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# Electrocatalytic Oxyesterification of Hydrocarbons by Tetravalent Lead

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TFA=trifluoroacetate

thermocatalysis, we demonstrate the room-temperature electrocatalytic oxyesterification of alkanes and benzene with  $Pb^{IV}(TFA)_4$  as catalysts. At 1.67 V versus SHE, alkanes and benzene yielded the corresponding trifluoroacetate esters at room temperature; typically, good yields and high faradaic efficiencies were observed. High intrinsic turnover frequencies were obtained, for example, of >1000 min<sup>-1</sup> for the oxyesterification of ethane at 30 bar. An analysis of the possible mechanistic pathways based on previously investigated stochiometric reactions, cyclic voltammetry measurements, kinetic isotope effects, and model compounds led to the conclusion that catalysis involves lead-mediated protoncoupled electron transfer of alkanes at and to the anode, followed by reductive elimination through an  $S_N 2$  reaction to yield the alkyl-TFA products. Similarly, lead-mediated electron transfer from benzene at and to the anode leads to phenyl-TFA. Cyclic voltammetry also shows the viability of in situ reoxidation of Pb(II) species. The synthesis results obtained as well as the mechanistic insight are important advances towards the realization of selective alkane and arene oxidation reactions.

KEYWORDS: alkane oxidation, benzene oxidation, electrocatalysis, electron transfer, lead

# **INTRODUCTION**

The sustainable oxidation of alkanes and arenes by activation of their strong carbon-hydrogen bonds remains a significant research goal, where the selective monofunctionalization of light alkanes, cyclohexane, and benzene is also of considerable practical interest. For liquid-phase oxidation under mild conditions, the possibility of using the mimics of monooxygenase enzymes for dioxygen activation and hydroxylation has long captivated researchers.<sup>1</sup> Recently, we demonstrated that an inorganic iron-tungsten oxide cluster is very effective for such monooxygenase reaction using cathodic electrocatalytic conditions.<sup>2</sup> Another common approach to activate strong C-H bonds is by metal complexes, as originally demonstrated for methane by Shilov and co-workers.<sup>3</sup> The arguably best Pt(II) catalysts were significantly improved by use of SO<sub>3</sub> as oxidant with the added advantage of the formation of bisulfate salts stable to further oxidation.<sup>4</sup> Oxidation of light alkanes has also been demonstrated using high-valent iodine compounds.<sup>5</sup> Electrocatalytic transformations are now very much in the vogue, leading to several reports on the anodic oxidation of aliphatic and aromatic

renewable energy resources as alternatives to high-temperature

hydrocarbons.<sup>6,7</sup> There is also a notable example for the use of electrochemically generated active Pd species for the oxidation of methane to a mixture of methyl bisulfate and methyl sulfonate.<sup>8</sup>

Although it was shown long ago that Pb(IV) trifluoroacetate can stoichiometrically oxidize cyclic alkanes in trifluoroacetic acid,<sup>9</sup> such and other similar (Tl(III), Au(III), and Sb(V)) stoichiometric transformations were more recently shown to be reactive for the stoichiometric oxidation of light alkanes in trifluoroacetic acid at elevated temperatures.<sup>10</sup> In the context of this research, our interest is focused on the first use of Pb(IV) in trifluoroacetic acid for the catalytic oxidation of alkanes for several reasons. First, the Pb(IV)/Pb(II) redox couple of 1.455 V versus NHE (in water) for the two-electron

 Received:
 April 13, 2021

 Revised:
 July 28, 2021

 Published:
 August 9, 2021





© 2021 The Authors. Published by American Chemical Society transformation provides a significant driving force for alkane oxidation. Second, lead is a relatively abundant and major industrial element.<sup>11</sup> Third, as shown in the past, two-electron oxidation of the reactive C-H bond leads to oxyesterification and prevents further oxidation of the reacted C-H bond. On the other hand, the high two-electron redox potential precludes the use of  $O_2$  as terminal oxidant, as well as the use of the more kinetically favored SO<sub>3</sub> as oxidant. Therefore, to the best of our knowledge, strong stoichiometric oxidants such as Pb(IV) tetrakis-trifluoroacetate ( $Pb^{IV}(TFA)_4$ ) have never been previously used for catalytic oxidations. It was, however, surmised in this research that it would be possible to use  $Pb(TFA)_4$  in an anodic electrochemical alkane and arene oxidation. Herein we will demonstrate the use of Pb(IV) in trifluoroacetic acid for the anodic room-temperature electrocatalytic oxidation of light alkanes, cyclohexane, and benzene, with a dissection also on possible mechanistic pathways to explain the reactivity that was observed.

