Matrix Isolation

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Chemistry on Single Atoms: Spontaneous Hydrogen Production from Reactions of Transition-Metal Atoms with Methanol at Cryogenic Temperatures**

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Methanol is widely used in industry as a fuel, solvent, and raw material for producing chemicals and other materials. Because of the promising applications of direct methanol fuel cells (DMFC) and the conversion of methanol to hydrogen by reforming, methanol is considered as a renewable alternative to petroleum-based hydrocarbons, thus opening the door for a possible future "methanol economy".[1] It is therefore vital to understand the interactions of methanol with metals as the latter are often used as catalysts for the chemical transformation of methanol. On the other hand, hydrogen is the ideal fuel for eco-friendly fuel cells and for onboard combustion vehicles since it has virtually zero emissions. Currently, processing by steam reforming of liquid fuels such as hydrocarbons and alcohols in the presence of a metal-based catalyst is a promising method for hydrogen production.[2] The catalytic conversions of hydrocarbons and alcohols to hydrogen are complex multiple-step chemical processes.[3] The interaction of metal atoms with methanol provides an ideal yet simple model system for understanding the complicated catalytic reaction mechanisms at the molecular level.

Numerous investigations[4–11] have been focused on the reactions of various metal atoms and methanol using matrix-isolation spectroscopy, a powerful method for delineating reaction mechanisms through the isolation and characterization of reactive intermediates.[12,13] These studies have shown that metal atoms are either thermally or photochemically inserted into the $H_3C{-}O$ and/or $O{-}H$ bonds of methanol.[4–11] Herein we report a joint matrix-isolation infrared spectroscopic and theoretical study of the reactions of early-transition-metal atoms with methanol. We have discovered an unusual reaction pathway: upon annealing, the ground-state atoms of early transition metals can react spontaneously with two methanol molecules to form low-valent $M(OMe)_2$ methoxide salts with release of dihydrogen rather than the anticipated high-valent $H_2M(OMe)_2$. This indicates that hydrogen can be produced directly from the reaction of metal atoms with methanol at cryogenic temperatures.

In this study, the metal atoms were produced by pulsed-laser evaporation of bulk metal targets. The laser-evaporated metal atoms were co-deposited with methanol/argon mixtures onto a 6 K CsI window as described elsewhere.[11,13] Infrared spectra were recorded on a Bruker IFS 66V spectrometer at 0.5 cm^{-1} resolution using a liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector. Experiments were performed by using different early transition metals including Sc, Ti, V, and Nb. With low (0.05 %) methanol concentrations, the early-transition-metal atoms Ti, V, and Nb, react with methanol to form the M(MeOH) complexes, which rearrange with insertion of the metal atom to give MeOMH molecules upon 532 nm laser irradiation.[10,11] In contrast, the ground-state Sc atoms react with methanol to directly form the inserted MeOScH molecule spontaneously on annealing.[9] When the experiments were performed using relatively high methanol concentrations, additional product absorptions were observed upon sample annealing. Taking the vanadium system as an example, a selected region of the spectra recorded using a vanadium target are shown in Figure 1, and the product absorptions are listed in Table 1. Besides the V(MeOH) absorption, new product absorptions at 2835.5, 1168.2, and 618.0 cm^{-1} appear on sample annealing to 30 K (Figure 1b). These absorptions increase together at the expense of the V(MeOH) absorption upon sample annealing to 35 K (Figure 1c). When the sample is subjected to 532 nm laser irradiation (Figure 1d), site absorptions at 2837.0, 1171.9, and 622.5 cm^{-1} are produced. The spectra recorded for the other metal systems (Sc, Ti, and Nb) are very similar to those of vanadium, and the results are shown in Figures S1–S5 of the Supporting Information.

Isotopic substitutions ($^{13}CH_3OH$, $CH_3{}^{18}OH$, $^{12}CH_3OH$ + $^{13}CH_3OH$, and $CH_3{}^{16}OH$ + $CH_3{}^{18}OH$) were employed for product identification based on isotopic shifts and absorption splitting. The absorptions at 2835.5, 1168.2, and 618.0 cm^{-1} are assigned to different vibrational modes of the $V(OMe)_2$ molecule (Table 1). The 1168.2 cm^{-1} absorption shifts to

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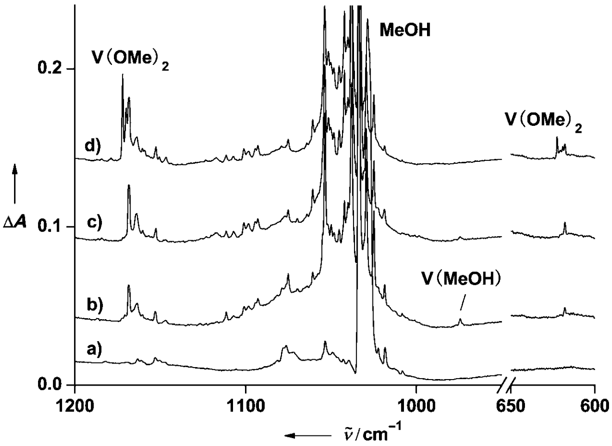

