Reactions and Reaction Intermediates on Iron Surfaces

II. Hydrocarbons and Carboxylic Acids

J. B. BENZIGER[1] AND R. J. MADIX

Department of Chemical Engineering, Stanford University, Stanford, California 94305

The reactions of hydrocarbons and carboxylic acids on Fe(100) were studied by temperature-programmed reaction spectroscopy (TPRS) and X-ray photoelectron spectroscopy (XPS). Adsorbed methyl groups were observed to be stable surface intermediates formed from CH_3Cl adsorption. The methyl groups reacted to form H_2 and surface carbide; the rate of this reaction was given by $-d\sigma_{CH_3}/dt = (8 \times 10^{12} \text{ s}^{-1})\sigma_{CH_3} \exp(-110 \text{ kJ/mole/RT})$. TPRS results did show that olefins formed stable surface intermediates, though no definitive identification was possible from the studies reported here. Carboxylic acids were found to form stable carboxylate intermediates, which decomposed by first-order kinetics to form H_2 and either CO_2 or CO and adsorbed oxygen. The rates for formate and acetate decomposition were $-d\sigma_{HCOO}/dt = (7 \times 10^{13} \text{ s}^{-1})\sigma_{HCOO} \exp(-130$ kJ/mole/RT), $-d\sigma_{CH_3COO}/dt = (8 \times 10^{13} \text{ s}^{-1})\sigma_{CH_3COO} \exp(-140 \text{ kJ/mole/RT})$. The stability of surface formates on various metal surfaces were compared and shown to correlate with the oxygen metal bond strength.

INTRODUCTION

In Part I of this series the reactions of alcohols on Fe(100) were described (*1*). Alcohols were observed to form alkoxy intermediates, and it was suggested that these alkoxys were one of the important intermediates in Fischer–Tropsch synthesis, as they reacted to form hydrocarbons and oxygen-containing products. In addition to alcohols and aldehydes, carboxylic acids and hydrocarbons are also reaction products in the Fischer–Tropsch synthesis. Therefore the reations of simple hydrocarbons and carboxylic acids on Fe(100) have been studied, and the results are presented in this paper. The terms desorption-limited and reaction-limited signify reaction sequences in which evolution of the product into the gas phase is limited in rate by desorption or a prior surface reaction, respectively.

[1] Present address: Department of Chemical Engineering, Princeton University, Princeton, N.J. 08540.

EXPERIMENTAL

The experimental apparatus and procedures have been reviewed previously (*1, 2*). Samples of formic acid and acetic acid were prepared as described elsewhere (*4, 5*). Samples of methyl chloride (Liquid Carbonic 98%), ethylene (Matheson 99.9%), *cis*-2-butene (Liquid Carbonic 98%), and acetylene (Liquid Carbonic 99.5%) were attached to a gas manifold and admitted into the vacuum chamber through a 22-gauge needle connected to a variable leak valve. Preliminary studies showed methane and ethane had sticking probabilities of less than 10^{-6} (see Part I (*1*) on how sticking probabilities were determined).

RESULTS

Reactions of Hydrocarbons

The adsorption and reactions of CH_3Cl, C_2H_4, C_2H_2, and *cis*-2-butene were studied. Subsequent to the adsorption of CH_3Cl on Fe(100) at 180 K the only desorption prod-
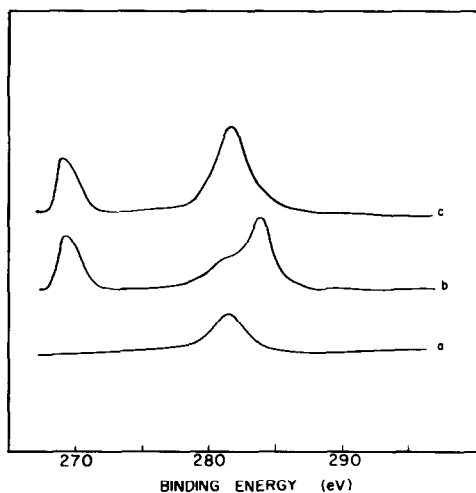
FIG. 1. C(1s) XPS of methyl chloride adsorbed on Fe(100). (a) before adsorption, (b) CH_3Cl adsorbed at 150 K, (c) heated to 500 K.

uct observed was H_2, which desorbed in a single peak at 475 K. This temperature was well above 400 K, the temperature at which H_2 desorbed subsequent to H_2 adsorption (the desorption-limited temperature of H_2) (3). The X-ray photoelectron (XP) spectra for methyl chloride adsorbed on Fe(100), shown in Fig. 1, gave a C(1s) peak at 283.4 eV and a Cl(2s) peak at 269.0 eV. There were no changes in the spectra for crystal temperatures up to 380 K. Upon heating to 500 K the C(1s) peak shifted to 282.2 eV, corresponding to carbon adsorbed on the Fe(100) surface; however, there was no change in the Cl(2s) peak. The fact that neither the magnitude nor the peak position of the Cl(2s) peak changed from low-temperature adsorption up to 900 K indicated that upon adsorption the $H_3C–Cl$ bond was broken to form a Fe–Cl bond. The chlorine could only be removed from the surface by argon sputtering, and no chlorine-containing products were observed to desorb from the surface.

