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Infrared Evidence for Reversibility in the Formation of Surface Carbonyl Complexes

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Received August 4, 1975 AIC50581V

Molybdenum hexacarbonyl adsorbed on γ-alumina is a heterogeneous catalyst for olefin metathesis when suitably activated.[1,2] A previous infrared study[3] showed that activation by mild heating in vacuo causes decomposition of the $Mo(CO)_6$, which occurs in a complex fashion through formation of several unidentified molybdenum subcarbonyl species. Recently, Brenner and Burwell[4] reported measurements of CO evolution during activation of $Mo(CO)_6$ on Al_2O_3 which confirmed the formation of stoichiometric surface molybdenum carbonyls and indicated that the decomposition of $Mo(CO)_6$ may be reversed under suitable conditions. Further infrared evidence is presented here in support of the contention that formation of surface carbonyl species is reversible.

Experimental Section

$Mo(CO)_6$, $Cr(CO)_6$, and $W(CO)_6$ were supplied by BDH Ltd. The γ-Al_2O_3 and SiO_2 supports were prepared as previously described.[3] Carbon monoxide labeled with ^{13}C (95%) was supplied by Merck Sharp and Dohme. Pressed wafers (10–20 mg cm^{-2}) of Al_2O_3 or SiO_2 were supported in a stainless steel sample holder mounted at the base of a cold finger in a Pyrex cell fitted with NaCl windows and connected to a vacuum line. The pressure inside the cell was monitored with a Penning gauge protected from hexacarbonyl vapor with a liquid nitrogen trap. The sample holder could be heated to 300°C. A Pyrex inlet tube leading from a reservoir of the appropriate hexacarbonyl terminated close to the sample holder. Spectra were recorded on a Perkin-Elmer 225 spectrophotometer equipped with an auxiliary recorder for absorbance and expanded transmittance scale measurements. A reduced source intensity was used to minimize the heating effect of the infrared beam, and spectra were recorded over the range 1600–2300 cm^{-1} with a spectral slit width of 5 cm^{-1}.

Al_2O_3 or SiO_2 wafers were outgassed at 25°C at a pressure of 10^{-5} Torr[5] and then cooled to ca. −100°C with liquid nitrogen in the cold finger. Hexacarbonyl vapor (at 25°C) was admitted through the inlet tube and allowed to condense on the sample holder and cold finger. Spectra were then recorded while warming to 45°C, the ambient temperature in the infrared beam, in vacuo, and on subsequent exposure to CO.

Results and Discussion

Figure 1 shows spectra recorded during warm-up of $Mo(CO)_6$ on Al_2O_3 in vacuo. After exposure to $Mo(CO)_6$ at −100°C the spectrum showed only a single very weak band at 2000 cm^{-1}. Most of the added $Mo(CO)_6$ is initially condensed on the colder surface of the liquid nitrogen cold finger, and only after warming above about −30°C does the vapor pressure of $Mo(CO)_6$ become sufficiently high (10^{-3} Torr at −20°C) for adsorption onto the Al_2O_3 surface warmed by the infrared beam to occur. At −30°C a single band appeared at 1985 cm^{-1}, which was immediately followed on further warming by the appearance of the complex series of bands in Figure 1. At the same time, the dynamic pressure in the cell increased from 10^{-5} to around 10^{-3} Torr, indicating evolution of CO and suggesting that the $Mo(CO)_6$ begins to decompose immediately following adsorption onto the Al_2O_3, at about −10°C. After warming to 45°C the pressure returned to 10^{-5} Torr and the spectrum showed the four bands described previously[3] which are stable to prolonged pumping at 45°C. The series of bands occurring at lower temperatures, evidently due to unstable carbonyl species, have not been previously observed.

