Hypervalent Compounds

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Selective CH Functionalization of Methane, Ethane, and Propane by a Perfluoroarene Iodine(III) Complex**

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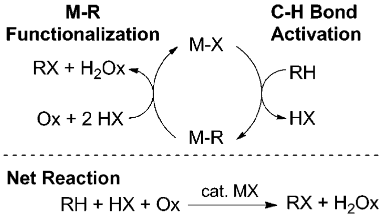
***Abstract:** Direct partial oxidation of methane, ethane, and propane to their respective trifluoroacetate esters is achieved by a homogeneous hypervalent iodine(III) complex in non-superacidic (trifluoroacetic acid) solvent. The reaction is highly selective for ester formation (> 99 %). In the case of ethane, greater than 0.5 M EtTFA can be achieved. Preliminary kinetic analysis and density functional calculations support a nonradical electrophilic CH activation and iodine alkyl functionalization mechanism.*



Scheme 1. Generalized catalytic cycle and net reaction for CH functionalization.

The direct conversion of C$_1$–C$_3$ alkanes in natural gas into upgraded commodities at low temperature and high selectivity remains a significant challenge.[1] Catalytic systems based upon nonradical homogeneous CH activation and metal–alkyl (M−R) functionalization, together designated herein as CH functionalization, remains a viable strategy to achieve this goal (Scheme 1).[2] Some of the most efficient systems we have developed utilize catalysts based on electrophilic transition metals with unfilled d orbitals (d$^{<10}$), such as platinum,[3] palladium,[4] and gold.[5] One difficulty limiting the reactivity of these electrophilic systems is the slow rate of alkane coordination, which is necessary for efficient CH activation.[2,6] To address this challenge, superacid solvents, such as H$_2$SO$_4$, have been used to facilitate anion ligand dissociation and alkane coordination.[2] However, the use of a superacid solvent is impractical because of the high costs for product separation and corrosivity, and is limited primarily to methane because of the instability of higher-order oxygenated products.[2]

We have recently reported that main-group electrophilic salts with filled d orbitals (d^{10}) such as Tl^{III}(TFA)$_3$ and Pb^{IV}(TFA)$_4$ (TFA = trifluoroacetate) promote efficient and selective stoichiometric CH activation and functionalization of methane (MeH), ethane (EtH), and propane (PrH) in more practical weaker acid solvents (HOAc, HTFA).[6] The high rates of these main-group electrophiles were attributed to substantially faster alkane coordination which could be conceptually ascribed to the lack of ligand-field stabilization energies for d^{10} systems.[6] Importantly, this work also suggested that other main-group electrophiles may promote CH functionalization.[6]

While the simplicity of main-group electrophilic salts is attractive, we are also interested in designing main-group electrophilic systems with stable ligands which can be elaborated to tune electronics and sterics, to control selectivity and reactivity. We were particularly interested in hypervalent iodine electrophiles, given their wide range of oxidation states, tunability by ligation, and extensive development for a wide variety of metal-free organic transformations.[7] Importantly, several stable organo-ligated species of this class [e.g. R-I(X)$_2$, R-I(X)$_4$] are well known,[7] thus opening the possibility for rational ligand design. Herein, we describe a homogeneous stoichiometric reaction for the oxy-functionalization of C$_1$–C$_3$ alkanes by a well-defined hypervalent iodine compound C$_6$F$_5$I^{III}(TFA)$_2$ (**1**). In the HTFA solvent, **1** cleanly and selectively oxidizes C$_1$–C$_3$ alkanes (RH) to generate the respective trifluoroacetate esters (RTFA) and C$_6$F$_5$I^{I} (**2**) in high yields for EtH and PrH. Experiments and density functional calculations disfavor a 1e$^-$ pathway and provide evidence supporting a CH activation and M−R functionalization mechanism, through the formation of an alkyl(perfluoroaryl)-λ^3-iodane intermediate.

