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Radical-Initiated Functionalization of Methane and Ethane in Fuming Sulfuric Acid

Naomi Basickes, Terrence E. Hogan, and Ayusman Sen*

Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802

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Methane and ethane are the least reactive and the most abundant of the hydrocarbon family with known reserves equal to that of petroleum.[1] Thus, the selective oxidative functionalization of these alkanes to more useful chemical products is of great practical interest.[2] Recently, building on a previous report,[3] a high-yield system for the oxidation of methane to a methanol derivative was described by Catalytica.[4] The system consists of Hg(II) ion in 100% sulfuric acid and operates at 180 °C. It was suggested that the C−H bond-breaking step involved an electrophilic attack by the Hg(II) ion. This was followed by a nucleophilic attack by sulfuric acid on the resultant Hg(II)−CH_3 species to yield the product CH_3OSO_3H. The sulfuric acid also served as the reoxidant for the metal. Our own work on the system suggested an alternative (or parallel) pathway involving outer-sphere electron transfer from the alkane leading, eventually, to the formation of an alkyl radical which was subsequently converted to the product.[5] Herein, we report that the radical-initiated functionalization of methane and ethane is quite facile in fuming sulfuric acid, leading to high reaction rates and long chain lengths. Our results also point to a novel and potential practical route to CH_3SO_3H from methane under mild conditions.

Typical reactions involving methane were carried out as follows. Initiator (0.1 mmol) was added to 3 mL of fuming sulfuric acid (27−33% SO_3 content by weight; 19−23 mmol of SO_3) in a glass liner which was then transferred to a 125-mL high-pressure vessel. The vessel was then pressurized to 1000 psi of methane (350 mmol) and heated. Following the reaction, the gases were vented, 1 mL of D_2O added to convert the remaining SO_3, and the solution analyzed by NMR spectroscopy. Conversions obtained with a number of initiators at 90 and 160 °C are shown in Table 1; no product formation was observed in the absence of the initiators. For the initiators examined, the product concentrations were invariably many times the concentration of the initiator; clearly, as in the Catalytica system, the actual oxidant was SO_3.

Except when $PdSO_4$ was used as the initiator/catalyst, CH_3SO_3H was invariably the favored product at 90 °C. In terms of total product formation at 90 °C, $K_2S_2O_8$ was clearly superior to the others with the yield of CH_3SO_3H exceeding 35% relative to SO_3, the limiting reagent. Only a small increase in product formation was observed when the reaction involving $K_2S_2O_8$ was run for 24 h instead of 2 h. Typical of radical initiators, a decrease in the amount of $K_2S_2O_8$ employed (from 0.1 to 0.01 mmol) did not lead to a significant decrease in the amount of product formed. The use of 0.01 mmol of $K_2S_2O_8$ resulted in the formation of 7.2 mmol of CH_3SO_3H, i.e., a chain length of 720! While not strictly comparable, it is noteworthy that 720 mol of product were formed per mol of initiator in 2 h at 90 °C compared to 70 mol of product per mol of Hg(II) formed in 2 h at 180 °C by the Catalytica system.[4] $PdSO_4$ was the only reagent that consistently formed CH_3OSO_3H as the principal product at 90 °C. One explanation for this is that unlike the other reagents, it functionalized methane through a non-radical (electrophilic) pathway leading to CH_3OSO_3H as the primary product. The Pd(II) ion is the only two-electron oxidant in the group, and such a mechanistic scenario would be consistent with the two-electron oxidation of methane by Pd(II)[6] (and the closely related Pt(II)[7]) that is observed in other protic solvents.

