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Methane oxidation to acetic acid catalyzed by Pd^{2+} cations in the presence of oxygen

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Abstract

Synthesis of acetic acid from methane catalyzed by Pd^{2+} cations dissolved in sulfuric acid was investigated to determine the effects of reaction conditions and the mechanism. Acetic acid yield was found to be a strong function of CH_4 and O_2 partial pressures. High O_2/CH_4 ratio and high total pressure delivered the highest yield of acetic acid (14.2 turnovers of Pd^{2+}) and the highest retention of Pd^{2+} in solution (96%). Byproducts were sulfur containing compounds (most notably methyl bisulfate) and CO_x, but the acetic acid selectivity was maximized (82%) by lowering the reaction temperature. Methane is activated by $Pd(OSO_3H)_2$, forming $(CH_3)Pd(OSO_3H)$. CO, generated from the oxidation of methyl bisulfate, inserts into the CH_3–Pd bond creating a $(CH_3CO)Pd(OSO_3H)$ species. Reaction of this complex with H_2SO_4 produces acetic acid. Pd^{2+} is reduced to Pd^0 during the oxidation of methyl bisulfate or CO, and Pd^0 is reoxidized to Pd^{2+} by H_2SO_4 and O_2.

Keywords: Methane; Acetic acid; Palladium; Methyl bisulfate; Pd^0 oxidation; Sulfuric acid; Homogeneous catalysis

1. Introduction

The conversion of methane to acetic acid is currently carried out in a three-step process [1]. Methane is first reformed in a heterogeneously catalyzed process that is energy- and capital-intensive to produce synthesis gas, a mixture of CO and H_2. The CO and H_2 then react at high pressure in a second step to produce methanol, and finally, in the third step, acetic acid is produced by homogeneous-phase carbonylation of methanol. Because of the strong demand for acetic acid (3.1 million tons/year [1]) by the plastics, textiles, paper, paints, and adhesives industries, there is considerable interest in finding ways to synthesize acetic acid directly from methane. Several studies have recently shown how this might be done. For example, methane will undergo oxidative carbonylation in either water or strong acid catalyzed by Rh [2] or Cu [3] cations, and the carboxylation of methane has been demonstrated in both water and strong acids using soluble V-based catalysts [4,5]. A particularly interesting approach for the direct synthesis of acetic acid from methane has been reported by Periana et al. [6,7], who describe the oxidation of methane to acetic acid catalyzed by Pd^{2+} cations in 96 wt% sulfuric acid. The only other products observed are methyl bisulfate (a precursor to methanol) [8] and carbon dioxide. Whereas the selectivity to the liquid-phase products is reported to be as high at 90%, Pd^{2+} is observed to precipitate from solution as Pd-black, causing the reaction to stop. Zerella et al. [9] reproduced these observations and showed that the addition of Cu^{2+} and O_2 to the reaction mixture enhances the yield of acetic acid without dramatically increasing the yield of methyl bisulfate or decreasing the selectivity.

The aim of the present study was to investigate the effects of CH_4 and O_2 partial pressure, temperature, and sulfuric acid concentration on the synthesis of acetic acid and on the retention of Pd^{2+} in solution. The pathways leading to the formation of CO and CO_2 were examined, as was the mechanism by which the carboxylate group in CH_3COOH is formed. A further aim of this study was to identify the effects of reaction conditions on the formation of sulfur-containing acids, such as methanesulfonic acid, methane disulfonic acid, and sulfoacetic acid.

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2. Experimental

All reactions were carried out in a 50-mL Parr autoclave made of Hastelloy C. To minimize problems with reproducibility due to trace amounts of water retained in crevices of the autoclave head, all parts of the reactor were cleaned and dried thoroughly before each run. The temperature of the reacting mixture was measured with a thermocouple located in a well made of Hastelloy C, wrapped with Teflon tape to minimize exposure of the metal to the reaction mixture. The reaction mixture was contained in a glass liner. In a typical run, 0.0121 g (20 mM) of $PdSO_4$ (Aldrich) and 3 mL of 96% H_2SO_4 (Aldrich) were added to the liner. After the glass liner was placed in the autoclave, it was sealed and purged with N_2. The autoclave was pressurized at room temperature with 400 psi of CH_4 (99.97%, Praxair) and then with the desired pressure of O_2 (99.993%, Praxair). The reactor was brought to 453 K in $\sim$15 min and then held at this temperature for 4 h. On completion of the reaction, the autoclave was quenched in ice water to $<$308 K and then vented. On opening the autoclave, the solution was chilled further before 3 mL of water was added.

