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Partial oxidation of light alkanes by periodate and chloride salts†

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The efficient and selective partial oxidation of light alkanes using potassium periodate and potassium chloride is reported. Yields of methane functionalization in trifluoroacetic acid reach >40% with high selectivity for methyl trifluoroacetate. Periodate and chloride also functionalize ethane and propane in good yields (>20%).

Natural gas is an abundant chemical feedstock and fuel that contributes nearly 25% of the world's energy demand.[1] A limitation to the widespread use of natural gas is the expense of the infrastructure required to transport it. As a result, natural gas is often flared at the source.[2] Thus, it is desirable to develop gas-to-liquid (GTL) processes that enable the efficient conversion of natural gas to liquid fuels.[3] The conversion of methane to methanol (MTM) provides a GTL route for methane, the dominant component of natural gas. Traditionally, the conversion of methane-to-methanol has been accomplished by initial methane reforming to give a mixture of carbon monoxide and hydrogen (syngas), which is subsequently converted to methanol. However, the syngas process for MTM is energy intensive, requiring high temperatures and pressures.[4] As a result, syngas plants are expensive, which has reduced the viability of using this technology for widespread GTL processes. The ability to convert light alkanes (R–H) into mono-functionalized products (R–X) selectively at moderate temperatures (~200 °C) and pressures (~250–1000 psi) would allow the widespread use of natural gas as a precursor for high value chemicals and liquid fuel.[4–13]

One strategy to access selective R–H to R–X conversion under mild conditions is the use of transition metal catalysts. Similar to enzymatic processes for C–H functionalization, high valent oxo complexes that functionalize C–H bonds have been reported.[14–21] Moreover, metal complexes that directly interact with C–H bonds have shown promise for C–H functionalization.[4,6,22–27] Examples of methane functionalization using late transition and main group metals such as Pt, Pd, Hg and Au in super-acidic media have been reported.[28–32] These systems suffer drawbacks including product inhibition of catalysis and challenges with product separation in super-acidic solvents such as oleum. An example of a Pd complex that functionalizes propane in trifluoroacetic acid has been described.[33] Metal complexes have also been shown to functionalize hydrocarbons by radical-based mechanisms.[34–36] In another approach, Ag complexes are capable of converting alkanes to esters using ethyl diazoacetate.[37,38] Recently, main group metals have been demonstrated to functionalize hydrocarbons in non-superacids.[39]

Halogens such as bromine have also been used to functionalize methane.[40,41] Hypervalent iodine species have been reported to functionalize C–H bonds by non-radical routes; however, these reactions typically take place in either super-acidic media or suffer from low selectivity.[42–48] For example, elemental iodine and KIO_3 have been shown to functionalize methane in oleum.[49–52] A recent report highlighted the efficacy of a well-defined iodine(III) compound that mediates selective partial oxidation of hydrocarbons, which was demonstrated to proceed by a non-radical mechanism.[53] Recently, we reported the selective mono-oxidation of methane and other light hydrocarbons using iodate salts, I^{V}, and sub-stoichiometric (*i.e.* catalytic) amounts of chloride.[54] In that study, we observed a ~24% yield of MeTFA (TFA = trifluoroacetate) relative to methane and ~30% yield of EtTFA for ethane functionalization. These high yields in non-super-acidic media are rare, especially the conversion and selectivity observed for ethane. Our study demonstrated that both iodate and chloride are necessary for the high alkane conversions. We have considered whether iodine in other oxidation states, such as periodate, I^{VII}, is viable for this transformation. Herein, we disclose the efficient partial oxidation of light hydrocarbons using a periodate salt along with catalytic amounts of chloride. We find that

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the periodate–chloride system operates at low pressures of methane (860 kPa) to give >40% yield of MeX within 1 h at 200 °C (eqn (1)). The results in this report demonstrate that periodate–chloride mixtures can be used to achieve monofunctionalization of light alkanes in high yields, in some cases with increased efficacy compared to iodate–chloride, which highlights the potential broad application of iodine oxides and chloride to mediate alkane functionalization.

