

Steady-state rate of decomposition of formaldehyde on Ru(001)

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The steady-state, absolute rate of decomposition of formaldehyde on the Ru(001) surface has been measured as a function of surface temperature from 310 to 750 K and for reactant pressures between 9.7×10^{-8} and 1.6×10^{-6} Torr. The only observed reaction products were carbon monoxide and hydrogen. Postreaction Auger spectroscopic analysis revealed a clean surface. Two distinct kinetic regimes are observed. At relatively low surface temperatures (and/or high formaldehyde pressures), the rate is zero order in formaldehyde pressure with an apparent activation energy of 23 ± 0.5 kcal/mol and an apparent preexponential factor of $4 \times 10^{11} \text{ s}^{-1}$. The rate becomes flux limited and first order in formaldehyde pressure with an apparent activation energy of zero at relatively high surface temperatures (and/or low formaldehyde pressures). Perdeutero-formaldehyde decomposes on Ru(001) with the same kinetic parameters as HCHO. The lack of a kinetic isotope effect indicates that C-H bond cleavage is not the rate-limiting step under these experimental conditions. In the low-temperature regime, the surface is saturated with CO, and the rate is CO desorption limited. Dissociative chemisorption of formaldehyde is irreversible since no isotopic exchange products were observed by reacting a mixture of HCHO and D₂ with a molar ratio of 1:4 at a total pressure of 1×10^{-6} Torr.

I. INTRODUCTION

The decomposition of formaldehyde has been studied on a number of transition-metal surfaces including W(111) and W(100),¹ Ru(110),^{2,3} Ru(001),⁴ Ni(110),^{5,6} clean and sulfided Pt(111),⁷ clean and oxygen precovered Cu(110),⁸ and oxygen precovered Ag(110).⁹ The possibility that the methanation reaction may proceed via HCHO or HCHO-derived intermediates¹⁰ makes a study of the chemistry of formaldehyde on transition-metal surfaces quite relevant. Carbon monoxide and hydrogen are the major reaction products of formaldehyde decomposition, as determined by temperature programmed desorption. Small quantities of other products were also observed on these surfaces, however, including CH₄,^{1,2} CH₃OH,⁵⁻⁷ CO₂,¹⁻⁷ and H₂O.^{2,5,6} The presence of impurities in the formaldehyde sample (methyl formate, for example) may account for the observation of CO₂ and CH₄ in some cases. On the Ru(001) surface, stable reaction intermediates including η^1 -formaldehyde, η^2 -formaldehyde, and η^1 -formyl have been identified by electron energy-loss spectroscopy following formaldehyde adsorption at 80 K.⁴ In this study, we have made mass spectrometric measurements of the steady-state and transient isothermal rate of decomposition of formaldehyde on an initially clean Ru(001) surface as a function of surface temperature, parametric in the formaldehyde pressure. We have determined the kinetics and mechanism of the formaldehyde decomposition reaction, as well as the surface coverages of carbon monoxide and hydrogen during the steady-state reaction.

II. EXPERIMENTAL DETAILS

The experiments were carried out in an ion-pumped (200 l/s) stainless-steel, ultrahigh vacuum chamber equipped with quadrupole mass spectrometry, Auger electron spectroscopy, low-energy electron diffraction, and x-ray photoelectron spectroscopy.¹¹ The base pressure of the belljar was

below 8×10^{-11} Torr of reactive gases. The Ru(001) surface (8 mm in diameter and 0.8 mm thick) was cut from a single-crystalline ruthenium boule by spark erosion. It was polished to within 0.5° of the (001) orientation and mounted on a manipulator by two 0.010-in. tantalum wires spotwelded on the back of the crystal. The Ru(001) crystal could be heated resistively, and cooled conductively by liquid nitrogen. The temperature of the Ru(001) surface was measured by a 0.003-in. W/5% Re-W/28% Re thermocouple spotwelded to the back of the crystal. Oxygen cleaning was routinely performed prior to each measurement by cycling the temperature of the Ru(001) crystal between 400 and 1100 K in 7×10^{-8} Torr of oxygen backfilled into the belljar. Chemisorbed oxygen was removed by annealing the crystal to over 1600 K.¹² The cleanliness of the surface was verified by Auger electron spectroscopy.