Liquid-phase reaction products were analyzed using ^1H nuclear magnetic resonance (NMR). D_2O was used in a capillary as the lock reference. A known amount of t-butanol was added to each sample and used as an internal standard for quantification. The liquid-phase products observed were acetic acid (CH_3COOH), methanesulfonic acid (CH_3SO_3H), methanol (CH_3OH), methyl bisulfate (CH_3OSO_3H), sulfoacetic acid (HO_3SCH_2COOH), and methane disulfonic acid ($CH_2(SO_3H)_2$). The chemical shifts for these products were as follows: acetic acid, 2.0 to 2.1 ppm; methanesulfonic acid, 2.8 to 2.9 ppm; methanol, 3.3 to 3.4 ppm; methyl bisulfate, 3.6 to 3.7 ppm; sulfoacetic acid, 4.0 to 4.1 ppm; and methane disulfonic acid, 4.4 to 4.5 ppm.

For analysis of the gas products, a sample of the autoclave head-space gas was taken using a gas-tight syringe on venting the autoclave. Analysis of the sample was carried out by gas chromatography to determine the concentrations of CH_4, CO, and CO_2. The concentrations of liquid-phase products were determined from the ^1H NMR analyses, and these measurement were combined with the gas chromatography analyses of the autoclave head space to determine the amount of CO_x ($x = 1, 2$) produced.

The yield of each liquid-phase product is reported in terms of the concentration of that product observed after a fixed reaction period. Even though water is added to the reaction mixture before the ^1H NMR analysis, the reported concentrations are calculated on the basis of the volume of liquid present in the autoclave liner before the addition of water. In this prehydrolized state, no methanol is observed [8]. Only after the addition of water is some of the methyl bisulfate hydrolyzed to methanol. Because methanol derives from methyl bisulfate, any methanol measured is reported as methyl bisulfate. The carbon selectivity to acetic acid, S_{AcOH}, is the moles of carbon in acetic acid divided by the sum of the moles of carbon appearing in all liquid- and gas-phase products. In calculating S_{AcOH}, the volume of the gas head space in the autoclave and the volume of liquid in the autoclave liner are taken into account.

The concentration of Pd^{2+} retained in solution after reaction (but before water addition) was determined by UV–vis spectroscopy. The peak located at 440 nm, ascribed to $Pd(OSO_3H)_2$ [10], was used to determine the concentration of Pd^{2+} cations in solution. A solution of known concentration of Pd^{2+} was used as a standard for the comparison of peak areas.

3. Results

The effects of CH_4 and O_2 partial pressures were explored to determine the influence of these variables on the yields of acetic acid and methyl bisulfate, the selectivity of methane conversion to these products, and the retention of Pd^{2+} in solution. Unless specified otherwise, all reactions were carried out in 96 wt% H_2SO_4 containing 20 mM of $PdSO_4$ at 453 K. The initial partial pressures of CH_4 and O_2 were chosen to avoid compositions that would result in an explosive mixture during any part of the reaction [11]. The results of these experiments are given in Tables 1 and 2. Table 1 shows that for an initial CH_4 partial pressure of 200 psi, the yield of acetic acid rose from 65.7 to 181 mM as the initial partial pressure of O_2 increased from 0 to 125 psi. Over the same range of O_2 partial pressures, the yield of methyl bisulfate increased from 2.5 to 4.8 mM, whereas the production of methanesulfonic acid increased from 3.0 to 29.4 mM. The other two sulfur-containing byproducts, sulfoacetic acid and methane disulfonic acid, re-

Table 1
Effect of O_2 pressure at 200 psi CH_4[a]

	O_2 pressure (psi)				
	0	30	60	75	125
CH_3COOH (mM)	65.7	52.1	136	154	181.2
CH_3OSO_3H (mM)	2.5	1.7	3.1	3.9	4.8
CH_3SO_3H (mM)	3.0	7.7	15.9	25.3	29.4
HO_3SCH_2COOH (mM)	5.9	6.2	11.6	9.9	9.3
$CH_2(SO_3H)_2$ (mM)	18.2	65.1	31	31	32.9
S_{CH_3COOH} (%)	46	22	41	37	39
S_{CO_x} (%)	44	60	50	54	53
Pd retained (%)	6.5	11	13	48	96

[a] Reaction conditions: 3 ml 96% H_2SO_4; 0.0121 g (20 mM) $PdSO_4$; 200 psi CH_4; X psi O_2; 180 °C; 4 h.

