INFRARED SPECTRA OF METHYL ISOCYANIDE CHEMISORBED ON RHODIUM (U)

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The chemisorption of CH$_3$NC on dispersed Rh supported on Al$_2$O$_3$ has been investigated using transmission infrared spectroscopy. Evidence for the chemisorption of undissociated CH$_3$NC is presented. It is shown that at 300K the isomerization of CH$_3$NC to CH$_3$CH does not occur on Rh. The spectra obtained for adsorbed CH$_3$NC suggest an analogous chemistry of the Rh surface sites to that found in organometallic chemistry.
INFRARED SPECTRA OF METHYL ISOCYANIDE CHEMISORBED ON RHODIUM

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The similarity between the inorganic chemistry of the carbon monoxide ligand and the isocyanide ligand is well known.\(^1\) In transition metal carbonyl chemistry, CO ligands and isocyanide ligands are often interchangeable moieties. To date, the extension of this analogy to surface chemistry has not been fully tested. Although some work on the chemisorption and thermal properties of adsorbed methyl isocyanide on nickel has been reported,\(^2\) local bonding properties have not been examined. Since CO and \(\text{CH}_3\text{NC}\) are isovalent, and as their frontier orbitals are strikingly similar,\(^3\) we have investigated the chemisorptive binding of methyl isocyanide to a metal whose local bonding to CO is well-documented. In this note, we report the observation of the infrared spectrum of methyl isocyanide chemisorbed by rhodium supported on \(\text{Al}_2\text{O}_3\).

Methyl isocyanide was synthesized by established methods,\(^4\) and its purity was verified by infrared spectroscopy on the gas. Preparation of the supported metal sample by hydrogen reduction has been described elsewhere.\(^5\) The highly dispersed rhodium is 2.8% by weight in the \(\text{Rh/Al}_2\text{O}_3\) samples. Upon cooling the reduced Rh sample to room temperature, a background spectrum was recorded on a Perkin-Elmer Model 180 infrared spectrometer. After exposure of the sample to 3 torr equilibrium pressure of \(\text{CH}_3\text{NC}\) vapor, the cell was evacuated and a second spectrum was recorded. Control \(\text{CH}_3\text{NC}\) adsorption experiments on pure \(\text{Al}_2\text{O}_3\) were carried out at 300K following the same thermal and \(\text{H}_2\) treatment used to prepare the supported Rh.

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Comparison of the spectra obtained at 300°K on Al₂O₃ and on Rh/Al₂O₃ is shown in Figure 1b and 1c. Predominant features in the Rh sample are clearly absent in the Al₂O₃ spectrum. Carbon-hydrogen stretching modes are observed at 3003(s), 2946(s), 2918, 2883, 2861, and 2813 cm⁻¹. The features between 2300 and 2100 cm⁻¹ are assigned to N≡C, as is the feature at 1910 cm⁻¹. For liquid CH₃NC the C≡N stretching mode is at 2161 cm⁻¹. The bands at 1448(s), 1415(s), and 1391 cm⁻¹ are assigned to CH₃ bending modes. Comparable CH₃ modes for liquid CH₃NC are at 3002 and 2951 cm⁻¹ and 1456 and 1414 cm⁻¹.

Subsequent exposure to 50 torr of CO is shown in Figure 1d. A single new feature at 2020 cm⁻¹ is observed. The low intensity of this CO feature and the absence of the well-established intense spectrum of CO on Rh/Al₂O₃ indicates that methyl isocyanide has almost completely blocked specific Rh-CO binding sites.

Similar chemisorption experiments were conducted with methyl cyanide (CH₃CN). At 300K, no spectral features associated with CH₃CN adsorption on Rh were detected at 10 torr pressure. Following this experiment, the CH₃CN(g) was pumped away and CO chemisorption was carried out. The CO spectrum which developed was identical to that found for freshly prepared rhodium surfaces. The absence of spectral features for CH₃CN and the capacity of the surface for CO adsorption following CH₃CN exposure suggests that CH₃CN is not chemisorbed by Rh at 300°K. These results, when combined
with the evidence for strong CH$_3$NC chemisorption and CO-blockage by the CH$_3$NC(ads) suggest the absence of surface-induced isomerization of CH$_3$NC to CH$_3$CN at 300°K, a process which is ~63 kJ mole$^{-1}$ exothermic in the gas phase, with an activation energy of 161 kJ mol$^{-1}$.6

The possibility that the methyl isocyanide dissociates to CH$_3$ and CN fragments on the metal sites has also been addressed. Confirmation of the lack of dissociation of CH$_3$NC on Rh at 300K was obtained by comparison of the CH$_3$ (stretching and bending) features for Rh-CNCH$_3$ and physisorbed CH$_3$NC on Al$_2$O$_3$ at 190°K. In both regions the primary spectral features agree to within 10 cm$^{-1}$, although major changes are observed in relative band intensity within the C-H bending region.

These preliminary results indicate that at least in the Rh/Al$_2$O$_3$ system, the analogy between the chemistry of CO and isocyanides can be extended to surfaces. Experiments are underway to further explore the behavior of isocyanides on supported metals and on single crystals.
REFERENCES


Figure 1. Infrared spectra at 300K for CH$_3$NC on Rh/Al$_2$O$_3$. Spectrum (a): Background spectrum of Al$_2$O$_3$ (11.4 mg/cm$^2$) following H$_2$ reduction; spectrum (b): Saturation coverage of CH$_3$NC on Al$_2$O$_3$ followed by evacuation; spectrum (c): CH$_3$NC saturation of 2.8% Rh/Al$_2$O$_3$ (16.3 mg/cm$^2$) followed by evacuation; spectrum (d): Addition of ~50 torr CO to (c).
INFRARED SPECTRUM OF CH₃NC CHEMISORBED ON Rh SUPPORTED ON Al₂O₃

T = 300 K

-CH₃ (str)
-N≡C (str)
-C≡O
-CH₃ (bend)
-N≡C (str)

WAVENUMBER (cm⁻¹)