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An Inelastic Electron Tunneling Spectroscopic Investigation of the Interaction of Molybdenum Hexacarbonyl with an Aluminum Oxide Surface

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Abstract: Molybdenum hexacarbonyl chemisorbs reversibly on fully hydroxylated aluminum oxide surfaces at room temperature to form a molybdenum carboxylic acid which desorbs at room temperature. Heating the surface during the vapor phase exposure of the hexacarbonyl leads to decomposition to a molybdenum oxide (of undetermined oxidation state) and molybdenum carbonyl oxides at 100 °C and to complete decomposition to multilayers of metallic molybdenum at 140 °C. Exposure of multilayers of molybdenum hexacarbonyl, deposited on the alumina surface from hexane solution, to 594 $\mu W/cm^2$ of 366-nm UV irradiation failed to produce any identifiable irreversibly adsorbed molybdenum species. The exposure of the molybdenum oxide, formed on a 100 °C surface by adsorption and reaction of the hexacarbonyl, to ethylene at 2 Torr and 100 °C failed to form any detectable molybdenum carbene type complexes that are proposed to be active metathesis catalysts. Indeed, there was no evidence of any adsorption or reaction of the ethylene with the surface.

I. Introduction

Inelastic electron tunneling spectroscopy is a highly sensitive, moderate resolution vibrational technique for studying molecules adsorbed on insulator surfaces. Although many substrates can be used, the majority of the existing studies have been concerned with adsorption on aluminum oxide employing aluminum–aluminum oxide–lead tunnel junctions. Several recent reviews discuss both the theory and the practice of tunneling spectroscopy,[1-10] including a recent general overview of tunneling spectroscopy.[11]

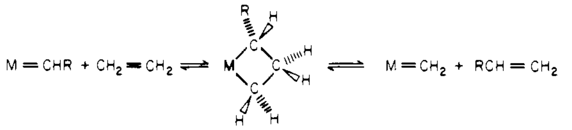
Tunneling spectroscopy has been applied previously to the study of both adsorbed metal carbonyls and evaporated metal clusters with postadsorbed carbon monoxide. These studies have been reviewed extensively by Weinberg[9] and Kroecker.[12] Specific systems include $Ru_3(CO)_{12}$,[13] $[Rh(CO)_2Cl]_2$[14] on alumina, and CO adsorbed on alumina-supported rhodium,[15] iron,[16] and nickel[17] crystallites. The sensitivity and wide spectral range (240–4000 cm^{-1} in our experiments) permit the observation of the $\nu(CO)$, $\delta(M–C–O)$, and $\nu(M–CO)$ vibrational modes. Broadening and downshifting of the $\nu(CO)$ modes limits, however, the spectral resolution. A discussion of the perturbation on vibrational frequencies by the upper metal electrode has been given by Kroecker and Hansma.[18]

The extensive study of molybdenum hexacarbonyl adsorbed on aluminum oxide including its decomposition products dates back to the observation by Banks and Bailey[19] of the catalytic metathesis of propylene by alumina supported molybdenum hexacarbonyl decomposition products. This catalyst was prepared by impregnating an activated alumina (approximately equivalent to the partially dehydroxylated alumina discussed below) with a solution of $Mo(CO)_6$ in cyclohexane at 65 °C. The cyclohexane was removed by flushing the catalyst with dry nitrogen and then evacuating at 120–140 °C. The catalyst was activated with dry air at 540 °C for 5 h. Although various decomposition products of the adsorbed molybdenum hexacarbonyl can catalyze other reactions such as isotopic exchange between deuterium and alkanes[20] or Fischer–Tropsch synthesis,[21] much of the work has centered on the identification of those species responsible for the metathesis reaction.[22,23]

The metathesis reaction may be written as

$$2\,RCH{=}CH_2 \rightarrow RCH{=}CHR \text{ (cis and trans)} + CH_2{=}CH_2$$

where the ratio of the cis-to-trans olefin that is formed is a function of both the reactant and the catalyst. The Chauvin–Herisson (carbene) mechanism[24]



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has been established by a series of isotopic labeling experiments.[25] On the basis of the work of Mocella et al.,[26] this mechanism was extended for the molybdenum catalyzed systems in order to explain the necessary presence of oxygen to activate the catalyst. This led to the oxo–molybdenum carbene hypothesis, which was given theoretical support by Goddard and Rappē,[27] who determined that the reaction mechanism

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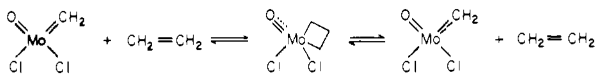

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was favored due to the change in the nature of the molybdenum–oxygen bond in the metallocycle. This calculation explained the origin of the reduction in the activation energy for the insertion reaction. Recently, isolatable tungsten oxo–alkylidene complexes, which are quite active for metathesis in solution, have been synthesized and characterized.[28,29] A review of the field has been given by Grubbs.[30]

The study of the adsorption and reaction of molybdenum hexacarbonyl has involved primarily the use of transmission infrared spectroscopy of the carbonyl stretching region (1700–2100 cm^{-1}), in addition to an analysis of thermally desorbed decomposition products. The majority of the experiments have involved partially or fully dehydroxylated aluminas as opposed to fully hydroxylated alumina. These materials are prepared by heating γ-alumina in flowing helium to a temperature of 500 °C (partially dehydroxylated) or 1000 °C (fully dehydroxylated) for 1 h.[31] The reaction of the hexacarbonyl proceeds quite differently on the three supports. On hydroxylated alumina, the hexacarbonyl adsorbs weakly and decomposes readily with the loss of carbon monoxide at 25 °C and the oxidation of molybdenum at 265 °C (monitored by the desorption of hydrogen).[22] On partially dehydroxylated alumina, the initial adsorption is stronger, and the subsequent thermal decomposition produces a variety of surface species, e.g., $Mo(CO)_3(ads)_3$, $Mo(O)_2(CO)_2(ads)_2$, and $(Al\text{-}O)_2Mo$[22] [(ads) represents a surface Lewis base site]. Since this surface produces the most active metathesis catalysts, it has been studied extensively.[22,23,31-34] The exact species that form and their relative concentrations appear to depend critically on initial preparation conditions and thermal decomposition parameters such as temperature and time of decomposition.

