

# Oxygenate reaction pathways on transition metal surfaces

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## Abstract

The importance of various oxygenates as fuels and as chemical intermediates and products continues to grow. Alcohols and aldehydes have also been the subjects of numerous surface reactivity studies. We review here the decomposition mechanisms of oxygenates on transition metal surfaces focusing primarily on metals of Groups VIII and IB. Common pathways as well as deviations from these serve to illustrate the patterns of oxygenate reactions. Several major divisions in the preferred pathways can be rationalized in terms of the affinities of metals for making metal–oxygen and metal–hydrogen bonds. Other important factors determining oxygenate reactivities include surface crystallographic structure and the detailed molecular structure of the oxygenate. Differences in product distribution between metals are frequent, even in cases where many of the reaction steps are common, primarily because of the plethora of elementary reaction steps usually involved in oxygenate decomposition on transition metal surfaces. As a result, differences late in the reaction sequence can obscure important similarities in the overall reaction network. Spectroscopic identification of common surface reaction intermediates including alkoxides, acyls, and oxametallacycles, has become increasingly important in revealing the underlying similarities in seemingly diverse oxygenate reaction pathways on transition metal surfaces. © 1998 Elsevier Science B.V.

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## 1. Introduction

Among Brian Bent's most important contributions to surface science and catalysis were his elegant studies of the synthesis and reactivity of discrete alkyl ligands and other hydrocarbon fragments on metal surfaces, and his thorough review of this chemistry [1]. We attempt here an overview of a related area of surface chemistry and catalysis, that of oxygenates on transition metal surfaces. These two areas of surface chemistry, those of hydrocarbon and oxygenate ligands on transition metal surfaces, appear to have a growing overlap, and developments in one most likely are important for the other. In

particular, the production of surface hydrocarbon ligands is very common in processes involving oxygen removal or decarbonylation of oxygenates on a variety of metal surfaces [2–5]. Conversely, oxygenate synthesis on various metals has been clearly demonstrated to proceed via oxygen addition to hydrocarbon fragments, such as alkyls or alkylidenes, adsorbed on the corresponding metal surfaces [6–12].

The literature of oxygenate surface chemistry and catalysis on transition metal surfaces has grown enormously over the past 20 years, with an increasingly large proportion focusing on fundamental mechanistic studies employing surface science techniques. It is beyond the scope of this brief review to present an exhaustive compilation of the whole body of work related

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to the chemistry of oxygenates on transition metals. Our primary goal is to illustrate common threads in reactivity patterns characterizing oxygenate chemistry on different transition metal surfaces, as well as to draw attention to major differences in reaction pathways demonstrated by the same oxygenates on different metals or different oxygenates on the same metals. By means of such contrasts and comparisons, one can hope that new principles of surface chemistry might be elucidated.

Alcohols, aldehydes, ketones, and carboxylic acids are among the most extensively studied oxygenates on transition metal surfaces. There are a number of motivations supplied by heterogeneous catalysis for interest in the surface chemistry of these molecules: (i) they have been traditionally used as probe reagents in catalysis, (ii) selective oxidations of alcohols and hydrocarbons lead to useful oxygenate chemicals, (iii) reduction of  $\alpha, \beta$ -unsaturated aldehydes can lead to unsaturated alcohols or saturated aldehydes, presumably reflecting the competition between different functional groups for surface sites, and (iv) the synthesis of higher alcohols and oxygenates from CO and H<sub>2</sub> for fuels and chemicals continues to be of interest. In short, the reactions of oxygen-containing species at metal surfaces are relevant to a wide variety of catalytic processes, and a fundamental understanding of these reactions may therefore contribute to catalytic synthesis of a surprising array of products.

In virtually all of the catalytic reactions just noted on metals, it is worth remembering that surface hydrocarbon species appear, either as intermediates on the path to oxygenate formation, or as products of oxygenate decomposition. For example, higher oxygenate synthesis from syngas has been performed on rhodium and other Group VIII metals. It is typically proposed [13–16] that hydrocarbon ligands are assembled by stepwise addition of CH<sub>x</sub>-monomeric units, and the chain-growth of the hydrocarbon backbone is terminated by CO insertion to form surface-bound acyl species. Hydrogena-

tion of the acyl may lead to aldehydes or alcohols. Oxygenate synthesis by oxidation of hydrocarbons is similar in that one again has insertion into a surface metal–hydrocarbon bond [6–12], however in these examples the species inserted is an adsorbed oxygen atom rather than CO.

Microscopic reversibility suggests that elementary reaction steps involved in oxygenate synthesis should be the same as those characterizing the decomposition of the same oxygenates on the corresponding surfaces used as catalysts for their synthesis. Hence, by studying the reaction network followed by oxygenates during their decomposition on transition metal surfaces, one can hope to gain substantial insight into mechanistic details concerning oxygenate synthesis. The focus of this review is on the decomposition pathways of alcohols and aldehydes on single crystal transition metal surfaces, as demonstrated by UHV studies.

