

Photoinduced Ethane Formation from Reaction of Ethene with Matrix-Isolated Ti, V, or Nb Atoms

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The reactions of matrix-isolated Ti, V, or Nb atoms with ethene (C_2H_4) have been studied by FTIR absorption spectroscopy. Under conditions where the ethene dimer forms, metal atoms react with the ethene dimer to yield matrix-isolated ethane (C_2H_6) and methane. Under lower ethene concentration conditions ($\sim 1:70$ ethene/Ar), hydridic intermediates of the types HMC_2H_3 and $H_2MC_2H_2$ are also observed, and the relative yield of hydrocarbons is diminished. Reactions of these metals with perdeuterioethene, and equimolar mixtures of C_2H_4 and C_2D_4 , yield products that are consistent with the production of ethane via a metal atom reaction involving at least two C_2H_4 molecules. The absence of any other observed products suggests the mechanism also involves production of small, highly symmetric species such as molecular hydrogen and metal carbides. Evidence is presented suggesting that ethane production from the ethene dimer is a general photochemical process for the reaction of excited-state transition-metal atoms with ethene at high concentrations of ethene.

Introduction

The reactions of hydrocarbons with metal atoms are of interest due to their value as prototypes for metal cluster and metal surface reactions. Such studies often provide opportunities to spectroscopically characterize chemical species which may exist as intermediates in overall processes. These characterizations, often achieved using the technique of matrix isolation, provide insight into reaction processes that are important in both industrial and catalytic contexts.

Of the hydrocarbons, ethene (C_2H_4) is one of the most important molecules for industrial synthesis and is the prototypical molecule for the study of alkene reactions. Many matrix isolation studies have been carried out on the reactions of ethene with transition-metal atoms.^{1–12} Most of this work has focused on determining the structure of the initial ethene–metal reaction product, often leading to the conclusion that formation of a π -bonded complex is the primary reaction process. In some works, such as that of Lee et al. with Ti atoms and ethene,¹⁰ C–H bond insertion products are observed. C–H insertion is believed to follow π -coordination of ethene, although Lee et al. did not find evidence for a π -coordinated complex. Their work demonstrates the photoproduction of vinyltitanium hydride ($HTiC_2H_3$), as well as a dihydridoorganotitanium complex ($H_2-TiC_2H_2$). As well, the laser ablation matrix isolation work of Cho and Andrews for Zr atoms reacting with ethene¹¹ shows evidence for C–H insertion intermediates that have been implicated in H_2 elimination chemistry. These examples show C–H insertion for early transition metals; however, similar insertion products have also been observed recently by Cho and Andrews for the reaction of Pt atoms with ethene.¹²

Transition-metal atom insertions into C–H bonds have received a fair amount of attention in theoretical studies.^{13–22} These studies together predict reaction trends for metal atoms on insertion into the C–H bonds of small hydrocarbons, in

particular with ethene. Specifically, the reactions of Zr and Y with ethene investigated by Porembski and Weisshaar^{21,22} suggest that the thermodynamic barriers associated with a stepwise conversion from a coordination complex of the form MC_2H_4 through an intermediate, HMC_2H_3 , to a final complex, $H_2MC_2H_2$, are either nonexistent or reasonably small. Products predicted in this theoretical study have been observed in the gas-phase kinetics work of Carroll et al. with Zr atoms and ethene.²³ In contrast, the theory work of Siegbahn concerning the reaction of metal hydrides (MH_x , $x = 1–3$) with ethene suggests exoergicity for the insertion of ethene into the M–H bond of the metal hydride to form $H_{x-1}MC_2H_5$.¹⁷ Thus, gas-phase transition-metal atoms have been shown to be capable of dehydrogenation or hydrogenation of unsaturated organic molecules.

Gas-phase work from our laboratory on the reaction of C_2H_4 with the niobium atom and small niobium clusters²⁴ shows that these reactions lead to formal dehydrogenation of ethene. However, these results have been characterized only by mass spectrometry, thereby providing no insight into the detailed structure(s) of the product species involved in the reaction mechanism. Our motivation for the present study was to identify spectroscopically the intermediates involved in these gas-phase reactions. To our surprise, the major product observed in the present study at high ethene concentrations is the *hydrogenated* product ethane (C_2H_6). This serendipitous result has given us unexpected insight into the reactions of metal atoms with ethene, as discussed in detail below.