# RESULTS AND DISCUSSION

The catalytic oxidant,  $Pb^{IV}(TFA)_4$ , was prepared by the literature method<sup>12</sup> from red lead  $Pb_3O_4$  (2PbO, PbO<sub>2</sub>) to yield a 1.56 M solution of 1:2  $Pb^{IV}(TFA)_4/Pb^{II}(TFA)_2$ . The cyclic voltammogram of  $Pb^{II}(TFA)_2$  separately prepared from PbO, shown in Figure 1, indicates a nonreversible electro-



**Figure 1.** Cyclic voltammogram of 5 mM  $Pb^{II}(TFA)_2$  in 0.2 M TFAK; the working, counter, and reference electrodes were Pt; scan rate: 50 mV/s.

chemical oxidation of Pb<sup>II</sup>(TFA)<sub>2</sub> where the onset potential is at ~1 V. The current at 1.87 V versus SHE, the potential used for the electrocatalytic oxyesterification reactions (see below), is sufficient for an efficient oxidation of Pb<sup>II</sup>(TFA)<sub>2</sub> to Pb<sup>IV</sup>(TFA)<sub>4</sub>. Indeed, the electrochemical oxidation of the 1.56 M solution of 1:2 Pb<sup>IV</sup>(TFA)<sub>4</sub>/Pb<sup>II</sup>(TFA)<sub>2</sub> yielded a quantitative formation of Pb<sup>IV</sup>(TFA)<sub>4</sub>.

The room-temperature electrocatalytic oxidation of light alkanes (methane, ethane, and propane) in trifluoroacetic acid (TFAH) with potassium trifluoroacetate (TFAK) as electrolyte in an electrochemical autoclave was carried out using a homogeneous reaction mixture with dissolved Pb(TFA)<sub>4</sub> and Pt working, counter, and quasi reference electrodes.

The results shown in Table 1 lead to the following insights. (1) Reactivity was a function of the bond dissociation energy (BDE) of the active C-H bond; propane > ethane  $\gg$  methane. This is an indication that the rate-determining step of the reaction is C-H bond activation, where the bond dissociation energies (BDE) for ethane and methane are 100.5 and 105.0 kcal/mol, respectively. The support for this indication is that the oxidation of propane (5 bar) produced

Table 1. Electrocatalytic Oxyesterification of Light Alkanes<sup>a</sup>

substrate	products (µmol)	TOF $(\min^{-1})^{b}$	FE <sup>c</sup>
CH <sub>4</sub> , 30 bar	MeTFA, 23	50	2
C <sub>2</sub> H <sub>6</sub> , 5 bar	EtTFA, 165	800	84
	1,2-CH <sub>2</sub> CH <sub>2</sub> (TFA) <sub>2</sub> , 135		
C <sub>2</sub> H <sub>6</sub> , 5 bar <sup>d</sup>			
C <sub>2</sub> H <sub>6</sub> , 5 bar	EtTFA, 176	1290	91
CH <sub>4</sub> , 30 bar	1,2-CH <sub>2</sub> CH <sub>2</sub> (TFA) <sub>2</sub> , 264		
C <sub>2</sub> H <sub>6</sub> , 5 bar	EtTFA, 130	1180	68
N <sub>2</sub> , 30 bar	1,2-CH <sub>2</sub> CH <sub>2</sub> (TFA) <sub>2</sub> , 255		
C <sub>3</sub> H <sub>8</sub> , 5 bar	i-PrTFA, 420	780	92
	n-PrTFA, 2		

1,2-CH<sub>3</sub>CHCH<sub>2</sub>(TFA)<sub>2</sub>, 2

<sup>*a*</sup>Reaction conditions: 50  $\mu$ mol 1:2 Pb(TFA)<sub>4</sub>/Pb(TFA)<sub>2</sub>, 10 mL TFAH, 0.2 M TFAK, *T*: 23 °C, *t*: 7 h, 1.87 V versus SHE; working electrode Pt mesh (2.5 cm<sup>2</sup>), counter electrode Pt wire, reference electrode Pt wire. <sup>*b*</sup>The TOF (assuming all the lead trifluoroacetate was Pb(TFA)<sub>4</sub>) was calculated as follows: TOF = mol<sub>2-electron oxidations/</sub> (mol<sub>cat on electrode</sub> × time), where mol<sub>products</sub> is the total of all products. The surface of the Pt anode was 2.5 cm<sup>2</sup> = 2.5 × 10<sup>14</sup> nm<sup>2</sup>; the crosssection of Pb(TFA)<sub>4</sub> was taken as 1 nm<sup>2.13</sup> Arbitrarily, at 33% coverage, mol<sub>cat on electrode</sub> = (2.5 × 10<sup>14</sup> nm<sup>2</sup>) (0.33)/(1 nm<sup>2</sup> molecule<sup>-1</sup>) (6.02 × 10<sup>23</sup> molecule mol<sup>-1</sup>) = 1.3 nmol. <sup>c</sup>FE—faradaic efficiency. Note that the faradaic efficiency is also a function of the distance between electrodes. This was difficult to keep constant in the high-pressure autoclave reactor. <sup>*d*</sup>No Pb.

