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Coordination of NH_3 and C_2H_4 onto $W(CO)_5$ in the Gas Phase

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The coordination process of NH_3 and C_2H_4 onto "naked" $W(CO)_5$, having one coordinatively unsaturated site, was investigated using a laser-based time-resolved infrared absorption spectroscopy in the gas phase. $W(CO)_5$, selectively prepared by a pulsed 355-nm laser photolysis of $W(CO)_6$, was observed to react with either reactant gas L to make a simple coordination complex, $W(CO)_5(L)$, where L is NH_3 or C_2H_4.

Recent studies of pulsed UV laser photolysis of transition metal carbonyls in the gas phase have elucidated their primary photophysical and photochemical processes and also provided a convenient means for selective production of "naked" coordinatively unsaturated sites, which are free from the effects of surrounding molecules such as solvent.[1)] If an appropriate reactant molecule is added to the gaseous photolysis system of metal carbonyl, the coordination process of the molecule onto the photoproduced "naked" coordinatively unsaturated site(s) can be directly pursued by a time-resolved spectroscopy.

Ammonia and ethylene are typical σ-donor and π-acceptor ligands and a considerable amount of spectroscopic works concerning $W(CO)_5(NH_3)$ or $W(CO)_5(C_2H_4)$ in the condensed phase have been published.[2,3)] However, none of their infrared absorption spectra in the gas phase has been reported probably owing to their thermally instability. In this letter, we report the direct observation of coordination process of NH_3 and C_2H_4 onto $W(CO)_5$ and the infrared absorption spectra of resultant $W(CO)_5(NH_3)$ and $W(CO)_5(C_2H_4)$ in the C–O stretching frequency region in the gas phase at room temperature. The C–O stretching frequencies of transition metal carbonyl compounds are well known to be very sensitive to the oxidation state on the metal center.[4)] As the oxidation state varies with number of coordinatively unsaturated sites or with coordination species, the observation of C–O stretching frequencies has an good potentiality to provide information about interaction between "unsaturated" transition metal center and coordination molecules, that is, *d*-orbitals and ligand's molecular orbitals.

The experimental setup of laser-based time-resolved infrared absorption (TRIR) spectroscopy employed in this study consists of a home-made liquid-N_2 cooled cw-CO