The reaction pathways and product selectivities observed during the decomposition of alcohols and aldehydes on clean or oxygen-covered transition metal surfaces appear at first glance to be quite diverse and strongly dependent on the identity of the metal and the detailed molecular structure of the reactants. Nevertheless, spectroscopic identification of surface-bound reaction intermediates provides evidence for the fundamental similarities in the reaction mechanisms governing the decomposition of alcohols and aldehydes on many transition metal surfaces. For example, the typical reaction sequence characteristic of alcohol decomposition on Pt-group metals (including Pd [17,18], Ni [2], and Pt [3]) involves formation of an alkoxide intermediate via hydroxyl-hydrogen elimination, followed by  $\alpha$ -H abstraction leading to an aldehyde intermediate bonded to the surface either via both carbon and oxygen atoms of its carbonyl function (designated as  $\eta^2(\text{C},\text{O})$ -conformation) or via its oxygen atom only ( $\eta^1(\text{O})$ -conformation). Oxygen precovered surfaces promote the  $\eta^1(\text{O})$  configuration of aldehyde intermediates, which tend to desorb rather than decompose further, as is

the case with the  $\eta^2(\text{C},\text{O})$  configuration of aldehyde intermediates. The latter route leads to acyl intermediate formation followed by CO elimination and the release of volatile hydrocarbons. Carboxylates may also be formed from aldehydes in the presence of surface oxygen or by dissociative adsorption of carboxylic acids. Thus the roster of surface intermediates needed to account for oxygenate chemistry includes alkoxides,  $\eta^1$ - and  $\eta^2$ -aldehydes, acyls, and carboxylates, shown schematically in Fig. 1. Considerable spectroscopic evidence for each of these species has been developed on a number of metal surfaces and much, but not all, surface oxygenate chemistry can be explained in terms of their formation and reaction. One advantage of establishing the framework of surface oxy-

genate chemistry around these common intermediates is that it permits one to identify examples of chemistry that they cannot explain, leading to the proposal of new surface intermediates and reaction pathways. Examples include the suggested formation of oxametallacycles from ethanol on Rh(111) [19] and the proposed scission of the C–O bond of methanol on Pt-group metals [20,21].

### 1.1. Alkoxide synthesis from alcohols

Cleavage of the O–H bond of alcohols upon their adsorption on transition metals appears to be a general phenomenon, occurring at low temperatures and leading to the formation of stable alkoxide intermediates [2,17,3,22–29] [30–34]. For example, HREELS and isotopic labelling experiments have shown that methanol decomposition starts by initial cleavage of the O–H bond on many Group VIII and IB metal surfaces to form stable methoxy ( $\text{CH}_3\text{O}$ ) intermediates. This reaction step occurs at temperatures between 100 K and 200 K on the Group VIII metals. Copper and silver generally require the addition of oxygen atoms to the surface, facilitating the proton transfer to the basic surface oxygen [35]. This requirement can be removed on Cu, with the use of higher adsorption temperatures [36].

Alkoxide formation as the first step in alcohol decomposition is not surprising, since any alternative scenario would involve alcohol activation via interaction at an alkyl carbon, in addition to or instead of at the oxygen. Initial adsorption of alcohols in general appear to occur via donation of a lone pair of electrons from the oxygen to the surface [36]. In methanol for example, C–H or C–O scission would require the formation of a surface intermediate or transition state with a five-coordinate carbon atom. The greater difficulty of activating ethers vs. alcohols on metal surfaces [37] illustrates the barriers to C–H and C–O vs. O–H bond activation. Thus alkoxide formation is the expected first step in alcohol decomposition.

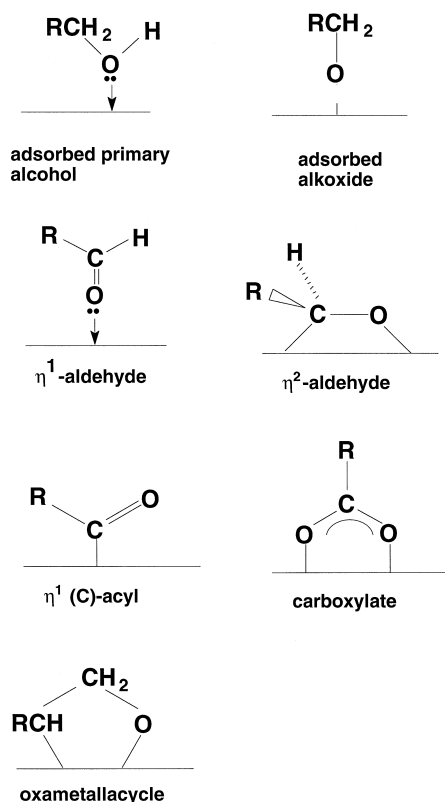


Fig. 1. Important oxygenate intermediates observed on transition metal surfaces. Details of coordination to the metal surface, e.g., the specific metal atoms involved, are not depicted, as these are less well known than the identities of the organic ligands, and may vary with surface composition and structure.

