to be easily convertible to each other under physiological conditions, their coexistence may be useful for MgATP to bind to a variety of ATP-utilizing enzymes and to become an active substrate without or through isomerization.

Conclusion

Vibrational spectroscopy in conjunction with ^{18}O isotopic substitution have been shown to be a useful method to reveal the sites of coordination of Mg^{2+} to ATP. From the isotopic frequency shifts, several infrared bands have been found to be due to vibrations localized or nearly localized at individual phosphate groups of the triphosphate. Frequency shifts on complexation with Mg^{2+} observed for such localized vibrations indicate that the MgATP complexes exist as a mixture of α,β-, β,γ-, and α,γ-bidentates when the γ-phosphate is protonated. At pH 7.5, where the γ-phosphate is not protonated, ATP forms β,γ-bidentate and α,β,γ-tridentate complexes with Mg^{2+}. The variety of MgATP complex forms may be related to the fact that various enzymes utilizing ATP require Mg^{2+} as cofactors.

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Registry No. ATP, 56-65-5; α-ATP, 111616-21-8; β-ATP, 73135-75-8; γ-ATP, 73116-39-9; Mg^{2+}, 22537-22-0.

Active Oxygen on Group VIII Metals: Activation of Formic Acid and Formaldehyde on Pd(100)

Scott W. Jorgensen and R. J. Madix*

Contribution from the Department of Chemical Engineering, Stanford University, Stanford, California 94305. *Received June 12, 1987*

Abstract: The reactions of formic acid and formaldehyde were studied individually on the clean and oxygen-predosed Pd(100) surface by using temperature-programmed reaction and vibrational spectroscopies. On the clean surface formic acid partially decomposes to give CO, while formaldehyde dehydrogenates to CO and H_2. The formate species was identified on the oxygen-precovered surface in each case. This result clearly shows that the pattern of activation by oxygen via nucleophilic attack of electron-deficient centers or Brønsted basicity previously reported on copper, silver, and gold single-crystal surfaces is also exhibited on the group VIII metal palladium.

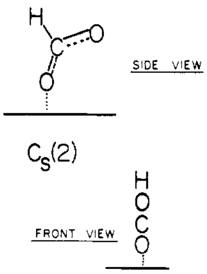
Direct activation by adsorbed oxygen plays a major role in the selective oxidation of alcohols,[1-3] nitriles,[4] and amines[5] on silver surfaces. In addition, it has been shown that C–H bonds in allyls or alkynes are activated in the same fashion.[6] These reactions indicate that the oxygen has an appreciable Brønsted basicity. Furthermore, the nucleophilicity of this type of oxygen has been established for oxidations of aldehydes and methyl formate.[3] Similar reactivity exists for oxygen on both copper[7] and gold surfaces,[8,9] so that these general patterns of reactivity appear well established for the group IB metals. The behavior of adsorbed oxygen on group VIII metals is, however, not yet well characterized. Brønsted basicity of adsorbed oxygen has been established on Pt(111)[10] and Pd(100)[11] for reaction with water to form hydroxyl groups. Similarly, the hydroxyl proton in methanol is transferred directly to surface oxygen on Pd(100).[12]

Table I. Comparative Vibrational Frequencies (cm^{-1}) for HCOOH and H_2CO[a]

	Pd(100)		Pt(111)	Ag(110)
mode	HCOOH	D_2CO	HCOOH	H_2CO
δ(OCO)	700		715	
π(CH/CD)	1220	855	1235	1250 (935)
	1385	1090	1385	1490 (1115)
ν(CO)	950		970	
	1685	1635	1720	1710
ν(CH/CD)	2660	2195	2500	2850 (2135)
	3000		3050	
ν(OH)	3320		>3000	

[a] All spectra taken at 80 K and 1–2 eV beam energy. The values in parentheses are estimates of the CD frequencies for D_2CO based on the data from ref 17.

