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FTIR Matrix-Isolation Study of the Reaction Products of Vanadium Atoms with Propene: Observation of Allylvanadium Hydride As a Precursor to Sacrificial Hydrogenation of Propene

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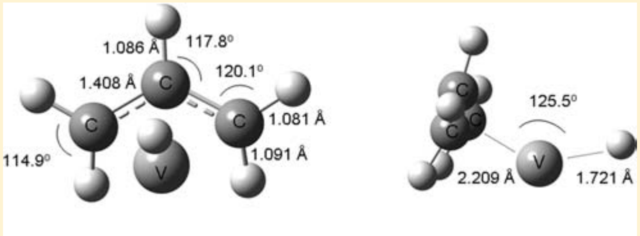
S *Supporting Information*



Doublet H-V-(η^3-C_3H_5)
(point group: C_s)

ABSTRACT: Vanadium atoms have been reacted with different partial pressures of propene in Ar under matrix-isolation conditions, and the products have been observed using Fourier transform infrared (FTIR) spectroscopy. Under dilute propene in Ar conditions, new features are observed in the IR spectra corresponding to a C−H insertion product, identified here as H−V−(η^3-allyl). Use of d_3-propene ($CD_3-CH{=}CH_2$) demonstrates that the initial V-atom insertion occurs at the methyl group of the propene molecule, and DFT calculations have been used to support the identity of the initial product. Upon increasing the partial pressure of propene, additional features corresponding to propane (C_3H_8) are observed, with the hydrogen-atom source for the observed hydrogenation demonstrated to be additional propene units. Analysis of a systematic increase in the partial pressure of propene in the system demonstrates that the yield of propane correlates with the decrease of the allyl product, demonstrating the H−V(allyl) species as a reactive intermediate in the overall hydrogenation process. An overall mechanism is proposed to rationalize the formation of the insertion product and ultimately the products of hydrogenation, which agrees with previous gas-phase and matrix-isolation work involving propene and the related system, ethene.

INTRODUCTION

Metal-based reactions with hydrocarbons play a key role in understanding many industrial and catalytic processes.[1] Many of these metal-based processes incorporate early transition metal atoms, and while these can be very catalytically active, the specific reaction steps of the catalytic processes are rarely known precisely. Given the paucity of detailed structural and spectroscopic information about some of the simplest organometallic species, overall reaction mechanisms in this field are difficult to confirm. Thus, techniques that can directly explore intermediate steps of an overall reaction pathway can provide invaluable insight into the mechanism of metal-based catalytic processes.

The technique of matrix isolation coupled with infrared spectroscopy provides one method by which metal-atom reactions with hydrocarbons can be straightforwardly investigated[2,3] while providing detailed information about the structure of metal−organic reactive intermediates and their reactivity. Early transition metal atoms reacting with ethene have been previously investigated by Thompson and Parnis,[2] as well as by Cho and Andrews,[3] under matrix-isolation conditions. Such results demonstrate that excited-state V atoms insert into C−H bonds to yield a vinylvanadium hydride intermediate.[3] Increasing ethene partial pressure yields ethane (C_2H_6), with the implication that the H atoms are transferred to an additional ethene unit via the V−H bond in vinylvanadium hydride, thereby transferring hydrogen from one ethene to another (sacrificial hydrogenation).[4] The current investigation uses propene to confirm previous mechanistic aspects and to provide new spectroscopic insights into the nature of the reaction products.

The reactivity of ground- and excited-state V atoms with ethene and propene has been investigated in the gas phase.[5,6] The initial products are identified as atomic metal and alkene π-coordination products, but exact structures of the final products are not confirmed. Song and co-workers also investigated vanadium atom and cluster reactions with propene and halopropenes using mass spectrometry.[7] Following alkene monomer pickup, all clusters, save the ground-state metal atom, demonstrated products consistent with C−H bond insertion and elimination of H_2.[7]

The present work is aimed toward further investigating the C−H bond insertion chemistry of V atoms with propene. A C−H bond insertion intermediate is observed, which is identified as allylvanadium hydride. At higher partial pressures of

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propene, the allylvanadium hydride also undergoes further reactivity to yield propane as the major product.

