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A Thermal Desorption Study of Methyl Formate from W(100) and Its Relevance to the Catalytic Production of Methane

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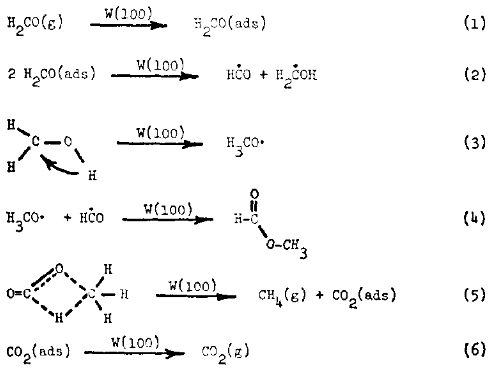
Previous work has suggested that methyl formate is a possible intermediate in the catalytic production of methane from formaldehyde on a tungsten (100) single crystal. To test this hypothesis, a study of methyl formate interaction with W(100) has been performed. The major products desorbed upon heating a saturated layer of methyl formate on W(100) were hydrogen and carbon monoxide. However, a significant yield of formaldehyde and small amounts of methane, carbon dioxide, and several organic products believed to be methyl formate, glycolaldehyde, and methyl alcohol were also observed. The thermal desorption products and their desorption kinetics from methyl formate adsorbed on W(100) were very similar to those from formaldehyde on W(100). A sequence of reactions which might account for this similar behavior is suggested.

I. INTRODUCTION

A catalytic reaction which is receiving wide attention today is the catalytic methanation reaction in which $CO + H_2$ are catalytically converted to CH_4 and H_2O (*1*, *2*). This reaction will be of major significance in the conversion of coal into synthetic natural gas. At the present time, the mechanism and intermediates involved in this reaction are not known. In an attempt to learn more about the chemistry of CH_4 production by heterogeneous catalytic processes, several recent studies have been conducted of the decomposition of organic adsorbates known to produce CH_4 as a product. For example, an early thermal desorption study of formaldehyde adsorbed on a W(100) single-crystal surface conclusively demonstrated that methane and carbon dioxide are produced in low yield when the crystal is covered with more than about one-half monolayer of H_2CO (*3*). A more recent X-ray photoelectron spectroscopy/thermal desorption study of H_2CO adsorbed on W(100) confirmed these findings and led to the proposal of the following sequence of reactions as being responsible for the catalytic decomposition of H_2CO to yield CH_4 and CO_2 (*4*).



The gas-phase reaction of two molecules of

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H_2CO to produce one molecule of CH_4 and one molecule of CO_2 is thermodynamically favorable (*5*), the change of enthalpy at 298°K being -56.54 kcal/mol, and the Gibbs free-energy change being -53.87 kcal/mol. Although some of the steps in the proposed mechanism are not thermodynamically favorable in the gas phase [e.g., ΔH for step (2) is ca. $+44$ kcal/mol], such processes should be more probable on a catalytic surface due to stabilization of the species involved. Step (2) has been postulated because a bimolecular process would seem reasonable in explaining the observed CH_4 and CO_2 *only* when the surface coverage reaches approximately one-half monolayer (*3*, *4*). Furthermore, a recent theoretical study has indicated that adsorbed HCO is a possible intermediate in catalytic methanation over Ni (*6*), and, in an early thermal and electron-impact desorption investigation, Baldwin and Hudson (*7*) suggested that HCO is an intermediate in the decomposition of H_2CO on Pt(111). Of course, $H\dot{C}O$ and $\cdot CH_2OH$ have been observed in the gas phase and in condensed phases by various spectroscopic techniques (*8*). Step (3) of the proposed mechanism involves a hydrogen atom shift to form $CH_3O\cdot$. The latter radical has not been observed spectroscopically, but has been postulated to be an intermediate in the photolytic decomposition of methyl alcohol (*9*). Step (4) represents the combination of $H\dot{C}O$ and $CH_3O\cdot$ to form methyl formate. Step (5) represents the decomposition of methyl formate through a four-center intermediate similar to those often invoked in explaining the mechanisms of a variety of organic reactions (*10*). Alternatively, step (5) could be achieved in two steps: via the formation of $HCOO + CH_3$, followed by decomposition of HCOO to CO_2 and $CH_3 + H$ reacting to produce CH_4. Step (6) was necessary because our flash desorption (*3*) and XPS studies (*4*) indicated that CO_2 was still present on the surface of the W(100) single crystal after all the CH_4 was evolved. It is clear from this proposed mechanism that a thermal-desorption study of methyl formate on W(100) would be desirable for testing the proposed mechanism. Such a study has been performed and will be described in this paper.

