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Synthesis of Mixed Acid Anhydrides from Methane and Carbon Dioxide in Acid Solvents

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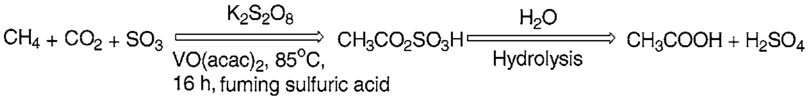
ABSTRACT



$$CH_4 + CO_2 + SO_3 \xrightarrow[\text{VO(acac)}_2,\ 85^{\circ}C,\ 16\ h,\ \text{fuming sulfuric acid}]{K_2S_2O_8} CH_3CO_2SO_3H \xrightarrow[\text{Hydrolysis}]{H_2O} CH_3COOH + H_2SO_4$$

Direct reaction of methane and CO_2 in fuming sulfuric acid

The reaction of CH_4 with CO_2 has been performed in anhydrous acids using VO(acac)$_2$ and $K_2S_2O_8$ as promoters. NMR analysis establishes that the primary product is a mixed anhydride of acetic acid and the acid solvent. In sulfuric acid, the overall reaction is $CH_4 + CO_2 + SO_3 \rightarrow CH_3C(O)–O–SO_3H$. Hydrolysis of the mixed anhydride produces acetic acid and the solvent acid. When trifluoroacetic acid is the solvent, acetic acid is primarily formed via the reaction $CH_4 + CF_3COOH \rightarrow CH_3COOH + CHF_3$.

The discovery and development of catalytic processes for the conversion of methane to commodity chemicals and liquid fuels has been the subject of considerable research.[1] Today, such products are produced in a multistep process, which begins with the reforming of methane to synthesis gas followed by the catalyzed conversion of this mixture of H_2 and CO_x ($x = 1, 2$) to produce hydrocarbons and/or oxygenated products (e.g., aldehydes, alcohols, carboxylic acids). Since 65−75% of the capital cost of this indirect approach is associated with methane reforming, there is an ongoing interest in identifying strategies for the direct conversion of methane to products.

One of the targeted products for the direct conversion of methane is acetic acid. Due to favorable thermodynamics ($CH_4 + CO + 1/2O_2 \rightarrow CH_3COOH$, $\Delta G^{\circ}_{rxn} = -202$ kJ/mol), a number of authors have focused on the liquid-phase carbonylation of methane to acetic acid.[2] As an alternative, it is interesting to consider the reaction of CH_4 with CO_2. Fujiwara and co-workers have reported that VO(acac)$_2$ in combination with $K_2S_2O_8$ promotes the reaction of methane with CO_2 to acetic acid in CF_3COOH as the solvent.[3] The conversion of methane to acetic acid is reported to be as high as 97%. Spivey and co-workers have questioned whether the acetic acid observed by Fujiwara and co-workers was formed by the reaction of methane with carbon dioxide, since this reaction is thermodynamically unfavorable ($CH_4 + CO_2 \rightarrow CH_3COOH$, $\Delta G^{\circ}_{rxn} = +55$ kJ/mol), and, hence, the fractional conversion of methane is predicted to be no more than 1.6×10^{-6} at any operating conditions. As an alternative, Spivey and co-workers proposed that acetic acid is formed by the reaction of methane with the solvent, CF_3COOH.[4] Since this reaction ($CH_4 + CF_3COOH \rightarrow CH_3COOH + CHF_3$, $\Delta G^{\circ}_{rxn} = -52$ kJ/mol) is thermo-

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dynamically favorable, it could readily explain the observed conversions of methane to acetic acid. In the present study, we have confirmed that the reaction proposed by Spivey and co-workers occurs. More importantly, we have discovered that under completely anhydrous conditions, CH_4 and CO_2 react with the acid solvent to form a mixed anhydride, $CH_3C(O)-O-C(O)CF_3$. Upon hydration, the mixed anhydride forms acetic acid and trifluoroacetic acid. We have also found that formation of mixed acid anhydrides will occur in sulfuric acid and trifluoromethanesulfonic acid.