$$\underset{\substack{860\,\text{kPa}\\2.9\,\text{mmol}}}{CH_4} \xrightarrow[\substack{\text{HTFA}\\200\,°\text{C},\ 800\,\text{rpm},1\,\text{h}}]{KIO_4/KCl} \underset{1.18\,\text{mmol}}{CH_3TFA} + \underset{0.03\,\text{mmol}}{CH_3Cl} \quad \textit{42\% yield} \tag{1}$$

As an initial probe into the reactivity of periodate and chloride, we subjected a mixture of KIO_4 (7.7 mmol) and KCl (0.67 mmol) to 3450 kPa of CH_4 (10.6 mmol) in HTFA (eqn (2)). After stirring at 180 °C for 1 h, analysis of the reaction mixture by ^1H NMR revealed the formation of 0.86 mmol of MeTFA along with 0.10 mmol of MeCl, which corresponds to ~9% yield of total MeX relative to methane.

$$\underset{\substack{3450\,\text{kPa}\\10.6\,\text{mmol}}}{CH_4} \xrightarrow[\substack{\text{HTFA}\\180\,°\text{C},\ 800\,\text{rpm},\ 1\,\text{h}}]{KIO_4/KCl} \underset{0.86\,\text{mmol}}{CH_3TFA} + \underset{0.10\,\text{mmol}}{CH_3Cl} \tag{2}$$

To optimize yields of MeX, we studied several features of this reaction. To examine the effect of temperature (Fig. 1), KIO_4 (7.7 mmol) and KCl (0.67 mmol) in HTFA were heated over a range of temperatures (150–220 °C) for 1 h with 3450 kPa of CH_4 (10.6 mmol). Increasing the reaction temperature has a positive effect on the yield of MeX. At 200 °C, the yield of MeX reaches 1.55 mmol MeTFA and 0.10 mmol MeCl, and then appears to plateau. This corresponds to ~16% yield of MeX relative to methane. These data suggest that at temperatures ≥200 °C the reaction is complete within 1 h. Importantly, since the overall reaction is exothermic (*e.g.*, CH_4 (g) + $\frac{1}{2}O_2$ (g) → CH_3OH (l), $\Delta H = -163$ kJ mol^{-1}), an industrially viable reaction would ideally be performed between 200 °C and 250 °C.[7]

We next explored the effect of chloride on the yield of MeX (Fig. 2). In the absence of chloride, we observed a small amount of MeTFA (0.19 mmol) compared to 1.55 mmol of MeTFA observed with the addition of 0.67 mmol of KCl. The yield of MeX increased with increasing concentration of KCl. Adding 0.33 mmol KCl resulted in the production of 0.56 mmol MeX and increasing the KCl loading further to 0.67 mmol resulted in 1.65 mmol MeX. Increasing the concentration of chloride above 0.67 mmol had minimal effect on increasing MeX yields.

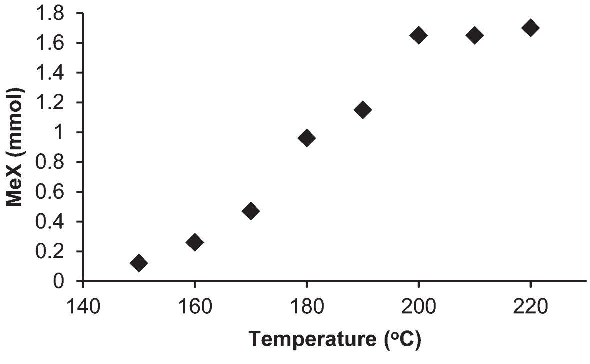


Fig. 1 Dependence of temperature on MeX yield. Conditions: 7.7 mmol KIO_4; 0.67 mmol KCl; 8.0 mL HTFA; 3450 kPa (10.6 mmol) CH_4; 800 rpm; 1 h.

