 °C; time, 18 h.**

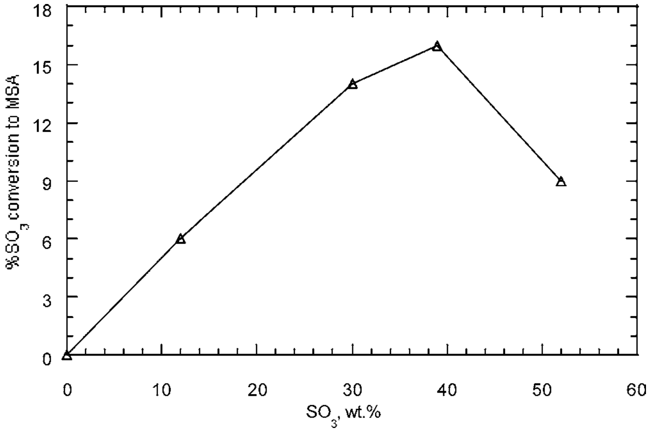

Figure 5. **Effect of SO_3 initial concentration on the conversion of SO_3 to MSA. *Reaction conditions:* solvent, fuming sulfuric acid; methane, 300 psig (84.9 mmol); KO_2, 0.98 mmol; $RhCl_3$, 0.31 mmol; temperature, 95 °C; time, 18 h.**

species.[12,13] The I• abstracts hydrogen from CH_4 to form $CH_3\bullet$ radicals (reaction 1) which react with SO_3 (reaction 2) to form $CH_3SO_3\bullet$ radicals which in turn abstract hydrogen from methane to form MSA according to reaction 3.

$$CH_4 + I\bullet \rightarrow CH_3\bullet + IH \tag{1}$$

$$CH_3\bullet + SO_3 \rightarrow CH_3SO_3\bullet \tag{2}$$

$$CH_3SO_3\bullet + CH_4 \rightarrow CH_3SO_3H + CH_3\bullet \tag{3}$$

While the nature of the composition of I• has not been confirmed, we have recently demonstrated that $RhCl_3$ in combination with urea$-H_2O_2$ is a particularly effective free radical initiator for the direct sulfonation of CH_4 by SO_3 to form MSA.[8e]

The observed lowering in the conversion of SO_3 to MSA when more than 0.98 mmol of metal superoxide is used can be attributed to an increase in the rate of O_2 formation. Since O_2 is known to act as a free radical scavenger,[7a] it would be expected to inhibit 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 40 psig of O_2.

It is noted that KO_2 can initiate the reaction in the absence of a promoter (Table 1, entry 1), suggesting that H_2O_2 generated by the reaction of KO_2 with the acid solvent can activate methane. Consistent with this observation, no reaction was observed in a nonacidic solvent such as DMSO. When $RhCl_3$ is added to the reaction mixture, the conversion of SO_3 to MSA increases up to a maximum value and then decreases, as shown in Figure 2. The rising portion of this plot can be attributed to an increase in the amount of the metal$-$peroxo species formed via the reaction of $RhCl_3$ with H_2O_2. The decrease in the conversion to MSA for a KO_2/$RhCl_3$ ratio of less than 3 might be associated with the catalyzed decomposition of H_2O_2 by excess $RhCl_3$. Two other observations support the in situ formation of a metal$-$peroxo species. The first is that after reaction for 18 h in the presence of $RhCl_3$ and KO_2 ($KO_2/RhCl_3 = 3$), the addition of more KO_2 resulted in an additional 11% conversion of SO_3 to MSA after an additional 18 h of reaction. On the other hand, when the same experiment was carried out in the absence of $RhCl_3$, no additional MSA was observed after an additional 18 h of reaction. These experiments suggest that a part of the $RhCl_3$ may be recycled during the reaction. To examine whether $Rh_2(SO_4)_3$ might have formed by the reaction of $RhCl_3$ and H_2SO_4, we performed a reaction with $Rh_2(SO_4)_3$ as a promoter instead of $RhCl_3$. In this case, hardly any MSA formation was observed. This suggests that during the reaction $RhCl_3$ does not dissociate completely in fuming H_2SO_4 and that the chloride anion is not replaced fully by sulfate or bisulfate anions.

The decrease in SO_3 conversion above 95 °C seen in Figure 3 might be due to rapid decomposition of H_2O_2 and the release of O_2. As noted above, the presence of O_2 in the reaction mixture inhibits the formation of MSA. This is attributed to the formation of alkylperoxide species via the reaction of methyl radicals with O_2, which are less active for reaction with SO_3 than methyl radicals.

The effect of SO_3 concentration on the conversion of SO_3 to MSA seen in Figure 5 can be explained as follows. Below 40 wt % SO_3, the increase in conversion is attributed to the increase in the driving force for reaction 2. However, for higher SO_3 levels, MSA formation is reduced by the formation of CH_3OSO_3H and $CH_3(SO_3)_2H$. A similar effect has been observed in several other reaction systems utilizing a free radical initiator to produce MSA from CH_4 and SO_3.[8]

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Conclusions

We have demonstrated a synthetic approach for the direct, liquid-phase sulfonation of methane with SO_3. Under the best suitable reaction conditions, 24% conversion of SO_3 to MSA was achieved. $RhCl_3$ emerged as an effective promoter when used with KO_2 serving as the radical initiator. It is proposed that a rhodium−peroxo or hydroperoxo species is formed in situ, which is a more effective free radical initiator than KO_2 in activating methane.

Experimental Section

Reactions were carried out in a 100 cm^3 high-pressure autoclave (Parr Instruments: 3000 psig maximum) constructed of Hastelloy B. Unless otherwise stated, the following procedure was used for all experiments. Typically, 0.98 mmol of KO_2 (Aldrich Chemical Co.) and 0.31 mmol of $RhCl_3$ (Aldrich Chemical Co., 99.98%) were added to 5.7 g of fuming sulfuric acid (Aldrich Chemical Co., 27−33% SO_3) taken in the glass liner containing a Teflon-encased stirring bar at 0−5 °C. For some experiments, additional SO_3 (Aldrich Chemical Co., 99%) was added to the liquid in the liner. The glass liner was then transferred to the reactor, after which the reactor was sealed and attached to a gas handling system. The reactor was purged twice with N_2 (Matheson) and then twice with CH_4 (Matheson, ultrahigh purity) and then pressurized with CH_4 to 300 psig. The reactor was heated to 95 °C, a process which took 8−10 min, and this temperature was then maintained for up to 18 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 Carbusorb to remove sulfur (II) compounds. The system was then purged with N_2 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_2O to convert any unreacted SO_3 to H_2SO_4. Reaction products were characterized by ^1H NMR. All spectra were acquired using a Bruker AMX-400 MHz FT-NMR spectrometer. A capillary containing D_2O and CH_3OH, immersed within the NMR tube containing the sample, was used as a lock, reference, and integration standard. All other chemicals were purchased from Aldrich Chemical Co. and used without further purification. Products were identified by ^1H NMR. The chemical shift for methyl group of MSA was observed to be 2.9−3.07 ppm, depending on the concentration of MSA in the reaction mixture.

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