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Effects of Solvent Acidity on the Free-Radical-Initiated Synthesis of Methanesulfonic Acid from CH_4 and SO_3

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The effects of solvent acidity on $K_2S_2O_8$-initiated synthesis of methanesulfonic acid (MSA) from CH_4 and SO_3 have been investigated. Dimethyl sulfoxide, sulfuric acid, and trifluromethane-sulfonic acid were used as the solvents. The initial rate of MSA synthesis increased with solvent acidity, being lowest in DMSO and highest in triflic acid. This effect is attributed to the influence of solvent acidity on the extent of decompostion of the $S_2O_8^{2-}$ anion, which dissociates to form $SO_4^{-\bullet}$. The latter species is responsible for activation of CH_4 to form $CH_3^{\bullet}$. The maximum conversion of SO_3 to MSA also depends on the solvent, increasing in the order DMSO < TFMSA < H_2SO_4. The highest conversion of SO_3 to MSA observed for the conditions of these studies was 87% when H_2SO_4 containing 0.2 M TFMSA was used as the solvent. The limit on the maximum conversion of SO_3 to MSA is set by the reaction $CH_3SO_3H + SO_3 \rightleftharpoons CH_3(SO_3)_2H$, which removes unconverted SO_3 from solution as MSA is formed. Although the extent to which this reaction proceeds decreases with increasing solvent acidity, the use of TFMSA as the solvent is detrimental because it appears to stabilize the formation of $CH_3(SO_3)_2H$, possibly in the form of $CH_3(SO_3)_2H\cdot(CF_3SO_3H)_2$. The influences of the initial concentrations of SO_3 and $K_2S_2O_8$ and of the reaction temperature on the maximum conversion of SO_3 to MSA are discussed in terms of a proposed mechanism for MSA synthesis.
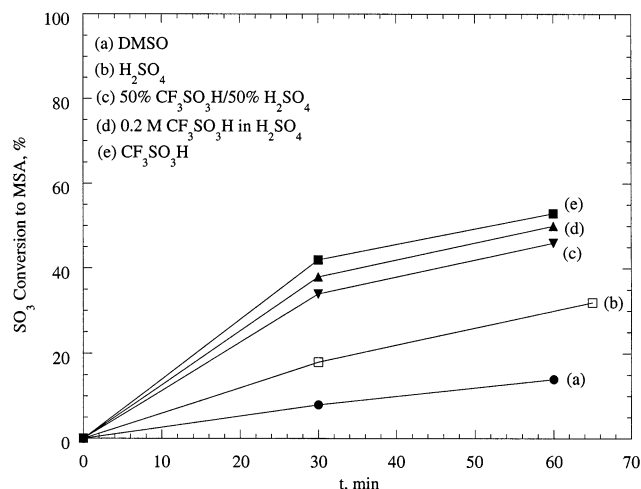
Introduction

The current commercial process for the synthesis of methanesulfonic acid (MSA) occurs via the chlorine oxidation of methylmercaptan.[1,2] Although this process is highly productive, it produces 6 mol of HCl per mole of MSA, resulting in a coupling of the demand for the primary product and the byproduct. As an alternative route to MSA, it is interesting to consider the reaction of methane with sulfur trioxide, as it is thermodynamically favorable. Sen and co-workers have demonstrated that MSA can be produced from CH_4 and SO_3 via a radical-initiated pathway.[3] Of the several radical initiators they investigated, $K_2S_2O_8$ was found to be the most effective. We have recently shown that, by optimizing the reaction conditions, i.e., CH_4 pressure, SO_3 concentration, $K_2S_2O_8$ concentration, and reaction temperature, yields of 60−65% could be achieved using this approach.[4] In the course of these studies, it was observed that the conversion of SO_3 to MSA reached a plateau of less than 100% after a certain reaction time, even though the thermodynamically expected maximum was 100% for all of the conditions explored. The present study was undertaken to obtain an understanding of the limit in SO_3 conversion to MSA and to investigate the effects of solvent composition on the rate of SO_3 reaction and the maximum conversion of SO_3 to MSA. Dimethyl sulfoxide (DMSO), fuming sulfuric acid, and triflic acid (TFMSA) were used as solvents, and all reactions were initiated with $K_2S_2O_8$.

