

Isolation and Identification of Surface-Bound Acetone Enolate on Ni(111)

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Metal enolate complexes are key intermediates in carbon-carbon bond-forming reactions in both organometallic chemistry and heterogeneous catalysis. Enolate ions coordinated to alkali, main group, and transition metals are extensively used in well-established procedures for contemporary organic synthesis.¹ Enolate species have also been implicated as surface intermediates in the industrially important process of acetone (CH_3COCH_3) condensation over transition-metal oxide catalysts, largely on the basis of studies performed on powdered samples of ill-defined surface structure and composition.² Paradoxically, with the exception of preoxidized Ag where an enolate species was postulated,³ ultrahigh vacuum (UHV) surface science studies of acetone adsorption on all other metal single-crystal surfaces to date have suggested that the dominant adsorption states of acetone are that of the intact molecule bonding to the surface either through the O lone pair electrons ($\eta^1(\text{O})$ -acetone) or via di- σ bonding of both the carbonyl C and O atoms ($\eta^2(\text{C,O})$ -acetone).⁴ Here we report the first detailed high-resolution vibrational spectroscopic characterization of stable surface-bound acetone enolate (CH_3COCH_2) fragments on a metal single-crystal surface produced by the reaction of either acetone or acetylacetone ($\text{CH}_3\text{COCH}_2\text{COCH}_3$) with clean and preoxidized Ni(111). The results obtained from reflection absorption infrared spectroscopy (RAIRS), isotopic substitution studies, and density functional theory (DFT) calculations unambiguously fingerprint the surface species present.

RAIRS experiments were performed in a newly built UHV chamber with a base pressure of $<2 \times 10^{-10}$ Torr coupled to a Nicolet Magna-IR 560 FTIR spectrometer with a narrow band MCT detector. The Ni(111) sample was cleaned by repeated Ar ion sputtering and annealing cycles. O-precovered surfaces were obtained by dissociative adsorption of O_2 on the clean crystal at 320 K, with the O coverages calibrated by RAIRS of the CO post-adsorbed surface.⁵

Exposing clean Ni(111) to a saturation dose (>0.2 L, $1 \text{ L} = 1 \times 10^{-6}$ Torr s) of CH_3COCH_3 at 260 K yields absorption bands at 1260, 1353, and 1545 cm^{-1} (Figure 1a) that are assigned to the mixed vibrational modes involving essentially the CC stretch $\nu(\text{CC})$, CH_3 symmetric deformation $\delta_s(\text{CH}_3)$, and CO stretch $\nu(\text{CO})$ of a surface-bound acetone enolate species. Repeating the experiment with CD_3COCD_3 results in little change in the frequencies of $\nu(\text{CC})$ and $\nu(\text{CO})$ but leads to the disappearance of the $\delta_s(\text{CH}_3)$ band (Figure 1b). The same sets of acetone enolate absorption bands are obtained if the Ni(111) surface is precovered with 0.1 monolayers of O prior to dosing the acetone isotopomers at 340 K (Figure 1, c and d). In this case, acetate and CO are also formed, as evidenced by their respective characteristic symmetric OCO stretching $\nu_s(\text{OCO})$ (1425 cm^{-1} for CH_3COO and 1415 cm^{-1} for CD_3COO) and carbonyl stretching $\nu(\text{CO})$ bands (1808 cm^{-1}). The acetate absorption bands are identical to those of acetate species