Figure 1. Infrared spectra in the 1200–950 and 650–600 cm^{-1} regions from co-deposition of laser-evaporated vanadium atoms with 0.2% CH_3OH in argon. a) After 1 h of sample deposition at 6 K, b) after annealing to 30 K, c) after annealing to 35 K, and d) after 10 min of laser irradiation ($\lambda = 532$ nm).

Table 1: Observed and calculated vibrational frequencies [cm^{-1}] of the $V(OMe)_2$ molecule.

Mode	CH_3OH		$CH_3{}^{18}OH$		$^{13}CH_3OH$	
	calcd.	obs.[a]	calcd.	obs.	calcd.	obs.
C–H stretch (a_{2u})	2986.4	2835.5	2986.4	2836.6	2984.7	2834.3
antisymmetric C–O stretch (a_{2u})	1181.0	1168.2	1141.4	1131.2	1163.6	1151.5
antisymmetric V–O stretch (a_{2u})	617.1	618.0	613.6	614.1	609.4	610.2

[a] Only the major site absorptions are listed.

1131.2 cm^{-1} with $CH_3{}^{18}OH$, exhibiting an $^{16}O/^{18}O$ isotopic frequency ratio of 1.0327. Upon $^{12}C/^{13}C$ substitution, the 1168.2 cm^{-1} absorption shifts to 1151.5 cm^{-1} with a $^{12}C/^{13}C$ isotopic frequency ratio of 1.0145. The band position and isotopic frequency ratios imply that this absorption is due to a C–O stretching vibration. In the experiment with an equimolar mixture of $CH_3{}^{16}OH$ and $CH_3{}^{18}OH$, one intermediate absorption at 1138.1 cm^{-1} together with an additional absorption at 1180.6 cm^{-1} was observed (Figure 2). Similar splitting was also observed in the experiment with a 1:1 mixture of $^{12}CH_3OH$ and $^{13}CH_3OH$. These spectral features indicate that the absorber involves two equivalent CO subunits that are central symmetric; in other words, it is a reaction product from two methanol molecules. The absorption at 1168.2 cm^{-1} is due to the antisymmetric C–O stretching vibration of $V(OMe)_2$. The symmetric C–O stretching mode is IR inactive in keeping with the selection rule, but this mode of the $V(^{16}OMe)(^{18}OMe)$ isotopomer is IR active because of the reduced symmetry. The absorptions at 1138.1 and 1180.6 cm^{-1} observed in the mixed-isotope experiments are due to the antisymmetric and symmetric C–O stretching modes of $V(^{16}OMe)(^{18}OMe)$. The absorptions at 2835.5 and 618.0 cm^{-1} are due to the antisymmetric C–H and V–OMe stretching modes of $V(OMe)_2$.

To validate the experimental assignment, we performed quantum chemical calculations using density functional theory (DFT) and wavefuction-based ab initio methods.[14] Besides the equilibrium geometries and vibrational spectra of the intermediates and products, energetic and potential energy surfaces of the observed reactions were also calculated. DFT calculations predict that the $V(OMe)_2$ molecule has a quartet ground state with C_{3v} symmetry (Figure 3); the COVOC fragment is linear. The calculated vibrational frequencies and isotopic frequency ratios are compared with the experimental values in Table 1. Three modes in the spectral range of 4000–400 cm^{-1} are predicted to be IR active with appreciable intensities. These adsorptions are experimentally detected and the calculated frequencies and isotopic frequency ratios are in good agreement with the experimental values; this provides unequivocal support to the experimental assignment.

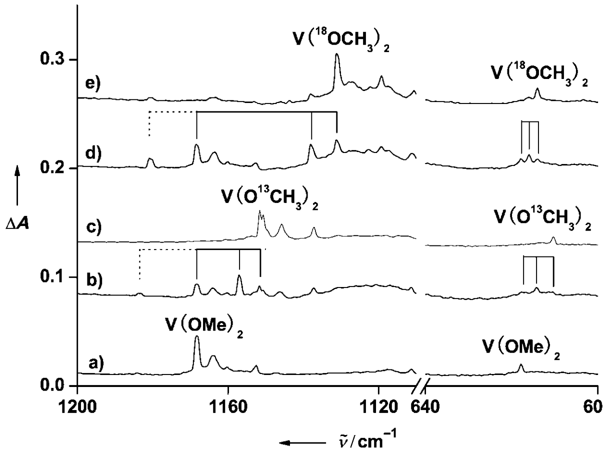

Figure 2. Infrared spectra in the 1200–1110 and 640–600 cm^{-1} regions from co-deposition of laser-evaporated vanadium atoms with the isotopic-labeled methanol in excess argon. Spectra were recorded after 1 h of sample deposition at 6 K followed by annealing at 35 K. a) 0.2% CH_3OH, b) 0.1% CH_3OH + 0.1% $^{13}CH_3OH$, c) 0.2% $^{13}CH_3OH$, d) 0.1% CH_3OH + 0.1% $CH_3{}^{18}OH$, e) 0.2% $CH_3{}^{18}OH$.

