

Experimental and Computational Studies of the Homogeneous Thermal Decomposition of the Tungsten Dimethylhydrazido Complexes Cl₄(RCN)W(NNMe₂)

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The thermal decomposition pathways of the tungsten dimethylhydrazido complexes $Cl_4(RCN)W(NNMe_2)$ (1a: R=CH₃; 1b: R=Ph), precursors for single source deposition of WN_xC_y , were investigated using a combination of experiments and calculations. Raman scattering studies were performed in an impinging-jet, up-flow, aerosol-assisted CVD reactor to identify reaction intermediates. Density Functional Theory calculations (B3LYP/LanL2DZ) were used to estimate Raman active frequencies and explore the reaction surface. Dimethylamine and methylmethyleneimine, products from N–N cleavage of the hydrazido ligand, were observed under deposition conditions and identified by comparison with previously reported Raman shifts and calculated frequencies. © 2012 The Electrochemical Society. [DOI: 10.1149/2.002206jes] All rights reserved.

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Continual reduction of the average feature size found in integrated circuits and the concomitant changes in via and line resistivity, current density, and RC time delays have driven the gradual replacement of Al-based metallization to that based on Cu given its lower electrical resistivity and higher resistance to electromigration. Use of Cu metallization requires prevention of Cu migration into the underlying Si and SiO₂, which can produce an increase in contact resistance, leaky pn junctions, variations in the barrier height, and contact layer embrittlement.^{1,2} To avoid Cu-Si interaction an amorphous diffusion barrier layer at a thickness well below the via dimension is conformally deposited at low temperature. As these requirements become more demanding, a chemical deposition method will likely be required. WN_xC_y films grown by both chemical vapor deposition (CVD)^{3,4} and atomic layer deposition⁵ have shown promise as a suitable diffusion barrier material. Tungsten-based barriers have demonstrated improved adhesion to Cu and ease of chemical mechanical planarization as compared to the commonly used TaNx.^{6,7} We recently reported the preparation of the diorganohydrazido(2-) tungsten complexes $Cl_4(CH_3CN)W(NNR_2)$ ($R_2 = Me_2$, Ph_2 , and $-(CH_2)_5-$) and Cl_4 (pyridine)W(NNPh₂)⁸ as precursors for the CVD of WN_xC_y films for use as Cu diffusion barriers.^{9,10} Other than these, researchers also have reported tungsten carbonitride film deposition using single source precursors.^{11–13}

This study reports the mechanism of depositing tungsten carbonitride from the hydrazido complex $Cl_4(CH_3CN)W(NNMe_2)$ (1a). The synthesized precursor 1a was dissolved in benzonitrile to allow transport by nebulization. The precursor rapidly coverts to its benzonitrile derivative $Cl_4(PhCN)W(NNMe_2)$ (1b) upon dissolution in benzonitrile. The gas-phase decomposition kinetics of 1b were investigated using in situ Raman spectroscopy in a vertical up-flow, cold-wall CVD reactor. Additional experiments involved NMR kinetics and observation of the fragmentation of 1b during electrospray ionization (ESI) in a Fourier transform ion cyclotron resonance (FTICR) mass spectrometer. Comparison of the experimental results with literature data and DFT calculations was used for assignment of the observed Raman bands and evaluation of likely decomposition pathways.

Experimental and Theoretical Methods

The homogeneous thermal decomposition of mixtures of the tungsten dimethylhydrazido complex **1a** and its benzonitrile derivative **1b** was studied in a custom designed CVD reactor (Fig-

