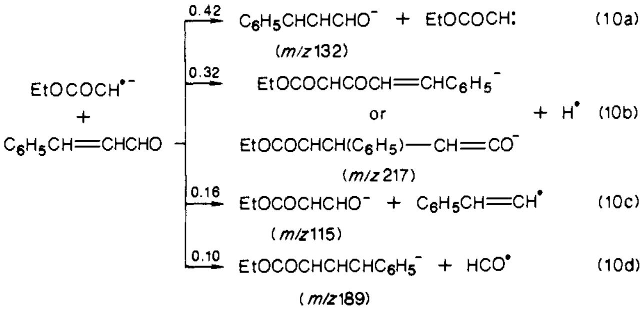
be favored for the carbon-centered anion radical.

Reaction of $EtOCOCH^{\bullet -}$ with $C_6H_5CH{=}CHCHO$ produced at least four anionic products (reactions 10a–10d). Electron transfer (i.e., a charge exchange reaction) produces the major product. Formation of the anions with m/z 217 and 115 may result from nucleophilic attack at carbonyl carbon with subsequent loss of either $H^{\bullet}$ or $C_6H_5CH{=}CH^{\bullet}$. However, the loss of a hydrogen atom could also occur following radical attack at the β carbon generating a radical center of the α carbon, followed by loss of a hydrogen atom (a 1,4-addition process). Observation of the minor product (m/z 189) is somewhat unexpected and may be rationalized as arising from radical attack at the α carbon (a 1,3-addition process) followed by loss of formyl radical.



Reactions of $EtOCOCH^{\bullet -}$ with CH_3X (X = Cl and Br), O_2, N_2O, CO_2, and CS_2

Carboethoxycarbene anion radicals undergo slow and moderate rate S_N2 displacement reactions with CH_3Cl and CH_3Br, to yield chloride and bromide, respectively, suggesting that $EtOCOCH^{\bullet -}$ is a weak to moderate nucleophile. Although no reaction was observed with O_2, N_2O, or CO_2, $EtOCOCH^{\bullet -}$ reacts rapidly with CS_2 via S atom abstraction to yield $EtOCOCHS^-$.

Summary and Conclusion

In contrast to results from flowing afterglow studies, ethyl diazoacetate produces abundant carboethoxycarbene anion radical ($EtOCOCH^{\bullet -}$) under low-pressure FTMS conditions. Collision-induced dissociation studies suggest that $EtOCOCH^{\bullet -}$ eliminates C_2H_4 via a six-membered transition state, yielding $C_2H_2O_2^-$ anion. For the reactions studied, the reactions of carboethoxycarbene anion radical are best understood by considering two resonance structures: I, a carbon-centered radical anion, and II, an oxygen-centered anion. The reactions of $EtOCOCH^{\bullet -}$ with carbonyl compounds and activated olefins are consistent with more carbon-centered anionic character. Competitive D^+ transfer, H/D exchange, and D atom abstraction reactions with EtOD support this interpretation. By bracketing proton transfer and H atom abstraction reactions, $PA(EtOCOCH^{\bullet -}) = 377 \pm 2$ kcal/mol and $D(EtOCOCH\text{-}H) \geq 101 \pm 1$ kcal/mol are determined. Using the PA together with other thermochemical data, $\Delta H_f(EtOCOCH^{\bullet -})$ is estimated to be -48.5 ± 3 kcal/mol.

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Registry No. $EtOCOCHN_2$, 623-73-4; $EtOCOCH^{\bullet -}$, 119638-74-3; H, 1333-74-0.

Thermal Stability of the C–O Bond of Methanol on the Pd(111) Surface: An Isotopic Mixing Study

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Abstract: The isotopic mixing method was employed to study the thermal desorption of CO molecules produced from methanol decomposition on Pd(111). Using $^{13}CH_3{}^{16}OH$ and $^{12}CH_3{}^{18}OH$ adsorbate molecules, no isotopic exchange in thermally desorbing CO to produce $^{13}C^{18}O$ and $^{12}C^{16}O$ was observed. This observation, combined with measurements indicating that no H_2O or CH_4 desorbs, indicates that C–O bond scission does not occur in any of the surface species derived from adsorbed CH_3OH.