II. EXPERIMENTAL METHODS

These studies were performed in an ultrahigh vacuum chamber on a W(100) single-crystal disk (0.60 cm in diameter by 0.036 cm thick) having a W(100) geometrical surface area equal to 89% of the entire crystal area. Both sides of the crystal disk were ground and polished to within 0.4° of the (100) direction. The crystal was welded to a 0.025-cm-diameter 97% W/3% Re support wire which served as one thermocouple lead. The second thermocouple lead (0.013 cm in diameter) of 74% W/26% Re was welded to the crystal edge. The emf of the thermocouple was tested at 373°K, and the measured temperature was found to be within 1°K of the true value. The crystal could be heated to 2600°K by electron bombardment from a pancake-W spiral emitter mounted 0.2 cm behind the crystal. Radiation from the emitter was used alone to heat the crystal to ~1000°K in thermal desorption experiments.

Methyl formate was purified from reagent-grade methyl formate by distillation. The middle fraction boiling at 304°K was collected, and this portion was then subjected to vacuum distillation at 195°K in a greaseless vacuum system. Breakseal ampoules of the final product were sealed to a metal–glass gas-dosing system connected to the ultrahigh vacuum (uhv) apparatus. Gas chromatographic analysis (stationary phase: polyphenyl ether–6 rings) of the methyl formate indicated that its purity was greater than 99%, with methanol being the major impurity.

A molecular beam doser within the uhv apparatus was used to deposit methyl

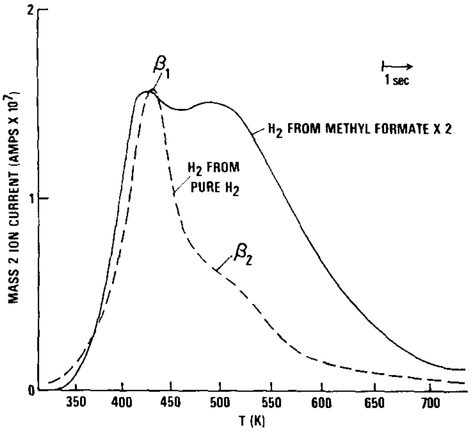

Fig. 1. Comparison of H_2 desorption from hydrogen monolayer and from saturated methyl formate layer on W(100). Since methyl formate is deposited only on the front surface of the crystal, the H_2 desorption from methyl formate has been multiplied by 2 for comparison with H_2 desorption from both faces of the crystal.

formate on the front surface of the W(100) crystal. This technique effectively prevented a major gas load from being introduced into the uhv chamber, leading to unacceptable levels of residual gases. The doser is a cylindrical "short tube," for which $L/R = 1$, where L = length, and R = radius = 0.625 mm, mounted 12 mm from the W(100) crystal. We calculate (*11*) that 8.5% of the effluent methyl formate molecules are incident on the W(100) crystal and that the uniformity of deposition is constant to within 20% over the crystal surface. Since the sticking coefficient falls during adsorption, there will be a tendency for a more uniform surface coverage to be produced as coverage rises. The flow of methyl formate to the effusion source was controlled by adjusting the pressure of methyl formate behind a glass capillary within the gas-dosing vacuum system. At our beam flux, it was found that a 180-s dose of methyl formate was sufficient to saturate the crystal, and all the desorption spectra shown here were obtained at this level of initial coverage.

A stainless steel uhv apparatus was used in this work. The base pressure was 2×10^{-10} Torr, with residual-gas relative peak heights of 64% H_2, 8% CH_4, 8% H_2O, 10% CO, 4% CO_2, 6% Ne. A quadrupole mass spectrometer was used in all thermal desorption measurements, operating at an electron energy of 70 eV.

