ELSEVIER

Catalysis Today 35 (1997) 407–413

CATALYSIS TODAY

Activation of methane with organopalladium complexes

Charles E. Taylor *, Richard R. Anderson, Richard P. Noceti

US Department of Energy, Pittsburgh Energy Technology Center, P.O. Box 10940, Pittsburgh, PA 15236-0940, USA

Abstract

Selective, direct oxidation of methane to methanol is a process of scientific interest and industrial importance. Reports have appeared in the literature describing the use of organometallic complexes to effect this transformation [1–5]. Investigation of one of these reaction schemes in our laboratory has produced interesting results. Our research effort was an extension of work reported by Sen et al. [3]. The reported reaction occurs between methane (at 800 psig 5.52 MPa) and palladium(II) acetate in trifluoroacetic acid at 80°C (Eq. (1)). The product, methyl trifluoroacetate, is readily hydrolyzed to produce methanol and trifluoroacetic acid. It is reported that methyl trifluoroacetate is produced with reported conversions, calculated on palladium metal recovery, of ~ 60 percent.

$$CH_4 + Pd(O_2CCH_3)_2 \xrightarrow[80°C,\,800\,PSIG]{CF_3COOH} CF_3CO_2CH_3 + Pd. \qquad (1)$$

Keywords: Methane activation; Methanol; Organopalladium complexes; Palladium

1. Introduction

Selective, direct oxidation of methane to methanol is a process of scientific interest and industrial importance. There are vast proven reserves of geologic methane in the world but, unfortunately, a large fraction of these reserves are in regions where there is little local demand for methane and where it is not economically feasible to transport it to a market. Methanol, the initial product of methane oxidation, is a desirable product of conversion because it retains much of the original energy of the methane while satisfying transportation and storage requirements. A liquid at room temperature, methanol could be transported to market utilizing the existing petroleum pipeline, tanker network, and distribution infrastructure. Methanol may be used directly as a fuel or be converted to other valuable products (i.e. other transportation fuels, fuel additives, or chemicals). The feasibility of an oxidative conversion of methane to methanol by organometallic reagents was the subject of recent investigations in our laboratory.

2. Background

Recently, several reports have discussed the activation of methane's carbon–hydrogen bond by the use of organometallic complexes [1–5]. One of these reactions [3] appeared to be

---

* Corresponding author.

PII S0920-5861(96)00213-1

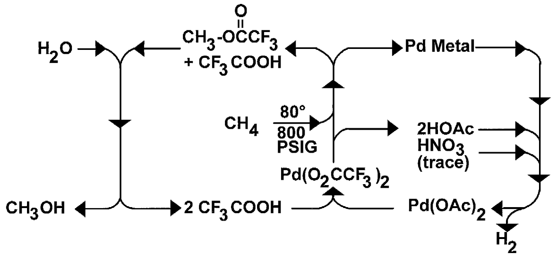

Fig. 1. Reaction pathway for the conversion of methane to methanol using organopalladium complexes.

promising and was selected for study. The reaction of interest occurs between methane (at 800 psig 5.52 MPa) and palladium(II) acetate in trifluoroacetic acid at 80°C (Eq. (1)). The product, methyl trifluoroacetate, is readily hydrolyzed to produce methanol and trifluoroacetic acid. Our objective was to investigate this reaction scheme, attempt to reproduce the results reported in the literature, and explore the possibility of using this reaction pathway in a commercial process. On initial examination, this reaction scheme appeared not to have much commercial application because of long reaction times (~ 150 hours) and batch mode operation. The reported conversions of 60% were intriguing, but were calculated on the amount of Pd metal recovered from the reactor system. When conversions are calculated on the basis of methane consumed, they are on the order of about 3 percent, of which about 33 percent of the converted methane is methyl trifluoroacetate, a net conversion of methane to product of 1 percent. In spite of this and in light of the reported catalytic reaction, it was decided to examine this reaction in some detail. A reaction scheme similar to that shown in Fig. 1 could be of commercial interest if all steps could be realized at reasonable conversions and with minimal side reactions. For purposes of discussion, the scheme may be separated into three major parts: (1) conversion of methane to methyl trifluoroacetate, (2) hydrolysis of methyl trifluoroacetate to methanol and trifluoroacetic acid, and (3) conversion of palladium metal to palladium(II) trifluoroacetate. The focus of the work and this report is the conversion of methane to methyl trifluoroacetate because parts 2 and 3 are known reactions which can be made to occur quantitatively.

