

Facile and Selective Carbonylation of Methane in Superacids

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This paper is dedicated to Professor Roger Sheldon on the occasion of his 60th birthday.

Abstract: The carbonylation of CH₄ with carbon monoxide in superacids HF/SbF₅ or HSO₃F/SbF₅ leads to the *exclusive and quantitative* formation of the acylium ion ([CH₃CO]⁺[SbF₆]⁻) with the concomitant stoichiometric formation of SbF₃.

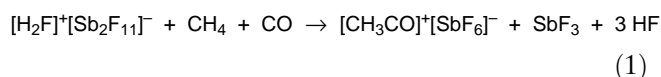
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Methane (CH₄), the primary component of natural gas, is mostly available in large quantities only in remote locations. Since the transportation of liquid natural gas is expensive, conversion of CH₄ to transportable chemicals at remote sites could be a very attractive approach for natural gas utilization.^[1] Protection of the initial product (CH₃-X) from secondary reactions remains a central challenge in the development of CH₄ conversion schemes.^[2] The stabilization of the C-H bonds in CH₃-X by electron-withdrawing groups such as -OSO₃H has shown success in overcoming this limitation.^[3] As part of our programs on alkane activation^[4-6] and high-pressure NMR for catalyst development (HP-NMR),^[7] we have found that the carbonylation of CH₄ with carbon monoxide in superacids HF/SbF₅ or HSO₃F/SbF₅ leads to the *exclusive and quantitative* formation of acylium ion [CH₃CO]⁺ with the concomitant stoichiometric formation of SbF₃. This unprecedented selectivity is achieved because the positively charged primary activation product [CH₃CO]⁺ will react with neither CH₄, CO, nor the extremely strong electrophile HF/SbF₅ to yield secondary products.

When HF/SbF₅ (1:1, a source of [H₂F]⁺[Sb₂F₁₁]⁻) is allowed to react with CH₄ and CO at 80 °C in a sapphire HP-NMR tube, the sole product derived from CH₄ is [CH₃CO]⁺ (Figure 1) {in this extremely strong acid CO is in equilibrium with the formyl cation [HCO]⁺ and formyl fluoride H(F)CO^[6]}. Reaction of CH₄ and CO

with the 1000-fold weaker^[8] superacid HSO₃F/SbF₅ (1:1) at 80 °C also yields exclusively [CH₃CO]⁺ (Figure 2). If the reaction mixture is quenched with H₂O, quantitative formation of acetic acid is achieved (Figure 2) and the antimony species is hydrolyzed. When CO (7.9 mmol) and CH₄ (8.5 mmol) (total pressure 80 atm) were reacted with HSO₃F/SbF₅ (1:1) (5.46 mmol) at 120 °C, no further reaction occurred once 2.7 mmol of CH₄ and CO (one-half the total moles of SbF₅ available) were consumed.

Furthermore, visual inspection of the HP-NMR tubes under pressure revealed the formation of a colorless solid which was isolated and shown by infrared analysis to be a mixture of [CH₃CO]⁺[SbF₆]⁻ [bands at 1618 and 662 cm⁻¹]^[9] and SbF₃ [bands at 619 and 575 cm⁻¹].^[10] In accordance with these results, we conclude that the formation of [CH₃CO]⁺[SbF₆]⁻ proceeds with the concomitant stoichiometric formation of SbF₃ and HF, as shown in Equation 1.



Unlike previously examined examples of CH₄ activation in liquid superacids,^[13-16] the reported carbonylation reactions are completely selective within HP-NMR detection limits. Reaction in a sapphire NMR tube of ethane (CH₃CH₃) (17 atm) and ¹³CO (20 atm) with HF/SbF₅ at 80 °C for 4 h yields a mixture of [CH₃¹³CO]⁺ (δ¹³C = 149 ppm, see Figures 1–3) and [CH₃CH₂¹³CO]⁺ (δ¹³C = 151 ppm). Under these conditions [CH₃CH₂-CO]⁺ did not convert to [CH₃CO]⁺, indicating that the latter is derived directly from CH₃CH₃. Since [CH₃CH₂-CO]⁺ was not observed during CH₄ carbonylation, we conclude that no CH₄ coupling took place in the presence of CO.