The W(100) crystal was cleaned by repeated heating to ~2400°K in O_2 at 2×10^{-8} Torr to remove residual carbon. Following O_2 treatment, the crystal was flashed to 2600°K in an ultrahigh vacuum. The thermal desorption spectrum of pure hydrogen from W(100) was an indicator of surface contamination; it was found that the H_2 desorption spectrum was in good agreement (see Fig. 1) with that obtained in other work on clean W(100) (*13–15*).

In all adsorption experiments, the crystal was flashed in vacuum two times to 2600°K, and then was cooled to ~340°K. Methyl formate was admitted using the beam doser to any desired coverage level. The beam was then shut off, the throttle valve to the

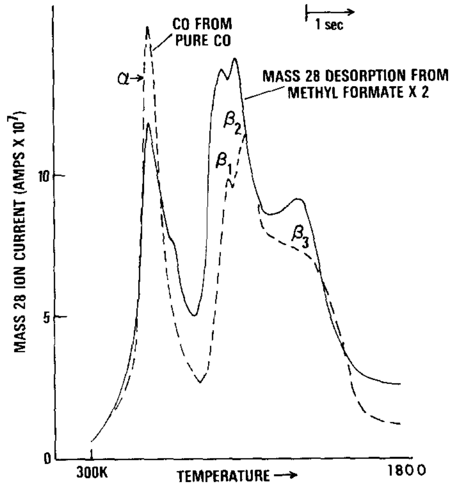

Fig. 2. Comparison of mass 28 desorption from a saturated CO monolayer and from a saturated methyl formate layer. Since methyl formate is deposited only on the front surface of the crystal, the CO desorption from methyl formate has been multiplied by 2 for comparison with CO desorption from both faces of the crystal.

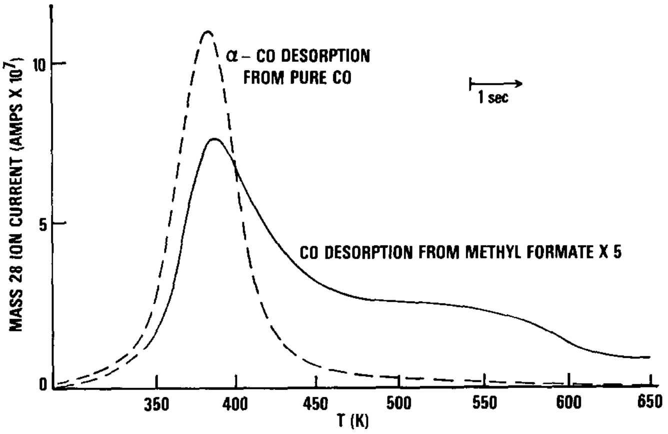

FIG. 3. Comparison of α-CO desorption from CO monolayer and from saturated methyl formate layer on W(100).

ion pump was partially closed to enhance the thermal desorption signal, and the crystal was heated by radiation from the W-pancake spiral emitter. In some cases, even though the emitter was shielded from the molecular beam by the crystal, slight desorption from the emitter occurred prior to reaching a crystal temperature of 350°K; in these cases, the lower part of the leading edge of the thermal desorption is uncertain, as shown by dashed lines in the figures.

III. RESULTS

Figure 1 compares the thermal desorption spectra of H_2 ($m/e = 2$) desorbed from a saturated methyl formate layer (solid curve) and from a pure H_2 monolayer (dashed curve) on W(100). As will be shown later, this characteristic two-peak H_2 evolution from methyl formate on W(100) is quite similar to that observed for H_2 evolution from formaldehyde on W(100) (*3*) and contrasts with the characteristic 2:1 ratio of β_1- and β_2-H_2 desorption states for pure H_2 on W(100) (*13*, *14*). The H_2 evolution curve is also distinctly different from that obtained by interaction of adsorbed CO with adsorbed hydrogen on W(100) (*15*) and was the first indicator that neither H_2CO nor $HCOOCH_3$ completely dissociates to CO and hydrogen upon adsorption at ~300°K. Figure 2 shows the thermal desorption spectra of CO ($m/e = 28$) from a saturated layer of methyl formate (solid curve) and from a