■ EXPERIMENTAL SECTION

The specific details of the apparatus used in these experiments have been described previously.[2] All gas samples were prepared using standard manometric techniques and contained 0.1−2% propene ($CH_3{-}CH{=}CH_2$, 99+% propene, Aldrich), perdeuteriopropene ($CD_3{-}CD{=}CD_2$, 99.7% atom D, C/D/N Isotopes), or d_3-propene ($CD_3{-}CH{=}CH_2$, 99.9% atom D, C/D/N isotopes) diluted in argon. Some experiments included 0.1−1% H_2O or D_2O (99% atom D, Aldrich), purified by freeze−pump−thaw cycles. Experiments involving D_2O also involved exposure of the entire interior of all components of the apparatus with D_2O vapor in three repetitions to dissociatively chemisorb D_2O, minimizing conversion of D_2O to HOD, by H/D exchange. Additionally, propane (C_3H_8, C.P. grade, Matheson) was used for verification as a spectroscopic reference material where necessary. All gas samples were prepared by diluting the reagent gases in ultra-high-purity argon (UHP grade, 99.9995%, Praxair).

Vanadium atoms were generated by resistively heating a thin strip of the pure metal (0.25 mm thickness, 99.5% metal basis, Alfa Aesar) placed between water-cooled copper electrodes using a 30 A alternating current variable-power supply under high-vacuum conditions (10^{-7}−10^{-8} Torr system base pressure). The rate of deposition of metal atoms was monitored by use of a quartz crystal microbalance. Typical metal introduction rates were between 0.3 and 0.5 μmol/h. Metal atoms were mixed in a flow of argon (up to ∼10 mmol/h), which contained the above-listed reagent species, using an MKS 1100 series mass flow controller. Note that the resistive heating of the filament unavoidably irradiates the matrix during sample preparation with orange light.

Argon/propene mixtures containing the metal atoms were condensed on a cold CsI spectroscopic window maintained near 17 K using an APD Cryogenics (model HC-2) closed cycle helium refrigeration unit. Additional irradiation of deposited matrices with light was performed using a Kratos LH150 150W Xe arc lamp and various band-pass filters, where indicated. Typical matrix deposition times were 75 min. In all cases, IR absorption spectra of the condensed matrices were collected using a 1 cm^{-1} resolution Bomem MB 102 spectrometer, operating in absorption mode.

To confirm the identity of molecular species associated with observed infrared absorptions, complementary density functional theory (DFT) calculations were carried out using the Gaussian 03 software package[8] using the B3LYP density functional and the 6-311G(3df,3pd) basis set for all of the atoms used. Geometries were fully relaxed during the optimization cycles, and the optimized geometries were confirmed by analysis of the calculated vibrational wavenumber values.

■ RESULTS

When V atoms are codeposited with dilute propene in Ar (1 to 1000, C_3H_6 to Ar) a number of new features can be observed in the corresponding infrared spectra. Figure 1 provides the full infrared spectra obtained from replicate matrices containing 0.1% propene in Ar with and without inclusion of V atoms. The use of difference spectra obtained by subtracting the metal-free spectrum from the metal-containing spectrum serves to illuminate product-related absorptions. All product absorptions are observed in the difference spectrum as positive features, while negative features are associated with consumed precursor.

Analysis of the difference spectrum for 0.1% propene with and without V atoms shows a series of new features. The main wavenumber values associated with product absorptions are summarized in Table 1. All of these product absorptions are consistent with new hydrocarbon or organometallic intermediate species. (Spectrally expanded portions of the infrared spectra, highlighting the key absorption regions, are given in the Supporting Information.) Of the main product features observed, one group (referred to as species A) is identified below as allylvanadium hydride, H−V−(η^3-C_3H_5). In addition, several features (2973.2, 1466.8, and 743.9 cm^{-1}) correspond well to absorptions of propane isolated in argon (referred to as species B). Additional features are observed corresponding to matrix-isolated CO_2[9] and matrix-isolated CO,[9] which are unavoidably present in a trace amount during metal experiments. Similarly, an absorption at 1305 cm^{-1} is also observed, corresponding to CH_4.[9] When a similar set of experiments was performed using 1 to 1000 d_6-propene in Ar, related absorptions were observed with absorption positions shifting in accordance with deuterium substitution (see Table 1). Additionally, a very weak absorption is observed at 993 cm^{-1}, an indication of CD_4 isolated in Ar.[9]