3. Experimental

All reactions were conducted in a sealed, 0.5-in (1.27-cm) o.d. × 12-in (30.5-cm) silica-lined stainless-steel batch reactor (Fig. 2). Total volume of the reactor system was < 35 mL. The reactor was lined by Restek, Inc. utilizing a chemical vapor deposition technique that is used to coat capillary GC columns. In order to reproduce the earlier work, experimental conditions were the same as those reported by Sen et al. [3]. In a typical experiment, 0.15 g of palladium(II) acetate was dissolved in 5.00 g of trifluoroacetic acid and placed in the reactor. After being connected to the gas manifold, the reactor was purged several times with helium at 1000 psig (6.89 MPa), followed by several purges of methane with a final methane pressure of 800 psig (5.52 MPa). The reactor was then isolated from the gas manifold and heated by immersion in a silicone–oil bath. Pressure was monitored during the experiment by a pressure transducer. Blank runs followed the same proce-

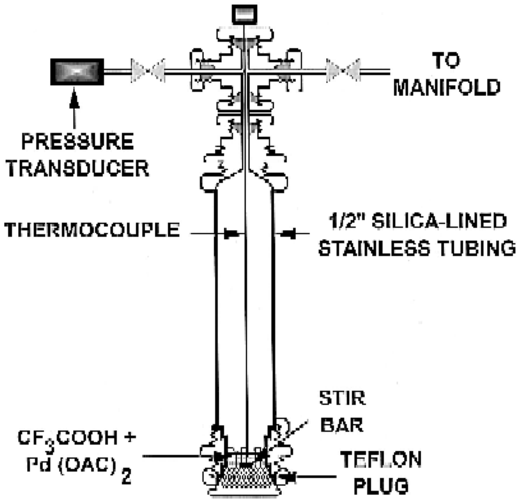

Fig. 2. Schematic reactor.

dure with the exception of helium replacing methane.

After removal of the reactor's liquid contents, the reactor was filled with deionized water, capped, and placed in an 720-W ultrasonic cleaner for one hour. The reactor contents plus washings were then passed through a preweighed 0.50-μm Teflon® filter and the residue air dried. This material was removed and identified by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS).

For labeling studies, $^{13}CH_4$, rated by the supplier at 99 + % isotopic purity, was supplied in 1-L cylinders at 20 psig (0.14 MPa) pressure. The contents of two cylinders were required to obtain the necessary >800 psig (5.52 MPa) pressure for reaction. The reactor was rinsed with 5.0 g (3.3 mL) of dry trifluoroacetic acid, purged several times with helium at 1000 psig (6.89 MPa), charged with reactants, and purged again several times with helium at 1000 psig (6.89 MPa). The reactor was then immersed in a liquid nitrogen bath. When the temperature had reached −190°C, the reactor was connected to a mechanical vacuum pump and evacuated. The reactor was then isolated from the vacuum pump and, while still immersed in liquid nitrogen, was connected to the cylinders of $^{13}CH_4$ to allow transfer of the cylinder's contents to the reactor. After transfer of the cylinder's contents, the reactor was sealed and placed in the silicone oil bath.

When necessary, the gases were dried prior to entering the reactor by passing through an 8-ft (2.44-m) × 1/4-in (0.64-cm) coil of stainless-steel tubing immersed in an acetone/dry ice bath.

Gaseous components were analyzed on a Hewlett-Packard 5730 gas chromatograph. Isotopic ratios of the gaseous samples were determined on an Extrel EL-150 mass spectrometer. Liquid samples were analyzed on a Hewlett-Packard 5988A GC/MS system.