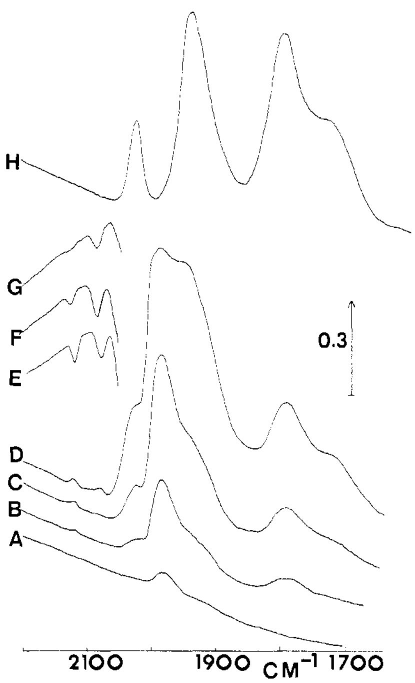

Figure 1. Infrared spectra in the ν(CO) region during warm-up of $Mo(CO)_6$ on Al_2O_3. Spectra recorded at (A) −20°C, (B) −10°C, (C) 0°C, (D) 10°C, (E) 15°C, (F) 20°C, (G) 25°C, and (H) 45°C, in vacuo, on a linear absorbance scale, except for (E)–(G) which were recorded on a 2X expanded transmittance scale.

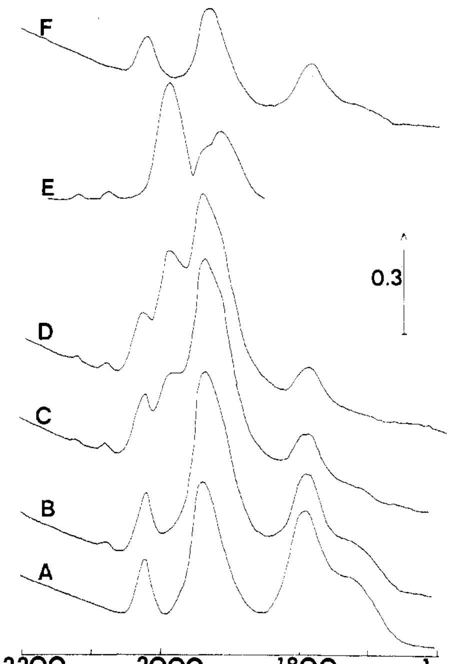

Figure 2. Infrared spectra in the ν(CO) region after exposure to CO: (A) sample from Figure 1 outgassed at 60°C for 1 hr, (B) sample exposed to 4 Torr of CO at 45°C for 5 min, (C) sample exposed to 65 Torr of CO for 5 min, (D) sample exposed to 65 Torr of CO for 1 hr, (E) difference spectrum of (D) − (A), (F) sample evacuated at 45°C for 5 min. Linear absorbance scale is used.

A clearer picture of the decomposition process is gained by examining the changes in the spectra on exposure to CO. Figure 2 shows spectra recorded after warming $Mo(CO)_6$ on Al_2O_3 to 45°C in vacuo and then exposing to CO. The 2120- and 2075-cm^{-1} bands observed during warm-up were restored in the presence of CO. Of the stable carbonyl bands, those at 2020 and 1935 cm^{-1} were relatively unaffected by CO,

Table I. Observed ν(CO) Bands[a]

Species	M = Mo ^{12}CO	M = Mo ^{13}CO	M = W ^{12}CO	M = Cr ^{12}CO
$M(CO)_6$(ads) on Al_2O_3 or SiO_2	2120 w	*b*	2120 w	2120 w
	1985 s	1950	2015 sh	2015 sh
			1980 s	1980 s
$M(CO)_5$ on Al_2O_3	2075 w	2030		
	1950 sh	1900		
	1910 m	1860		
$M(CO)_x$ on Al_2O_3, "stable species"	2020 m	1970		
	1935 s	1895		
	1790 s	1755		
	1725 sh	1695		

[a] Frequencies in cm^{-1}, ±5 cm^{-1}. [b] Not observed.

whereas the 1790- and 1725-cm^{-1} bands were significantly reduced in intensity. New bands between 1850 and 2050 cm^{-1} can be seen by subtracting the spectrum recorded in vacuo from the spectrum in CO (on an absorbance scale), as in trace E, which shows new bands at 1985, 1950 (sh), and 1910 cm^{-1}. The intensities of the bands at 2075, 1950, and 1910 cm^{-1} fell in a constant ratio with several different samples and were relatively insensitive to the CO pressure and time of exposure to CO. The 2120- and 1985-cm^{-1} bands, on the other hand, were considerably enhanced at higher CO pressures and increased in intensity on standing in CO for several hours. Evacuation at 45°C after exposure to CO at low pressures (below 10 Torr) restored the original spectrum, but after exposure to higher CO pressures the carbonyl bands restored on evacuation were considerably reduced in intensity (trace F). This reduction in intensity could be continued by repeating the CO exposure and evacuation cycle.

