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High yield conversion of methane to methyl bisulfate catalyzed by iodine cations

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Iodine in 2% oleum is an efficient catalyst for the selective, high yield oxidation of methane to methyl bisulfate.

Recently, several reports of alkane CH activation by homogeneous, cationic metal complexes with poorly coordinating anions in poorly coordinating solvents have been reported.[1] The success of this strategy relies on the ease of substitution of the weakly coordinating anion or solvent by the poorly coordinating alkanes. A related strategy that lends itself well to net CH functionalization *via* the CH activation reaction is to generate such poorly coordinated, redox-active, cationic species by use of strongly acidic, oxidizing solvents.

Attesting to the utility of this strategy, to date, the highest reported yields and selectivities for the low temperature oxidation of methane to methanol are with cationic catalysts in sulfuric acid solvent.[2] A key requirement for working in such strongly acidic, poorly coordinating, oxidizing media is that the catalysts be stable.

Herein we report that 1–10 mM elemental iodine dissolved in sulfuric acid containing 2–3% SO_3 (oleum) generates a stable, active species that at 165–220 °C catalyzes the functionalization of methane (500 psig) to methyl bisulfate, eqn. (1).[3] Concentrations of methyl bisulfate of up to 1M, 45% yields (based on methane) at $>90\%$ selectivity, volumetric productivities of $\sim 10^{-7}$ mol per cc.s, turn-over numbers of 300 and turn-over-frequencies of 3×10^{-2} s^{-1} have been observed. Iodine is required for the reaction as no methyl bisulfate is formed in the absence of added iodine, Table 1, # 7. Use of enriched ^{13}C methane and ^{1}H, ^{13}C NMR and HPLC analyses of the crude reaction mixtures confirmed that methyl bisulfate is the only liquid-phase product generated from methane; no methanol, methyl iodide, methane sulfonic acid (CH_3SO_3H) or other liquid phase produced were observed. Only SO_2 and very low levels ($<1\%$ based on added CH_4) of CO_2 were observed in the gas phase. Carbon mass-balances of $>95\%$ based on unreacted methane and methyl bisulfate confirmed the high reaction selectivity and yield. The reaction rates and selectivities are reproducible and first order dependence on both methane (Table 1, # 4 and 8) and iodine (Table 1, # 4–7) are observed. The reaction rate is also strongly dependent on the concentration of SO_3 in the sulfuric acid solvent and does not proceed in $<98\%$ H_2SO_4 where free SO_3 is not present, Table 1, # 1–4.[4] Reactions of higher alkanes with oleum catalyzed by iodine were briefly examined but while oxidation to esters was observed, the reactions are much less selective than with methane. Evidently, the increased rates of proton catalyzed side reactions with these higher alkanes make them unsuitable substrates in oleum.

$$CH_4 + 2\,SO_3 \xrightarrow[H_2SO_4/SO_3]{I_2^+\ HS_2O_7^-} CH_3OSO_3H + SO_2 \qquad (1)$$

Table 1 Yield of CH_3OSO_3H in different reaction conditions[a]

#	SO_3 Wt	X_2 (mM)	CH_4 psig	% CH_4 Conv	TOF s^{-1}	[CH_3X^b] mM, % sel
1	0[c]	I_2 (5)	500	0	0	0, 0
2	0.5	I_2 (5)	500	—	0.003	54, 95
3	1	I_2 (5)	500	10	0.012	218, 95
4	2.5	I_2 (5)	500	30	0.033	600, 95
5	2.5	I_2 (10)	500	53	0.03	1050, 95
6	2.5	I_2 (1)	500	5	0.035	95, 95
7	2.5	none	500	0	0	0, 0
8	2.5	I_2 (5)	200	10	0.01	205,95
9	2.5	Br_2 (10)	500	20	—	240. 50
10	2.5	Cl_2 (10)	500	25	—	150, 30
11	2.5	I_2 (5)	500[d]	31	0.033	610, 95
12	2.5	I_2 (5)	500[e]	28	0.025	575, 94

[a] Reaction time and temperature: 60 min at 195 °C. [b] 96% H_2SO_4. [c] X = OSO_3H. [d] 50 psig O_2 added. [e] 10 mM $K_2S_2O_8$ added.

Other researchers have reported on the use of sulfuric acid and other strong acid solvents for conversion of methane but in these cases, the product yields, selectivities and volumetric productivities were significantly lower and relatively expensive oxidants, such as persulfate were utilized.[4,5] Given the simplicity of the catalyst and high reaction efficiency and selectivity, it is of interest to provide some information on the reaction mechanism.