It has been shown that the reaction of CH₄ and CO proceeds slowly in neat SbF₅ at 60 °C resulting in [CH₃CO]⁺ and, upon aqueous work-up, acetic acid.^[11,12] It was proposed that SbF₅ oxidizes CH₄ to methyl cation

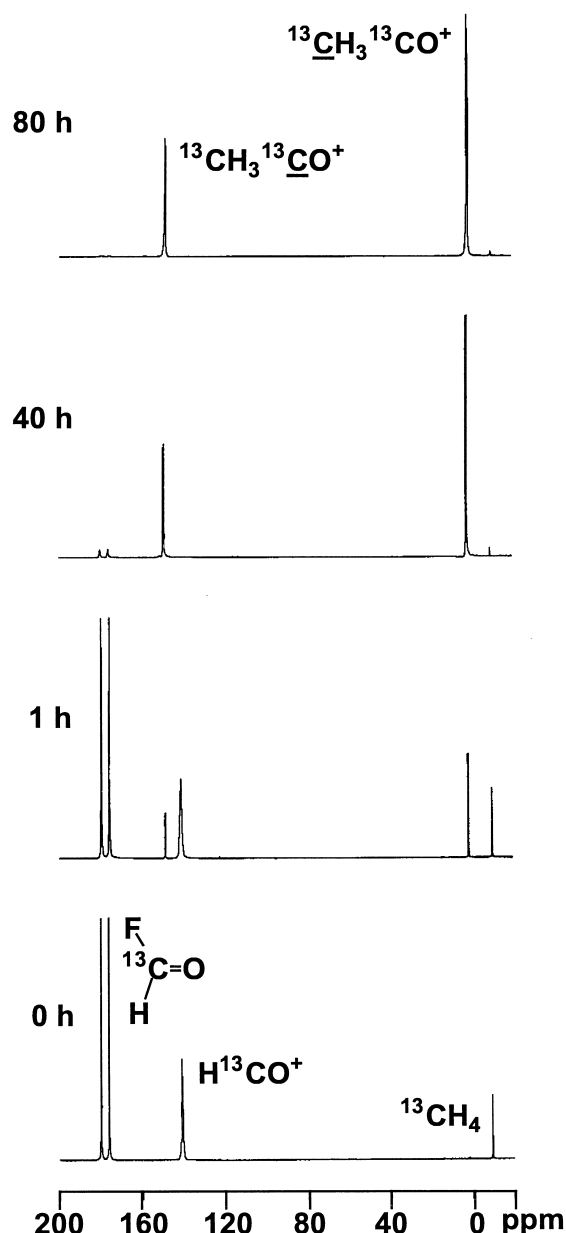
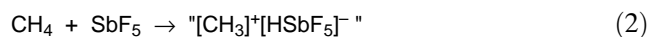


Figure 1. ^{13}C HP-NMR of reaction of $^{13}\text{CH}_4$ (34 atm), ^{13}CO (19 atm), and HF/SbF_5 (1:1) (15.0 mmol) at 80°C (spectra obtained at 25°C).

$[\text{CH}_3]^+$, which is readily trapped by CO to give $[\text{CH}_3\text{CO}]^+$ (Equations 2 and 3).