Can the C–O bond of methanol be thermally dissociated on the Pd(111) surface? In a recent SIMS (secondary ion mass spectroscopy) and XPS (X-ray photoelectron spectroscopy) study,[1] the results were interpreted to indicate efficient C–O bond scission of chemisorbed methanol on Pd(111) at 175 K. This report of the thermal activation of the C–O bond of methanol on the Pd surface differs from current models of CH_3OH interaction with transition-metal surfaces, where decomposition to CO and H_2 is postulated to occur via the methoxy intermediate. In order to directly examine the possibility of C–O bond scission, we have performed experiments involving coadsorption of $^{13}CH_3{}^{16}OH$ and $^{12}CH_3{}^{18}OH$ on the Pd(111) surface at various adsorption temperatures from 87 to 265 K. Any isotopic mixing in the desorbing CO products would be indicative of C–O bond breaking and recombination in $CH_3OH(a)$, $CH_3O(a)$, or CO(a). However, our study shows negative results: no measurable production of $^{13}C^{18}O$ and $^{12}C^{16}O$ is observed compared to the isotope abundance in the labeled methanol adsorbate; no methane or water desorbs within detection limits conservatively estimated to be ~1% of a monolayer based on calibration experiments. Our experimental observations are therefore consistent with other studies on Pd surfaces,[2-6] as well as with the selective methanol formation (with respect to methane) from synthesis gas (CO + H_2) on supported Pd catalysts at high pressure.[7-9]

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Table I. Isotopic CO Yields (%) from Methanol Adsorption on Pd(111) (T_{ads} = 87 K)

adsorbate	isotopic CO product yield %[a] $^{12}C^{16}O$ 28 amu	 $^{13}C^{16}O$ 29 amu	 $^{12}C^{18}O$ 30 amu	 $^{13}C^{18}O$ 31 amu	notes
a. 100% "$^{13}CH_3{}^{16}OH$"	18.5	78.9	0.0	2.6	experiment (Figure 2b)
b. 100% "$^{12}CH_3{}^{18}OH$"	20.3	6.2	73.2	0.3	experiment (Figure 2c)
c. 50% "$^{13}CH_3{}^{16}OH$" 50% "$^{12}CH_3{}^{18}OH$"	19.0	42.8	36.6	1.6	experiment (Figure 2a)
d. 50% "$^{13}CH_3{}^{16}OH$" 50% "$^{12}CH_3{}^{18}OH$"	19.4	42.6	36.5	1.5	calcd from a and b, assuming no C–O bond scission
e. 50% "$^{13}CH_3{}^{16}OH$" 50% "$^{12}CH_3{}^{18}OH$"	34.7	27.3	21.2	16.8	calcd from a and b, assuming complete C–O bond scission

[a] The absolute error in these measurements is estimated to be ±0.5%.

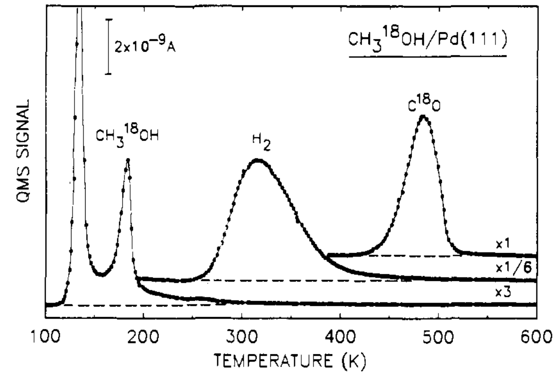

Figure 1. Thermal desorption spectra of $^{12}CH_3{}^{18}OH$, H_2, and $^{12}C^{18}O$ from $^{12}CH_3{}^{18}OH$ adsorbed on Pd(111) at 87 K. The QMS signals shown are not corrected for mass spectrometer sensitivity. $^{12}CH_3{}^{18}OH$ exposure = ~4 × 10^{15} molecules/cm^2. Heating rate = 2 K/s. Lines have been drawn through the data points for clarity.