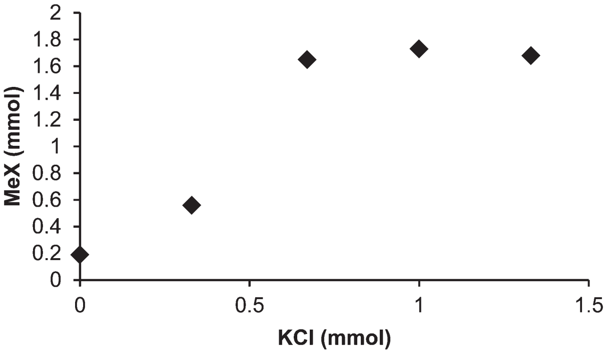


Fig. 2 Dependence of KCl loading on MeX yield. Conditions: 7.7 mmol KIO_4; 8.0 mL HTFA; 3450 kPa (10.6 mmol) CH_4; 200 °C; 800 rpm, 1 h.

We studied the influence of methane pressure on the yield of MeX (Fig. 3). Varying the pressure has a negligible effect on mmol of MeX produced over 1 h. We observed a slightly higher MeX production at 3450 kPa CH_4, but within the deviation of the experiment there is little difference in amount of MeX produced as CH_4 pressure is increased. Thus, percent yields of MeX are optimized at lower CH_4 pressures with a yield of 42% MeX with 7.7 mmol KIO_4 and 0.67 mmol KCl at 200 °C with 860 kPa CH_4 (2.9 mmol) after 1 h.

We also studied the effect of periodate loading. Since the chloride : periodate ratio must be at least ~1 : 10 to obtain optimal yields (see Fig. 2), the amount of chloride was scaled with added periodate. Using 3450 kPa CH_4, we increased the loading of KIO_4 by ~55%. At lower concentrations of KIO_4 there is a linear correlation with MeX production (Fig. 4).

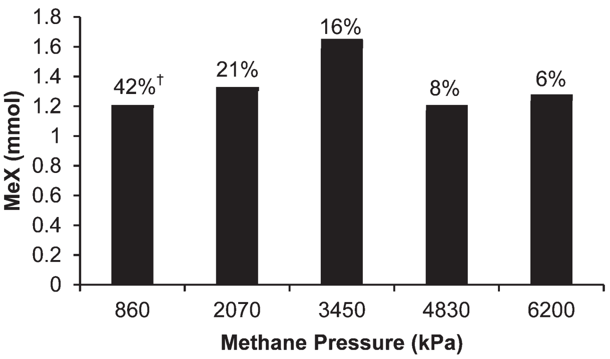


Fig. 3 Dependence of methane pressure on MeX yield. Conditions: 7.7 mmol KIO_4; 0.67 mmol KCl; 8.0 mL HTFA; 200 °C; 800 rpm; 1 h. †Yields based on starting CH_4 loading shown above each bar (860 kPa = 2.9 mmol, 2070 kPa = 6.3 mmol, 3450 kPa = 10.6 mmol, 4830 kPa = 15.6 mmol, 6200 kPa = 21.9 mmol).

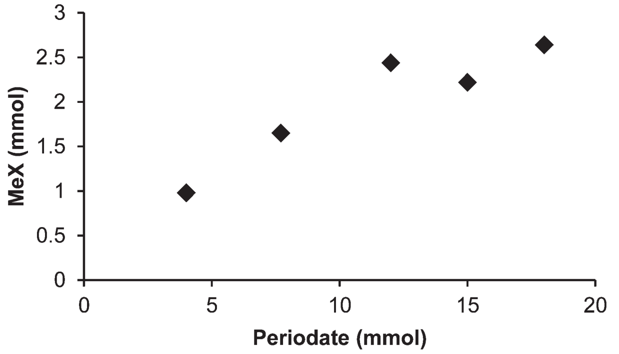
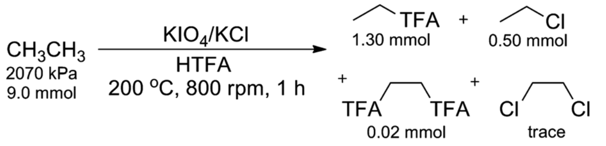


Fig. 4 Dependence of KIO_4 loading on MeX yield. Conditions: 0.47 mmol KCl (4.0 mmol KIO_4), 0.67 mmol KCl (7.7 mmol KIO_4), 1.4 mmol KCl (12 mmol KIO_4), 1.8 mmol KCl (15 mmol KIO_4), 2.1 mmol (18 mmol KIO_4); 8.0 mL HTFA; 3450 kPa (10.6 mmol) CH_4; 200 °C; 800 rpm, 1 h.