Chart I



The oxidation reactions of formic acid and formaldehyde have been studied on several single-crystal surfaces[13-21] with a combination of temperature-programmed reaction and vibrational spectroscopies.[15-17] In these studies the formate intermediate has

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Table II. Vibrational Frequencies (cm^{-1}) for Formate on Metal Surfaces[a]

	Pd(100)		Ag(110)[18]				Pt(111)[15]	
mode	HCOO	DCOO	HCOO$_{mono}$	HCOO$_{bi}$	DCOO$_{mono}$	DCOO$_{bi}$	HCOO$_{mono}$	HCOO$_{bridge}$
M–O	370	320	280	280	260	270	360	360
δ(OCO)	775	775	770	760	770	750	780	780
π(CD/CH)		1025	1050	1060	1010	1020		
ν_s(OCO)	1340	1305	1340	1340	1310	1300	1290	1330
ν_a(OCO)	1660	1630	1640	1570	1640	1570	1620	
ν(CD/CH)	2865	2190	2900	2870	2150	2150	2920	2920

[a] All spectra were taken at 80 K with a 1–2 eV beam energy. Mono denotes monodentate and bi denotes bidentate.

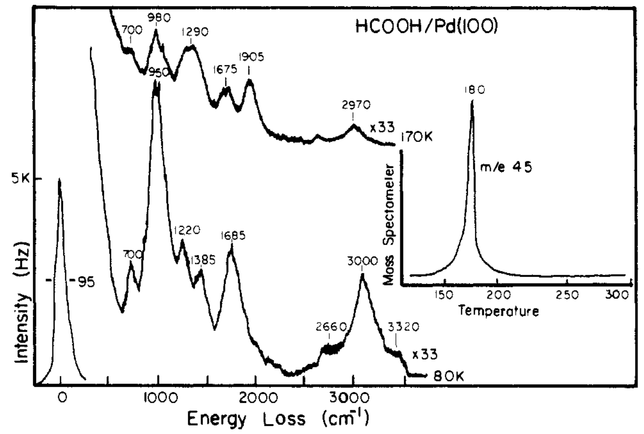

Figure 1. Formic acid on clean Pd(100): A saturated layer of formic acid was formed at 80 K on the clean surface. The loss spectrum at 80 K is in good agreement with previous studies of molecular formic acid.[15,18] At 165 K most of the loss intensity for the acid dissappears due to partial decomposition shown by the presence of a CO mode at 1905 cm^{-1} (carbon monoxide) and the temperature-programmed reaction spectrum. Further heating fully removes the acid peaks leaving only CO and hydrogen on the surface. The peak temperature of the HCOOH desorption is 180 K.

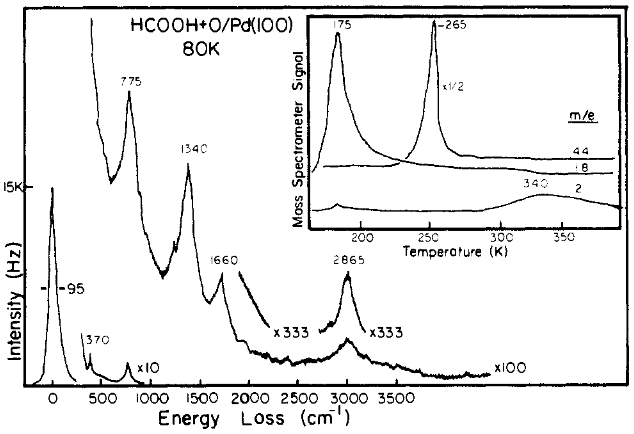

Figure 2. Formic acid oxidation: 0.15 ML of oxygen was formed initially by O_2 dosing at 300 K. The crystal was then exposed to ≈0.4 ML of HCOOH at 80 K. The HREELS spectra taken at 80 K with a beam energy of 1–2 eV indicate that formate forms immediately upon adsorption. The reaction spectra at the upper right indicate that the formic acid was converted selectively to formate. At lower O_a coverages or higher formic acid doses molecular formic acid is also adsorbed, giving rise to desorption-limited CO at 515 K and formic acid multilayers at 180 K, respectively.

been identified either by its characteristic vibrational spectrum (Table I) or by the evolution of characteristic reaction products, CO_2 and H_2. In this work we report evidence obtained with vibrational spectroscopy and temperature-programmed reaction spectroscopy for both Brønsted basicity and nucleophilicity of surface oxygen for reactions with formic acid and formaldehyde, respectively, on the group VIII metal palladium.

