

Reactions and Reaction Intermediates on Iron Surfaces

IV. Thermodynamics of Surface Reactions

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The reactions of methanol, formaldehyde, and formic acid on copper, silver, iron, and tungsten surfaces have been examined in terms of reaction mechanisms and thermodynamic driving forces. Thermochemical techniques were used to estimate the heats of formation of adsorbed surface intermediates. The enthalpies of reaction were then compared to determine the thermodynamic feasibility of the reactions. It was found that common surface intermediates were found for the reactions on all surfaces. Methanol reacted via a methoxy surface intermediate and formic acid reacted via a formate surface intermediate. Formaldehyde was found to undergo nucleophilic addition forming either methoxy or formate. The observed reaction paths could be accounted for in terms of their thermodynamic driving forces, including the effect of preadsorbed oxygen on the adsorption of methanol on copper and silver. The thermochemical model could also quantitatively account for the "volcano plot" correlation between catalytic activity and the heats of formation of metal formates for formic acid decomposition on transition metal catalysts.

I. INTRODUCTION

The application of thermochemistry to problems in reaction kinetics has resulted in several useful techniques for estimating the feasibility of a reaction and the kinetic parameters. Cox and Pilcher have compiled extensive lists of thermochemical data and have shown how these data may be applied to evaluate the feasibility of a chemical reaction (1). Benson has shown that quantitative estimates of kinetic parameters for gas-phase reactions may be obtained from thermochemical data for elementary reaction steps (2). The techniques outlined by Cox and Pilcher, and Benson have proved tremendously useful when applied to homogeneous reactions. However, the lack of knowledge of surface intermediates has hindered the application of these techniques to heterogeneous reactions.

In previous papers the reactions of alcohols, aldehydes, and carboxylic acids on an Fe(100) surface have been described (3-5). Surface intermediates and reaction pathways were identified using temperature-programmed reaction spectroscopy (TPRS) and X-ray photoelectron spectroscopy (XPS). Similar studies have been performed on W(100), Cu(110), and Ag(110) surfaces (6-14). The interesting feature of these studies was that similar surface intermediates were involved for the reactions on all four metals; however, the reaction pathways were much different. In an effort to account for differences in the reaction pathways on different metal surfaces the thermodynamic driving forces for the reactions of methanol, formaldehyde, and formic acid on Fe(100), W(100), Cu(110), and Ag(110) have been examined. Thermochemical data were used to provide esti-

mates for the heats of reactions. Comparing estimates of the thermodynamic driving forces provided a criterion for evaluating the feasibility of the various mechanistic pathways proposed for the different surfaces. It was found that most of the observed reactions could be accounted for by this analysis.

II. REVIEW OF EXPERIMENTAL RESULTS

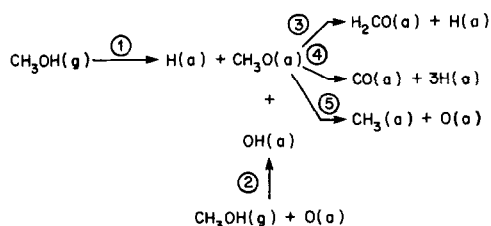
The reactions of methanol, formaldehyde, and formic acid have been studied on Fe(100), W(100), Cu(110), and Ag(110) surfaces. The results of those studies will be reviewed here. In the case of tungsten the results for a W(100)-(5 × 1)C surface will be presented. The clean W(100) surface was so reactive that it caused complete decomposition of the molecular species to adsorbed atomic species at low temperature. However, the reaction mechanisms were clearly identifiable for a W(100)-(5 × 1)C surface. The carbide surface is closely related to a clean tungsten surface, as the surface region is reconstructed with the carbon occupying an interstitial layer beneath a tungsten surface layer (15), and can be considered representative of tungsten.