In a typical reaction,[5] CH_4 and CO_2 were reacted at 85 °C in a high pressure, glass-lined autoclave. $K_2S_2O_8$ and a small amount of $VO(acac)_2$ were dissolved in an anhydrous acid (CF_3COOH, H_2SO_4, or CF_3SO_3H). Reactions were carried out for 16 h. Upon completion of the reaction, 2 g of water were added to the liquid phase in order to hydrolyze any anhydrides. The acetic acid thus formed was identified and quantified by ^1H NMR. The only major byproducts were the methyl esters of the acid solvents (Figure 1).

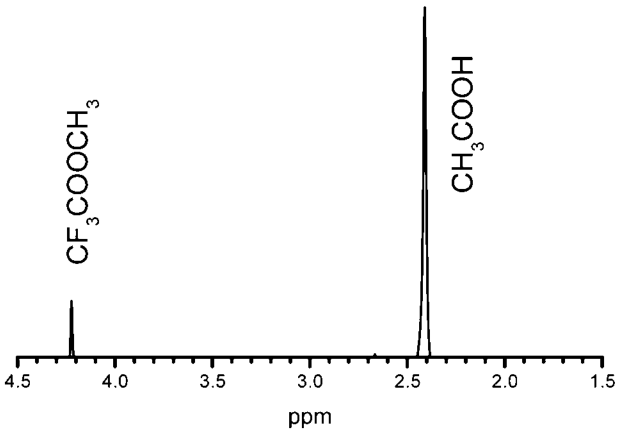

Figure 1. ^1H NMR of the reaction mixture in CF_3COOH. Reaction conditions: CF_3COOH (29.5 g), $(CF_3CO)_2O$ (0.9 g), $K_2S_2O_8$ (10 mmol), $VO(acac)_2$ (0.5 mmol), CH_4 (80 psig), CO_2 (120 psig), 17 h, 80 °C. Yield (based on methane conversion) is 40% acetic acid and ~3.6% methyl trifluoroacetate.

Under the best conditions reported by Fujiwara et al.,[3] we observed a 40% methane conversion to acetic acid for CO_2 pressure of 120 psig (Figure 1). This was lower than the methane conversion reported by Fujiwara et al., 97%, because of the larger headspace volume of our autoclave, which results in a larger reservoir of methane. ^{13}C NMR showed that $^{13}CH_3COOH$ is formed when $^{13}CH_4$ reacts with CO_2. In the absence of CO_2, the conversion of CH_4 to acetic acid was 26%. To verify whether CO_2 contributes to the formation of acetic acid, we carried out the reaction of CH_4 with $^{13}CO_2$ in CF_3COOH. As seen in Figure 2, $CH_3{}^{13}COOH$ was detected by ^{13}C NMR. Thus, 14% of the CH_4 was converted to CH_3COOH via a reaction involving CO_2. To confirm that the balance of the acetic acid formed arises from the reaction of CH_4 with the solvent, CF_3COOH, the liquid phase was analyzed by ^{19}F NMR to look for the anticipated coproduct, CHF_3.[6]

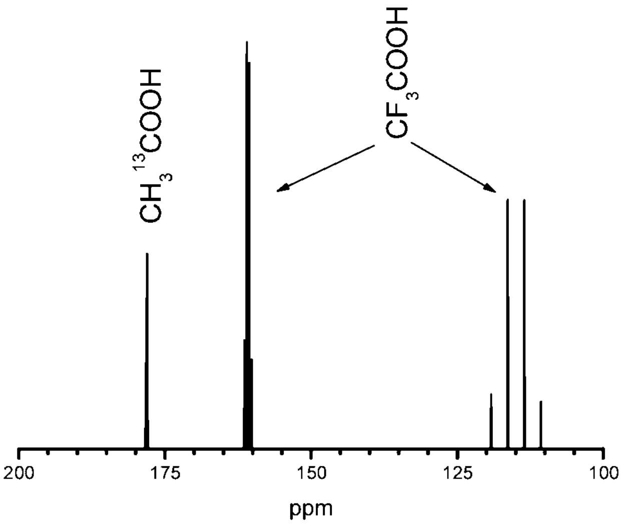

Figure 2. ^{13}C NMR of the reaction mixtures in CF_3COOH. Reaction conditions: CF_3COOH (29.5 g), $(CF_3CO)_2O$ (0.9 g), $K_2S_2O_8$ (10 mmol), $VO(acac)_2$ (0.5 mmol), CH_4 (80 psig), $^{13}CO_2$ (115 psig), 17 h, 80 °C.