ure 1).¹⁴ Since under deposition conditions (1a in benzonitrile solvent and delivered as aerosol to substrate at temperature >250°C), the equilibrium between 1a and 1b is dominated by 1b (vide *infra*), these mixtures will subsequently be referred to as "1b." The reactor is interfaced with an in situ Raman spectrometer (Ramanor U-1000, Jobin Yvon), which uses the 532.08 nm line of Nd:YAG solid-state laser as the light source and includes a double additive monochromator fitted with a diffraction grating of 1800 grooves/mm. The Raman system was calibrated against the 546.07 nm emission line of mercury. As described elsewhere,¹⁴ this up-flow, impingingjet CVD reactor was designed to produce a stable 2-D flow pattern while isolating the reactants from the reactor walls to prevent parasitic reactions. Since the entire CVD reactor chamber assembly could be translated in the x-y-z directions, it was possible to measure gas-phase composition and temperature profiles inside the reactor to quantitatively study the gas phase decomposition kinetics of complex 1b. The three concentric inlet tubes shown in Figure 1 are packed with 3 mm glass beads to establish an equal velocity and uniform-flow inlet boundary condition. Aerosol-assisted CVD (AACVD) was carried out for the Raman experiment with 1b because this complex has low volatility.¹⁵ The precursor 1b was prepared by dissolving solid 1a in benzonitrile (PhCN, 0.0174 mol/L). The solution is then pumped into a nebulizer from a syringe. A piezoelectric material in the nebulizer vibrates at a frequency of 1.44 MHz, which generates an aerosol of precursor 1b and benzonitrile. The aerosol is introduced into the reactor with N₂ (99.999%, Airgas) carrier at a flow rate of 2.5 cm/s, which transports the mixture of 1b and solvent that was injected at a rate of 1.0 mL/h. The susceptor is heated by a resistive ceramic heater placed on the inside of the quartz flat-one-side tube and the experiments were conducted at a set point of 850°C. For the concentric annular and sweep flows, pure N2 gas was delivered with the same flow velocity (2.5 cm/s) and sufficient gas flow time was allowed for the reactor to reach steady state before measurements were made. Based on a previous study¹⁶ that validated a steady-state, two-dimensional mass transport model and included CH4 tracer experiments, disruptive recirculation flow patterns in the reactor are not anticipated. A 3W Nd: YAG solid-state laser line (532.08 nm) was used to excite 1b and benzonitrile, while the N2 vibrational Raman excitation lines were recorded along the centerline to estimate the temperature profile.

To assist in the assignment of these additional Raman bands as well as to assess possible reaction pathways, DFT calculations were performed using the Gaussian 03 program suite.¹⁷ For all bond dissociation, recombination, activation energy, thermodynamic properties, and frequency calculations, the spin polarized hybrid density functional B3LYP was combined with the LanL2DZ basis set for all

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Figure 1. Schematic of the nebulizer-assisted experimental reactor for in situ Raman spectroscopic measurements.

elements. Crystallographic structure data⁸ of complex **1a** collected at 173 K were used to obtain the starting geometry for calculations.

NMR kinetic studies of the dissociation of acetonitrile from **1a** were conducted on a Varian Inova at 500 MHz. Compound **1a** along with a molar equivalent of acetonitrile was dissolved in toluene- d_8 . The ¹H spectrum displayed signals for **1a** at 0.53 ppm and acetonitrile at 0.83 ppm with a ratio of 1:2.09.

For ESI-FTICR mass spectrometric analyzes solutions of **1b** were prepared by dissolving **1a** at a concentration of 100 μ M in dry benzonitrile (purchased from Sigma-Aldrich as anhydrous grade in 99.9% purity and degassed by purging with Ar) in a dry-box under N₂. The complex was ionized (negative ionization mode) using a commercial electrospray ionization (ESI) source (Analytica of Branford, Branford; CT, USA) with a user-modified heated metal capillary^{18–20} modified with a conical capillary inlet²¹ set at a temperature of 125°C. The ESI source was confined in a purge box maintained at a positive pressure of dry nitrogen gas. The complex was introduced in benzonitrile solution with no additional solvents (e.g., water, methanol). Mass spectra of the WCl₄N⁻ (nominal m/z 340) ions were obtained with a Bruker 47e FTICR mass spectrometer (Bruker Daltonics; Billerica, MA, USA) equipped with a 4.7 T superconducting magnet (Magnex Scientific Ltd.; Abington, UK) and Infinity cell.²²

Results and Discussion

Kinetics of acetonitrile dissociation from 1a.— To estimate the rate of loss of acetonitrile from 1a to form $Cl_4W(NNMe_2)$ (2) in the CVD reactor, the kinetics of acetonitrile exchange were determined via variable temperature NMR spectroscopy. The exchange rate k was determined by line shape analysis in the temperature interval 50 to $84^{\circ}C$. A plot of ln(k/T) vs. 1/T (Figure 2) afforded an activation enthalpy of 23.0 ± 0.2 kcal/mol and an activation entropy of 28.8 ± 0.6 cal/mol·K, consistent with dissociative exchange. The corresponding Gibbs energy of activation is 14.4 kcal/mol, indicating that dissociation of acetonitrile from 1a should be facile under CVD conditions.