The new species formed on exposure to CO are identical with those observed during the initial decomposition of $Mo(CO)_6$. The bands at 2075, 1950, and 1910 cm^{-1} are attributed to a pentacarbonyl species with C_{4v} symmetry, $Mo(CO)_5L$, where L is an OH group on the alumina surface, as discussed previously.[3] The bands at 2120 and 1985 cm^{-1} are attributed to $Mo(CO)_6$ physically adsorbed on alumina. Octahedral $Mo(CO)_6$ has Raman-active carbonyl vibrations at 2114 cm^{-1} (A_{1g}) and 2005 cm^{-1} (E_g) in addition to the infrared-active T_{1u} vibration at 1990 cm^{-1}.[6] Interaction with the surface will lower the symmetry of the molecule and may allow one or both of the Raman-active vibrations to become infrared active.

Exposure of the stable carbonyl species to ^{13}CO gave the same changes in the spectrum with all of the bands shifted by the expected amounts for $Mo(^{13}CO)_5$ and $Mo(^{13}CO)_6$. No new bands due to mixed $^{13}CO^{12}CO$ species were observed. Small concentrations of mixed species such as $Mo(^{13}CO)_5(^{12}CO)$ may be expected from statistical exchange with 95% ^{13}CO but were presumably obscured by the large bandwidths and the relatively complex band structure. After evacuation of ^{13}CO the stable carbonyl bands at 1790 and 1725 cm^{-1} were found to be completely shifted to lower frequency, consistent with rapid exchange between the surface species and the gas phase. The 2020- and 1935-cm^{-1} bands, on the other hand, were only partially shifted after exposure to ^{13}CO for 3 h and subsequent evacuation, implying a significantly slower rate of exchange of the species responsible for these bands. The frequencies and assignments of the observed bands are summarized in Table I.

The spectra recorded during decomposition of $Mo(CO)_6$ on alumina may now be interpreted as follows. Initially, $Mo(CO)_6$ vapor is physically adsorbed onto the surface. The $Mo(CO)_6$(ads) is not stable in vacuo and immediately loses CO to form $Mo(CO)_5$, which then decomposes further in vacuo to give the stable carbonyl species. On exposure to CO, both of these steps may be reversed. $Mo(CO)_5$ is formed initially, and at higher CO pressures $Mo(CO)_6$ slowly reappears. Subsequent evacuation at 45°C removes at least part of $Mo(CO)_6$ through sublimation, resulting in a net loss of molybdenum from the surface.

$$Mo(CO)_6(ads) \xrightleftharpoons[+CO\ (slow)]{-10^\circ C,\ in\ vacuo} Mo(CO)_5 \xrightleftharpoons[+CO\ (rapid)]{+10^\circ C,\ in\ vacuo} Mo(CO)_x$$

This interpretation of the infrared spectra is in complete agreement with the scheme given by Brenner and Burwell.[4] However, the spectra recorded after evacuation at 45°C are not consistent with the single stable $Mo(CO)_3$ species suggested by them. At least two and possibly three stable carbonyl species are present on the alumina surface, as discussed previously.[3] While the average ligand number may be 3, as implied by the CO evolution measurements,[4] the stable carbonyl species cannot be unambiguously identified from their infrared spectra. We note further that only the species responsible for the lower frequency bands (1790 and 1725 cm^{-1}) undergo rapid reaction and exchange with gas phase CO. Carbonyl frequencies below 1900 cm^{-1} are generally associated with either bridging CO groups or anionic species,[7] but it is not clear which of these possibilities applies to the reactive molybdenum carbonyl species on alumina.

Identical experiments were carried out with $Mo(CO)_6$ on a fully hydroxylated SiO_2 surface and with $W(CO)_6$ and $Cr(CO)_6$ on both Al_2O_3 and SiO_2, but in none of these systems were stable subcarbonyl species formed from decomposition of the parent hexacarbonyl. During initial warm-up, the only bands observed were those due to $M(CO)_6$(ads) (see Table I), which disappeared slowly on warming above 10°C in vacuo. Subsequent exposure to high pressures of CO (>50 Torr) at 45°C did however partially restore the $M(CO)_6$ bands, to an extent depending on the CO pressure and time of exposure.

$$M(CO)_6(ads) \xrightleftharpoons[CO,\ \geq 50\ Torr]{>10^\circ C,\ in\ vacuo} M(ads)$$