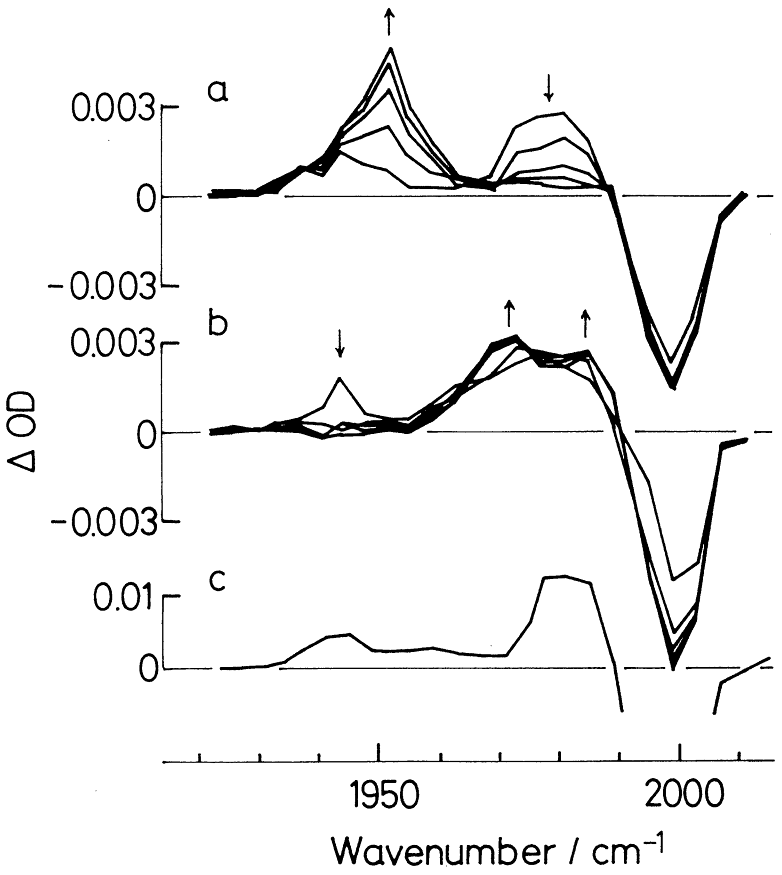

Fig.1. TRIR spectra following the 355-nm laser photolysis of mixtures of $W(CO)_6$ and NH_3 (a) and C_2H_4 (b) in Ar buffer gas. The five spectra (a) were taken at 1.0-μs intervals over a 1.0 - 5.0 μs range and the five spectra (b) at 0.4-μs intervals over a 0.4 - 2.0 μs range. The spectrum (c) illustrates the absorption of "fully relaxed" $W(CO)_5$ in the gas phase. An up arrow indicates an increase of ΔOD and a down arrow a decrease.

laser (spectral range, 1650 - 2050 cm^{-1}; spectral resolution, ca. 4 cm^{-1}) as a monitoring infrared source and a pulsed Nd:YAG laser (Spectron SL803, λ = 355 nm) as a UV photolysis source, which is similar to an existing TRIR spectroscopy apparatus.[5-7] The accuracy of the CO laser wavenumber, monitored with a calibrated monochromator (Ritsu Ouyou-Kougaku Co., MC-20L), was estimated to be less than ± 4 cm^{-1}. TRIR difference absorption spectra are constructed from a series of kinetic absorption measurement using a fast infrared detector system (≈ 800 ns rise time). The gases, $W(CO)_6$ (Alfa), ethylene (Takachiho Co., ≥ 99.9%), ammonia (Nihon Sanso Co., ≥ 99.999%), and Ar (Air Products, Research grade), were used without further purification except several degassing. A gas flow cell was employed to prevent metal deposition on the windows.

Figure 1a shows the TRIR spectra observed following 355-nm laser photolysis of $W(CO)_6$(≈ 10 mTorr)(1 Torr = 133.322 Pa) in the presence of NH_3(≈ 0.1 Torr) at a total pressure of 4.0 Torr, balance Ar. The TRIR spectrum observed at 1 μs shows the photoproduction of "hot" $W(CO)_5$ with broad bands at ca. 1980 and 1942 cm^{-1} associated with the decomposition of $W(CO)_6$, corresponding to ΔOD decrease at ca. 1999 cm^{-1}. Shown in Fig.1c for comparison is the "fully relaxed" $W(CO)_5$ absorption spectrum obtained in the similar photolysis of "neat" $W(CO)_6$ in Ar buffer gas. The 1942-cm^{-1} band has been assigned as the low-frequency band of the A_1 mode and the 1980-cm^{-1} band as the E mode of C_{4v} symmetry.[8)] As Ar, used as buffer gas, does not coordinate on