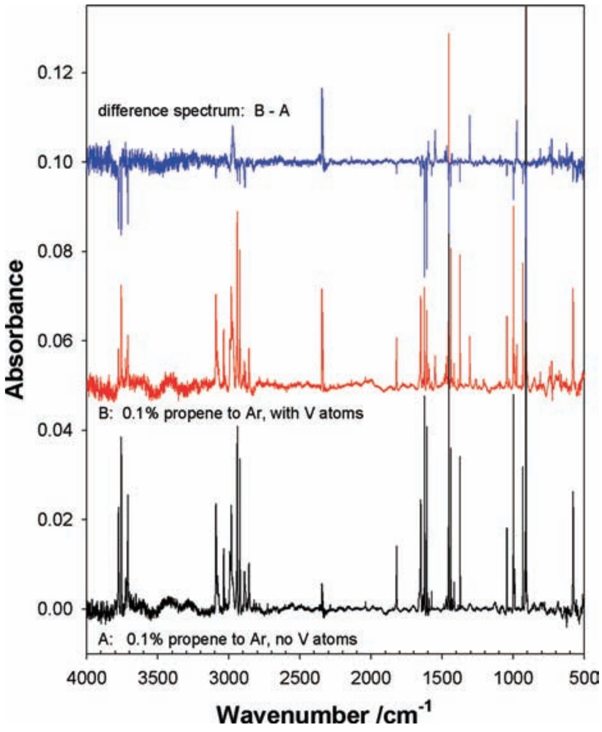

Figure 1. Comparison of the infrared spectra obtained from replicate Ar matrices formed containing (A) 1 to 1000 propene to Ar and (B) 1 to 1000 propene to Ar with V atoms. The uppermost trace is a subtraction (difference spectrum) of B − A. Negative features are consumed precursor, while positive absorptions represent product features.

When a similar set of experiments was performed using 1 to 1000 d_6-propene in Ar, related absorptions were observed with absorption positions shifting in accordance with deuterium substitution. Additionally, a very weak absorption is observed at 993 cm^{-1}, an indication of CD_4 isolated in Ar.[9]

The wavenumber ratio of the most intense absorptions in the h_6-propene and d_6-propene at 1549 and 1117 cm^{-1}, respectively, suggests a V−H-containing product arising from metal-atom insertion into the C−H bond of propene. To further investigate this and determine which of the propene C−H bonds is the site of insertion, additional experiments were performed using 3,3,3-d_3-propene, $CD_3{-}CH{=}CH_2$. When the difference spectrum for matrices containing 1 to 400 3,3,3-d_3-propene to Ar is analyzed, a series of related features is observed, along with absorptions at

Table 1. Comparison of Product Absorption Features for V atoms Reacting with Varied Concentration of Propene Isotopomers under Matrix-Isolation Conditions[a]

1 to 1000 propene to Ar		1 to 100 propene to Ar		1 to 1000 propane in Ar	1 to 1000 d_6-propene to Ar		1 to 100 d_6-propene to Ar		gas-phase d_8-propane	1 to 400 d_3(methyl)-propene to Ar	
wavenumber/ cm^{-1}	identity	wavenumber/ cm^{-1}	identity	wavenumber/ cm^{-1}	wavenumber/ cm^{-1}	identity	wavenumber/ cm^{-1}	identity	wavenumber/ cm^{-1}	wavenumber/ cm^{-1}	identity
1549.2	A	1549.2 (very weak)	A		1117.2	A				1435.1	A
1480.9	A				1092.5	A				1117.2	A
1207.5	A									1081.1	A
974.5	A									772.5	A
810.1	A				780.8	A				576.4	A
728.7	A				638.4	A					
624.1	A				561.7	A					
2973.2	B	2973.8	B	2973.1	2226.6	B	2226.6	B	2225		
		2941.2	B	2941.6			2150.4	B	2148		
		2902.8	B	2902.8			2119.9	B	2120		
		2882.1	B	2882.7			2077.8	B	2080		
1473.5	B	1473.2	B	1473.5	1080.4	B	1080.6	B	1064		
1466.8	B	1466.7	B	1467			1063.5	B	712		
		1387.1	B	1387.2							
		obscured by precursor		1372.6							
		1050.4	B	1050.4							
		obscured by precursor		918.5							
743.9	B	743.1	B	744.1			573.9	B	572		
1305.1	CH_4						993.7	CD_4			

[a] Gas-phase d_8-propane values obtained from Gough et al., ref 10.

new positions. Major new product features are observed (see Table 1), along with weak C$-$H and C$-$D stretching region absorptions. No feature is observed at 1549 cm^{-1}.