Because the standard conditions (7.7 mmol KIO_4 and 0.67 mmol KCl) at 2070 kPa and 860 kPa gave higher yields relative to CH_4, we investigated the effect of higher periodate loading at these pressures. Increasing the periodate loading at 2070 kPa had minimal effect on overall yields, especially when compared to the effect at 3450 kPa (see above). Heating an HTFA mixture of 12 mmol KIO_4 and 1.4 mmol KCl with 2070 kPa of CH_4 gave 1.48 mmol MeX, which corresponds to a yield of ~23%. This is only ~10% increase in yield upon increasing the oxidant loading by ~55%. Similarly, at 860 kPa the yield of MeX does not increase with added periodate (ESI†).

The periodate–chloride system is effective at functionalizing other light alkanes. Using the optimized conditions from methane functionalization (12 mmol KIO_4 and 1.4 mmol KCl), we studied the partial oxidation of ethane. Heating a trifluoroacetic acid mixture of 12 mmol KIO_4 and 1.4 mmol KCl with 2070 kPa of ethane (9.0 mmol) at 200 °C for 1 h yielded 1.30 mmol EtTFA and 0.50 mmol of EtCl, which corresponds to a ~20% yield based on ethane (eqn (3)). We also observed 0.02 mmol of the bisTFA-ester of ethylene glycol and trace (<0.02 mmol) 1,2-dichloroethane. Notably, the yield of EtCl is higher than what was observed for the iodate–chloride system (see below).[54]



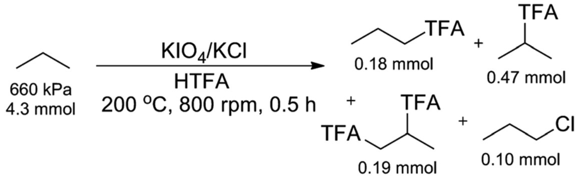
(3)

Applying the optimized conditions to the partial oxidation of propane (660 kPa, 4.3 mmol) resulted in a deep red reaction mixture from which analysis by ^1H NMR spectroscopy was challenging due to broad resonances. Decreasing the oxidant loading to 5.2 mmol KIO_4 and 0.61 mmol KCl as well as shortening the reaction time to 30 min allowed for the observation of 0.18 mmol *n*PrTFA, 0.47 mmol iPrTFA, 0.19 mmol 1,2-TFA-propane, and 0.10 mmol *n*PrCl (eqn (4)). The total yield of functionalized product (based on initial propane loading) is ~22%.

Table 1 Comparison of alkane functionalization with periodate–chloride and iodate–chloride

	Periodate	Iodate
Yield at 3450 kPa CH_4 [a]	23%	23%
Yield at 3450 kPa CH_4 [b]	16%	21%
Yield at 860 kPa CH_4 [b]	42%	30%
EtTFA : EtCl[b]	3.3 : 1	16 : 1[c]
iPrTFA : *n*PrTFA	2.6 : 1	1.7 : 1[c]
PrTFA : $PrTFA_2$	3.4 : 1	1.3 : 1[c]
[iPrTFA + $PrTFA_2$] : *n*PrTFA	3.7 : 1	3.6 : 1[c]

[a] High loading: 12 mmol IO_x^- and 1.4 mmol KCl. [b] Low loading: 7.7 mmol IO_x^- and 0.67 mmol KCl. [c] Ref. 54.