An IBM PC/XT microcomputer with a Data Translation 2805 board was utilized as a temperature controller,¹³ which controls a programmable dc power supply. The emf of the thermocouple was measured with a Hewlett-Packard 3455A digital voltmeter at a rate of 25 readings/s, and the readings are transferred to the computer through a general purpose interface bus (GPIB) interface. This controller allows the crystal temperature to follow a predefined temperature profile, a staircase function in the case of the steady-state decomposition rate measurements. The software performs temperature control, mass spectrometric multiplexing, and mass spectrometric signal measurements simultaneously.

Deuterated paraformaldehyde (99.6 at.% D) was obtained from MSD Isotopes and paraformaldehyde (with H₂O < 1%) from Fluka. They were transferred in powder form into a preevacuated 50-ml Pyrex flask in a plastic bag purged with dry nitrogen gas. The flask with the paraformaldehyde sample was evacuated in a gas manifold which is pumped by a Varian M-2 diffusion pump and has a base

pressure of 6×10^{-6} Torr. Formaldehyde in monomer form was prepared in a similar way to that described by Yates *et al.*,¹ and was stored at room temperature in a 500-ml Pyrex bulb at pressures from 0.2 to 8 Torr. A mass spectrum of the HCHO sample exhibits m/e peaks only at 30, 29, 28, 16, 14, 13, 12, and 2 with peak height ratios of 0.73:1.00:0.34:0.02:0.04:0.03:0.05; that of the DCDO sample exhibits m/e peaks at 32, 30, 28, 16, 14, 12, and 4 with intensity ratios of 0.80:1.00:0.36:0.07:0.05:0.04:0.05, in reasonable agreement with the reported values.¹⁴ Most importantly, there are no peaks at masses 44 and 60, indicating that the samples were free of methyl formate.¹ The mass spectra remain unchanged for up to one week following storage at room temperature.

The formaldehyde was introduced from the storage bulb onto the Ru(001) surface through a directional beam doser consisting of a type 304 stainless-steel plate with collimated hole structures (Brunswick Corporation). The hole diameters are 0.1 mm; the thickness of the plate is 1.3 mm; and the open area of the plate is 50%. The diameter of the plate is 9 mm, slightly larger than that of the Ru(001) single crystal, in order to improve the pressure profile across the Ru(001) surface. The Ru(001) surface is parallel to and 3 mm away from the doser when the crystal is in front of the beam doser. The crystal so positioned intercepts $\sim 50\%$ of the formaldehyde flowing through the doser.¹⁵

The absolute HCHO beam flow rate through the doser was determined by the rate of pressure drop in the formaldehyde storage bulb, measured by a Baratron manometer. The cryopan in the UHV system was cooled by liquid nitrogen, and the ion gauge was turned off during the steady-state rate measurements in order to decrease the background pressure. The ratio of the formaldehyde "beam pressure" to the background formaldehyde pressure was determined to be greater than 40:1 by measuring the formaldehyde decomposition rate when the crystal was in and out of the formaldehyde beam at high surface temperatures (where the reaction kinetics are first order).

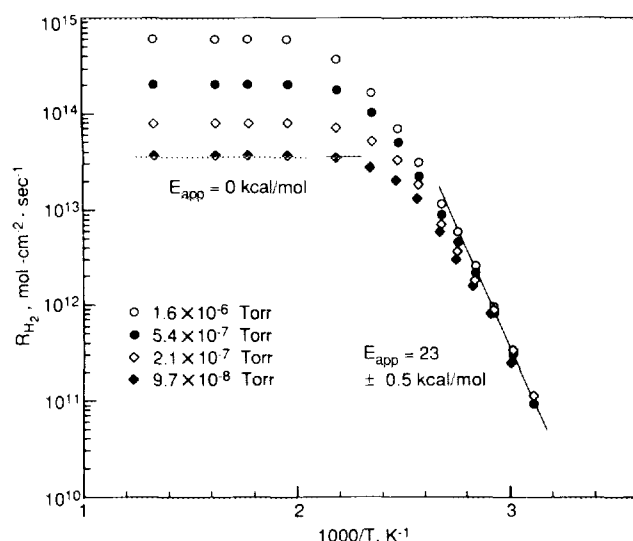


FIG. 1. Arrhenius plots of the steady-state rate of decomposition of formaldehyde on Ru(001). Note that the reaction is zero order in the low-temperature regime and first order in the high-temperature regime.