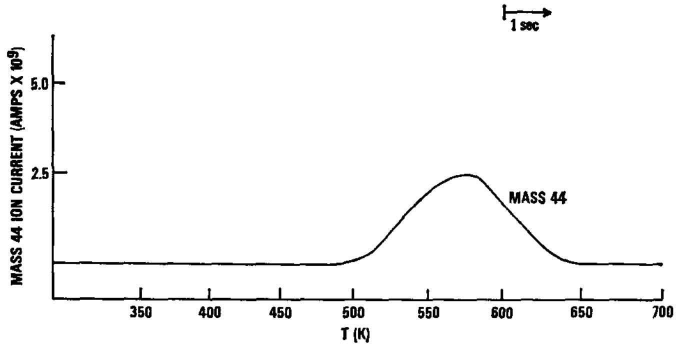

FIG. 4. CO_2 desorption from saturated methyl formate layer on W(100).

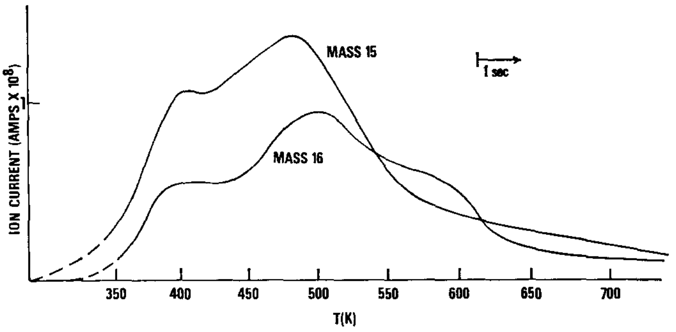

FIG. 5. Mass 15 and 16 desorption from saturated methyl formate layer on W(100).

monolayer of pure CO (dashed curve) on W(100). The two curves are again structurally similar, except for the presence of a pair of α-CO-like states for the CO evolved from the methyl formate, which are shown in more detail in Fig. 3.

The thermal desorption spectrum for CO_2 ($m/e = 44$) desorbed from a saturated layer of methyl formate on W(100) is shown in Fig. 4. The temperature of evolution of this CO_2 state is almost identical to that obtained for CO_2 evolved from formaldehyde on W(100) (*3*). Figure 5 shows the thermal desorption spectra for species having $m/e = 15$ and 16. These spectra correspond to the desorption of primarily CH_4, although the $m/e = 15$ spectrum does contain a component from an organic product, and the $m/e = 16$ spectrum contains a small component from CO (4% of the $m/e = 28$ fragment). Again, the two spectra resemble those obtained for CH_4 evolved from formaldehyde on W(100) (*3*), except for the extra peak in the $m/e = 16$ curve near 580°K.

Figure 6 represents the thermal desorp-

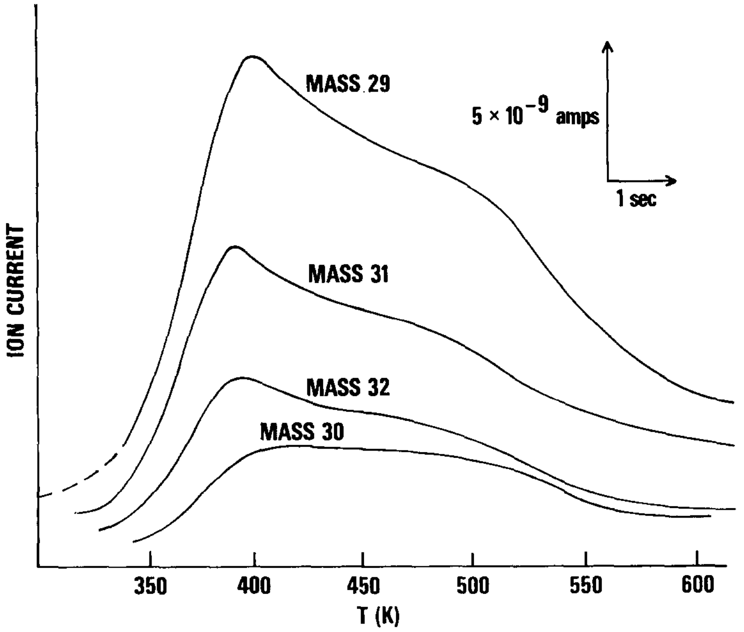

FIG. 6. Mass 29, 30, 31, and 32 desorption from saturated methyl formate layer on W(100).