Experimental Details

Metal atoms were generated by resistively heating a thin filament of the pure metal (Nb, V, or Ti (A.D. McKay, New York, 99.999%)) in a water-cooled furnace. The rate of metal atom deposition was continuously monitored with the use of a quartz crystal microbalance built into the resistive furnace assembly.²⁵ Note that the generation of metal atoms using metal filaments results in the unavoidable generation of visible light,

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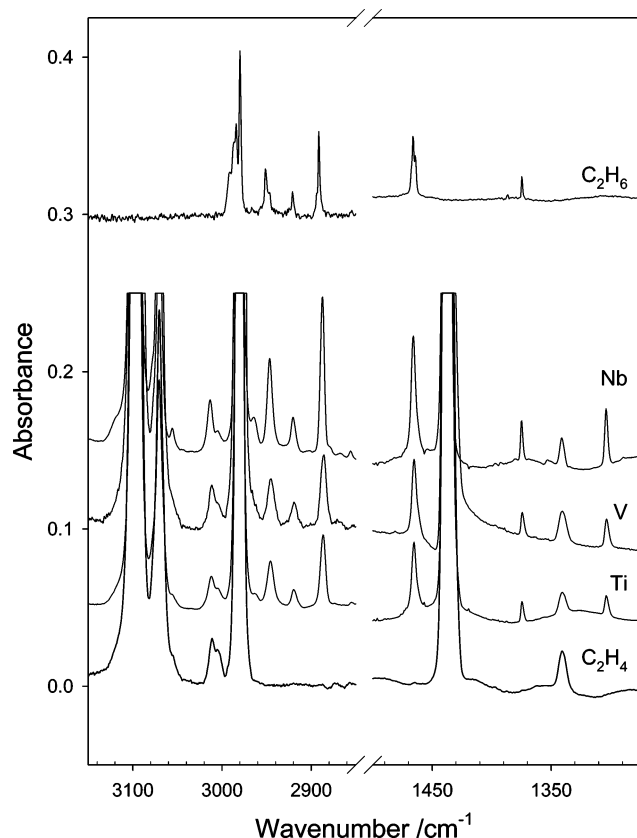


Figure 1. Portions of the FTIR absorption spectra of argon matrices containing (from bottom to top) 10% ethene, 10% ethene with Ti atoms, 10% ethene with V atoms, 10% ethene with Nb atoms, and 0.1% ethane.

which irradiates the sample during matrix deposition. Ethene (C.P. grade, 99.5%, Matheson of Canada) or ultra-high-purity ethene (99.99%, Sigma-Aldrich) was used without further purification. Perdeuterioethene (99.99 atom % D) was obtained from C/D/N Isotopes (Quebec, Canada). For verification of the spectrum of ethane, chemical-purity ethane (99.5%, Matheson) and *d*₆-ethane (C/D/N Isotopes, 99.99 atom % D) were also employed. For all of the matrices, argon (99.995%, Matheson) was employed as the host gas. Unless stated otherwise, matrices were of the mole ratio metal:C₂H₄:Ar = 0.5:10:100. Matrices were deposited for 1.5 h (unless otherwise noted) with a gas flow rate of 0.5 sccm onto a KBr optical window maintained at 17 K using an APD Displex refrigeration apparatus. Fourier transform infrared absorption spectroscopic analyses were performed using a Bomem Michelson MB-102 FTIR spectrometer in the range of 4000–400 cm⁻¹. Where performed, sample irradiations were done using a 150 W Hg arc lamp (Kratos model LH-150), using either the full focused output of the lamp (UV–vis irradiation) or the focused lamp output filtered to remove wavelengths below 400 nm (visible irradiation).

Results

Portions of the infrared spectra obtained prior to, and following, the co-condensation of gas-phase Ti, V, or Nb atoms with 10% ethene in argon are given in Figure 1. For comparison, the spectrum of 0.1% ethane in argon is also shown, which demonstrates clearly that the major product obtained in the metal-containing matrices is unperturbed matrix-isolated ethane. The major unobscured ethane absorptions obtained by metal atom reactions with ethene are observed at 2944.9, 2919.4, 2885.9, 1465.0, and 1373.1 cm⁻¹, wavenumber positions that are identical to those observed for matrix-isolated ethane