mainly isopropyl trifluoroacetate with a ratio of 450:1 in favor of oxidation at the secondary position, for which the BDE of the C–H bond is 98.1 kcal/mol. (2) Methane was less reactive even at higher pressures as measured by the yield, turnover frequency (TOF), and faradaic efficiency (FE). (3) Ethane reacted to yield both the TFA esters of ethanol and 1,2ethanediol. (4) Mixtures of ethane (5 bar) and methane (30 bar) yielded the selective oxidation of ethane only, indicating also a mechanism that excludes the reactions of an alkane intermediate with an additional alkane molecule. (5) The reaction is not catalyzed by Pt, as shown by the absence of a product in the entry where a Pt anode was used in the absence of  $Pb(TFA)_4$ . Therefore, considering that only a less amount of the Pb(IV) species is actually on the electrode, and is in the nanomole range (see the footnote of Table 1), high intrinsic electrocatalytic turnover frequencies are obtained. Support for this high intrinsic activity can be obtained from the observation that the oxyesterification reactions are efficient at room temperature, in contrast to the previously studied stochiometric reactions that were carried out at 180 °C.<sup>10a</sup> In addition, reasonably good total turnovers can be obtained. For example, in the oxidation of 5 bar ethane in the presence of 30 bar methane (Table 1, entry 4), a TON of 25 in 7 h was obtained.

An attempt was also made to evaluate the possibility of replacing Pb(TFA)<sub>4</sub>, which was used as a molecular catalyst, by a heterogeneous analog, PbO<sub>2</sub> supported on FTO, taking into consideration that PbO<sub>2</sub> should at least partially react with TFAH to yield trifluoroacetate esters on the electrode surface.<sup>12</sup> A typical PbO<sub>2</sub>/FTO electrode that was prepared (see Experimental Section) contained 11 mg (46  $\mu$ mol) of PbO<sub>2</sub>. Thus, a reaction of 5 bar C<sub>2</sub>H<sub>6</sub> in 10 mL of TFAH, 0.2 M TFAK at T = 23 °C for 7 h at 1.87 V versus SHE, using a PbO<sub>2</sub>/FTO working electrode, and a Pt wire as counter electrode and quasi reference electrode yielded 145  $\mu$ mol EtTFA and 125  $\mu$ mol 1,2-CH<sub>2</sub>CH<sub>2</sub>(TFA)<sub>2</sub>. These results were similar to entry 2, Table 1. Further examination of the use of

## Scheme 1. Electrocatalytic Oxyesterification of Cyclohexane and Benzene<sup>a</sup>



<sup>*a*</sup>Reaction conditions:  $50 \mu$ mol 1:2 Pb(TFA)<sub>4</sub>/Pb(TFA)<sub>2</sub>,10 mL of TFAH, 0.2 M TFAK, T: 23 °C, t: 7 h, 1.67 V versus SHE; working electrode Pt mesh (2.5 cm<sup>2</sup>), counter electrode Pt wire, reference electrode Pt wire. The TOF was calculated as described in the footnote of Table 1.