The results of temperature-programmed desorption experiments strongly suggested that the C(1s) peak at 283.4 eV was due to surface methyl groups. Upon heating, all of the H_2 was desorbed alone at 475 K, and

there was no desorption-limited H_2 at 400 K. These observations ruled out the possibility of the formation of CH or CH_2 intermediates below 475 K. The hydrogen evolved was apparently still bound to the carbon, although the methyl chloride dissociated to give chlorine atoms at 150 K. The kinetic parameters for the methyl decomposition were estimated from a plot of ln(rate/coverage) versus $1/T$; the rate of decomposition was described by

$$\text{rate} = (8 \times 10^{12} \text{ s}^{-1})\sigma_{CH_3}$$
$$\exp(-110 \text{ kJ/mole/RT}).$$

After adsorption of ethylene and acetylene the only desorption products observed were the parent molecules and H_2. Ethylene adsorption at 180 K led to ethylene desorption at 250 K (with smaller amounts desorbing up to 450 K) and H_2 desorption at 390 K (see Fig. 2). The behavior of acetylene was similar; after acetylene adsorption at 180 K acetylene desorbed at 240 K, and H_2 desorbed at 350 K. The fact that the H_2 reaction product from ethylene and acetylene desorbed at different temperatures indicated that the hydrogen apparently came from different surface intermediates.

The XPS results provided some insight into the intermediates that existed on the surface. The C(1s) XPS spectra for ethylene adsorbed on Fe(100) are shown in Fig. 3. For ethylene adsorbed at 180 K there was evidence for two peaks in the C(1s) spectrum, neither of which corresponded to
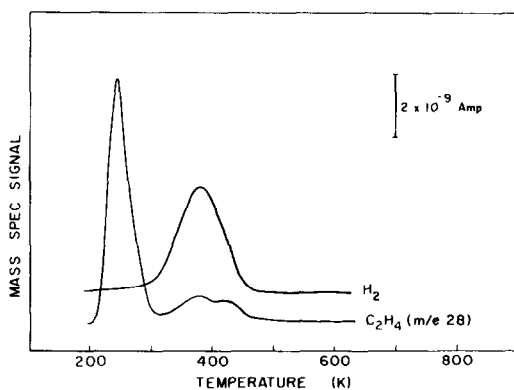

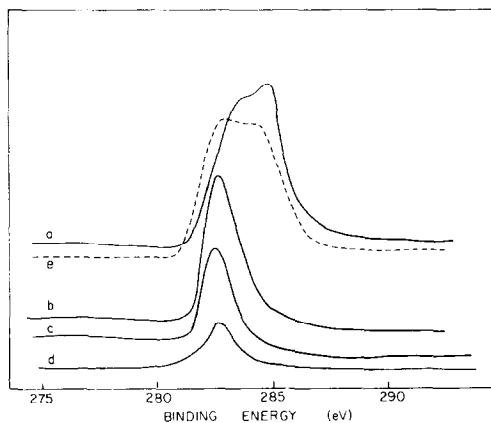FIG. 2. Ethylene decomposition on Fe(100).

FIG. 3. C($1s$) XPS of ethylene adsorbed on Fe(100). (a) C_2H_4 adsorbed at 200 K, (b) heated to 400K, (c) heated to 600 K, (d) heated to 800 K, (e) C_2H_2 adsorbed at 200 K.

FIG. 4. Reactions of cis-2-butene on F(100).

adsorbed carbon, and the spectrum showed no change for heating the crystal up to 300 K other than a slight decrease in the C($1s$) intensity. Heating to 400 K led to decomposition of the surface intermediate and desorption of H_2. At the same time the C($1s$) spectrum shifted to lower B.E. and indicated the buildup of carbon on the surface with a single peak at 282.2 eV. An interesting feature seen in Fig. 3 was the decrease of the C($1s$) peak at 282.2 eV as the temperature of the crystal was raised, indicating diffusion of carbon into the bulk of the iron crystal. Adsorption of acetylene on Fe(100) gave similar results; the C($1s$) spectra showed two peaks for low-temperature adsorption (see Fig. 3) and a single peak at 282.2 eV after heating to 400 K.