Based on these results it can be assumed that benzonitrile solutions of **1a** have been converted almost completely to **1b** by dissociative exchange of the acetonitrile ligand with solvent before the solution is introduced into the CVD reactor. Thus complex **1b** can be con-



Figure 2. Plot of ln(k/T) vs. 1/T(K) for acetonitrile exchange in complex 1a.

sidered as the predominant precursor species during deposition of WN_xC_y from solutions made from **1a**. Because the rates for dissociation of acetonitrile and benzonitrile from transition metal complexes are similar,²³ these experiments also establish that the coordinately unsaturated intermediate **2** will be readily accessible from either **1a** or **1b** under deposition conditions.

Ion cyclotron resonance experiments.— We have previously demonstrated that mass spectrometry can provide insight into the gas phase dissociation chemistry of the related tungsten imido complexes $Cl_4(CH_3CN)W(NR)$ where $R = {}^iPr$, Ph and $allyl^{3,24,25}$ as well as the series of tungsten hydrazido complexes $Cl_4(CH_3CN)W(NR_2)$.⁸ The chemical ionization mass spectra of **1a**, however, were anomalous in that the tungsten nitrido fragment Cl_4WN^+ , which is a marker for the ability of the imido complexes to deposit high quality films at low temperatures, could not be detected unambiguously in the spectra of **1a**, despite the fact that **1a** is an excellent CVD precursor for WN_xC_y . To further investigate the gas phase ion dissociation pathways of **1a** and their relevance to the deposition conditions, a mass spectrometric study with negative electrospray ionization and FTICR ion trapping and detection was carried out.

Figure 3 shows the ions detected (negative ion mode) following electrospray ionization of **1b** prepared by dissolving **1a** in



Figure 3. Mass spectrum of $Cl_4(PhCN)W(NNMe_2)$ (**1b**). Negative ions were generated through electrospray ionization (ESI) technique and detected using a Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometer. The most abundant peak in the array was a combination of the ions WCl_4N^- and WCl_4O^- , in a ratio of 21:79. Inset: comparison of experimental intensities to calculated intensities using the 21:79 ratio determined through least squares analysis.



trile as a function of distance below the heated susceptor along the reactor centerline. Spectra in panel E (nitrogen vibrational mode) are marked with reduced scale for concentration reference. Raman shift values for the primary modes are specified at the top of each panel. Raman spectra profiles are marked as a function of position from the heated susceptor surface as (a) 1 mm, (b) 3 mm, (c) 4 mm, (d) 5 mm, (e) 7 mm, (f) 9 mm and (g) 11.5 mm. Panels D and F show only three high resolution scans acquired in a single run.

benzonitrile. The envelope of peaks centered about m/z 340 corresponds to WCl₄N⁻, and a second, lower intensity, envelope of peaks centered about m/z 323 corresponds to WO₂Cl₃⁻. Observing the latter oxidation products suggested that the major peaks in the mass spectrum might represent overlapping WCl₄N⁻ and WCl₄O⁻ distributions, which are displaced by 2 amu. Comparison of the observed mass spectrum with simulations based on mixtures of the calculated distributions of the nitrido- and oxo- species revealed that the major envelope of peaks in Figure 3 is actually composed of 21% WCl₄N⁻ and 79% WCl₄O⁻ (Figure 3, inset). Although the configuration of the sample inlet resulted in formation of the oxo anion WCl₄O⁻due to unavoidable brief exposure of the samples to the atmosphere, the observation of the nitrido cleavage product provides evidence of N-N bond cleavage of the hydrazido ligand of 1b in the gas phase under mass spectrometry conditions.

In situ Raman experiments.- To investigate the thermal decomposition of hydrazido complex 1b, in situ Raman experiments were performed using a susceptor set point temperature of 850°C. Figure 4 shows the observed Raman bands along the centerline at seven distances below the heated susceptor (labeled a-g in Figure 4). To minimize the influence of blackbody radiation, Raman signals of the blank reactor were recorded and subtracted for each measurement position. For the results shown in panels A and D, each spectrum was deconvolved using the Gaussian-Lorentzian peak shape routine in the commercial software package PeakFIT (v4.12). An example deconvolution of spectrum (g) from Panel A (Figure 4) is shown in Figure 5A. Measurements on neat benzonitrile provided frequency values for the C-H in plane bending coupled with \hat{C} -CN stretching (1181 cm⁻¹) and the C–H in plane bending (1197 cm^{-1}) modes in this region. Other modes detected in this region include C-CN stretching for complex 1b (1178 cm⁻¹), W \equiv N1 stretching with methyl scissoring for complex 2 Cl₄W(NNMe₂) (1189 cm⁻¹), and C-Ph stretching, W–N1 and W–N3 stretching with C–N–C torsion for complex **1b** (1193 cm^{-1}) with the assignments based on DFT calculations. Estimation of the local gas phase temperature along the reactor centerline was made by analysis of the N₂ rotational state distribution with accuracy 20 to 30°C in the temperature range of interest.²⁶ The measured temperature is plotted in Figures 5B and 5C as a function of reactor position and the position associated with each spectrum listed in Figure 4. The concentration profiles were obtained as shown in Figures 5B and 5C. In Figure 5B, detected species concentrations are shown in relative concentration because the Raman cross section of 1b is not available. Since the inlet concentration of benzonitrile is known the Raman scattering cross-section was estimated and the concentration profiles indicated in Figure 5C estimated values.