Adsorbed methoxide intermediates have been proposed for the reaction of methanol on a variety of Group VIII metals. Experiments exploring the kinetic isotope effect in combination with HREELS studies have clearly illustrated the formation of methoxides on a Ni(111) surface [38]. Similarly, HREEL spectroscopic signatures of methoxide intermediates have been obtained on clean Ni(110) surfaces [26], during methanol decomposition to CO and H<sub>2</sub>. In spite of the fact that HREELS studies were not conclusive with respect to the presence of surface methoxides, the methanol decomposition pathway on clean Pd(111) and Pt(111) surfaces was proposed to be similar to the one observed on Ni single crystals [17,18,39,40]. Similarly, ultraviolet photoelectron spectroscopy (UPS) provided evidence for adsorbed methoxides on the clean Pd(100) surface and the stoichiometry of CO and H<sub>2</sub> desorption products observed between 200 K and 600 K was in good agreement with the decomposition of adsorbed methoxy intermediates [41]. Dissociative methanol adsorption leading to stable adsorbed methoxide species has also been observed on Ru(001) [24], Fe(100) [42,43], Rh(100) [30], and Rh(111) [28,29].

Oxygen-predosed Pd(100) and Pd(111) surfaces stabilized adsorbed methoxides up to temperatures above 200 K, allowing the observation of a pathway leading to formaldehyde production [18,44,45]. Similarly, oxygen-predosed Pt(111) stabilized methoxides which were detected by HREELS; however, these decomposed to adsorbed H-atoms and CO, without desorption of the intermediate dehydrogenation product, formaldehyde. Although oxygen preadsorbed on metal surfaces acts as a basic agent facilitating proton abstraction from the hydroxyl function of alcohols thus promoting alkoxide formation, the presence of oxygen on the most oxophilic metals may inhibit alkoxide formation. There is strong evidence for such an effect for oxygen on metals of Group VI (W, Mo) [46,47] and metals of the first column of Group VIII (Fe, Ru) [43].

The formation of alkoxides by dissociative adsorption of alcohols on Group VIII metal surfaces is ubiquitous, and appears to be relatively insensitive to surface structure. There is some evidence, however, for alternative reaction pathways which may be sensitive to surface structure. For example, C–O bond cleavage of methanol on Pd(111) has been reported to lead to adsorbed methyl and hydroxyl functions, instead of methoxide formation [48,49]. Other workers were unable to reproduce key features of these results [44,50]. There still exists a question regarding the extent of damage caused by the original use of SIMS [48,49] to examine this chemistry. The low coverage of methyl groups measured subsequently [39,40] suggests that this chemistry may occur at surface defect sites. A more recent study [51] utilizing SIMS, XPS, and TPD has suggested that C–O scission of methanol on Pd(111) is coverage and temperature dependent, and in the most favorable case (monolayer methanol coverages), ultimately leads to carbon deposition on the surface at the level of 0.07 monolayers. Along the same lines, Wang and Masel [20,21] have reported methanol decomposition to produce CH<sub>4</sub> with high selectivity on an unreconstructed Pt(110) surface but not on the reconstructed (2 × 1) surface. This latter case merits special attention because it includes the effect of more than one factor simultaneously. The C–O scission pathway emphasizes the importance of surface crystallographic structure in connection with electronic factors in determining the local driving force for metal–hydrogen bond formation. Another exception to the pattern of alcohol dissociation to form alkoxides has been suggested by Papa-georgopoulos et al. [52]. They examined desorption and decomposition of ethanol on a Rh(111) surface, and interpreted their data as ruling out ethoxide formation. They propose a reaction mechanism involving competition between molecular desorption and direct decomposition to final products CO and H<sub>2</sub> only. Houtman and Barteau [19] had previously studied the same system, proposing the formation of an oxametal-

lacycle intermediate via  $\beta$ -H-elimination of the ethoxide intermediate. Even in the latter proposal,  $\beta$ -H-elimination is somewhat surprising with respect to the usual  $\alpha$ -H-elimination, which would lead to acetaldehyde formation, a product not observed in these experiments.

### *1.2. Aldehyde and ketone adsorption and preferred binding modes on transition metal surfaces*

Carbonyl compounds adsorb on clean and modified transition metal surfaces via two alternative bonding configurations:  $\eta^1(\text{O})$  or  $\eta^2(\text{C},\text{O})$ . In the  $\eta^1(\text{O})$  configuration, the carbonyl compound is bonded to the surface through the oxygen lone pair orbital, acting as a Lewis base. Bonding of the carbonyl compounds to the surface in the  $\eta^2(\text{C},\text{O})$  configuration occurs through the carbonyl  $\pi$  orbital with back-donation from the metal to the adsorbate occurring through the carbonyl  $\pi^*$  orbital. On surfaces predosed with electronegative agents, such as oxygen or sulfur, the reduced electron density of the metal induced by the presence of these surface modifiers decreases the amount of back-donation to the carbonyl function [53–55]. Thus, on such surfaces, carbonyl compounds tend to preferentially adsorb in the  $\eta^1(\text{O})$  configuration, suggesting that the interaction of the Lewis acid site in these molecules (i.e., the unfilled  $\pi^*$  carbonyl orbital) with the surface is suppressed. The specific bonding configuration of the carbonyl compounds on transition metal surfaces is directly correlated to their thermal stability on the corresponding metal surfaces. As might be expected,  $\eta^2(\text{C},\text{O})$  bonded carbonyl compounds are more stable than those bonded to surfaces through an  $\eta^1(\text{O})$  configuration, and as a result the latter generally desorb at lower temperatures. Moreover, manipulation of the bonding configuration of carbonyl compounds on metal surfaces, e.g., via preadsorption of chemical surface modifiers, may lead to changes in kinetics and consequently alter reaction selectivities towards the desired pathway.