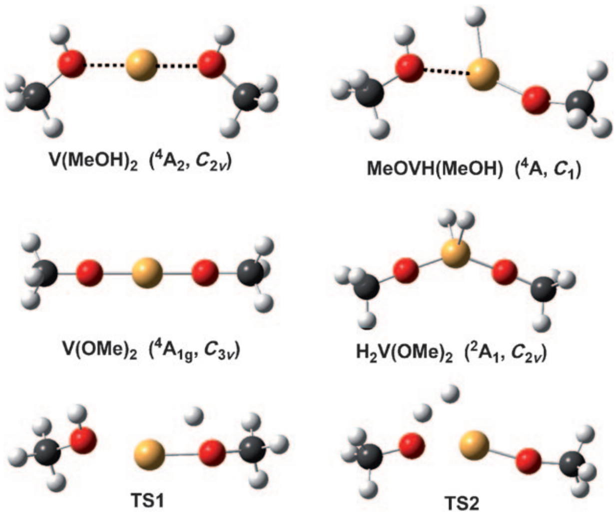

Figure 3. Optimized structures of the intermediates and transition states involved in the reaction $V + 2\,MeOH \rightarrow V(OMe)_2 + H_2$.

The spectra in Figure 1 clearly demonstrate that the $V(OMe)_2$ molecules are formed spontaneously on annealing, which suggests that the ground-state vanadium atom reacts with two methanol molecules in solid argon to form $V(OMe)_2$ with release of one hydrogen molecule [Eq. (1)]. The dihydrogen molecule is IR inactive and cannot be observed.

$$V + 2\,MeOH \rightarrow V(OMe)_2 + H_2 \qquad (1)$$

Our experiments find that other early-transition-metal atoms including Sc, Ti, and Nb are also able to undergo spontaneous replacement reactions with two methanol molecules to form $M(OMe)_2$ and one hydrogen molecule (see Table S1 and Figures S1–S5 in the Supporting Information). These results are at variance with previous investigations of similar reactions between early transition metals and water.[15] At first glance, it is quite surprising that the reaction $M + 2\,MeOH$ gives the divalent $M(OMe)_2$ molecule instead of the tetravalent $H_2M(OMe)_2$ molecule, in which two more H–M bonds are formed. However, our calculations show that the doublet ground state of $H_2V(OMe)_2$ lies 8.6 kcal mol^{-1} higher in energy than $V(OMe)_2 + H_2$ at the CCSD(T)//B3LYP level of theory, indicating that the formation of tetravalent vanadium complex $H_2V(OMe)_2$ from $V + 2\,MeOH$ is energetically unfavorable. This result can be rationalized in terms of the difference in the strengths of the V–H and H–H bonds. In fact, the H–H bond strength (104.2 kcal mol^{-1}) is more than twice that of the V–H bond (49.1 kcal mol^{-1}).[16,17] Therefore formation of H_2 is thermodynamically more favorable than that of the two V–H bonds. In contrast, it was found that reactions of the early-transition-metal atoms with two water molecules give high-valent $H_2M(OH)_2$ instead of low-valent $M(OH)_2$, consistent with the theoretical prediction that $H_2M(OH)_2$ is more stable than $M(OH)_2 + H_2$.[15] The higher acidity of the MeOH hydrogen compared to H_2O is responsible for the different reactivity. Meanwhile the stronger donating capacity of OMe relative to OH can stabilize the divalent $M(OMe)_2$ complexes.

The mechanism of the reaction neutral metal atoms is different from that of metal cations. The reactivity of atomic vanadium cation and vanadium cluster cations toward methanol has been investigated recently in the gas phase using mass spectrometry.[18] In the case of atomic vanadium cation, the oxygen atom is transferred to the metal and methanol is reduced to methane or methyl radical; efficient dehydrogenation of methanol to produce V_nOC^+ and two hydrogen molecules takes place only for the vanadium cluster cations.

