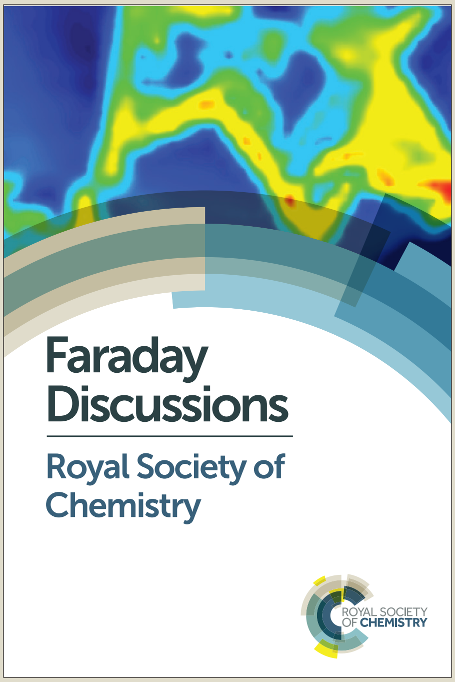
Faraday Discussions

Accepted Manuscript

This manuscript will be presented and discussed at a forthcoming Faraday Discussion meeting. All delegates can contribute to the discussion which will be included in the final volume.

Register now to attend! Full details of all upcoming meetings: http://rsc.li/fd-upcoming-meetings



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/faraday_d

Faraday Transactions

ARTICLE

Designing for Selectivity: Weak interactions and the competition for reactive sites on gold catalysts

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

C.G.F. Siler, R.J. Madix, C.M. Friend

Abstract: A major challenge in heterogeneous catalysis is controlling reaction selectivity, especially in complex environments. When more than one species is present in the gas mixture, the competitiion for binding sits on the surface of a catalyst is an important factor in determining reaction selectivity and activity. We establish an experimental hierarchy for the binding of a series of reaction intermediates on Au(111) and demonstrate that this hierarchy accounts for reaction selectivity on both the single-crystal surface and under operating catalytic conditions at atmospheric pressure using a nanoporous Au catalyst. A partial set of measurements of relative binding has been measured by others on other catalyst materials, including Ag, Pd and metal oxide surfaces; comparison demonstrates the generality of this concept and identifies differences in the trends. Theoretical calculations for a subset of reactants on Au(111) show that weak, van der Waal's interactions are key to predicting the hierarchy of binding strengths for alkoxides bound to Au(111). This hierarchy is key to the control of the selectivity for partial oxidation of alcohols to esters on both Au surfaces and over nanoporous Au catalysts under working catalytic conditions using nanoporous gold. The selectivity depends on the competition for active sites among key intermediates. New results probing the affect of fluorine substitution are also presented to extend the concept relating reaction selectivity to the hierarchy of binding are also presented. Motivated by an interest in synthetic manipulation of fluorinated organics, we specifically investigated the influence of the –CF_3 group on alcohol reactivity and selectivity. 2,2,2-Trifluoroethanol couples on O-covered Au(111) to yield CF_3CH_2O-C(=O)(CF_3), but in the presence of methanol or ethanol it preferentially forms the respective 2,2,2-trifluoroethoxy-esters. The ester is *not* the dominant product in any of these cases, though, indicating that the rate of β-H elimination from adsorbed trifluoro-ethoxy is slower than for either adsorbed methoxy or ethoxy, consistent with their relative estimated β-C-H bond strengths. The measured equilibrium constants for the competition for binding to the surface are 2.4 and 0.38 for ethanol and methanol, respectively, vs. 2,2,2-trifluoroethanol, indicating that the binding strength of 2,2,2-trifluoroethoxy is weaker than ethoxy, but stronger than methoxy. These results are consistent with weakening of the interactions between the surface and the alkyl group due to Pauli repulsion of the electron-rich CF_3 group from the surface, which offsets van der Waals attraction. These experiments provide guiding principles for understanding the effect of fluorination on heterogeneous synthesis and further demonstrate the key role of molecular structure in determining reaction selectivity.

Introduction

An important facet of the design of efficient catalytic processes is understanding the factors that determine reaction selectivity, especially in complex environments. One factor in determining reaction selectivity in heterogeneous catalysis is competition for active sites among the various reactants and products of reactions. The competition for active sites will depend on the relative binding strengths of these disparate species. The relative binding strengths, in turn, are known to depend on the composition and structure of the surface and the functionality of the primary moiety bound to the surface. Generally, periodic trends in relative binding strengths have been described in terms of the relative metal-atom binding strengths calculated using Density Functional Theory (DFT) leading to so-called linear scaling relationships.[1] While there is no question that many aspects of reactivity trends are predicted using these scaling relationships, this approach does not capture variability in reactivity within a homologous series of molecules, e.g. alcohols with different chain lengths.

