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Surface-Bound Ketenylidene (CCO) from Acetone Decomposition on Ag{111}-*p*(4×4)−O

W. S. Sim and D. A. King*

Department of Chemistry, University of Cambridge
Lensfield Road, Cambridge CB2 1EW, U.K.

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Metal ketenylidene (CCO) complexes have emerged as a growing class of compounds whose structure and reactivity bear potential implications in many branches of chemistry.[1,2] The facile formation of several transition metal CCO complexes by reductive CO cleavage or insertion has led to postulation of the possible existence of CCO moieties on metal surfaces, particularly as reaction intermediates in the Fischer−Tropsch process.[3−6] However, with the exception of a single known report in the literature,[7] such a surface fragment has proved to be highly elusive. Partial oxidation of organic molecules over Ag surfaces has shown great promise as a synthetic technique for generating new, stable surface species.[8] We describe here a novel reaction of acetone ($(CH_3)_2CO$) with preoxidized Ag{111} that yields surface-coordinated CCO groups, which have been unambiguously fingerprinted using reflection−absorption infrared spectroscopy (RAIRS).

Experiments were performed in an ultrahigh-vacuum chamber with a base pressure of $<1 \times 10^{-10}$ mbar.[9] Ag{111}-*p*(4 × 4)−O was prepared by heating the clean crystal to 425 K in ~1 mbar of O_2.[10] Dosing of the modified surface phase with a saturation exposure (>5 L) of $(CH_3)_2CO$ between 240 and 280 K yields CCO and formate (HCOO) as the only detectable surface species,[11] as identified by their characteristic vibrational signatures (Figure 1). These are for CCO, the out-of-phase C=C=O stretch ν_{op}(CCO), which gives rise to a strong band at 2026 cm^{-1}, and a weak band at 1972 cm^{-1} due to another CCO species adsorbed at a different site;[12] and for HCOO, the symmetric O−C−O stretch ν_s(OCO) at 1320 cm^{-1}, and the Fermi resonance doublet consisting of the C−H stretch ν(CH) coupled to the C−H bending overtone 2δ(CH) or the combination band ν_{as}(OCO) + δ(CH) at 2886 and 2808 cm^{-1}.

Selectively labeled acetone isotopomers were used to confirm these assignments (Figure 1). $(CD_3)_2CO$ forms CCO (no shift in associated vibrational frequencies) and DCOO (ν_s(OCO) at 1298 cm^{-1} and ν(CD) at 2130 cm^{-1}); $(CH_3)_2{}^{13}CO$ gives $C^{13}CO$ ($\nu_{op}(C^{13}CO)$ at 1974 and 1920 cm^{-1}) and HCOO (no change in associated vibrational frequencies); while $(^{13}CH_3)_2CO$ produces ^{13}CCO ($\nu_{op}(^{13}CCO)$ at 2022 and 1968 cm^{-1}) and $H^{13}COO$ ($\nu_s(O^{13}CO)$ at 1298 cm^{-1} and $\nu(^{13}CH)/2\delta(^{13}CH)$ or $\nu_{as}(O^{13}CO) + \delta(^{13}CH)$ at 2862 and 2784 cm^{-1}). The formate absorption bands are identical to those in the RAIR spectra of formate acquired for other precursor molecules partially oxidized on Ag{111},[13] while the change in the behavior of the bands in the C−H/C−D stretching region is due to changes in the degree of Fermi resonance coupling between the corresponding stretching and overtone/combination bands caused by isotope-induced frequency shifts.

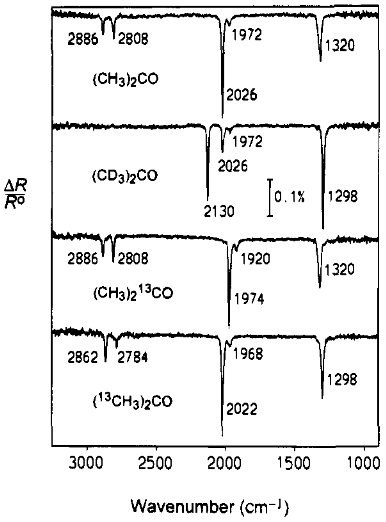

Figure 1. RAIR spectra of ketenylidene and formate obtained by exposing preoxidized Ag{111} to saturation doses (>5 L) of the respective acetone isotopomers at 240 K.