To better identify the carrier of the observed absorptions, irradiation of the metal-containing matrices was performed. A series of 5 min irradiations, with wavelength ranges of light >495, 455, 400 nm and finally with a band-pass range with maximum transmittance at 320 nm showed no changes in the matrix spectra, indicating no photochemical reactivity of the species within the matrix environment. In addition, to investigate any influence of deposition temperature on the reaction chemistry during matrix formation, a set of comparison experiments was performed where the matrix-deposition temperature was raised to 25 K. The comparison with experiments done at lower temperature showed no significant effect on hydrogenation product yield.

Experiments employing increased concentration from 1 to 1000 propene to Ar through to a maximum concentration of 1 to 50 propene to Ar were performed to investigate the dependence of the products on the availability of the precursor. With 1 to 100 propene to Ar, the features associated with species A showed decreased intensity in the higher concentration experiments while those of species B increased in intensity, with new features observed at 2941.2, 2902.1, 2882.1, 1387.1, and 1051.1 cm^{-1}. On the basis of this behavior, we can identify species A as a primary product and species B (propane) as a secondary product. A comparison of the major product absorptions with an infrared spectrum of 0.1% propane isolated in Ar is given as Figure 2. The complete set of absorptions and their tentative identity is given in Table 1.

Figure 3 shows the comparative yield of each species as a function of propene concentration. With increasing propene concentration, the measured area of the main features attributed to species A decrease while the main features for species B increase. In addition, it was observed that increasing the gas-flow rate for matrix deposition showed marked enhancements of species B, with only modest increases in species A. Together, these results suggest that net formation of species B involves more than one propene molecule, while species A requires a single propene unit.

Results from samples of V co-condensed with 1 to 100 d_6-propene to Ar show two sets of absorptions also corresponding to species A and B. The former decrease with increasing propene partial pressure, while those of species B increase. The absorptions due to species B are consistent with the spectrum of gas-phase d_8-propane,[10] providing further support for the species B identification as propane. Matrices formed containing 1 to 100 3,3,3-d_3-propene ($CD_3{-}CH{=}CH_2$) to Ar with and without metal atoms showed many C$-$H and C$-$D modes corresponding to isotopic propane species. However, the relative complexity of the isotopic products makes it difficult to assign the specific isotopomer of propane conclusively. The complexity of the pattern suggests that more than one propane isotopomer may be generated.

Using $CD_3CH{=}CH_2$ at various concentrations, a similar set of features demonstrating the behavior of species A can also be identified. Again, no H$-$V stretch is observed near 1550 cm^{-1}. Furthermore, at higher concentration, these species A features do not appear. Instead, spectra yield features with characteristics similar to species B, described above. The pattern of behavior is consistent with species B, but in the isotopic case, it is possible that there is more than one isotopomeric form of the species B product, depending on the H-atom source for hydrogenation (i.e., d_6-propene or impurity H_2O).

Finally, that species B demonstrates an apparent hydrogenation of propene when V atoms are present along with an observed consumption of unavoidable impurity H_2O in the corresponding gas implies that hydrogenation could occur by reaction of V atoms with H_2O and propene. Experiments were performed where 1% D_2O was added to a sample containing 1% propene in Ar. No evidence for new C$-$D modes was observed. Similarly, samples containing d_6-propene with H_2O showed no evidence for new C$-$H features following codeposition with V atoms.

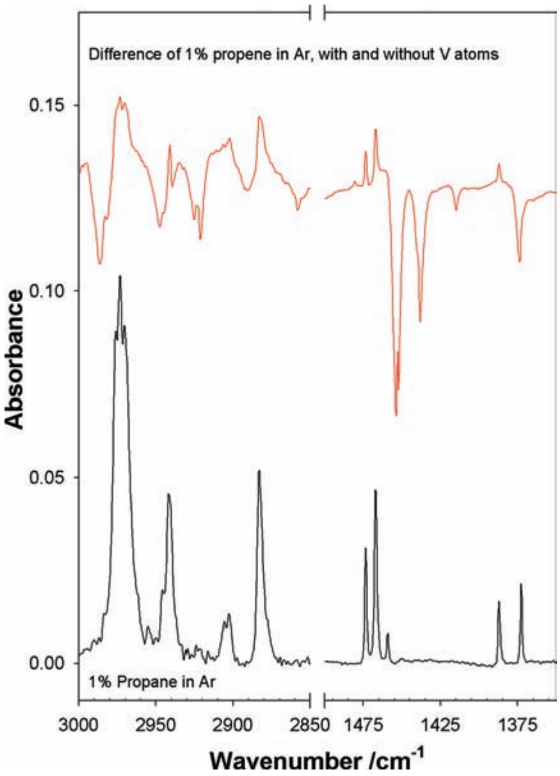

Figure 2. Comparison of the infrared spectrum of 0.1% propane in Ar with the difference spectrum obtained when V atoms react with 1% propene in Ar. Unless obscured by the propene precursor, all propane modes are observed in the product matrix at the same position with similar relative intensities as the reference propane sample matrix.

