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# Selective C−C Bond Activation of Methyl Pyruvate on Ni(111) to Yield Surface Methoxycarbonyl

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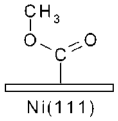
The preferential activation of CC bonds using transition metal complexes relies heavily on driving forces such as the release of ring strain energy in the reactant, the introduction of aromaticity in the product, or the eventual liberation of products such as $H_2$ or $CH_4$. In the absence of these driving forces, the preferential cleavage of CC over CH bonds is rarely favored despite the fact that CH bonds are stronger than CC bonds by about 10 kcal mol$^{-1}$. CC bond activation is disfavored because the CH bonds are more abundant and more easily accessible, and also because the highly directional nature of the sp$^3$ C hybrid orbital leads to an energy barrier for CC bond breaking that is about 6−12 kcal mol$^{-1}$ greater than that for CH bond activation.[1,2] Herein we present reflectance-infrared (RAIRS) and static secondary ion mass spectrometry data showing the preferential CC bond scission of methyl pyruvate, $CH_3COCOOCH_3$, on Ni(111). Apart from providing a new case of selective CC bond breaking, this surface reaction leads to the first report of the isolation and spectroscopic identification of surface methoxycarbonyl (**1**). The proposed dissociation mechanism is also, we believe, relevant to an understanding of the enantioselective hydrogenation of α- and *β*-ketoesters on chirally modified metal particles.[3] The experiments were performed using standard ultrahigh vacuum procedures.[3d]



**(1)**

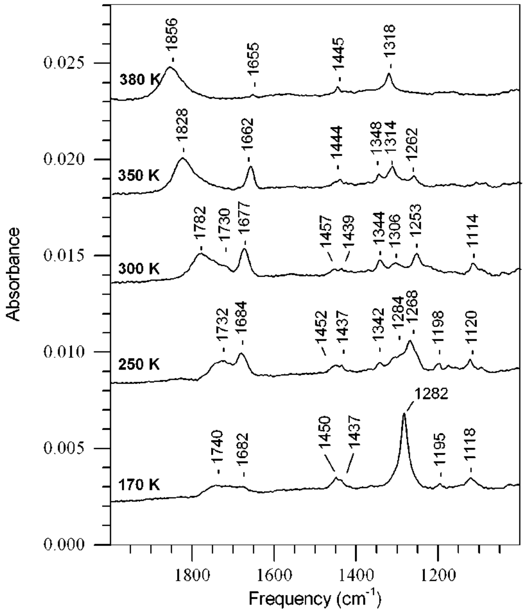


**Figure 1.** RAIRS spectra of methyl pyruvate on Ni(111) acquired at 105 K following anneals to the specified temperatures. The initial exposure at 105 K was sufficient to populate the multilayer. The 170 K spectrum is characteristic of *cis*-adsorbed molecular methyl pyruvate.[3d]

**Table 1.** Comparison of Vibrational Data for Adsorbed Methoxycarbonyl Species Prepared by Annealing Methyl Pyruvate on Ni(111) to 300−325 K with Data for Free Methyl Pyruvate and Methyl Acetate

| | assignment | frequency data for comparison | |
|---|---|---|---|
| band frequency (cm$^{-1}$) | methoxycarbonyl on Ni (111) | methyl pyruvate[a] | methyl acetate[b] |
| 3050 | $\nu_a(OCH_3)$ | 3035 | 3028 |
| 2969 | $\nu_s(OCH_3)$ | 2958 | 2955 |
| 1677 | $\nu(C{=}O)$ | | |
| 1457 | $\delta_a(OCH_3)$ | 1448 | 1462 |
| 1439 | $\delta_s(OCH_3)$ | 1438 | 1438 |
| 1253 | $\nu(C{-}OCH_3)$ | 1299 | 1249 |

[a] Reference 6. [b] Reference 7.