To help elucidate the reaction intermediate in ethylene decomposition, cis-2-butene decomposition was also studied. The reaction product spectrum for cis-2-butene is shown in Fig. 4. Butene was observed to desorb at 260 K after adsorption at 180 K, similar to what was observed for ethylene; CH_4 and H_2 desorbed near 390 K; at 480 K, H_2 desorbed alone. The desorption of H_2 at 390 K corresponded to H_2 desorption from ethylene, indicating the presence of analogous intermediates for both C_2H_4 and cis-2-butene decomposition, while the de-
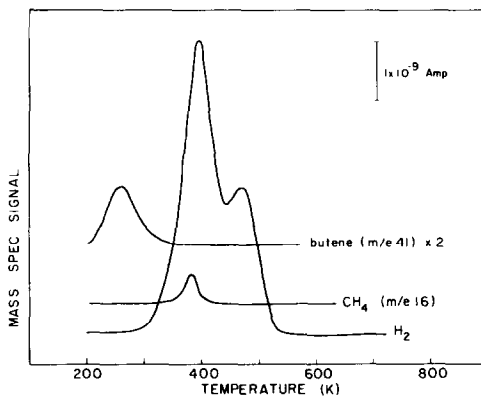
sorption at H_2 at 480 K corresponded to the decomposition of methyl groups noted above for $CH_{3(a)}$ from CH_3Cl. The evolution of the XP spectra with heating was very similar to that for C_2H_4 shown in Fig. 3.

Reactions of Carboxylic Acids

The reaction product spectrum subsequent to formic acid adsorption on Fe(100) is shown in Fig. 5. The reaction appeared to proceed in two steps. The hydrogen originally bound to the oxygen was evolved at 350 K in what appeared to be a desorption-limited step. At 490 K, CO_2, CO, and H_2 were evolved simultaneously, presumably from formate decomposition. There was also a small amount of CO that desorbed at 800 K as the result of the reaction between
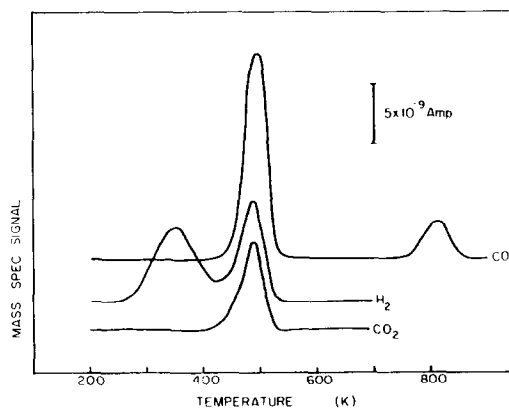

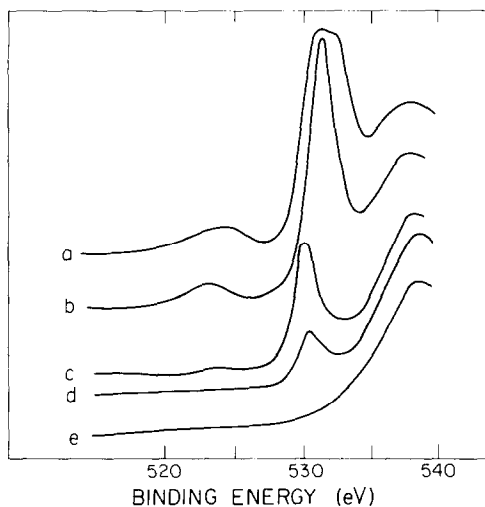FIG. 5. Reactions of formic acid on Fe(100).

FIG. 6. O(1s) XPS of formic acid adsorbed on Fe(100). (a) HCOOH adsorbed at 160 K, (b) heated to 360 K, (c) heated to 500 K, (d) heated to 900 K, (e) before adsorption.

TABLE 1

Formic Acid Adsorption on Fe(100)

Conditions	Binding energies (eV)		Coverages (mono-layers)[a]	
	$C(1s)$	$O(1s)$	θ_C	θ_O
(a) HCOOH adsorbed at 160 K	282.3 288.3	531.2 532.5	0.36	0.62
(b) Heated to 360 K	282.3 288.3	531.7	0.35	0.60
(c) Heated to 500 K	282.3	530.0	0.12	0.20
(d) Heated to 900 K	—	530.0	—	0.07
(e) Before adsorption	282.3	—	0.06	—

[a] 1 monolayer $= 1.2 \times 10^{15}$ atoms/cm^2.

adsorbed carbon and oxygen atoms. No other reaction products (e.g., H_2O) were detected. These results are discussed below.