Although it was later suggested that this reaction probably involves protic acid impurities inadvertently present in the "neat" SbF_5 used (Equation 4),^[13] to the

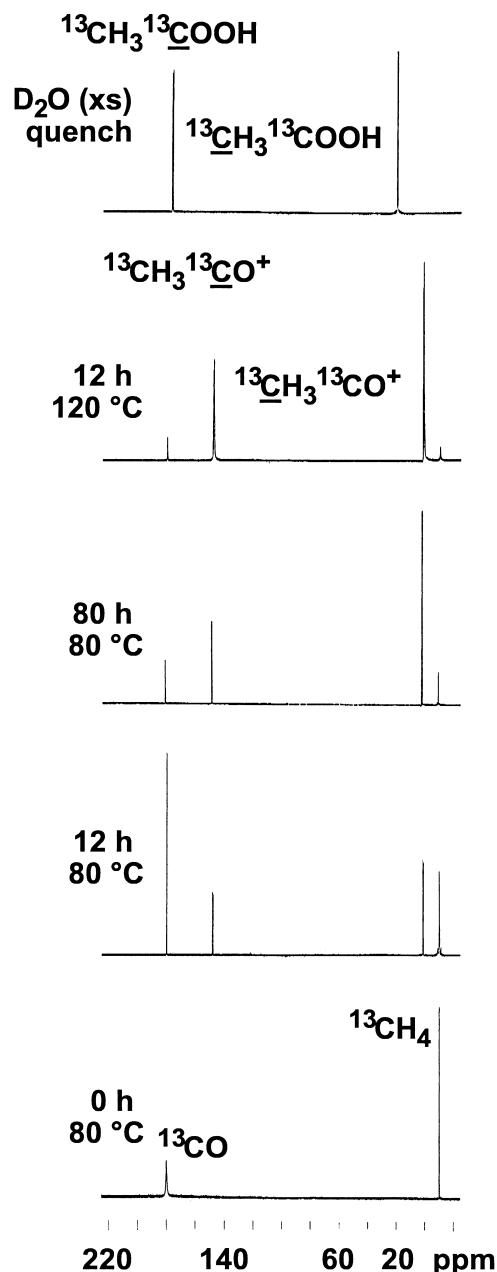


Figure 2. ^{13}C HP-NMR of reaction of $^{13}\text{CH}_4$ (3.5 mmol), ^{13}CO (3.5 mmol), and $\text{HSO}_3\text{F/SbF}_5$ (1:1) (11.5 mmol) at 80°C (spectra obtained at 25°C).

best of our knowledge no supporting data on reaction stoichiometry or yield has been reported at all.



Unpublished results of Olah et al. pertaining to this issue have been noted.^[14] We therefore re-examined the reaction of CH_4 and CO in "neat" SbF_5 . HP-NMR (Figure 3) confirms that protic impurities are present in the SbF_5 as received, and reveals that $[\text{CH}_3\text{CO}]^+$ is the