Table 2
Effect of O_2 pressure at 400 psi CH_4[a]

	O_2 pressure (psi)			
	0	30	100	150
CH_3COOH (mM)	78.5	118	191	284
CH_3OSO_3H (mM)	3.2	5.1	5.4	6.8
CH_3SO_3H (mM)	9.2	8.2	27.0	55.5
HO_3SCH_2COOH (mM)	8.3	10.1	12.2	16.3
$CH_2(SO_3H)_2$ (mM)	44.6	26.3	25.4	36.8
S_{CH_3COOH} (%)	51	57	50	44
S_{CO_x} (%)	27	31	41	47
Pd retained (%)	3.8	3.3	16	40

[a] Reaction conditions: 3 ml 96% H_2SO_4; 0.0121 g (20 mM) $PdSO_4$; 400 psi CH_4; X psi O_2; 180 °C; 4 h.

mained relatively constant at about 9 and 30 mM, respectively. Notably, the overall selectivity of methane conversion to acetic acid decreased only slightly, from 46 to 39%. The most remarkable effect of O_2 partial pressure, however, was on the retention of initially dissolved Pd in solution at the end of the reaction. Table 1 shows that this value rose from 6.5 to 96% as the initial O_2 partial pressure increased from 0 to 125 psi. Raising the initial CH_4 pressure to 400 psi increased the yields of acetic acid and, to a much lesser degree, methyl bisulfate, as shown in Table 2. Here again, increasing the initial partial pressure of O_2 increased the yields of acetic acid and methanesulfonic acid, slightly increased the yield of methyl bisulfate, slightly decreased the selectivity to acetic acid, and significantly increased the percentage of Pd retained in solution. The yields of sulfoacetic acid and methane disulfonic acid also increased slightly. Comparing the results in Tables 1 and 2 reveals that for the same O_2/CH_4 ratio, operation at higher initial pressures of both reactants resulted in an increased yield of acetic acid that was essentially proportional to the increase in total initial pressure and to only a small increase in the yield of methyl bisulfate. The overall selectivity of methane conversion to acetic acid and methyl bisulfate increased slightly for operation at higher pressure, but retention of the initially dissolved Pd as Pd^{2+} remained essentially the same. Note that although reaction with O_2 and CH_4 pressures of 250 and 400 psi would be expected to result in complete retention of Pd^{2+} in solution, these conditions were not used, because this reaction mixture lies within the explosive region [11].

Periana et al. [6] reported that the carboxylate group of acetic acid derives from a “CO species” produced in situ. Reactions conducted with the addition of ^{13}C-labeled methanol (which is methyl bisulfate in solution) showed that ^{13}C is transferred only to the carboxylate group of acetic acid (viz., as $CH_3{}^{13}COOH$), leading to the suggestion that the “CO species” is produced by oxidation of the added $^{13}CH_3OH$. As a part of the present study, we have confirmed that methyl bisulfate is oxidized to CO (see below) and have observed that adding a small amount of ^{13}CO to the feed gas results in the formation of $CH_3{}^{13}COOH$.

Several experiments were carried out to confirm the formation of CO from methyl bisulfate. For these experiments, 0.09 g of methanol was added to the sulfuric acid solution (where it was converted to methyl bisulfate) normally used for the synthesis of acetic acid. Table 3 shows the effects of the presence or absence of $PdSO_4$ in the solution and the presence or absence of O_2 in the autoclave head space. Sulfuric acid itself converted 16% of the methyl bisulfate to CH_4, CO, and CO_2. In the presence of O_2, the conversion of methyl bisulfate increased to 44%, with CO_2 becoming the major product. When Pd^{2+} was present in the absence of O_2, methyl bisulfate was consumed completely to form primarily methane and some CO_2, but no CO. Introducing O_2 led to total conversion of methyl bisulfate to CO_2. These data demonstrate that methyl bisulfate is highly reactive, particularly when Pd^{2+} is present. CO is observed as a product, and in the presence of Pd^{2+} it assumed to be the precursor to CO_2. However, under normal reaction conditions, the rate of CO reaction (to CO_2 or CH_3COOH) is rapid, so that very little of it accumulates in the gas phase.

Table 3
Methyl bisulfate conversion to products[a]

Reactant(s)	Methyl bisulfate conversion		
	CH_4 (%)	CO (%)	CO_2 (%)
H_2SO_4	6	2	8
H_2SO_4, Pd^{2+}	91	0	9
H_2SO_4, O_2	14	4	26
H_2SO_4, Pd^{2+}, O_2	0	0	100

[a] Reaction conditions: 3 ml 96% H_2SO_4; 0.0121 g (20 mM) Pd^{2+} (when added); 0.090 g (94 mM) CH_3OH; 30 psi O_2 (when added); 180 °C; 4 h.

Because CO is established to be an intermediate in the reaction and is incorporated into acetic acid, we explored the effects of adding CO into the gas phase. At very low pressures (∼0.02 atm), CO had a beneficial effect, boosting the acetic acid yield from 78 to 109 mM. However, as shown in Fig. 1, further increasing the CO pressure inhibited the reaction. Once the partial pressure of CO reached 1 atm, acetic acid production dropped to 20 mM. The effect of CO partial pressure on the yield of methyl bisulfate was similar to, but less dramatic than, that on the yield of acetic acid for pressures below about 0.2 atm. Note, however, that raising the CO partial pressure to 1 atm produced a small increase in the yield of methyl bisulfate (see Fig. 1).