### Scheme 2. Reaction Pathways Considered for the Oxyesterification of Alkanes

 $\begin{array}{c} \mathbf{A} \\ \mathbf{R}_{3}\mathbf{CH} + \mathbf{Pb}^{IV}(\mathbf{TFA})_{4 \ (sol)} \longrightarrow \\ \mathbf{Pb}^{II}(\mathbf{TFA})_{2 \ (sol)} \longrightarrow \mathbf{Pb}^{II}(\mathbf{TFA})_{2 \ (anode)} \longrightarrow \mathbf{Pb}^{IV}(\mathbf{TFA})_{2 \ (anode)} \longrightarrow \\ \mathbf{Pb}^{IV}(\mathbf{TFA})_{2 \ (sol)} \longrightarrow \\ \mathbf{Pb}^{IV}(\mathbf{TFA})_{2 \ (sol)} \longrightarrow \\ \mathbf{Pb}^{IV}(\mathbf{TFA})_{2 \ (anode)} \longrightarrow \\ \mathbf{Pb}^{IV}(\mathbf{TFA})_{3 \ (anode)} \longrightarrow \\ \mathbf{Pb}^{IV}(\mathbf{TFA})_{4 \ (anode)} \longrightarrow \\ \mathbf{Pb}^{IV}(\mathbf{TFA})_{3 \ (R_{3}C)]^{+} \xrightarrow{anode} \\ \mathbf{Pb}^{IV}(\mathbf{TFA})_{3 \ (R_{3}C)]^{+} \xrightarrow{anode} \\ \mathbf{Pb}^{IV}(\mathbf{TFA})_{3 \ (R_{3}C)]^{+} \xrightarrow{anode} \\ \mathbf{Pb}^{IV}(\mathbf{TFA})_{4 \ (anode)} \longrightarrow \\ \mathbf{Pb}^{IV}(\mathbf{TFA})_{4 \ (anode$ 

 $PbO_2$  as anode revealed by ICP-MS measurements that although only a very small amount, 0.25  $\mu$ g (0.12  $\mu$ M), of Pb was leached into the solution, the  $PbO_2/FTO$  electrode proved to be very unstable in the recycle experiments, Figure S1, and therefore further studies in this direction were not pursued.

The oxyesterification of room-temperature liquid hydrocarbons, notably cyclohexane and benzene, is also of practical interest as they are potential precursors to cyclohexanol and phenol, Scheme 1.

It should be noted that only small amounts of dioxyesterification products were obtained in these two reactions. In fact, using cyclohexanol as substrate (500  $\mu$ mol under the conditions described in the footnote of Scheme 1) yielded only 18  $\mu$ mol of a mixture of diesters. This is in contrast to the significant amounts of 1,2-CH<sub>2</sub>(TFA)<sub>2</sub> found in the oxyesterification of ethane. Additional oxyesterification results for various alkanes and different electrolytes can be found in the Supporting Information, Tables S1 and S2. Notably, (1)  $Pb(OAc)_4$  in acetic acid with potassium acetate as electrolyte yielded only small amounts of cyclohexylacetate (12  $\mu$ mol) and phenyl acetate (18  $\mu$ mol) from cyclohexane and benzene, respectively; (2) Oxyesterification of cyclohexane with Pb<sup>II</sup>(TFA)<sub>2</sub> instead of Pb<sup>IV</sup>(TFA)<sub>4</sub> yielded equivalent results; (3) addition of trifluoroacetic anhydride in order to remove water also had no significant effect on the results; (4) the presence of chloride severely inhibited the reaction, and (5)exchange of the Pt mesh anode with FTO yielded significantly lower amounts of the product. (6) In addition, it should be noted that only a miniscule amount of PbO<sub>x</sub> was deposited on the anode from the reaction solution. By removing the electrode at the termination of the reaction, washing with water, and then dissolving any residual PbO<sub>x</sub> with a 1 M solution of KOH, ICP-MS analysis showed 1.9  $\mu$ g of Pb in solution, which corresponds to 8.0 nmol of PbO<sub>2</sub>.

The observation that electrocatalytic oxyesterification occurred with high intrinsic TOFs at room temperature while  $Pb(TFA)_4$  is only a stoichiometric oxidant in solution raises important mechanistic questions, which need to take into account also the difference between the molecular electrocatalytic and homogeneous stoichiometric reactions. Previous experimental and computational evidence has supported the idea of  $Pb(TFA)_4$  acting as an electrophile for the homogeneous stoichiometric reaction that entails, e.g., for ethane:<sup>10a</sup> (i) deligation of a TFA ligand, (ii) endergonic coordination of ethane, (iii) intramolecular C–H bond activation via a cyclic transition state to yield a metal-ethyl species and bound TFAH, followed by (iv) a reductive elimination to yield EtTFA via a  $S_N2$  pathway or ethylene via a  $E_2$  pathway where ethylene further reacts to yield 1,2- $CH_2CH_2(TFA)_2$ .

Based on this previously supported mechanism, various pathways for the electrocatalytic reaction were evaluated. A first possibility is that  $Pb^{IV}(TFA)_4$  reacts in solution with the substrate to yield an oxidation product and reduced  $Pb^{II}(TFA)_2$ . The latter can then be reoxidized at the anode to complete a catalytic cycle, Scheme 2A. Such a pathway seems very improbable based on the observations (i) that the  $PbO_2/FTO$  anode is similarly efficient to a Pt anode with dissolved  $Pb(TFA)_4$  although in the former case only 0.12  $\mu M$  lead was found in solution and (ii) the stoichiometric oxidation of ethane at ~35 bar, for example, required 3 h at 180 °C for 0.9 turnovers based on Pb(TFA)\_4, while under electrocatalytic conditions around 25 turnovers (5 bar ethane, 30 bar N<sub>2</sub>) based on Pb(TFA)\_4 were obtained at room temperature after 7 h.

