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Reactions and Reaction Intermediates on Iron Surfaces

III. Reactions of Aldehydes and Ketones on Fe(100)

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The reactions of formaldehyde, acetaldehyde, and acetone on Fe(100) were studied by temperature-programmed reaction spectroscopy and X-ray photoelectron spectroscopy (XPS). Formaldehyde and acetaldehyde were observed to react with adsorbed hydrogen to form adsorbed alkoxy intermediates. These reactions occurred at low temperature (ca. 200 K). In the absence of adsorbed hydrogen, formaldehyde and acetaldehyde decomposed to adsorbed CO and hydrogen. This reaction was also observed at low temperatures. On an initially clean surface the aldehydes first decomposed, forming adsorbed hydrogen which subsequently reacted with adsorbed aldehyde to form an alkoxy intermediate. The alkoxy intermediates reacted to form CO and H_2 primarily, with lesser amounts of alcohol, aldehyde, and hydrocarbon products. Acetone reacted differently from the aldehydes and did not appear to form an alkoxy intermediate. XPS results suggested that acetone and acetaldehyde did not adsorb in their keto form on the surface and it is suggested that they adsorbed as enol intermediates. The distinct reaction behavior of acetone may be due to these enol intermediates.

INTRODUCTION

The reactions of organic molecules on iron and other transition metals are the basis for much of CO hydrogenation chemistry. We have undertaken a comprehensive study of the reactions and a variety of organic molecules on iron surfaces in an effort to contribute further understanding to Fischer–Tropsch reaction systems. In previous studies the reactions of alcohols, hydrocarbons, and carboxylic acids were examined (*1*, *2*). The results of these studies indicated the involvement of alkoxy, alkyl, and carboxylate surface intermediates.

Aldehydes and ketones have also been observed as reaction products from the Fischer–Tropsch synthesis over iron catalysts (*3*). Fischer speculated that aldehyde surface intermediates were involved in the formation of oxygenated products during Fischer–Tropsch synthesis (*4*). In our previous study aldehydes were observed as products from the reaction of alkoxy intermediates (*1*). In this work the reactions of formaldehyde, acetaldehyde, and acetone on Fe(100) were studied using temperature-programmed reaction spectroscopy (TPRS) and X-ray photoelectron spectroscopy (XPS) to complete a survey of the reactions of oxygenated Fischer–Tropsch products on Fe(100). These studies show that alcohols and aldehydes both form the same stable alkoxy intermediates, in contrast to the enol and aldehyde intermediates proposed by previous investigators (*3*, *4*).

EXPERIMENTAL

The experimental procedures have been reviewed previously (*1*, *5*). Briefly, the experiments were carried out in an ultrahigh vacuum system equipped with low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), and temperature-programmed reaction spectroscopy

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(TPRS). A clean Fe(100) surface, as verified by LEED, AES, and XPS, was prepared by argon sputtering and high-temperature annealing as described elsewhere (*5*).

Formaldehyde was prepared by heating paraformaldehyde to 360 K while pumping on the vapor until the mass spectrum showed no impurities (*6*). Acetaldehyde (ICN 99.9%) was kept in a constant-temperature bath at 190 K and was pumped on until the mass spectrum showed no impurities. The vapor pressure at 190 K was greater than 100 Pa as measured by a thermocouple gauge. The gas manifold was filled to 100 Pa and subsequently evacuated to 20 Pa for admission of acetaldehyde to the vacuum chamber. Acetone (Fischer 99.9%) was held at 230 K; at this temperature the vapor pressure of acetone was approximately 80 Pa. Acetone was prepared for use in the same way as acetaldehyde. The gases were admitted to the vacuum chamber through a 22-gauge needle which provided a directed flux onto the front surface of the crystal.

The reactions were followed by TPRS and XPS. The desorption of products from the surface was monitored with TPRS. Typically, the reactant gas was adsorbed at or below 200 K, and the crystal temperature was linearly ramped to 1000 K at a rate of 20 K/s. Products were detected in line-of-sight by a quadrupole mass spectrometer and verified against fragmentation patterns. XPS was used to follow changes in the nature of adsorbed intermediates. After adsorption of the reactant gas at 200 K the sample was heated to a desired temperature and subsequently quenched rapidly to 200 K; a series of O(1*s*) and C(1*s*) spectra was obtained as a function of this temperature. Coverages of adsorbed carbon and oxygen were determined from the XPS results as described previously (*5*); relative coverage determinations were accurate to ±0.02 monolayer (2.4×10^{13} atoms/cm^2). The XPS results provided an accurate analysis of the state of the surface at several states of the reaction.

RESULTS

Formaldehyde

The reaction product spectrum subsequent to formaldehyde adsorption on Fe(100) at 200 K is shown in Fig. 1. The major desorption products were CO and H_2, with lesser amounts of CH_3OH, H_2CO, and CH_4. All the reaction products could be clearly distinguished by their mass fragmentation pattern as discussed previously (*1*). The reaction product spectra for formaldehyde on Fe(100) showed similarities to those observed for methanol. The simultaneous desorption of CO, CH_3OH, H_2CO, CH_4, and H_2 at 450 K from the reactions of both methanol and formaldehyde indicated common surface intermediates existed for both reactants. Additionally, the evolution of CO at 800 K from the associative desorption of CO was observed from both formaldehyde and methanol.