TABLE 1

Mass Spectral Cracking Patterns Obtained in This Study[a]

Molecule (MW)	*m/e*							
	15	16	28	29	30	31	32	60[b]
Carbon monoxide (28)	0	4	100	1	0	0	0	0
Methyl formate (60)	13	1	13	63	8	100	37	<16
Glycolaldehyde (60)	25	2	11	69	6	100	35	<2
Methyl alcohol (32)	100	6	13	82	9	94	59	0
Formaldehyde (30)	2	5	35	100	62	1	0	0
Methane (16)	77	100	0	0	0	0	0	0

[a] Quadrupole mass spectrometer; electron energy = 70 eV.

[b] Amplitude uncertain due to change in mass range.

tion spectra from a saturated layer of methyl formate on W(100) for organic fragments having *m/e* values of 29, 30, 31, and 32. It is clear from the curve shapes that *m/e* = 31 and *m/e* = 32 refer to the same organic species; however, the *m/e* = 29 and *m/e* = 30 curves peak at slightly different temperatures and have slightly different shapes; therefore, these must contain contributions from other organic species. Table 1 lists the mass spectral cracking patterns obtained with our quadrupole mass spectrometer for several likely candidates for the organic species in this study and will be useful to the reader in the interpretation to follow.

IV. DISCUSSION

One of the more intriguing aspects of this work is the identification of the various organic species which give rise to the *m/e* = 29, 30, 31, and 32 thermal desorption spectra. Many organic fragment-cracking patterns were considered in this work; those which have not been eliminated from consideration are given in Table 1. It is evident from Table 1 that the only species considered which has a substantial *m/e* = 30 contribution is formaldehyde. Thus, in this work, it was assumed that the entire *m/e* = 30 spectrum represents desorption of formaldehyde from the saturated layer of methyl formate.

Therefore, a portion of the *m/e* = 29 desorption spectrum in Fig. 6 can also be attributed to formaldehyde. However, Table 1 indicates that methyl formate, glycolaldehyde, and methyl alcohol also have substantial *m/e* = 29 contributions. To measure the contribution of the *m/e* = 29 fragment which is not due to formaldehyde, we subtracted the *m/e* = 30 desorption curve [corrected by a factor 100/62 using the cracking pattern (Table 1) for formaldehyde] from the *m/e* = 29 curve. The result

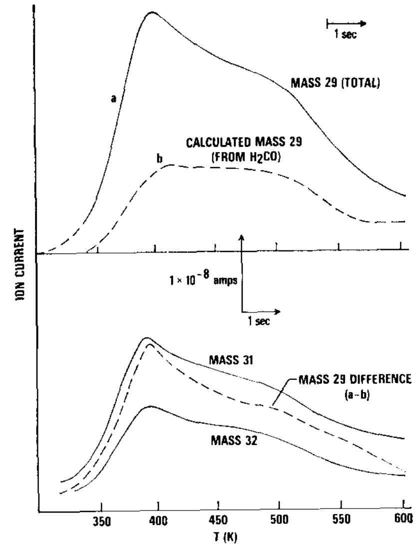

FIG. 7. Resolution of mass 29 desorption products from saturated methyl formate layer on W(100). See text for explanation of the method used here.