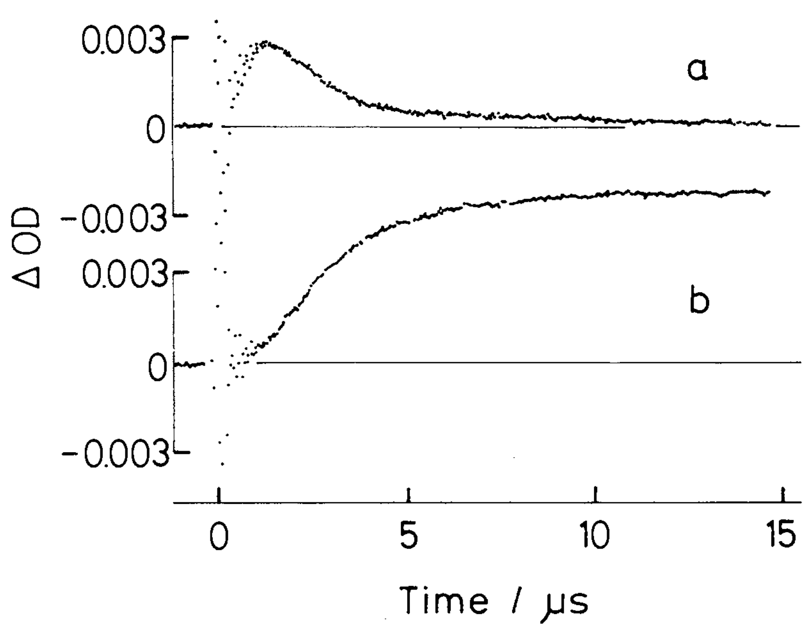

Fig.2. Typical transient absorptions following the 355-nm laser photolysis of $W(CO)_5$ in the presence of NH_3 in Ar buffer gas: (a) $W(CO)_5$ monitored at 1981 cm^{-1}; (b) $W(CO)_5(NH_3)$ monitored at 1952 cm^{-1}. The rapid initial spikes are due to an electromagnetic interference from the photolysis laser.

$W(CO)_5$ at room temperature,[9)] the species which has these two absorption bands can be considered as a "naked" $W(CO)_5$. In the presence of NH_3 (Fig.1a), a new absorption band centered at 1950 cm^{-1}, with a shoulder around 1940 cm^{-1} (not obvious owing to the overlap with the intense absorption band), has grown up along with the decrease of $W(CO)_5$ band(s). Typical time dependence of absorption features at 1981 cm^{-1} (identified with $W(CO)_5$) and at 1952 cm^{-1} are shown in Fig.2. The decay of $W(CO)_5$ well corresponds to the production of the new complex and also both rates linearly depend on the NH_3 pressure with a similar slope. These experimental results suggest that the new complex can be

$$W(CO)_5 + NH_3 \rightarrow W(CO)_5(NH_3) \qquad (1)$$

reasonably assigned to a simple coordination compound $W(CO)_5(NH_3)$. In the presence of C_2H_4($\approx$ 0.4 Torr)(Fig.1b), the transient spectrum development in the early-time region ($\leq$ 1 μs) is similar to those observed in the absence of reactant, where the "hot" $W(CO)_5$ is relaxed. In the later-time region (> 1 μs), the bands attributable to "naked" $W(CO)_5$ gradually disappear and synchronously new absorption bands grow up at 1985 and 1968 cm^{-1}. Kinetic analysis also supports the assignment of these two absorption bands to

$$W(CO)_5 + C_2H_4 \rightarrow W(CO)_5(\eta^2\text{-}C_2H_4) \qquad (2)$$

$W(CO)_5(\eta^2\text{-}C_2H_4)$. From the comparison with the infrared absorption frequencies of $W(CO)_5(\eta^2\text{-}C_2H_4)$ in hexane solution at room temperature (1953(E) and 1973 $cm^{-1}(A_1)$),[2a)] the bands centered at 1985 and 1968 cm^{-1} are assigned to a low frequency A_1 and E symmetry C-O stretching modes, respectively.

When the $W(CO)_5$ is bonded to a strong σ-donor ligand such as NH_3, the frequency for E_1 mode (equatorial C–O stretching) are lowered (1980 → 1950 cm^{-1}) but that for A_1 mode (axial C–O stretching) does not show a large shift. This can be interpreted by the interaction of a direct overlap of the σ-orbital of NH_3 with the a_1-orbital (mixing of π^*(equatorial CO) and 5d),$^{10)}$ resulting in a weakening of equatorial C–O bonds. On the other hand, the coordination of π-acceptor such as C_2H_4 decreases somewhat the E_1 mode frequency (1980 → 1968 cm^{-1}) and increases appreciably the A_1 mode frequency (1942 → 1985 cm^{-1}). It suggests that the main interaction exists in an overlap of π^*-orbital of C_2H_4 and the e-orbital (mixing of 5d and π^*(axial CO)). Then a bond strength of axial C–O increases owing to an electron flow from π^*-orbital of axial CO to π^*-orbital of C_2H_4.

The coordination rate constants for both reactions 1 and 2 are tentatively estimated to be about (1.4 ± 0.2) and (0.7 ± 0.2) $\times 10^{-10}$ $molecule^{-1}$ cm^3 s^{-1}, respectively. However, the absolute pressure of reactants in the reaction cell is not certain because of the use of a gas flow cell. A more precise kinetic study is now being performed.

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