It has also been recently suggested that oxidation reactions of light hydrocarbons, even for example methane, can be propagated by trifluoromethyl radicals.<sup>14</sup> Based on such reactivity, one can propose a catalytic cycle, Scheme 2B, where an anode-initiated reaction leads to homolytic cleavage of a trifluoroacetate ligand coordinated to Pb to yield a trifluoromethyl radical  $CF_3^{\circ}$ ,  $CO_2$ , and  $Pb^{III}(TFA)_3$ . A



Figure 2. Cyclic voltammograms of a representative alkane (hexane) and arene (benzene) in the presence of 1:2  $Pb^{IV}(TFA)_4/Pb^{II}(TFA)$ , 5 mM Pb trifluoroacetate esters, and 0.2 M TFAK; the working, counter and reference electrodes were Pt; scan rate: 50 mV/s.





subsequent hydrogen atom transfer reaction to yield a hydrocarbon radical would be followed by one-electron redox reaction to vield the oxvesterification product and  $Pb^{II}(TFA)_2$ , which would be oxidized back to  $Pb^{IV}(TFA)_4$  at the anode. There are various lines of evidence that support such a reaction pathway, including the reactivity  $3^{\circ} > 2^{\circ} > 1^{\circ}$ (Table S1), the general trend of reactivity being a function of the BDE of the reactive C-H bond (propane 98.1 kcal/mol < ethane 100.5 kcal/mol < methane < 105.0 kcal/mol)<sup>15</sup> and the presence of a planar intermediate as shown by the formation of equal amounts of cis- and trans-1,2-dimethylcyclohexyl-2-TFA from trans-1,2-dimethylcyclohexane (see Table S1). These observations also support other pathways as shown below. Importantly, however, such a reaction pathway would require the formation of equimolar amounts of fluoroform and oxyesterification products. GC-MS and GC-TCD analysis of the reaction mixture (including the gas phase) revealed the formation of some CF<sub>3</sub>H, however in quantities of only 5–10% of the amount of oxyesterification product. Further, one must take into account that such a mechanism requires the homolytic C-C bond cleavage of a carboxylate ligand. A comparison of the C-C BDEs of three liquid carboxylic acids as solvents for oxyesterification was carried out and showed the following: acetic acid (92.0 kcal/mol) > trifluoroacetic acid

(88.6 kcal/mol) > 2,2'-dichloracetic acid (79.8 kcal/mol).<sup>14</sup> The limited reactivity of Pb<sup>IV</sup>(OAc)<sub>4</sub> would be consistent with the relative C–C BDEs of acetic acid versus trifluoroacetic acid, but a reaction carried out in dichloroacetic acid yielded no oxyesterification of cyclohexane but a large amount of 1,1,2,2-tetrachloroethane, the homocoupled product of Cl<sub>2</sub>HC<sup>•</sup>. One may conclude that there may be some contribution to oxyesterification initiated by F<sub>3</sub>C<sup>•</sup>, but probably this pathway is only of minor importance.

Based on the notion that the oxyesterification reactions occur via similar reaction steps as proposed for the stoichiometric homogeneous reaction, one can postulate that the reaction at the anode lowers the free energies of the endergonic alkane coordination and/or the free energy of the transition state required for C–H bond activation, Scheme 2C, thereby increasing the overall rate. Evidence for the validity of this postulate was obtained by cyclic voltammetry measurements, Figure 2, showing that the onset potential for the electron transfer (ET) of representative alkane and arene substrates, hexane and benzene, is decreased in the presence of Pb<sup>IV</sup>(TFA)<sub>4</sub>, while the current increases.