4. Results and discussion

The results of our experiments are summarized in Table 1. During the early experiments (Runs 241 and 242) we were able to reproduce the results reported by Sen et al. [3]. We observed the production of methyl trifluoroacetate concomitant with a fine metallic powder. Analysis of the powder by SEM and EDS showed it to be palladium metal with crystallites of the

Table 1
Experimental results

Run number	$CF_3C(O)$-OCH_3	H_2O	Pd metal recovered (mole%)	CH_4 difference (mole%)	Moles Pd recovered ($x10^4$)	Moles CH4 difference ($x10^3$)	CH_4/Pd metal	% conversion to $CF_3C(O)OCH_3$
241	X	X	83.50	3.00	4.70	4.69	9.98	N/A
242	X	X	77.00	3.13	5.14	3.59	6.99	N/A
243a	X	X	68.30	N/A	4.30	N/A	N/A	N/A
244b			0.00	N/A	N/A	N/A	N/A	N/A
244c			0.00	N/A	0.00	N/A	N/A	N/A
245d	X	X	83.20	N/A	5.76	N/A	N/A	N/A
246	X		39.20	6.42	2.72	4.54	16.72	0.4
248e	Xf		7.88	4.08	0.55	3.07	56.32	N/A
250	X		4.21	4.01	0.29	5.94	203.84	N/A
252	X		7.46	10.30	0.49	6.90	141.15	N/A
254	X		8.29	9.87	0.55	8.44	153.45	0.8

N/A = Not applicable.[a] No CH_4, wet CF_3COOH.[b] No CH_4, dry CF_3COOH before heating in 800 PSIG He.[c] No CH_4, dry CF_3COOH after heating in 800 PSIG He.[d] Product of Run 244 with $10X$ excess H_2O added, heating in 800 PSIG He.[e] $^{13}CH_4$ used.[f] Mixture of $CF_3C(O)O^{13}CH_3$ and $CF_3C(O)O^{12}CH_3$.

order of 1 micron in size. Quantitative analysis of the palladium metal residue indicated that $>80\%$ of the palladium acetate was recovered as palladium metal. Methane conversion, calculated by the difference in pressure from the beginning to the end of the run, was on the order of 3 mol%. A typical plot of temperature and pressure as a function of time during the course of a typical run shows that the majority ($\sim 93.5\%$) of the methane was consumed during the first 30 hours of the reaction (Fig. 3).

Analysis of the reaction mixture from Run 241 identified several other oxygenated compounds and water. To determine the source of these compounds, the palladium(II) acetate dissolved in trifluoroacetic acid for Run 242 was analyzed prior to the introduction of methane. This analysis revealed the presence of methyl trifluoroacetate, the product of methane oxidation, prior to introduction of methane, and the same components identified before (Table 2).

The trifluoroacetic acid was then analyzed, without added palladium(II) acetate, to determine if the methyl trifluoroacetate and other compounds found in Runs 241 and 242 were present. All the oxygenated compounds previously found, except methyl trifluoroacetate, were detected in the trifluoroacetic acid including a significant quantity of water. A blank run (243) was conducted wherein the methane was replaced with helium at 800 psig, 5.52 Mpa. All reaction conditions and operations were identical to previous runs. This experiment resulted in the production of methyl trifluoroacetate and a 68.30% recovery of palladium metal. The only logical origin of the ester's methyl group is via decarbonylation of the starting material's acetate ligand.