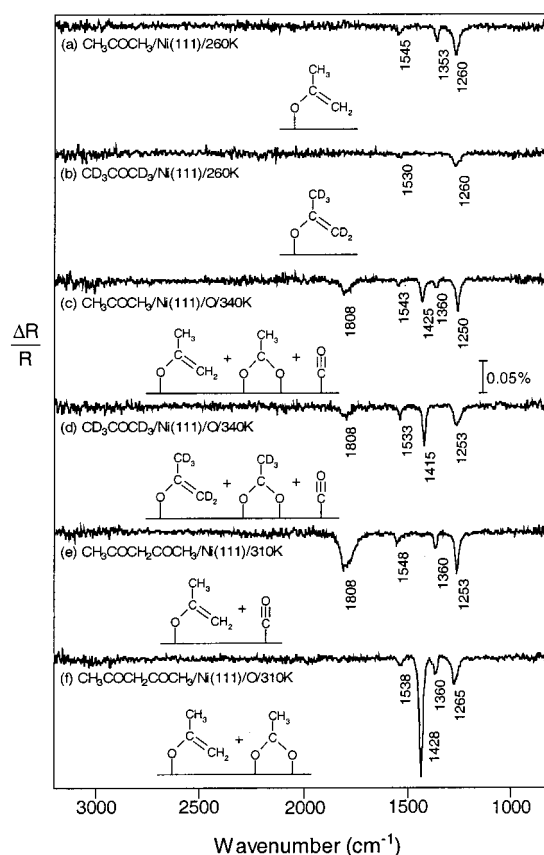


Figure 1. RAIR spectra of Ni(111) and Ni(111)/O exposed to >0.2 L of acetone or acetylacetone at the temperatures indicated.

produced from corroborative experiments involving acetic acid and acetyl bromide adsorption on preoxidized Ni(111) as shown in the Supporting Information. Acetone enolate can also be synthesized on Ni(111) at 310 K using acetylacetone as the precursor molecule as shown by the presence of the identical trio of absorption bands at 1253, 1360, and 1548 cm^{-1} (Figure 1, e and f). Here clean Ni(111) yields CO ($\nu(\text{CO})$ at 1808 cm^{-1}), while preoxidized Ni(111) gives acetate ($\nu_s(\text{OCO})$ at 1428 cm^{-1}) as byproducts of the surface reaction.

The interaction between acetone and a transition metal can give rise to a range of products, the most probable ones being $\eta^1(\text{O})$ -acetone, $\eta^2(\text{C,O})$ -acetone, $\eta^1(\text{C})$ -acetyl, $\eta^1(\text{C})$ -acetyl, $\eta^1(\text{O})$ -acetone enolate, and bridging $\mu(\text{C,O})$ -acetone enolate. To distinguish between these species, calculations utilizing the perturbative Becke-Perdew density functional method have been performed to predict the vibrational spectra of the energy-minimized structures of a series of model Ni complexes containing these ligands.⁶ The results as shown in the Supporting Information clearly demonstrate that only the computations for $\eta^1(\text{O})$ - and $\mu(\text{C,O})$ -acetone enolate

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complexes give rise to a pair of $\nu(\text{CC})$ and $\nu(\text{CO})$ bands at 1260–1264 and 1511–1574 cm^{-1} that remain essentially invariant on deuteration, plus a $\delta_s(\text{CH}_3)$ band that shifts from 1311–1312 to 1053–1065 cm^{-1} , in full agreement with the RAIRS observations.⁷

The other possible surface complexes can be effectively ruled out on the basis of the current DFT frequency calculations and vibrational spectra of these species on surfaces and in organometallic compounds. $\eta^1(\text{O})$ -acetone is predicted to have a $\nu(\text{CO})$ frequency of 1647 cm^{-1} , which is in fact observed at 1655 and 1682 cm^{-1} when acetone is dosed on clean and preoxidized Ni(111), respectively, below 180 K as shown in the Supporting Information. This vibrational mode has also been detected at 1638, 1670, 1665, and 1690 cm^{-1} on Pt(111),^{4a} Pd(111),^{4b} Rh(111),^{4c} and Ru(001)^{4d} respectively; and at 1680–1694 cm^{-1} for a range of complexes $[\text{M}((\text{bz})_2\text{SO})_4(\eta^1(\text{O})\text{-acetone})_2]^{2+}$ ($\text{M} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Zn}, \text{or Cu}$).⁸ For $\eta^2(\text{C},\text{O})$ -acetone, the $\nu(\text{CO})$ frequency is predicted to be 1191 cm^{-1} , which is consistent with that observed for complexes such as $\text{Ta}(\text{C}_5\text{Me}_5)_2\text{Me}_2(\eta^2(\text{C},\text{O})\text{-acetone})$ (1200 cm^{-1})⁹ and $\text{W}(\eta^2(\text{C},\text{O})\text{-acetone})_2\text{Cl}_2(\text{PMePh}_2)_2$ (1230 cm^{-1}).¹⁰ However, higher $\nu(\text{CO})$ frequencies have been reported for the complex $[\text{Os}(\text{NH}_3)_5(\eta^2(\text{C},\text{O})\text{-acetone})]^{2+}$ (1330 cm^{-1}),¹¹ as well as $\eta^2(\text{C},\text{O})$ -acetone species adsorbed on Pd(111) (1435 cm^{-1}),^{4b} Rh(111) (1380 cm^{-1})^{4c} and Ru(001) (1300 cm^{-1}).^{4d} In the case of $\eta^1(\text{C})$ -acetyl, the calculated $\nu(\text{CO})$ frequency is 1634 cm^{-1} , again in excellent agreement with adsorbed acetyl species on a Rh catalyst surface (1693 cm^{-1})¹² and a range of PtX(acetyl)(PEt₃)₂ and PdX(acetyl)(PEt₃)₂ complexes (1629–1675 cm^{-1}).¹³ The $\eta^1(\text{C})$ -acetyl species is similar to acetone enolate in structure, except that it binds via the terminal C atom and has an expected $\nu(\text{CO})$ frequency of 1634 cm^{-1} , as is indeed observed at 1632–1636 cm^{-1} for a series of Pd($\eta^1(\text{C})$ -acetyl)L₂Cl complexes (L₂ = tmeda, phen, bpy, or dbbpy)¹⁴ and at 1636 cm^{-1} for Pt($\eta^1(\text{C})$ -acetyl)(bpy)-Cl.¹⁵