[a] Dr. C. G. F. Siler, Prof. R. J. Madix, Prof. C. M. Friend
School of Engineering and Applied Science
Harvard University
12 Oxford St, Cambridge, MA 02138
E-mail: friend@fas.harvard.edu
[b] Prof. C. M. Friend
Dept. of Chemistry and Chemical Biology
Harvard University
12 Oxford St, Cambridge, MA 02138

Supporting information for this article is given via a link at the end of the document.

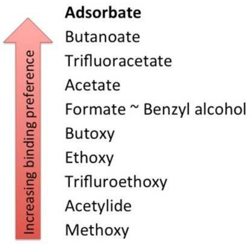


Figure 1: Hierarchy of relative binding affinities of various molecules on Au(111).

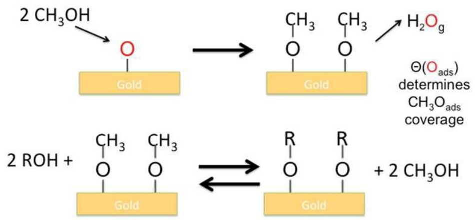


Figure 2: Schematic of displacement reactions on Au(111). Adsorbed O is required to activate an alcohol on Au (top). Competition for binding sites occurs through displacement which establishes an equilibrium concentration of two dissimilar alcohols because of their different adsorption energies.

We have shown that variation in molecular structure, even for a homologous series, has a significant impact on the competition for active sites. Experimentally, we established a hierarchy for the binding of a broad range of molecules on Au single-crystals by studying displacement reactions (Figs. 1, 2).[2] Clearly, the functional group through which the molecule is primarily bound to the surface is important in determining binding strength; e.g. carboxylates are more strongly bound that alkoxides. There are also important differences in binding strength depending on the alkyl group within a homologous series, e.g the alkoxides. Generally, an increase in chain length strengthens binding. On the other hand, fluorination of the terminal group in ethoxy weakens the binding.

In selected cases, equilibrium constants for this competition (Figure 1) were measured in order to quantify the relative binding affinity. Specifically, the equilibrium constants for displacement of methoxy (CH_3O_{ads}) by ethanol or 1-butanol on Au(111) were measured to be 5 and 10, respectively.[3] These studies raised the important question of the underlying physical basis of these differences in relative binding strengths and also suggested that additional quantitative measurements of equilibrium constants would be valuable in predicting reaction selectivity when one or more of these intermediates competes for reactive sites.

The generality of the use of displacement reactions to establish a hierarchy of the relative binding affinities of various molecules on surfaces has been demonstrated by other studies. On coinage metals, Ag(110) and Cu(110), the experimentally determined hierarchy of binding is similar to Au(111) and was related to the gas phase acidities of the molecules. On Ag(110), the order of binding of adsorbed species was determined to be HCOO ≈ $CH_3COO > C_2H_5O > C_2H > CH_3O$.[4] A somewhat different set of molecules was studied on Cu(110) but with a similar hierarachy: HCOO > 1-propoxy ~ 2-propoxy > C_2H > C_2H_5O > CH_3O.[5] Analogous studies on ZnO and MgO established a different order of binding affinities.[6] Although the carboxylates (HCOO and CH_3COO) still had higher binding affinities to these oxide surfaces than any of the alcohols investigated, similar to the coinage metals, the relative behaviour of methanol and ethanol was different. On ZnO, methoxy and ethoxy were similarly bound and on MgO methanol displaced ethoxy—the opposite of the coinage metals. The behaviour on the oxides was explained in terms of charge stabilization of the anion of the gas-phase acidity by cation sites on these oxides; however, advanced theoretical methods were not yet available to test this postulate. Nevertheless, these investigations illustrate the generality of using displacement reactions to establish a qualitative hierarchy for binding affinity.

Table 1: The significant role of van der Waal's interactions in determining relative binding strengths is revealed by DFT calculations.

Adsorbate	E_b (eV) PBE	E_b (eV) PBE+ vdW	Difference due to vdW (eV)
CH_3O	1.15	1.29	0.14
CF_3CH_2O	1.11	1.41	0.30
CH_3CH_2O	1.38	1.64	0.28
1-$CH_3(CH_2)_3O$	1.33	1.80	0.47

Theoretical studies of a selected set of alkoxides on Au(111) demonstrated the key role of weak, van der Waal's interactions in determining relative binding for the specific case of alkoxide binding (Table 1).[2] The van der Waal's interactions of the alkyl group with the surface increase with increasing alkyl chain length by ~ 0.13 eV per CH_2 group. The presence of the electron-rich group, e.g. CF_3, also affects relative binding strength via Pauli repulsion with the surface leading to a decrease in the binding energy of 0.27 eV for trifluorethoxy vs. ethoxy. The combination of model studies on gold single crystals and theoretical investigations establish the important parameters that dictate relative binding energy—functional group binding and weak van der Waal's forces. The similarities in binding trends on Ag and Cu suggest that weak interactions are also important on these metals. On the other hand, the experimental hierarchy on the oxides, ZnO and MgO, suggest that the van der Waal's interactions play less of a role on the oxides due to lower polarizability. This important point needs further study using theoretical tools.