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Experimental Section

Reactions were carried out in a 100-cm^3 high-pressure autoclave (Parr Instruments, 3000 psi maximum) constructed of Hastelloy B. Unless otherwise stated, the following procedure was used for all experiments. $K_2S_2O_8$ (Mallinckrodt, 99.1%) and 3 cm^3 of solvent [DMSO (Aldrich Chemical Co., 99%), fuming sulfuric acid (Aldrich Chemical Co., 27−33% SO_3), or TFMSA (Aldrich Chemical Co., 99%)] were added to a glass liner containing a Teflon-encased stirring bar. 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 with CH_4 (Matheson, ultrahigh purity) and then pressurized to the desired level. The reactor was heated to the preset temperature, a process that took 8−12 min, and this temperature was then maintained for up to 2 h, unless stated otherwise. Following reaction, the reactor was cooled in an ice bath to room temperature (~0.5 h), and the system was then purged with N_2 purified by passage through oxysorb, ascarite, and molecular sieve traps. The gases exiting the reactor were passed through scrubbers containing NaOH and Carbusorb to remove sulfur(II) compounds. The liquid product was removed from the glass liner and added slowly to 0.5−1.0 cm^3 of H_2O to convert any unreacted SO_3 to H_2SO_4. Reaction products were characterized by ^1H NMR spectroscopy. All spectra were acquired using a Bruker AMX-400 MHz FT-NMR spectrometer. A capillary containing D_2O and CH_3OH,

**Figure 1.** Effect of solvent acidity on the temporal evolution of the conversion of SO_3 to MSA.
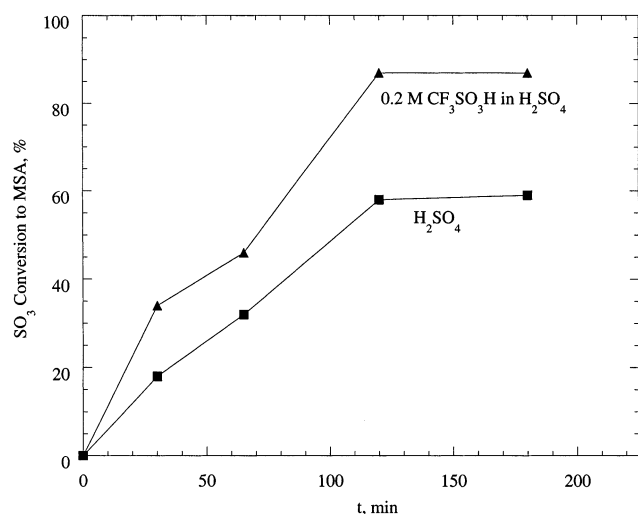
Figure 2. Comparison of the temporal evolution of the conversion of SO_3 to MSA carried out in H_2SO_4 and H_2SO_4 containing 0.2 M TFMSA.

immersed within the NMR tube containing the sample, was used as a lock, reference, and integration standard.

Results

The effects of reaction medium on the conversion of SO_3 to MSA were explored for reaction times of 60 min. Figure 1 demonstrates that the conversion of SO_3 is a strong function of the solvent. In a nonacidic solvent, such as DMSO, the conversion rises to 15%, but in fuming H_2SO_4, the conversion is 30%. If pure TFMSA is used as the solvent, the conversion rises further to 50%. An only slightly lower conversion, 45%, is achieved if fuming H_2SO_4 containing 0.2 M TFMSA is used as the solvent. It is interesting to note, however, that, for longer reaction times, e.g., >2 h, the conversion of SO_3 to MSA is significantly higher in fuming H_2SO_4 containing 0.2 M TFMSA (87%) than in pure TFMSA (50%). For this reason, all further experiments were conducted in fuming H_2SO_4 with or without the addition of TFMSA.