The XPS results shown in Figs. 6 and 7, and summarized in Table 1, showed that decomposition proceeded above 360 K and led to a buildup of oxygen on the surface. Figure 7 shows the presence of carbon contamination before adsorption of formic acid; after heating to 900 K to desorb dissociated CO, the carbon was removed, and there was an oxygen buildup (see Fig. 6). The spectra suggested that the formate was bonded to the surface through both oxygens. The O(1s) XPS spectrum for formic acid adsorbed at 160 K showed a very broad peak, which would result from the two different oxygens in formic acid. Heating to 350 K resulted in the loss of the acid hydrogen and formation of the surface formate. The two oxygens in the formate should be equivalent, which indeed appeared to be the case as there was a detectable shift to O(1s) intensity into the lower B.E. peak with a FWHM equal to that of adsorbed atomic oxygen. However, the C(1s) spectra showed no change between

the formic acid adsorbed at 160 K and the formate formed by heating to 350 K. These results suggested that the changes that occurred during formic acid adsorption were due to the formation of oxygen surface bonds. The fact that an O(1s) peak was observed with a FWHM equal to that of adsorbed atomic oxygen was consistent with the view that the formate was bonded to the surface via the two oxygens equally.
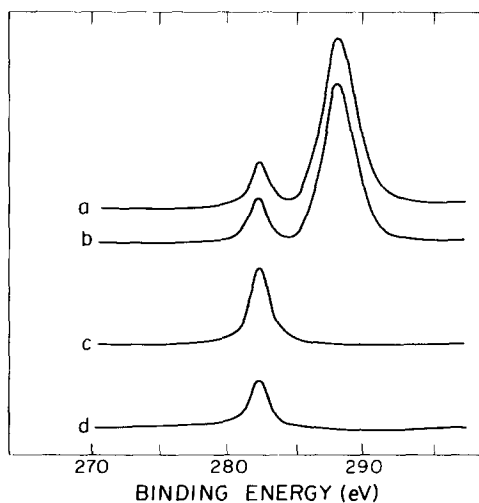

FIG. 7. C(1s) XPS of formic acid adsorbed on Fe(100). (a) HCOOH adsorbed at 160 K, (b) heated to 360 K, (c) heated to 500 K, (d) before adsorption.

The last thing to note from the spectra is that the buildup of surface oxide and dissociation of CO to atomic species only occurred when the formate decomosed at 490 K. This was evident from the shift of the O(1s) peak from 531.7 to 530.0 eV and from the increase in the C(1s) peak at 282.3 eV.

The results in Table 1 allow the selectivity for the two pathways $HCOO_{(a)} \to CO_{(g)} + O_{(a)} + H_{(a)}$ and $HCOO_{(a)} \to CO_{2(g)} + H_{(a)}$ to be estimated. The total amount of formate decomposing to CO and adsorbed oxygen is equal to the amount of carbon consumed in the adsorption/reaction cycle, plus the net oxygen buildup (0.13 monolayer). The selectivity for oxidation of the surface was then 0.13/0.30 = 0.43.

The kinetic parameters for the formate decomposition were estimated from peak shape analysis. One approach employed was based on peak temperature and the peak width at half maximum rate (6). The CO_2 desorption peak was asymmetric, consistent with a first-order process. Assuming the formate decomposition was a first-order process, we calculated the rate of decomposition to be

$$\text{rate} = (7 \times 10^{13} \text{ s}^{-1})\sigma_{HCOO}$$
$$\exp(-130 \text{ kJ/mole/RT}),$$

where σ_{HCOO} was the coverage of surface formate. An alternative method of determining the kinetic parametrers was to plot $\ln(\text{rate}/\sigma)$ versus $1/T$, which has a slope of E_A/R. This method gave an activation energy of 128 kJ/mole, in excellent agreement with the value obtained from the peak width method.