The relationship between reaction selectivity and competitive binding is specifically illustrated by the oxidative coupling of dissimilar alcohols on Au. Detailed mechanistic studies on Au(111) using surface science techniques established the mechanism for selective oxidative coupling of

Figure 3: Schematic of the mechanism for oxidative coupling of ethanol on Au activated by adsorbed O.

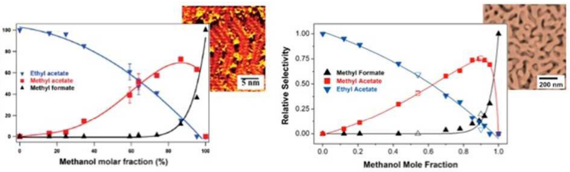


Figure 4: The dependence of the selectivity as a function of the mole fraction of methanol in the oxygen-assisted reaction of ethanol and methanol is similar for Au(111) under ultrahigh vacuum conditions (left) and over a nanoporous Au catalyst under steady state reaction conditions at atmospheric pressure (right).

methanol and subsequently of other longer-chain alcohols, e.g. ethanol (Figure 3). Adsorbed O is required to activate alcohols on gold, [7,8] the first step being hydrogen transfer from the O-H to adsorbed O to yield an adsorbed alkoxy (RO_{ads}) and hydroxyl. An aldehyde is formed in an ensuing β-C-H scission step and three reaction pathways are available thereafter: (1) coupling to a neighbouring unreacted alkoxy to form an ester; (2) reaction with excess adsorbed O to form a carboxylate; or (3) desorption from the surface. The relative contributions of these pathways depend on the ratio of adsorbed O to alkoxy on the surface and on the molecular structure of the alkyl group in the alkoxy. [2 9]

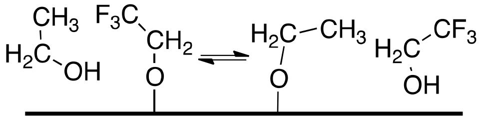
The same general mechanism leads to the coupling of dissimilar alcohols on gold. The *selectivity* for production of specific esters from a mixture of different alcohols depends strongly on the composition of the reactant mixture (Figure 3). The optimum selectivity for production of methyl acetate from coupling of methanol with ethanol on gold has essentially the same dependence both under the controlled conditions of ultrahigh vacuum and catalytic flow conditions (Fig. 4). [3,10,11] A similar correspondence was also measured for methanol coupling with 1-butanol on Au(111) and over nanoporous Au. The two main factors that control reaction selectivity are: (1) the relative rate of β-H elimination from the adsorbed alkoxy species to form the aldehyde, and (2) the relative concentrations of the reactant alkoxys, which is, in turn, determined by the equilibrium between the adsorbed intermediates and the ambient reactant gas phase.

In this work, we extend the study of reaction selectivity and its relationship to competitive binding to the study of fluorinated ethanol. Fluorinated organic compounds are widely used in the synthesis of specialized polymers and pharmaceuticals. The fascinating chemistry of fluorinated organics is due to the stability of the C-F bond and high electronegativity and low polarizability of fluorine, which can change the electron density distribution, molecular conformations, and intramolecular forces of organic compounds, among other effects, altering their physical and chemical properties.[12] These unique interactions of fluorine have been applied to enable phase separation in catalysis, enhanced medicinal effectiveness of drugs, pesticide potency, and more favorable environmental compatibility, to name a few examples.2 [12,13] Hydrofluoroalcohols in particular are used as solvents for enantioselective catalysis, in lubricants, electronic components, and as refrigerants. [14,15] They are environmentally-friendly alternatives for chlorofluorocarbons or hydrofluorocarbons, because they cause less greenhouse warming and no stratospheric ozone depletion. [15,16]

Considerable effort has been made to develop homogeneous catalysts for stereoselective transformations of fluorinated compounds; fluorine has also been used as a steering group to build novel homogeneous catalysts. [13,17,18] In contrast, there has been little effort to develop heterogeneous catalysts, which have potential advantages from a process standpoint.[19] Therefore, we set out to develop fundamental understanding of the surface chemistry of fluorinated organics on gold in order to provide the understanding necessary for controlling the heterogeneous catalysis involving these fascinating systems. We specifically investigated the effect of fluorination in 2,2,2-trifluoroethanol on O-covered Au(111) by generalizing the mechanism for alcohol transformations on gold.