The ultra-high-vacuum apparatus (background pressure ≤1.0 × 10^{-10} Torr during experiment) and the labeled methanol, $^{13}CH_3{}^{16}OH$ (Cambridge Isotopes, 99 atom % ^{13}C) and $^{12}CH_3{}^{18}OH$ (Cambridge Isotopes, 95 atom % ^{18}O), have been used previously for a similar experiment on the Ni(111) surface.[10] The desorbing species from the center of the Pd(111) surface were monitored by a multiplexed quadrupole mass spectrometer (QMS) located inside a differentially pumped and apertured (1.6 mm diameter) random flux shield. The "$^{13}CH_3{}^{16}OH$" and the "$^{12}CH_3{}^{18}OH$" were subjected to 3 freeze–pump–thaw cycles before use and were mass spectrometrically analyzed. The methanol vapor was delivered to the crystal surface through a calibrated and collimated molecular beam doser.

The Pd(111) crystal was cut, oriented, and polished by standard methods to within ±0.5° of the (111) surface. The Pd(111) surface was cleaned *rigorously* by prolonged cycles of Ar$^+$ sputtering (600 eV, 2 μA/cm^2, 1000 K), annealing (1200 K), and oxygen treatment (1000 K) using a beam doser producing a local oxygen pressure of ~10^{-6} Torr. The crystal cleanliness was checked not only by Auger spectroscopy (which on Pd is sensitive to oxygen and sulfur impurity), but also by the well-known O_2-adsorption/CO,CO_2-desorption cycle commonly used to accurately determine carbon impurity levels on Pd surfaces.[11] The carbon, oxygen, and sulfur impurity on the cleaned surface were estimated to be less than 0.1% of a monolayer. It has been well established[12,13] that Ar$^+$ sputtering alone (up to 400 h) is not sufficient to remove carbon completely from Pd surfaces. Extensive oxygen treatment at 900–1000 K is essential to obtain a carbon-free Pd surface. The experiments in ref 1 employed only Ar$^+$ sputter cleaning.