Acetic acid appeared to decompose by a mechanism similar to that for formic acid. The reaction product spectra shown in Fig. 8 indicated the acid hydrogen was lost at or below 300 K and subsequently desorbed by a desorption-limited process at 350 K. The acetate intermediate remaining on the surface decomposed at 535 K yielding H_2, CO, CO_2, and a small amount of CH_4. The methane product most probably resulted
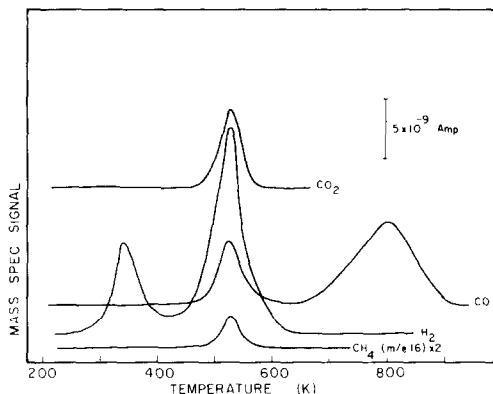

FIG. 8. Reactions of acetic acid on Fe(100).

from the hydrogenation of the methyl group in the acetate intermediate. At 800 K there was a very substantial CO product, much more than was observed for any other reaction. This apparently resulted from the buildup of oxygen and carbon on the surface from the carboxylate end of the acetate (as was observed for formate) and the methyl group of the acetate, respectively. The carbon and oxygen then recombined to desorb as CO at 800 K.

The acetate on Fe(100) was a more stable intermediate than the formate, as we obvious from the higher decomposition temperature for the acetate. The kinetic parameters for the decomposition of acetate were determined by the same methods as used for formate decomposition discussed above. The rate of decomposition of the acetate was described by

$$\text{rate} = (8 \times 10^{13} \text{ s}^{-1})\sigma_{CH_3COO}$$
$$\exp(-140 \text{ kJ/mole/RT}).$$

The XPS results for acetic acid adsorbed on Fe(100) were also similar to those for formic acid. The O(1s) peak for acetic acid adsorbed at 180 K was broader than would be expected for a single peak; however, heating to 350 K resulted in the peak's narrowing (see Fig. 9). Heating to 580 K, which caused the acetate to decompose, resulted in the O(1s) peak diminishing in intensity and shifting to a lower binding energy characteristic of adsorbed oxygen.
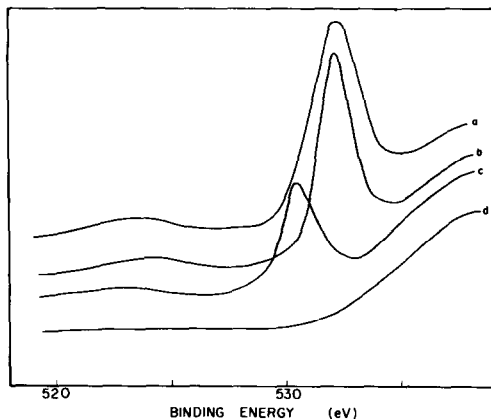
FIG. 9. O(1s) XPS of acetic acid adsorbed on Fe(100). (a) CH₃COOH adsorbed at 190 K, (b) heated to 360 K, (c) heated to 580 K, (d) Heated to 900 K.

Lastly, heating to 900 K caused the dissociated CO to desorb, and the O(1s) peak vanished. The C(1s) spectra showed two peaks for acetic acid corresponding to the methyl and carboxylate carbons at 285.8 and 288.8 eV, respectively, as well as a small amount of carbon contamination with a peak at 282.3 eV (see Fig. 10). The two peaks could be assigned to specific carbons by comparing the positions with other adsorbates. The peak at 288.8 eV was at approximately the same energy as the formate peak and was assigned to the carboxylate carbon. The

peak at 285.8 eV was nearly the same energy as the methyl group for ethoxy (1), and acetone (2) and was assigned to the methyl group. No change was observed in the C(1s) spectra until the temperature reached 580 K, when the acetate decomposed, and a buildup in surface carbon was seen. The C(1s) peak at 282.3 eV then decreased when the crystal was heated to 900 K to desorb the dissociated CO. The XPS results are summarized in Table 2.