This current work was also motivated our recent study of the relative stability of surface intermediates in which the stability of 2,2,2-trifluoroethoxy formed from 2,2,2-trifluoroethanol was compared to intermediates formed from other primary alcohols and acids on Au(111). Displacement reactions showed that fluorine substitution weakened the binding on Au(111). Theoretical studies demonstrated that the van der Waals forces that are important in predicting the order of stability for alkoxys with varying chain length were essentially the same for ethoxy and 2,2,2-trifluoroethoxy (Table 1) but that repulsion between the electron-rich CF_3 group and the Au surface has a destabilizing effect. The net result is that adsorbed 2,2,2-trifluoroethoxy is predicted to be slightly more stable than methoxy but less stable than either ethoxy or 1-butoxy on Au(111). In this work we quantify the effect of fluorine substitution on the competition for binding to the surface by measuring the equilibrium demonstrate the steering effect of fluorine substitution on the reaction selectivity in the complex reaction environment of coadsorbed alkoxy intermediates.

Results and discussion



Scheme 1. Competitive equilibrium of alkoxys on a gold surface, shown for 2,2,2-trifluoroethoxy and ethoxy.

We established the influence of fluorine substitution on the two factors that determine reaction selectivity—competition for reactive sites and the rate of β-H elimination—using 2,2,2-trifluoroethoxy, derived from CF_3CH_2OH, as a prototype. By measuring selectivity and total product yields for mixtures of CF_3CH_2OH and either ethanol or methanol, we were able to determine the relative rates of β-H elimination of the different alkoxy species, equilibrium constants for competitive binding (Scheme 1) and overall trends in selectivity. First, for reference, we address oxidation of the fluorinated ethanol and ethanol on gold in isolation. Then we will explore the mixtures of alcohols, first addressing the difference in β-H elimination, then the binding equilibrium constants and overall selectivity trends.

Reaction of CF_3CH_2OH on O/Au(111) produces 2,2,2-trifluoroacetaldehyde and 2,2,2-trifluoroethyl-2,2,2-trifluoroacetate at 240-300 K and 277, K, respectively, and CO_2 and CF_3 produced via trifluoroacetate decomposition at 595 K (Fig. 5a). These results demonstrate that the same overall mechanism for selective alcohol oxidation on Au applies to the fluorinated species. [20,21] However, there are interesting selectivity differences, which can be clearly observed by placing oxidation of both 2,2,2-trifluoroethanol and ethanol side-by-side under the same oxidizing conditions (Fig. 5a, b).

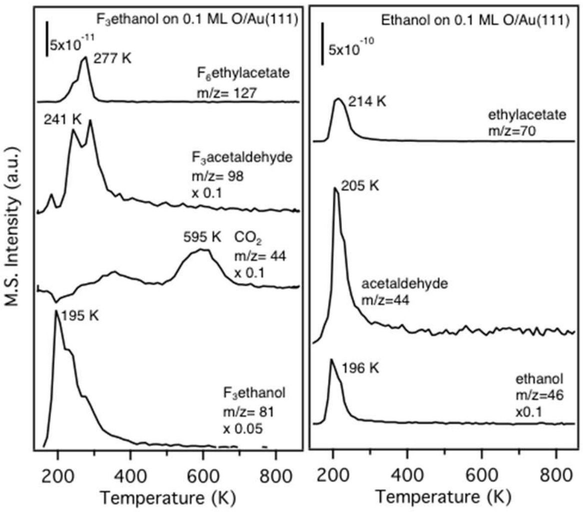


Figure 5. Oxidation of (a) 2,2,2-trifluoroethanol and (b) ethanol on 0.1 ML O/Au(111). Each alcohol was dosed in excess at 120 K the heating rate was 5 K/s. The m/z traces have been corrected for fragmentation and ionization cross-section, and then the multiplication factor was applied so that all products could be seen. Also note different scales.

In contrast to ethanol oxidation, for which our results are consistent with previous results [21] oxidation of trifluoroethanol results in a much larger molar ratio of aldehyde vs. ester production: ~16:1 vs. ~1.6:1 with and without F substitution, respectively. Furthermore, there is also a considerable amount of CO_2 production at high temperature for $CF_3CH_2O_{ads}$ but no detectable CO_2 for reaction of $CH_3CH_2O_{ads}$ under the same conditions. This pattern of CO_2 production indicates the presence of trifluoroacetate from over-oxidation on the surface.[20]

There are four possible ester products that can be derived from oxidative coupling of mixtures of two different alcohols: two cross-coupling esters and two self-coupling esters. However, as previously established, only one of the cross-coupling products is observed.[3] The relative β-H elimination rates between different alcohols are reflected in the identity of the coupling products—the alcohol with the faster β-H elimination makes up the acyl portion of the alkyl-ester product (Scheme 2).