The selective oxidation of unactivated alkanes by hypervalent iodine is rare,[7,8] with only a few reports describing

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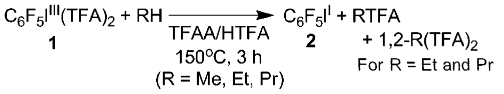
selective alkane oxygenation.[9–12] To our knowledge only one electrophilic, non-oxo system (which was limited to MeH and operated in superacid media) has been reported for high-yielding, selective light-alkane oxygenation with hypervalent iodine,[11] with no reports concerning EtH and PrH. In a prior report,[9] I(TFA)$_3$ was found to functionalize tertiary alkanes to esters within minutes at room temperature, however secondary CH functionalization was sluggish (requiring days or weeks), primary CH functionalization could not be observed (neopentane), and C$_1$–C$_3$ alkanes were not examined. To begin, we evaluated the reactivity of I(TFA)$_3$ in HTFA as the solvent towards MeH, EtH, and PrH under more forcing reaction conditions (3 h, 150 °C) than previously described.[9] We also examined the commonly utilized hypervalent iodine reagent C$_6$H$_5$I(OAc)$_2$ (DIB). While I(TFA)$_3$ and DIB both indicated the formation of alkane-derived products by ^{1}H NMR spectroscopy, quantitative analysis was complicated by either the formation of I$_2$[9] or a side reaction where DIB reacts with the aryl backbone of a second DIB equivalent.

Perfluorous aryl and alkyl iodine(III) reagents are useful and potentially recyclable electrophilic oxidizing agents, which contain a stable R$_F$–I^{III} bond and no oxidizable CH functionality.[7l,13] These traits made the commercially available C$_6$F$_5$I^{III}(TFA)$_2$ (**1**), an ideal candidate for alkane oxidation. Upon heating a 100 mM solution of **1** at 150 °C for 3 hours in 100 mM TFAA/HTFA under 500 psi of MeH or EtH (125 psi for PrH), ^{1}H NMR analysis of the crude reaction mixtures indicated the generation of the respective trifluoroacetate monoesters and 1,2-TFA-diesters (for EtH and PrH) [Eq. (1), Table 1].[14,15] The reactions are highly selective and no hydrocarbon-derived products are observed other than the respective monoesters and 1,2-diesters (see Figure S1 in the Supporting Information). ^{19}F NMR analysis of the solutions post-reaction showed that **1** is cleanly converted into **2** as the reaction proceeds with no intermediate iodine species observed in greater than 90 % mass balance (Figure S1). Control experiments showed that **1** was stable under the reaction conditions (under 500 psi Ar) in the absence of the hydrocarbons and that the hydrocarbons did not react in the absence of **1**. Consistent with the expected relative reactivity of an electrophilic system, the order of reactivity was determined to be PrH (ca. 89 %) > EtH (80 %) ≫ MeH (5 %; Table 1, entries 1–3). The reaction was highly efficient with EtH and PrH, and at the saturation concentration of **1** (ca. 0.8 M), 0.56 M EtTFA could be observed (see Figure S2 in the Supporting Information). Notably, the selectivity for the monofunctionalized and 1,2-difunctionalized products depended upon substrate. The monoester is heavily favored (24:1) for EtH while about a 1:1 ratio is observed for propane. Control experiments suggest that this difference likely arises because of the relative reactivity of the monoester products: while EtTFA is completely unreactive towards **1**, 2-PrTFA is readily converted into 1,2-Pr(TFA)$_2$ under our standard reaction conditions (see Table S1 and Figures S3 and S4 in the Supporting Information) in the presence of **1**.