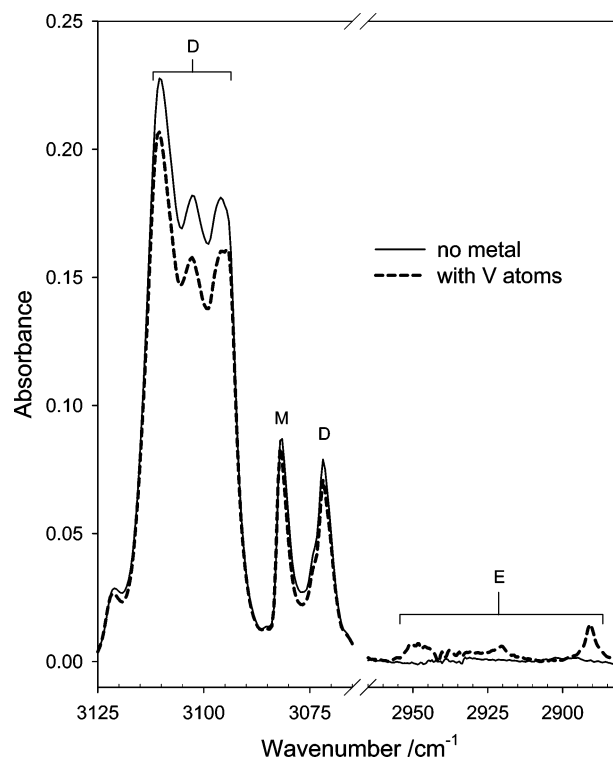


Figure 2. Portions of the infrared spectra of argon matrices containing ethene (1:70 ethene/Ar), with (dotted line) and without (solid line) V atoms. Features associated with ethane, the ethene monomer, and ethene dimer are labeled E, M, and D, respectively.

deposited using an ethane/argon mixture. Methane is also formed as a product, giving rise to an absorption at 1304 cm⁻¹. No other products from reaction of ethene with metal atoms were observed under 1:10 ethene/Ar conditions.

When production of ethane was observed, it was in all cases accompanied by measurable depletion of absorptions due to matrix-isolated ethene dimers,²⁶ which give rise to absorptions at 3096 and 2980 cm⁻¹ in the C–H stretching mode region. Note that ethene exists only in the dimer form at, and above, concentrations of 1:10 ethene/Ar. Under conditions where features associated with the ethene dimer are not present, no ethane production is observed. Where the ethene monomer and dimer coexist, depletion of both the monomer and dimer is observed, with concomitant production of ethane and hydridic species (see below). This effect is evident in Figure 2, where spectra are shown from the C–H stretching region of matrices generated with a 1:70 ethene/argon mixture, with and without the inclusion of V metal atoms. Similar experiments were done with Ti, V, or Nb atoms in pure ethene matrices. In these cases, the yield of ethane was substantially greater than in 1:10 ethene/Ar matrices, but otherwise no other significant changes were noted beyond some changes in peak shape. Methane was also produced in amounts that appear to be correlated with the increase in ethane production.

Co-deposition of Ti or V atoms with lower concentration mixtures of ethene in Ar (1:70 ethene/Ar) gave rise to diminished yields of ethane, accompanied by new features in the region of 1650–1450 cm⁻¹. In the case of Ti, these absorptions have been previously identified in 1:200 ethene/Ar matrices by Lee et al.¹⁰ as being associated with HTiC₂H₃ (1500 cm⁻¹) and H₂TiC₂H₂ (1585 and 1611 cm⁻¹). These features show photochemical behavior identical to that described previously by Lee et al.; e.g., irradiation of deposition samples containing both species with 466 nm light gave rise to depletion