DISCUSSION

Reactions of Hydrocarbons

The reactions of ethylene, butene, and acetylene on Fe(100) all appeared to proceed by similar reaction pathways. The XPS data and TPRS results suggested that both ethylene and butene formed intermediates which decomposed near 390 K. Ethylene decomposed to form H_2 at 390 K, while cis-2-butene formed an analogous intermediate that reacted to form H_2, and CH_4 at 390 K. If one rules out the fortuitous possibility that the rates of $H_{(a)} + H_{(a)} \rightarrow H_{2(g)}$ and $n\ H_{(a)} + CH_{4-n(a)} \rightarrow CH_4$ are identical, the formation of CH_4 at 390 K indicated that the hydrogen evolved at 390 K from both ethylene and cis-2-butene was the result of a reaction of a surface intermedi-
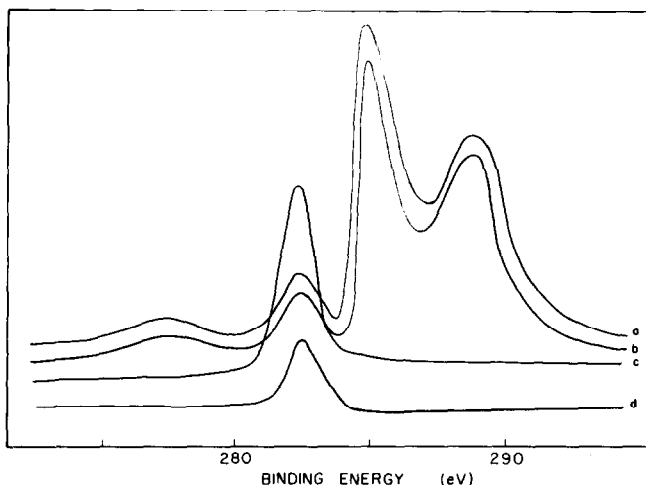

FIG. 10. C(1s) XPS of acetic acid adsorbed on Fe(100). (a) CH₃COOH adsorbed at 190 K, (b) heated to 360 K, (c) heated to 580 K, (d) heated to 900 K.

ate, and not the result of desorption-limited H_2. The H_2 desorption peak at 480 K from the decomposition of *cis*-2-butene can be attributed to methyl groups decomposing. The decomposition of methyl groups at 475 K to give H_2 and surface carbon has also been observed from the reactions of methyl chloride, ethanol (1), and acetone (2).

The nature of the surface intermediates formed during the reactions of acetylene, butene, and ethylene cannot be answered definitively from the results at hand. The $C(1s)$ XP spectra for ethylene and acetylene adsorbed on Fe(100) showed two peaks, which seemed to discount the possibility of a symmetric π-bonded intermediate, as the two carbons would be equivalent in such an intermediate. Brucker and Rhodin (7) found that UPS results of ehtylene and acetylene adsorbed on Fe(100) above 123 K were not consistent with a π-bonded ethylenic or actylenic intermediate, and speculated that ethylene and acetylene decomposed at low temperature to CH_2 and CH intermediates, respectively. Two such intermediates should possess nearly equal $C(1s)$ binding energies, which is not consistent with PES results (8).

Numerous other possibilities for surface intermediates exist. One is that there are two different types of surface intermediates formed, which have similar reaction kinetics. As an example there could be a mixture of π-bonded and di-σ-bonded olefin intermediates

$$(\text{e.g., } H_2C{=}CH_2 + H_2C{-}CH_2).$$
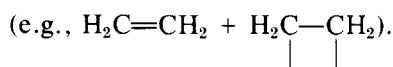
Other possibilities are ethylidene intermediates

$$(*{-}\overset{H}{\underset{}{C}}{-}CH_3)$$
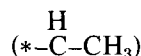
similar to what has been proposed by Ibach and Lehwald (9), or vinylidene intermediates

$$(*{-}C{\overset{H}{\underset{CH_2}{\diagdown}}})$$

which have analogs in organometallic complexes (*10, 11*). The TPRS results for ethylene on Fe(100) tend to rule out the ethylidene intermediate. The reaction of such an intermediate would be expected to yield CH_4, since experimental evidence suggests that surface intermediates with methyl groups attached to a carbon give rise to CH_4 (e.g., ethoxy, butene, acetate). Both the vinylidene intermediate and the mixture of two different intermediates are consistent with the TPRS results. The H_2/C_2H_4 TPRS results showed the H_2 desorption peak consisted of two overlapping peaks. If there were a mixture of two types of intermediates, their decomposition kinetics must be virtually identical to be unresolved by TPRS. On the other hand, if there were vinylidene intermediates there would be desorption-limited H_2 as a product at 350 K, which would overlap the decomposition peak at 390 K to produce a broad peak. Unfortunately we are unable to distinguish these two possibilities. However, the existence of a stable surface intermediate is clearly established.

The stabilities of the ethylene and acetylene intermediates should be related to the thermodynamic stabilities of the two. As the average bond energy in the triple bond is less than in the double bond, the ethylene

TABLE 2

Acetic Acid Adsorption on Fe(100)

Conditions	Binding energies (eV)		Coverages (monolayers)	
	$C(1s)$	$O(1s)$	θ_C	θ_O
(a) CH_3COOH adsorbed at 190 K	282.3 285.8	532.0	0.64	0.60
(b) Heated to 360 K	282.3 285.8 288.8	532.0	0.61	0.56
(c) Heated to 580 K	282.3	530.3	0.28	0.25
(d) Heated to 900 K	282.3	—	0.04	—
(e) Before adsorption	282.3	—	0.02	—

intermediate should be the more stable toward reaction. The stabilities are reflected in the decomposition temperatures, acetylene decomposed at or below 350 K (it was not possible to ascertain whether the H_2 evolution was desorption or reaction limited), while both ethylene and cis-2-butene decomposed at 390 K indicating greater stability of the ethylene intermediates.