Figure 5. A) Peak deconvolution of spectrum at probe position (g) 11.5 mm, panel A, Figure 4; B) Relative species concentration and gas phase temperature profile (x) along the reactor centerline for 1b and 2; C) Concentration for benzonitrile (BN) and gas phase temperature profile (x).



Figure 6. Peak deconvolution results: (A) spectrum g in panel D of Figure 4 and (B) N_2 vibrational bands from additional experiment (spectrum a) and peaks associated with N_2 vibrational modes and with $C \equiv N$ stretching frequencies (spectra b, c, and d are the same as spectra g, d, and a of panel D in Figure 4, respectively).

The results shown in panel D (Figure 4) support the presence of two C≡N vibrational modes. It is noted, however, that since this region also includes signal from the periodic vibration of excited N₂, these two vibrations can be extracted from the spectra in panel D by comparison with the gas-phase data from authentic benzonitrile. Peak deconvolution of spectrum g in Panel D (Figure 4) reveals six components: four peaks associated with the N2 vibrational mode and two with $C \equiv N$ stretching (Figure 6A). Examination of the spectra (a) from additional N₂ only experiment with (b), (c) and (d) reveals the four periodic N2 vibrational peaks (spectrum a) at 2221, 2229, 2237, and 2245 cm⁻¹. Two additional C≡N stretching frequencies are detected at 2234 and 2241 cm⁻¹ as shown in Figure 6B (spectra b, c, and d). These last two frequencies lie in the reported ranges for v_{CN} of benzonitrile as observed in gas-phase Raman experiments^{27–29} and the origin of the second band under our experimental conditions is not yet understood.

To probe for additional Raman active species that were not detected in the gas-phase experiments, supplementary liquid phase Raman experiments were performed for 1b generated by dissolving 1a in benzonitrile. Using a standard liquid chamber, the 532.08 nm line of a Nd: YAG solid-state laser at 0.1 W was used to excite neat benzonitrile and the vibrational Raman excitation lines were recorded in the range $100 \sim 4000 \text{ cm}^{-1}$. Solution phase Raman spectra of **1b** (the solutions are prepared as 0.0174 mol/L 1a in benzonitrile) and pure benzonitrile were measured and spectra for three selected wave number ranges are shown in Figure 7. It is evident that the higher liquid phase density affords strong scattering intensity to produce very good signal to noise (S/N) ratio. It is also evident that spectra for the liquid samples show features not detected in the gas-phase experiments. Specifically, the three spectra show peaks at 361 cm⁻¹, associated with the W-Cl₄ vibrational mode, 1133 cm⁻¹, assigned to the C-N-C asymmetric vibrational mode, and 1396 cm⁻¹ assigned to the symmetrical umbrella mode of two terminal CH₃ groups. These Raman shifts were not detected in the gas-phase experiments and more detailed experiments are in progress.

DFT calculations.— DFT calculations were performed to better interpret the experimental results and evaluate possible mechanistic steps in the thermal decomposition of **1b**. We have reported further comparison of DFT calculations to experimental results for aryl- and alkylimido precursors.³⁰ The initial calculations were a geometry optimization (B3LYP/LanL2DZ) using experimentally determined bond lengths and angles for **1a** as a test of the computational method (Figure 8). Although the results of the NMR study indicate that **1a** will



Figure 7. Liquid Raman spectra of 1b in benzonitrile solution (solid line) compared to pure liquid benzonitrile (dashed line). Note that the red spectra are intensity shifted for clarity.