(4)

It is of interest to compare our previously reported iodate–chloride system with the periodate–chloride system highlighted in this report.[54] Because of differences in experimental design and conditions, we performed some reactions with NH_4IO_3 and KCl in order to provide a more accurate comparison with the data presented in this report. This comparison is summarized in Table 1. Using 7.7 mmol NH_4IO_3 and 0.67 mmol KCl at 200 °C with 3450 kPa CH_4 (10.6 mmol) produced 2.22 mmol MeTFA and 0.05 mmol MeCl, which corresponds to a 21% yield of MeX (eqn (5)). The periodate–chloride system gives 16% yield of MeX under these conditions. However, increasing the amount of periodate–iodate and chloride to 12 mmol and 1.4 mmol, respectively, gave similar yields for both systems (~23%).

With low pressures (860 kPa), the periodate–chloride system is considerably more effective. As mentioned above, reacting 7.7 mmol KIO_4 and 0.67 mmol KCl with 860 kPa of CH_4 (2.9 mmol) gave 42% yield of MeX. Under these conditions, iodate–chloride gave 30% yield MeX. At this point, the source for this difference is not known. For the iodate–chloride system, we observed highly irreproducible yields with very broad ^1H NMR spectra under these conditions.

$$\underset{\substack{3450\ \text{kPa}\\ 10.6\ \text{mmol}}}{CH_4} \xrightarrow[\text{200 °C, 800 rpm, 1 h}]{\substack{NH_4IO_3/KCl\\ \text{HTFA}}} \underset{2.22\ \text{mmol}}{CH_3TFA} + \underset{0.05\ \text{mmol}}{CH_3Cl} \tag{5}$$

Another striking difference is the increased amount of RCl produced for functionalization reactions using periodate. We have previously shown that MeCl is not a kinetic product that is converted to MeTFA under reaction conditions, and, thus, may be attributed to a second competitive pathway.[54] The difference is most readily observed for the functionalization of ethane. For iodate–chloride, only ~6% of the total functionalized product from ethane is EtCl. In contrast, we observed

~28% EtCl relative to total functionalized product when using periodate–chloride. One explanation is that there is a higher concentration of chloride present in the reaction with periodate (1.4 mmol *vs.* 0.67 mmol). However, even running the ethane functionalization reaction with 7.7 mmol KIO_4 and 0.67 mmol KCl, we still observe ~23% EtCl (ESI†).

Previously, we observed ~1.7 : 1 ratio of iPrTFA to *n*PrTFA for propane functionalization when using NH_4IO_3 and KCl. For KIO_4–KCl, that ratio is increased to ~2.6 : 1. Likewise, the ratio of mono- and difunctionalized products for the iodate system was ~1.3 : 1, while the ratio is ~3.4 : 1 for the periodate reaction described herein.[54] Thus, the periodate system reported herein is more selective for both the monofunctionalized product and the branched product. However, a potentially relevant comparison is the ratio of the sum of iPrTFA and 1,2-difunctionalized product to *n*PrTFA. If the difunctionalized product forms *via* further reaction of iPrTFA, one would expect these ratios to be similar between iodate and periodate, assuming a similar mechanism was operative. Indeed, for both iodine species, the ratio is ~3.6 : 1 (Table 1).

In summary, we have demonstrated that the mixture of KIO_4 and KCl in HTFA is an efficient system for the monofunctionalization of light alkanes even at low pressures. Yields of functionalized products from methane, ethane and propane reach over 20%, and in the case of methane at 860 kPa, a 42% yield of MeX is observed. Additionally, comparison to our previously reported hydrocarbon functionalization using iodate and chloride salts provides evidence that these two systems operate *via* a similar pathway.[54] By optimizing the reaction conditions, a greater yield of MeX is observed for the periodate system reported here than for the iodate system at 200 °C. The high activity observed at 200 °C is important for the development of industrially viable systems, considering the exothermic nature of the reaction and the energy and cost needed to cool large scale industrial reactions.[7] Understanding the mechanism of these transformations may allow for the development of more active and efficient catalytic systems for the conversion of natural gas into liquid fuels. Efforts into elucidating the mechanism are currently underway in our laboratories and will be reported in due course.

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