It was hypothesized that the decrease in acetic acid yield at high CO partial pressures may be due to Pd-catalyzed CO oxidation to CO_2, resulting in the reduction of Pd^{2+} to Pd^0. To test this hypothesis, the autoclave was pressurized with 1 atm of CO, but no CH_4 or O_2 was added to the gas phase. After proceeding as in a normal reaction (raising the temperature to 453 K for 4 h), all of the Pd^{2+} was reduced to Pd-black. In contrast, in an inert atmosphere, all of the Pd^{2+} remains in solution. Increasing the CO pressure to 2–3 atm caused the Pd^{2+} reduction to proceed more rapidly. Analysis of the reactor headspace after reduction of Pd^{2+} shows that CO_2 was the only gaseous product; thus, it is reasonable to conclude that acetic acid formation is limited by CO reduction of Pd^{2+} to Pd-black.

Fig. 2 illustrates the effects of the initial concentration of $PdSO_4$ on the yields of acetic acid and methyl bisulfate. The percentage of the initially charged $PdSO_4$ retained in solution at the end of the reaction, and the number of moles of acetic acid

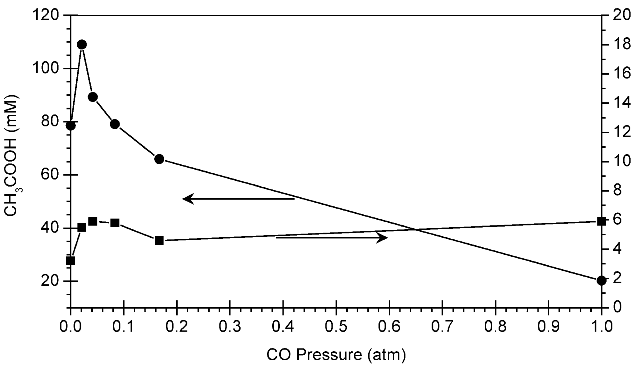

Fig. 1. Effect of CO pressure on acetic acid and methyl bisulfate yields. Reaction conditions: 3 ml 96% H_2SO_4; 0.0121 g (20 mM) $PdSO_4$; 400 psi CH_4; 180 °C, 4 h.

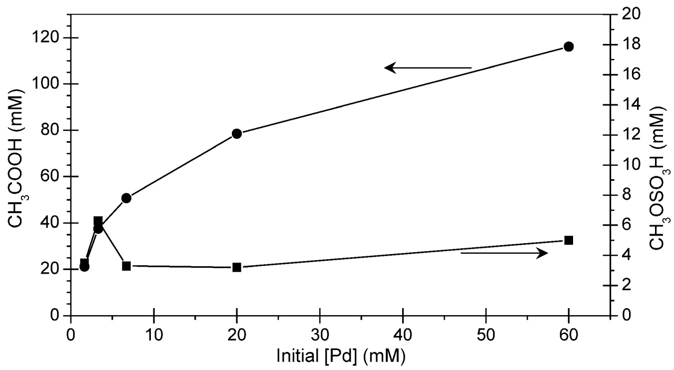

Fig. 2. Effect of initial palladium concentration. Reaction conditions: 3 ml 96% H_2SO_4; X mM $PdSO_4$; 400 psi CH_4; 180 °C; 4 h.

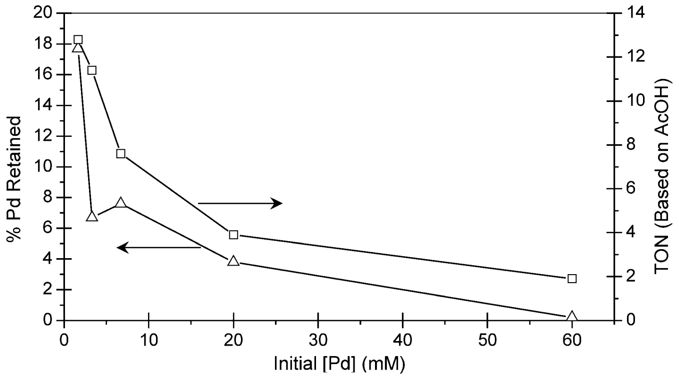

Fig. 3. Pd^{2+} Retention and TON. Reaction conditions: 3 ml 96% H_2SO_4; *X* mM $PdSO_4$; 400 psi CH_4; 180 °C; 4 h.

Table 4

Effect of reaction temperature[a]

	180 °C	160 °C
CH_3COOH (mM)	284	266
CH_3OH (mM)	6.8	15.8
CH_3SO_3H (mM)	55.5	17.0
HO_3SCH_2COOH (mM)	16.3	4.3
$CH_2(SO_3H)_2$ (mM)	36.8	1.1
S_{CH_3COOH} (%)	44	82
S_{CO_x} (%)	47	13
Pd retained (%)	40	51

[a] Reaction conditions: 3 ml 96% H_2SO_4; 20 mM $PdSO_4$; 400 psi CH_4; 150 psi O_2; 4 h.