The reactions of formaldehyde did show contrasting behavior from methanol as well. Formaldehyde decomposition led to two low-temperature CO product peaks; one at 450 K, which methanol also showed, and the second one at 330 K. Desorption of CO from CO adsorption was also observed at these temperatures (*5*), suggesting that some formaldehyde decomposed at or below room temperature and CO subsequently desorbed by a desorption-limited step. Low-temperature reactions of formaldehyde were also indicated by the coincident evolution of CH_3OH and H_2CO at 270 K. Another difference between the reactions of methanol and formaldehyde was the CO/H_2 product ratio at 450 K. Methoxy intermediates formed from methanol yielded a CO/H_2 ratio of 2/3, whereas the CO/H_2 ratio at 450 K with formaldehyde as the reactant was 4/3.

The similarity of reaction products formed at 450 K on Fe(100) from methanol and formaldehyde indicated that both reactants formed a common surface intermediate. This intermediate was previously identified as an adsorbed methoxy (*1*). The

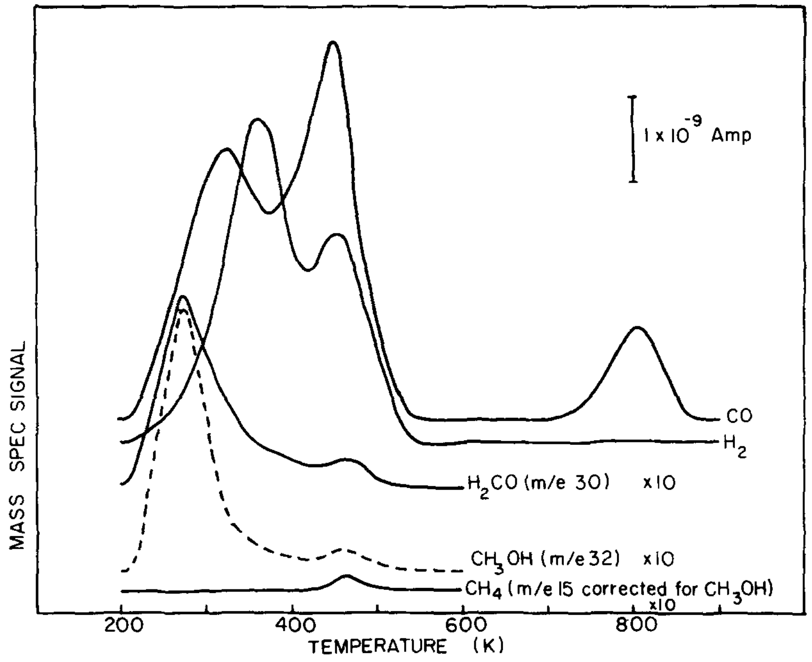
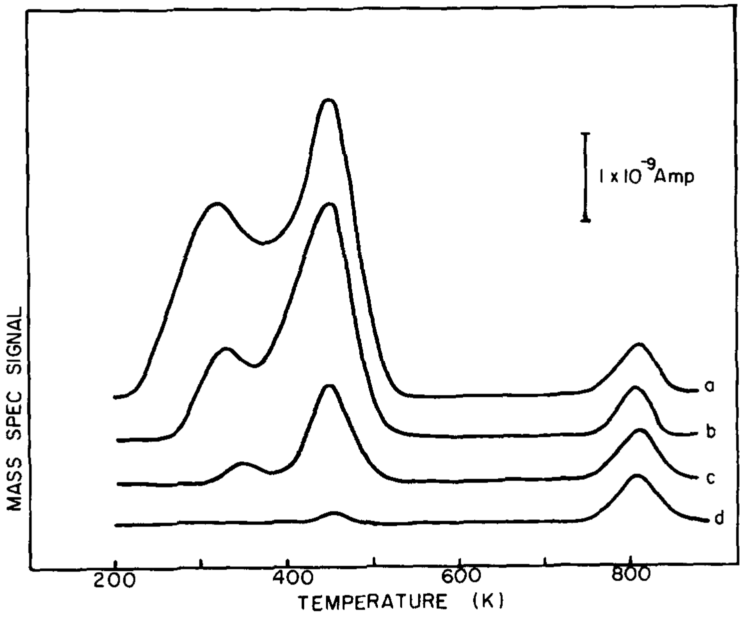


FIG. 1. Formaldehyde decomposition on Fe(100): Reaction product Spectrum (from Fe(100) subsequent to a 10-L exposure of formaldehyde at 185 K).

formation of adsorbed methoxy from formaldehyde was found to be dependent on formaldehyde coverage. The evolution of reaction products was followed as a function of formaldehyde exposure onto the Fe(100) surface. Desorption of CO at 450 K was observed for all initial coverages of H_2CO (Fig. 2A), whereas desorption of H_2, CH_3OH, and CH_4 at 450 K (Fig. 1) was only observed for high coverages of H_2CO (Fig. 2B). These results indicated that for low initial coverages of H_2CO only decomposition occurred leading to desorption-limited CO evolution at 330, 440, and 800 K, and H_2 desorption between 350 and 400 K. Increasing the H_2CO coverage led to the formation of methoxy intermediates and the emergence of the H_2, CH_3OH, and CH_4 products at 450 K. Both the reaction products and reaction temperature indicate the existence of the methoxy intermediates.