Reactions of Methanol

The reactions of methanol on Fe(100), W(100)-(5 × 1)C, Cu(110), and Ag(110) all involved the formation of methoxy intermediates (3, 7, 9, 10). However, the formation of the methoxy and its subsequent reactions on copper and silver contrasted sharply with what was observed on iron and tungsten. On a clean Fe(100) surface methanol was observed to dissociatively adsorb and form a methoxy intermediate (3). Similar behavior was observed for a W(100)-(5 × 1)C surface (7). The dissociative adsorption on both these surfaces was irreversible. In contrast to the dissociative adsorption of methanol on Fe and W, methanol did not dissociatively adsorb on clean Ag(110) (10), and dissociative adsorption of methanol on clean Cu(110) was observed to be reversible (14, 16). However, oxygen

preadsorbed on Cu(110) or Ag(110) was observed to induce the subsequent dissociative adsorption of methanol to form methoxy. The adsorbed oxygen reacted with the hydroxyl hydrogen of methanol to form water and methoxy, each oxygen inducing the adsorption of two methanol molecules (9, 10).

The subsequent reactions of the adsorbed methoxy on Fe and W also contrasted with those on Cu and Ag. The primary reaction products on Cu and Ag were H₂CO and H₂ (9, 10), whereas on Fe and W, CO and H₂ were the major products (3, 7). Methane and adsorbed oxygen were also observed as products from the reaction of methoxy on Fe and W. This presumably resulted from the breaking of the C-O bond to form adsorbed oxygen and methyl, followed by the subsequent hydrogenation of methyl to give methane. The reactions of methanol that have been observed on the four metal surfaces are summarized below.



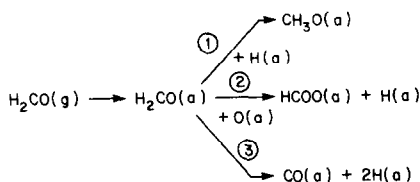
On Fe and W the overall reaction proceeded via reaction ① followed by ④ and ⑤, whereas reaction ② followed by ③ was observed on Cu and Ag.

Reactions of Formaldehyde

Formaldehyde reacted in two ways on the metal surfaces studied. It was observed to decompose to adsorbed CO and hydrogen on Fe(100) (5) and W(100)-(5 × 1)C (8) surfaces. Decomposition was not observed on Cu(110) (12) or Ag(110) (11). The second type of reaction observed for formaldehyde was addition at the acyl carbon. On Fe(100) and W(100)-(5 × 1)C surface hydrogen addition led to the formation of adsorbed methoxy intermediates (5, 8). Hydrogen addition was not observed on

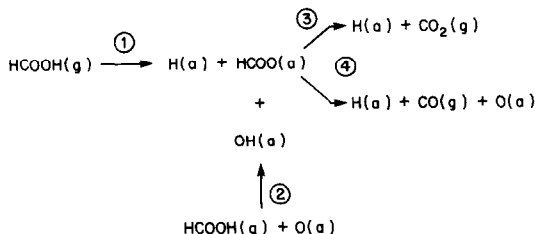
Cu(110) or Ag(110) surfaces (11, 12). However, the addition of adsorbed oxygen to adsorbed formaldehyde, resulting in the formation of adsorbed formate intermediates, was observed on both Cu(110) and Ag(110) (11, 12).

The reactions of formaldehyde are summarized below. Reactions ① and ③ were observed on Fe(100) and W(100)-(5 × 1)C, only reaction ② was observed on Cu(110) and Ag(110).



Reactions of Formic Acid

Formic acid was observed to dissociatively adsorb on Fe(100), W(100)-(5 × 1)C, and Cu(110) surfaces to form a formate intermediate (4, 6, 13). Formic acid did not dissociatively adsorb on clean Ag(110) (11). However, a Ag(110) surface with preadsorbed oxygen did dissociatively adsorb formic acid forming adsorbed formate and hydroxyl groups. The surface formates on all four surfaces were observed to decompose to yield CO₂ and hydrogen. On Fe and W surfaces the surface formate was also observed to decompose to CO, hydrogen, and adsorbed oxygen. On Cu(110) and Ag(110) the oxidation of the surface by formate decomposition was not observed. The reactions of formic acid are summarized below. Reactions ① and ③ were observed on Cu(110), reactions ② and ③ were observed on Ag(110), and reactions ①, ③, and ④ were observed on Fe(100) and W(100)-(5 × 1)C.