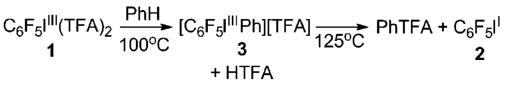
$$\underset{\mathbf{1}}{C_6F_5I^{III}(TFA)_2} + RH \xrightarrow[\substack{150^{o}C,\ 3\ h \\ (R = Me, Et, Pr)}]{TFAA/HTFA} \underset{\mathbf{2}}{C_6F_5I^{I}} + \underset{\text{For R = Et and Pr}}{RTFA + 1,2\text{-}R(TFA)_2} \quad (1)$$

Table 1: Oxidation of C$_1$–C$_3$ alkanes and benzene by **1**.[a]

Entry	RH	*T* [°C]	Conv.[b]	Product (yield [%])[b]
1	MeH	150	5 %	MeTFA (5 %)
2	EtH	150	80 %	EtTFA (73 %); 1,2-Et(TFA)$_2$ (3 %)[c]
3[d]	PrH	150	89 %	2-PrTFA (30 %); 1,2-Pr(TFA)2 (27 %)[c]
4[e]	PhH	125	99 %	C$_6$H$_5$TFA (91 %)
5[e]	PhH	100	99 %	[C$_6$F$_5$I^{III}(C$_6$H$_5$)][TFA] (99 %)[f]

[a] General reaction conditions: 100 mM **1**, 500 psi RH (2.78 mmol, 27.8 equiv based on ideal gas law), 1 mL 100 mM TFAA/HTFA, 3 h.
[b] Conversions and product yields are reported relative to [**1**]$_0$; and were determined by ^{19}F and ^{1}H NMR spectroscopy, respectively, by comparison to an internal standard (C$_6$F$_6$ and CH$_2$Cl$_2$) which was added post reaction. [c] 2 equiv of **1** are consumed per 1 equiv 1,2-product.
[d] 125 psi PrH (0.70 mmol, 7.0 equiv based on ideal gas law).
[e] 690 mM C$_6$H$_6$, 250 mM **1**, 500 psi Ar. [f] Tentative product identification.

In addition to alkanes, **1** is also effective for the selective monofunctionalization of benzene (PhH) to PhTFA at lower temperatures (125 °C; Table 1, entry 4). Reducing the temperature of this reaction to 100 °C resulted in the complete consumption of **1** with the generation of a new species in solution. By using ^{1}H and ^{19}F NMR spectroscopy, we tentatively identified the new species as the diaryl-λ^3-iodane [C$_6$F$_5$I^{III}(C$_6$H$_5$)][TFA] (**3**). Only trace levels of PhTFA and **2** were observed (entry 5; see Figure S5 and S6 in the Supporting Information). Further heating of this solution (at 125 °C) resulted in the complete conversion of **3** into PhTFA and **2**. This transformation is consistent with **3** as an intermediate in the conversion of PhH into PhTFA [Eq. (2)]. Although both the generation of diaryl-λ^3-iodanes from a λ^3-iodane and arene in acidic media and the functionalization of nucleophiles by diaryl-λ^3-iodanes are well established,[7,16] only a few examples of direct one-pot aromatic CH oxygenation by λ^3-iodanes have been reported in the literature.[7a,b,e,17]



$$\underset{\mathbf{1}}{C_6F_5I^{III}(TFA)_2} \xrightarrow[100^{o}C]{PhH} \underset{\substack{\mathbf{3} \\ + HTFA}}{[C_6F_5I^{III}Ph][TFA]} \xrightarrow[125^{o}C]{} PhTFA + \underset{\mathbf{2}}{C_6F_5I^{I}} \quad (2)$$

Analogous to the observed chemistry of benzene with **1** [Eq. (2)], one mechanistic possibility for alkane functionalization is a reaction that proceeds by the formation of an alkyl(perfluoroaryl)-λ^3-iodane intermediate ([C$_6$F$_5$I(alkyl)]-[TFA]), which is then rapidly functionalized to generate RTFA. The reductive functionalization of alkyl-λ^3-iodanes to oxygenated and olefinic products has long been known.[18] However, alkyl-λ^3-iodanes are known to be highly susceptible to reductive functionalization by weak nucleophiles at low temperatures (< 0 °C),[7a,b,e] and it is unlikely that this intermediate could be detected during our reactions described above. Therefore, in an effort to probe the reactivity of the proposed [C$_6$F$_5$I(alkyl)][TFA] intermediate directly, we examined the reaction of SnEt$_4$ with **1** in HTFA (see the