Perhaps the most important result from the hydrocarbon reactions was the observation of stable alkyl intermediates (e.g., *–CH_3). Blyholder and co-workers also observed alkyl intermediates in their ir studies of adsorbates on iron (12). In the work presented here methyl groups were observed to form from C–C bond scission, as in the case of ethanol, acetone, and butene, or by breaking the weak carbon–halogen bond in methyl chloride. The methyl groups decomposed to H_2 and adsorbed carbon; no methane or ethane was observed as a reaction product. One point to note was that there was no indication in any of the reactions studied for stable methylene (*=CH_2) intermediates. This observation is important because in many of the mechanisms proposed for Fischer–Tropsch synthesis, methylene was suggested as the surface intermediate.

The results obtained here support the hypothesis that carboxylic acids decompose on iron via the formation of a surface carboxylate. The XPS results suggested that the carboxylate was bound with both oxygen bonding in equivalent fashion to the surface. The formation of carboxylate intermediates has been previously established by Blyholder and co-workers on iron powders (12) and by a variety of other investigators on other metal surfaces (13). The carboxylates were observed to be exceptionally stable on iron surfaces, both by Blyholder and in the present study. The surface acetate was more stable than the formate. The present study further quantified these findings and provided kinetic parameters for formate and acetate decomposition. The selectivity for the for-

mate decomposition was a bit surprising, as typically the decomposition of formic acid is envisioned as proceeding via a formate surface intermediate to yield CO_2 and hydrogen. Consideration of two reaction pathways for formate decomposition helped to clarify this dilemma. The formate could decompose to either adsorbed hydrogen and CO_2, or hydrogen, CO, and surface oxide.

$$HCOO(a) \diagup\diagdown \begin{array}{l} H(a) + CO_2(g) \\ H(a) + CO(g) + O(a) \end{array}$$
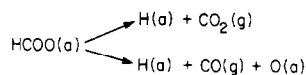
The difference in enthalpy for these reaction pathways is equal to the difference between the heat of formation of CO_2 and the heats of formation of CO and FeO, which is small (less than 8 kJ/mole). The two reaction pathways would thus be expected to compete on thermodynamic grounds alone.

It is instructive to compare the reactions of carboxylic acids on different metals. Carboxylate intermediates have been observed on most metal surfaces (e.g., Cu, Ag, W), with the only known exception being nickel, on which anhydride intermediates were reported (14–16). The reason for this different behavior is not known, although it appears to be related to the formation of surface oxygen bonds. The reactions of alcohols, aldehydes, and acids on iron, copper (17, 18), silver (19), and tungsten (20, 21) all were found to proceed via the formation of stable intermediates which were bound to the surface by oxygen–metal bonds. Nickel was different in that these types of intermediates (alkoxys and carboxylates) were not stable at room temperature.

For those metals on which the carboxylate intermediates were stable a comparison of the kinetic parameters for the decomposition should provide some insight into the differences between metals. The peak temperatures for the decomposition of a formate are shown below for studies on clean metal surfaces.

Metal	Metal oxygen bond strength (kJ/mole)	T_p (K)	Reference
Ag	140	410	(9)
Cu	202	470	(18)
Fe	258	495	This study
W	263	560	(20)

A striking feature to note is that the peak temperature for decomposition increases with increasing oxygen–metal bond strength, suggesting that the strength of the metal–oxygen bond determines the stability of these intermediates on the surface. Qualitatively, it would be expected that the peak temperatures be related to the difference between the surface single-bond energies for hydrogen and oxygen atoms, since the final state of the reaction system results in the formation of adsorbed hydrogen atoms. The bond energies for adsorbed hydrogen atoms increase systematically by about 63 kJ/mole from Ag to W (22). The very strong increase in the bonding to oxygen on these surfaces appears to dominate the kinetics and offset any increased bonding strength to hydrogen which might provide a higher driving force for reaction.