The major peak vibrational frequencies of the CCO isotopomers have been fitted to a modified valence force field model involving the C=O and C=C bond stretching coordinates that includes the coupling interaction between them.[14] Adapting the respective force constants k_{CO} = 1644 Nm^{-1} and k_{CC} = 891 Nm^{-1} determined for the $[Ru_3(CO)_6(\mu\text{-}CO)_3(\mu_3\text{-}CCO)]^{2-}$ cluster[4] yields an interaction force constant k_{CO-CC} = 282 Nm^{-1} for surface-bound CCO and predicts correctly the observed vibrational frequencies for each of the isotopically substituted species. The analysis also shows that ν_{op}(CCO) involves essentially motion of the O atom and central C atom, with little involvement of the terminal C atom. This is entirely consistent with the observed frequency shifts, where ^{13}C substitution of the central C atom causes a large shift of 52 cm^{-1}, while that for the terminal C atom only results in a small shift of 4 cm^{-1}.

We can confidently rule out all other surface species (restricted to C-, H-, and O-containing moieties) which absorb at ~2000 cm^{-1}. Preoxidation of Ag{111} with $^{18}O_2$ results in new bands for all the CCO isotopomers through partial incorporation of ^{18}O. This implies that the vibration involves O atom motion, which precludes acetylenic (C≡C) and allene-type (C=C=C) chromophores. The absence of C−H/C−D modes associated with the species in question also means that no H-containing fragments are involved. The only other possibility, chemisorbed CO, can be effectively excluded as the different ^{13}C-labeled acetone isotopomers give rise to surface species that show different frequency shifts. Moreover, the lifetime of adsorbed CO on low Miller index Ag single crystal surfaces is very short above 100 K.[15,16]

There is considerable evidence from the infrared spectra of other CCO-based systems to further support our conclusions. Each of the noble metal complexes with empirical formulas $Cu_2(CCO)$,[17] $Ag_2(CCO)$,[18,19] and $Au_2(CCO)$[20] exhibits a strong characteristic ν_{op}(CCO) absorption band at 2030, 2060, and 2015

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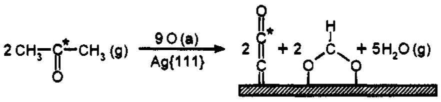
cm^{-1}, respectively. Isotopically labeled $Ta(CCO)(t\text{-}Bu_3SiO)_3$ complexes show frequency shifts that mimic the present results, with $\nu_{op}(CCO)$ at 2076 cm^{-1}, $\nu_{op}(^{13}CCO)$ at 2065 cm^{-1}, and $\nu_{op}(C^{13}CO)$ at 2022 cm^{-1}.[5] The crystal structure of $Zr_3Cp_2(O_2CN\text{-}i\text{-}Pr_2)_6(\mu_3\text{-}O)(\mu_2\text{-}CCO)$ has been recently established and reveals a bridging CCO ligand that absorbs at 2013 cm^{-1}.[6] The coupled $\nu_{op}(CCO)$ and $\nu(CO)$ bands of the $[Ru_3(CO)_6(\mu\text{-}CO)_3(\mu_3\text{-}CCO)]^{2-}$ cluster have been identified at 1977 and 2022 cm^{-1}.[3,4] Of even more significance is the assignment of a band at 2038 cm^{-1} to $\nu_{op}(CCO)$ of CCO fragments produced by the decomposition of β-diketonate ligands on Cu{111} and Cu{100} surfaces.[7] We do not observe the in-phase C=C=O stretch $\nu_{ip}(CCO)$ as this mode is known to show only very weak infrared absorption at 1200−1350 cm^{-1} for the trimetallic CCO clusters[4] and was not detected at all for the other complexes.

A recent investigation of $(CH_3)_2CO$ oxidation on Ag{110} over a wider temperature range indicated a fairly complicated series of events with several competing mechanisms.[21] Our results reveal a hitherto unreported reaction pathway involving essentially O-induced C−C and C−H bond cleavage. The isotope labeling studies clearly demonstrate that CCO retains the acetone C=O group (with some O exchange with the surface) while HCOO is solely derived from the acetone CH_3 group and surface O (including exchanged) atoms, as depicted in Scheme 1. Excess H and O are eliminated as H_2O, which desorbs during the dose. The mild conditions under which bulk $Ag_2(CCO)$ can be synthesized from the deprotonation of ketene (H_2CCO) by Ag salts[19] suggest that a H_2CCO-like intermediate could be involved as a precursor to the surface-bound CCO. Just as acetic anhydride, enol acetates, and phenyl acetates can act as in situ H_2CCO sources for bulk $Ag_2(CCO)$ formation,[19] $(CH_3)_2CO$ could presumably do the same under the present conditions.

Scheme 1



Surface-bound CCO has not been assigned from previous studies of $(CH_3)_2CO$,[21−25] H_2CCO,[26−28] or indeed any other adsorbate (with the noted exception[7]) on metal surfaces. In the light of the present results, it would be prudent to give this possibility much more serious consideration.

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