Under conditions of rigorous water removal, the hexacarbonyl decomposes to zero valent molybdenum at submonolayer coverages. Residual hydroxyl protons produce some oxidation, yielding an average oxidation number of 0.4.[22] The average oxidation number is the formal oxidation state, as determined by quantitative oxidation of the surface species to MoO_3. The oxygen uptake, corrected for other oxidation products (such as hydrogen), is converted to an oxygen/molybdenum ratio and then subtracted from three (MoO_3 has an O/Mo ratio of three) and doubled (since the formal oxidation state of oxygen is 2–). We emphasize that the oxidation number represents a *formal* oxidation state and does not imply, for example, that Mo^{6+} exists on the surface. The chemistry that occurs on the fully dehydroxylated surface corresponds to that which occurs on dispersed molybdenum metal, although the extent of dehydroxylation must be extremely high to avoid side reactions from the residual oxidized species.

The accumulated data from the decomposition studies on various alumina surfaces have led to the development of models for the adsorption and decomposition reactions by Brown,[35] Bailey and Langer,[36] and Phillips and Dumesic,[37] the latter summarizing available experimental evidence for characterizing the adsorption and decomposition of various carbonyls (including molybdenum hexacarbonyl) on alumina surfaces. In addition to structural information derived from transmission infrared spectroscopy of thin pressed alumina disks, information is available concerning the oxidation state of the molybdenum species from X-ray photoelectron spectroscopy (XPS) and electron spin resonance (ESR) measurements [on molybdenum(V) species]. These data support the carbene mechanism indirectly by indicating both a correlation of the metathesis activity with the molybdenum(IV) concentration and also the difficulty of oxidizing the molybdenum species beyond molybdenum(V) under all but the most severe conditions. For example, decomposition at 600 °C in helium produces an average oxidation number of 4.6,[34] while heating in oxygen at 500 °C is necessary to produce molybdenum(VI).[23]

Brown[35] also provides a summary of work on alumina supported carbonyl complexes, emphasizing molybdenum hexacarbonyl, and formulates a series of plausible mechanisms for the adsorption and decomposition reactions consistent with the experimental data. This includes the initial adsorption (through a Lewis acid–carbonyl interaction, a molybdenum carboxylate species, or a surface hydroxyl–carbonyl interaction), the formation of various gas-phase products (CO, CO_2, H_2, and CH_4), and the formation of a surface carbene species for the metathesis reaction. We shall be concerned here with the initial adsorption reaction and the final decomposition to molybdenum oxide.

Bailey and Langer[36] have presented a comprehensive review of supported carbonyl catalysts. They include systems supported on functionalized polymers and inorganic supports, including the alumina system considered here. They provide an exhaustive summary of the research performed on the molybdenum hexacarbonyl–aluminum oxide system, including discussions of models proposed by experimentalists, but they do not provide a formalism to unify the data.

Finally, the synthesis and vibrational characterization of stable metal carboxylic acids [MCOOH, e.g., M = Pt[38]] and their considerably more stable esters [MCOOR, e.g., M = Co[39]] provide direct information concerning the vibrational frequencies of carboxylate species. In general, the high-frequency bands [ν_a(OCO) ~1550 cm^{-1} or ν(C=O) ~1650 cm^{-1}] are observable in the transmission infrared spectra of high-surface-area alumina-supported catalysts. Lower frequency modes [including the metal–carboxyl stretch and deformations and the δ(OCO) mode] occur in regions that are highly absorbing in the high-surface-area systems, and they are rarely observed for the organometallic complexes. The identification of intermediate frequency modes such as ν(CO) at ~1200 cm^{-1}, δ(COH) at ~1350 cm^{-1}, or ν_s(OCO) at ~1400 cm^{-1}, which are known both from homogeneous systems and several supported systems, can be used to link the high-surface-area alumina data with the information from the wider spectral range of inelastic electron tunneling spectroscopy.

II. Experimental Procedures

The inelastic electron tunnel junction fabrication system and experimental procedures are described in detail elsewhere.[40] Briefly, a lower aluminum electrode is formed by evaporating high-purity aluminum metal through a mask onto a clean glass slide. The aluminum surface is oxidized in an oxygen/water vapor glow discharge to form the thin insulating aluminum oxide film. The reactant under study is then deposited on this aluminum oxide surface either by adsorption from the vapor phase or by exposure to a solution of the reagent in an inert solvent (hexane). Heating, if used, is accomplished by the resistive heating method of Bowser and Weinberg.[41] The system is then evacuated to below 5×10^{-7} Torr, and the upper lead electrode is vacuum evaporated to complete the tunnel junction.

The tunneling spectra are measured with a constant-current modulation system described elsewhere.[42] This system incorporates near-real-time display of the spectra to aid in optimizing the phase setting of the lock-in detector. The spectrum in Figure 2 was processed with use of an algorithm to remove the linearly sloping background from the measured spectra.[43]

The fractional surface coverages of hydroxyl groups (θ_{OH}) are estimated by normalizing the area of the alumina vibration to unity in each

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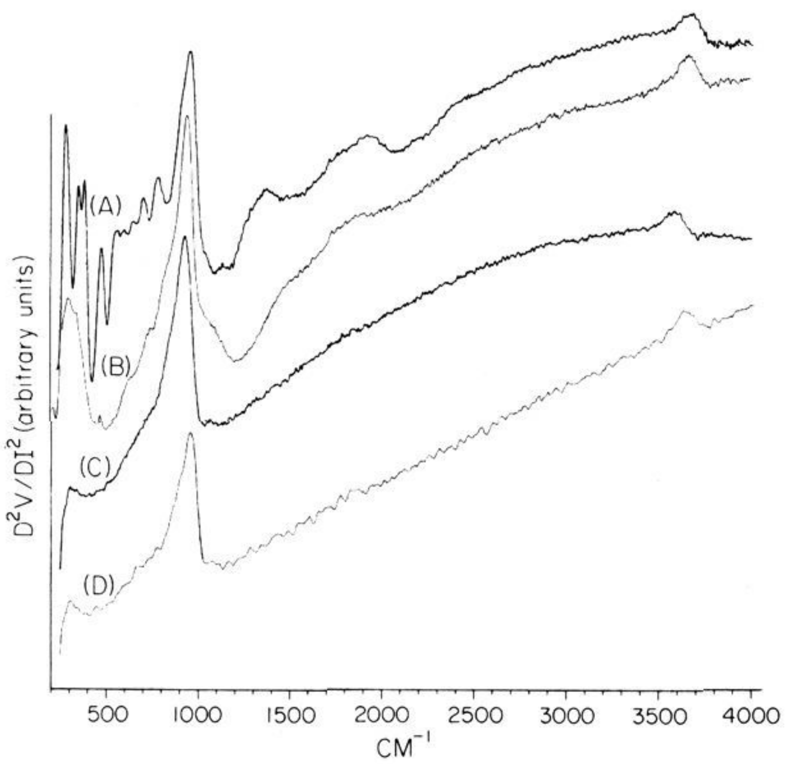