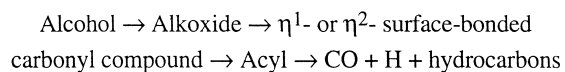
While adsorption of carbonyl compounds on Group IB metal surfaces occurs exclusively in the  $\eta^1$  mode [56], on Group VIII metal surfaces both adsorption geometries ( $\eta^1(\text{O})$  and  $\eta^2(\text{C},\text{O})$ ) for carbonyl compounds have been observed [53–58]. It is clear from the work of Anton et al. [53], Henderson et al. [58], and our group [19,55] that the preferred bonding configuration of aldehydes and ketones on clean Ru and Rh surfaces is  $\eta^2$ , as on the platinum group metals. The  $\eta^2$  species formed from higher aliphatic aldehydes are easily isolated on Rh(111) [19,59], and exhibit characteristic  $\nu(\text{CO})$  frequencies between 1350 and 1450  $\text{cm}^{-1}$ . HREELS studies of formaldehyde and acetone adsorbed on Ru(001) and acetone on Pt(111) have identified both bonding geometries,  $\eta^1$  and  $\eta^2$ , on clean surfaces of these metals [53,56,60]. However, on oxygen-precovered surfaces of the same metals, carbonyl compounds preferentially adsorb in the  $\eta^1$  configuration. Although the possibility that oxygen prevents adsorption in the  $\eta^2$  configuration by simple site-blockage cannot be entirely excluded, direct analogies from studies of the effect of preadsorbed oxygen on olefin adsorption [61], as well as theoretical results for interaction of unsaturated functional groups with metal clusters and surfaces [62], suggest that adsorption configuration is influenced much more strongly by surface electronic properties rather than by the geometry of surface sites. TPD and HREELS studies of acetaldehyde adsorption on Pd(111) have clearly shown that the  $\eta^2$  state is preferred on the clean surface [63], whereas the  $\eta^1$  state is preferred in the presence of oxygen [64]. A similar preference for the  $\eta^1$  adsorption mode has been observed for acetaldehyde and acetone on oxygen-predosed Rh(111) surfaces [55,65]. Since desorption of aldehydes from the  $\eta^1$  state occurs at approximately 100 K less than from the  $\eta^2$  state, aldehyde desorption from the  $\eta^1$  state, induced by the presence of oxygen, competes effectively with aldehyde decomposition, whereas decomposition is the major pathway for aldehydes adsorbed on clean Pd(111) [64]. Therefore, one

can easily envision how the presence of oxygen can critically affect product selectivity in the decomposition of even simple oxygenates on transition metal surfaces. It is important to emphasize that these selectivity changes are not the result of direct oxygen participation in a chemical reaction, but are due to the influence of oxygen via through-surface interactions on the relative kinetics of oxygenate desorption and decomposition.

Another important bonding mode of carbonyl compounds on transition metal surfaces involves oligomerization. Oligomerization occurs primarily on oxygen-dosed surfaces of Group VIII [63,66] and IB metals [67,68], but has also been reported on some clean Group VIII surfaces. For example, formaldehyde reacted upon adsorption on a clean Pd(111) surface at 170 K via decomposition to CO and H, and polymerization to paraformaldehyde [63]. However, no evidence was found for polymerization of either acetaldehyde or propionaldehyde on the clean Pd(111) surface, although such reactions were observed on Rh(111) [19] and Pd(110) following aldehyde adsorption at lower temperatures. Oxygen adatoms were found to initiate formaldehyde polymerization on a Pd(111) surface, but no polymerization of the higher aldehydes was detected on the oxygen-dosed Pd(111) surface [64]. Formaldehyde polymerization has also been reported on a clean Rh(111) surface [66], in which case the model proposed to explain the reaction mechanism suggested that formyl (HCO) surface intermediates derived from formaldehyde dissociation initiate formaldehyde polymerization. The extent of paraformaldehyde polymerization is governed by the competition between formyl decomposition and formyl addition to formaldehyde molecules on the surface.

### 1.3. Reaction pathways of alkoxides and aldehydes on transition metal surfaces

As noted above, the following sequence of elementary steps represents the most general



Scheme 1. Alcohol  $\rightarrow$  Alkoxide  $\rightarrow$   $\eta^1$ - or  $\eta^2$ -surface-bonded carbonyl compound  $\rightarrow$  Acyl  $\rightarrow$  CO + H + hydrocarbons

reaction scheme oxygenates follow for their decomposition on transition metal surfaces (Scheme 1).