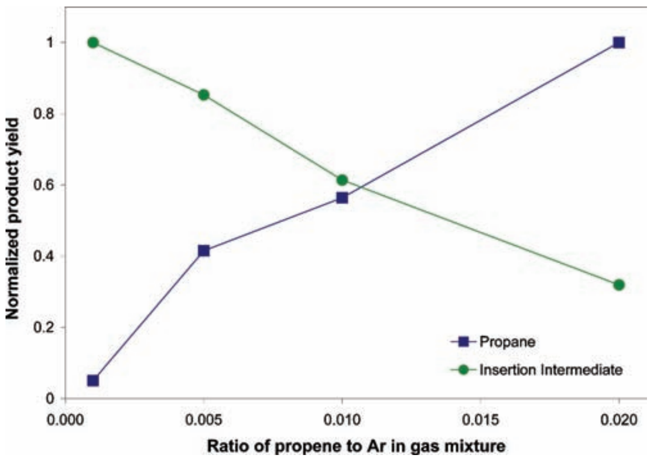

Figure 3. Comparison of the yield of the metal C—H insertion product "A" and the yield of propane with propene availability. For each product, the measured peak areas has been normalized relative to the largest area in the corresponding data set.

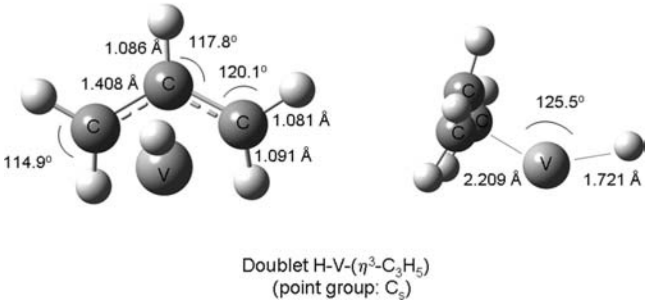

Figure 4. Optimized B3LYP/6-311(3df,3pd) structure of doublet H—V(η^3-CH_2CHCH_2). The molecule is predicted to belong to the C_s point group and is pictured from two sides for clarity.

Thus, when hydrogenation is observed, it involves hydrogen transfer from propene precursor molecules only.

Computational Results. To confirm the proposed structure of species A as H—V—(η^3-allyl), B3LYP/6-311G(3df,3pd) calculations were performed for the main spin states expected for this structure. The doublet, quartet, and sextet spin states of the molecule are possibilities; however, of these, only the doublet and quartet are lower in energy than the starting products. As a result, the observed features corresponding to species A were compared with calculated frequencies for both the doublet and the quartet species. Only the doublet insertion species provides a good match for the calculated wavenumber values. The structure of the optimized geometry for the doublet species is given as Figure 4.

In Table 2, the comparison of the calculated wavenumber values for the doublet H—V—(η^3-allyl) with those observed in the experiment are given. A comparison of the same data for the quartet spin state of the same species is given in the Supporting Information.

■ DISCUSSION

Identification of Species A and B. Analysis of the infrared spectra of matrices formed by co-condensation of V atoms with dilute propene in Ar shows that a clear series of product features appears in the spectra. The lack of change in any of the spectra following irradiation suggests that either the product species are quite stable or these species have no chromophore for UV—vis absorption in the employed range. By directly comparing the relative amounts of these species as the availability of propene is increased, species B maximizes at the expense of species A (see Figure 3). These facts imply that species A is a primary product, which upon increase of availability of propene is transformed into product B.