Figure 8. Computationally optimized geometry of 1a.

have been converted to 1b before it is injected into the reactor, only the substituent of the nitrile ligand is different and the critical bond lengths and bond angles of 1a should carry over to 1b. The computationally optimized geometry of 1a (Figure 8) is summarized in Table I along with experimental data⁸ and previous calculations using a split valence basis set.³¹ For most of the calculated values in Table I, the B3LYP/LanL2DZ geometry optimization more closely approximates the experimental solid state structure.

Since the dissociation of acetonitrile from 1a was observed to be facile near room temperature, calculations assumed that loss of the nitrile was a rapid first step in decomposition of 1a in the reactor. Further calculations on possible intermediates thus began with $Cl_4W(NNMe_2)$ (2), the product of acetonitrile loss from 1a (or loss of benzonitrile from 1b). The experimental observation of dimethylamine and methylmethyleneimine among the decomposition products suggest two possible dissociative reactions of 2 as depicted in Scheme 1. We have considered both dissociation reactions since AACVD from 1b involves high deposition temperature. Values for the enthalpy and Gibbs energy of W-N¹ and N¹-N² dissociation (Table II) were obtained using statistical thermodynamics. Homolysis of W-N¹ affords open shell products and the spin states were set accordingly during calculations. In the case of $N^1 - N^2$ homolysis, the products are doublets. The calculated W-N¹ bond dissociation enthalpy is significantly higher than the N¹-N² dissociation energy over the 298 to 900 K temperature range. These bond strengths can be viewed in terms of the limiting resonance structures A and B (Figure 9). Crystallographic data are consistent with representation B being the major

Table I. Experimental and Computationally Optimized Bond Lengths (Å) and Bond Angles (°) for Complex 1a.

	Experimental ⁸	Split Basis Set ^{31,a}	This Work ^b
W1-N1	1.769(5)	1.749	1.757
W1-N3	2.224(7)	2.268	2.220
W1-Cl	2.347(16)	2.388	2.429
N1-N2	1.271(8)	1.289	1.283
N2-C1	1.438(7)	1.467	1.478
N1-W1-Cl	95.9(4)	96.8	96.2
N3-W1-Cl	84.07(4)	83.24	83.75
N2-N1-W1	180.0(0)	178.0	179.6

^a B3LYP/LanL2DZ for W, 6-311G for other elements, ^b B3LYP/LanL2DZ for all elements

Table II. Calculated Bond Dissociation Enthalpy (ΔH°) and Gibbs Energy Change (ΔG°) for the W–N¹ and N¹–N² Bonds.

	BDE(W–N ¹) (kcal/mol) ^a	BDE(N ¹ –N ²) (kcal/mol) ^a
ΔH ^o (298 K)	113.1	88.0
ΔH ^o (900 K)	111.4	86.9
ΔG ^o (298 K)	101.0	73.2
ΔG ^o (900 K)	77.8	43.7

^a B3LYP/LanL2DZ



Figure 9. Limiting resonance structures of complexes 1a and 1b.

contributor, which is in accord with calculated N1-N2 BDE values that are higher than the experimental value for free 1,1-dimethylhydrazine (49.6 kcal/mol).32

The dissociation of benzonitrile to form $Cl_4W(NNMe_2)$ (2) (Scheme 2) is postulated to be the first step in thermal decomposition of 1b on the basis of the nitrile dissociation rates for conversion of **1a** to **1b**. The assumed parallel between the reactivity of **1a** and



Scheme 1. Products of cleavage of the W-N¹ and N¹-N² bonds of complex 2. Gibbs energy values (ΔG°) are in kcal/mol.



Scheme 2. Gibbs energy change (ΔG°) for initial ligand substitution and dissociation reactions of complex 1. All energy values are in kcal/mol at 298 K.

the imido complex $Cl_4(CH_3CN)W(N^iPr)$ is consistent with computational assessment of the bond strength between W and N³ using the Wiberg bond index in the natural bond orbital (NBO) analysis of complex **1a**. As shown in Figure 10, the coordinate covalent bond of the acetonitrile ligand with W has the weakest bond order (0.3310).

Dimethylaminyl radical $(3)^{33-35}$ and 1,1-dimethyldiazene (5) have been previously generated by other methods and their reactions have been reported. Dimerization of 1,1-alkyldiazenes is known to form tetrazene derivatives, which in the case of 5 would afford tetramethyl-2-tetrazene (7). Since decomposition of 7 affords two equivalents of dimethylaminyl radical 3 (Scheme 3), the critical reactive intermediate from cleavage of either the W–N¹ or N¹–N² bond of 2 (Scheme 1) will be 3.