Oxidation of CF_3CH_2OH in the presence of ethanol or methanol on O/Au(111) yields coupling products, as exemplified for specific mixtures (Fig. 6). In the example shown for the CH_3CH_2OH and CF_3CH_2OH mixture, the only esters formed are trifluoroethylacetate and ethylacetate; no trifluoroethyltriflouroacetate or

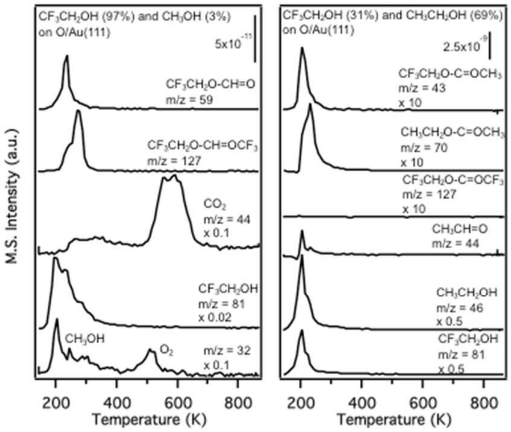


Figure 6. Oxidation of a mixture of 2,2,2-trifluoroethanol and either methanol (left) or ethanol (right) on 0.1 ML O/Au(111).The mixtures used are 0.31: 0.69 ratio of CF_3CH_2OH: CH_3CH_2OH and 0.97: 0.03 CF_3CH_2OH: CH_3OH. The mixture of alcohols was dosed in excess at 120 K, to ensure equilibrium is reached. The heating rate was 5 K/s. The relative amounts of the alcohols were determined from condensation of the alcohol mixture onto clean Au(111) followed by desorption. The m/z traces have been corrected for fragmentation and ionization cross-section, and then the multiplication factor was applied to emphasize the ester products. No trifluoroacetaldehyde is detected in the experiment with ethanol.

ethyltriflouroacetate is detected. Both of the esters formed are derived from acetaldehyde formed from ethanol oxidation (Scheme 2) - clear evidence that β-H elimination from the ethoxy is significantly faster than from 2,2,2-trifluoroethoxy. If β-C-H bond breaking occurred at a similar rate for the two alkoxys, all coupling products would be observed. This faster rate of β-H elimination from the ethoxy is observed for all compositions tested (see below). It appears as if acetaldehyde also preferentially adds to $CF_3CH_2O_{ads}$ over CH_3CH_2Oads based on the lower temperature for production of trifluoroethylacetate relative to ethylacetate (Fig. 6), with a peak onset approximately 20 K lower. There is a qualitatively similar shift in the peak onset for neat desorption of the products, but only 10 K. Notably there is no CO_2 produced.

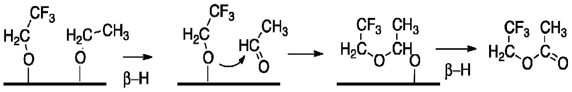
Table 2. Homolytic bond dissociation energies for relevant β-C-H bonds. Bond dissociation energies taken from[26] except for F_3CH_2COH, which was estimated using calculated enthalpies of formation from [23].

Bond broken (bold)	Bond dissociation energy (kJ/mol)	Distance between C1 of alkoxy and Au surface
H_2**C-H**OH	402	2.83
H_3CH**C-H**OH	401	2.81
F_3CH**C-H**OH	409	2.86

Selective oxidation of a mixture of methanol and 2,2,2-trifluoroethanol yields 2,2,2-trifluoroethylformate at 238 K and 2,2,2-trifluoroethyltrifluoroacetate at 270 K on O/Au(111) (0.1 ML initial O coverage) for a mixture dilute in methanol (Fig. 6). Therefore, the rate of β-H elimination is faster for methoxy than 2,2,2-trifluoroethoxy, as there was no methyltrifluoroacetate detected for any experiment.

In contrast, coupling of methoxy with other longer-chain alkoxys on O/Au(111) exclusively yields methyl esters because of the generally slower rate of β-C-H bond scission for methoxy. Formaldehyde is formed from methoxy at ~210 K, below the temperature of formation of $CF_3CH(=O)$ from CF_3CH_2O, ~240 K. A large amount of CO_2 is formed at ~580 K, resulting for oxidation of the $CF_3CH=O$ to form an acetate. CO_2 from methanol oxidation would be formed at ~295 K. Notably, there is also excess oxygen present, observed in the m/z=32 peak at ~520 K. This feature was present for all of the methanol mixtures tested.

There are two principal factors that are expected to affect the rate of C-H bond breaking: (1) the proximity of the β-H to the surface; and, (2) the β-C-H bond strength. The proximity to the surface is important because the abstraction of the β-H requires interaction with the surface or another surface-bound species.[22] Based on the recent density functional calculations that include van der Waals interactions, the distance between the β-H and Au surface is closer in the non-fluorinated alkoxy species (as measured by the distance from the C1 carbon of the alkoxy to the Au surface (Table 2) because of repulsion between the CF_3 group and the surface.



Scheme 2. Coupling of dissimilar alkoxys depends on relative rates of β-H elimination, shown for 2,2,2-trifluoroethanol and ethanol.

Hence, the rate of β-C-H dissociation should be faster for ethoxy and methoxy in comparison to the trifluoro-ethoxy all other factors being equal. The second factor, β-C-H bond strength, is not experimentally known for the CF_3CH-HOH bond; however, from recent calculations for ΔH_f for CF_3CHOH and CF_3CH_2OH,[23] the bond dissociation energy for the CF_3CH-HOH bond is estimated to be 409.3 kJ/mol, compared to 401 and 402 kJ/mol for methoxy and ethoxy, respectively (Table 2).