There was one unusual feature in the C(1s) XPS results for acetic acid adsorbed on Fe(100). Though the peak heights of the two carbon peaks in Fig. 10 were different, the integrated areas were the same, as the peak at 288.8 eV was broader than the peak at 285.8 eV. One possible explanation of the broadening of the carboxylate carbon peak is multiplicity of the final state due to spin–spin coupling with the valence electrons. If the actual bonding of the carboxylate were a hybrid of the three resonance structures shown below
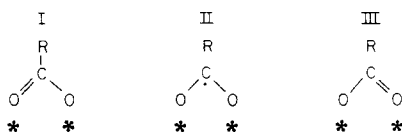
then the unpaired electron in structure II would cause a splitting of the energy of the C(1s) photoelectron, similar to what has been observed for O_2 and NO in the gas phase (23). Note that such splitting would not be of major importance for the other atoms in the molecule as they are more shielded from the unpaired electron. The C(1s) peak for formate also showed this same broadening, although it was not as apparent because there was not a second peak for comparison.

CONCLUSION

The reactions of hydrocarbons and carboxylic acids on Fe(100) were studied with TPRS and XPS. Olefinic hydrocarbons were observed to form stable surface intermediates which decomposed between 350 and 400 K. Ethylene and acetylene both reacted to give H_2 and surface carbon, whereas cis-2-butene formed methane and surface methyl intermediates as well. The XPS results suggested that olefins did not form symmetrically π-bonded intermediates solely. Methyl chloride was observed to dissociatively adsorb on Fe(100) to form methyl groups. The methyl groups decomposed at 475 K to give H_2 and surface carbon.

Carboxylic acids were found to form carboxylate surface intermediates. The carboxylates were stable surface intermediates decomposing around 500 K. Both formate and acetate were observed to decompose via two pathways, giving either CO_2 or CO and adsorbed oxygen as reaction products. The stability of formates on various metal surfaces was discussed and was shown to correlate with the bond energy of metal–oxygen bonds.

REFERENCES

1. Benziger, J. B., and Madix, R. J., J. Catal. 65, 36 (1980).

2. Benziger, J. B., Ph.D. thesis. Stanford University, Stanford, Calif., 1979.

3. Benziger, J. B., and Madix, R. J., *Surface Sci.* **94,** 119 (1980).

4. McCarty, J. G., Falconer, J. L., and Madix, R. J., *J. Catal.* **30,** 235 (1973).

5. Madix, R. J., Falconer, J. L., and Suszko, A. M., *Surface Sci.* **54,** 6 (1976).

6. Edwards, D., Jr., *Surface Sci.* **54,** 1 (1976).

7. Brucker, C., and Rhodin, T., *J. Catal.* **47,** 214 (1977).

8. Broden, G., Gafner, G., and Bonzel, H. P., *Appl. Phys.* **13,** 333 (1977).

9. Ibach, H., and Lehwald, S., *J. Vac. Sci. Technol.* **15,** 407 (1978).

10. Keister, J. B., and Shapley, J. R., *J. Organometal. Chemc.* **85,** 29 (1975).

11. Ugo, R., *Catal. Rev. Sci. Eng.* **11,** 225 (1975).

12. Blyholder, G., Shihabi, D., Wyatt, W. V., and Bartlett, R., *J. Catal.* **43,** 122 (1976).

13. Sachtler, W. M. H., and Fahrenfort, J., "Actes du duxieme congres internationale de catalyse, Paris 1960," p. 831. Edition Technip, Paris, 1961.

14. Falconer, J. L., and Madix, R. J., *Surface Sci.* **46,** 473 (1974).

15. Madix, R. J., Falconer, J. L., Suszko, A. M., *Surface Sci.* **54,** 6 (1976).

16. Benziger, J. B., and Madix, R. J., *Surface Sci.* **79,** 394 (1979).

17. Wachs, I. E., and Madix, R. J., *J. Catal.* **53,** 208 (1978).

18. Ying, D., Ph.D. thesis. Stanford University, Stanford, Calif., 1978.

19. Wachs, I. E., and Madix, R. J., *Surface Sci.* **76,** 531 (1978).

20. Benziger, J. B., Ko, E. I., and Madix, R. J., *J. Catal.,* **58,** 149 (1979).

21. Ko, E. I., Benziger, J. B., and Madix, R. J., *J. Catal.,* **62,** 264 (1980).

22. Madix, R. J., and Benziger J. B., *Annu. Rev. Phys. Chem.* **29,** 285 (1978).

23. Siegbahn, K., Nordling, C., Johansson, G., Hedman, J., Meden, P. F., Hamrin, K., Gelius, U., Bergmark, T., Werme, L. O., Manne, R., and Baer, Y., *in* "ESCA Applied to Free Molecules. North-Holland, Amsterdam, 1969.