III. THERMOCHEMISTRY OF SURFACE REACTIONS

The thermodynamic feasibility of a reaction may be determined from the free energy of reaction. Those reactions with negative free-energy changes will move toward completion, whereas those reactions with a positive free energy will not occur to a marked extent. Provided that the temperature is not too high the entropy contributions to the free energy will generally be small in comparison to the enthalpy contributions, so that the enthalpy should be a good indication of the thermodynamic driving force. However, it should be noted that when the enthalpy is small, or adsorption or desorption steps are involved the entropic contributions will be important and the enthalpy may not be a sufficient criterion for determining thermodynamic feasibility. Furthermore, it will be convenient to neglect temperature corrections to the enthalpies of reaction, as these corrections are small and will be of secondary importance. In order then to compare the reactions of methanol, formaldehyde, and formic acid on Fe, W, Cu, and Ag surfaces the enthalpies of reaction were estimated and compared to identify the thermodynamic feasibility of the various reactions.

The required thermodynamic data are the heats of formation of gas-phase species, the heats of adsorption of those species, and the heats of formation of the surface intermediates. Enthalpies of formation of gas-phase species are readily available and are listed in Table 1. Heats of adsorption for the various species are only partially available. In those cases where the heats of adsorption were not available they were estimated as being equal to the activation energy for desorption. For H₂ adsorption on Ag a lower limit for the heat of adsorption of -25 kJ/mole was estimated from H₂ desorption resulting from decomposition reactions (11). Lastly, the heats of adsorption of oxygen and the heats of formation of adsorbed hydroxy, methoxy, formate, and

TABLE I
Enthalpies of Formation and Adsorption

Species	ΔH_f (kJ/mole)	ΔH_{ad} (kJ/mole)	Ref.
H ₂ O(g)	-240		(17)
CH ₃ OH(g)	-201		(17)
H ₂ CO(g)	-115		(17)
HCOOH(g)	-363		(17)
CO(g)	-108		(17)
CO ₂ (g)	-393		(17)
CH ₃ O(g)	+15		(2)
HCOO(g)	-151		(2)
CH ₃ (g)	+142		(2)
OH(g)	+5		(17)
C(g)	+718		(17)
O(g)	+248		(17)
FeO(s)	-267		(17)
Fe ₃ C(s)	+21		(17)
WO ₃ (s)	-544		(17)
WC(s)	-38		(17)
Ag ₃ O(s)	-31		(17)
Ag ₃ N(s)	+255		(23)
Cu ₃ O(s)	-163		(17)
Cu ₃ N(s)	+75		(23)
H ₂ /Fe(100)		-86	(18)
CO/Fe(100)		-105	(18)
H ₂ CO/Fe(100)		-60	(5)
CH ₃ OH/Fe(100)		-60	(3)
H ₂ /W(100)-(5 × 1)C		-70	(15)
CO/W(100)-(5 × 1)C		-82	(15)
H ₂ CO/W(100)-(5 × 1)C		-60	(7)
CH ₃ OH/W(100)-(5 × 1)C		-60	(8)
H ₂ /Cu(311)		-40	(19)
CO/Cu(110)		-54	(19)
H ₂ CO/Cu(110)		-60	(12)
CH ₃ OH/Cu(110)		-60	(9)
H ₂ /Ag(110)		-25	(11)
CO/Ag(110)		-27	(20)
H ₂ CO/Ag(110)		-55	(11)
CH ₃ OH/Ag(110)		-55	(10)

methyl intermediates must be estimated. These enthalpies were estimated assuming that the bonds to the surface are highly localized so that a bond additivity approach may be used. The enthalpies may be estimated from knowledge of metal-oxygen and metal-carbon bond strengths, as indicated below.

$$\begin{aligned}\Delta H_{ad}(\text{O}_2) &= 2\Delta H_f(\text{O}\cdot) - 4D(\text{M}-\text{O}), \\ \Delta H_f(\text{OH}(\text{a})) &= \Delta H_f(\cdot\text{OH}) - D(\text{M}-\text{O}), \\ \Delta H_f(\text{CH}_3\text{O}(\text{a})) &= \Delta H_f(\text{CH}_3\text{O}\cdot) - D(\text{M}-\text{O}), \\ \Delta H_f(\text{HCOO}(\text{a})) &= \Delta H_f(\text{HCOO}\cdot) - D(\text{M}-\text{O}), \\ \Delta H_f(\text{CH}_3(\text{a})) &= \Delta H_f(\cdot\text{CH}_3) - D(\text{M}-\text{C}).\end{aligned}$$