Figure 1. Tunneling spectra of molybdenum hexacarbonyl adsorbed from the vapor phase on alumina at 22 °C with increasing time delays between the end of the exposure and the start of the lead evaporation. Exposure of 30 Torr·s (10^{-1} Torr for 300 s). (A) Delay ~15 min, (B) delay ~22 min, (C) delay ~25 min, (D) blank (unexposed) junction for comparison. 1000 scans, τ = 1 ms, and V_{mod} = 1.7 mV rms.

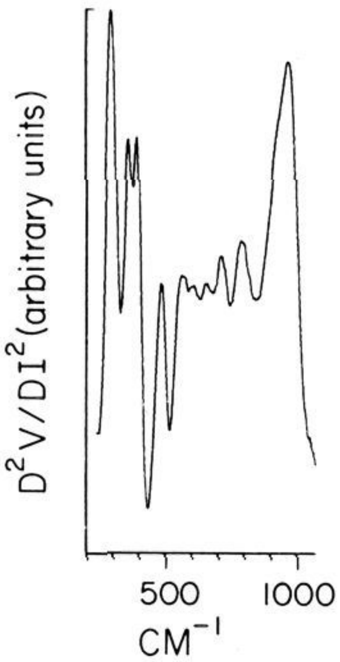

Figure 2. Spectrum of Figure 1A with the background removed for the region between 240 and 1050 cm^{-1}.

spectrum and evaluating the area of the hydroxyl stretching peak. The latter for a clean junction at room temperature is assumed to correspond to a monolayer of hydroxyl groups. Values of θ_{OH} for other spectra are obtained by taking the ratio of the integrated intensities of the ν(OH) modes. Since the intensity does not scale strictly linearly with coverage, this estimate is only approximate.

The molybdenum hexacarbonyl from Pressure Chemical was purified by the method of Laniecki and Burwell[31] (sublimed twice in vacuo). The ethylene was CP grade (99.9%) from Matheson, and the hexane was Photrex grade (99%) from Baker. Both were used as received.

III. Results

A. Surface Carbonyl Hydroxyl Reaction. Due to the nature of tunneling spectroscopy, it is impossible to follow the course of a surface reaction as a function of time on a single junction. Several junctions prepared under different conditions must be used to study "dynamic" processes, such as reversible adsorption and sequential irreversible reactions. The tunneling spectrum of molybdenum hexacarbonyl adsorbed at 22 °C on a fully hydroxylated ($\theta_{OH} = 1$) aluminum oxide surface is shown in Figure 1A. This spectrum was obtained by minimizing the time (15 min) between the end of the carbonyl exposure and the start of the lead electrode evaporation. An intermediate stage in the desorption is observed with a 22-min delay, and the spectrum is shown in Figure 1B. The tunneling spectrum that results from a 25-min delay is shown in Figure 1C. The spectrum in Figure 1C is comparable to the spectrum of a clean junction shown in Figure 1D. This suggests that the reaction of the carbonyl with the fully hydroxylated surface is reversible at room temperature. The spectrum in Figure 1A has been processed to remove the background, and the region from 240 to 1050 cm^{-1} is shown in Figure 2.

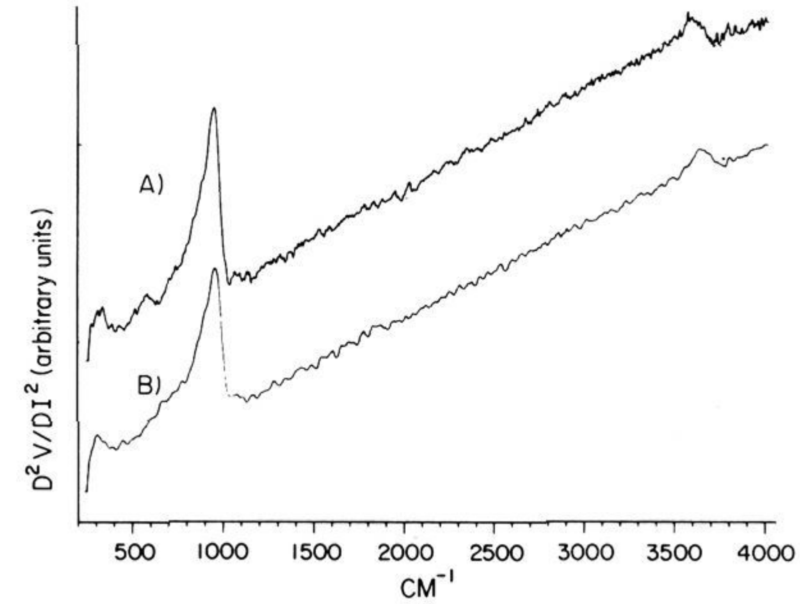

Figure 3. (A) Tunneling spectrum of molybdenum hexacarbonyl adsorbed from the vapor phase on an alumina surface heated to 200 °C for 600 s to partially dehydroxylate it. Exposure of 30 Torr·s (10^{-1} Torr for 300 s). 750 scans, τ = 3 ms, and V_{mod} = 1.7 mV rms. (B) Tunneling spectrum of a blank junction for comparison. 1000 scans, τ = 1 ms, and V_{mod} = 1.7 mV rms.