Experimental Section

The apparatus and crystal treatment are the same as described previously.[11] The oxygen used was obtained from Matheson (99.998%). The formaldehyde was obtained by heating paraformaldehyde purchased from Merck; formic acid was obtained from Aldrich. Each dose was performed with a new portion of sample, as the reactants began to degrade in the stainless steel line after only 10 min.

Results and Discussion

Adsorption of formic acid on the clean surface was briefly studied in order to better understand the influence of oxygen (Figure 1 and Table I). At 80 K the vibrational spectrum of molecular formic acid was observed with electron energy loss spectroscopy. Strong loss features at 950 and 1685 cm^{-1} are indicative of the molecular species.[18] The OH stretch at 3320 cm^{-1} is visible as a shoulder on the CH stretch (3000 cm^{-1}). Annealing the surface to 170 K partially desorbs the formic acid, and the vibrational spectrum of the remaining surface species shows no indication of the formate. The appearance of the mode at 1905 cm^{-1} is strongly suggestive of molecular CO formation. Carbon monoxide was indeed evolved at 515 K in a desorption-limited step in support of this conclusion; no CO_2 was formed.

When the surface was dosed with 0.15 monolayer (ML) of oxygen at 300 K and exposed to a 1-L dose of formic acid applied at 80 K, the formate intermediate formed immediately. Under these conditions no excess oxygen remained after temperature-programmed heating to 400 K, showing complete titration of the preadsorbed oxygen by the acid. The vibrational frequencies observed (Figure 2) are in good agreement with the formate spectra observed previously on Pt(111) and Ag(110) (Table II). The OCO stretching (1340, 1660 cm^{-1}) and bending (780 cm^{-1}) modes are present while the formic acid modes at 950, 1220, 1385, and 3320 cm^{-1} are absent (Table I). The 320-cm^{-1} difference between the symmetric and asymmetric OCO losses and the presence of the strong asymmetric OCO mode (1660 cm^{-1}) indicate a monodentate species.[4]

The TPRS spectra also indicate a formate intermediate is present. Water evolution at 170 K is clear indication of proton transfer to the surface oxygen. Hydrogen evolution at 340 K is desorption limited, but the CO_2 evolution at 265 K indicates that decarboxylation of the formate occurs at or below 265 K. In order to test whether this CO_2 peak was desorption limited, the adsorption behavior of CO_2 was studied. CO_2 could not be molecularly adsorbed on Pd(100) at 80 K; neither was there any significant amount of CO desorption when the surface exposed to CO_2 was heated. Thus, the CO_2 peak at 265 K must be assigned to formate decomposition and not to desorption of bound CO_2. If the initial oxygen coverage utilized was 0.1 ML or lower and a saturation dose of HCOOH was applied, there was significant CO evolution at the desorption-limited temperature of 515 K, and the amount of H_2 desorption increased. Formic acid desorbed as well at 180 K. These products are due to decomposition of the formic acid on the clean surface without oxygen activation. Thus at low oxygen precoverages the formate group is coadsorbed with molecular formic acid. The desorption temperature of formic acid and the stability of the formate were insignificantly altered by their coadsorption under the conditions described.

Carbon dioxide formation was clearly not due to the oxidation of CO released via decomposition of formic acid without formation

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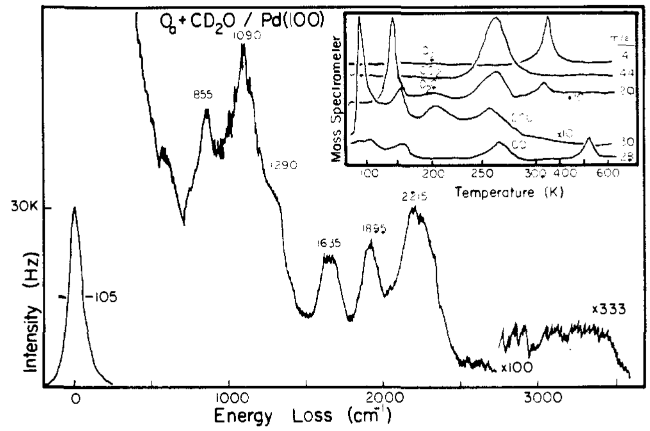

Figure 3. Formaldehyde oxidation: A saturated CD_2O layer adsorbed on 0.15 ML of predosed O_a was heated to 225 K and cooled to 80 K for the HREELS spectrum. The losses are those of formaldehyde, though the shoulder at 1290 cm^{-1} could be due to some formate. All the reaction products are shown at upper right. The formaldehyde peak below 100 K grew without bound under extended dosing indicative of a multilayer. Note the temperature scale above 300 K.