The first step involves the elimination of the hydroxyl hydrogen, whereas the  $\eta^1$ - or  $\eta^2$ - surface-bound carbonyl compounds are derived via another hydrogen elimination, this time one of the  $\alpha$  hydrogens of the alkoxide intermediate. Further hydrogen abstraction leads to the formation of an acyl intermediate. Subsequent C–C bond scission, in some cases preceded by additional C–H scission, is necessary for the production of surface-bound hydrocarbon species with simultaneous release of CO adsorbed on the metal surface. Adsorbed hydrocarbon fragments may undergo both hydrogenation and dehydrogenation, depending on the metal, the identity and extent of saturation of the hydrocarbon intermediate, and the availability of hydrogen atoms on the surface. We have already discussed in detail alkoxide formation and to some extent the subsequent formation of the surface bonded carbonyl compound in an  $\eta^1$ - or  $\eta^2$ - configuration, depending on the specific molecular structure of the initial oxygenate, the identity of the metal, and the presence of surface modifiers, such as oxygen, sulfur, or other coadsorbates. In particular, the detailed mechanism of methoxide decomposition has been studied on both Ni(111) and Ni(110) surfaces [26,38]. Kinetic experiments for the case of CH<sub>3</sub>OH decomposition on Ni(111), and TPD and HREELS studies of CH<sub>3</sub>OH on Ni(110) have clearly demonstrated that cleavage of the C–H bond of the methoxide is the rate-limiting-step in methanol decomposition to surface-bound H<sub>2</sub>CO species. In good agreement with these data, studies of ethanol adsorption on Ni(111) have shown that cleavage of the  $\alpha$  C–H bond is the rate-limiting step. Cleavage of

this bond was followed by rapid decomposition with the final products being CO and H<sub>2</sub>. There is a remarkable parallelism between the methanol and ethanol decomposition pathways on Pd(111) and nickel surfaces, suggesting that the sequence of elementary reaction steps proposed for nickel surfaces can be extended to include Pd(111) surface as well [17,18].

Higher oxygenates, while less frequently studied than their C<sub>1</sub> counterparts, provide both important evidence in support of the reaction (shown in Scheme 1) above, and important warning signs about the danger of attempting to generalize this scheme too broadly. That some differences should arise when one replaces one or more hydrogens in a C<sub>1</sub> compound with alkyl ligands is not surprising; alkyl groups not only influence the electronic environment and reactivity of the carbonyl carbon, but provide alternative sites for interaction with the surface. Higher aldehydes and acyl ligands tend to exhibit greater thermal stability than formaldehyde and formyl species, and thus are more readily isolated for spectroscopic examination. On Pd(111), for example, vibrational spectra were obtained for each of the oxygenates in the sequence ethanol → ethoxide → η<sup>2</sup>-acetaldehyde → acyl → CO [18], and the chemistry of adsorbed acetaldehyde was the same, whether adsorbed directly on the surface or produced by ethanol dehydrogenation [63]. The same sequence of reaction intermediates appears to adequately describe higher alcohol decomposition on Ni(111) [2] and Pt(111) [3] surfaces as well. The latter half of this reaction sequence: decarbonylation of aldehydes via acyl intermediates appears to be applicable to other Group VIII metals; acyl intermediates from reaction of aldehydes have been observed spectroscopically on Rh (111) [19,59], Ru (001) [58,69], and stepped Pt surfaces [57].

On Pd(111) [17,18] and (110) [70] surfaces, the decarbonylation of ethanol proceeds via the sequence of spectroscopically identified intermediates in the scheme above, ultimately yielding CO, CH<sub>4</sub> and H<sub>2</sub> with high selectivity. It

should be realized, however, that this ‘simple’ reaction must involve at minimum six bond-making or bond-breaking events: OH scission, 2 × C–H scission, C–C scission, C–H formation, and H–H recombination. Thus there exist numerous opportunities for variations on the oxygenate reaction scheme above; these may involve differences in the sequence of bond-breaking and -making events, or the inclusion of additional such events in the sequence. These variations may occur early or late in the reaction sequence, they may or may not require one to consider additions to the menagerie of oxygenate surface intermediates considered thus far. A few examples serve to illustrate such phenomena.

In Scheme 1 above, the sequential formation of ethoxide, aldehyde, and acyl intermediates involve a single bond scission (considering only the organic ligand in each case, and not its bonds to the surface). Not so the final step depicted: decarbonylation of an acetyl group and formation of CH<sub>4</sub>, H<sub>2</sub>, and CO must involve at least three of the six minimum bond-making or -breaking steps noted above. Here, ‘late’ in the reaction sequence, mechanistic variations with surface structure and metal identity may be observed. For example, we previously examined the decarbonylation of CH<sub>3</sub>CHO and CD<sub>3</sub>CDO on Pd(111) using TPD and temperature programmed HREELS techniques [63]. These experiments demonstrated a kinetic isotope effect on the rate of decarbonylation of surface acetyl intermediates. This implies that C–H, not C–C scission is the rate-determining step in acetyl decomposition, and thus that acetyl species react on this surface by dehydrogenation to a reactive ketene species [63]. This species undergoes rapid C–C scission, depositing CO plus methylene groups, CH<sub>2</sub>, on the surface. In effect this adds one additional bond-breaking event, C–H scission of the acetyl, and one bond-making event, hydrogen addition to surface methylenes to form surface methyl groups, to the minimum reaction sequence which involves C–C scission of the acetyl to produce