Coadsorption of D_2 and H_2CO suggested that the methoxy intermediates were formed from the reaction of adsorbed formaldehyde and adsorbed deuterium. After sequential adsorption of D_2 and H_2CO at 200 K the reaction product spectra showed deuterated products D_2, HD, and CH_3D evolved at 450 K. As H_2/H_2 desorption occurred below 400 K, the deuterated products at 450 K indicated that adsorbed deuterium was incorporated into formaldehyde to form methoxy. This reaction appeared to have a low activation barrier because CH_2DOD (*m/e* 34) was also detected at 270 K in the coadsorption experiment.

Several adsorbed species apparently existed on the surface simultaneously (e.g., H_2CO, CO, CH_3O) subsequent to H_2CO adsorption. These intermediates could be partially distinguished by XPS. The sequence of C(1*s*) spectra shown in Fig. 3 suggests the presence of four intermediates. For H_2CO adsorbed at 200 K there were at least three species evident in the C(1*s*) spectrum, characterized by peaks at 282.1, 284.7, and 287.0 eV. The peak at 282.1 eV was characteristic of adsorbed carbon (*5, 7*). There was significantly more adsorbed carbon on the surface after H_2CO



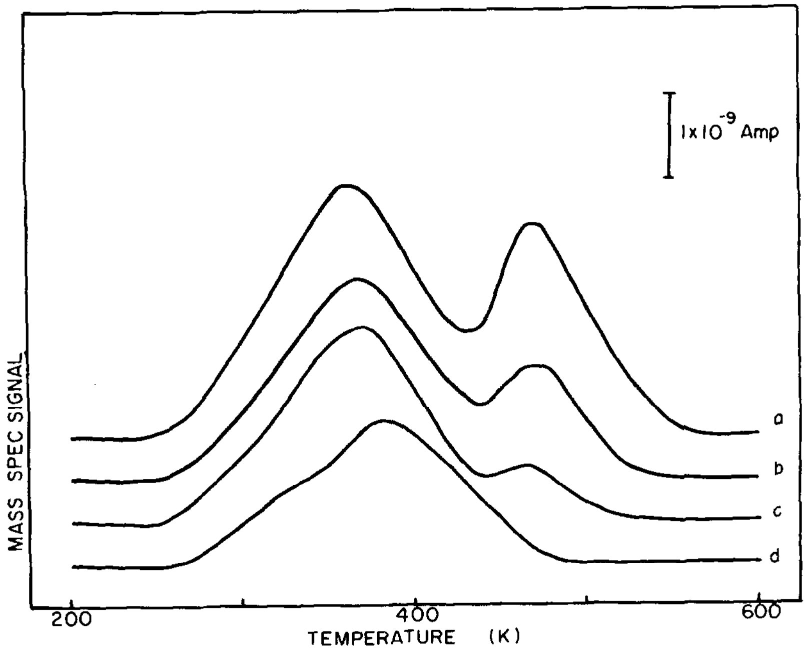


FIG. 2. (A) CO/H_2CO (200 K) coverage variation on Fe(100). (B) H_2/H_2CO (200 K) coverage variation on Fe(100). Initial coverages of formaldehyde: (a) θ_{H_2CO} = 0.28 monolayers; (b) θ_{H_2CO} = 0.23 monolayers; (c) θ_{H_2CO} = 0.17 monolayers; (d) θ_{H_2CO} = 0.13 monolayers.

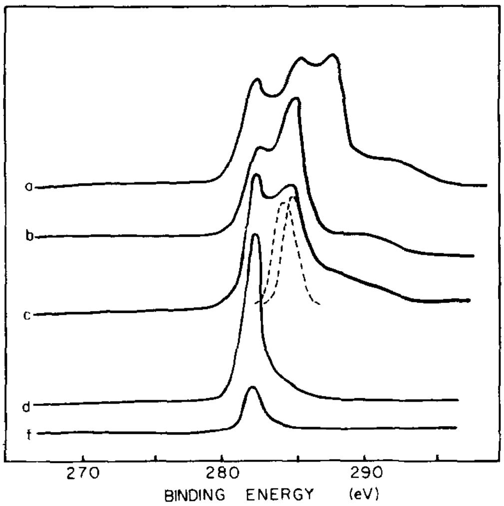


FIG. 3. C(1*s*) X-ray photoelectron spectra of surface intermediates from formaldehyde reacting on Fe(100). (a) H_2CO adsorbed at 200 K; (b) heated to 280 K; (c) heated to 360 K; (d) heated to 500 K; (e) heated to 900 K—no visible signal; (f) before adsorption.