TFMSA has two effects on the conversion of SO_3 to MSA, as shown in Figure 2. The first is to increase the rate of SO_3 conversion to MSA, and the second is to increase the plateau in the SO_3 conversion. The maximum in SO_3 conversion after 4 h of reaction increased
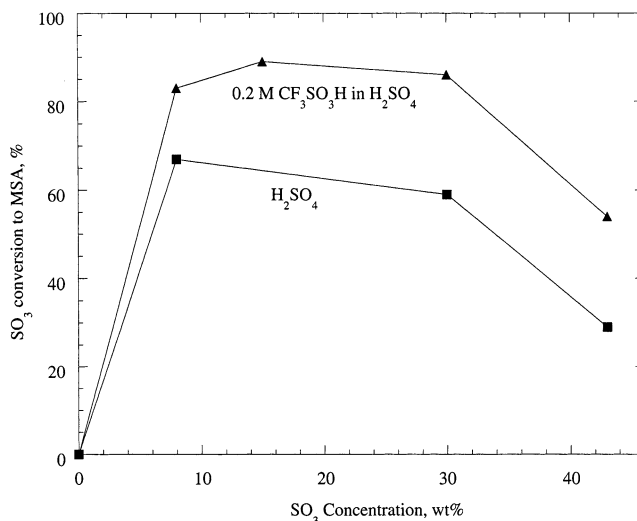
Figure 3. Effect of initial SO_3 concentration on the conversion of SO_3 to MSA after 2 h of reaction in H_2SO_4 and H_2SO_4 containing 0.2 M TFMSA.
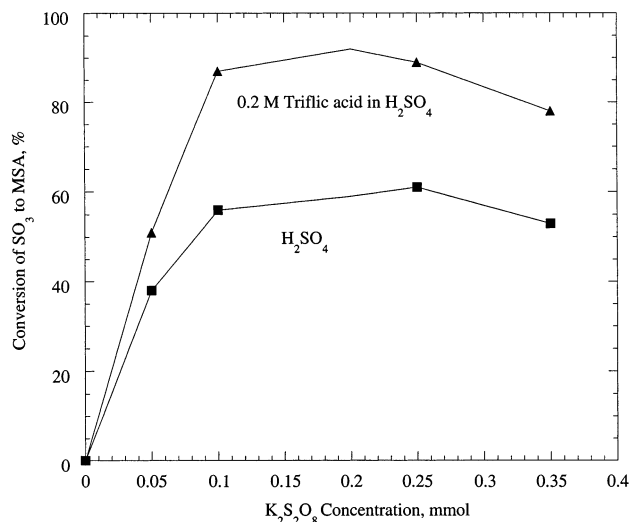
Figure 4. Effect of $K_2S_2O_8$ concentration on the conversion of SO_3 to MSA after 2 h of reaction in H_2SO_4 and H_2SO_4 containing 0.2 M TFMSA.

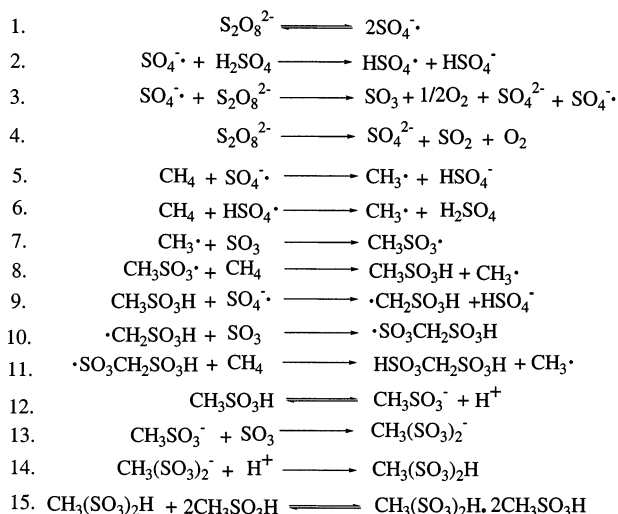from 67 to 80%. In separate experiments (results not shown), it was found that the maximum conversion of SO_3 increased linearly with increasing TFMSA addition in the range of 0−0.33 M.