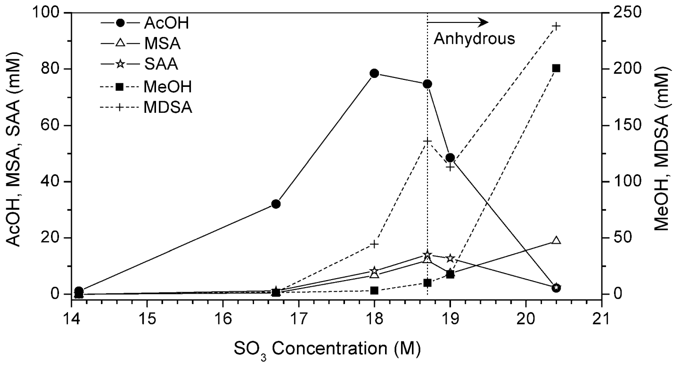

Fig. 4. Impact of SO_3 concentration. AcOH, acetic acid; MSA, methanesulfonic acid; SAA, sulfoacetic acid; MeOH, methanol and methyl bisulfate; MDSA, methane disulfonic acid. Reaction conditions: 3 ml X M SO_3; 0.0121 g $PdSO_4$; 400 psi CH_4; 180 °C; 4 h.

produced per mole of $PdSO_4$ charged to the reaction (TON), are shown in Fig. 3. The yield of acetic acid increased with the initial charge of $PdSO_4$ but with a decreasing slope, which led to a decrease in TON. In contrast, the yield of methyl bisulfate changed to a much lesser degree with an increasing charge of $PdSO_4$. Fig. 3 shows that the percentage of Pd retained in solution at the end of the reaction decreased as the magnitude of the initial charge of $PdSO_4$ increases. These latter results suggest that <1 mM of Pd^{2+} was retained in solution after reaction for the reaction conditions chosen, independent of the initial charge of $PdSO_4$. To test this hypothesis, a reaction was carried out starting with Pd-black [12]. Acetic acid was formed (a yield of 37.9 mM after 4 h), and the final concentration of Pd^{2+} in solution was 0.45 mM. These results support the proposition that only a limited amount of Pd^{2+} can be maintained in solution during reaction. However, as demonstrated by the results given in Tables 1 and 2, the percentage of Pd^{2+} retained in solution is a strong function of the ratio of O_2 to CH_4 partial pressures and, to a lesser extent, the total system pressure. Taken together, these results suggest that under reaction conditions, the concentration of Pd^{2+} retained in solution is dictated by a balance between the rates of Pd^{2+} reduction and Pd^0 oxidation.

The reaction temperature was found to affect the distribution of products and the retention of Pd^{2+} in solution. As shown in Table 4, decreasing the reaction temperature from 180 to 160 °C resulted in only a modest decrease in the yield of acetic acid. This was accompanied by a dramatic increase in selectivity, noticeable increases in the yield of methyl bisulfate and Pd retention, and significant decreases in the yields of methanesulfonic acid, methane disulfonic acid, and sulfoacetic acid. The high selectivity of acetic acid at 160 °C is due primarily to the low production of CO_x at this temperature. The strong increase in the yield of acetic acid relative to sulfur-containing acids reflects the higher activation energies associated with the latter products. The increase in the methyl bisulfate yield and Pd retention on temperature reduction can be attributed to less extensive combustion of methyl bisulfate, with the resulting lower CO_x production.

The effect of the concentration of the sulfuric acid solution on the distribution of products was also investigated. Fig. 4 shows the yields of acetic acid, methyl bisulfate, methanesulfonic acid, methane disulfonic acid, and sulfoacetic as a function of the concentration of SO_3. Below 18.7 M, all of the SO_3 was present as H_2SO_4, and above this molarity an increasing fraction of the SO_3 was present as free SO_3 dissolved in 100% H_2SO_4. The yield of acetic acid increased to up to a maximum value of 78.5 mM at 18.0 M SO_3, after which it decreased to nearly zero. In contrast, the yield of methyl bisulfate was negligible for SO_3 molarities below 18.0, but rose rapidly thereafter. Below an SO_3 concentration of 18.0 mM, the yields of methanesulfonic acid, methane disulfonic acid, and sulfoacetic acid were very small. However, above this SO_3 concentration, the yield of methanesulfonic acid increased from 6.7 up to 18.8 mM; the yields of methane disulfonic acid and methyl bisulfate increased sharply from 44.6 and 3.2 up to 238 and 201 mM, respectively; and the yield of sulfoacetic acid increased from 8.3 up to 14.1 mM.