methyl groups directly. Which sequence is followed, methyl or methylene elimination from surface acetyls, appears to depend on both surface composition and crystallographic structure. For example, decarbonylation of  $\text{CH}_3\text{CHO}$  and  $\text{CD}_3\text{CDO}$  on Rh(111) shows no evidence for a kinetic isotope effect, and decomposition of  $\text{CH}_3\text{CHO}$  in the presence of preadsorbed deuterium atoms on the surface yields  $\text{CH}_3\text{D}$  but little  $\text{CH}_2\text{D}_2$  [19]. These results demonstrate that the acetyl intermediates react by direct elimination of methyl groups on Rh(111) rather than by dehydrogenation and methylene elimination as on Pd(111). Surprisingly, the chemistry of acetaldehyde on Pd(110) resembles that on Rh(111) more in this regard than it does that on Pd(111). No kinetic isotope effect was observed in the decomposition of  $\text{CD}_3\text{CDO}$  vs.  $\text{CH}_3\text{CHO}$ . The distribution of methane isotopomers for experiments in which these reactants were adsorbed in the presence of a D- or H-adlayer clearly supported the conclusion that methyl groups were eliminated in the decarbonylation step and then converted to methane by addition of a single H or D atom [70].

These variations arise 'late' in the oxygenate reaction sequence, they do not require one to revise the sequence of stable oxygenate intermediates, and they may have relatively minor effects on the distribution of volatile products observed. For example, if one decomposes  $\text{CH}_3\text{CH}_2\text{OH}$  on Pd(111) or (110), 100% of the original C–O bonds are preserved in the product CO, and > 80% of the original methyl groups are converted to methane, regardless of whether the hydrocarbon fragment eliminated is  $\text{CH}_2$  or  $\text{CH}_3$  [17,18,71].

Deviations 'early' in the sequence of reactions in Scheme 1 appear less frequently in studies of oxygenate chemistry on metal surfaces reported to date. Indeed, if this were not the case, there would be little point to the attempt to produce a general scheme of surface oxygenate reactions. Fig. 2 depicts the reaction sequence of  $\text{C}_2$  oxygenates on rhodium and palladium surfaces, and some of the deviations

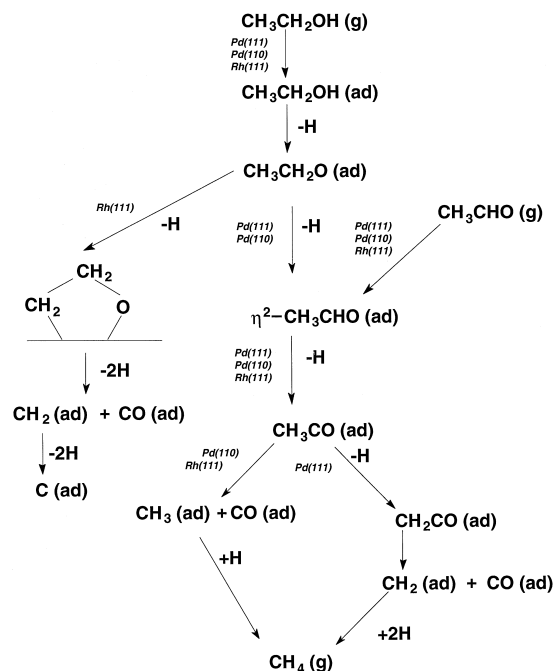


Fig. 2. Reaction pathways observed for  $\text{C}_2$ -oxygenates on palladium and rhodium surfaces.

from Scheme 1 observed. Perhaps the clearest anomaly arises in the reactions of ethanol and higher alcohols on Rh(111). Our studies of saturated and unsaturated alcohols on this surface have shown clearly that although they decarbonylate to produce CO plus hydrocarbon species one carbon atom shorter than the parent, they do not do so via a path which includes adsorbed aldehyde intermediates. Acetaldehyde, propionaldehyde, and acrolein on Rh(111) all produce volatile hydrocarbons by decarbonylation in TPD experiments; ethanol, 1-propanol, and allyl alcohol do not [4,19,59,72]. In addition, TPHREELS experiments with these adsorbates demonstrate that molecular CO is liberated on the surface at lower temperatures from the alcohols than from the corresponding aldehydes, suggesting that the alcohols cannot be reacting on this surface via formation of adsorbed aldehyde intermediates. A wealth of circumstantial evidence, including the correspondence of alcohol and epoxide reactions on this surface [4,73], and the ability to force alcohols