Two key considerations of our work were to determine the nature of the species that reacts with methane and whether free radicals are involved. It is well known that methane can react with super-acids such as $HF:SbF_5$ *via* the formation of CH_5^+.[6] Consequently, it is possible that added iodine catalyses the oxidation of CH_5^+ species by SO_3 to generate methyl bisulfate. To investigate this we examined the extent of deuterium incorporation into methane as well as methyl bisulfate in the presence and absence of added iodine when the reaction was carried out in D_2SO_4/SO_3. Consistent with earlier reports,[6] we find extensive, $\sim 50\%$, deuterium exchange into methane even at short reaction times (30 min) in the absence of iodine. Interestingly, the extent of deuterium exchange between the D_2SO_4/SO_3 solvent and gas-phase methane is suppressed when iodine is added presumably due to a net decrease in solvent acidity on addition of iodine and the known[6] strong dependence of the exchange on solvent acidity. More significantly, the methyl bisulfate produced (which as noted above is only formed in the presence of added iodine) shows only low levels ($<5\%$) of deuterium incorporation under the same conditions. This observation makes it unlikely that the methyl bisulfate is formed from iodine catalyzed oxidation of a putative CDH_4^+ intermediate as statistically, (ignoring isotope effects) this should lead to the formation of a minimum of $\sim 20\%$ CDH_2OSO_3H.[7]

It has been reported that S_8^{2+} cations reacts slowly with methane at room temperature in liquid SO_2 to generate low yields of methane thiol although no catalysis or mechanistic results were reported.[8] Gillespie has shown that the characteristic bright blue color formed on dissolution of iodine in oleum is due to the formation of the paramagnetic species I_2^+.[9] The reported disproportionation of I_2^+ in oleum with decreasing SO_3[9] to form the more stable, poly-iodo cations, I_3^+ or I_4^+, coupled with our observations of the strong dependence of the methane oxidation reaction on SO_3 concentration is consistent with either I_2^+ or possibly I^+ (which could be formed at the elevated reaction temperatures although it has never been synthesized) being the reactive species. Other possible reactive

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species are iodyl sulfate ($IO_2^+HSO_4^-$),[10] iodosyl sulfate ($IO^+HSO_4^-$)[10] and $I(HSO_4)_3$[11] as these are also reported to be formed on oxidation of iodine in sulfuric acid.

To determine which of these species could be the active catalyst we explicitly examined the stoichiometric reactions of methane at 50 °C with independently synthesized samples of $I_2^+[Sb_2F_{11}]^-$, $IOHSO_4$, IO_2HSO_4 and $I(HSO_4)_3$ in oleum and SO_2 solvents. Significantly, only the $I_2^+[Sb_2F_{11}]^-$ shows stoichiometric reactions under these mild conditions. Thus, reaction of 15 ml of 100 mM $I_2^+Sb_2F_{11}^-$ (1.5 mmols) with excess methane (30 mmols) at 50 °C for 1 h in 2.5 wt% oleum led to 30% yield of methyl bisulfate based on the added $I_2^+Sb_2F_{11}^-$. Importantly, no reaction is observed at these mild conditions if the $I_2^+Sb_2F_{11}^-$ is replaced with 100 mmol of either elemental iodine, $IOHSO_4$, IO_2HSO_4 or $I(HSO_4)_3$. Repeating the reaction with 100 mmols of $I_2^+[Sb_2F_{11}]^-$ in 96% sulfuric acid also gave no methyl bisulfate and is consistent with reported instability of I_2^+ species in SO_3-free sulfuric acid solutions.[9] We also examined the reaction of SO_2 solutions of $I_2^+Sb_2F_{11}^-$ with methane at 35 °C as, unlike oleum, this solvent is not oxidizing and is unlikely to oxidize the I_2^+ to higher oxidation state species. As was reported for the case of S_8^{2+},[8] there is a clear reaction with methane as the blue color of the $I_2^+Sb_2F_{11}^-$ is bleached on exposure to 500 psig of methane after 10 h. However, the reaction is not as clean as in oleum and NMR analysis shows that several methyl products, among them $(CH_3)_2I^+$ and CH_3F, are formed.