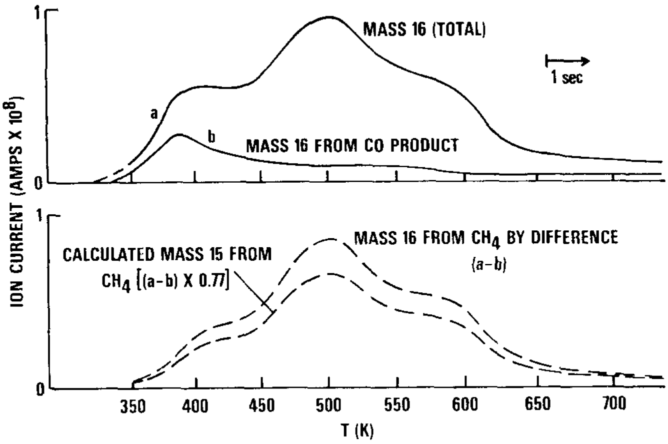

FIG. 8. Resolution of mass 16 desorption products from saturated methyl formate layer on W(100). See text for explanation of the method used here.

is shown graphically in Fig. 7. The difference curve, which can be attributed to organic species other than formaldehyde, is shown at the bottom of Fig. 7, together with the $m/e = 31$ and 32 curves. Comparison of the integrated areas under these three curves suggests that the most likely organic species from Table 1 which could give rise to these thermal desorption spectra is methyl alcohol. However, the $m/e = 15$ results to be described later preclude methyl alcohol as being the only desorbing molecule contributing to $m/e = 29$. We believe that methyl formate and glycolaldehyde may also be thermally desorbed from the methyl formate layer on W(100).

Figure 8 shows how the $m/e = 16$ contribution was corrected for the small $m/e = 16$ fragment from CO. Curve (b) represents 4% of the $m/e = 28$ contribution from Fig. 3. The corrected $m/e = 16$ methane contribution is represented at the bottom of Fig. 8, as well as the expected $m/e = 15$ methane contribution (77% of $m/e = 16$, from the cracking pattern of pure methane in our mass spectrometer).

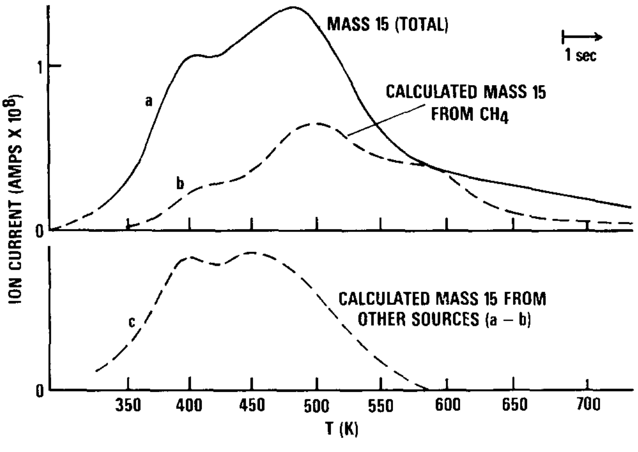

FIG. 9. Resolution of mass 15 desorption products from saturated methyl formate layer on W(100). See text for explanation of the method used here.

TABLE 2

Relative Mass Spectrometer Yields of Desorption Products from Saturated Methyl Formate Layer on W(100)

Desorption product	m/e	Relative yield (%)
CO	28	100
H_2	2	25
H_2CO and other organics	29, 30, 31, 32	8.8
CH_4	15, 16[a]	3.9
CO_2	44	0.4

[a] Corrected for $m/e = 16$ for CO and $m/e = 15$ for organics.

Figure 9 shows how the $m/e = 15$ contribution was resolved. Subtracting the corrected CH_4($m/e = 15$) contribution (curve b) from that of the total $m/e = 15$ contribution (curve a) yields curve c which represents the $m/e = 15$ contribution from other organic species. The integrated area under curve c is not as large as the areas under the $m/e = 31$ curve or $m/e = 29$ difference curve in Fig. 7. Therefore, using the cracking patterns in Table 1, the desorption of methyl alcohol cannot account for the entire product distribution detected at $m/e = 31$, 29, and 32. Since methyl formate was originally adsorbed on the W(100) surface, it is logical to assume that some methyl formate would evolve upon heating the saturated crystal. Also, from a photoelectron spectroscopy/thermal desorption study, Egelhoff has reported the desorption of glycolaldehyde, in addition to formaldehyde, from a formaldehyde layer on W(100) (*12*). Thus, it seems reasonable to postulate that the organic species desorbing from the saturated methyl formate layer are methyl formate, methyl alcohol, and glycolaldehyde, but this work cannot definitively discriminate among these products.