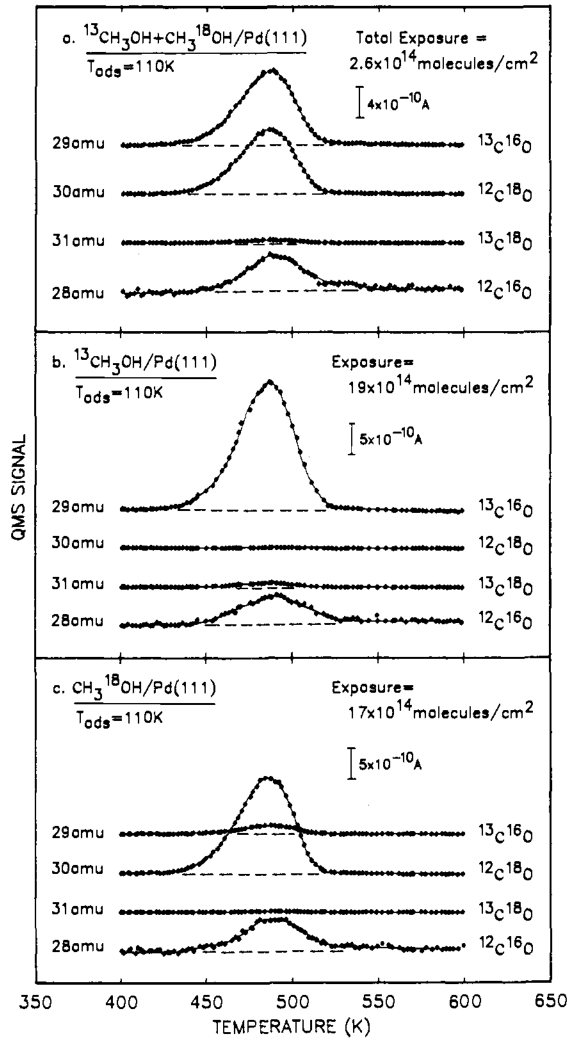

Figure 2. Thermal desorption spectra of all CO isotopes from methanol adsorption on Pd(111) at 110 K: (a) 50% "$^{13}CH_3{}^{16}OH$" + 50% "$^{12}CH_3{}^{18}OH$"; (b) 100% "$^{13}CH_3{}^{16}OH$"; (c) 100% "$^{12}CH_3{}^{18}OH$". Heating rate = 2 K/s. See Table I for percentage yields. For other adsorption temperatures see text. Lines have been drawn through the data points for clarity.

Figure 1 shows the thermal desorption spectra from $^{12}CH_3{}^{18}OH$ adsorbed on the Pd(111) surface at 87 K. The $^{12}CH_3{}^{18}OH$ exposure used for the experiment in Figure 1 was about 4 × 10^{15} molecules/cm^2. During the thermal desorption all possible product masses from 2 to 34 amu were monitored, with special attention being paid to possible methane (15 and 16 amu monitored) and water (19 and 20 amu monitored) desorption. The only desorbing species detected from $^{12}CH_3{}^{18}OH$ were H_2 and $^{12}C^{18}O$ (~0.06 ML). After all of the desorption is completed (~600 K), no carbon (sensitivity limit = 0.1% of a monolayer) was left on the surface as judged from the O_2-adsorption/CO,CO_2-desorption method.[11] The lack of CH_4 desorption and the absence of residual

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C(a) following CO desorption indicate that all carbon from dissociative CH_3OH adsorption on Pd(111) leaves the surface as CO. The lack of H_2O desorption and the absence of residual O(a) (<0.1% of a monolayer) following CO desorption indicate that all oxygen from dissociative CH_3OH adsorption on Pd(111) leaves the surface as CO.

Since the above results for $^{12}CH_3{}^{18}OH$ are in good agreement with the literature regarding the behavior of CH_3OH on clean Pd(111),[5,6] the thermal desorption method was used to study the coadsorption of $^{13}CH_3{}^{16}OH$ and $^{12}CH_3{}^{18}OH$ on the Pd(111) surface. The isotopic CO desorption spectra resulting from methanol adsorption at 110 K are shown in Figure 2a–c. In the case of Figure 2a, 2.6 × 10^{14} molecules/cm^2 of a 50% "$^{13}CH_3{}^{16}OH$" and 50% "$^{12}CH_3{}^{18}OH$" mixture of isotopically labeled methanol molecules was exposed to the surface. This exposure to methanol corresponds closely to that used in ref 1. Separate experiments involving exposures of 100% "$^{13}CH_3{}^{16}OH$" and 100% "$^{12}CH_3{}^{18}OH$" are shown in Figure 2, b and c, respectively, as a control. The percentage yields for each CO isotope are listed in Table I as obtained from the integrated areas of the corresponding CO desorption peaks in Figure 2. Small yields of $^{13}C^{18}O$ are obtained from 100% "$^{13}CH_3{}^{16}OH$" and 100% "$^{12}CH_3{}^{18}OH$" due to isotopic impurities in these alcohols (Figure 2, b and c). The mixture of 50% "$^{13}CH_3{}^{16}OH$" and 50% "$^{12}CH_3{}^{18}OH$" leads to the evolution of 19.0% $^{12}C^{16}O$ and 1.6% $^{13}C^{18}O$. In fact, if one assumes that there is *no isotopic exchange*, the percentage yield for each CO isotope from a mixture of 50% "$^{13}CH_3{}^{16}OH$" and 50% "$^{12}CH_3{}^{18}OH$" can be easily calculated based on the data from the separate isotopic methanol adsorption experiments shown in Figure 2, b and c. This calculation assuming no isotopic mixing (see Table I, row d) gives 19.4% of $^{12}C^{16}O$ and 1.5% of $^{13}C^{18}O$; this isotopic composition is very close to the experimental results shown in row c of Table I. The ~20% yield of $^{12}C^{16}O$ in the control and the mixed methanol experiments is higher than expected from the analysis of the methanol isotopic abundance and is due primarily to the adsorption of ~0.007 ML of $^{12}C^{16}O$ from background during these experiments. If complete isotopic exchange had occurred, which would be the case for the C–O bond dissociation in the chemisorbed methanol molecules as proposed in ref 1, *the calculated isotopic CO yields would differ significantly from the yields observed experimentally* (*see row e, Table I*). The lack of production of $^{13}C^{18}O$ is a particularly sensitive indicator that C–O bond scission does not occur.