adsorption, indicating H_2CO decomposition to adsorbed atomic species occurred at 200 K. The peak at 287.0 eV disappeared after heating to 270 K (cf. spectra a and b). The TPRS spectra showed desorption of H_2CO at 270 K, which suggested that the C(1*s*) peak at 287.0 eV was due to adsorbed H_2CO. Heating the crystal to 360 K resulted in desorption of CO, and a decrease in the C(1*s*) peak at 284.7 eV. The peak at 284.7 eV appeared to be too broad for a single species, and was attributed to two peaks, one due to methoxy at 285.4 eV (*1*) and one due to molecularly adsorbed CO at 284.3 eV (*5*). These two components are sketched in Fig. 3. After desorption of CO and reaction of the methoxy at 450 K there was a large increase in the C(1*s*) peak at 282.1 eV due to the buildup of dissociated CO. Heating to 900 K caused associative desorption as indicated by the disappearance of the C(1*s*) signal. It was also observed that after heating to 900 K the small carbon impurity on the surface before H_2CO adsorption was removed, and oxygen buildup was noted (see Table 1), consistent with the formation of CH_4 from methoxy, which led to adsorbed oxygen as a reaction product (*1*).

The O(1*s*) XPS results were of limited use. Low-temperature adsorption resulted in two peaks in the O(1*s*) spectrum. One peak occurred at approximately 532.0 eV and disappeared upon heating to 270 K, suggesting that it was due to adsorbed H_2CO. There was a second peak at 531.0 eV, apparently the result of both adsorbed CO and adsorbed methoxy. It should be noted that both methoxy and molecular CO on Fe(100) have O(1*s*) binding energies of 531.0 eV, making it impossible to distinguish them by their O(1*s*) spectrum. Heating to 500 K left dissociated CO as the only surface species, consistent with the O(1*s*) peak at 530.2 eV. Lastly, the buildup of oxygen was verified by the O(1*s*) spectrum taken after heating to 900 K. The XPS data for formaldehyde adsorption on Fe(100) are summarized in Table 1.

Acetaldehyde

The reactions of acetaldehyde were analogous to those observed for formaldehyde. Just as formaldehyde was hydrogenated to form methoxy, acetaldehyde appeared to

TABLE 1

Formaldehyde Adsorption on Fe(100)

	Binding energies (eV)		Coverages (monolayers)	
	O(1*s*)	C(1*s*)	θ_C	θ_O
(a) H_2CO adsorbed at 200 K	532.0 531.0	287.0 284.7 282.1	0.30	0.27
(b) Heated to 280 K	531.0	284.7 282.1	0.26	0.25
(c) Heated to 360 K	531.0	284.7 282.1	0.20	0.21
(d) Heated to 500 K	530.0	282.1	0.10	0.12
(e) Heated to 900 K	530.0	—	—	0.04
(f) Before adsorption	530.0	282.1	0.02	0.01

be hydrogenated to form ethoxy. The product desorption spectra for the reactions of acetaldehyde on Fe(100) (Fig. 4) indicated CO, H_2, CH_3CH_2OH, CH_3CHO, CH_4, and C_2H_4 desorbed simultaneously at 420 K, similar to the spectrum observed for the reactions of ethanol (*1*). There was a H_2 desorption peak at 480 K, resulting from adsorbed methyl groups, that was also observed in the reaction of ethanol. This similarity of products indicated a common intermediate, which was shown to be ethoxy (*1*). The formation of ethoxy probably resulted from the decomposition of a fraction of the CH_3CHO to adsorbed CO and hydrogen and the subsequent reaction of adsorbed hydrogen with acetaldehyde. The evidence for the decomposition of acetaldehyde was the desorption-limited CO and H_2 peaks between 300 and 350 K. Furthermore, the evolution of ethanol at 270 K indicated the occurrence of reactions even at rather low temperatures.

The C(1*s*) X-ray photoelectron spectra for adsorbed acetaldehyde, shown in Fig. 5, indicated that some CH_3CHO decomposition occurred at 185 K, since the C(1*s*) peak at 282.2 eV, which is attributable to surface carbon, showed a slight increase in magnitude after CH_3CHO adsorption at 185 K. Two other peaks in the C(1*s*) spectra appeared to be due to molecular intermediates. These two peaks were of unequal magnitude, suggesting that they were due to more than a single adsorbed species. For a single adsorbed species two peaks of equal magnitude would be expected as was observed for ethoxy (*1*) and acetate (*2*). TPRS results were helpful in identifying the intermediates. The XPS results showed that heating to 360 K caused the C(1*s*) peaks at 284.2 and 285.6 eV to decrease in magnitude, while the peak for surface carbon at 282.2 eV increased in magnitude (cf. spectrum band c). This conversion was accompanied by the desorption of CH_4, CO, and H_2. The C(1*s*) peaks may be identified with molecular CO and a surface intermediate that produces methane. Molecular CO has a C(1*s*) binding energy at 284.3 eV (*5*), partially accounting for the C(1*s*) peak at 284.2 eV. The methane-producing intermediate may be associated with C(1*s*) peaks at both 284.2 and 285.6 eV. Above 360 K the TPRS results indicated that ethoxy intermediates remained on the surface in addition to molecular CO and adsorbed carbon and oxygen. The H_2 desorption spectra showed a peak at 480 K which indicated the presence of methyl intermediates (*2*). The combination of the C(1*s*) peaks for ethoxy (284.4 and 285.4 eV), CO (284.3 eV), and methyl intermediates (283.4 eV) could account for the peaks observed at 284.0 and