The proposed electrocatalytic steps leading to product formation are summarized in Scheme 3 for the alkanes. Generally, it is possible that octacoordinate  $Pb^{IV}(TFA)_4^{15,16}$ 

Scheme 4. Key Reaction Steps for the Oxyesterification of Benzene



will bind the alkanes at one coordination site to yield I by ligand exchange, Scheme 3A. Then, C–H bond activation can occur through an electrochemical proton-coupled electron transfer (PCET) at the anode for alkanes to yield a Pb(III) intermediate (II), as shown in Scheme 3 for ethane. Subsequent 1-electron oxidation<sup>16</sup> will lead to a Pb(IV) species (III), which would be followed by a  $S_N2$  reductive elimination leading to the alkyl-TFA products. Pb<sup>II</sup>(TFA)<sub>2</sub> would be reoxidized to Pb<sup>IV</sup>(TFA)<sub>4</sub> at the anode. Alternatively, or in parallel, a [Pb<sup>III</sup>(TFA)<sub>2</sub>]<sup>+</sup> intermediate (IV), Scheme 3B, formed at the anode from Pb<sup>III</sup>(TFA)<sub>2</sub> may bind ethane in the presence of TFA. The Pb<sup>III</sup>(TFA)<sub>3</sub>(CH<sub>3</sub>CH<sub>3</sub>) intermediate (V) so formed would then undergo a PCET reaction leading to the Pb(IV) species (III) and then the product as noted above.

A kinetic isotope effect (KIE) at a constant current of 1 mA was measured for the intermolecular competitive reaction between cyclohexane  $C_6H_{12}$  and  $C_6D_{12}$ , where a primary KIE of  $k_{\rm H}/k_{\rm D}$  = 3.0 ± 0.1 was obtained, Figure S2. This KIE is a strong indication that the PCET reaction for C-H bond activation is rate determining. This conclusion is also supported by the relative reactivity, showing that the order of reactivity of C-H bonds is  $3^{\circ} > 2^{\circ} > 1^{\circ}$ . Using trans-1,2dimethylcyclohexane as substrate, Table S1, equimolar amounts of the cis- and trans isomers of 1,2-dimethylcyclohexyl-2-TFA were formed, indicating that the reductive elimination reaction is sequential to PCET, i.e., C-H bond activation. Notable was the observation that substrates such as cyclohexane or octane did not form diester products and propane only formed a small amount of 1,2- $CH_3CHCH_2(TFA)_2$  under electrocatalytic conditions, although diesters were formed in homogeneous stoichiometric reactions as reported<sup>10a</sup> and verified by us. Ethane is definitely an outlier with a significant formation of 1,2-CH<sub>2</sub>CH<sub>2</sub>(TFA)<sub>2</sub>.  $1,2-CH_2CH_2(TFA)_2$  is not formed sequentially from EtTFA in considerable amounts, since the latter yielded only 1.6% 1,2- $CH_2CH_2(TFA)_2$  (reaction conditions: 500 µmol EtTFA, 10 mL of TFAH, 0.2 M TFAK, T: 23 °C, t: 7 h, 1.87 V versus SHE; 50  $\mu$ mol 1:2 Pb(TFA)<sub>4</sub>/Pb(TFA)<sub>2</sub>, working electrode Pt mesh (2.5 cm<sup>2</sup>), counter electrode Pt wire, reference electrode Pt wire). The reasons for this may be the possibility of coordination of ethane via both carbon atoms at two positions of the octacoordinated Pb(IV) catalyst combined with the absence of steric effects, e.g., compared to cyclohexane, and the fact that both carbon atoms are primary with intrinsically identical reactivity, e.g., compared to propane, which reacts by a large preference at the 2° carbon atom.

The oxyesterification of benzene, Scheme 4, could start with a Pb<sup>IV</sup>(TFA)<sub>3</sub>-benzene complex where an ET process to the anode will lead to a Pb<sup>IV</sup>-based phenyl cation radical that can react with a TFA anion to yield Ph-TFA. Alternatively, beginning with a Pb<sup>II</sup>(TFA)<sub>2</sub>-benzene complex, an ET process will yield a Pb<sup>II</sup>-based phenyl cation radical, which could undergo an additional 1-electron oxidation and deprotonation

to yield a Pb(IV)-phenyl intermediate and then product formation by reductive elimination.<sup>17</sup> Beyond the evidence provided by the cyclic voltammetry measurements, there are various lines of evidence that support these postulated scenarios. Since PCET for benzene would require the cleavage of a prohibitively strong C-H bond and the unlikely formation of a phenyl radical, an ET activation benzene is more probable. Indeed, the KIE found in a competitive reaction between  $C_6H_6$ and  $C_6D_6$  yielded  $k_H/k_D = 1.07 \pm 0.02$ , indicative of only a secondary isotope effect, Figure S3. Further, it should be noted that this ET reaction is significantly more facile than PCET for cyclohexane since a competitive reaction between benzene and cyclohexane yielded a ratio of 99.2% Ph-TFA versus 0.8% cyclohexyl-TFA.