Supporting Information for details). Sn−R species (including examples where R is a sp^3-hybridized carbon center)[19] are well known to undergo facile R-transfer reactions with I^{III} species to generate I^{III}−R.[7] While the species [$C_6F_5I(Et)(TFA)$] could not be observed, addition of $SnEt_4$ to a solution of **1** in HTFA at 50 °C resulted in clean formation of EtTFA and smaller amounts of 1,2-Et$(TFA)_2$.[20] This is consistent with the product selectivities observed for the reaction of EtH and **1** described above.

To further examine the reaction mechanism, we performed a more detailed experimental and theoretical analysis of the oxidation of EtH by **1**. A time-course study, monitored by ^{1}H and ^{19}F NMR spectroscopy, indicated that the reaction is well behaved and first-order in **1**, thus displaying clean exponential decay through three half-lives with matching exponential growth of EtTFA and 1,2-Et$(TFA)_2$ as the reaction proceeds (Figure 1). Importantly, the ratio of [EtTFA] and [1,2-Et$(TFA)_2$] was determined to remain constant throughout the reaction (ca. 25:1). Additionally, control experiments have shown EtTFA is completely unreactive towards **1** (see Table S1 and Figure S4). These results support a mechanism where both the EtTFA and 1,2-Et$(TFA)_2$ products are formed from an unobserved common intermediate, and not a sequential functionalization of EtH to EtTFA to 1,2-Et$(TFA)_2$. Variation of EtH pressure indicated that the reaction is also first-order in EtH (Figure 2). The reaction of 1,2-[^{13}C]-EtH with **1** showed that both Et−TFA and 1,2-Et$(TFA)_2$ are derived solely from EtH (see Figure S7), and GC/MS analysis of the headspace gases post-reaction indicated that minimal levels of over oxidation occurs (< 1 % $^{13}CO_2$).[21] An intramoleuclar H/D KIE value of 3.0 (± 0.5) was obtained for the reaction by examining CH_3CD_3 (see the Supporting Information for details). Similar to the reported Tl^{III} and Pb^{IV} chemistry,[6] the examination of **1** with EtH in DTFA indicated no H/D exchange occurs (see Scheme S8), thus suggesting that if a I^{III}−Et intermediate is formed, functionalization occurs rapidly relative to protonolysis.

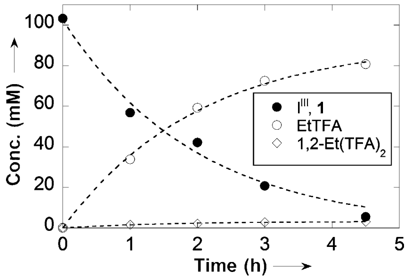


Figure 1. Reaction timecourse of the oxidation of EtH by **1**. Reaction conditions: $[\mathbf{1}]_0 = 103$ mM, 500 psi EtH, 150 °C, 1 mL 100 mM TFAA/HTFA, 0–4.5 h.

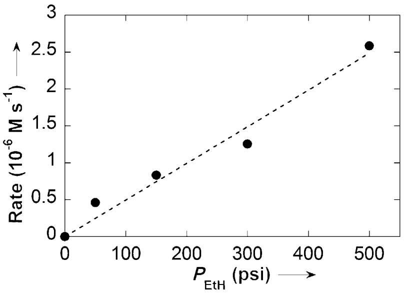
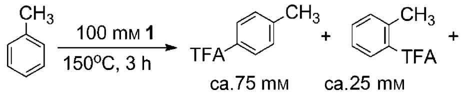


Figure 2. Initial rate dependence of EtH pressure on the generation of EtTFA from EtH and **1**. Reaction conditions: $[\mathbf{1}]_0 = 101$ mM, 50–500 psi EtH, 140 °C, 1 mL TFAA/HTFA, 0.5 h.