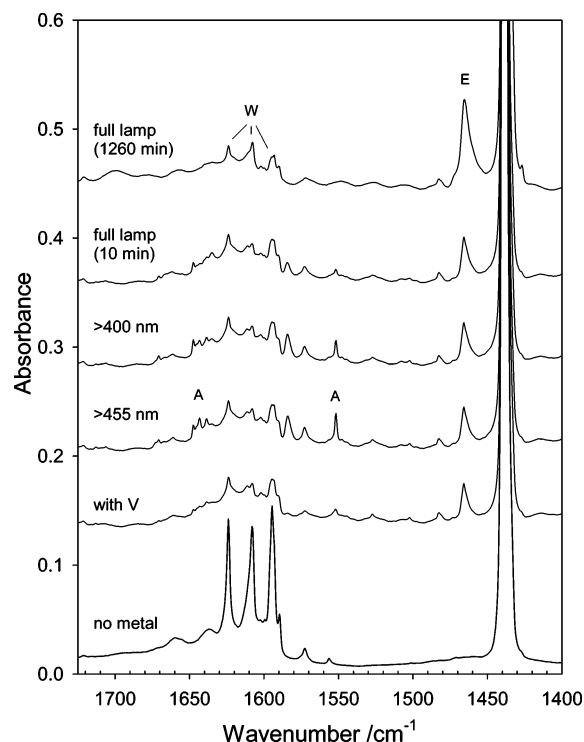


Figure 3. Portions of the infrared spectra of argon matrices containing ethene (1:70 ethene/Ar) with (from bottom to top) 5 h of deposition with no metal, with 4.5 h of deposition with V atoms, following 10 min of irradiation at >455 nm, following an additional 10 min of irradiation with full UV-vis output of the lamp, and following an additional 1260 min of irradiation with full UV-vis output of the lamp. Features associated with matrix-isolated ethane and water and those assigned in the text to $\text{H}_2\text{VC}_2\text{H}_2$ are denoted E, W, and A, respectively.

of HTiC_2H_3 and significant growth of $\text{H}_2\text{TiC}_2\text{H}_2$. Prolonged irradiation of such matrices resulted in the complete destruction of both titanium hydride species, in accord with the observations of Lee et al. However, in the present work, such prolonged irradiation also resulted in concomitant production of both ethane and methane, an observation not previously reported.

Features analogous to those of the $\text{H}_2\text{TiC}_2\text{H}_2$ species were seen at 1552 and 1644 cm^{-1} when V atoms were employed with 1:70 ethene/Ar gas mixtures (see Figure 3). The sample was subjected to a sequence of irradiations similar to those employed by Lee et al. in the Ti work noted above. Irradiation with light of wavelength >455 nm for 10 min resulted initially in the growth of these features; however, further irradiation at these wavelengths resulted in their modest depletion. Subsequent irradiation with broad-band UV-vis light for 10 min resulted in further depletion of these features, with the complete destruction of these features following prolonged irradiation (~ 15 h). Given that the modes we observe with V under these conditions have a relative intensity profile and photochemical behavior similar to those of the dihydridotitanium species of Lee et al., we tentatively assign these new features at 1552 and 1644 to $\text{H}_2\text{VC}_2\text{H}_2$. Following irradiations of the sample containing V atoms with visible light, there is a very small increase in the features associated with ethane. Subsequent broad-band UV-vis irradiation of the sample gave a more pronounced growth of the ethane features, particularly following prolonged irradiation (see Figure 3, top spectrum).

For vanadium atoms, the analogous reactions were carried out with argon containing 10% perdeuterioethene (C_2D_4). Portions of the resultant spectra are given in Figure 4, along with the corresponding spectrum for 0.1% perdeuterioethane

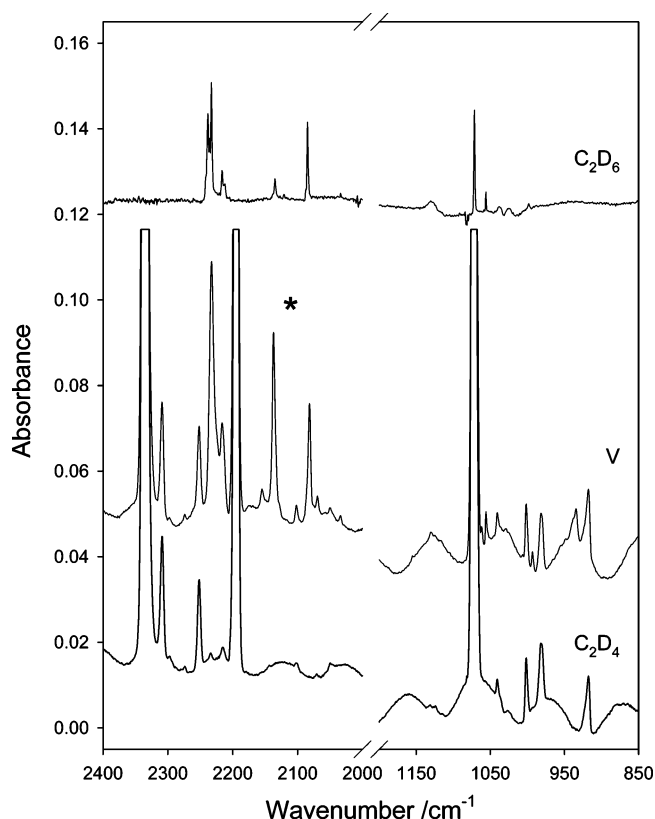


Figure 4. Portions of the FTIR absorption spectra of argon matrices containing (from bottom to top) 10% perdeuterioethene, 10% perdeuterioethene with V atoms, and 0.1% perdeuterioethane. The asterisk denotes a feature due to matrix-isolated CO, generated by thermal desorption of CO in the apparatus during sample preparation.