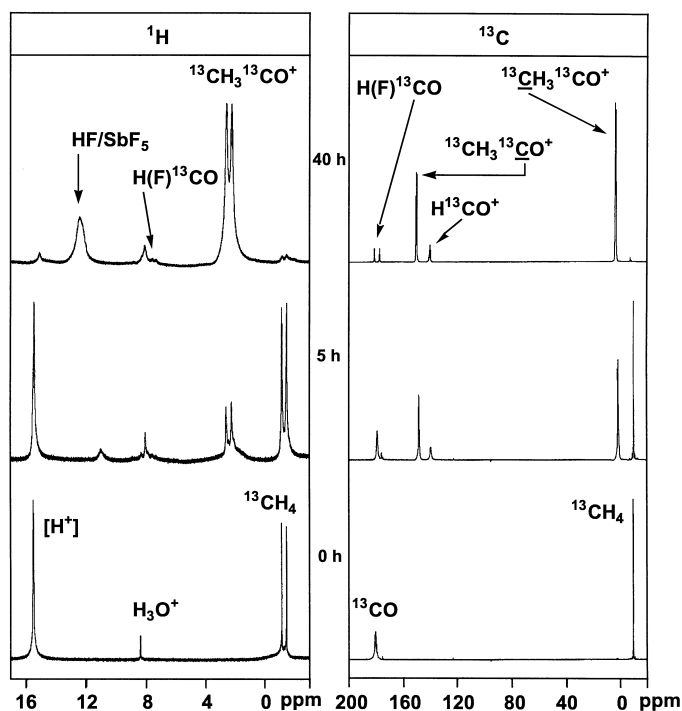


Figure 3. ^1H and ^{13}C HP-NMR of reaction of $^{13}\text{CH}_4$ (4.1 mmol), ^{13}CO (5.5 mmol) (total pressure 43 atm at 25°C), and SbF_5 (11.8 mmol) at 80°C (spectra obtained at 25°C). “[H_3O^+]” represents a protic impurity in the SbF_5 , probably of the type $[\text{H}_2\text{F}]^+ [\text{Sb}_x\text{F}_{5x+1}]^-$.

sole product derived from CH_4 . Furthermore, ^1H and ^{19}F NMR clearly indicate that HF is produced as the reaction proceeds. Indeed, $[\text{HCO}]^+$, which is only observable in HF/SbF_5 (1 : 1),^[6] is present in the reaction mixture (Figure 3). As with CH_4 carbonylation in HF/SbF_5 and $\text{HSO}_3\text{F}/\text{SbF}_5$, formation of a colorless solid (SbF_3) and reaction stoichiometry of $\text{CH}_4:\text{CO}:\text{SbF}_5$ equal to 1:1:2 is observed. These data lead us to conclude that the carbonylation of CH_4 in SbF_5 is also best described by a process analogous to that in Equation 1.

A commonly proposed mechanism^[13–16] that might explain the observed reactivity is a Koch–Haaf^[17] type alkylation of CO by methyl cation (Equation 3), which could form by the elimination of H_2 from $[\text{CH}_5]^+$ (Equation 4). In CH_4 activation with superacids in the absence of CO to yield a mixture of C_n ($n \geq 4$) carbocations, the H_2 evolution predicted by Equation 4 has indeed been observed, but less than one equivalent of H_2 was produced per mole of CH_4 activated.^[15,16] This has been explained in terms of partial consumption of H_2 by SbF_5 .^[13–16] We were unable to observe any H_2 production in the course of CH_4 carbonylation with CO in liquid superacids. While H_2 is known to react readily with SbF_5 at 80°C to form SbF_3 and HF,^[18] ^1H HP-NMR reveals that both H_2 and HF/SbF_5 are still present in spectroscopically observable amounts

after treatment of HF/SbF_5 with H_2 (100 atm) at 80°C for 12 h. This suggests that the reaction of SbF_5 with H_2 is not rapid enough to explain the absence of H_2 under our conditions. We attempted to examine the fate of the hydrogen atom extracted from methane utilizing DF/SbF_5 but were impeded by rapid exchange of deuterium into methane at room temperature, even in the presence of CO. Although this rapid exchange process has been reported before as evidence for the existence of $[\text{CH}_5]^+$ in superacidic media,^[15] its further reaction to $[\text{CH}_3]^+$ and H_2 is clearly much slower in HF/SbF_5 , if it occurs at all. Therefore, an alternative pathway should be operational for the initial activation of CH_4 resulting in the formation of $[\text{CH}_3]^+[\text{SbF}_6]^-$, SbF_3 , and HF followed by the facile conversion of $[\text{CH}_3]^+[\text{SbF}_6]^-$ to the final product $[\text{CH}_3\text{CO}]^+[\text{SbF}_6]^-$.

In conclusion, the selective carbonylation of CH_4 with CO in liquid superacids is remarkable in that the primary activation product is trapped selectively. The underlying design principle is that electrophilic activation of CH_4 leading to a cationic species will protect the product from further electrophilic activation. Furthermore, the product is not electrophilic enough to activate CH_4 or CO. Our approach therefore successfully combines full protection of the initial product from the species activating CH_4 and fine-tuning of the reactivity of this initial product resulting in total control of selectivity.