The high reproducibility, selectivity, well-defined kinetics, and constant EtTFA to 1,2-Et$(TFA)_2$ product ratios observed with EtH and **1** suggest that the reaction does not proceed by a free-radical chain mechanism. A comparison of the reaction of EtH with **1** to the reaction of EtH with other strong oxidants known to promote free-radical pathways ($K_2S_2O_8$, $NaBO_3$) under otherwise identical reaction conditions supports this proposal, as these reactions are much less selective for EtTFA and generate significant amounts of unidentified aliphatic products (see Scheme S9). To probe for the presence of a free-radical pathway or other 1 e$^-$ homolytic pathways (such as hydrogen-atom transfer; HAT) further, we next examined the reactivity of toluene (which contains homolytically weak benzylic CH bonds) with **1**. Under our standard reaction conditions (3 h, 150 °C; see the Supporting Informatino for details), quantitative generation (based upon starting [**1**]) of *p*-MeC_6H_4TFA and *o*-MeC_6H_4TFA in approximately a 3:1 ratio was observed with no formation of any benzylic oxy-functionalized products expected from a radical pathway [Eq. (3)].



(3)

Importantly, the observed selectivity with **1** (e.g. a preference for homolytically stronger, aromatic CH bonds) sharply contrasts with the previously described work by Ochiai et al., where the I^{III} complex **4** (see below) displayed a clear preference for benzylic (over aromatic or vinylic) CH oxygenation.[22] Mechanistic work by Ochiai et al. indicated that functionalization with **4** proceeds by a HAT mechanism where after I-OO*t*Bu bond homolysis to generate **5**, abstraction of a hydrogen atom from a CH bond by **5** (or the benzoyloxy-centered radical analogue of **5**) occurs.[22] Supporting this proposal, large H/D KIE effects of 10–14 were observed for CH/D oxygenation with **4**,[22] and is characteristic of HAT from a CH bond.[23] This result also differs greatly from the H/D KIE value of 3.0 observed with **1** and EtH as described above.

M06/6-31 + G(d,p)[LANL2DZ(d,p)] density functional calculations were carried out to predict the alkane oxidation mechanism and understand the high selectivity for the monoester product over the diester product for reaction of **1** with EtH. Calculations were carried out with an explicit HTFA solvent embedded in an implicit HTFA solvent model (see the Supporting Information for details). The ground state of the $C_6F_5I^{III}(TFA)_2$ complex involves *trans*-κ^1-TFA ligands interacting with $C_6F_5I^{III}$. Calculations indicate prohibitively high energies for one-electron oxidation between **1** and EtH at $\Delta H^{\ddagger} > 80$ kcal mol^{-1} (see Scheme S10). We also explored hydrogen-atom abstraction, which has a reasonable $\Delta H^{\ddagger}$ value of 38.8 kcal mol^{-1}, but is higher in energy than a CH activation pathway.

Calculations suggest that CH activation and M–R functionalization provides a viable mechanism for EtH oxidation (Figure 3). In this pathway, EtH coordination occurs with TFA ligand displacement (with the TFA anion remaining within the solvation sphere of the I^{III} center), thus requiring $\Delta H = 9.4$ kcal mol^{-1}. Subsequent deprotonation of the CH bond by the TFA (**TS1**) requires $\Delta H^{\ddagger} = 31.6$ kcal mol^{-1}, and exothermically generates the alkyl(perfluoroaryl)-λ^3-iodane intermediate [$C_6F_5I(Et)$][TFA] (**6**). Importantly, the $\Delta H^{\ddagger}$ value for CH activation of the methyl group of EtTFA by **1** was calculated to be 36.3 kcal mol^{-1}. This ΔH value is 5 kcal mol^{-1} larger for EtTFA (relative to **TS1**) and supports our mechanism where the 1,2-diester is not formed from functionalization of EtTFA by **1**. Our CH activation model is further validated by the approximate calculated KIE of 3.4 for CH_3CD_3 based on **TS1**, and is within the error range of the experimental value described above.