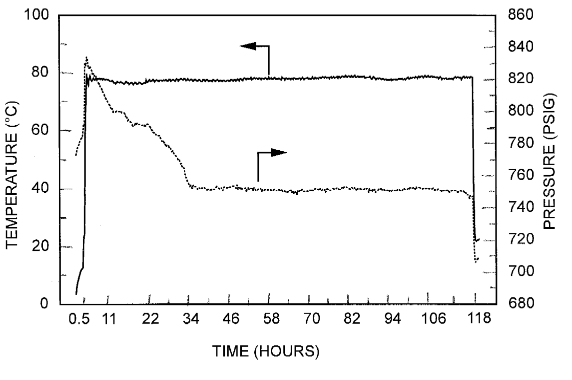

Fig. 3. Temperature and pressure profile of a methane conversion experiment. Reactor charge: 0.15 g of palladium(II) acetate, 5.00 g of trifluoroacetic acid and 800 psig (5.52 MPa) methane. Temperature ————, Pressure · · · · · · ·.

During the above experiments, the gas in the reactor was sampled prior to venting and recovery of liquid products. Analysis of the gas samples by GC showed only the components present in the feed gas.

In order to minimize artifacts in the remaining experiments, dry, high purity trifluoroacetic acid was obtained in sealed ampules, each containing enough acid for a single use. Analysis of this trifluoroacetic acid revealed no detectable quantities of water or the other impurities previously detected. The blank run was repeated. After 150 hours at 80°C and 800 psig (5.52 Mpa) helium, the reactor was opened and the solution removed for analysis and comparison with the starting material. No difference in composition was detected between the two samples. Water (8×10^{-3} moles, a 10 fold excess) was then added to the mixture of Run 244, the reactor was charged with helium at 800 psig, and held at 80°C for 150 hours. Analysis of the products of reaction (Run 245) revealed the presence of methyl trifluoroacetate and methyl acetate. Since no methane was present in the system, the only source of the methyl group in the products is from the displaced acetate. This observation is inconsistent with that of Sen [3] in that he did not observe any deuterium incorporation into the methyl trifluoroacetate when $Pd(O_2CCD_3)_2$ was used.

The first experiment (Run 246) to use both methane and the dry, high purity trifluoroacetic acid resulted in products similar to previous experiments with the exception that the amount of palladium metal recovered was only 39.20 mol%, a reduction of $>50\%$. We attribute this decrease to the absence of side reactions caused by the water in the trifluoroacetic acid.

Table 2
GC / MS analysis of methane / palladium trifluoroacetate reactions

Compound identified	241	242 before	242 after	243 (No CH_4)	244 before (No CH_4)	244 after (No CH_4)	245 run 244 + H_20	246	248 $^{13}CH_4$	250	252	254
CO_2	X	X	X	X	X	X	X	X	X	X	X	X
$CF_3C(O)CH_3$	X	X	X	X			X	X	X	X	X	X
$CH_3C(O)H$	X	X	X	X	X	X	X	X			X	X
$CH_3C(O)OCH_3$							X	X	X	X	X	X
H_2O	X	X	X	X			X					
CH_3COOH	X	X	X	X	X	X	X	X			X	X
$CF_3C(O)CF_3$							X	X	X	X	X	X
CF_3COOH	X	X	X	X	X	X	X	X	X	X	X	X

An experiment (Run 248) was conducted using methane that was isotopically enriched in carbon-13. Oxidation products arising solely from the labelled methane, determined by GC-MS, would eliminate the possibility of products arising from the acetate ligand on the palladium(II) acetate. The reactor was filled as described above. Operating under conditions similar to previous experiments resulted in similar methane conversions but a recovered palladium metal amount of only 7.88 mol%. Analysis of the product mixture revealed both $CF_3C(O)O^{13}CH_3$ and $CF_3C(O)O^{12}CH_3$. Single Ion Monitoring (SIM) analysis of the isotopic ratio of the labeled products gave a $^{13}C/^{12}C$ ratio of 4.98. The composition of the labeled methane was determined by mass spectroscopy to be 93.5% $^{13}CH_4$ and 6.5% $^{12}CH_4$; a ratio of 14.38. This means that $\sim 11\%$ of the methyl carbon in the methyl trifluoroacetate comes from a source other than the labeled methane and confirms our postulate that not all of the product arises from the methane introduced as a reactant.