to form aldehydes by replacement of the  $\text{CH}_3$  group of ethanol with  $\text{CF}_3$  or a tertiary butyl group [74,75], has led us to propose that ethanol decomposition on Rh(111) proceeds not via  $\alpha$ -CH scission of the ethoxide to form acetaldehyde, but by  $\beta$ -CH scission to form an oxametallacycle [4,19,73]. The same intermediate has been proposed by Xu and Friend [76–80], who have suggested that such species are pivotal intermediates in reactions such as olefin oxidation to ketones on the Rh(111)-(2 × 1)O surface. While these proposed intermediates, which have also been proposed as key species in epoxide ring opening reactions on a number of metals [73,81,82], offer intriguing parallels with oxametallacycle complexes in organometallic chemistry, they have yet to be isolated on rhodium or any other Group VIII metal. We have recently addressed the case of surface oxametallacycles with both theoretical and experimental tools. Calculations using density functional theory (DFT) methods have shown that epoxide ring opening to form an oxametallacycle is thermodynamically favorable on all Group VIII and IB metals examined [83]. We have recently succeeded in synthesizing the first stable surface oxametallacycle by reacting 2-iodoethanol ( $\text{ICH}_2\text{CH}_2\text{OH}$ ) on the Ag(110) surface [84], and have obtained vibrational spectra which confirm its identity [85]. It remains to be seen whether this or other techniques succeed in producing isolable oxametallacycles on Group VIII metals.

Returning to the ‘anomalous’ behavior of ethanol and higher alcohols on Rh(111), however, the ‘common sequence’ of oxygenate reactions generalized from the Pt-group metals has clearly served a useful purpose. Held up against this template, the chemistry of aldehydes on Rh(111) fits, but that of alcohols does not. This has added to proposals [76–80,86,87] of a new class of surface intermediates, oxametallacycles, and to the first synthesis of a stable, isolable member of this class [84]. There is perhaps as much to be gained by such examples which do not fit the generalized reaction scheme of oxy-

genates on transition metal surfaces, as from those which do.

## 2. Beyond pattern recognition

Prediction of stable surface intermediates, of reaction pathways, kinetics, and selectivities should be the aim of surface reactivity studies, both theoretical and experimental. Quantum chemical calculations by methods such as DFT and others have begun to provide insights into the identity, bonding, and reaction pathways of oxygenates on transition metal surfaces and clusters [83,88–92]. Given the continuing dramatic growth of computational power, it is safe to predict that the contributions of such methods to the understanding of surface chemistry, including that of oxygenates, will grow apace. What is also needed are frameworks to reduce the wealth of experimental observations, both already in hand and yet to come, to propositions testable by theory and to models with predictive utility in catalysis.

One of the classical approaches to developing quantitative reactivity correlations with predictive utility in homogeneous catalysis is the formulation of Linear Free Energy Relationships (LFERs). Such relationships have also been formulated and utilized in heterogeneous catalysis [93] and in fact are implicit in construction of ‘volcano’ plots [94] correlating catalytic rates with thermodynamic properties of the catalyst or catalyst–adsorbate complex. In principle, the development of LFERs for surface oxygenate reactions could provide the means to correlate and predict variations in activity and selectivity from metal to metal and from crystal plane to crystal plane. In practice, relatively few such correlations have been advanced for oxygenates on well-defined surfaces, and it is worthwhile to consider both successful examples and the limitations to this approach in the context of the chemistry discussed in this review.

Extant examples include correlations of dehydrogenation rates of  $\text{C}_1$  oxygenate intermedi-

ates on Group VIII and IB metal surfaces [95], and correlations of substituent effects in oxygenate decomposition reactions on IB metals [96,97]. In the first of these it was shown that the decomposition temperatures of formate and methoxide intermediates on metal surfaces followed linear correlations with the heats of formation of the corresponding metal oxides as illustrated in Fig. 3. The reactions chosen to develop these correlations were relatively insensitive to surface crystallographic structure, but others have suggested methods to account for kinetics which are structure dependent by correlation with heats of adsorption oxygen on the specific surface structures of interest [98].

The quantitative relationships developed for  $C_1$  oxygenate decomposition kinetics are shown below.

HCOO decomposition:

on Group VIII:  $E_a$  (kcal/mol) = 0.157  $[-\Delta H_{fMO}^{\circ}] + 12.66$

on Group IB:  $E_a$  (kcal/mol) = 0.162  $[-\Delta H_{fMO}^{\circ}] + 23.0$

$CH_3O$  decomposition:

on Group VIII:  $E_a$  (kcal/mol) = 0.157  $[-\Delta H_{fMO}^{\circ}] + 7.47$

on Group IB:  $E_a$  (kcal/mol) = 0.138  $[-\Delta H_{fMO}^{\circ}] + 15.4$

where  $E_a$  is the activation energy for decomposition of the surface intermediate and  $-\Delta H_{fMO}^{\circ}$  is the standard enthalpy of formation for the corresponding metal oxide per mole of metal [95]. Beyond the fact that such correlations are feasible, there are two surprising aspects to these correlations. First, one finds a slope for all four linear equations that is nearly independent of  $C_1$  oxygenate structure and of metal position in the periodic table. Since the slope reflects the nature of the transition state, this suggests that the transition states for hydrogen abstraction from both formates and methoxides on metal surfaces are quite similar. Not anticipated previously by others who developed volcano plots for the kinetics of  $C_1$  oxygenate decomposition [94] was the observation that different LFERs are needed to account for the activities of Group VIII vs. IB metals. The higher values of the intercepts in the equations representing IB metals indicate that these metals are less active for C–H scission. A IB metal with comparable affinities for oxygen to a Group VIII metal (e.g., Cu and Rh) exhibit much lower affinities