These observations are consistent with I_2^+ (or I^+) species as the active catalyst but do not indicate whether free radical mechanisms are involved. While the free radical reaction of atomic iodine with methane can be discounted,[12] free radical reactions are plausible with the stronger oxidants I_2^+, $IOHSO_4$, IO_2HSO_4 or $I(HSO_4)_3$. However, given the high reaction yield and selectivity as well as reproducible, first order kinetics with respect to both methane and iodine, we are biased toward a non-free radical pathway. This bias is strengthened by the observation that added oxygen gas or $K_2S_2O_8$ (Table 1, #11) has no affect on the reaction rate or selectivity. Oxygen and persulfate are known radical scavengers and initiators, respectively, and these species could be expected to lead to changes in rate or selectivity. We also investigated elemental bromine and chlorine as methane oxidation catalysts in 2–3% oleum. In both of these cases, both the reaction rates and selectivities to methyl bisulfate were lower (Table 1, # 9 and 10), than with iodine and extensive poly-halogenated methanes typical of free-radical reactions were observed. This marked difference in reactivity between chlorine, bromine and iodine is consistent with the proposed involvement of iodo cations such as I_2^+ as it has been reported that the related cations of bromine and chlorine are not stable in oleum.[9]

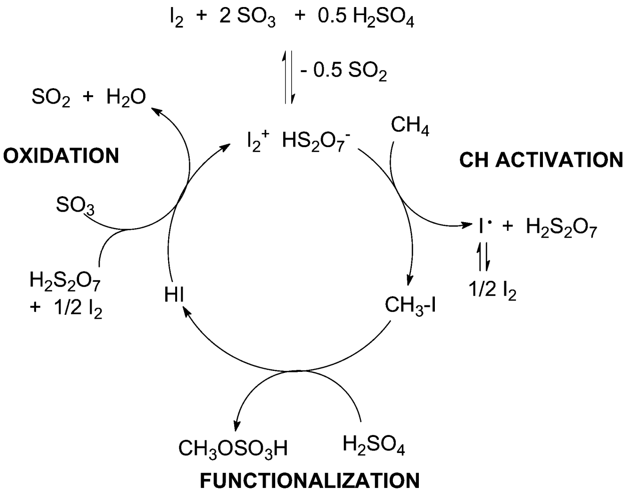

Fig. 1 Proposed electrophilic CH activation mechanism for the iodine catalyzed oxidation of methane in oleum.

The unusually high reaction efficiency and product selectivity for methane conversion, along with the strong dependence on solvent acidity is very similar to the reported, high yield oxidation of methane in sulfuric acid solvent to methyl bisulfate catalyzed by the soft, stable, redox-active electrophile, Hg(II).[2] Based on the proposal that Hg(II) catalyzes methane oxidation *via* CH activation by electrophilic substitution,[2] it is possible that the poorly coordinated $I_2^+H_2S_2O_7^-$, in spite of its known radical character,[9] is sufficiently electrophilic, soft and stable to also react with methane by a predominantly electrophilic substitution pathway as shown in Fig. 1, that does not involve the formation of free radicals. The proposed electrophilic substitution by I_2^+ shown in Fig. 1, is not without precedent. Similar electrophilic substitutions of CH bonds have been proposed for the reaction of alkanes with H^+, O_3^+, NO_2^+, and other electrophiles.[6,13] The electrophilic substitution of arenes by aryl iodo cations is also known.[14] Consistent with the proposed functionalization step in Fig. 1 and the observation that no free methyl iodide is formed, we find that addition of methyl iodide to 2.5% oleum at 150 °C leads to the immediate and quantitative formation of methyl bisulfate and blue colored species due to I_2^+. Consistent with the observation that I_2 does not catalyze H/D exchange between D_2SO_4/SO_3 and CH_4, no methane is produced in this reaction. The proposed oxidation step in Fig. 1 has been reported.[9,11] Elemental sulfur, selenium and tellurium are also reported to generate cationic species on dissolution in oleum and we have found that these species also catalyze reaction between methane and oleum, but at much lower efficiencies as compared to iodine.

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3 In a typical reaction, a 50 ml glass-lined, stirred, high-pressure reactor containing 5 mM iodine and 2.5 wt% sulfur trioxide dissolved in 15 ml of concentrated sulfuric acid was pressurized with methane to a final pressure of 500 psig. This reaction mixture was vigorously stirred and maintained at 195 °C for 2 h before analysis by NMR and HPLC. The reaction must be properly mixed to avoid mass-diffusion control with respect to CH_4.

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