The effect of the initial concentration of SO_3 on the conversion of SO_3 to MSA after 2 h is shown in Figure 3. Both with and without the addition of TFMSA, the conversion of SO_3 rises to a broad maximum at an initial SO_3 concentration of about 20% and then decreases above a SO_3 concentration of about 30%. This fall off in SO_3 conversion to MSA is associated with the appearance of byproducts such as methanedisulfonic acid and methyl bisulfate. The addition of 0.2 M of TFMSA increases the SO_3 conversion to MSA for all initial concentrations of SO_3.

The effects of the $K_2S_2O_8$ concentration on the conversion of SO_3 to MSA in the absence and presence of TFMSA are illustrated in Figure 4. Here again, the addition of TFMSA increases the conversion of SO_3 by a significant amount. It is interesting to note, however, that the presence of TFMSA has no effect on the shape of the curve of SO_3 conversion versus $K_2S_2O_8$ concentration.
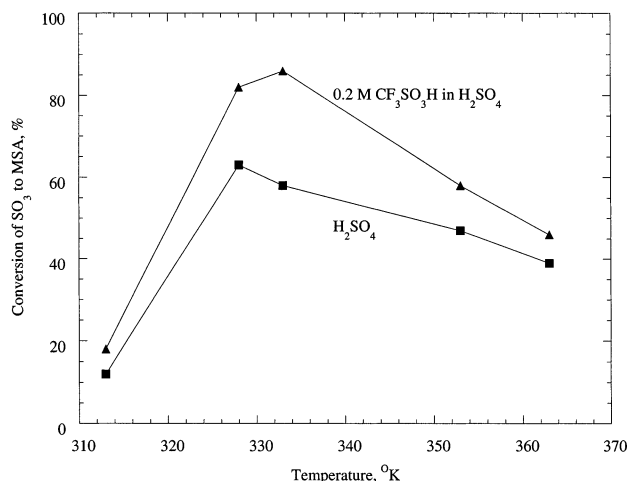
Figure 5. Effect of temperature on the conversion of SO_3 to MSA after 2 h of reaction in H_2SO_4 and H_2SO_4 containing 0.2 M TFMSA.

1. $S_2O_8{}^{2-} \rightleftharpoons 2SO_4{}^-\cdot$

2. $SO_4{}^-\cdot + H_2SO_4 \longrightarrow HSO_4{}^-\cdot + HSO_4{}^-$

3. $SO_4{}^-\cdot + S_2O_8{}^{2-} \longrightarrow SO_3 + 1/2O_2 + SO_4{}^{2-} + SO_4{}^-\cdot$

4. $S_2O_8{}^{2-} \longrightarrow SO_4{}^{2-} + SO_2 + O_2$

5. $CH_4 + SO_4{}^-\cdot \longrightarrow CH_3\cdot + HSO_4{}^-$

6. $CH_4 + HSO_4{}^-\cdot \longrightarrow CH_3\cdot + H_2SO_4$

7. $CH_3\cdot + SO_3 \longrightarrow CH_3SO_3\cdot$

8. $CH_3SO_3\cdot + CH_4 \longrightarrow CH_3SO_3H + CH_3\cdot$

9. $CH_3SO_3H + SO_4{}^-\cdot \longrightarrow \cdot CH_2SO_3H + HSO_4{}^-$

10. $\cdot CH_2SO_3H + SO_3 \longrightarrow \cdot SO_3CH_2SO_3H$

11. $\cdot SO_3CH_2SO_3H + CH_4 \longrightarrow HSO_3CH_2SO_3H + CH_3\cdot$

12. $CH_3SO_3H \rightleftharpoons CH_3SO_3{}^- + H^+$

13. $CH_3SO_3{}^- + SO_3 \longrightarrow CH_3(SO_3)_2{}^-$

14. $CH_3(SO_3)_2{}^- + H^+ \longrightarrow CH_3(SO_3)_2H$

15. $CH_3(SO_3)_2H + 2CH_3SO_3H \rightleftharpoons CH_3(SO_3)_2H \cdot 2CH_3SO_3H$

Figure 6. Proposed reaction mechanism for $K_2S_2O_8$-initiated synthesis of MSA from CH_4 and SO_3 in fuming sulfuric acid.

Figure 5 shows the effects of temperature on the conversion of SO_3 to MSA. In both the presence and absence of TFMSA, the conversion passes through a maximum. The position of the maximum conversion shifts to a slightly higher temperature when TFMSA is present, as does the conversion of SO_3 to MSA observed after 2 h.