Figure 1 displays a sequence of RAIRS (reflectance absorbance infrared spectroscopy) spectra obtained by exposing clean Ni(111) to multilayer methyl pyruvate at 105 K and annealing the sample to the indicated temperatures. Only molecularly adsorbed methyl pyruvate is present at 210 K.[3d] The intense band at 1282 cm$^{-1}$ may be assigned to the C−O stretching mode of chemisorbed *cis*-methyl pyruvate.[3d] The initial decomposition step for methyl pyruvate on Ni(111) occurs at approximately 250 K and leads to a severe attenuation of the $\nu$(C−O) band and its replacement by a band at 1268 cm$^{-1}$, the emergence of peaks at 1684, 1342 and 1116 cm$^{-1}$ and, as shown in the Supplementary Information, sharp $\nu$(CH) bands at 3050 and 2969 cm$^{-1}$. All of the latter bands except the one at 1116 cm$^{-1}$ simultaneously disappear on annealing above 360 K; the band at 1116 cm$^{-1}$ disappears at around 330 K. The intense carbonyl band at 1684 cm$^{-1}$ is characteristic of both alkoxycarbonyl[4] and acetyl ligands.[5] For example, bis-methoxycarbonyl platinum,[4a] palladium alkoxycarbonyl[4b] and platinum aryloxycarbonyl[4c] complexes all display carbonyl bands in the 1650−1680 cm$^{-1}$ region. The band at 1268 cm$^{-1}$ (shifted to 1253 cm$^{-1}$ at 300 K) is attributed to the $\nu$(C−O) vibration of methoxycarbonyl, by analogy to data (Table 1) for methyl pyruvate[3d,6] and methyl acetate.[7] Similarly, the bands at 3050 and 2969 cm$^{-1}$ are very close in frequency to CH stretching vibrations of the $O{-}CH_3$ group of methyl pyruvate and methyl acetate. The simultaneous detection of acetyl and methoxycarbonyl surface groups would be a reasonable proof of selective scission of the central CC bond. Surface acetyl groups on Ni(111) prepared from 2,3-butanedione decomposition[8] display a relatively weak broad band at approximately 1664 cm$^{-1}$ and hence may be hidden by the intense carbonyl band due to methoxycarbonyl in the present case. Temperature-resolved SSIMS data (Figure 2), however, distinguish between surface methoxycarbonyl (**1**) and surface acetyl in a way that is consistent

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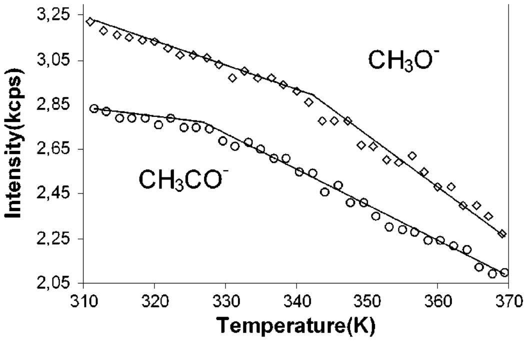

**Figure 2.** SSIMS data for the temperature dependence of the $CH_3O$ and $CH_3CO$ negative ion signals for methyl pyruvate on Ni(111).

with the temperature-resolved RAIRS data. The SSIMS $OCH_3$ negative ion signal, which in the absence of RAIRS evidence for methoxy groups is taken to be characteristic of methoxycarbonyl, displays a change in slope at 345 K. This corresponds to the temperature at which the intensity of the RAIRS bands assigned to methoxycarbonyl begin to decrease rapidly in intensity. Similarly, the change in slope of the $CH_3CO$ negative ion intensity plots occurs at 325 K, simultaneous to the removal of the RAIRS bands at 1720 and 1116 $cm^{-1}$. The presence of a weak $\nu$(CH) band at 2989 $cm^{-1}$ (Supporting Information) up to 325 K is also consistent with the presence of acetyl groups, since the most intense $\nu$(CH) band for $CH_3CO$ on Rh particles appears at 2984 $cm^{-1}$.[9] Indirect evidence for the presence of acetyl groups is provided by the RAIRS bands arising from hydrocarbon fragments deposited on the surface. Of the two hydrocarbon bands that remain on annealing methyl pyruvate exposed Ni(111) to 380 K (Figure 1), the relatively intense band at 1318 $cm^{-1}$ is most likely due to the symmetric $CH_3$ deformation of a species containing both CC bonds and a $CH_3$ group.[10,11] This generic assignment suggests that surface acetyl releases methyl groups to the surface, and that the methyl groups undergo CC coupling reactions to give the species displaying the observed hydrocarbon bands. This interpretation is consistent with the chemistry of acetyl on Pd(111)[12] and the chemistry of methyl on Pt(111),[13] and provides indirect evidence for the presence of acetyl groups. Both methoxycarbonyl and acetyl undergo decarbonylation generating the intense $CO_{ads}$ peak at 300−380 K in Figure 1. The onset for decarbonylation is highly coverage-dependent as may be seen from the data shown in Figure 3. The coverage dependence is discussed in a separate publication.[10] RAIRS data specific to a monolayer of methyl pyruvate on Ni(111) are included as Supporting Information.