As seen in Figure 3, the presence of CHF_3 is clearly identified by the peaks at −15.1 and −15.3 ppm; the peaks at −12.4 and −13.5 ppm are due to the solvent. Although not quantitatively, these data clearly demonstrate that CF_3COOH has reacted with CH_4 to produce CH_3COOH and CHF_3.

To isolate the reaction of CH_4 with CO_2, CF_3COOH was replaced by other solvents, while holding all other reaction conditions constant. Table 1 shows the effect of solvent composition on the conversion of CH_4 to acetic acid. Not surprisingly, the highest conversion was obtained in trifluoroacetic acid, since we now know the solvent directly contributes to the yield. Approximately 7% conversion of

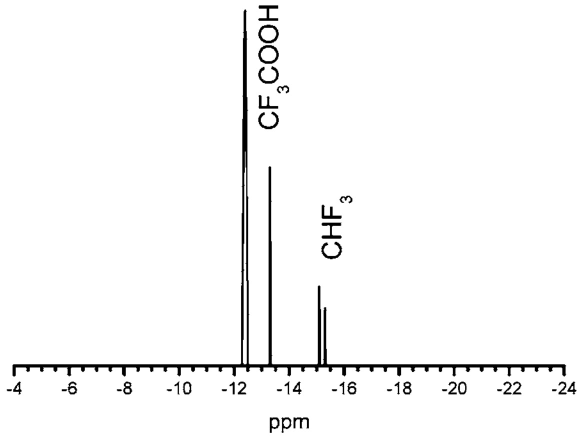

Figure 3. ^{19}F NMR of the reaction mixture in CF_3COOH. Reaction conditions: CF_3COOH (7 g), $(CF_3CO)_2O$ (3 g), $K_2S_2O_8$ (10 mmol), $VO(acac)_2$ (0.16 mmol), CH_4 (100 psig), CO_2 (120 psig), 85 °C, 10 h. The peaks at −12.4 and −13.3 ppm are associated with CF_3COOH. The peaks at −15.1 and −15.3 ppm are CHF_3.

Table 1. Direct Reaction of CH_4 and CO_2 in Different Solvents

entry	solvent	% conversion of CH_4 to CH_3COOH	byproducts
1	CF_3COOH^b	16	CF_3COOCH_3
2	C_9F_{20}	0	
3	$H_2SO_4{}^c$	7	CH_3OSO_3H
4	$CF_3SO_3H^d$	13	$CF_3SO_3CH_3$

[a] Reaction conditions: CH_4, 80 psig; CO_2, 120 psig; $K_2S_2O_8$, 1 g (3.7 mmol); $VO(acac)_2$, 0.043 g (0.16 mmol); solvent, 10.0 g; 85 °C; 16 h. [b] Trifluoroacetic acid anhydride, 3.0 g, was used to make the system anhydrous. [c] SO_3, 3.0 g, was used. [d] Trifluoromethanesulfonic acid anhydride, 3.0 g, was used.

CH_4 to acetic acid was obtained when sulfuric acid was used as the solvent, whereas 13% conversion of CH_4 to acetic acid was obtained using trifluoromethanesulfonic acid. Small amounts of methyl esters of the acidic solvents were produced as byproducts in each reaction. Interestingly, in fuming H_2SO_4, the presence of CO_2 seems to inhibit the production of CH_3SO_3H. To ensure that any CO or CO_2 produced by the oxidation of CH_4 by $K_2S_2O_8$ under the reaction conditions was not responsible for acetic acid formation, a blank reaction was performed in the absence of CO_2. The absence of an acetic acid peak in the ^1H NMR spectrum (Figure 4) demonstrates clearly that the only source of CO_2 is that which is originally supplied to the reactor.