The major features associated with species A are maximized when propene concentration is lowest. In the most dilute experiments, a major absorption is observed near 1549 cm^{-1} for V/C_3H_6, and this absorption shifts to 1117 cm^{-1} when V/C_3D_6 experiments are performed. The ratio of the absorptions for the observed V—H/V—D is 1.404, and this is precisely the value that would be anticipated for the ratio of a V—H/V—D stretching absorption. This is strong evidence in support of assignment of this mode as an uncoupled single V—H stretching mode. The absorption position of organometallic species having a vanadium monohydride unit is in the vicinity of 1560 cm^{-1}.[2,3] Thus, the V atom has clearly inserted into a C—H bond of the propene molecule, and species A is consistent with a metal monohydride, with likely chemical formula HV(C_3H_5).

There are four unique C—H bonds in propene, CH_3—CH=CH_2: one allylic position and three vinylic positions. The bond strength of the C—H bond at the allylic position is 361 kJ·mol^{-1}, much weaker than the other vinylic C—H bonds, which are closer to 444 kJ·mol^{-1}.[11] Therefore, it is energetically favorable for a metal atom to preferentially insert into the methyl

Table 2. Comparison of the Predicted Wavenumber Values (Unscaled) for Isotopomers of Doublet (η^3-Allyl) Vanadium Hydride

6-311G(3df,3pd)	rel int	expt
doublet, $HV(\eta^3-CH_2CHCH_2)$		
232.8	0.21	
273.8	0.05	
304.2	0.03	
348.4	0.05	
364.4	0.15	
412.7	0.06	
569.5	0.00	
697.2	0.01	624.1
796.7	0.12	728.7
833.7	0.00	
929.6	0.00	
947.9	0.01	
1011.3	0.07	974.5
1230.5	0.02	
1240.7	0.05	1207.5
1415.4	0.00	
1480.9	0.01	
1520.1	0.08	1480.9
1601.3	1.00	1549.2
3051.4	0.00	
3058.1	0.03	
3125.3	0.01	
3196.2	0.00	
3199.0	0.00	
doublet, $DV(\eta^3\text{-}CD_2CDCD_2)$		
185.92	0.30	
219.06	0.12	
271.77	0.02	
283.59	0.01	
300.74	0.08	
333.40	0.03	
425.77	0.00	
542.53	0.02	
617.99	0.13	561.7
638.30	0.01	
687.62	0.00	638.4
762.69	0.01	
839.99	0.11	
930.62	0.02	
1015.37	0.01	
1060.24	0.00	
1144.61	1.00	1117.2
1230.82	0.02	
1432.41	0.25	1406.6
2223.80	0.01	
2227.08	0.04	
2306.13	0.00	
2370.04	0.00	
2374.37	0.01	
doublet - $DV(\eta^3\text{-}CD_2CHCH_2)$		
195.38	0.33	
222.51	0.12	
286.34	0.03	
289.93	0.02	
321.30	0.07	
369.51	0.04	
466.30	0.02	
607.89	0.07	576.7
683.01	0.03	
783.43	0.03	
814.46	0.10	772.9
927.96	0.10	
942.62	0.00	
1071.63	0.03	
1145.00	1.00	1117.6
1219.35	0.03	
1250.59	0.10	
1440.78	0.03	
1506.32	0.14	1475.9
2226.04	0.02	
2371.24	0.00	
3054.75	0.03	
3126.42	0.02	
3197.61	0.01	

C−H bond. When experiments were performed using dilute 3,3,3-d_3-propene, $CD_3-CH{=}CH_3$ in Ar, the 1549 cm^{-1} absorption was completely absent and no new features were observed in this area. However, the 1117 cm^{-1} absorption was present and as intense as in related experiments where perdeuteriopropene was employed. Using this observation, it seems clear that insertion of the metal atom occurs selectively at the allylic position of the hydrocarbon. Additionally, the complete shifting to almost the exact wavenumber position observed in pure C_3D_6 suggests that this observed feature is a pure uncoupled V−H (V−D) stretch.

In the reaction of V atoms with ethene, photoexcitation was required,[3−7] provided by the metal source during sample deposition.[4] In the case of propene, ground-state V atoms have been shown to react with propene,[5] though reaction of excited-state V atoms is faster.[6] Thus, when considering reactivity factors, the initial V atom may be a ground state V or a photoexcited V* atom, and in this particular case, it is likely that both reactions proceed via a parallel set of reaction steps.