## CONCLUSIONS

The first catalytic and electrocatalytic oxidative transformation of gaseous alkanes (methane, ethane, and propane) as well as cyclohexane and benzene with Pb<sup>IV</sup>(TFA)<sub>4</sub> was demonstrated. From a synthesis, practical point of view, the formation of mono-oxyesterification products was obtained except in the case of ethane, where TFA esters of both ethanol and 1,2ethanediol were obtained in similar amounts. Intrinsic TOFs were typically quite high except in the case of methane. Interestingly, however, the lower reactivity of methane demonstrates the possibility of an effective pathway of productive removal of ethane from natural gas, ethane being often burnt off on site. The use of lead, a relatively abundant element in a catalytic oxidative transformation, is a step forward in the framework of sustainability; however, alternatives to TFAH should still be discovered. From a mechanistic point of view, cyclic voltammetry, kinetic isotope effects, model compounds, as well as the activity of PbO<sub>2</sub>/FTO suggest that the oxyesterification reaction occurs at the anode. For alkanes, there is strong support for PCET as the ratedetermining step, where alkanes are coordinated either to the Pb(IV) or to the Pb(III) species. PCET at and to the anode yields an alkyl-Pb intermediate as the rate-determining step, as supported by the relative reactivity of substrates  $(3^{\circ} > 2^{\circ} >$ 

 $1^{\circ}$  > methane) and the KIE measurements. Subsequent reductive elimination yields alkyl-TFA and  $Pb^{II}(TFA)_2$ , where the latter is reoxidized at the anode and  $H_2$  is released at the Pt cathode. The unique diesterification of ethane may be related to a combination of 2 equiv primary carbons and the lack of steric hindrance. Benzene is proposed to react in a similar manner, except that an ET reaction leads to a phenyl radical cation moiety that reacts with TFA to yield phenyl-TFA as the only product.

## EXPERIMENTAL SECTION

Chemicals. All chemicals were reagent grade and used as supplied.  $Pb(TFA)_4$  was prepared by a known literature method.<sup>12</sup> Red lead, Pb<sub>3</sub>O<sub>4</sub> (2PbO, PbO<sub>2</sub>) (15.3 g, 0.023 mol), trifluoroacetic acid (50 g, 0.43 mol), and trifluoroacetic anhydride (30 g, 0.14 mol) were stirred for 2-4 days at RT until the red color disappeared. The mixture was filtered by centrifugation and the yellow solution of Pb(TFA)<sub>4</sub> was decanted and used directly. The concentration of Pb(TFA)<sub>4</sub> was measured by adding 0.05 mL of the TFA solution to water (25 mL), reduced with KI (0.05 g), and then saturated with NaOAc. Back titration was done with a standard Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution containing 32%  $Pb(TFA)_4$  and 68%  $Pb(TFA)_2$ . This solution, at 1.67 V versus SHE, can be transformed quantitatively to form a 1.56 M solution of  $Pb(TFA)_4$ . When TFAK was used as electrolyte, it was prepared in situ by slow addition of solid KOH in the required amount to TFAH.

**Preparation of the PbO<sub>2</sub>-FTO Electrode.** FTO glass, 10  $\Omega$ /sq, from XinYan Technology was cleaned with isopropanol and then dried. An FTO anode and a Cu wire cathode were placed in a 0.1 M Pb(NO<sub>3</sub>)<sub>2</sub>, 0.1 M Cu(NO<sub>3</sub>)<sub>2</sub>, and 1 M nitric acid in water. A potential of 2.5 V at 23 °C was applied for 10 min, during which black layers of PbO<sub>2</sub> (11 mg, 46  $\mu$ mol) were formed on the conducting surface of FTO. A similar fluorinated PbO<sub>2</sub>-FTOF electrode was prepared under the same conditions in the presence of 0.1 M solution of NaF.

**Cyclic Voltammetry and Electrolysis.** All experiments were carried out using a BioLogic Science VSP-201 potentiostat. CV was measured using a three-electrode setup in which all the electrodes were of Pt wire. All of the measurements were performed in 0.2 M TFAK in TFA, with 0.5 mM Pb(TFA)<sub>4</sub>.