(C_2D_6). The results of these experiments confirm that perdeuterioethane is the only major hydrocarbon product in these reactions. Absorptions due to CO_2 , CO, and traces of CH_4 associated with the metal vaporization approach were also observed, as noted below for the C_2H_4 reactions. A feature at 993 cm^{-1} is also observed which is assigned to CD_4 ²⁷ by comparison with spectra of CD_4 in an Ar matrix.

The reaction of an equimolar mixture of 5% each of C_2H_4 and C_2D_4 with vanadium atoms was also studied. Infrared spectra obtained for this reaction show numerous weak and broad features in the C-H and C-D stretching regions. Many of these absorptions correspond to features associated with C_2H_6 and C_2D_6 . We speculate that the additional observed absorptions are associated with one or more isotopomers of ethane, due to the close proximity of these absorptions to the known modes of the isotopically pure ethanes. Spectral congestion did not allow for the identification of mixed-isotope product(s).

Other minor features sometimes appear in the spectra of the metal-containing matrices associated with CO_2 (2349 and 667 cm^{-1}) and CO (2137 cm^{-1}).²⁸ Both species are well-known matrix isolation impurities, in this case generated as byproducts of metal vaporization by desorption from the apparatus walls during sample formation. In accord with this supposition, the intensities of these features varied from experiment to experiment in a manner that did not correlate with production of ethane or methane. For each metal used, a new absorption was sometimes observed at 1193 (Ti), 1205 (V), or 1263 (Nb) cm^{-1} . In each case, the absorption could be photobleached during irradiation of the matrix with visible light. There was no other apparent change in the recorded spectra upon elimination of this species. The yield of this species varied significantly between similarly prepared samples, despite the fact that

production of ethane was essentially constant. Therefore, we conclude that this set of absorptions is due to the production of a metal-containing species, via a competitive metal atom reaction which we are unable to identify.

Discussion

Ethane Production in Low-Temperature Matrices. The results presented above demonstrate that ethane is the major infrared-observable, matrix-isolated product for the reactions of Ti, V, or Nb atoms with ethene in matrices containing the ethene dimer. Organometallic species that are believed to be precursors to dehydrogenation products are observed in our work when relatively low concentrations of ethene are employed, where the ethene monomer is present. In the case of Ti, these species have been identified previously as titaniacyclopropene dihydride and vinyltitanium hydride.¹⁰ At intermediate concentrations, where a relatively low abundance of the ethene dimer coexists with the matrix-isolated ethene monomer, production of ethane and metal hydride species can be observed simultaneously.

At higher ethene concentrations (1:10 ethene/Ar and higher), metal hydride species are not observed, which suggests that, if they are formed, they exist only as transient species under these conditions due to their consumption in the formation of ethane. This is supported by the work of Siegbahn which suggests that second-row transition-metal hydride species can incorporate an ethene molecule¹⁷ by a barrierless process involving direct insertion of the ethene molecule into the M–H bond. For Ti and V, this process may involve photoexcitation of the metal hydride species. Such a process would result in formation of $\text{HM}(\text{C}_2\text{H}_2)\text{C}_2\text{H}_5$, which would be expected to be the direct precursor to ethane in our experiments by reductive elimination of the hydride and alkyl fragments. Note that, since insertion of bare transition-metal atoms into C–H bonds is generally exothermic, such a reductive elimination process would be expected to exhibit a significant potential energy barrier. To overcome such a barrier, the process would need to be photon-assisted or exhibit thermodynamics significantly different from that of the bare metal atom, the latter possibly resulting from the presence of one or more additional ligands on the metal atom.