We propose the following mechanism for the selective CC bond scission of methyl pyruvate on Ni(111). The organometallic literature on selective CC bond activation point to the role of carbonyl groups in activating adjacent CC bonds.[1,14] The CC bond in methyl pyruvate is situated between two carbonyl groups. There is little conjugation, however, between the carbonyl functions, and the central C−C bond length is typical for a single bond.[15] The organometallic literature also points to the role of chelating or proximity effects in CC bond activation.[1,16] Methyl pyruvate on Ni(111) can achieve the latter effect perfectly. We have previously shown that methyl pyruvate adopts the *cis*-conformation on Ni(111) with the molecular plane oriented perpendicularly to the surface,[3d] thereby implying facile rotation about the CC bond. Further, the strongest chemisorption interaction is through the keto carbonyl-surface bond.[17] The facile rotation about the CC bond observed at 105 K for 2,3-butanedione on Ni(111) is due to the noncovalent molecule surface interaction possible for the half-rotated structure.[8] For methyl pyruvate attached to Ni(111) via the keto carbonyl, the noncovalent interaction in question is that between the methoxycarbonyl moiety, twisted out of the molecular plane, and the extended metal. Since little energy is required to change the C−O−Ni angle in the lone pair Lewis acid-type bonding of the keto-carbonyl to the surface,[18] the noncovalent interaction between $COOCH_3$ group and the surface can tilt the CC bond toward the surface, thereby achieving ideal nonobstructed proximity conditions. The coordinative unsaturation of the extended metal surface then permits facile CC scission. This interpretation is, of course, consistent with the use of Lennard-Jones potential plots to explain the low or zero activation energy barriers in many dissociative chemisorption processes. Since both α- and $\beta$-ketoesters are dicarbonyls, the present study suggests they can undergo reactions in which one carbonyl serves to attach the molecule to the surface while the other side of the molecule rotates into the geometries leading to reaction. This type of structural effect should be considered in mechanistic proposals for their asymmetric hydrogenation on chirally modified surfaces.[19]

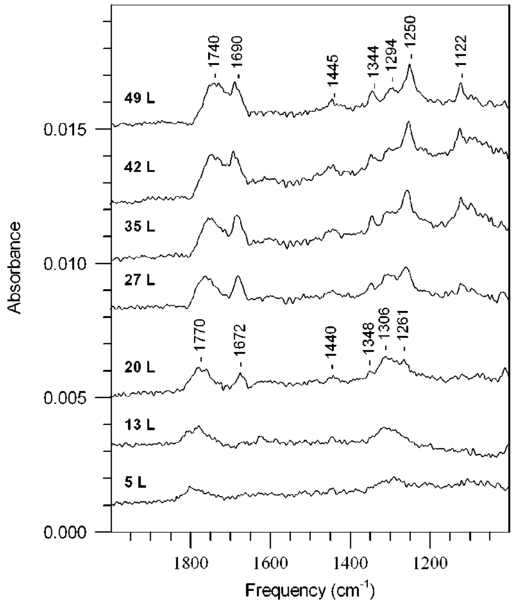

**Figure 3.** Sequential RAIRS spectra recorded with the sample held at 250 K in a background pressure of $1 \times 10^{-8}$ Torr.

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**Supporting Information Available:** CH stretching region RAIRS spectra; monolayer RAIRS spectrum at 105 and 300 K (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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