The electrolysis experiments were performed in a thermostated microcell at 23 °C with a platinum gauze anode working electrode (3 cm<sup>2</sup> effective area), a platinum wire cathode counter electrode, and a Pt pseudo reference electrode. In a typical reaction for liquid substrates, a magnetically stirred solution of substrate and Pb(TFA)<sub>4</sub> (25  $\mu$ mol) in 10 mL of TFAH containing 0.2 M electrolyte was electrolyzed at a constant potential (1.67 V versus the Pt wire pseudo reference electrode). This electrode was calibrated using a solution of Ru(bpy)<sub>3</sub>Cl<sub>2</sub> in TFAH and was compared to Ag/AgNO<sub>3</sub> in TFAH yielding a potential of 0.07 V versus SHE. To the reaction was added water; the reaction mixture was extracted with ethyl ether; the collected organic extracts were washed with aqueous NaHCO<sub>3</sub>, then with water, and finally dried with anhydrous Na2SO4. The conversion of the substrate and yield of products and selectivity were determined by GC, GC-MSD, or by <sup>1</sup>H NMR. GC-MSD was used for the KIE measurements.

For gaseous alkanes, a 25 mL Hastelloy C Parr reactor was adapted with a Pave Technology high-pressure electrical feedthrough seal, Figure S4. All electrochemical measurements using this cell were performed using a Biologic VSP 5-channel potentiostat and a three-electrode undivided electrochemical cell. A Pt net (2.5 cm<sup>2</sup>) or Pb<sub>2</sub>O/FTO-coated glass slides cut into 1 × 2.5 cm<sup>2</sup> rectangular pieces were used as the working electrodes. A tungsten wire was wrapped tightly around the upper half of the FTO-coated slide to ensure a contact between the working electrode and wire current collector. To prevent the exposure of the tungsten wire to the corrosive TFA solution, a Teflon tape was wrapped around the tungsten wire and the FTO-coated slide, leaving a 1 × 1 cm<sup>2</sup> area of Pb<sub>2</sub>O/FTO in the reaction solution.

Intrinsic TOFs were computed as follows: TOF =  $mol_{2-electron oxidations}/(mol_{cat on electrode} \times time)$ , where  $mol_{products}$ is the total of all products. When using a Pt anode  $(2.5 \text{ cm}^2 =$  $2.5 \times 10^{14} \text{ nm}^2$ ), the cross-section of Pb(TFA)<sub>4</sub> was taken as 1 nm<sup>2</sup>. Arbitrarily at 33% coverage, The faradaic efficiency for formation of organic products was calculated by dividing the number of products (taking into account each two-electron oxidation) by the number of electrons that were passed through the electrochemical cell. Combined NMR, GC, and GC-MSD measurements (see the Supporting Information) were carried out to quantify and identify the reaction products. For GC, a HP 6890 instrument with a flame ionization detector and a HP 5973 instrument with a mass-selective detector were used. Liquid chromatographic separations were carried out using a 30 m (Restek 5MS, 0.32 mm internal diameter) column with a 5% phenylmethylsilicone coating of 0.25  $\mu$ m; helium was used as the carrier gas. A split/splitless injector was applied with a split ratio of 50:1 and a split flow of 50 mL/min. Both instruments were operated with an oven temperature of 40 °C, an inlet temperature of 220 °C, a column pressure of 7 psi, and a flow rate of 1 mL/min using helium as the carrier gas. After 5 min at 40 °C, the temperature was increased by 15 °C/min to 280 °C. The gas phase was analyzed using a HP 6890 GC equipped with a thermalconductivity detector using a 15 m Carbonplot capillary column (0.53 mm ID). <sup>1</sup>H NMR spectra were measured using a Bruker Avance 400 MHz instrument with  $C_6H_6$  as the external reference in a capillary tube.

**Caution.** Alkyl lead compounds may be present in the reaction mixtures and appropriate care should be taken to prevent exposure.

## ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.1c01674.

Tables and figure of additional oxyesterification reactions, figures for the analysis of the kinetic isotope effects, a picture of the gas phase electrochemical reactor, NMR spectra, GC-FID chromatograms, mass spectra, current versus time plots, and charge versus time plots (PDF)

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#### **Author Contributions**

The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

#### Notes

The authors declare no competing financial interest.

# ACKNOWLEDGMENTS

This research was supported by the Israel Science Foundation grant 1237/18. R.N. is the Rebecca and Israel Sieff Professor of Organic Chemistry.

# **ABBREVIATIONS**

BDE, bond dissociation energy; CV, cyclic voltammetry; ET, electron transfer; FE, faradaic efficiency; FTO, fluorinated tin oxide; GC-MSD, gas chromatograph with a mass-selective detector; ICP-MS, inductively coupled plasma mass spectrometry; KIE, kinetic isotope effect; NHE, normal hydrogen electrode; NMR, nuclear magnetic resonance; PCET, protoncoupled electron transfer; SHE, standard hydrogen electrode; TFA, trifluoroacetate; TFAH, trifluoroacetic acid; TFAK, trifluoroacetate potassium salt; TOF, turnover frequency

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