Table 1. Methane Functionalization in Fuming Sulfuric Acid

initiator (mmol)	substrate (psi or mmol)	temp, °C	time	CH_3SO_3H mmol	CH_3OSO_3H mmol
none	CH_4 (1000)	90	1 d	tr	tr
none	CH_4/O_2 (1000/100)	90	1 d	tr	tr
none	CH_4 (1000)	160	1 d	tr	tr
none	CH_3SO_3Na (1.3)	160	1 d		1.2
$K_2S_2O_8$ (0.1)	CH_4 (1000)	90	2 h	7.6	tr
$K_2S_2O_8$ (0.01)	CH_4 (1000)	90	2 h	7.2	tr
$K_2S_2O_8$ (0.01)	CH_4/O_2 (1000/100)	90	2 h	2.0	tr
$K_2S_2O_8$ (0.1)	CH_4 (1000)	160	1 d	tr	1.6
$HgSO_4$ (0.1)	CH_4 (1000)	90	1 d	0.9	0.1
$HgSO_4$ (0.1)	CH_4 (1000)	160	1 d	6.4	4.0
$Ce(SO_4)_2$ (0.1)	CH_4 (1000)	90	1 d	0.4	tr
$PdSO_4$ (0.1)	CH_4 (1000)	90	1 d	tr	0.3
$PdSO_4$ (0.1)	CH_4 (1000)	160	1 d	tr	1.5
H_2O_2 (0.1)	CH_4 (1000)	90	1 d	2.2	0.2

While CH_3SO_3H was generally the favored product at 90 °C, it was quantitatively converted to CH_3OSO_3H simply by heating in fuming sulfuric acid at 160 °C (Table 1). As shown in Table 1, the radical-initiated methane functionalization could be carried out at 160 °C to directly yield CH_3OSO_3H as the principal product in most cases. The product yield obtained using $K_2S_2O_8$ as the initiator was lower at 160 °C than at 90 °C, presumably due to decomposition at the higher temperature to inactive species. $HgSO_4$ gave the highest yield of products at 160 °C, but unlike other initiators, more CH_3SO_3H than CH_3OSO_3H was formed. However, since stoichiometry demands the consumption of 1 and 2 equiv of SO_3 for every CH_3SO_3H and CH_3OSO_3H formed, respectively (eqs 1 and 2), the yield and product distribution may be constrained by the SO_3 content of the reaction mixture (see above).

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[1] (a) Axelrod, M. G.; Gaffney, A. M.; Pitchai, R.; Sofranko, J. A. In *Natural Gas Conversion II*; Curry-Hyde, H. E., Howe, R. F., Eds.; Elsevier: Amsterdam, 1994; p 93. (b) Masters, C. D.; Root, D. H.; Attanasi, E. D. *Science* **1991**, *253*, 146. (c) Starr, C.; Searl, M. F.; Alpert, S. *Science* **1992**, *256*, 981.

[2] Recent reviews: (a) Olah, G. A.; Molnár, A. *Hydrocarbon Chemistry*; Wiley: New York, 1995. (b) Crabtree, R. H. *Chem. Rev.* **1995**, *95*, 987. (c) Labinger, J. A. *Fuel Process Technol.* **1995**, *42*, 325. (d) Fierro, J. L. G. *Catal. Lett.* **1993**, *22*, 67. (e) Srivastava, R. D.; Zhou, P.; Stiegel, G. J.; Rao, V. U. S.; Cinquegrane, G. *Catalysis (London)* **1992**, *9*, 183.

[3] Snyder, J. C.; Grosse, A. V. U.S. Patent 2,493,038, 1950.

[4] Periana, R. A.; Taube, D. J.; Evitt, E. R.; Löffler, D. G.; Wentrcek, P. R.; Voss, G.; Masuda, T. *Science* **1993**, *259*, 340.

[5] Sen, A.; Benvenuto, M. A.; Lin, M.; Hutson, A. C.; Basickes, N. *J. Am. Chem. Soc.* **1994**, *116*, 998.

[6] (a) Sen, A. *Platinum Met. Rev.* **1991**, *35*, 126. (b) Kao, L.-C.; Hutson, A. C.; Sen, A. *J. Am. Chem. Soc.* **1991**, *113*, 700. (c) Nakata, K.; Yamaoka, Y.; Miyata, T.; Taniguchi, Y.; Takaki, K.; Fujiwara, Y. *J. Organomet. Chem.* **1994**, *473*, 329. (d) Nakata, K.; Miyata, T.; Jintoku, T.; Kitani, A.; Taniguchi, Y.; Takaki, K.; Fujiwara, Y. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 3755.

[7] (a) Reference 5. (b) Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Complexes*, D. Reidel: Dordrecht, 1984; Chapter V.