Although these relative β-C-H bond energies are generally consistent with the more rapid elimination from ethoxy and methoxy, the differences may be too small relative to the error in the calculated energies to be definitive, and refinement of these values is necessary. Nevertheless, this factor also indicates that fluorination will retard aldehyde formation. A similar trend was previously reported on copper: the barrier for β-C-H dissociation was 8.4 kcal/mol higher for $CF_3CH_2CH_2$-Cu vs. $CH_3CH_2CH_2$-Cu. This effect was attributed to destabilization of the carbo-cation in the transition state.[24] An alternative explanation is that weak interactions between the alkyl groups and the surface affect the relative rates. This concept requires further exploration using density functional calculations that include van der Waal's interactions in the calculation of the transition state energies.

The other significant factor in determining the product distribution for oxidation of CF_3CH_2OH mixtures with either methanol or ethanol is the competition of the different alcohols for binding to the surface. This factor was quantitatively evaluated by measuring the equilibrium constants for binary mixtures of CF_3CH_2OH with either CH_3CH_2OH or CH_3OH exposed to O/Au(111) over a range of compositions. A series of mixtures of the two alcohols was dosed in excess on the gold surface with 0.1 monolayers of pre-adsorbed atomic O . The adsorbed O is required for initial activation of the O-H bonds in alcohols. The alcohols then form an equilibrium mixture consisting of adsorbed alcohols and alkoxys (Scheme 1) and the equilibrium constant was determined from quantitative analysis of the respective product formed (Fig. c,d) using a method described previously.[3] The equilibrium constant, K, is measured for the displacement reaction, $\mathrm{RO}_{ads} + \mathrm{R'OH} \leftrightarrow \mathrm{ROH} + \mathrm{R'O}_{ads}$, (1) assuming equilibrium of the alcohols with the condensed phase of co-dosed (in excess) alcohols. Therefore, $K = \frac{\theta_{R'O}\,\theta_{ROH}}{\theta_{RO}\,\theta_{R'OH}}$, (2) where θ_{RO} and $\theta_{R'O}$ are the relative coverages of reacted surface alkoxy species are determined by quantitative analysis of the product distribution of the coupling reactions, and θ_{ROH} and $\theta_{R'OH}$ are the relative amounts of alcohols in the mixture dosed on the surface. The relative amounts of reacted alkoxys in turn reflect the outcome of the competitive equilibrium and are used to calculate the equilibrium constant. In this work, ROH will always refer to the 2,2,2-trifluoroethanol, while R'OH will be either ethanol or methanol.

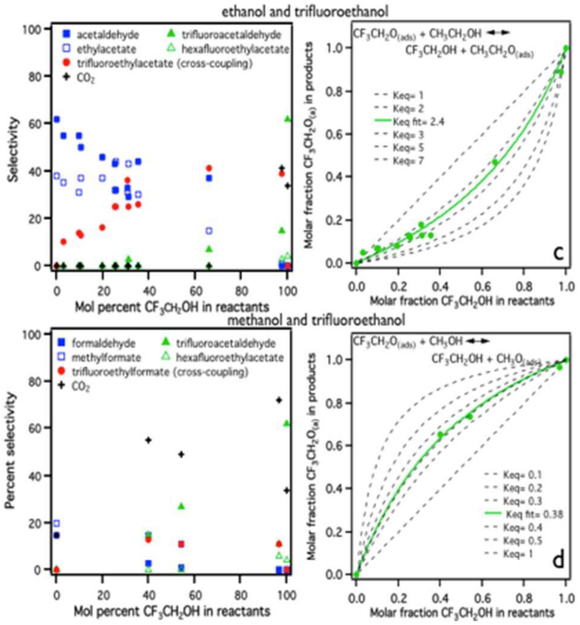


Figure 7: Variation in the reactant composition affects the product distributions (left) for coupling of CF_3CH_2OH with ethanol (top) or with methanol (bottom). These same measurements were used to estimate the equilibrium constants (right) for the competitive binding of the two different pairs of alcohols. The dashed curves are the predicted behaviour for various values of Keq and the solid curve represents the experimental data. All measurements were performed after exposing an excess of the alcohols mixtures onto Au(111) containing 0.1 ML of O_{ads} initially. In the case of methanol, only a few data points were measured in the region of composition exhibiting the biggest differences in curvature for different values of K_{eq}.

The equilibrium constants for 2,2,2-trifluoroethanol and ethanol and (Fig. 7a) and 2,2,2-trifluoroethanol and methanol (Fig. 7b) are determined to be 2.4 and 0.38, respectively, in qualitative agreement with the trend indicated by DFT calculations that included van der Waals interactions which indicate relative binding strengths of 1-butoxy > ethoxy > trifluoro-ethoxy> methoxy (Table 3). Using our values for the equilibrium constants between methanol or ethanol with 2,2,2-trifluoroethanol, the K_{eq} for ethanol with methanol can then be estimated by taking the ratio of these numbers (2.4/0.38), which gives K_{eq}~6. This is quite close to the previously measured value of 5, indicating that our results are internally consistent.