To elucidate the pathway of acetic acid formation from CH_4 and CO_2 in acid solvents, the same reaction in sulfuric acid was run, but ^1H NMR was performed prior to addition of water to the product mixture (Figure 5). The product obtained in this reaction was identified as the mixed anhydride of acetic acid and sulfuric acid, $CH_3C(O)-O-SO_3H$. Upon the addition of water, this mixed anhydride hydrolyzes to produce acetic acid and H_2SO_4. The presence of acetic acid was confirmed by distilling a water−acetic acid azeotrope and then analyzing this mixture by ^1H NMR and Raman spectroscopy.[7]

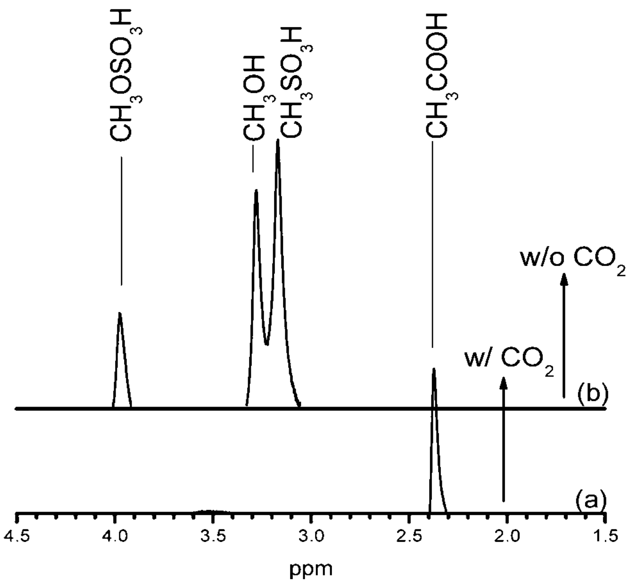

Figure 4. ^1H NMR of the reaction mixtures in H_2SO_4. Reaction conditions: H_2SO_4 (10.0 g), SO_3 (3.0 g), $K_2S_2O_8$ (3.7 mmol), $VO(acac)_2$ (0.16 mmol), 80 psig of CH_4 (24.6 mmol), 16 h, 85 °C. (a) CO_2 (120 psig, 34.9 mmol) was added to the autoclave, and acetic acid was formed. (b) No CO_2 was added to the reaction, and only byproducts were formed. The excess water added after completion of the reaction enables CH_3OH to exist in equilibrium with CH_3OSO_3H for case b.

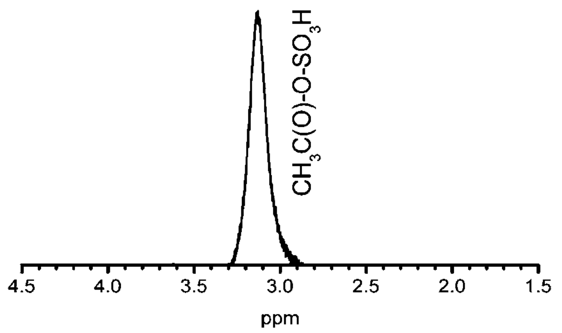

Figure 5. ^1H NMR of the reaction mixtures in H_2SO_4. Reaction conditions: H_2SO_4 (10.0 g), SO_3 (3.0 g), $K_2S_2O_8$ (3.7 mmol), $VO(acac)_2$ (0.16 mmol), CH_4 (80 psig), 16 h, 85 °C. Spectrum was taken prior to hydrolysis of the product solution.

Thus, it appears that the formation of acetic acid involves the following stoichiometric reactions:

$$CH_4 + CO_2 + H_2SO_4 \rightarrow CH_3C(O)-O-SO_3H + H_2O \quad (1)$$

$$\Delta G^\circ_{rxn} \cong +60 \text{ kJ/mol}$$

$$H_2O + SO_3 \rightarrow H_2SO_4 \quad (2)$$

$$\Delta G^\circ_{rxn} = -79 \text{ kJ/mol}$$

$$CH_3C(O)-O-SO_3H + H_2O \rightarrow CH_3COOH + H_2SO_4 \quad (3)$$

$$\Delta G^\circ_{rxn} \cong -5 \text{ kJ/mol}$$

While reaction 1 is thermodynamically unfavorable, when it is coupled with reaction 2, the overall thermodynamics

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(5) In a 100 mL glass-lined Parr autoclave, 3.7 mmol (1 g) of $K_2S_2O_8$, 0.16 mmol (0.043 g) of VO(acac), 3 g of $(CF_3CO)_2O$, and 7 g of CF_3COOH were charged together with a small Teflon-coated magnetic stir bar. (The solvent was chilled to 5−8 °C during these additions to minimize the thermal decomposition of $K_2S_2O_8$.) The reactor was then purged with N_2 to expel the air out of the system. It was then pressurized first with 120 psig of CO_2 and then finally with 80 psig of methane from the adjacent connecting cylinders. The reactor was heated to 85 °C under stirring and maintained for 16 h. After the stipulated period of time, the reactor was quenched with ice and opened to collect the reaction mixture. Then, 2.0 g of water was slowly added to the mixture that was then filtered before taking it to ^1H NMR analysis. D_2O was used in a capillary as the lock reference. The corresponding chemical shift for acetic acid was 2.3 to 2.4 ppm, depending on the concentration of acetic acid in the mixture.