These expressions implicitly assume each oxygen atom forms a total of two electron

pair bonds and each carbon atom forms four bonds. The bond dissociation energies can be estimated from the heats of formation of metal oxides and carbides (21). If we assume that the oxygen and carbon add interstitially so as to not disrupt the metal lattice, then oxygen adsorption proceeds with the formation of 2y metal-oxygen bonds, and the carbon adsorption proceeds with the formation of 4y metal-carbon bonds. The bond dissociation energies are then given by

$$D(\text{M}-\text{O}) = \frac{1}{2y} [-\Delta H_f(\text{M}_x\text{O}_y)] + \frac{1}{2} \Delta H_f(\text{O}(\text{g})),$$

$$D(\text{M}-\text{C}) = \frac{1}{4y} [-\Delta H_f(\text{M}_x\text{C}_y)] + \frac{1}{4} \Delta H_f(\text{C}(\text{g})).$$

The bond dissociation energies calculated in this fashion are tabulated in Table 2. The heats of formation of Ag and Cu carbides are not known, but are expected to be greater than the heats of formation of Ag and Cu nitrides, so that $\Delta H_f(\text{Ag}_3\text{N})$ and $\Delta H_f(\text{Cu}_3\text{N})$ were used as estimates for the lower limits of the heats of formation of Ag and Cu carbides. (Note that for all transition metals for which data are available (Ti, V, Cr, Mn, Fe, Co, Ni, Zr, Nb, Mo, Ta, W) the heat of formation of the metal nitride is less than the heat of formation of the metal carbide (22).)

In Table 3 the heats of adsorption of O₂ on Ag, Cu, Fe, and W as calculated by the above technique are compared with experimental values. The estimated values are in qualitative agreement with experimental values; the quantitative aspects are difficult to judge because of the large uncertainty for most of the experimental values. For adsorption on Ag quantitative checks may be made and they reveal a discrepancy of 105 kJ/mole between the experimental and calculated heats of adsorption, which corresponds to an error of 26 kJ/mole for the

TABLE 2
 Bond Dissociation Energies^a

Metal	$\Delta H_f(M_xO_y)$	$\Delta D(M-O)$	$\Delta H_f(M_xC_y)$	$D(M-C)$		
Fe	FeO	-267	258	Fe ₃ C	-21	176
W	WO ₂	-554	263	WC	-38	189
Cu	Cu ₂ O	-163	202	Cu ₉ N	+75 ^b	160
Ag	Ag ₂ O	-31	140	Ag ₃ N	+255 ^b	115

^a All values are in kilojoules per mole.

^b These values are lower limits of $\Delta H_f(M_xC_y)$. See text for explanation.

calculated Ag-O bond strength, or approximately a 15% error. The figure of 15% is probably a reasonable estimate on the error in the bond strengths although the scatter in the experimental data makes it impossible to give precise limits on the error. It should be emphasized that the assumption has been made throughout of localized bonding. For solids the localized bonding assumption is not particularly good. Long-range bonding is an important feature of metals and the ionic stabilization of the metal oxides is also a long-range effect. It may well be fortuitous that the technique described above gives any agreement at all; and the reason for success could be that the error in neglecting the long-range bonding in the metal is cancelled by neglecting the long-range bonding in the metal oxide. However, the approximations made here are simple and do give semiquantitative agree-

ment, so they provide a useful starting point.