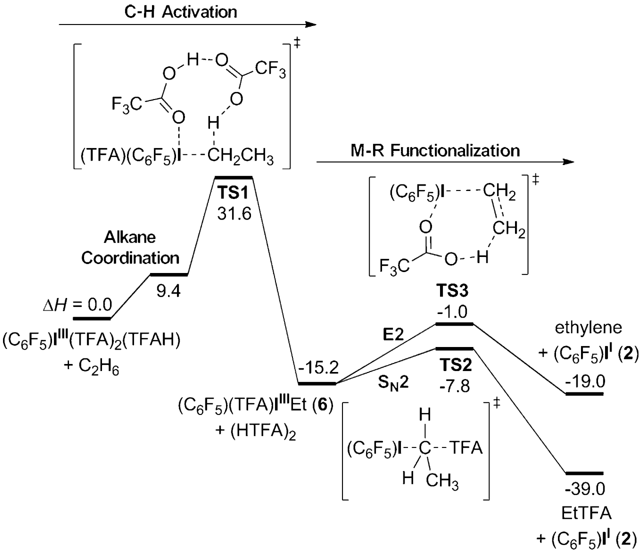


Figure 3. DFT-calculated CH activation and M–R functionalization pathway. Enthalpies are in kcal mol^{-1}. (M06/6-31 + G(d,p)[LANL2DZ-(d,p)]).

Calculations identified two low-energy I^{III}-Et functionalization pathways (Figure 3), which explains the lack of direct observation of the intermediate **6**. An S$_N$2 functionalization pathway forms EtTFA via **TS2** with a 7.4 kcal mol^{-1} $\Delta H^{\ddagger}$ value relative to **6**. The E2 pathway forms ethylene via **TS3** with a 14.2 kcal mol^{-1} $\Delta H^{\ddagger}$ value relative to **6**. Ethylene is then proposed to be converted into the 1,2-diester by **1**.[24] The calculated functionalization pathways from **6** are consistent with the high selectivity for EtTFA over 1,2-Et(TFA)$_2$.

The calculated CH activation mechanism for reaction of **1** with EtH contrasts with the free-radical alkane functionalization mechanism described with **4**.[22] The difference between **1** and **4** is clearly revealed by the calculated I–O bond homolysis enthalpies (Figure 4). The I–O bond dissociation enthalpy for **4** is compatible with a radical mechanism at 30.6 kcal mol^{-1}. Whereas with **1**, the bond dissociation enthalpy is much higher (60.1 kcal mol^{-1}), thus suggesting that homolysis to form **7** is unlikely.

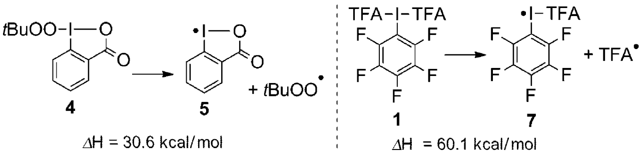


Figure 4. DFT-calculated I–O bond dissociation enthalpies for **4** and **1** in HTFA solvent. (M06/6-31 + G(d,p)[LANL2DZ(d,p)]).

In summary, we report that efficient and selective oxyfunctionalization of light alkanes to oxy-esters in a non-superacid solvent (HTFA) can be mediated by hypervalent iodine. Experiment and theory disfavors one-electron mechanisms and provides evidence supporting alkane CH activation and M–R functionalization by the hypervalent iodine complex **1**. Considering the recent developments on the use of hypervalent iodine catalytically,[7f,i,j,25] it is feasible that further studies may allow development of catalytic systems designed to selectively transform unactivated alkanes and arenes into alcohols and phenols, respectively. These investigations are currently underway.

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