Though the *relative* K_{eq} values are qualitatively consistent with the order of calculated binding energies for the adsorbed alkoxy intermediates, additional calculations are required to theoretically estimate the equilibrium constants. Based on recent work evaluating the entropy of bound species, we expect the relative differences in entropy between the three alkoxys to have negligible effect.[25] In order to theoretically determine the equilibrium constants, the different stabilities and entropies of the gas-phase alcohols must also be included.

The preference for ethoxy adsorption over trifluoethoxy on the Au surface is manifested in the product distributions in that there are few fluorinated products formed below 0.60 mole fraction of CF_3CH_2OH in the mixture (Fig. 7). On the other hand, fluorinated products are formed from the CF_3CH_2OH/CH_3OH mixtures starting at a CF_3CH_2OH mole fraction of ~0.4 (Fig. 7).

Unfortunately, the selectivity for production of fluorinated esters is not high In any case studied. In the CF_3CH_2OH/CH_3CH_2OH mixtures, acetaldehyde and ethyl acetate always predominate because of the combination of more rapid aldehyde production and stronger binding of ethoxy. The best selectivity for CF_3CH_2O-C(=O)(CH_3) is ~20-30% and is achieved for a mole fraction of the CF_3CH_2OH of ~30%. It is worth noting that the oxygen coverage was not adjusted to optimize for selectivity toward esters in this study. In previous studies, sometimes an oxygen coverage of lower than 0.1 ML O/Au was required to obtain optimum selectivity.[21]

Table 3. Relative K_{eq} values are consistent with the differences in calculated binding energies between alkoxies.

Alcohol Pair RO_{ads} + R'OH ↔ ROH + $R'O_{ads}$	Computed difference in BE of alkoxys (eV)	Measured K_{eq}
$CH_3O_{(a)} + CH_3(CH_2)_3OH \leftrightarrow CH_3OH + CH_3(CH_2)_3O_{(a)}$	0.51	10 ref. [3]
$CH_3O_{(a)} + CH_3CH_2OH \leftrightarrow CH_3OH + CH_3CH_2O_{(a)}$	0.35	5 ref. [3]
$CF_3CH_2O_{(a)} + CH_3CH_2OH \leftrightarrow CF_3CH_2OH + CH_3CH_2O_{(a)}$	0.23	2.4
$CF_3CH_2O_{(a)} + CH_3OH \leftrightarrow CF_3CH_2OH + CH_3O_{(a)}$	- 0.12	0.38

The difference in binding energy, and hence efficiency of alkoxy formation may explain part of this low selectivity. The higher rates of CO_2 production may be explained in part by the presence of excess oxygen. In our experiments, there was excess O for all of the methanol/trifluoroethanol experiments. However, there was not excess O for the ethanol/trifluoroethanol experiments. Interestingly, there is also a small amount of excess oxygen in the oxidation of pure methanol, but although the trifluoroethanol oxidation is much less selective than ethanol oxidation, we did not observe excess oxygen. This supports the hypothesis as the binding energy of the alkoxy increases, it competes more effectively and uses the surface oxygen more completely. When using less strongly bound alkoxys, therefore, one might expect to improve selectivity by using a lower initial oxygen coverage with excess alcohol.

In previous studies of aliphatic alcohols, it has been found that the longer chain alcohols have both a stronger binding energy and a faster rate of β-H elimination.[3] The case of trifluoroethanol having a binding energy between ethanol and methanol, yet having a slower β-H elimination than either of them stands out as a unique contrast. As discussed above, this is due to the fluorination of the methyl carbon, part of the effect of which is to lengthen the distance between the C1 carbon and the surface due to Pauli repulsion. The observation that such a subtle chance in distance between a carbon and the surface can have such a marked effect on reaction rate, and thereby control the reaction pathway, may lead to new ways of understanding and designing reactions in the future, particularly when using fluorinated compounds.

Conclusions

By establishing a hierarchy of binding for a range of adsorbates on gold, we establish that small differences in the binding of reactive species has a significant impact on reaction selectivity by affecting the competition for binding sites. The coupling of dissimilar alcohols is used to illustrate that the dependence of the selectivity for production of various esters on the composition of the reactant mixture is the same on O-covered single crystals and under working catalytic conditions using nanoporous Au catalysts. Density functional theory calculations show that weak van der Waal's interactions play an important role in determining this competition for binding of a homologous series of reactants; thus, providing an explanation for the observed trends in selectivity and binding.