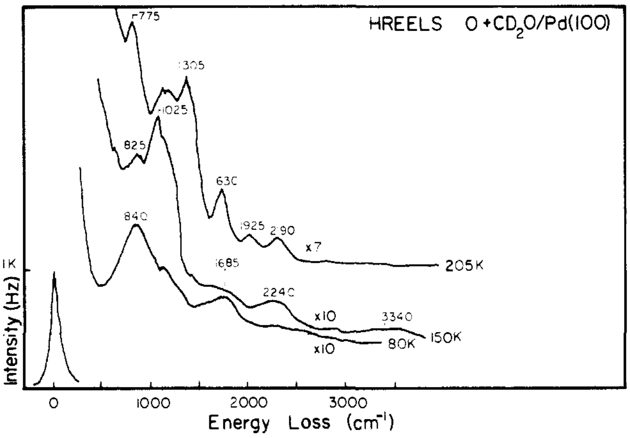

Figure 4. Formate HREELS: 0.2 ML of preadsorbed O_a was dosed with multilayers of CD_2O at 80 K. All spectra are taken at 80 K following annealing to the indicated temperature. The beam energy was 1–2 eV. The vibrational spectrum observed following annealing to 205 K is a strong indication of formate creation. Above 265 K there was no sign of formate or formaldehyde.

of the formate. The oxidation of CO was studied previously on Pd(100)[23] for a wide range of oxygen and CO coverages. At any coverage of CO and coadsorbed oxygen which reacted below 300 K to form CO_2 substantially more oxidation to form CO_2 occurred above 300 K. In the experiments reported here, however, there was no CO_2 formation above 300 K. It is possible that the initial reaction could yield surface hydrogen and CO. In turn, the CO could react with surface oxygen at 265 K, and the surface hydrogen could then deplete the oxygen by reaction at the temperature known for this reaction of 340 K, preventing further CO oxidation. This sequence would produce water at 340 K and CO at 515 K. There was, however, insufficient water and CO evolved at these temperatures for this to be a significant pathway.

The reaction to surface formate occurs via a through-space (direct) transfer of hydrogen from the acid to the oxygen. As shown elsewhere[24,26] a through-space transfer is indicated by water desorption below room temperature in the temperature-programmed reaction spectrum. In the case of formic acid the strong acid can protonate both O_a and OH_a leading to water desorption at the molecular desorption-limited temperature of 175 K.[24] Formic acid is a stronger acid than methanol in both aqueous solution[27] and the gas phase.[28] The fact that formic acid doubly protonates the oxygen on the surface while methanol singly protonates adsorbed oxygen, yielding water by hydroxyl disproportionation, strongly implies that the relative acidity of these species is relected by the degree of proton transfer to the surface hydroxyl groups initially formed. On Ag(110) this order of acidity for reaction with the surface-bound oxygen was rigorously established.[13]

The case of formaldehyde is more complex. On the clean surface formaldehyde decomposed solely to CO and hydrogen, as determined by temperature-programmed reaction spectroscopy. The temperature-programmed reaction spectrum from the oxygen-predosed surface indicates that a formate is present, however, since the CO_2 and H_2 desorptions are the same as observed in the formic acid reaction (Figure 3). In spite of this, the vibrational spectra taken at temperatures below the temperature at which CO_2 starts to desorb show only formaldehyde. The presence of formate is not obvious in the vibrational spectrum of formaldehyde added to preadsorbed oxygen at 0.15 monolayer coverage of oxygen. At 80 K the vibrational spectrum was not well resolved, but heating to any temperature under 230 K gave well resolved losses expected for D_2CO (Table I). The strong 1090-cm^{-1} loss is assigned to the DCD deformation, while the much broader 2215-cm^{-1} loss is assigned to the unresolved symmetric and asymmetric CD_2 stretches in accord with previous work.[17] The CO stretch is observed at 1635 cm^{-1}, and the CD_2 wag modes were observed at 855 cm^{-1}. The loss at 1895 is due to CO. If either paraformaldehyde or methylene dioxide were the dominant surface species, the loss at 1635 cm^{-1} would be absent while OCO modes at 950 cm^{-1} would be observed.[17] The CO stretch is 75 cm^{-1} lower than that on Ag, indicating a stronger metal–adsorbate interaction on Pd.