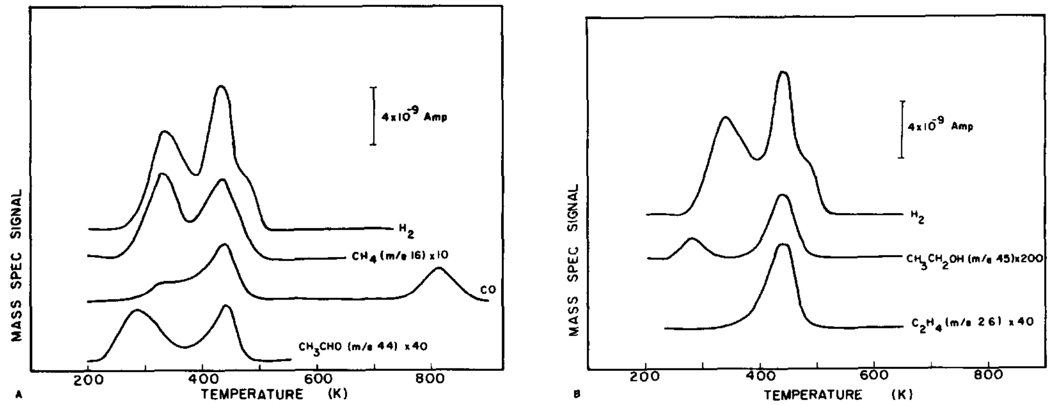


FIG. 4. Acetaldehyde decomposition on Fe(100): Reaction product spectrum of acetaldehyde on Fe(100) subsequent to a 10-L exposure at 190 K (A and B).

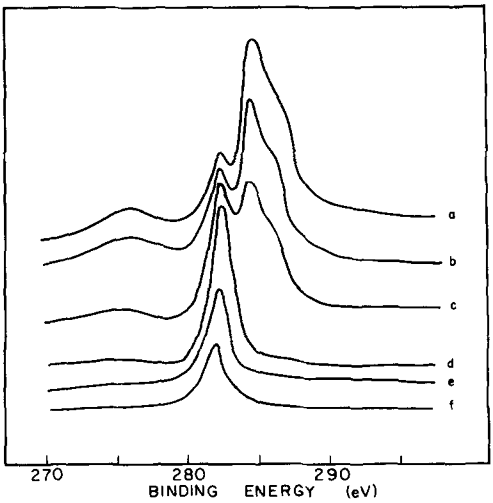


FIG. 5. C(1*s*) X-ray photoelectron spectra of surface intermediates from acetaldehyde reacting on Fe(100). (a) CH_3CHO adsorbed at 185 K; (b) heated to 270 K; (c) heated to 360 K; (d) heated to 500 K; (e) heated to 900 K; (f) before adsorption.

285.6 eV shown in spectrum c. These intermediates would be expected to yield the observed TPRS results. All of these intermediates reacted and/or desorbed between 400 and 500 K leaving only adsorbed carbon and oxygen. Heating to 900 K caused recombination and desorption of dissociated CO which resulted in the decrease of the C(1*s*) peak at 282.2 eV. It should be noted that acetaldehyde caused carbon deposition on the surface, as seen in the increase of the C(1*s*) peak at 282.2 eV after the complete adsorption/reaction cycle (see Table 2).

The XPS results for low-temperature adsorption of acetaldehyde differed significantly from formaldehyde. Molecularly adsorbed H_2CO showed a C(1*s*) binding energy of 287.0 eV due to the acyl (C=O) group. It was expected that molecularly adsorbed CH_3CHO would have a similar C(1*s*) binding energy, as the two aldehydes have nearly the same C(1*s*) binding energies in the gas phase (*8*). However, adsorption of CH_3CHO at temperatures down to 150 K gave no C(1*s*) peak at an energy greater than 285.5 eV (see Fig. 6). Furthermore, the O(1*s*) spectra for H_2CO adsorption showed a peak at 532.0 eV, which was not observed for acetaldehyde adsorption. From these results it is apparent that these two aldehydes bind differently to the surface.