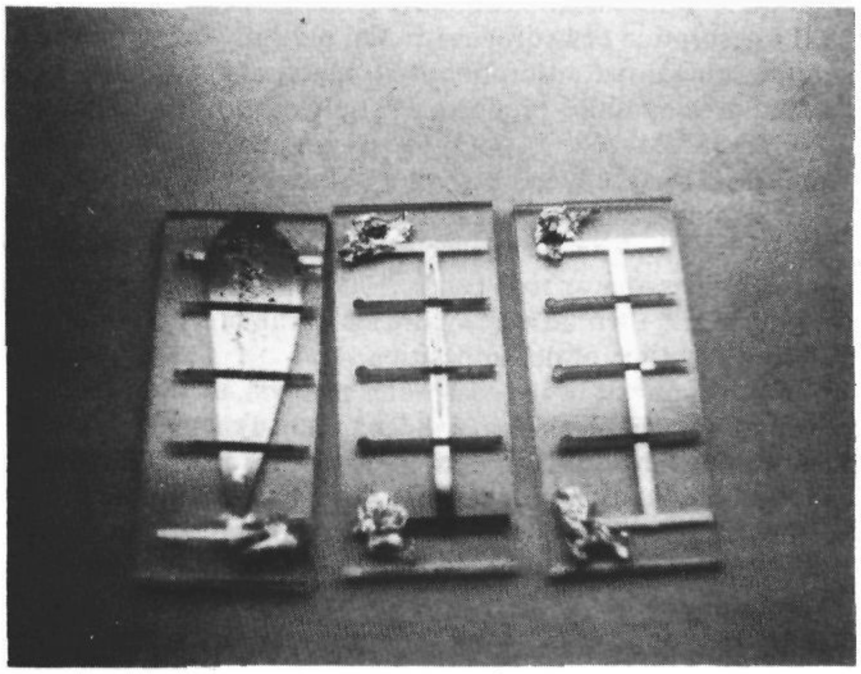

Figure 4. Photograph of actual junctions heated to 140 °C during exposure to molybdenum hexacarbonyl in the vapor phase at 10^{-1} Torr. (Left) Heated for 300 s. (Center) Heated for 30 s. (Right) Unexposed junction for comparison.

B. Surface Carbonyl Decomposition Reaction. The tunneling spectrum that results after heating the junction to 200 °C for 600 s to partially dehydroxylate ($\theta_{OH} \cong 0.85$) the alumina surface, followed by adsorption of molybdenum hexacarbonyl at 22 °C, is presented in Figure 3A. An unheated blank junction is shown for comparison in Figure 3B. The partially dehydroxylated surface produces a very small amount of decomposition of the carbonyl. The extent of dehydroxylation is approximately 15% as judged by a comparison of the intensities of the (Al)OH stretching mode at approximately 3600 cm^{-1}. The time delay is not important in this case because we are interested in irreversibly chemisorbed products, as discussed in section IVC.

C. Activated Adsorption and Decomposition. Pure molybdenum hexacarbonyl has been reported to decompose at its own vapor pressure at 150 °C.[44] The tunnel junctions shown in Figure 4

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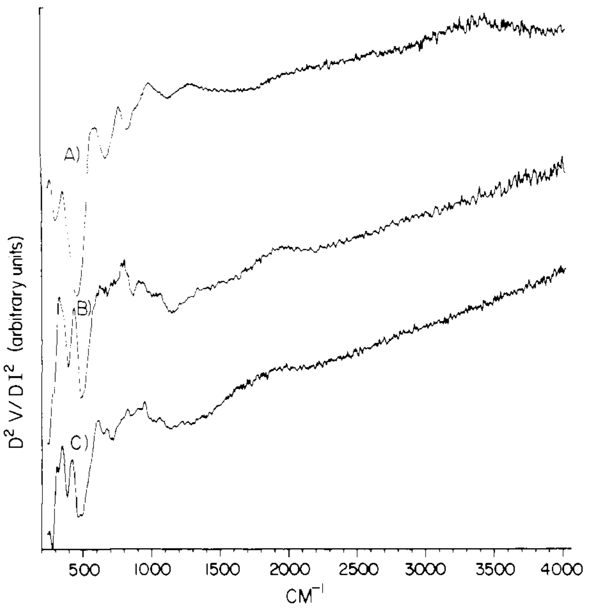


Figure 5. (A) Tunneling spectrum of molybdenum hexacarbonyl adsorbed from the vapor phase at 100 °C. Exposure of 30 Torr·s (10^{-1} Torr for 300 s). 1000 scans, τ = 3 ms, and V_{mod} = 1.7 mV rms. (B) As in spectrum A except the junction was subsequently heated in vacuum at 100 °C for 300 s to further decompose the adsorbed species. 100 scans, τ = 10 ms, and V_{mod} = 1.7 mV rms. (C) As in spectrum A except the surface species was exposed to ethylene at 100 °C. Exposure of 1800 Torr·s (2 Torr for 900 s). 1000 scans, τ = 3 ms, and V_{mod} = 1.7 mV rms.

(left and center) were heated to approximately 140 °C for 5 min and 30 s, respectively. The molybdenum hexacarbonyl has decomposed to form a molybdenum metal zone, which appears darker than the aluminum strip by reflected light. A standard, unexposed junction is shown for comparison in Figure 4 (right). These experiments also indicate qualitatively the thermal gradient present in the junctions during heating and will be discussed further in section IVC.

The molybdenum hexacarbonyl decomposes without metal deposition when the junctions are heated to approximately 100 °C. The tunneling spectrum that results after exposure to 10^{-1} Torr of molybdenum hexacarbonyl vapor for 300 s at 100 °C is shown in Figure 5A. The decomposition can be carried to completion by further heating of the junction under vacuum at 100 °C for 300 s after prior hexacarbonyl exposure at 100 °C (post-heating). The tunneling spectrum that results from this treatment is shown in Figure 5B.