Such reversal of the complete decomposition of the group 6B hexacarbonyls under mild conditions has not previously been observed, although Mond's original preparation of $Mo(CO)_6$ involved reaction between the metal and CO at several hundred atmospheres.[8]

Watters et al.[9] have observed that the removal of the ν(CO) spectrum of $Rh_6(CO)_{16}$ supported on Al_2O_3 by treating with O_2 may be reversed by exposure to CO. This observation is clearly related to the decarbonylation of the group 6B hexacarbonyls described here. The role of the oxide support as a catalyst in these novel reactions and the possibility of observing similar behavior with other transition metal carbonyls warrant further investigation.

Acknowledgment. This work was carried out in the Chemistry Department, University of Edinburgh, Edinburgh, Scotland, and supported by a Science Research Council Grant for Organometallic Chemistry. I thank Professors C. Kemball and E. A. V. Ebsworth for providing laboratory facilities.

Registry No. $Mo(CO)_6$, 13939-06-5; $Cr(CO)_6$, 13007-92-6; $W(CO)_6$, 14040-11-0; $Mo(CO)_5(OH)^-$, 57527-30-7; Al_2O_3, 1344-28-1.

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(5) This treatment leaves the surface fully hydroxylated. Brenner and Burwell used a partially dehydroxylated Al_2O_3; however, we found no significant differences in behavior if the Al_2O_3 was outgassed up to 300°C before adding the hexacarbonyl.

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Chemistry of Quinquevalent Chromium. 2,2'-Bipyridinium Oxopentabromochromate(V)

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Received August 5, 1975 AIC50588C

We report here for the first time the isolation of oxopentabromochromate(V), $[CrOBr_5]^{2-}$, as the bipyridinium salt, using a method similar to that used by one of the authors to synthesize oxopentabromomolybdates,[1-3] with some necessary modifications. Similar oxopentachlorochromates(V) have been isolated long ago[4-8] and studied,[9,10] but corresponding bromo complexes could not be isolated, presumably due to the fact that reduction of Cr(VI) with hydrobromic acid proceeds to Cr(III) at ordinary temperatures. However it has been observed, that the Cr(V) which is formed as an intermediate can be trapped at low temperatures and the $[CrOBr_5]^{2-}$ species has been isolated as the corresponding bipyridinium salt. The salt isolated is fairly stable but, when kept for weeks, slowly decomposes, especially in the presence of moisture, chromium being reduced to Cr(III), while the bromide is oxidized to bromine. Thus, the analysis and measurements were carried out with freshly prepared samples.

Experimental Section

Preparation of 2,2'-Bipyridinium Oxopentabromochromate(V), $BpyH_2[CrOBr_5]$. About 1 g of $K_2Cr_2O_7$ was finely ground and cooled to −5°C in a freezing mixture. Saturated hydrobromic acid (saturated by passing hydrobromic acid gas through available AR hydrobromic acid at 0°C) was cooled to −5°C and was added slowly and dropwise with stirring till the dichromate dissolved, the temperature being kept always below 0°C. To this was added the hydrobromide of 2,2'-bipyridyl (prepared by adding saturated hydrobromic acid slowly and dropwise with stirring to 1 g of 2,2'-bipyridyl, till it dissolved and the solution was just acidic). A brownish yellow solid was obtained which was quickly filtered under cold conditions, drained under suction, washed once with ice-cold saturated hydrobromic acid, and dried under vacuum over solid KOH; yield 3.3 g.

Analysis. Chromium in the compound was estimated by oxidizing with sodium peroxide, adding ferrous ammonium sulfate solution along with excess silver sulfate to precipitate bromide, destroying excess silver ion with HCl, and then back-titrating the excess ferrous ion with standard potassium dichromate solution (the modifications being necessary due to the presence of bromide).

Bromide in the compound was estimated as silver bromide and nitrogen was estimated using the semimicro Kjeldahl method.

The conductance measurement was carried out in freshly distilled nitrobenzene (as the compound decomposes in water at ordinary temperature).

Magnetic susceptibility was measured on a Gouy balance at room temperature using a field strength of 10160 G.

The ir spectrum was recorded on a Perkin-Elmer 621 spectrophotometer using a KBr pellet.