The TPRS results also showed some distinctive features for the reactions of acetaldehyde. Methane evolution was observed at two temperatures from the reactions of acetaldehyde. The CH_4 product at 420 K was readily explained as resulting from the reaction of ethoxy. However, CH_4 was also observed at 330 K, well above the temperature for desorption-limited CH_4, suggesting that it was formed by the reaction of another surface intermediate. The possible identity of this intermediate will be discussed in greater detail below. Another feature of note was the desorption of H_2 at 480 K in the absence of any other reaction products. This result is the consequence of the decomposition of methyl intermediates as observed for CH_3Cl decomposition of Fe(100) (*2*) and for the reactions of ethanol and isopropanol on Fe(100) (*1*). The results

TABLE 2

Acetaldehyde Adsorbed on Fe(100)

	Binding energies (eV)		Coverages (monolayers)	
	C(1*s*)	O(1*s*)	θ_C	θ_O
(a) CH_3CHO adsorbed at 185 K	282.2 284.2 285.6	531.0	0.55	0.23
(b) Heated to 270 K	282.2 284.2 285.6	531.0	0.48	0.20
(c) Heated to 360 K	282.2 284.0 285.6	531.0	0.40	0.19
(d) Heated to 500 K	282.2	530.0	0.28	0.10
(e) Heated to 900 K	282.2	—	0.15	—
(f) Before adsorption	282.2	—	0.10	—

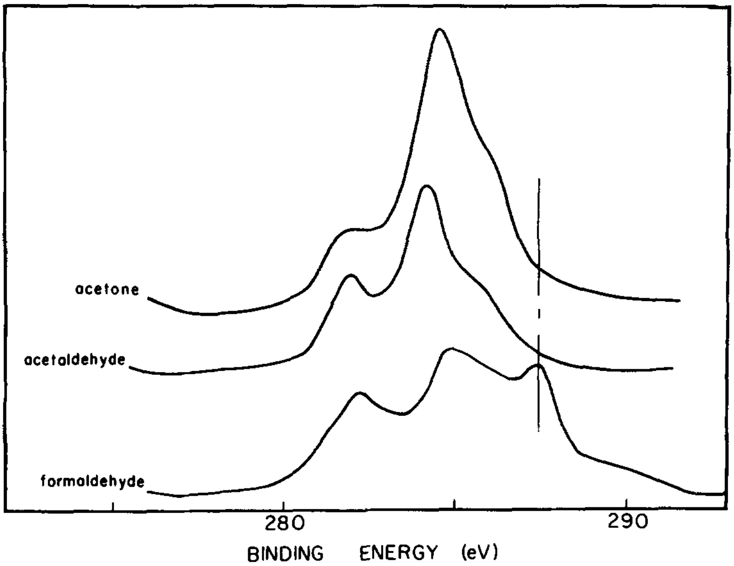


FIG. 6. C(1*s*) X-ray photoelectron spectra of aldehydes and ketones adsorbed on Fe(100) at 180 K.

indicate that methyl groups are formed by breaking C–C bonds.

Acetone

The reactions of acetone were similar to those previously observed for isopropanol (*1*), but they both behaved much differently from the methanol–formaldehyde and ethanol–acetaldehyde pairs. Subsequent to acetone adsorption the only products observed to desorb were $(CH_3)_2CO$, CO, and H_2 as shown in Fig. 7. All three CO peaks corresponded to desorption-limited CO. Acetone desorbed at 225 and 400 K, and H_2 desorbed at 390 and 480 K; the reactions of isopropanol also led to acetone desorption at 400 K and H_2 desorption at 390 and 480 K. The H_2 peak at 480 K can be ascribed to the decomposition of methyl intermediates, as noted above. The simultaneous evolution of H_2 and $(CH_3)_2CO$ at 400 K suggests they are products from the reaction of a surface intermediate. Desorption of acetone at 225 K appeared to be desorption limited.

The changes in the XPS data with temperature reflect the reactions already identified. Heating to 300 K caused the C(1*s*) peak shape to change slightly due to decomposition of some acetone to form CO, hydrogen, and adsorbed methyl groups (see Fig. 8). There were two peaks in the C(1*s*) spectrum after heating to 400 K, one at 282.2 eV due to surface carbon, and another at 283.6 eV characteristic of adsorbed methyl intermediates (*2*). The methyl intermediates decomposed after heating to 550 K causing an increase in the surface carbon. Finally heating to 900 K caused dissociatively adsorbed CO to desorb. A buildup of carbon was obvious from an increase of the C(1*s*) peak at 282.3 eV after the adsorption/reaction cycle. Further support for the existence of methyl intermediates came from the O(1*s*) XPS results, summarized in Table 3. The O(1*s*) spectrum taken after heating to 400 K showed only a peak at 530.1 eV, characteristic of adsorbed atomic oxygen (*5*, *7*). Heating to 550 K caused no change in the O(1*s*) spectrum, while the C(1*s*) spectrum changed. This suggested that the intermediate reacting at 480 K did not contain oxygen and was probably a hydrocarbon intermediate.