D. Attempted Activation of Decomposition Products of Molybdenum Hexacarbonyl with Ethylene. Molybdenum oxides, primarily ammonium molybdate, have been used as metathesis catalyst precursors.[45] After being calcined to remove ammonia and water, the resulting molybdenum oxide is activated with an olefin, typically propylene, at a temperature of 400 °C in 1 atm of the olefin for 1 to 4 h.[45]

The molybdenum hexacarbonyl decomposition products, formed in the activated adsorption experiments described in section IIIC, were exposed to 2 Torr of ethylene at 100 °C for 900 to 3600 s. The tunneling spectrum that results from the 900-s exposure is shown in Figure 5C. There is no evidence of reaction of the ethylene with the surface under these conditions. Longer exposures also showed no evidence of hydrocarbon adsorption or carbene formation.

E. Attempted Decomposition of Molybdenum Hexacarbonyl via UV Photolysis. A series of junctions was prepared by depositing 10 μL of a 1% (w/v) Mo(CO)$_6$/hexane solution (approximately 0.04 M) on the aluminum oxide surface at 22 °C, allowing the solvent to evaporate (~30 s) and exposing the junctions to 366 nm (3.39 eV) ultraviolet radiation through a Huntington Mechanical Labs VP-151 viewport constructed of type 7056 glass. This viewport has a minimum transmission coefficient of 0.8 from 320 to 2700 nm. The source has a stated light intensity of 330 μW/cm^2 at 6 in. The junctions were positioned approximately 4 in. from the source, which should provide an intensity of 594 μW/cm^2 [330 μW/cm^2 × $(6/4)^2$ × 0.8]. The exposure to this UV irradiation was 300 s in duration. The delay time between the end of the UV exposure and the start of the lead evaporation was approximately 60 min. The tunneling spectra of a UV-exposed junction and a non-UV-exposed junction, prepared at the same time, are shown in spectra A and B in Figure 6, respectively.

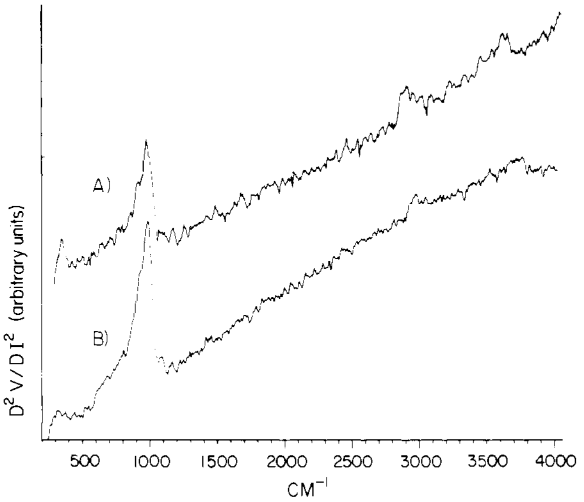
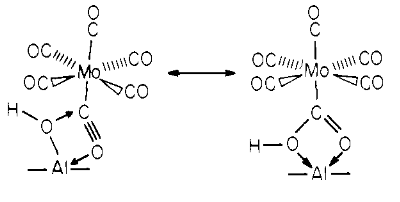


Figure 6. (A) Tunneling spectrum of a junction exposed to molybdenum hexacarbonyl in the liquid phase, (1% w/v [0.04 M] Mo(CO)$_6$ in hexane, 10^{17} molecules/cm^2), then ~600 μW/cm^2 of 366-nm UV irradiation for 300 s. 100 scans, τ = 10 ms, and V_{mod} = 1.7 mV rms. (B) As in spectrum A without exposure to UV irradiation.

IV. Discussion

A. Molybdenum Hexacarbonyl–Surface Complex Formation. As discussed by Brown,[35] three major types of surface carbonyl complexes can occur: (1) a carboxylate-type species which can be subdivided into a "carboxylic acid", represented by a resonance structure in IA that can occur on partially or fully hydroxylated oxide surfaces and a carboxylate IB that can occur on partially or fully dehydroxylated oxide surfaces, (2) a carbonyl–Lewis acid adduct II that can occur on partially or fully dehydroxylated oxide surfaces, and (3) a carbonyl–surface hydroxyl adduct III that can occur on partially or fully hydroxylated oxide surfaces. Each structure has certain characteristic vibrational frequencies that, if sufficiently intense, can be used to identify the species. The



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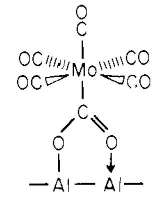

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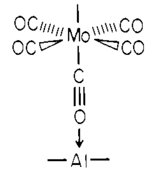

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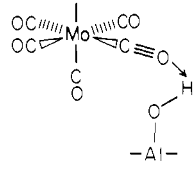

III

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Table I. Vibrational Frequencies of Gas-Phase and Adsorbed Molybdenum Hexacarbonyl

	gas phase[48]			chemisorbed on alumina	
mode	symmetry	assignment[a]	freq (cm^{-1})	freq (cm^{-1})	assignment[a]
13	f_{2u}	δ(CMoC)	60		
9	f_{1u}	δ(CMoC)	82		
11	f_{2g}	δ(CMoC)	86		
5	f_{1g}	β(MoCO)	342	298	β(MoCO)
8	f_{1u}	β(MoCO)	367	366	β(MoCO)
4	e_g	ν(MoC)	392	398	ν(MoC)
2	a_{1g}	ν(MoC)	402		
10	f_{2g}	β(MoCO)	448		
12	f_{2u}	β(MoCO)	507	491	β(MoCO)
7	f_{1u}	ν(MoC)	596	585 br	ν(MoC)
				725	carboxylic acid
				819	deformation modes
				945	ν(Al-O)
				1166 w	carboxylic acid
				1200–1650 v br	stretching modes
6	f_{1u}	ν(CO)	2003	1650–2100 v br	ν(CO)
3	e_g	ν(CO)	2019		
1	a_{1g}	ν(CO)	2117		
				3650 v br	ν(OH)

[a] ν = stretching mode, δ = deformation mode, β = bending mode, w = weak, br = broad, v br = very broad.