The production of ethane in the matrix isolation environment following the reaction of iron atoms with ethene has been previously reported by Kafafi et al. at 13.5–15 K.⁷ Cardenas and Shevlin also observed production of ethane following warm-up of matrices containing iron atoms in ethene deposited at 77 K.²⁹ In the work of Kafafi et al., absorptions assigned to ethane (C_2H_6) at 1465.9 and 1374.5 cm^{-1} and methane (CH_4) at 1305.1 cm^{-1} were observed on co-condensation of iron atoms with high concentrations of ethene in argon ($\text{Fe}:\text{C}_2\text{H}_4:\text{Ar} = 0.6:12.4:100$).⁷ Prolonged UV irradiation of such matrices resulted in an increase in ethane and methane absorptions, with a concomitant decrease in the diethene–iron complex ($\text{Fe}(\text{C}_2\text{H}_4)_2$). They propose that methane and ethane are produced following the disproportionation of the diethene–iron π -complex, in which production of an unobserved iron carbide species is also speculated. Note that we also observe an increase in the amount of ethane upon prolonged irradiation of our matrices. Gentle annealing of the matrix is always a feature of prolonged irradiations with broadband light, and we propose that such annealing results in additional metal atom–ethene dimer reactions occurring.

Vibrational modes of ethane are also evident in earlier published matrix isolation work on the reaction of transition-metal atoms with ethene in argon. Huber et al. have studied the

reaction of nickel atoms with ethene under relatively concentrated conditions of ethene in argon, and in pure ethene.² They have assigned several observed vibrational modes to $\text{Ni}(\text{C}_2\text{H}_4)_2$, which appear at exactly the same positions as major ethane modes (2945, 2886, and 1465 cm^{-1} , for 1:10 $\text{C}_2\text{H}_4/\text{Ar}$) observed here in argon. The published spectra also show absorptions at 2918 and ~ 1375 cm^{-1} . The first of these modes has been assigned to $\nu(\text{C–H})$ of $\text{Ni}(\text{C}_2\text{H}_4)_3$,² but given both the close wavenumber matching and observation of the other three fundamental modes of ethane, it is highly likely that these absorptions are also due to ethane. A similar group of bands (2943, 2888, and 1463 cm^{-1} , average values quoted from various ethene, Ar, or Xe matrix experiments) assigned by Huber et al. to $\text{Pd}(\text{C}_2\text{H}_4)_2$ ⁴ are almost certainly due to ethane features as well. The remaining modes of the group of bands assigned by Huber et al. to $\text{Ni}(\text{C}_2\text{H}_4)_2$ have been reassigned to $\text{Ni}(\text{C}_2\text{H}_4)$ by Merle-Mejean et al.,⁸ and confirmed in the work of Lee et al.⁹ Interestingly, Merle-Mejean et al. did not observe the feature at 1465 cm^{-1} under their experimental conditions, though they do predict a vibrational mode of $\text{Ni}(\text{C}_2\text{H}_4)$ to occur at about 1460 cm^{-1} , resulting from the coupling of C=C stretching and CH_2 deformation motions. This mode has subsequently been reported by Lee et al.⁹ at 1468 cm^{-1} , following co-condensation of Ni vapor with ethene in argon matrices. As the spectra of Lee et al. show no evidence for any of the other modes of ethane, and the experiments were carried out at relatively low ethene concentrations where ethene dimers are not present, we believe that the mode observed by Huber et al.² at 1465 cm^{-1} is due to matrix-isolated ethane, but the mode reported at 1468 cm^{-1} by Lee et al. is due to NiC_2H_4 . The latter assignment is confirmed by the observation of a ^{13}C shift in the 1468 cm^{-1} mode of -15.5 cm^{-1} , as anticipated for a metal–ethene π -complex,^{9,11} and far greater than the shift of -4 cm^{-1} observed in our work for ethane. The observation of features attributable to ethane in the work of Huber et al. is most likely due to metal atom reactions with ethene dimers present in their samples at the high ethene concentrations employed. We suggest that, in cases where there is doubt about the origin of the 1465 cm^{-1} mode, ^{13}C -isotopic substitution could be used profitably to distinguish between formation of ethane and the formation of a metal–ethene π -complex.