Discussion

The results presented in Figures 1–5 can be interpreted in light of the mechanism for MSA synthesis presented in Figure 6, which is based on that originally proposed by Sen and co-workers[3] and later modified by Lobree and Bell.[4] The formation of MSA is initiated by the reaction of CH_4 with the radical anion $SO_4{}^-\cdot$ (reaction 5). This latter species is formed via the reversible decomposition of $S_2O_8{}^{2-}$ (reaction 1). The resulting methyl radical can react with SO_3 to form the radical $CH_3SO_3\cdot$ in reaction 7. MSA is formed via reaction 8, which involves the reaction of $CH_3SO_3\cdot$ with CH_4.

The remaining reactions listed in Figure 6 relate to the loss of the initiator and to secondary reactions involving MSA. Reaction 2 consumes $SO_4{}^-\cdot$ via reaction with H_2SO_4 and results in the formation of a new

radical, $HSO_4\cdot$, as well as $HSO_4{}^-$. $HSO_4\cdot$ can also initiate the formation of $CH_3\cdot$ radicals but is not expected to be as effective as $SO_4{}^-\cdot$. High concentrations of $K_2S_2O_8$ can also lead to the consumption of $SO_4{}^-\cdot$ by reaction 3 or decomposition of $S_2O_8{}^{2-}$ to $SO_4{}^{2-}$, SO_2, and O_2 via reaction 4, a process believed to be catalyzed by $SO_4{}^-\cdot$.[5]

MSA can undergo at least two types of types of secondary reactions. Reactions 9–11 constitute a pathway through which mathanedisulfonic acid, $CH_2(SO_3H)_2$, can be formed by a set of free-radical processes similar to those involved in the formation of CH_3SO_3H (reactions 5–8). As discussed below, MSA can react with SO_3 via reactions 12–15 to form a product containing two units of SO_3, $CH_3(SO_3)_2H$, which is then stabilized as a complex through hydrogen bonding with two additional molecules of MSA.

It can be seen in Figure 2 that the conversion of SO_3 increases with time and then approaches a plateau after about 2 h of reaction. The addition of TFMSA increases both the rate of MSA formation and the magnitude of the plateau. Thermodynamic calculations indicate that, for the conditions of the present experiments, the ultimate conversion of SO_3 to MSA should be 100%.[4,6] Failure to achieve 100% SO_3 conversion suggests that unreacted SO_3 is being consumed in secondary reactions or that the initial charge of initiator, $K_2S_2O_8$, is fully consumed prior to the completion of the reaction. The latter explanation can be eliminated, because, as reported by Lobree and Bell,[4] the addition of a new charge of initiator after attainment of the plateau in SO_3 conversion did not further increase the conversion of SO_3. The more probable interpretation is that a portion of the MSA formed reacts with SO_3 via reactions 11 and 12 to form a complex containing $CH_3(SO_3)_2H$. To confirm the possibility of forming such a product, samples of pure MSA containing increasing amounts of SO_3 were prepared. ^{1}H NMR spectra of these samples are shown in Figure 7A. The ^{1}H peak for protons associated with the methyl group of MSA appears at 2.5 ppm. Upon addition of SO_3, a new peak appears downfield of that for pure MSA at 3.1 ppm. The position of this feature is consistent with its assignment to $CH_3(SO_3)_2H$, because an increase in the shielding of the methyl protons is expected as a consequence of the addition of a second unit of SO_3. As the concentration of SO_3 increases, the position of this new peak shifts upfield, and its relative intensity increases. The presence of SO_3 also causes the MSA peak to shift downfield, and eventually the new feature and that for MSA merge into a single peak. The trends in peak position are likely due to solvent effects (Figure 7A). The change in the relative intensity of the MSA peak and of the new peak with increasing SO_3 concentration support also support the assignment of the new feature to $CH_3(SO_3)_2H$. The distribution of these two compounds with SO_3 concentration is shown in Figure 7B. Almost a 1:1 product distribution is achieved at around 50% SO_3 concentration.