"carboxylic acid" (IA) would have modes due to ν(C═O) [~1600–1680 cm^{-1}],[38,39] ν(C–O) [~1200 cm^{-1}],[38] and δ(C–O–H) [~1350 cm^{-1}],[46] as well as lower frequency carboxylic acid deformation modes, which occur in the metal–carbonyl bending region [~600–800 cm^{-1}].[46] The carboxylate (IB) would have asymmetric and symmetric carboxylate stretching modes [ν_a(OCO) ~1580 cm^{-1} and ν_s(OCO) ~1460 cm^{-1} for formate on alumina[47]]. The carbonyl–Lewis acid adduct (II) would produce a broad, downshifted carbonyl stretch, extending as low as 1700 cm^{-1}.[33] Finally, the carbonyl–surface hydroxyl adduct (III) would, in addition to a carbonyl downshift, produce the characteristically downshifted ν(OH) modes of a hydrogen-bonded complex [ν(OH) $\lesssim$3400 cm^{-1}].[46]

The tunneling spectrum of the surface molybdenum carbonyl complex adsorbed at 22 °C is shown in Figure 1A, with the spectral region from 240 to 1050 cm^{-1} shown in greater detail in Figure 2. The vibrational frequencies are listed in Table I. The tunneling spectrum of Figure 1A was obtained by evaporating the lead overlayer 15 min following the molybdenum hexacarbonyl exposure at a system pressure of approximately 5×10^{-7} Torr. Shorter delay times produce poor quality junctions due to a higher background pressure. The tunneling spectrum in Figure 1C was obtained with a delay time of 25 min prior to the lead evaporation. By comparison with the tunneling spectrum of the blank junction shown in Figure 1D, there is no evidence of any molybdenum hexacarbonyl (or decomposition products therefrom) remaining on the surface. From this, we infer that the interaction of the molybdenum hexacarbonyl with the fully hydroxylated alumina surface is rather weak and completely reversible. On the basis of these data we can calculate an approximate heat of adsorption. If we assume a steady state between a 5×10^{-7} Torr background molybdenum hexacarbonyl partial pressure and a fractional surface coverage of 0.01 (the detection limit of 10^{12} molecules/cm^2) with a preexponential factor of the desorption rate coefficient of 10^{13} s^{-1} and a probability of adsorption of unity, we estimate ΔH_{ads} = 15.1 kcal/mol. By varying the approximations, we find ΔH_{ads} = 15 ± 3 kcal/mol. As noted in section IIIA, the need to deposit the lead upper electrode to synthesize the tunneling junction does not allow a single junction to be observed as a function of time. Rather, a series of junctions must be prepared with increasing delay times between the end of the vapor-phase exposure to the molybdenum hexacarbonyl and the beginning of the lead evaporation. An example is given in Figure 1B for which the delay time is 22 min.

Both Burwell and co-workers[22,31] and Howe and co-workers[23,32,33] have reported the formation of a $Mo(CO)_3(ads)_3$ type species on partially dehydroxylated alumina surfaces on the basis of CO desorption studies. The $Mo(CO)_3(ads)_3$ complex is formed over approximately 1 h by sweeping the alumina-supported carbonyl with pure helium at 100 °C. Molybdenum hexacarbonyl can be recovered quantitatively by flowing CO containing helium through the sample cell. However, $Mo(CO)_3(ads)_3$ is reported to be stable indefinitely to flowing helium below 100 °C on hydroxylated aluminas.[31] Since the desorption observed in our work occurs under vacuum and hence does not involve recarbonylation of CO, and considering the short time (~20 min) and low temperatures (~22 °C) involved, the surface species formed here cannot be $Mo(CO)_3(ads)_3$.

The vibrational frequencies of the surface species are compared with the frequencies of gas-phase molybdenum hexacarbonyl in Table I. The free molybdenum hexacarbonyl frequencies are listed with the assignments and mode symmetries given by Shimanouchi.[48] Unlike infrared or Raman spectroscopy, inelastic electron tunneling spectroscopy has no strict selection rules comparable to the dipolar allowed modes of infrared spectra or the polarization rules of Raman spectra.[49] Thus the number of observed modes is not a useful guide to the symmetry of the adsorbed molecule in tunneling spectroscopy.

The relatively good correspondence between the low-frequency modes of the surface species and the free hexacarbonyl suggest, in agreement with the observation of reversible adsorption, that relatively minor modifications in the structure of the molecule have occurred. In addition to several new low-frequency modes (below 1000 cm^{-1}), a broad peak occurs from approximately 1200 to 1650 cm^{-1} and a second from approximately 1650 to 2100 cm^{-1}. The hydroxyl stretching mode at 3550–3700 cm^{-1} is essentially unshifted from its position on the clean alumina surface [cf. Figure 1D].

Of the three surface species discussed above, only the surface carboxylic acid (IA) or the surface carboxylate (IB) would be expected to produce vibrational frequencies in the 1200–1600-cm^{-1} range. Relatively few carboxylic acid complexes (as opposed to carboxylate esters) are sufficiently stable for infrared spectra to be obtained. The platinum complex $Pt(COOH)(C_6H_9)(P–P)$ [$(P–P) = Ph_2P(CH_2)_nPPh_2$, n = 2, 3, 4], discussed in section I, has a ν(C═O) of 1555–1651 cm^{-1} and a ν(C–O) of 1137–1215 cm^{-1}.[38] In addition, $CpFe(CO)(PPh_3)(COOH)$ has a ν(C═O) of 1565 cm^{-1}.[50] Several additional examples of carboxylate esters are known with most having a ν(C═O) of approximately 1685 cm^{-1},[37,51,52] due primarily to the lack of hydrogen bonding that exists in the carboxylic acid dimer. In the surface species, the carbonyl frequency is downshifted by the analogous interaction with the aluminum site.

Two bulk oxide systems provide additional evidence for metal carboxylate formation. Fubini et al.[53] have studied the adsorption of chromium hexacarbonyl on calcium oxide. The oxide was dried by heating under vacuum to remove all hydroxyl groups, and it provides a useful infrared window down to 900 cm^{-1}. They assign

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(49) See, for example, ref 8, Chapter 1.