Mechanistic Considerations. It is obvious by stoichiometric considerations alone that the production of ethane from ethene must involve the reaction of at least two ethene molecules, provided there is no other source of hydrogen available. However, the ubiquitous presence of water in all matrix samples raises the concern that water may be the source of hydrogen incorporated into ethane. When metal atoms are co-deposited with samples containing ethene and argon, there is a significant loss of features associated with water. To investigate water as a hydrogen donor in our work, experiments which incorporated D_2O in the sample gas were performed to determine if any D atoms would be included in the observed ethane. No evidence for inclusion of deuterium was observed, thereby eliminating water as the formal source of hydrogen in our experiments. Since the depletion of water is evident in all metal-containing experiments, it is clear that some reaction of metal atoms with water is occurring on deposition. Indeed, we see a feature near 1584 cm^{-1} which may be attributed to a metal hydride stretch associated with a metal–water reaction product (see Figure 3). Note that such a feature near this position has been attributed to HVOH by Kauffman et al.,³⁰ and to a vanadium cluster–water reaction product by Zhou et al.³¹ Thus, it would appear that we have observed vanadium water chemistry occurring,

and that such chemistry is unrelated to the formation of ethane in this work.

The hydrogenation of ethene involving a second ethene molecule requires one of the ethene molecules to act as a sacrificial hydrogen atom donor, while the other ethene molecule acts as a hydrogen atom acceptor. Mechanistic steps required for such a process are supported by the calculations of Porembski and Weisshaar for early transition metals,^{21,22} experimental and theoretical investigations by Carroll et al.,¹⁹ and the theoretical work on metal hydrides and ethene by Siegbahn.¹⁷ In the first of these, early second-row transition-metal atoms are predicted to coordinate ethene through the π -bond to form a metallocyclopropane species. Zr atom reactions with C_2D_4 ³² show no kinetic isotope effect in the rate of atom removal, thus supporting the supposition that π -complexation of ethene is the initial reaction step. For Ti and V, π -complexation must involve photoexcitation of the metal atom, since experimental gas-phase measurements of the rate of depletion of both of these metals by ethene show that the ground states of both elements are not reactive.³³ Further, the first allowed excited states of Ti and V are accessible with visible light corresponding to wavelengths (629 and 611 nm)³⁴ present in emission from the heated Ti or V filaments in our experiments. In both cases, such excitation would lead to an electronic configuration similar to that of ground-state niobium atoms (having partial occupancy of the valence s-orbital), and therefore, it is reasonable to suggest that this excitation will result in similar chemistry between the three metallic elements, as observed.

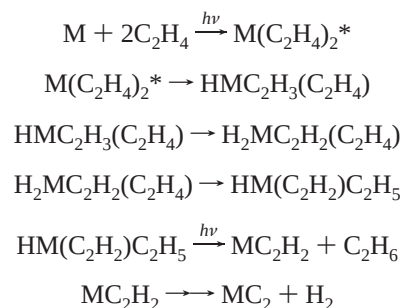
This coordination step is believed to be followed by insertion of the coordinated metal into a C–H bond to form hydrido-, and subsequently dihydrido-, organometallic intermediates. The barrier for the first of these insertions for early transition metals has been calculated to be fewer than 2 kcal/mol for Y and Zr,^{19,21,22} and nonexistent for Nb.¹⁹ In the work of Siegbahn,¹⁷ metal hydrides are predicted to be able to insert ethene directly into an M–H bond without prior formation of a π -bonded ethene complex. Such a direct insertion is predicted to be barrierless¹⁷ for early second-row transition metals up to Nb, for each of the mono-, di-, or trihydrides, and increasingly thermodynamically favored for the di- and trihydrides compared with the monohydride.

These studies together provide the basis for development of a formal scheme for alkene hydrogenation through sacrificial hydrogen donation by another alkene. The observation of perdeuterioethane in our work for the analogous reaction of V atoms with perdeuterioethene conclusively demonstrates that the formal hydrogen atom source must be ethene. The observation of ethane production only under conditions where the ethene dimer exists implicates one ethene molecule in the ethene dimer as the *actual* source of hydrogen in our work. We believe that the production of ethane by disproportionation of ethene at transition-metal atom centers is a general reaction of ethene under high-concentration conditions in low-temperature matrices. The generality of this process is demonstrated by the production of ethane both in our work with early-transition-metal atoms and in the work of others using late transition metals. The general observation of ethane production under conditions of higher ethene concentration demonstrates that there exists a richer chemistry for metal atom reactions with ethene than has been previously recognized, specifically under conditions where a second ethene molecule is available to react immediately with primary products.

We propose Scheme 1 as a framework for understanding the present work. All steps in this scheme must be fast under

irradiation from the filament, since we observe no other intermediates on deposition that show concentration relationships that link them to ethane production.