Similar results to those in Figure 2 were also obtained for methanol adsorption temperatures of 87, 160, 210 and 265 K (data not shown). At 110 K, the adsorption temperature used in ref 1, the isotopic methanol coadsorption experiment was performed also with various methanol exposures from 2 to 34 × 10^{14} molecules/cm^2. No measurable $^{13}C^{18}O$ production (<3%, due entirely to the abundance of $^{13}C^{18}O$ in the adsorbed methanol isotopic species) was detected for all the methanol exposures used. In addition, adsorbing $^{13}CH_3OH$ using a fluence from our beam doser of 2 × 10^{14} molecules/s on the Pd(111) surface at 580 and 800 K for more than 600 s left no ^{13}C on the surface, as measured by the O_2-adsorption/CO,CO_2-desorption method.

Finally, to eliminate the possibility that the molecular methanol desorption occurs via $CH_3(a) + OH(a)$ recombination, the isotopic methanol content was analyzed in the two molecular desorption states (cf. Figure 1). No evidence of $^{12}CH_3{}^{16}OH$ or $^{13}CH_3{}^{18}OH$ was found in either methanol desorption state.

In conclusion, we observe no C–O bond scission for the thermal decomposition of methanol on the Pd(111) surface as demonstrated by the absence of isotopic exchange in the desorbing CO and methanol products from coadsorbed $^{13}CH_3{}^{16}OH$ and $^{12}CH_3{}^{18}OH$. The accuracy of measurement is such that if ≥1% of the adsorbed CH_3OH was dissociated, it could be detected by the production of $^{13}C^{18}O$ or isotopically mixed methanol species. This conclusion differs significantly from that of ref 1, where, using different Pd(111) surface cleaning methods and different surface measurement techniques, efficient C–O and scission in either adsorbed CH_3OH or CH_3O is proposed on Pd(111). Our results, in distinction to the conclusions of ref 1, also exclude the possibility of the formation of appreciable surface concentrations of $CH_3(a)$ from CH_3OH, since CO formation from $CH_3(a)$ would be accompanied by isotopic mixing in our experiments.

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Autocatalysis and Apparent Bistability in the Formose Reaction

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Abstract: The homogeneous formose reaction has been studied under continuous-flow stirred-tank reactor conditions and under batch conditions. Several classes of mechanisms have been examined, and simulations of a model accounting for the observed autocatalysis and isotope effects in the reaction are presented. Hysteresis loops seen under flow conditions are thought to arise from insufficient observation times.

Under basic conditions in the presence of certain divalent cations, aqueous formaldehyde reacts to form a complex mixture of sugars and other compounds in a process called the formose reaction. The reaction has aroused interest as a potential source of carbohydrates,[1-4] as a model for the prebiotic synthesis of sugars,[5-8] and because of its resemblance to carbohydrate metabolism.[9] Our interest in the reaction derives from the autocatalytic nature of the reaction under batch conditions and from

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