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$$CH_4 + SO_3 \rightarrow CH_3SO_3H \quad (1)$$

$$CH_4 + 2SO_3 \rightarrow CH_3OSO_3H + SO_2 \quad (2)$$

A plausible mechanism for the $K_2S_2O_8$-initiated conversion of methane to CH_3SO_3H by fuming sulfuric acid is sketched in Scheme 1. We had previously demonstrated the facile H-atom abstraction from methane by $KSO_4^{\bullet}$ in aqueous medium.[8] Also consistent with a radical mechanism was the observation that the addition of the radical quencher, O_2, led to greatly diminished yield for the $K_2S_2O_8$-initiated reaction. That the yield in the latter reaction was still many times the initiator concentration may be due to fast reaction of $CH_3^{\bullet}$ with SO_3 which was present in much higher concentration than O_2. The preference for H-atom abstraction from methane rather than the methyl group of CH_3SO_3H by $CH_3SO_3^{\bullet}$ may be ascribed at least in part to its electrophilic nature (the "polar effect").[9]

Unlike methane, product formation from ethane was observed at 90 °C even in the absence of any added initiator. The dominant product was $HO_3SCH_2CH_2OSO_3H$ with 0.3 mmol being formed when the reaction was run for 1 d with 600 psi of ethane. Under identical conditions, the addition of 0.1 mmol of $K_2S_2O_8$ resulted in only a modest increase in product formation (0.8 mmol). The formation of this unusual product was also observed in 100% sulfuric acid.[5] The use of $CH_3CH_2SO_3H$, as well as ethene, as substrates also led to the same product at 90 °C and thus either of these molecules could conceivably be an intermediate.

In conclusion, we have demonstrated that methane can be converted at moderate temperatures to CH_3SO_3H and, eventually, CH_3OSO_3H in high yields using radical initiators. In light of our observations, the possibility of a radical pathway operating in the Catalytica system[4] must be considered seriously, particularly since Hg(II) is a $1e^-$-oxidant. It should also be noted that even for the reaction of Hg(II) with arenes where an electrophilic mechanism is often assumed, Kochi has clearly shown that the reaction occurs by an initial one-electron transfer step.[10] Additionally, although not directly related, the mercury-photosensitized sulfonation of alkanes through a radical pathway has been demonstrated by Crabtree.[11]

Scheme 1. Radical Mechanism for the Formation of Methanesulfonic Acid

$$\left.\begin{array}{lcl} K_2S_2O_8 & \longrightarrow & 2\,KSO_4^{\bullet} \\ KSO_4^{\bullet} + CH_4 & \longrightarrow & KSO_4H + CH_3^{\bullet} \end{array}\right\}\ \text{Initiation}$$

$$\left.\begin{array}{lcl} CH_3^{\bullet} + SO_3 & \longrightarrow & CH_3SO_3^{\bullet} \\ CH_3SO_3^{\bullet} + CH_4 & \longrightarrow & CH_3SO_3H + CH_3^{\bullet} \end{array}\right\}\ \text{Propagation}$$

From a practical standpoint, our observations point to a novel and potential practical route to CH_3SO_3H from methane under mild conditions. The current technology for methane to CH_3SO_3H involves high temperature (ca. 300 °C) gas-phase reaction of methane with SO_3 in the presence of a catalyst (usually mercury).[12] The $S_2O_8^{2-}$ initiated conversion occurs at a much lower temperature. Moreover, a separation step becomes unnecessary since the initiator is converted to SO_4^{2-} and becomes part of the solvent.

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[8] Lin, M.; Sen, A. *J. Chem. Soc., Chem. Commun.* **1992**, 892.

[9] Walling, C. In *Energetics of Organic Free Radicals*; Simoes, J. A. M., Greenberg, A., Liebman, J. F., Eds.; Blackie Academic: London, 1996; p 15. Russell, G. A. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. I, p 275.

[10] Review: Kochi, J. K. In *Advances in Free Radical Chemistry*; Tanner, D. D., Ed.; JAI: Greenwich, CT, 1990; Vol. 1, p 53.

[11] Ferguson, R. R.; Crabtree, R. H. *J. Org. Chem.* **1991**, *56*, 5503.

[12] *The Merck Index*; Merck: Rahway, NJ, 1989; p 938. (b) Snyder, J. C.; Grosse, A. V. U.S. Patent 2,493,038, 1950.