The heats of formation of adsorbed intermediates are given in Table 4. Although not explicitly stated each of these values has error limits of approximately ± 40 kJ/mole for reasons explained above. Furthermore, crystallographic orientation effects and adsorbate-adsorbate interactions have been neglected. These effects are of secondary importance, typically being less than 20 kJ/mole in magnitude. It has also been assumed that the heats of formation of the surface intermediates on W(100)-(5 \times 1)C are the same as those for a clean W(100) surface because of the surface reconstruction which resulted in tungsten being the topmost surface layer. Spectroscopy has indicated that oxygen adsorbed on clean tungsten, oxygen adsorbed as dissociated CO on tungsten, and oxygen adsorbed on W(100)-(5 \times 1)C all appear to be identical (18), which suggests that the W-O bond strength should be approximately the same on the clean and carbide surfaces. However, reaction differences between the clean and carbide surfaces are substantial so this assumption should be regarded with some skepticism.

TABLE 3

Heats of Adsorption of Oxygen

Metal	Estimated ΔH_{ad} (kJ/mole)	Experimental ΔH_{ad} (kJ/mole)	
Fe	-534	-569	(23) ^a
		-414 \rightarrow -502	(24)
W	-554	-812	(23)
		-767	(25)
		-680	(26)
Cu	-310	-459 \rightarrow -84	(27)
		-209	(28)
Ag	-62	-167	(29)

^a Reference numbers are in parentheses.

Reactions of Methanol

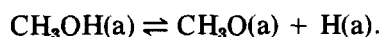
A comparison of the enthalpies of reaction for the reactions of methanol on iron, tungsten carbide, copper, and silver is given in Table 5. In the case of methanol adsorption on the metal surfaces it is apparent that iron and tungsten have a highly

TABLE 4
Heats of Formation of Surface Intermediates^a

Metal	$\Delta H_f(\text{OH(a)})$	$\Delta H_f(\text{CH}_3\text{O(a)})$	$\Delta H_f(\text{HCOO(a)})$	$\Delta H_f(\text{CH}_3\text{(a)})$
Fe	-253	-243	-409	-36
W	-258	-248	-414	-49
Cu	-197	-187	-353	-19
Ag	-135	-125	-291	+25

^a All values are in kilojoules per mole.

favorable thermodynamic driving force for methoxy formation, consistent with the experimental results that showed methanol was dissociatively adsorbed on iron and tungsten carbide surfaces. The enthalpies of reaction indicated that methanol may be dissociatively adsorbed on copper, and should not appreciably dissociate on silver. UPS and ELS results indicated that, in fact, methanol dissociated on Cu(100) (14, 16), but no dissociation on Ag(110) has been observed. Reversible dissociation of methanol comes about due to the surface equilibrium



As the enthalpy for dissociative adsorption on Cu is only slightly endothermic equilibrium will be established between molecu-

larly adsorbed methanol and dissociatively adsorbed methanol. On iron and tungsten the enthalpy change for dissociative adsorption is highly exothermic so that the equilibrium greatly favors dissociation; on silver the enthalpy of dissociation is highly endothermic favoring no dissociation.

In contrast to the results on the clean copper and silver surfaces are those for surfaces with preadsorbed oxygen. When methanol was adsorbed on copper and silver surfaces with preadsorbed oxygen the hydroxyl hydrogen was abstracted by the surface oxygen forming a strong O-H bond instead of a weak M-H bond, thus providing a favorable driving force for dissociative adsorption. This is quite evident for the case of silver as shown in Table 5. One should note in Table 5 for reaction (2) all the enthalpies are the same. This results from the net change in every case being the breaking of the OH bond in methanol and the formation of an OH bond in hydroxy or water so that to first order the surface had no influence.

The differences in the adsorption of methanol on the various metal surfaces are primarily a function of the metal-oxygen bond strength. A strong metal-oxygen bond stabilized the methoxy relative to methanol, as observed for iron and tungsten carbide surfaces; copper and silver did not form strong metal-oxygen bonds and required preadsorbed oxygen to change the reaction pathway so that the methoxy would form.