The effect of solvent acidity on the rate of MSA formation and the maximum SO_3 conversion to MSA can be explained in the following manner. The acceleration of MSA formation can be ascribed to an increase in the concentration of $SO_4{}^-\cdot$, as the dissociation of $S_2O_8{}^{2-}$ via reaction 1 has been reported to be more extensive under acidic conditions.[7] Consistent with this, we have observed that the rate of MSA formation increases with increasing acidity of the medium (see Figure 1), i.e., DMSO < H_2SO_4 < TFMSA. The effect of
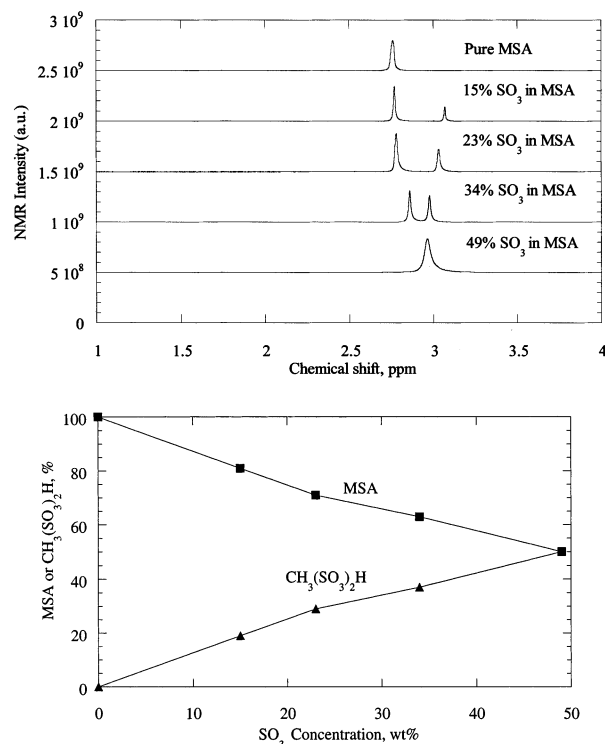
Figure 7. (A) ^{1}H NMR spectra of MSA with varying concentrations of SO_3 and (B) relative proportions of MSA and $CH_3(SO_3)_2H$ as a function of SO_3.

solvent acidity on the maximum conversion of SO_3 to MSA is more difficult to explain. With increasing acidity, the dissociation of MSA (reaction 12) should be suppressed, resulting in a lowering of the concentration of $CH_3SO_3^-$ anions. This, in turn, would decrease the formation of $CH_3(SO_3)_2^-$ anions and, hence, the loss of unreacted SO_3 via reaction 10. Therefore, the net effect of increasing solvent acidity is to increase the maximum possible yield of MSA. Consistent with this reasoning, the maximum convsersion of SO_3 to MSA increases when H_2SO_4 is used as the solvent instead of DMSO. This effect of acidity is further observed when a small amount of TFMSA is added to H_2SO_4, as TFMSA is a stronger acid than H_2SO_4. However, in pure TFMSA, the benefit of higher acidity is lost. This might be due to the sequestration of free SO_3 in the form of CF_3-$(SO_3)_2H$, a process that has been observed experimentally.[8]

The mechanism presented in Figure 6 can also be used to explain the observed effects of SO_3 concentration, $K_2S_2O_8$ concentration, and reaction temperature on the conversion of SO_3 to MSA. Because SO_3 is an essential component of MSA, the increase in SO_3 conversion to MSA with increased initial concentration of SO_3 is not surprising. The decrease in SO_3 conversion to MSA once the initial SO_3 concentration rises above $10-15\%$ is possibly due to the removal of dissolved SO_3 through the formation of products such as $H_2S_2O_7$, $H_2S_3O_{10}$, $H_2S_4O_{13}$, etc.[9,10] Another contributor to the decrease in the conversion of SO_3 to MSA is the formation of methanedisulfonic acid ($2-3\%$) and CH_3-$(SO_3)_2H$ ($3-5\%$), which are observed at SO_3 concentrations above 40%. The formation of methanedisulfonic acid can be explained by the attack of $SO_4^{-\bullet}$ radicals on the methyl group of CH_3SO_3H (reaction 9), followed by reactions 10 and 11. The formation of $CH_3(SO_3)_2H$ can be explained by reactions $12-14$.