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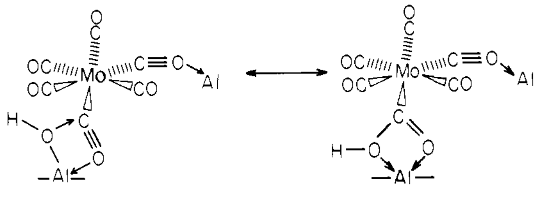
broad modes at 1425 [ν_s(OCO)], 1075 [δ_a(OCO)], and 975 cm^{-1} [δ_s(OCO)] to a surface carboxylate similar to IB. In addition, they observe a series of broad infrared bands from 2120 to 1715 cm^{-1} in the carbonyl stretching frequency region. Guglielminotti and Zecchina[54] have studied the adsorption of molybdenum hexacarbonyl on magnesium oxide and observed similar bands at 1472–1436 cm^{-1} [ν_s(OCO)] and 1060 cm^{-1} [δ_s(OCO)] which they assigned to a surface carboxylate. Their magnesium oxide surface was stated to be free of hydroxyl groups, precluding the formation of a carboxylic acid species IA.

The broad structure at 1200–1650 cm^{-1} in Figure 1A, produced by the surface molybdenum hexacarbonyl, precludes any attempt to differentiate between IA and IB on the basis of the carboxyl modes. However, the carboxylic acid, as opposed to the carboxylate, would be expected to produce a downshifted ν(OH) mode due to the surface hydroxyl–carbonyl carbon interaction and to reduce the intensity of the ν(Al)OH mode. Although the downshifted ν(OH) mode is too weak to observe, the 3650-cm^{-1} ν(OH) mode in the carboxylic acid spectrum is attenuated relative to a blank junction spectrum. Since our surfaces are fully hydroxylated in the untreated state, we tentatively favor the assignment of the "carboxylic acid" type structure.

Finally, the broad carbonyl stretching mode from approximately 1650 to 2100 cm^{-1} may be due to an interaction with the surface aluminum sites, as in II, or a downshift caused by the lead upper electrode.[18] Generally, the lead-induced downshift is ≤6%,[18] which cannot account for these observed shifts. Rather, the observed low frequency of ν(C≡O) is consistent with a Lewis-acid-induced downshift [e.g., Kazusaka and Howe[33]] as in II. A surface species such as III is unlikely, due to the lack of a broad ν(OH) mode at approximately 3300 cm^{-1}.

On the basis of these combined observations, we propose a surface "carboxylic acid" (IV) to represent best the structure of the surface species. It incorporates both the carboxylic acid moiety as well as the aluminum–carbonyl acid–base adduct. The vibrational modes are too broad to exclude the alternative of two species (IA and II), the vibrational modes of which are superposed to give the observed spectrum.



(IV)

B. Carbonyl Adsorption on the Partially Dehydroxylated Surface. The high-surface-area alumina studies of Burwell et al.[22,31] and Howe et al.[23,32,33] have each demonstrated significantly greater reactivity on partially or fully dehydroxylated alumina surfaces compared to the fully hydroxylated surface. To investigate this possibility, we attempted to dehydroxylate our alumina surface partially by heating the junctions to 200 °C for 300 to 600 s prior to exposure to the molybdenum hexacarbonyl vapor. A comparison of the resulting tunneling spectrum in Figure 3A with that of a blank junction in Figure 3B indicates that very few decomposition products are observed.

The extent of dehydroxylation, as judged by the relative areas of the ν(OH) mode centered at 3650 cm^{-1}, is rather small (approximately 15%, or $\theta_{OH} \sim 0.85$ after annealing to 200 °C). The partially dehydroxylated aluminas used by Burwell et al.,[31] for example, were prepared by heating the alumina to 450 °C in flowing helium for 1 h, while the fully dehydroxylated aluminas were heated to 1000 °C for 1 h. Our method of heating the junctions prevents us from reaching these elevated temperatures.

C. Reaction at Elevated Temperatures. Molybdenum hexacarbonyl vapor is reported to decompose at 150 °C[44] to give molybdenum metal and CO. To test the reactivity of molybdenum hexacarbonyl with the alumina surface, we prepared several tunneling junctions by exposing them to 10^{-1} Torr of molybdenum hexacarbonyl vapor while heating the aluminum strips from 100 to 150 °C. The measured temperatures show significant (±10 °C) fluctuations when the temperature reaches 140 °C. The result of heating for 5 min and for 30 s beyond the observation of the first fluctuations is shown in Figure 4, left and center, respectively. This figure is a photograph of the completed junctions after removal from the vacuum system. The negative heating lead is connected at the upper left of each junction as oriented in the figure, while the positive lead is connected at the lower right. The junction in Figure 4 (left) shows a large, approximately oval metal film deposited asymmetrically with respect to the heating leads. In addition, a small metal film is deposited on the back side of the glass slide and located on the central aluminum strip lines near the upper crossbar of the I-shaped aluminum strip. The formation of this second film, between the glass slide and the slide holder (see ref 40 for details), indicates that decomposition of the vapor produced the film, and the source was the heat produced by the aluminum strip heating, transmitted through the glass slide. No direct line of sight exists between the second metal film and any metal evaporation source.

The 30 s heating exposure shown in Figure 4 (center) depicts the initial stages of the film formation and also indicates the asymmetric nature of the deposition. The localized nature of the metal film deposition suggests that a thermal gradient exists along the heated aluminum strip. Comparison of the measured decomposition temperature on the alumina surface, 140 ± 2 °C [±2 being the calibration accuracy[41]], as indicated by the start of the temperature fluctuations caused by the metal deposition, and the measured decomposition temperature of Mo(CO)$_6$ vapor at its own vapor pressure [150 ± 1 °C[44]], indicates that the maximum local deviation from the average temperature (140 °C) is approximately 10 °C.

Heating the junctions to 100 °C for 300 s during the molybdenum hexacarbonyl vapor exposure results in decomposition of the carbonyl with no evidence of metal deposition. The tunneling spectrum of the decomposition product is shown in Figure 5A. Heating the junction to 100 °C under vacuum for 300 s after the original thermal decomposition produces the tunneling spectrum in Figure 5B. We note the weak carbonyl vibrations in Figure 5A with the presence of hydroxyl vibrations, while the reverse is true in Figure 5B. This apparent discrepancy is explained by the presence of chemisorbed hexacarbonyl on the alumina surface for approximately 15 min after the initial pumpdown. The hexacarbonyl decomposes with loss of CO by reaction with surface hydroxyl groups.[37] In the case of no postheating, excess hexacarbonyl desorbs leaving a molybdenum suboxide and unreacted hydroxyl groups. The postheating allows the reaction between the residual chemisorbed hexacarbonyl and the surface hydroxyl groups to continue, until all of the hydroxyl groups are reacted. This produces a mixture of molybdenum suboxides and subcarbonyls.[37] A similar result is obtained if the initial heating in hexacarbonyl vapor is for 600 s. This suggests that the decomposition of the carbonyl is limited by the availability of protons from hydroxyl groups on the surface. This is in accord with previous observations of molybdenum carbonyl–aluminum oxide systems that all hydroxylated surfaces have a maximum reaction capacity, limited by the number of hydroxyl groups.[37] Further reaction requires much higher temperatures, or the addition of oxygen or water vapor to the system.