The XPS results for acetone adsorbed on Fe(100) also showed features nearly identi-

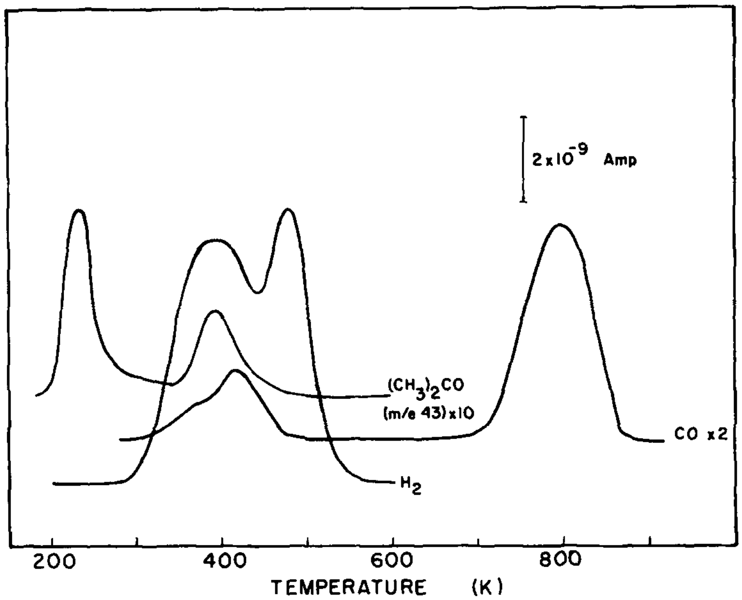


FIG. 7. Acetone decomposition on Fe(100): Reaction product spectrum of acetone on Fe(100) subsequent to a 15-L exposure at 175 K.

cal to acetaldehyde. There was no C(1*s*) peak at 287.0 eV from acetone adsorption, as was observed for formaldehyde adsorption (see Fig. 6). For acetone adsorbed at 180 K the C(1*s*) spectrum showed two peaks at 284.4 and 285.6 eV with relative magnitudes of 2: 1. The energy difference between these peaks was much less than the 3-eV difference between the methyl and acyl carbons for acetone in the gas phase (*8*). A comparison of the spectra for acetone and isopropanol adsorbed on Fe(100) showed them to be quite similar, indicating that they may have formed similar intermediates.

DISCUSSION

The major result of the studies reported here is the finding that aldehydes react to form stable alkoxy surface intermediates. In our previous studies of the reactions of alcohols on Fe(100) stable alkoxy intermediates were identified, which reacted to yield alcohol, aldehyde, and hydrocarbon products, as well as decomposing to CO and H_2 (*1*). These results complement earlier studies of Kummer and Emmett who reported that alcohol-related intermediates were significant in Fischer–Tropsch synthesis (*9*). On the combined basis of our studies and Kummer and Emmett's work it

TABLE 3

Acetone Adsorbed on Fe(100)

	Binding energies (eV)		Coverages (monolayers)	
	C(1*s*)	O(1*s*)	θ_C	θ_O
(a) $(CH_3)_3CO$ adsorbed at 180 K	282.2 284.4 285.6	531.2	0.57	0.18
(b) Heated to 300 K	282.2 284.4 285.6	531.2	0.50	0.16
(c) Heated to 400 K	282.2 283.7	530.1	0.41	0.10
(d) Heated to 500 K	282.2	530.1	0.38	0.09
(e) Heated to 900 K	282.2	—	0.07	—
(f) Before adsorption	—	—	—	—

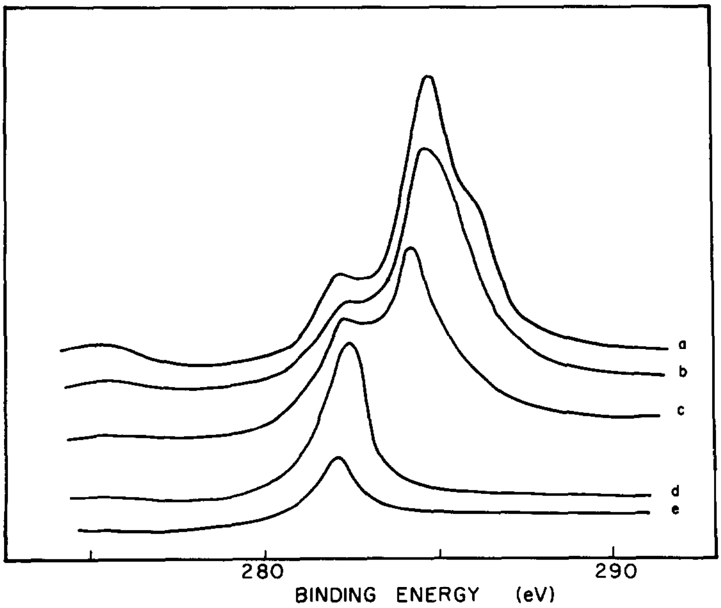


FIG. 8. C(1*s*) X-ray photoelectron spectra of surface intermediates for acetone reacting on Fe(100). (a) $(CH_3)_2CO$ adsorbed at 180 K; (b) heated to 300 K; (c) heated to 400 K; (d) heated to 500 K; (e) heated to 900 K.