As shown in Figure 4, the conversion of SO_3 to MSA obtained after a fixed reaction time passes through a maximum with increasing initial concentration of $K_2S_2O_8$. This rise in SO_3 conversion to MSA is attributed to an increasing concentration of $SO_4^{-\bullet}$, as a consequence of reaction 1 (see Figure 6). At higher $K_2S_2O_8$ concentrations, however, $SO_4^{-\bullet}$ will catalyze the irreversible loss of $S_2O_8^{2-}$ via reactions 3 and 4. The O_2 formed via reaction 4 can act as a radical scavenger and inhibit the formation of MSA. This effect was confirmed by performing a reaction under the conditions listed in Figure 2 in the absence of TFSMA but with the addition of 2 atm of O_2 to the gas phase. The presence of O_2 reduced the maximum conversion of SO_3 to MSA from 60 to 16%.

Both in the presence and in the absence of TFMSA, the conversion of SO_3 to MSA passes through a maximum with increasing temperature. This trend can be explained in the following manner. At lower temperatures, increasing the temperature increases the rate of MSA formation, but at temperatures above $328-333$ K, the decomposition of $S_2O_8^{2-}$ becomes rapid enough to offset the benefit of higher rates of MSA formation via reactions 5, 7, and 8 (see Figure 6). The formation of progressively higher concentrations of O_2 as a consequence of $S_2O_8^{2-}$ decomposition would also inhibit the formation of MSA, as noted above.

Conclusions

Solvent composition was found to have a strong influence on the radical-initiated synthesis of MSA from CH_4 and SO_3. For all solvents, the conversion of SO_3 to MSA increased with reaction time and then reached a plateau of less than 100%. The initial rate of SO_3 conversion increased with increasing acidity of the solvent. The lowest rate was observed in the nonacidic solvent DMSO. Higher rates were observed using either H_2SO_4 or TFMSA as the solvent, with the latter solvent resulting in the highest rates observed. Nearly equivalent initial rates could be achieved in H_2SO_4 containing 0.2 M TFMSA. The maximum conversion of SO_3 to MSA was lowest for DMSO and increased in the order DMSO $<$ TFMSA $<$ H_2SO_4 $<$ H_2SO_4 with 0.2 M TFMSA. The maximum conversion of SO_3 to MSA passed through a maximum with increasing initial concentrations of SO_3 and $K_2S_2O_8$ and with increasing reaction temperature. All of the observed effects of reaction conditions can be interpreted in terms of the reaction mechanism presented in Figure 6. The maximum conversion of SO_3 to MSA is attributed to the formation of $CH_3(SO_3)_2H^{\bullet}(CH_3$-$SO_3H)_2$, a complex that ties up unreacted SO_3 once MSA is formed. NMR evidence for the formation of such a complex is presented. The effect of solvent acidity on the rate of SO_3 conversion to MSA is attributed to the acid-catalyzed decomposition of $S_2O_8^{2-}$ to form $SO_4^{-\bullet}$, the species believed to be responsible for initiating the reaction of CH_4. Solvent acidity also influences the concentration of $CH_3(SO_3)_2H^{\bullet}(CH_3SO_3H)_2$. In general, the concentration of this species decreases with increasing acidity. However, when pure TFMSA is used as the solvent, this effect is offset by the formation of CF_3-$(SO_3)_2H$. The maximum in SO_3 conversion to MSA with increasing initial concentration of SO_3 is attributed to a tradeoff between the increase in the kinetics of forming MSA, the sequestration of SO_3 as $H_2(SO_3)_n$ ($n = 2, 3, 4, ...$), and the formation of $CH_2(SO_3H)_2$. The maximum in SO_3 conversion to MSA observed with

either increasing $K_2S_2O_8$ concentration or increasing reaction temperature is attributed to the opposing effects of these variables on the rate of MSA synthesis and the rate of initiator decomposition. Oxygen released upon the decomposition of $K_2S_2O_8$ is also reported to inhibit the conversion of SO_3 to MSA.

Acknowledgment

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