The complex nature of the spectra render more detailed assignments impossible. In particular, the very broad carbonyl stretching modes prevent any correlation with the oxidized subcarbonyls, such as Mo(O)$_2$(CO)$_2$(ads)$_3$, postulated by Brenner and Burwell.[22]

D. Reaction of Decomposed Molybdenum Hexacarbonyl with Ethylene. As noted in section IIIC, several tunneling junctions were prepared by reacting molybdenum hexacarbonyl vapor with the alumina surface heated to 100 °C. After evacuation of the vacuum system to a pressure below 5 × 10^{-8} Torr, the junctions

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were exposed to 2 Torr of ethylene vapor while being heated to 100 °C for 900 to 3600 s. Ethylene was used rather than propylene since the catalyst "activation" has been reported to occur at lower temperatures for this olefin,[23] although the resulting metathesis reaction cannot be observed by standard gas chromatographic detection (ethylene metathesis is degenerate). The tunneling spectrum that results from such a 900 s "activation" is shown in Figure 5C. None of the activation experiments provided any indication of hydrocarbon or carbene formation, as judged by the absence of C–H stretching modes in the 2800–3100-cm^{-1} region of the spectrum. Considering the rather severe conditions (400 °C and 1 atm of propylene) used to activate molybdenum(VI) oxide metathesis catalysts,[45] evidently our experimental conditions were insufficient to activate the decomposition product(s) of the molybdenum hexacarbonyl to the metathesis catalyst.

E. UV Exposure of Chemisorbed Molybdenum Hexacarbonyl. Photolysis of alumina-supported molybdenum hexacarbonyl by UV irradiation has been observed to produce CO and yield the proposed $Mo(CO)_3(ads)_3$ species.[36] We have attempted to prepare irreversibly adsorbed molybdenum hexacarbonyl by exposure to 366-nm radiation. Details of the experiment were given in section IIIE. The sample holder was oriented so that two junctions would be exposed to the light source and two junctions would be shielded. The resulting tunneling spectra for the exposed and unexposed junctions are shown in Figure 6, A and B, respectively. The similarity in the spectra indicates that the UV source was insufficiently intense to photolyze the carbonyl. Typically, light intensities of 4 mW/cm^2 (vs. 594 μW/cm^2 in our experiments) are used to initiate decomposition.[55] The observed weak ν(CH) modes are due to hydrocarbon contaminants from the solvent.

V. Summary

We have obtained the vibrational spectrum of a transient complex formed between molybdenum hexacarbonyl and a fully hydroxylated alumina surface. The spectrum shows significant similarities to the gas-phase or solid-state hexacarbonyl, and it is consistent with the carboxylic acid type intermediate (IV) proposed both by Burwell[31] and by Brown.[35] The complex is formed by the interaction of a surface hydroxyl group and a carbonyl from the molybdenum hexacarbonyl. Both the ease of desorption (~25 min at 22 °C) and the small perturbations from the gas-phase spectrum indicate relatively weak chemisorption on the surface. Attempts to dehydroxylate the surface partially or expose the adsorbed complex to ultraviolet irradiation proved insufficient to increase the reactivity of the carbonyl at room temperature. Heating the surface during the vapor exposure of molybdenum hexacarbonyl produced metallic molybdenum films at a temperature of 140 °C and a mixture of molybdenum suboxides and subcarbonyls at 100 °C. An attempt to react the molybdenum suboxides with ethylene to produce a molybdenum carbene species (the proposed metathesis catalyst) was unsuccessful. No evidence of hydrocarbon or carbene vibrational modes was observed.

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The Coadsorption of Hydrogen and Acetylene on the Ru(001) Surface

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Abstract: The adsorption of acetylene on Ru(001) surfaces with various coverages of preadsorbed hydrogen has been investigated by using high-resolution electron energy loss spectroscopy and thermal desorption mass spectrometry. The presence of a saturation coverage of dissociatively adsorbed hydrogen ($\theta_H \cong 0.85$) inhibits the subsequent adsorption of acetylene, reducing the fractional saturation coverage of chemisorbed acetylene at 80 K from approximately 0.25 to 0.11. Partial hydrogenation of the chemisorbed acetylene occurs as the surface is heated above 150 K, resulting in the formation of an η^2-$CHCH_2$ species. Further hydrogenation of η^2-$CHCH_2$ to ethylene occurs also, with 0.01 monolayer of ethylene desorbing at 175 K. The remainder of the chemisorbed acetylene is not hydrogenated to ethylene but undergoes carbon–hydrogen bond cleavage and formation to yield acetylide (CCH) and ethylidyne (CCH_3) above 230 K, as on clean Ru(001). The ratio of ethylidyne to acetylide is greater, however, on the hydrogen presaturated surface.

I. Introduction

The adsorption of acetylene has been studied on a number of single-crystalline transition-metal surfaces under ultrahigh vacuum (UHV) conditions,[1-15] both to gain insight into the interaction of alkynes with such surfaces and to isolate stable surface intermediates in order to make a connection with the bonding of similar ligands in organometallic complexes. In nearly all cases, acetylene adsorbs molecularly at low temperatures ($T \lesssim 250$ K) but with substantial rehybridization of the carbon–carbon triple bond occurring. We have recently reported the results of a study of acetylene adsorption and reaction on the hexagonally close-packed Ru(001) surface by using high-resolution electron energy loss spectroscopy (EELS) and thermal desorption mass spectrometry (TDMS).[16] It was found that acetylene chemisorbs molecularly on this surface below 230 K with rehybridization of

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