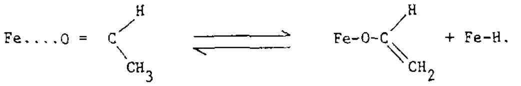
can be proposed that alkoxy intermediates are not insignificant in Fischer–Tropsch synthesis. The observation that aldehydes were readily hydrogenated on iron to alkoxys gives further support to the importance of alkoxy intermediates in Fischer–Tropsch synthesis. The results for the reactions of aldehydes and alcohols suggest that both products may be derived from alkoxy intermediates. Alkoxy intermediates also give rise to hydrocarbon products as previously discussed (*1*).

The results show that a portion of the adsorbed aldehydes were hydrogenated on Fe(100) to form alkoxy intermediates. This same result was obtained by Blyholder and Neff for aldehyde adsorption on iron powders (*10*). Blyholder and Neff employed infrared absorption spectroscopy with suspensions of iron powder in diffusion pump oil and found that alcohols and aldehydes formed intermediates with ir absorption bands corresponding to surface alkoxys. In contrast to the present work they did not observe aldehyde decomposition to adsorbed CO. This difference may be the result of the experimental conditions. In the present work, in order for the aldehyde to be hydrogenated some aldehyde had to decompose to adsorbed CO and hydrogen. In Blyholder and Neff's experiment there may have been hydrogen dissolved in the oil so that sufficient hydrogen could be adsorbed on the iron to hydrogenate the aldehyde.

The XPS results obtained for acetaldehyde and acetone raise interesting questions about the nature of the adsorbed intermediates. If acetaldehyde were adsorbed via the lone pair electrons on oxygen, as believed for H_2CO (*6, 11*), the C(1*s*) XPS results would be expected to show two widely separated peaks corresponding to the methyl and acyl carbons as observed for gas-phase species (*8*). Instead both acetaldehyde and acetone showed C(1*s*) spectra more similar to alcohols or alkoxys, where the methyl carbon and the alcoholic carbon have a C(1*s*) binding energy difference of 1.0–1.5 eV.

There are several possible explanations

for these results. One is the existence of structural isomers of aldehydes and ketones which produce an effective lowering of the C–O bond order. In the gas phase aldehydes and ketones exist in equilibrium with the appropriate enol (*12*, *13*); thermodynamics greatly favor the aldehyde form in the gas phase. For adsorption on the iron surface the comparable equilibrium is

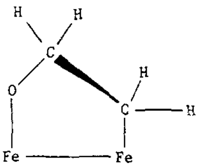


$$\text{Fe}\cdots\text{O}=\text{C}(\text{H})\text{CH}_3 \rightleftharpoons \text{Fe–O–C}(\text{H})=\text{CH}_2 + \text{Fe–H}.$$

An estimate of the thermodynamic driving force for this reaction may be obtained from bond energies. Listed below are approximate bond energies for the bonds being formed or broken in the above reaction.

Bond	Bond energy (kJ/mole)
Fe···O=	45
Fe – O–	258
$>$C = O	729
–C – O	383
–C – C–	368
$>$C = C$<$	653
–C – H	410
–O – H	430
Fe – H	260

All these energies were estimated from heats of formation and bond dissociation energies in the fashion suggested by Pauling (*14*), except for the Fe . . . O= bond which was estimated from the activation energy for desorption of H_2CO. The enthalpy of the above reaction is −2 kJ/mole, indicating the above reaction is nearly thermodynamically neutral. The enthalpy for the equilibrium between acetaldehyde and vinyl alcohol in the gas phase is +40 kJ/mole. This estimate indicates that the enol form of the aldehyde may be a stable surface intermediate. The C(1*s*) XPS of the enol should be quite similar to an alcohol which is consistent with the experimental results. Additionally it should be noted that formaldehyde has no enol form, and must exist as an aldehyde. Another possible conformation for this intermediate is a cyclic-type intermediate.



An estimate of the enthalpy of reaction between aldehyde and this intermediate shows it to be more stable than the aldehyde but less stable than the enol form suggested above. The experimental evidence cannot distinguish these two possibilities. The reaction of either of these two intermediates could account for the CH_4 product from acetaldehyde at 330 K.

CONCLUSIONS

The reactions of formaldehyde, acetaldehyde, and acetone on Fe(100) were studied with temperature-programmed reaction spectroscopy and X-ray photoelectron spectroscopy. Formaldehyde and acetaldehyde reacted below room temperature by either decomposition to CO and hydrogen, or hydrogenation to alkoxy intermediates. The alkoxy intermediates were identified by their reaction product spectra, as established from the reactions of alcohols on Fe(100) (*1*). Decomposition of the aldehydes below room temperature was verified by XPS from an increase of the C(1*s*) yield after adsorption of the aldehyde at 200 K. Acetone was also observed to react similarly to its corresponding alcohol, isopropanol. However, the reactions of acetone and isopropanol differed from the other aldehydes and alcohols in that they did not appear to form a stable alkoxy intermediate.

The XPS results for acetaldehyde and acetone adsorbed on Fe(100) below 200 K indicated that adsorption decreased the C–O bond order, whereas no such effect was observed for formaldehyde. It was suggested that enol-type intermediates could account for these results. The enol intermediates could also account for the difference in reaction behavior of isopropanol and acetone. However, the proposed enol structures should be viewed with caution, as further experiments are required to establish their true identity.

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