To test the postulate that the absence of water in the reactor system was responsible for the observed decrease in palladium metal recovery, three experiments were conducted (Runs 250, 252, and 254) where the gases were dried prior to entering the reactor as described above. The reactor was prepared as in the $^{13}CH_4$ experiment. After warming to room temperature, 4.8×10^{-3} grams (2.7×10^{-4} moles) of water was recovered from the drying trap. The result of these experiments is that the methane consumption and product distribution remained the same as previously observed, but that recovery of palladium metal was only 4.21, 7.46, and 8.29 mol%, respectively. This suggests that the presence of water in either the reactants or in the reactor system is responsible for the greater quantities of palladium metal reported in the literature. Water was not detected in the product mixture by GC/MS for these experiments. Quantization of reaction products for Run 254 revealed that 0.13 weight% of the product is methyl trifluoroacetate. This corresponds to a conversion of reactants to the desired product of 0.8%.

Sen et al. [3] postulated that the mechanism of this reaction is electrophilic attack on the methane by Pd(II), followed by reductive elimination to give Pd metal and the alcohol derivative. This mechanism is supported only by the fact that Pd(II) is a strong electrophile and a good two electron oxidant. Our observations do not support the original assumption that the reaction, as stated in Eq. (1), is a 1:1 stoichiometric reaction between methane and palladium(II) trifluoroacetate. The molar balance for the experiments showed that the ratio of methane consumed to palladium metal recovered in our experiments is far from 1:1. The data from the early experiments, when water was present, show that the molar ratio of methane consumed to palladium metal recovered is of the order of 10. In later experiments, when water was removed from the reactants, this ratio is an order of magnitude larger. These inconsistencies leave open the important questions about the reaction mechanism which is key to proper evaluation of this reaction as a method for direct oxidation of methane. If the methane is being consumed by some other reaction not involving palladium, is the palladium(0) being reoxidized to a palladium(II) complex, or are other impurities present in the system?

5. Conclusion

This study has shown that the reaction expressed in Eq. (1) does occur, as confirmed by the production of $CF_3CO_2^{13}CH_3$ from $^{13}CH_4$ and trifluoroacetic acid, but that this reaction is not responsible for all product methyl trifluoroacetate. When a blank experiment was performed using the highest purity starting materials and replacing methane with helium, methyl trifluoroacetate was detected in the product if water was not excluded from the system. The presence of water in the reaction mixture appears to cause the palladium acetate/trifluoroacetate complex to decompose and produce methyl trifluoroacetate and produce the high yields of palladium metal reported in the literature. While there are several unexplained observations and some interesting chemistry occurring in the reaction, further investigation of this process by our group is not warranted. Conversions are low ($>1\%$ of methane) and side reactions consuming the palladium(II) complex argue against future commercialization.

6. Disclaimer

Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

Acknowledgements

We would like to acknowledge the technical assistance of Donald V. Martello, Joseph P. Tamilia and Curt M. White.

References

[1] R.H. Crabtree, Chem. Rev., 85 (1985) 245–269.
[2] J. Schwartz, Acc. Chem. Res., 18 (1985) 302–308.
[3] (a) A. Sen, Platinum Metals Rev., 3 (1991) 126–132; (b) L.-C. Kao, A.C. Hutson and A. Sen, J. Am. Chem. Soc., 113 (1991) 700–701; (c) E. Gretz, T.F. Oliver and A. Sen, J. Am. Chem. Soc., 109 (1987) 8109–8111; (d) A. Sen, E. Gretz, T.F. Oliver and Z. Jiang, New J. Chem., 13 (1989) 755–760; (e) A. Sen, Acc. Chem. Res., 21 (1988) 421–428.
[4] M.N. Vargaftik, I.P. Stolarov and I.I. Moiseev, J. Chem. Soc, Chem. Commun. (1990) 1049–1050;
[5] G.T.P. Harper, R.S. Shinomoto, M.A. Deming and T.C. Flood, J. Am. Chem. Soc., 110 (1988) 7915–7916.