We further extended the concept of competitive binding to the investigation of fluorinated alcohols. Fluorinated organics are becoming prominent in chemical industry and synthesis because of their unique properties and myriad applications. In this study we established principles for reactive processes involving fluorinated alcohols on a surface, with specific aim toward ester synthesis. Subtle differences between β-H elimination rates and equilibrium constants between alkoxys on a surface have a marked effect on the products of reaction between two alcohols, and we have here evaluated these factors for trifluoroethanol as compared to ethanol and methanol. 2,2,2-Trifluoroethoxy has a slower rate of β-H elimination than both methoxy and ethoxy. These results are consistent with the estimated β-H bond dissociation energies of the alcohols and with the geometric structures of the adsorbed alkoxys predicted by DFT including van der Waals forces. The binding energy of adsorbed 2,2,2-trifluoroethoxy lies between ethanol and methanol, manifesting differences between the equilibrium constants for formation of the 2,2,2-trifluoroethoxy in the presence of ethanol or methanol, respectively.

Acknowledgements

We gratefully acknowledge the support of this work by the U.S. Department of Energy, Basic Energy Sciences, Grant no. DE-FG02-84ER13289

Notes and references

1 J. K. Norskov, T. Bligaard, J. Rossmeisl and C. H. Christensen, *Nat Chem*, 2009, **1**, 37–46.

2 J. C. F. Rodriguez-Reyes, C. G. F. Siler, W. Liu, A. Tkatchenko, C. M. Friend and R. J. Madix, *J. Am. Chem. Soc.*, 2014, **136**, 13333–13340.

3 B. Xu, R. J. Madix and C. M. Friend, *J. Am. Chem. Soc.*, 2010, **132**, 16571–16580.

4 M. A. Barteau and R. J. Madix, *Surf. Sci.*, 1982, **120**, 262–272.

5 S. W. Jorgensen and R. J. Madix, *Surf. Sci.*, 1983, **130**, L291–L293.

6 R. N. Spitz, J. E. Barton, M. A. Barteau, R. H. Staley and A. W. Sleight, *J. Phys. Chem.*, 1986, **90**, 4067–4075.

7 D. A. Outka and R. J. Madix, *J. Am. Chem. Soc.*, 1987, **109**, 1708–1714.

8 B. Xu, R. J. Madix and C. M. Friend, *Acc. Chem. Res.*, 2014, **{47}**, {761–772}.

9 B. Xu, X. Liu, J. Haubrich, R. J. Madix and C. M. Friend, *Angew. Chem. Int. Ed. Engl.*, 2009, **48**, 4206–4209.

10 K. J. Stowers, R. J. Madix and C. M. Friend, *J. Cat.*, 2013, **308**, 131–141.

11 L.-C. Wang, K. J. Stowers, B. Zugic, M. L. Personick, M. M. Biener, J. Biener, C. M. Friend and R. J. Madix, *J. Cat.*, 2015, **329**, 78–86.

12 R. Berger, G. Resnati, P. Metrangolo, E. Weber and J. Hulliger, *Chem Soc Rev*, 2011, **40**, 3496–3508.

13 D. Cahard and V. Bizet, *Chem Soc Rev*, 2014, **43**, 135–147.

14 J. P. Begue, D. Bonnet-Delpon and B. Crousse, *Synlett*, 2004.

15 T. J. Wallington and W. F. Schneider, *Environ. Sci. Technol.*, 1994, **28**, 1198–1200.

16 M. Lily, D. Sutradhar and A. K. Chandra, *Computational and Theoretical Chemistry*, 2013, **1022**, 50–58.

17 C. Hollingworth and V. Gouverneur, *Chem. Commun. (Camb.)*, 2012, **48**, 2929–2942.

18 S. Y. Lee, S. Neufeind and G. C. Fu, *J. Am. Chem. Soc.*, 2014, **136**, 8899–8902.

19 L. E. Manzer, *Catal. Today*, 1993, **18**, 199–207.

20 C. G. F. Siler, T. Cremer, J. C. F. Rodriguez-Reyes, C. M. Friend and R. J. Madix, *ACS Catal.*, 2014, **{4}**, {3281–3288}.

21 X. Liu, B. Xu, J. Haubrich, R. J. Madix and C. M. Friend, *J. Am. Chem. Soc.*, 2009, **131**, 5757–5759.

22 B. Xu, T. A. Baker, E. Kaxiras and C. M. Friend, *J. Phys. Chem. C*, 2011, **115**, 3703–3708.

23 Y. Wang, J.-Y. Liu, Z.-S. Li, L. Wang and C.-C. Sun, *Journal of Computational Chemistry*, 2007, **28**, 802–810.

24 J. G. Forbes and A. J. Gellman, *J. Am. Chem. Soc.*, 1993, **115**, 6277–6283.

25 C. T. Campbell and J. R. V. Sellers, *J. Am. Chem. Soc.*, 2012, **134**, 18109–18115.

26 Y.-R. Luo, *Comprehensive Handbook of Chemical Bond Energies*, CRC Press, Boca Raton, 2007.