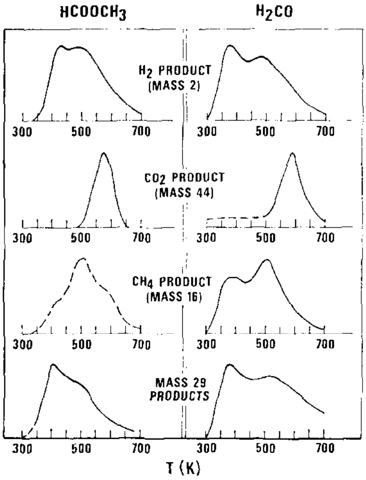

FIG. 10. Comparison of the thermal desorption spectra from methyl formate and formaldehyde adsorbates on W(100). The spectra, obtained in different vacuum systems, are normalized to the same maximum peak intensity.

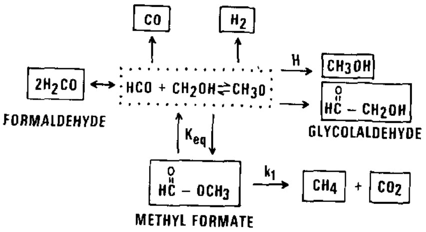

FIG. 11. Possible reaction scheme for formaldehyde and methyl formate decomposition on tungsten. Key intermediate species are indicated inside dotted region.

From the mass spectrometer currents, i_+, associated with the desorption products, we may make a crude estimate of the yields of CO, H_2, organics, CH_4, and CO_2 produced (by comparing $\int i_+ dt$ as measured with our mass spectrometer). These are shown in Table 2.

From Table 2 it can be seen that the major desorption products in this study were CO and H_2, but a substantial amount of CH_4 was also produced. The results of this study are remarkably similar to those obtained in the earlier work on formaldehyde adsorbed on W(100) (*3*, *4*). This point is clearly illustrated in Fig. 10, where various characteristic desorption spectra for H_2CO and $HCOOCH_3$ adsorbates are compared.[2] It appears, then, that the be-

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[2] It should be noted that a conclusion (*2*) previously reached in early work in which $m/e = 29$

havior of methyl formate and formaldehyde on W(100) is closely interrelated. This similarity in desorption product identity and in the kinetics of the various desorption processes as shown in Fig. 10 is indicative of the presence of similar surface species when either methyl formate or formaldehyde is adsorbed. A possible reaction scheme which expresses this interrelationship is given in Fig. 11, where methyl formate is shown to undergo decomposition to $H\dot{C}O$ and $\cdot CH_2OH$. This overall reaction scheme is similar to that proposed earlier for the decomposition of formaldehyde on W(100) (*4*), except that we now include provisions for the production of methyl alcohol and glycolaldehyde. The product yields from Table 2 indicate that the overall reaction rates for all steps leading to CO and H_2 are large, while the overall rate for the production of CH_4 and CO_2 from methyl formate is small, due to either a low surface concentration of methyl formate or to a low specific rate, k_1. The equilibrium (K_{eq}) between methyl formate and the organic fragments is strongly shifted toward the fragments. In summary, our proposed reaction scheme would suggest that, adsorption of formaldehyde, glycolaldehyde, or methyl formate on W(100) should all give rise primarily to CO and H_2, with small yields of CH_4, CO_2, and the organics upon thermal desorption.

It may also be seen from Figs. 3 and 10 that the desorption of H_2, α-CO, CH_4, and organics (mass 29 spectrum) occurs in nearly the same temperature region. This may indicate that the overall step for these products' formation may be controlled by the opening of filled sites due to desorption of a *predominant* surface species [H(ads); α-CO(ads)?]. The opening of these sites could then allow other more complex adsorbed species to interact with more surface sites, leading to fragmentation and desorption.

ACKNOWLEDGMENTS

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was thought to be due to ethane is clearly incorrect. The $m/e = 29$ from formaldehyde adsorbate is, in fact, predominantly formaldehyde, with the possibility of some glycolaldehyde (*12*), methyl alcohol, and methyl formate.