Experimental Section

NMR experiments were performed with an Oxford Instruments 400 MHz magnet with a Varian Associates Unity 400 System and VNMR Version 5.1. software for data collection and analysis and a Varian Associates 10 mm multinuclear broad-band probe. The high pressure experiments were performed in Sapphire NMR tubes.^[7] The tubes were charged with SbF_5 or HF/SbF_5 or $\text{HSO}_3\text{F}/\text{SbF}_5$ (all products of Aldrich Chemical Co. and used as received) within a dry-box under Ar atmosphere. ^{13}CO (Isotec, 99%) and $^{13}\text{CH}_4$ (Isotec, 99%) were added from lecture bottles in quantities determined by a pressure gauge and by difference in weight of the sample tube before and after addition of the gases. The tubes were heated in an oil bath for the required time, cooled back to room temperature, and then placed in the magnet for NMR measurements.

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References

- [1] E. Curry-Hyde, R. F. Howe, *Natural Gas Conversion II*, Elsevier, Amsterdam, **1994**
- [2] G. A. Olah, A. Molnár, *Hydrocarbon Chemistry*, Wiley, New York, **1995** b) A. Sen, *Acc. Chem. Res.* **1998**, *31*, 550–557; c) C. Jia, T. Kitamura, Y. Fujiwara, *Acc. Chem. Res.* **2001**, *34*, 633–639; d) M. Muehlhofer, T. Strassner, W. A. Herrmann, *Angew. Chem. Int. Ed.* **2002**, *41*, 1745–1747.
- [3] R. A. Periana, D. J. Taube, S. Gamble, H. Taube, T. Satoh, H. Fujii, *Science* **1998**, *280*, 560–564.
- [4] I. T. Horváth, R. A. Cook, G. Kiss, *U. S. Patent* 5,276,226, **1994**.
- [5] I. T. Horváth, R. A. Cook, J. M. Millar, G. Kiss, *Organometallics* **1993**, *12*, 8–10.
- [6] a) P. J. F. de Rege, J. A. Gladysz, I. T. Horváth, *Science* **1997**, *276*, 776–779; b) T. G. Sorensen, *Angew. Chem. Int. Ed.* **1998**, *37*, 603–604.
- [7] I. T. Horváth, J. A. Millar, *Chem. Rev.* **1991**, *91*, 1339–1351.
- [8] A. Olah, G. K. S. Prakash, J. Sommer, *Superacids*, Wiley, New York, **1985**.
- [9] G. A. Olah, W. S. Tolgyesi, S. J. Kuhn, M. E. Moffatt, I. J. Bastien, E. B. Baker, *J. Am. Chem. Soc.* **1963**, *85*, 1328–1334.
- [10] C. J. Adams, A. J. Downs, *J. Chem. Soc. A* **1971**, 1534–1542.
- [11] H. Hogeveen, J. Lukas, C. F. Roobeck, *Chem. Commun.* **1969**, 920–921.
- [12] H. Hogeveen, C. F. Roobeck, *Recl. Trav. Chim. Pays-Bas* **1972**, *91*, 137–140.
- [13] G. A. Olah, Y. Halpern, J. Shen, Y. K. Mo, *J. Am. Chem. Soc.* **1973**, *95*, 4960–4970.
- [14] A. Bagno, J. Bukala, G. A. Olah, *J. Org. Chem.* **1990**, *55*, 4284–4289.
- [15] G. A. Olah, R. H. Schlosberg, *J. Am. Chem. Soc.* **1968**, *90*, 2726–2727.
- [16] G. A. Olah, G. Klopman, R. H. Schlosberg, *J. Am. Chem. Soc.* **1968**, *90*, 3621–3265.
- [17] H. Bahrmann, in *New Syntheses with Carbon Monoxide*, (Ed.: J. Falbe), Springer-Verlag, Berlin, **1980**, pp 372–408.
- [18] P. L. Fabre, J. Devynk, B. Tremillon, *Chem. Rev.* **1982**, *82*, 591–614.