SCHEME 1: Reaction Mechanism for Production of Ethane from Ethene Disproportionation with Transition-Metal Atoms



One can understand why the yield of ethane increases nonlinearly with ethene concentration, since the ethene dimers have a very low concentration in 1:70 ethene/Ar samples, but are essentially the only form ethene takes in 1:10 ethene/Ar matrices. As well, the production of additional ethane following prolonged irradiation in 1:70 samples is in accord with the idea that photoannealing of the matrix over very long periods of time will cause an increase in the number of metal atoms in close proximity to ethene dimers, yielding additional production of ethane. Subsequent destruction of the MC_2H_2 species is implicit in the lack of observation of any other products save methane, which it cannot generate directly.

The overall reaction process would be $M^* + 2C_2H_4 \rightarrow MC_2 + C_2H_6 + H_2$, which would give rise to no new major spectroscopically observable hydrocarbon products, other than ethane. While we have no evidence for a metal carbide product, we speculate that it must be present for the validity of these reactions and that its infrared spectrum is not observed under our conditions. Note that Kafafi et al. propose the formation of a similar metal carbide with iron atoms following prolonged irradiation of their matrix samples, which was also not observed in their work.⁷ The fundamental of NbC has been experimentally determined to occur at 993 cm^{-1} (ω_e).³⁵ TiC and VC are predicted to have ω_e in the range $869\text{--}1006\text{ cm}^{-1}$. The MCC dicarbides of Ti, V, and Nb are known to have an M–C fundamental mode in the range of $500\text{--}600\text{ cm}^{-1}$.^{36–38} As ethene in argon matrices (1:10 ethane/Ar) has strong IR absorption in the range $920\text{--}985\text{ cm}^{-1}$, it is possible that spectral features due to metal monocarbides are obscured by the strong ethene absorptions in this spectral range. However, given the low concentration of metal in our samples, it is more likely that features due to metal carbide species are simply too weak to observe.

The reaction of niobium atoms with ethene has been studied in the gas phase, by both Weisshaar¹⁹ and ourselves,²⁴ using fast-flow metal atom reactors. In both cases, Nb atoms are removed by ethene at rates very close to the gas-kinetic collision frequency, supporting a barrierless association reaction to form a π -complex as a first, rate-limiting step. In our flow reactor work, product mass data indicate that production of NbC_2H_2 is the major active process in the gas phase. As well, the kinetic behavior of the reaction of this product with a second ethene molecule exhibits sequential addition behavior. The observation of NbC_2H_2 as the major product in the gas phase contrasts the current matrix isolation work, in which no product except ethane is observed. This difference is undoubtedly due to the fact that

the gas-phase processes involve only the ethene monomer, whereas our matrix work involves both the ethene monomer and the ethene dimer. Intermediates such as those identified by Lee et al.¹⁰ are likely the precursors to the gas-phase reactivity, leading to partial or full dehydrogenation of ethene. We predict that ethane production would be observed in the gas phase, if the gas-phase reaction process were to be carried out at high enough partial pressures of ethene for reaction of two ethene molecules at the metal center before any metal–hydride bond cleavage were to occur.

In both our work and the work of Kafafi et al., absorptions attributed to CH₄ are observed,⁷ the latter involving photoexcitation of a metal atom–ethene complex. In the analogous reactions with C₂D₄, the formation of CD₄ (993 cm⁻¹) demonstrates that the presence of methane in the resultant spectra must be due to a competitive metal atom–ethene reaction. In the absence of any further spectroscopic information related to methane production, we can only speculate on the mechanism for methane formation by early-transition-metal atoms. It is clear that the mechanism must involve a C–C bond cleavage as a critical step. Such a process likely involves further reaction of hydridic metal complexes from reactions of metal atoms with ethene, likely involving intermediates such as HMC₂H₃ and H₂-MC₂H₂ identified by Lee et al. for Ti and proposed for V in this work.

In summary, the production of ethane is a general process in the chemistry of matrix-isolated ethene with metal atoms, when the concentration of ethene is sufficiently high for the ethene dimer to be present. We have proposed a general mechanistic scheme for ethene disproportionation to form ethane, molecular hydrogen, and metal carbides which is supported by this work and by observations from previous work with ethene. We have shown that gas-phase and matrix isolation reaction chemistries are distinct, and that differences in the observed chemistry are due to the availability of a second ethene molecule to react promptly with primary organometallic products at high ethene concentrations.

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