Following insertion of the metal into the C−H bond of the methyl group, two isomeric forms are possible, specifically, an open structure where the π-bond is not coordinated to the V atom and a closed structure where π-coordination to V has occurred. The open $H-V-CH_2-CH{=}CH_2$ structure, bearing an η^1-propenyl substituent, should have an absorption in the region of 1650 cm^{-1}, since there is an asymmetric C=C in the structure. However, no evidence for such an absorption is apparent in any of the observed infrared spectra. Instead, it is likely that π-coordination of the alkene at the V atom is occurring. Such donation of the π-bond to an oxidized metal atom would reasonably be expected to be a near-barrierless association and would not be inhibited under the cryogenic conditions of matrix isolation. Therefore, it is likely that this association occurs spontaneously, forming a ring-like η^3-C_3H_5 structure on the metal center. Such η^3-propenyl species are well known in organometallic and complexation chemistry and can be considered as fluxionally interconvertible with isomeric resonance forms best considered as a coordinated allylic group.[1]

To confirm the structure, B3LYP/6-311G(3df,3pd) calculations were performed on the doublet, quartet, and sextet structures of the H−V(η^3-allyl) structure. Of these, only the doublet and quartet were lower in energy than the starting materials, and on the basis of the comparisons given in Table 2, the doublet structure shows a strong match between the observed and calculated wavenumber positions and relative intensities for absorptions. The quartet species (see the Supporting Information for summarized calculation data), by comparison, shows a very poor correlation. Therefore, on the basis of all of this evidence, the most likely structure of the species A product is the doublet state of H−V(η^3-allyl). The structure of the optimized doublet species is given in Figure 4.

Scheme 1. Proposed Reaction Scheme for V Atoms Reacting with Propene under Matrix-Isolation Conditions

$$\begin{gathered}
\mathrm{V} + h\nu \rightarrow \mathrm{V}^{*} \\
\mathrm{V}^{*} + \mathrm{CH_3} - \mathrm{CH{=}CH_2} \rightarrow (\mathrm{V}(\eta^{2}\text{-propene}))^{*} \rightarrow \mathrm{H} - \mathrm{V}(\eta^{1}\text{-propenyl}) \\
\text{Under low partial pressure of } \mathrm{C_3H_6}: \\
\mathrm{H} - \mathrm{V}(\eta^{1}\text{-propenyl}) \rightarrow \mathrm{H} - \mathrm{V}(\eta^{3}\text{-allyl}) \\
\text{Under high partial pressure of } \mathrm{C_3H_6}: \\
\mathrm{H} - \mathrm{V}(\eta^{1}\text{-propenyl}) + \mathrm{CH_3} - \mathrm{CH{=}CH_2} \rightarrow \mathrm{CH_3CH_2CH_2} - \mathrm{V}(\eta^{1}\text{-propenyl}) \\
\mathrm{CH_3CH_2CH_2} - \mathrm{V}(\eta^{1}\text{-propenyl})(+h\nu) \rightarrow \mathrm{CH_3CH_2CH_3} + \mathrm{V(C_3H_4)} \\
\mathrm{V(C_3H_4)}(+h\nu) \rightarrow\ \rightarrow \mathrm{V(C_2)} + \mathrm{CH_4}
\end{gathered}$$

Further literature observations of these types of coordination complexes can be used to support this identification. Allyl π-coordination complexes have been observed and well characterized by infrared and Raman techniques for some transition metals,[12−16] although no complexes containing only allyl groups and V atoms have been reported in the literature. The observed infrared features associated with species A are consistent with a coordinated allyl group. Thus, the experimental and computationally available data listed in Table 2 are consistent with the assignment of the features corresponding to species A as doublet H−V(η^3-allyl).

Identification of the H−V(η^3-allyl) species makes it possible to consider the behavior of this complex with increasing propene concentration to yield species B. The set of product absorptions listed as species B correlate very well with propane (and d_8-propane,[10] see Figure 2). The origin of the hydrogen for hydrogenation is demonstrated as propene, implicating a sacrificial hydrogenation mechanism. We previously observed sacrificial hydrogenation in the case of ethene reacting with V atoms,[2,4] in which ethane was similarly formed under high ethene concentration by a sacrificial hydrogenation mechanism.

As noted in the Results section, no enhancement of the hydrogenated product was observed when matrices were formed at the elevated temperature of 25 K. However, increasing reagent-gas flow rates during deposition resulted in increased hydrogenation product yield. These results suggest that the enhancement is due to increased availability of reactant in the reaction zone during matrix formation. The increase in reagent availability to metal atoms and metallic species provides enhanced opportunity for intermediate species to react with a second precursor molecule. Since H−V(η^3-allyl) is believed to be the direct precursor to propane formation, its dependence on conditions which provide only a single propene molecule for reaction supports such claims.