The reaction spectrum is, however, indicative of the reaction of D_2CO with $O_{(a)}$ to give the formate intermediate. At 265 K there is evolution of CO_2, D_2O, and formaldehyde. The m/q 28 signal at 265 K is due to fragmentation of CO_2 in the mass spectrometer. The CO_2 is evolved at the same temperature observed for formate decomposition. As discussed above, the CO_2 is indicative of surface formate, since there is no CO_2 evolution above 300 K in CO oxidation. However, there is significant desorption-limited CO evolution at 535 K, indicating that there is substantial decomposition of formaldehyde without formate formation. The evolution of water at 265 K further indicates that hydroxyls have been formed. Previous work has shown that hydroxyl recombination occurs at or below this temperature while the hydrogen–oxygen recombination reaction occurs at 340 K.[24] A smaller water desorption peak appears at 330 K. Thus two reactive pathways for water formation are indicated, a direct reaction to form hydroxyl and a path with hydrogen initially transferred to the surface which reacts with residual adsorbed oxygen.

The hydroxyl formation is due to either the reactions of $CD_2O + O \rightarrow CD_2O_2$ and $CD_2O_2 + O \rightarrow CDO_2 + OD$, or $CD_2O + O \rightarrow CDO + OD$ and $CDO \rightarrow CO + D$ or $CDO + O \rightarrow OCDO$. The first reaction pair is initiated by nucleophilic attack of formaldehyde by O_a, while the second pair is initiated by an acid–base reaction. Though the CD_2O_2 species has been shown to exist on group IB metals, it has not yet been identified on palladium, and the vibrational spectra show no indication that it as a *stable* intermediate on Pd(100). The nucleophilic reaction between surface oxygen and the aldehyde apparently occurs between associated partners in the temperature range 225–250 K. Since numerous attempts to isolate the CDO group on group VIII metals have failed, it is not expected to be stable and should lead to desorption-limited evolution of CO and D_2. The absence of the formate or the methylene dioxide species and the presence of CO in the vibrational spectrum following the anneal to 225

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K indicates that the proton-transfer reaction dominates as the source of the water.

Higher oxygen predoses do lead to formate. If a larger oxygen dose (0.2 ML) was preadsorbed, and the crystal heated to 205 K and rapidly cooled to quench the surface reaction, the vibrational spectrum showed losses characteristic of monodentate DCOO on silver[18] (see Figure 4 and Table I). The absolute values and the separation of the ν(OCO) frequencies are almost the same as for the HCOO formed from formic acid. However, in the case of DCOO the π(CD) modes are no longer obscured by the stronger OCO stretch, and the π(CD) mode is clearly observed at 1025 cm^{-1}. We conclude that at these higher oxygen coverages the aldehyde is nucleophilicly attacked by surface oxygen even at 80 K.

The preadsorption of oxygen not only leads to nucleophilic attack on adsorbed formaldehyde, but it also appears to lead to a more ordered overlayer. No low-energy electron-diffraction studies were performed; however, the much stronger elastic peak in the loss spectrum obtained with oxygen precoverage compared to the elastic peak observed for monolayer coverage of the aldehyde on the clean surface is indicative of a more ordered overlayer in the presence of adsorbed oxygen. Adsorbed oxygen forms islands on Pd(100).[23] The islands may force the adsorbed formaldehyde to assume a more ordered configuration. Oxygen clearly reacts with formaldehyde, although at low θ_O the formate appears to be a transitory intermediate due to the nearly coincident temperatures for formaldehyde oxidation and formate decomposition. At higher θ_O the reaction to formate occurs at ≈200 K. This strong shift in reaction temperature with an ≈20% change in θ_O indicates that excess oxygen aids the nucleophilic attack. A similar process in which methylene dioxide is a transient intermediate between formaldehyde and formate has been proposed for the oxidation of formaldehyde on Cu.[13]