The differences in the reactions of adsorbed methoxys can also be related to the

TABLE 5

Heats of Reaction of Methanol on Metal Surfaces

Metal	Reactions				
	ΔH_1	ΔH_2	ΔH_3	ΔH_4	ΔH_5
	(1) $\text{CH}_3\text{OH(g)} \rightarrow \text{CH}_3\text{O(a)} + \text{H(a)}$				
	(2) $\text{CH}_3\text{OH(g)} + \text{O(a)} \rightarrow \text{CH}_3\text{O(a)} + \text{OH(a)}$				
	(3) $\text{CH}_3\text{O(a)} \rightarrow \text{H}_2\text{CO(a)} + \text{H(a)}$				
	(4) $\text{H}_2\text{CO(a)} + \text{H(a)} \rightarrow \text{CO(a)} + 3\text{H(a)}$				
	(5) $\text{CH}_3\text{O(a)} \rightarrow \text{CH}_3\text{(a)} + \text{O(a)}$				
	Heats of reaction (kJ/mole)				
Metal	ΔH_1	ΔH_2	ΔH_3	ΔH_4	ΔH_5
Fe	-87	-28	+25	-124	-60
WC	-84	-28	+38	-85	-73
Cu	-8	-28	-8	-27	+13
Ag	+64	-28	-55	+10	+110

thermodynamic driving forces. As shown by Table 5, the decomposition of methoxy to formaldehyde was only favorable on copper and silver. On iron and tungsten the decomposition to formaldehyde was not favorable, although the decomposition to CO and hydrogen had a favorable thermodynamic driving force, which was consistent with the experimental results. The enthalpies of reaction also suggested that decomposition of methoxy on Cu should give CO and hydrogen as opposed to formaldehyde, contrary to the experimental results. One possible explanation for this discrepancy is that the methoxy may have decomposed sequentially, first to formaldehyde and hydrogen, and the formaldehyde subsequently desorbed or decomposed. The experimental results clearly indicate activation barriers for the decomposition of methoxy and formaldehyde on all the surfaces studied (decomposition was not observed at low temperature, but required heating to supply sufficient energy for the reactions to occur). If the rate of formaldehyde desorption was much greater than the rate of decomposition, the primary reaction products from the decomposition of methoxy would be H_2CO and H_2 , whereas if the decomposition were faster, CO and H_2 would be the primary products. Within this context the experimental results suggested that the rate of formaldehyde desorption was greater than decomposition on copper, and vice versa on iron and tungsten. It should be pointed out that the sequential reaction path is consistent with experimental results, small amounts of formaldehyde product resulted from methoxy decomposition on both iron and tungsten carbide. A caution is in order at this point as well. The thermodynamic driving forces are useful in suggesting what is feasible, but energy barriers can also influence the overall pathway, and must also be considered.

Experimentally it was also observed that the methoxy could react to give methane and adsorbed oxygen as products. This re-

action was observed on both Fe(100) and W(100)-(5 × 1)C surfaces, but not on Cu(110) or Ag(110). The reaction step for the formation of methane involves the breaking of the C–O bond to give adsorbed oxygen and adsorbed methyl groups. The methyl groups then react with surface hydrogen to form methane. The enthalpies of this reaction on the four surfaces are given in Table 5. The thermodynamic driving forces are highly favorable on iron and tungsten, consistent with the experimental results.

Reactions of Formaldehyde

The reactions of formaldehyde were much different on iron and tungsten carbide surfaces than on copper and silver surfaces, and these differences were reflected in the thermodynamic driving forces of the reactions. As shown in Table 6 the thermodynamic driving forces for the oxidation of formaldehyde to formate were much more favorable on copper and silver surfaces than on iron and tungsten surfaces. Experimentally it was observed that oxidation was the primary reaction on copper and silver, and only a negligible amount of oxidation was observed on Fe(100) and W(100)-(5 × 1)C. On both iron and tungsten the predominant reactions were hydrogenation of for-

TABLE 6
Heats of Reaction of Formaldehyde on Metal Surfaces

Metal	Reactions		
	ΔH_1	ΔH_2	ΔH_3
	(1) $\text{H}_2\text{CO}(\text{a}) + \text{O}(\text{a}) \rightarrow \text{HCOO}(\text{a}) + \text{H}(\text{a})$ (2) $\text{H}_2\text{CO}(\text{a}) + \text{H}(\text{a}) \rightarrow \text{CH}_3\text{O}(\text{a})$ (3) $\text{H}_2\text{CO}(\text{a}) \rightarrow \text{CO}(\text{a}) + 2\text{H}(\text{a})$		
	Heats of reaction (kJ/mole)		
Fe	-10	-25	-124
WC	-2	-38	-85
Cu	-43	+8	-27
Ag	-106	+55	+10

maldehyde to methoxy and decomposition to CO and hydrogen. The hydrogenation of formaldehyde to methoxy was only observed on iron and tungsten surfaces, and as indicated in Table 6 these were the only surfaces on which that reaction was exothermic.