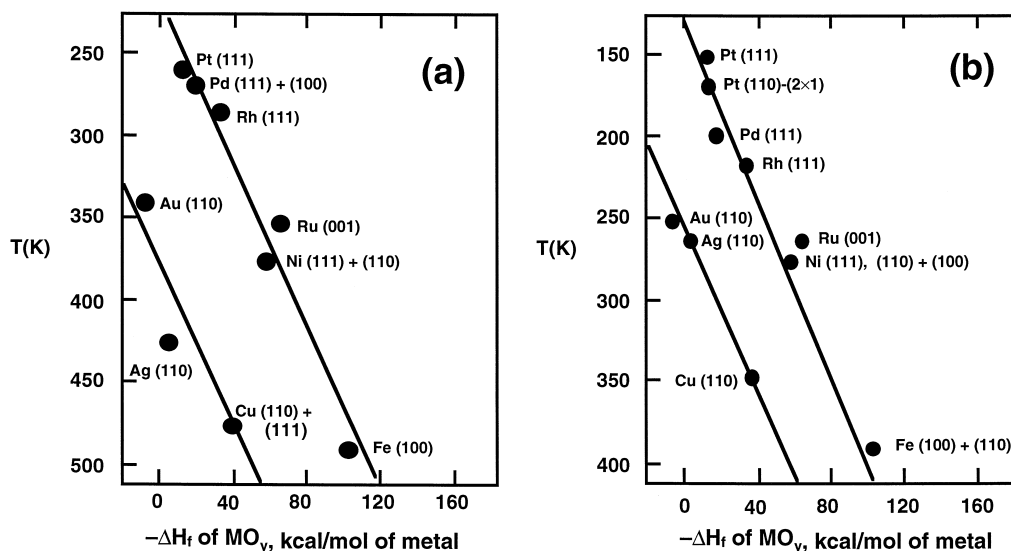


Fig. 3. Correlations of  $C_1$  oxygenate decomposition temperatures on metal surfaces with the corresponding metal oxide heats of formation [95]. (a) Formate (HCOO) decomposition temperatures. (b) Methoxide ( $CH_3O$ ) decomposition temperatures.

for hydrogen. The kinetics of formate and methoxide composition reflect the competition between the strength of the metal–oxygen bond which is broken in the course of intermediate decomposition, and the strength of the metal–hydrogen bond formed by that process. The IB metals require a different correlation between M–H and M–O bond energies than do the Group VIII metals, and one must therefore construct different LFERs to describe the kinetics of oxygenate dehydrogenation on these two groups.

Volcano plots in catalysis typically attempt to correlate reaction rates for a common reaction as one alters the catalyst, e.g., by varying the metal or by adding alloying components or surface modifiers [93,94]. The more common approach in organic chemistry is to vary substituents on the reactant and to observe changes in the kinetics of a common reaction. This approach has been applied by Gellman and Dai [96] and Dai and Gellman [97] in studies of the influence of fluorine substitution on the kinetics of alkoxide dehydrogenation to aldehydes on Ag and Cu surfaces. Quantitative measurements of ethoxide and fluoroethoxide decomposition kinetics demonstrate that fluorine substitution systematically decreases the rate of hydride elimination, effectively stabilizing the alkoxides to higher temperatures. Comparisons of adsorption equilibrium constants demonstrated that these were similar for the various fluorinated ethoxides, and thus that the differences in activation barriers resulted from the influence on the transition state for hydride elimination, rather than on the adsorbed state [96,97]. Gellman and Dai [96] and Dai and Gellman [97] have interpreted these results in terms of a polar transition state in which the carbon bears a net positive charge ( $C^{\delta+} \cdots H^{\delta-}$ ).

The key to development of quantitative LFERs in both of these cases is the selectivity of bond breaking. In the comparison of  $C_1$  oxygenate chemistry on different metal surfaces, the rate-determining step in all cases is the same, C–H scission. Likewise, ethoxides

and fluoroethoxides on silver and copper undergo hydride elimination cleanly; there are no competing reactions. Therein lies the challenge to constructing similar LFERs for higher oxygenates on Group VIII metals. As pointed out above, the sequence of C–H and C–C bond scission steps in the decomposition of  $C_2$  oxygenates such as ethanol and acetaldehyde can vary significantly with changes in surface composition on these metals: acetaldehyde decarbonylation occurs via release of  $CH_2$  groups on Pd(111) but via  $CH_3$  release on Pd(110) and Rh(111); ethanol decarbonylation proceeds via acetaldehyde on Pd(111) but via an oxametallacycle on Rh(111). These mechanistic differences within seemingly related reaction families present significant challenges to general methods for predicting oxygenate reaction pathways on transition metal surfaces.

### 3. Conclusions

Oxygenate chemistry on transition metal surfaces remains a growing field. There remains much to be learned about variations of reaction mechanisms with surface structure and composition, even among catalytically relevant metals of Groups VIII and IB. Many, but by no means all observations to date can be explained in terms of a limited set of surface intermediates and common reaction pathways. This framework provides a basis for comparison with new observations which may permit development of more comprehensive models to describe oxygenate surface reactivity and catalysis.

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