During steady-state rate measurements, formaldehyde flowed steadily through the gas doser. The temperature of the Ru(001) surface was programmed to follow a staircase function. Each time the surface temperature became constant, mass spectrometric signals of masses 2 and 29 were monitored as the Ru(001) surface was positioned in and out of the formaldehyde beam. The Ru(001) surface remained in the beam for a sufficiently long time that steady state was achieved. The difference in the mass spectrometric signal of mass 2 (in the case of HCHO) when the surface was in and out of the beam serves as a measure of the decomposition rate. Since the beam-to-background pressure ratio is > 40 , both the reaction rate when the Ru(001) surface was out of the beam and the reaction rate from the rear of the crystal when the Ru(001) was in the beam were negligible. The absolute rate of hydrogen production was calculated by calibrating the mass spectrometer with a known leak of hydrogen into the UHV system. The leak rate of hydrogen was determined in the same way as that of formaldehyde discussed above. Similar techniques have been employed in studying the kinetics of formic acid decomposition on the Ru(001) surface.¹⁶

III. RESULTS AND DISCUSSION

The measurement of the steady-state, absolute rate of formaldehyde decomposition on the Ru(001) surface was carried out at surface temperatures ranging from 310 to 750 K and pressures ranging from 9.7×10^{-8} to 1.6×10^{-6} Torr. The decomposition products are CO and H₂. No detectable quantities of CH₄, H₂O, or CO₂ were observed, unlike on the Ru(110) surface.² The temperature and pressure dependence of the reaction rate is presented in Arrhenius plots in Fig 1. Two distinct kinetic regimes are observed. At relatively low surface temperatures and/or high formaldehyde pressures, the reaction rate is nearly zero order in the formaldehyde pressure with an apparent activation energy of 23 ± 0.5 kcal/mol and an apparent preexponential factor of $4 \times 10^{11} \text{ s}^{-1}$. The rate levels off and becomes first order in the formaldehyde pressure with an apparent activation energy of zero at relatively high temperatures and/or low formaldehyde pressures. The reaction probability in this regime is essentially unity, i.e., the reaction rate becomes flux limited. The steady-state, absolute rate of DCDO decomposition was also measured under the same conditions. The kinetic parameters and absolute decomposition rates are the same as those for HCHO. The lack of a kinetic isotope effect indicates that C-H bond cleavage is not involved in the rate limiting step of the reaction under these experimental conditions. This observation also suggested a better way to measure the steady-state rate in the low surface temperature regime where the reaction rate is low. Instead of pure HCHO or DCDO, an equimolar mixture of both reagents was used. The intensity of mass 3 was monitored rather than mass 2 (or 4) in the case of pure HCHO (or DCDO). Since the background intensity of mass 3 in the UHV system is extremely low, the sensitivity of the rate measurements was increased by a factor of 10.

The fact that the reaction rate is nearly zero order in formaldehyde pressure in the low-temperature regime and the