The comparative reaction temperatures of the formic acid and formaldehyde oxidations give information on the relative activation energies of the the two paths to formate. The acid–base reaction for formic acid runs to completion at 80 K, while the nucleophilic attack occurs at ≈200 K or higher. The acid–base reaction is that of a very strong base with a strong acid. The driving force is obviously large, but the activation barrier need not be a priori small. However, the complete reaction at 80 K indicates that at least for formic acid the activation energy is less than 5 kcal/mol. By comparison, the activation energy for the nucleophilic attack leading to the same product, formate, has an activation energy of approximately 12 kcal/mol, based on the reaction temperature. Despite some uncertainty in these values, it is reasonable to infer that the activation energy of the acid–base reaction (H transfer) is significantly lower than the nucleophilic reaction (O incorporation) on this surface.

Conclusions

The formate group forms on Pd(100) as a result of both acid–base chemistry in the oxidation of formic acid and nucleophilic attack in the oxidation of formaldehyde. Formate adopts a monodentate form with the molecule tilted in a plane perpendicular to the surface. The formate is stable up to 265 K where is decomposes to CO_2 and hydrogen. The proton-transfer reaction in formic acid oxidation occurs via a direct path at 80 K while the nucleophilic attack in formaldehyde oxidation occurs at or above 200 K.

On Pd, as on silver, oxygen can act as both a nucleophile and a strong Brønsted base. Acids as weak as water, methanol, and presumably other alcohols react with oxygen in an acid–base fashion. Additionally, the nucleophilic reactivity of adsorbed oxygen, previously well documented on group IB metals, has also been demonstrated on Pd(100).

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Electron Affinities of Benzo-, Naphtho-, and Anthraquinones Determined from Gas-Phase Equilibria Measurements

Thomas Heinis, Swapan Chowdhury, Susannah L. Scott, and Paul Kebarle*

Contribution from the Chemistry Department, University of Alberta, Edmonton, Canada T6G 2G2. Received June 12, 1987

Abstract: The equilibrium constant K_{et} for gas-phase electron transfer equilibria $A^- + B = A + B^-$ between compounds A with known electron attachment energies and some 21 benzo-, naphtho-, and anthraquinones = B were determined. These lead to electron attachment free energies $\Delta G_a°(B)$ for the following process: $e + B = B^-$. Determination of the temperature dependence of K_{et} leads to $\Delta H_a°(B)$ and $\Delta S_a°(B)$. The electron affinities EA(B) correspond to $-\Delta H_a(B)$. The substituent effects on the electron affinities of the quinones are examined. Available half-wave reduction potentials for the quinones in water, dimethylformamide, and acetonitrile are used in order to evaluate the solvation free energies of the quinone radical anions in these solvents. The substituent effects on the solvation energies are examined. In general it is found that the exothermicity of the solvation free energy decreases as the electron affinity of the quinones increases.

The quinones are an extremely important group of compounds. In biological systems quinones attached to proteins are the prosthetic group involved in electron and hydrogen transfers.[1-3] The one- or two-electron reduction of quinone (quinone–hydroquinone) is reversible and represents one of the most important examples of organic electrochemistry.

Quantitative information on the stability of the radical anions resulting after single electron capture in solution can be obtained from the reduction potentials of quinones. The data that are generally available are polarographic half-wave potentials measured in different solvents. The corresponding quantity in the gas phase is the electron affinity and the related enthalpy $\Delta H_a°$ and free energy $\Delta G_a°$ of electron attachment shown in eq 1, where

$$e + B = B^- \tag{1}$$

$$\Delta H_1° = \Delta H_a°(B),\ \Delta G_1° = \Delta G_a°(B),\ -\Delta H_a°(B) \approx EA(B)$$

B is a molecule with electron affinity.

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