(6) After the stipulated reaction period, the reactor was cooled to 5 °C, and the gases were very slowly vented. Upon addition of 2 g of water, the residual reaction mixture was immediately taken for ^{19}F NMR analysis.

become favorable.[8] Reaction 3 represents the postreaction addition of water, which produces acetic acid and regenerates sulfuric acid.

VO(acac)$_2$ and $K_2S_2O_8$ are both essential to the formation of mixed acid anhydrides, since the exclusion of one or the other results in no products. The amount of $K_2S_2O_8$ required is greater by an order of magnitude than the amount of VO(acac)$_2$. When the amount of $K_2S_2O_8$ was reduced to the level of that of VO(acac)$_2$, no reaction was observed between CH_4 and CO_2, using fuming sulfuric acid as the solvent. This result stands in contrast to what we found in our studies of methanesulfonic acid, where only small amounts of $K_2S_2O_8$ were needed to promote the reaction $CH_4 + SO_3 \rightarrow CH_3SO_3H$ in fuming sulfuric acid.[9]

While the specific functions of VO(acac)$_2$ and $K_2S_2O_8$ have not been identified, it is possible to suggest a role for each component. $K_2S_2O_8$ cleaves thermolytically to $KSO_4^•$. In studies of the $K_2S_2O_8$-initiated sulfonation of CH_4 to methanesulfonic acid, it has been proposed that the radicals produced by dissociation of the initiator react with CH_4 and produce $CH_3^•$ radicals.[9] A similar function for $K_2S_2O_8$ is envisioned in the present study. By analogy to the reaction of $CH_3^•$ with SO_3 to form $CH_3SO_3^•$, it is possible to propose that $CH_3^•$ reacts with CO_2 to form $CH_3CO_2^•$. However, in contrast to $CH_3SO_3^•$, $CH_3CO_2^•$ is thermodynamically unstable. We propose that the role of V(IV) in VO(acac)$_2$ is to stabilize $CH_3CO_2^•$ as $CH_3CO_2^-$. In support of this proposal, it is observed that peracetic acid decomposes to CH_4 and CO_2 but that these products are not formed when VO(acac)$_2$ is added to the reaction mixture.[10] In fuming sulfuric acid, the formation of $CH_3C(O)-O-SO_3H$ can then be envisioned to proceed via the reaction of $CH_3CO_2^-$ with SO_3 and H^+.

In conclusion, we have shown that in anhydrous acid, CH_4 reacts with CO_2 to form an anhydride of acetic acid and the acid solvent. The water formed in this reaction must be absorbed in an accompanying reaction for the overall thermodynamics to be favorable. When the solvent is CF_3COOH, acetic acid is formed predominantly by the reaction of CH_4 with the solvent to produce CHF_3 and CH_3COOH. In this case, the formation of a mixed anhydride also produces acetic acid, but to a smaller extent. In all cases, the addition of water to the mixed anhydride produces acetic acid and the solvent acid.

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[7] C−H stretch (methyl group) of acetic acid was 2951 cm^{-1}.

[8] Free energy of formation of each species was taken from standard tables except the mixed anhydride for which the value was calculated using group contributions.

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[10] Into a 50 mL Parr autoclave was charged 7 g of peracetic acid (32% solution in dilute acetic acid) and heated to 110 °C under 110 psig N_2 for 2 h. The reactor was then cooled, and the gases in the headspace were analyzed by gas chromatography. The products contained a 1:1 mixture of CH_4 and CO_2. A similar reaction was carried out in which 1 g of VO(acac)$_2$ was added to the reaction mixture. Analysis of the autoclave headspace gas showed no CH_4 in this case.