absence of an isotope effect imply that the Ru(001) surface is saturated with the reaction product(s), carbon monoxide, and/or hydrogen. A determination of surface coverages of these species during the steady-state reaction is essential to a confirmation of the mathematical model describing the reaction. The coverages of carbon monoxide and hydrogen during the steady-state reaction were determined by temperature programmed thermal desorption. When the reaction reached steady state, the Ru(001) surface was swung rapidly away from the formaldehyde beam and positioned in front of the mass spectrometer, the temperature of the crystal was increased linearly at 3 K/s, and mass spectrometric signals of masses 2 and 28 were monitored. It took ~ 0.2 s from swinging the surface away from the doser to the start of the temperature ramp. The area under the thermal desorption spectra of CO and H₂ serves as a measure of the surface coverages of CO and hydrogen during the steady-state reaction. The mass spectrometer was enclosed in a glass envelope with an aperture of 3.7 mm in diameter during the coverage determination experiments, in order to reduce the contribution from any change in the background partial pressures and desorption from the rear of the crystal.¹⁷ The relative mass spectrometric sensitivities of CO and H₂ were determined from the thermal desorption spectra of CO and H₂ following the adsorption of HCHO on the Ru(001) surface at or below 200 K, when the ratio of the coverages of CO and hydrogen is 1:2. The results are shown in Fig. 2 for the decomposition of formaldehyde at 7×10^{-8} Torr. The surface is saturated with CO, whereas the coverage of hydrogen is only $\frac{1}{30}$ that of CO in the low-temperature regime. Furthermore, the coverage of CO remains essentially constant in the low-temperature regime. This demonstrates that the measured decomposition rate in the low-temperature regime corresponds to the rate of CO desorption. The activation energy of the desorption of CO is given by

$$\frac{E_{d,CO}}{k_B} = -\frac{d(\ln R)}{d(1/T)} + \frac{d(\ln \theta_{CO})}{d(1/T)},$$

where R is the reaction rate, and the first term on the right-hand side of the equation is the apparent activation energy determined from the Arrhenius plots. Since the second term

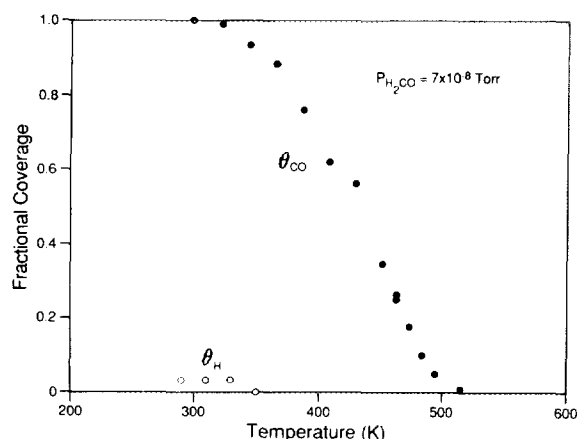


FIG. 2. The coverages of CO and hydrogen during the steady-state decomposition of formaldehyde on Ru(001) at an effective pressure of 7×10^{-8} Torr, determined by temperature programmed thermal desorption.

on the right-hand side is essentially zero in the low-temperature regime (cf. Fig. 2), the apparent activation energy (23 ± 0.5 kcal/mol) determined in this regime is the desorption energy of CO at saturation coverage.

A mixture of HCHO and D₂ with a molar ratio of 1:4 at a total pressure of 1.0×10^{-6} Torr was reacted on the Ru(001) surface, in order to determine if there are any isotopic exchange or reduction products. No DCHO, DCDO, or methanol was observed at any temperature from 300 to 750 K. Our detection sensitivity would allow us to have observed a rate of 1×10^{11} mol cm⁻² s⁻¹.

IV. SUMMARY

The decomposition kinetics of formaldehyde on the Ru(001) surface have been studied by measuring the steady-state, absolute rate of the reaction as a function of surface temperature from 310 to 750 K, parametric in the formaldehyde pressure from 9.7×10^{-8} to 1.6×10^{-6} Torr. Formaldehyde dissociates irreversibly on the Ru(001) surface, and only one reaction channel is observed, decomposition to CO and H₂. There are two distinct kinetic regimes in the Arrhenius plots, a low-temperature regime characterized by a Ru(001) surface which is essentially saturated with CO (the coverage of hydrogen is only $\frac{1}{30}$ of that of CO), and a high-temperature regime where the surface is essentially clean. In the low-temperature regime, the rate is nearly zero order in the formaldehyde pressure and has an apparent activation energy of 23 ± 0.5 kcal/mol and an apparent preexponential factor of 4×10^{11} s⁻¹. In the high-temperature regime, the rate is first order in the formaldehyde pressure, the apparent activation energy is zero, and the reaction probability is unity. No kinetic isotope effect is observed, indicating that C-H bond cleavage is not involved in the rate limiting step under these experimental conditions.

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