The decrease in the yield of all products at low concentrations of SO_3 is attributable to changes in the solubility of methane in sulfuric acid and the oxidation potential of the solution. As shown in Fig. 4, the acetic acid yield decreased by a factor of 2.4 when the SO_3 concentration was decreased from 18.0 to 16.7 M and by a factor of 71 when the SO_3 concentration was decreased from 18.0 to 14.1 M. Over the corresponding ranges of SO_3 concentrations, the solubility of methane decreased by factors of 1.9 and about 3.1, respectively [13]. Thus the very large decrease in the yield of acetic acid observed when the SO_3 concentration was reduced to 14.1 M is only partially attributable to the decreased methane solubility. The balance is very likely due to a loss in the oxidizing power of the solvent, which causes a decrease in the rate at which Pd^0 is reoxidized to Pd^{2+}.

The methyl bisulfate yield as a function of sulfuric acid concentration shown in Fig. 4 merits some comment. In contrast to the acetic acid, the yield of methyl bisulfate remained low for sulfuric acid concentrations $\leqslant 18.7$ M, but beyond this threshold increased rapidly to 201 mM at 20.4 M H_2SO_4 (27 wt% free SO_3). This dramatic increase in methyl bisulfate formation is attributed to a fundamental change in the reaction mechanism once the reaction system is anhydrous and free SO_3 is present. Two possible pathways for this have been proposed in the literature. In the first, palladium catalyzes the reaction of methane and SO_3 to form methanesulfonic acid [14]. At 180 °C, SO_3 oxidizes the methanesulfonic acid to methyl bisulfate [14b]. In the second proposed mechanism, Pd^{2+} catalyzes the direct formation of methyl bisulfate, in the process reducing to Pd^0 [15]. Because methyl bisulfate is stable under anhydrous conditions, it is not oxidized to CO, an essential intermediate in the formation of acetic acid. However, low yields of acetic acid are still observed, because CO can be generated via oxidation of the small amount of formaldehyde produced [15].

4. Discussion

The results presented in the preceding section clearly demonstrate that the yields of acetic acid and methyl bisulfate are strongly dependent on the initial partial pressures of CH_4, O_2, and CO; the concentration of $PdSO_4$ charged to the reaction solution; and the strength of the H_2SO_4 solution. For a particular charge of $PdSO_4$, the yield of acetic acid is maximized by using a high ratio of O_2/CH_4 partial pressures and a high total pressure of CH_4 and O_2. These conditions also increase the selectivity to acetic acid versus methyl bisulfate and the retention of Pd^{2+} in solution after reaction. The presence of a small amount of CO in the gas phase enhances the yield of acetic acid, but higher CO partial pressures have the opposite effect. A high yield of acetic acid also requires that the concentration of SO_3 in the solution be ~18.0 M. Sulfur-containing acids are also formed from methane, with the yield of these products strongly depending on the reaction conditions. The formation of methanesulfonic acid, methane disulfonic acid, and sulfoacetic acid relative to acetic acid are favored by high reaction temperatures, high SO_3 concentrations, and high O_2 partial pressures.

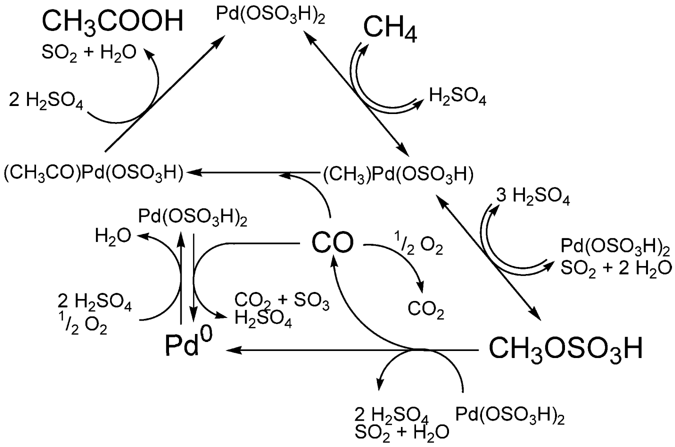

Fig. 5. Reaction pathway.

The effects of reaction conditions on the observed yields of acetic acid and methyl bisulfate and on the retention of Pd^{2+} in solution can be interpreted in terms of the scheme shown in Fig. 5. Although our scheme is similar in some aspects to the mechanisms proposed by Periana et al. [6,7] and by Zerella et al. [9], there are some significant differences, including (1) identification of CO as a reaction intermediate, (2) identification of CH_3OSO_3H and CO as reducing agents for the conversion of Pd^{2+} to Pd^0, (3) identification of the role of O_2 in the reoxidation of Pd^0, and (4) identification of an intermolecular process in the formation of CH_3COOH and CH_3OSO_3H.