The potential energy profile for the reaction $V(s^2d^3) + 2\,MeOH$ calculated at the CCSD(T)//B3LYP/6-311++G** level of theory is shown in Figure 4. Reaction (1) proceeds with the initial formation of the V(MeOH) and $V(MeOH)_2$ adduct complexes without any barrier. Both complexes are predicted to have a quartet ground state. The $V(MeOH)_2$ complex lies 21.0 kcal mol^{-1} lower in energy than the ground-state reactants, $V + 2\,MeOH$. We have not located a transition state for the one-step release of H_2 directly from the $V(MeOH)_2$ complex. Instead, the reaction is predicted to be a two-step process with the initial formation of a MeOVH(MeOH) intermediate via a transition state (TS1) lying 17.3 kcal mol^{-1} above the $V(MeOH)_2$ complex. From the MeOVH(MeOH) intermediate, the reaction proceeds to the $V(OMe)_2 + H_2$ products via another transition state (TS2). This step is exothermic by 24.0 kcal mol^{-1} with a very low barrier (3.6 kcal mol^{-1}). Overall, reaction (1) is predicted to be exothermic by 88.5 kcal mol^{-1}, and proceeds via two transition states, which lie 3.7 and 60.9 kcal mol^{-1} lower in energy than the ground-state reactants. The exothermicity of the overall reaction and the negative energy barrier heights as compared to the reactants imply that reaction (1) is both thermodynamically favorable and spontaneous in each kinetic steps. Owing to the small barriers, the intermediates involved in reaction (1) cannot be frozen in the solid argon matrix. Only the initially formed V(MeOH) complex was observed in our experiments. The calculations indicate that the reaction from the V(MeOH) complex to the inserted MeOVH isomer proceeds by a hydrogen-atom migration from O to V via a transition state, which lies 15.1 kcal mol^{-1} higher in energy than the ground-state reactants, $V + MeOH$ (Figure S6 in the Supporting Information). Therefore, the V(MeOH) complex is stabilized in the solid matrix, and the inserted MeOVH isomer is formed only under laser irradiation. As can be seen in Figure 4, the energy barrier for the metal-atom insertion decreases by about 18.8 kcal mol^{-1} upon coordination of a second methanol molecule. A dramatic increase in reactivity upon ligation has been reported for many transition-metal systems.[19] Calculations on the reaction $Sc + 2\,MeOH$ (Figure S7 in the Supporting Information) indicate that the overall reaction to form $Sc(OMe)_2$ and H_2 is also exothermic with low energy barriers for each elementary reaction step.

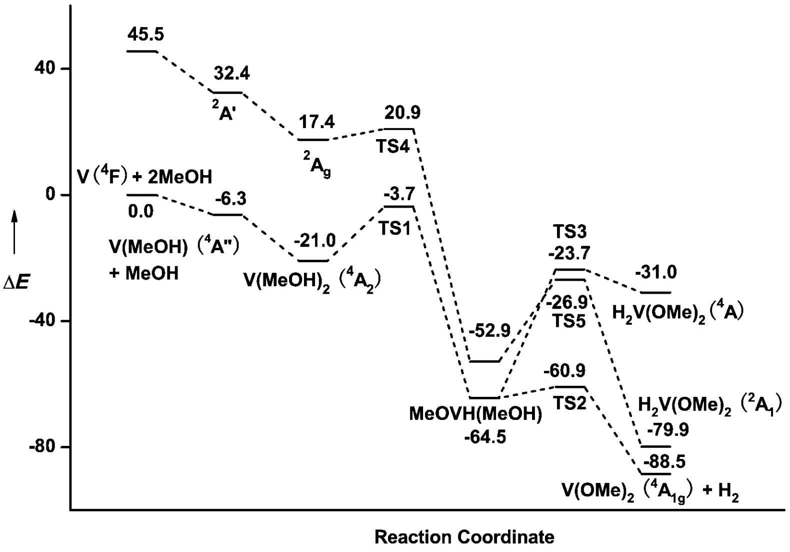

Figure 4. The quartet and doublet potential energy profiles of the reaction $V + 2\,MeOH$ calculated at the CCSD(T)//B3LYP/6-311++G** level of theory. The energies [kcal mol^{-1}] are corrected with zero-point energy.

In summary, our investigation clearly demonstrates that some early-transition-metal atoms are able to react with two methanol molecules to form the low-valent $M(OMe)_2$ methoxide molecules spontaneously upon annealing in solid argon. This indicates that hydrogen can be produced directly from the reaction of ground-state metal atoms with methanol even at cryogenic temperatures. The present finding points to new approaches to the design of catalysts such as supported single-atom systems or metal-atom-embedded polymer matrices for hydrogen production. As the dissociative adsorption of methanol ($MeOH + * \rightarrow CHO_{ads} + H_{ads}$) is the first elementary reaction step widely involved in methanol corrosion of metals and methanol chemisorption on metal surfaces, the results presented here may also help to understand methanol corrosion processes and catalytic mechanisms of methanol on metal surfaces.

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