The ESR spectrum was recorded in powder form using an Alfa EPR spectrophotometer, Model No. 340, by keeping the frequency constant at 340 MHz and changing the magnetic field at a rate of 32 G/min and at a run rate of 0.5 in./min. The spectrum is shown in Figure 1.

Results

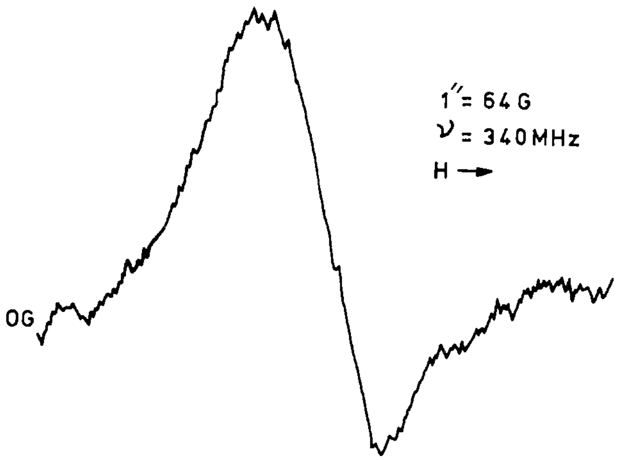

Figure 1. First-derivative ESR absorption spectrum of $bpyH_2[CrOBr_5]$ in solid powder form.

The molar conductance value of the compound in nitrobenzene using a saturated solution at 38°C was found to be 42.2 ohm^{-1} cm^2. The molar magnetic susceptibility (after diamagnetic correction) was found to be 1245.7 cgsu at 308 K, from which the effective magnetic moment is calculated to be 1.75 BM. Anal. Calcd for $C_{10}H_{10}N_2CrOBr_5$: Cr, 8.31; Br, 63.89; N, 4.47. Found: Cr, 8.40; Br, 64.52; N, 4.24.

The infrared spectrum of the compound shows the following absorption bands (in cm^{-1}): 365 s, 390 w, 585 m, 605 w, 755 vs, 895 s, 940 vs, 990 m, 1032 m, sh, 1085 s, 1150 s, 1170 s, 1218 s, sh, 1240 m, 1270 s, 1300 s, 1320 s, 1350 w, 1425 s, 1465 vs, 1518 vs, 1580 vs, 1595 vs, sh (w = weak, m = medium, s = strong, sh = shoulder, vs = very strong).

The first derivative of the ESR absorption is shown in Figure 1. The $\langle g \rangle$ value has been calculated using the relation $h\nu = g\beta H$ where h is Planck's constant, ν is the frequency of absorption, g is the gyromagnetic ratio, β is the Bohr magneton (0.927120×10^{-20} erg/Oe), and H is the magnetic field strength. The $\langle g \rangle$ value has been found to be 1.999.

Discussion

The value of the molar conductance in nitrobenzene is in conformity with that of a 2:2 electrolyte in nitrobenzene,[11] which is expected for the compound.

The value of the magnetic moment obtained from the bulk susceptibility measurement and the $\langle g \rangle$ value from the ESR spectrum show that the orbital moment is quenched in a low-symmetry ligand field as is expected in these types of compounds, the distortion being caused by the presence of a strong metal–oxygen bond. The presence of the metal–oxygen multiple bond is clearly proved by the presence of a very strong absorption band at 940 cm^{-1} in the infrared spectrum which is observed in similar chloro complexes[9,10] and corresponding molybdenum complexes.[12-15] The metal–halogen bond in the compound is characterized by a strong infrared absorption at 365 cm^{-1} as in the case of corresponding chloro complexes.[9,10]

The nature of the ESR spectrum in powder form also shows that there is a distortion from octahedral symmetry because in pure octahedral symmetry there would be excited states close to the ground state causing short spin–lattice relaxation times and very broad absorption lines at most temperatures. The situation is similar to that of corresponding chloro complexes.[16-18]

In view of the observations mentioned above we conclude that we have been able to isolate for the first time a species containing the $[CrOBr_5]^{2-}$ ion having chromium in the +5 oxidation state and bromide ion together. The anion is expected to belong to the C_{4v} point group, which is indicated by the presence of a metal–oxygen multiple bond observed in the infrared spectrum and a fairly narrow line width in the ESR spectrum.

Acknowledgment. We express our sincere thanks to Mr. Gulshan Roy and Mr. B. M. Sethi of the Physics Department,