The species involved in the activation of CH_4 is taken to be $Pd(OSO_3H)_2$, based on evidence from UV–vis spectroscopy and a theoretical analysis of Pd speciation as a function of acid strength. As noted above, the band in the UV–vis spectrum associated with Pd^{2+} cations shifted from 394 nm for 10% (1.1 M) H_2SO_4 to 440 nm for 96% (18.0 M) H_2SO_4. A similar shift was reported by Rudakov et al. [10] and assigned to the progressive displacement of H_2O by OSO_3H^- in the ligand sphere Pd^{2+}. To obtain a clearer picture of the speciation of Pd^{2+}, we carried out an estimate of the concentrations of equilibrium distribution of these species as a function of acid strength. The equilibrium constants required for these calculations were taken from a combination of experimental data and theoretical estimation [11,16,17]. On the basis of these calculations, we estimate that in 96% H_2SO_4, >99% of the Pd is present as $Pd(OSO_3H)_2$.

The oxidation of methane is assumed to begin via the reaction of CH_4 with $Pd(OSO_3H)_2$ to form $(CH_3)Pd(OSO_3H)$ and H_2SO_4. The bisulfate anions associated with $Pd(OSO_3H)_2$ are critical, because they act as nucleophiles for the proton abstracted of from CH_4 at the same time that Pd^{2+} acts as the electrophile for the methylide anion.

Recent theoretical calculations (unpublished results of S. Chempath and A.T. Bell) indicate that CH_3OSO_3H is produced not via an intramolecular process, as was proposed previously [6,7,9], but rather via an intermolecular process, as shown in Fig. 5. This process is assumed to be reversible, because adding methyl bisulfate to the reaction mixture results in the formation of CH_4, as well as CO and CO_2. Fig. 5 shows that CO is formed via the oxidation of CH_3OSO_3H. This step leads to the reduction of Pd^{2+} cations to Pd^0, which then precipitate from solution (see Table 3). The reduction of Pd^{2+} can also occur via reaction with CO (see above), leading to the formation of CO_2. Additional CO_2 is formed via the reaction of CO with O_2 when the latter species is present. The Pd^0 formed as a consequence of Pd^{2+} reduction by CH_3OSO_3H or CO is reoxidized by O_2 and H_2SO_4.

The formation of acetic acid starting from $(CH_3)Pd(OSO_3H)$ involves two steps. The first reaction is CO insertion into the Pd–CH_3 bond of the complex. Clear evidence for this step is given by studies carried out with ^{13}C-labeled CO and CH_3OH [6]. In the second step, $(CH_3CO)Pd(OSO_3H)$ is shown to react with H_2SO_4, resulting in the formation of CH_3COOH. Acetic acid formation via an intermolecular, rather than an intramolecular, process is suggested by theoretical calculations showing that the latter process is thermodynamically unfavorable. Although the scheme in Fig. 5 shows the formation of acetic acid to be irreversible, the formation of sulfoacetic acid indicates that secondary reaction of acetic acid can occur (see below). The high selectivity of acetic acid relative to sulfur-containing products suggests that CO insertion is much more facile than SO_2 insertion into the Pd–CH_3 bond. In addition, the data suggest that the rate of CO insertion must be as least as fast as the rate of CH_3OSO_3H formation. Both of these conclusions are supported by recent theoretical calculations.

The scheme presented in Fig. 5 shows that the final steps of acetic acid and methyl bisulfate formation do not involve the reduction of Pd^{2+} to Pd^0, as had been proposed previously [6]. The present study demonstrates that Pd^{2+} reduction occurs during the oxidation of CH_3OSO_3H and CO; therefore, maintenance of Pd^{2+} in solution requires a balance between the rate of Pd^{2+} reduction and Pd^0 oxidation. As shown in Tables 1 and 2, this can be achieved by adjusting the O_2/CH_4 ratio and operating at a high total pressure of CH_4 and O_2. For similar reasons, high partial pressures of CO should be avoided; however, a small amount of CO added to the feed can have a beneficial effect on the yield of acetic acid, because this facilitates the insertion of CO in the Pd–CH_3 bond of $(CH_3)Pd(OSO_3H)$ to form $(CH_3CO)Pd(OSO_3H)$. Yet another potential detrimental effect of CO is its interaction with $Pd(OSO_3H)_2$ to form $Pd(CO)(OSO_3H)_2$, a process that then competes with the formation of $Pd(CH_3)(OSO_3H)$.