Previous work with increased ethene concentration suggested that following the C−H bond insertion an additional alkene unit could directly insert into the V−H bond, yielding a coordinated alkyl group on the metal as well as a coordinated vinyl group.[2,4] In the current work, the same conditions apply, with the available hydrogen coming from the coordinated allyl unit. Initially, the V atom is inserted into the allylic position of propene, generating the H−V−(η^1-propenyl) complex. In the absence of collision with a second propene molecule, the observations suggest that the initially formed complex isomerizes to the H−V(η^3-propenyl), i.e., H−V(η^3-allyl) complex. However, at higher propene concentration, this isomerization to form the H−V-(η^3-allyl) complex is in direct competition with propene insertion into the H−V bond. The alkene insertion intermediate species proposed is therefore an analog to intermediates proposed in the case of hydrogenation of ethene by H−V−OH and by H−V−CH=CH$_2$.[4] Thus, it would not be unexpected for H transfer from the propenyl species to the propyl unit yielding propane and a V(C_3H_4) species. These proposals are the direct analogue to the hydrogen transfer observed for the case of ethyl−V−vinyl species in the V/ethene system.[2,4]

Although no new features are observed in the infrared spectrum that could be consistent with a V(C_3H_4) species, it is worth noting that under high concentration of propene there appears to be formation of CH_4. There is also a corresponding observation of CD_4 at 993 cm^{-1} when d_6-propene is used. Since no absorptions are observed consistent with a V(C_3H_4) species, it is believed that this species is able to continue to react spontaneously to yield a final product, in parallel with CH_4. In mass spectrometric results on the V/propene system, Song et al. did see loss of a C_1 fragment from propene units during dehydrogenation on clusters.[7] Therefore, it is conceivable that such a process also occurs here, and this process may be photoassisted during matrix formation by the prolonged and unavoidable irradiation from the metal filament prior to the initial infrared acquisition.

Assuming V(C_3H_4) yields CH_4 as a final product, the remaining fragment would have the molecular formula VC_2. This same final product is expected in the analogous reactions where sacrificial hydrogenation occurs with ethene,[2] and in those experiments, no conclusive spectral evidence for VC_2 was observed.[17] Formation of stronger C−H bonds in CH_4 would support thermochemical favorability in the proposed steps, as would the final product VC_2, which is known to have an overall binding energy between 550 and 590 kJ·mol^{-1}.[18] However, the absence of VC_2 (or other organometallic species) in any of the related experiments is perplexing and suggests that, if present, the molecule must be below the threshold for detection using infrared spectroscopy. To further examine this, we conducted DFT calculations on several isomers of VC_2 (see Supporting Information) for both doublet and quartet spin states. These computations indicate that if VC_2 were formed as a major final product, we would expect to observe at least one of its absorptions. The absence of such an observation remains a challenging point for further study (see Supporting Information).

An overall mechanism accounting for the observed products, over the range of concentrations studied in this work, is given in Scheme 1. According to Scheme 1, replacement of each of the H atoms with deuterium atoms would yield perdeuterio analogs of all products, consistent with the observed data. However, for the 3,3,3-d_3-propene case, hydrogenation of the propene molecule could lead to two possible hydrogenation products, depending on which of the two C atoms on propene receives the H atom formerly on the metal during alkene insertion. While it should be possible to identify CD_2H_2 on the basis of its infrared spectrum, the complexity of the potential propane isotopomers and their very similar spectra in the C−H and C−D absorption regions makes the current analysis difficult at best when considered with the wealth of propene precursor features in the same areas. Thus, while a full mechanistic investigation involving careful isotopic substitution should be possible, it would require a substantial investigation in order to confirm the geometric details of the latter part of this mechanism.

SUMMARY AND CONCLUSIONS

The nature of V-atom reactivity with propene evolves as the concentration of propene is increased. Under low partial-pressure conditions, a C−H bond insertion intermediate is observed, which is consumed with increasing partial pressures of propene to yield a hydrogenation product, propane. Additionally, under high propene concentration, products consistent with C−C bond cleavage appear to occur, as evidenced by the formation of CH_4 at high propene partial pressures. Given the current results, the only viable mechanism is one in which the final V-containing products are small, highly symmetric species that are unobserved under the present conditions. Otherwise, the mechanism and product distribution are very similar to previously reported observations wherein ethene is analogously hydrogenated sacrificially.

ASSOCIATED CONTENT

Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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