The decomposition of formaldehyde to CO and hydrogen was also found to be strongly exothermic on iron and tungsten, which accounted for the high reactivity of formaldehyde on these surfaces and suggested why formaldehyde which formed from methoxy decomposition on these surfaces would rapidly decompose to CO and hydrogen. On silver the reaction endothermicity opposed formaldehyde decomposition, which accounted for the absence of formaldehyde decomposition on Ag(110). The decomposition of formaldehyde on copper was calculated to be exothermic; the absence of the decomposition reaction on Cu(110) suggested an activation barrier for decomposition greater than that for desorption. An interesting point to note is that the nucleophilic addition reactions of oxidation and hydrogenation occurred at low temperature on all the metal surfaces, suggesting there was a negligible activation barrier for these reactions. On the other hand, the decomposition reactions of formaldehyde, methoxy, and formate on all the surfaces had substantial activation barriers.

Reactions of Formic Acid

Formic acid was observed to dissociatively adsorb on Fe(100), W(100)-(5 × 1)C, and Cu(110) to adsorbed hydrogen and adsorbed formate, but dissociative adsorption was not observed on Ag(110). This is exactly what one would predict from the enthalpies of the reactions as shown in Table 7. The weak M–O bonds to the silver surface resulted in a formate intermediate that is less stable than gas-phase formic acid, and thus dissociation was inhibited. It was observed that oxygen adsorbed on the Ag(110) surface changed the reaction path-

way to make the formation of a formate intermediate favorable. The adsorbed oxygen played the same role in formic acid adsorption on Ag(110) as it did in methanol adsorption; it abstracted the acid hydrogen to form a strong O–H bond instead of the weaker Ag–H bond.

Thermodynamic considerations also explain why the decomposition of formate oxidized the Fe(100) and W(100)-(5 × 1)C surfaces, but not the Cu(110) or Ag(110) surfaces. On iron and tungsten surfaces both CO and CO₂ formation were exothermic, whereas on copper and silver surfaces the favored reaction was formation of CO₂. It should be noted that the CO/CO₂ selectivity on iron and tungsten suggested that the two reaction pathways were of equal importance, consistent with the results shown in Table 7.

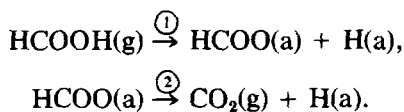
The application of thermochemical arguments has previously been applied in a more qualitative fashion to formic acid decomposition on metal surfaces. Sachtler and Fahrenfort (30) have shown the rate of formic acid decomposition on various metal surfaces may be correlated with the heat of formation of the metal formate through a "volcano plot." The volcano plot shows that the temperature necessary to achieve a fixed reaction rate goes through a minimum at a heat of formation of the metal formate

TABLE 7

Heats of Reaction of Formic Acid on Metal Surfaces

Metal	Reactions			
	ΔH_1	ΔH_2	ΔH_3	ΔH_4
	Reactions			
	(1) $\text{HCOOH(g)} \rightarrow \text{HCOO(a)} + \text{H(a)}$			
	(2) $\text{HCOOH(g)} + \text{O(a)} \rightarrow \text{HCOO(a)} + \text{OH(a)}$			
	(3) $\text{HCOO(a)} \rightarrow \text{CO}_2\text{(g)} + \text{H(a)}$			
	(4) $\text{HCOO(a)} \rightarrow \text{CO(g)} + \text{O(a)} + \text{H(a)}$			
Heats of reaction (KJ/mole)				
Metal	ΔH_1	ΔH_2	ΔH_3	ΔH_4
Fe	-89	-32	-27	-28
WC	-86	-32	-14	-1
Cu	-10	-32	-60	+60
Ag	+62	-32	-112	+143

of approximately -330 to -350 kJ/mole. This particular minimum may be explained by consideration of the two-step reaction sequence for formic acid decomposition shown below.