The elementary steps involved in the formation of sulfur-containing acids were not investigated in the course of this reaction; however, the observed effects of reaction conditions suggest that these products involve the following stoichiometric reactions:

$$CH_4 + SO_3 \rightarrow CH_3SO_3H, \tag{1}$$

$$CH_3SO_3H + SO_3 \rightarrow CH_2(SO_3H)_2, \tag{2}$$

$$CH_3COOH + SO_3 \rightarrow HSO_3CH_2COOH. \tag{3}$$

It is envisioned that the formation of methane sulfonic acid occurs in a manner analogous to that by which acetic acid is formed (see Fig. 5), the critical difference being that SO_3 rather than CO inserts into the Pd–CH_3 bond of $Pd(CH_3)(OSO_3H)$. This process is very similar to that proposed to explain the synthesis of CH_3SO_3H from CH_4 and a mixture of SO_2 and O_2 catalyzed by Pd^{2+} in fuming sulfuric acid [18]. Consistent with this reasoning, the yield of methanesulfonic acid is small for SO_3 concentrations below 18.0 M, then rises rapidly with increasing SO_3 concentration, because an increasing fraction of the dissolved SO_3 is present as free SO_3 rather than as H_2SO_4 (see Fig. 4). Previous studies have also shown that methanesulfonic acid can be readily oxidized by SO_3 in acid medium to form methyl bisulfate [14b]. The sharp rise in methyl bisulfate formation above an SO_3 concentration of 18.0 M seen in Fig. 4 is attributed to this phenomenon. The formation of methane disulfonic acid and sulfoacetic acid via reactions (2) and (3) are very likely initiated in the same manner as the sulfonation of methane. The high yields of these products suggest that the C–H bond of methyl group in methanesulfonic acid and acetic acid is easier to activate than the C–H bonds of CH_4 under conditions of high SO_3 concentration. Consistent with this reasoning, the yield of methane disulfonic acid was found to rise relative to the yield of methanesulfonic acid in studies of the synthesis of methane sulfonic acid from methane conducted in fuming sulfuric acid.

The effects of temperature presented in Table 4 merit some comment. It was shown there that a reduction in the reaction temperature from 180 to 160 °C caused a small decrease in the yield of acetic acid and a significant decrease in the yield of sulfur-containing acids. These trends suggest that the apparent activation energy for the formation of the latter class of products is higher than that for the formation of acetic acid.

5. Conclusion

The results of this study show that the selective oxidation of methane to acetic acid catalyzed by Pd^{2+} cations in sulfuric acid is strongly affected by the O_2/CH_4 ratio of the feed gas, the total pressure of the feed, the concentration of SO_3 in the sulfuric acid, and the concentration of Pd^{2+} present in solution at the onset of reaction. The yield of acetic acid, the primary product of methane oxidation, increases with increasing O_2/CH_4 ratio for a fixed CH_4 partial pressure and with increasing total reactant pressure for a fixed O_2/CH_4 ratio. The increase in acetic acid yield as a consequence of increasing O_2/CH_4 ratio is accompanied by only a modest loss in selectivity to oxygen-containing organic products, and the increase in total pressure of CH_4 and O_2 at a fixed O_2/CH_4 ratio results in a slight rise in the yield of acetic acid. A significant finding of this work is that the retention of initially dissolved Pd^{2+} can be raised to as high as 96%, by raising the O_2/CH_4 ratio and total feed pressure. The reducing agents for the reduction of Pd^{2+} to Pd^0 are found to be CH_3OSO_3H and CO, both of which are produced as intermediates in the oxidation of CH_4. CO is also established to be an essential intermediate in the formation of CH_3COOH and is the source of the carboxylate group in this product. The yield of acetic acid is also a strong function of the concentration of SO_3 in the sulfuric acid. Maximum acetic acid yield is achieved at an SO_3 concentration of 18.0 M, corresponding to 96% H_2SO_4. Below this level, the solubility of methane decreases, as does the oxidation potential of the solution. Above an SO_3 concentration of 18.7 M, corresponding to fuming sulfuric acid, the yield of acetic acid falls to negligible levels, and the yield of CH_3OSO_3H rises rapidly.

A possible mechanism for the oxidation of methane to acetic acid has been proposed, as shown in Fig. 5. In this mechanism, $Pd(OSO_3H)_2$ is envisioned as the species responsible for the activation of CH_4. CH_3OSO_3H is formed as an intermediate by reaction of $(CH_3)Pd(OSO_3H)$ with sulfuric acid. This product reduces Pd^{2+} to Pd^0 producing CO, which can in turn reduce additional Pd^{2+}. CO inserts into the Pd–CH_3 bond of $(CH_3)Pd(OSO_3H)$ to form $(CH_3CO)Pd(OSO_3H)$, which can then react with sulfuric acid to form CH_3COOH. Pd^0 is reoxidized by O_2 and H_2SO_4 to Pd^{2+}. The second role of O_2 is to oxidize CO to CO_2. Thus, O_2 is essential for maintaining Pd^{2+} in solution, as well as the level of CO in the system. Large concentrations of CO are undesirable, because CO adsorption by $Pd(OSO_3H)_2$ competes with the availability of this species to activate CH_4.

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