The existence of surface-bound acetone enolate has been previously postulated on the basis of infrared spectroscopic studies of acetone adsorption on various metal oxide catalysts. Absorption bands reported at 1558, 1540, and 1543–1595 cm^{-1} have been assigned to $\nu(\text{CO})$ of acetone enolate on NiO,^{2a} Fe₂O₃,^{2b} and Al₂O₃,^{2c,d} respectively. Organometallic complexes containing $\eta^1(\text{O})$ - and $\mu(\text{C},\text{O})$ -acetone enolate ligands are also known, with characteristic $\nu(\text{CO})$ frequencies observed for Ru(PMe₃)₄(H)($\eta^1(\text{O})$ -acetone enolate) (1579 cm^{-1}),¹⁶ [Pd($\mu(\text{C},\text{O})$ -acetone enolate)X]_n (X = Cl or I, 1554–1565 cm^{-1}),¹⁵ and (PdX)₂($\mu(\text{C},\text{O})$ -acetone enolate)₂ (X = *o*-C₆H₄CH₂NMe₂ or (AsPh₃)(C₆F₅), 1554–1560 cm^{-1}).¹⁷ These $\nu(\text{CO})$ frequencies fully corroborate with the values predicted for the model complexes (1511–1574 cm^{-1}) and the RAIR spectra acquired for the species on the Ni(111) surface (1545 cm^{-1}).

On the basis of the surface reaction products, we propose the following mechanisms for the formation of acetone enolate on Ni(111), which are consistent with the known abilities of Ni¹⁸ and O¹⁹ to activate C–C, C–H, and O–H bond scission. For acetone, the hydroxyl proton of the enol tautomer is abstracted by either Ni or basic O atoms to yield the enolate and H or OH, respectively.²⁰ This process is expected to be facile as acetone enol ($\text{p}K_a = 11$)²¹ is more acidic than methanol ($\text{p}K_a = 15$),²² which readily deprotonates on both clean and preoxidized Ni(111) surfaces.²³ In addition, the O atoms can nucleophilically attack the carbonyl group to yield acetate and CH₃, with the latter being further oxidized to CO. In the case of acetylacetone, C–C bond cleavage occurs to give acetone enolate and acetyl. On the clean surface, acetyl further

decomposes to CO, while on the preoxidized surface, it is scavenged by O to form acetate. The nucleophilic addition of O to the carbonyl groups of aldehydes and ketones on transition-metal surfaces is well documented,¹⁹ and we have observed similar behavior of O on Ni(111) toward other compounds such as acetaldehyde and acetyl bromide to produce acetate species.

The isolation and identification of acetone enolate on Ni(111) is not altogether unexpected, given its implicit role in heterogeneously catalyzed acetone condensation reactions.² Its unequivocal detection in this work is a result of optimization of the adsorption temperature for its maximum yield and accountability for the spectroscopic features of all surface species present. The ability to generate it from more than one precursor molecule suggests that several routes may be available for the preparation of surface-stabilized enolate species of a more general nature for synthetic purposes.

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Supporting Information Available: RAIR spectra of acetate and $\eta^1(\text{O})$ -acetone on Ni(111); computed frequencies and assignments for model Ni complexes (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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