The overall rate of decomposition will be maximized when both reaction steps are thermodynamically favorable, otherwise the rate will be reduced by having to overcome a thermodynamic energy barrier. To have both steps favorable requires

$$\begin{aligned} \Delta H_f(\text{HCOOH(g)}) \\ - \Delta H_f(\text{H(a)}) < \Delta H_f(\text{HCOO(a)}) \\ < \Delta H_f(\text{CO}_2\text{(g)}) + \Delta H_f(\text{H(a)}). \end{aligned}$$

The heat of adsorption of hydrogen varies from -20 to -130 kJ/mole with most metals having a value of approximately -80 kJ/mole. Assuming a value for the heat of adsorption of hydrogen of -80 kJ/mole one obtains the thermodynamic limitations on the maximum rate

$$\begin{aligned} -323 \text{ kJ/mole} > \Delta H_f(\text{HCOO(a)}) \\ > -433 \text{ kJ/mole}. \end{aligned}$$

This analysis shows the minimum of the volcano plot indeed corresponds to thermodynamic limitations. Thus when the heat of formation of a metal formate is greater than -320 kJ/mole (e.g., Ag) reaction $\textcircled{1}$ is unfavorable, and when the heat of formation of the metal formate is less than -430 kJ/mole (e.g., Fe, W) reaction $\textcircled{2}$ is unfavorable. Only when the heat of formation of the adsorbed formate intermediate goes to those extremes will any thermodynamic limitations be absent.

The thermodynamic limitations to formic acid decomposition of formic acid are essentially a statement of the principle of Sabatier (31). Several previous investigators recognized this fact and made qualitative comparisons of the rate of decomposition with the heats of formation of metal for-

mates (30) or the heats of formation of metal oxides (32). The rationale for plotting catalytic activities as a function of heats of formation of a metal oxide is a postulate of Balandin that the heat of formation of the stable intermediate is linearly related to the heat of formation of the metal oxide (33). The analysis we have presented quantifies that postulate.

IV. CONCLUSIONS

The intent of this paper was to show how a knowledge of reaction intermediates and the thermodynamic quantities associated with those intermediates may be used to identify differences in the reactions catalyzed by different metals. The reactions of alcohols, aldehydes, and carboxylic acids on Fe, W, Cu, and Ag surfaces were all found to be related by common reaction intermediates. Alcohols reacted via alkoxy formation, aldehydes reacted via nucleophilic addition at the acyl carbon, and carboxylic acids reacted via carboxylate intermediates. The thermodynamic feasibilities of various reaction pathways were compared by comparing enthalpies of reaction. Heats of formation of surface intermediates were estimated from bond additivities. A simple technique for estimating metal-oxygen and metal-carbon bond strengths was described which estimated these quantities from a knowledge of the heat of formation of the bulk metal oxide or carbide. The model was able to explain dissociative adsorption of methanol on iron and tungsten carbide surfaces, and show how preadsorbed oxygen induced dissociative adsorption of methanol on copper and silver surfaces. It was also possible to account for different reaction products formed from methoxy on the various surfaces. In particular it was clearly shown why Ag yielded only formaldehyde and hydrogen while Fe and WC yielded primarily CO and hydrogen as well as methane. The thermodynamic driving forces also showed why different nucleophiles reacted with formaldehyde on different surfaces. In the

case of formic acid decomposition the thermodynamics indicated why surface oxidation occurred on iron and tungsten carbide surfaces. The model was also shown to account for the "volcano plot" correlation between the rate of formic acid decomposition and the heat of formation of the metal formate.

Thermochemical data may also be used to evaluate an abundance of surface intermediates. Mars *et al.* have used thermochemical techniques to evaluate the abundance of NH_x surface intermediates during ammonia synthesis (34). Thermochemistry has also been useful in identifying the conditions under which metals will dissociatively adsorb diatomic molecules (35). These previous studies coupled with the present results suggest that with proper refinement thermochemical techniques may be useful for preliminary screening of catalyst materials.

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