Known reactions of dimethylaminyl radical (disproportionation, dimerization, dissociation and rearrangement) are summarized in Scheme 4. Two dimethylaminyl radicals can yield methylmethyleneimine (**8**) and dimethylamine (**9**)^{36–38} or tetramethylhydrazine (**7**) by disproportionation or recombination, respectively^{34,39} (Scheme 4, path a). Since bimolecular reactions of radicals have low activation energies, products of recombination and disproportion are



Figure 10. Wiberg bond indexes for 1a and 1b.

expected to be formed in similar quantities.⁴⁰ In addition to these reactions, dimethylaminyl radical undergoes dissociation into methylnitrene and methyl radical (Scheme 4, path b). Subsequent hydrogen shift in methylnitrene affords methyleneimine^{41–43} (Scheme 4, path c).

Comparison of experimental results with DFT calculations.— The calculated vibrational frequencies can be correlated to products postulated in the proposed decomposition mechanisms (Schemes 1 and 4a). Calculated and corrected Raman active stretching frequencies with experimental values for all compounds including the gas-phase authentic sample of benzonitrile are listed in Table III.

Assignments for 9 of the observed bands attributed to benzonitrile (462, 762, 1003, 1181, 1197, 2234, 3077, 3128, 3175 cm⁻¹) were derived from gas phase benzonitrile Raman spectra and deconvolution data as well as DFT calculations. The reported Raman bands of 1240 and 3377 cm⁻¹ of gas-phase dimethylamine⁴⁴ and DFT results were used for assigning 1247 and 3377 cm⁻¹ to the CH₃ rocking and N-H stretching motions in dimethylamine, respectively. In addition, 1638 cm⁻¹ was assigned to C=N stretching of methylmethyleneimine (8). This assignment is supported by IR data³⁹ and the Raman characteristic group frequency.⁴⁵ Given that dimethylamine (9) and imine 8 would ultimately result from homolysis of the N¹-N² bond followed by disproportionation of radical 3, observation of these products is consistent with N1-N2 cleavage. The possibility of W-N1 dissociation, however, cannot be excluded since this reaction can produce the same radical intermediate (3) through tetramethyltetrazene formation (Scheme 4).

The peak at 3426 cm⁻¹ is tentatively assigned to the N–H stretching mode of HNWCl₄ (**14**) based on the predicted gas phase reaction chemistry and the experimentally observed N–H vibrational frequencies of W(VI) model compounds with imido (NH) and amido (NH₂) ligands.⁴⁶ The N–N cleavage reaction (Scheme 1) would produce the nitrogen-centered radical \cdot NWCl₄ (**4**) as the inorganic product. Subsequent abstraction of a hydrogen atom by **4** would afford the W(VI) parent imido complex **14**. The N_{sp}-H bond of **14** would be expected to have a high bond dissociation energy, making hydrogen abstraction from several species in the reactor energetically favorable.⁴⁷

Estimate of aerosol evaporation time.— The analysis of this study assumes that the decomposition reactions that occur are for inlet species **1b**, benzonitrile, and acetonitrile, and that they occur in the gas phase along the probed centerline of the reactor. The aerosol assisted delivery of the low volatility precursor complicates the analysis of the experimental results since the precursor is initially in a liquid solution but quickly evolves to a gas mixture due to the high vapor pressure of the solvent. It is of interest therefore to estimate the position at which



Scheme 3. Production of dimethylaminyl radical (3) after $W-N^1$ cleavage to form 5. Gibbs energy values are in kcal/mol.



Scheme 4. Known reactions of dimethylaminyl radicals and their calculated (B3LYP/LanL2DZ) reaction energies at 298 K. Gibbs energy values are in kcal/mol.

Table III. Calculated and Corrected Raman Active Stretching Frequencies.					
Molecule	Experimental	Calculated	Corrected	Assignment	
BN	462	466	461	Ph ring stretching	
BN	762	769	761	Ph ring stretching	
BN	1003	1025	1005	Ph ring breathing	
1b	1177	1226	1177	C-H in plane bend	
BN	1181	1236	1187	C-H in plane bend+ C-CN vibration	
2	1189	1246	1196	CH_3 scissoring + W=N stretching	
1b	1193	1243	1193	C-Ph stretching + N3-W-N1 stretching + C-N-C torsion	
BN	1197	1248	1198	C–H in plane bend	
9	1247	1279	1228	CH ₃ rocking	
8	1638	1696	1638	C=N stretching	
_	1708			-	
BN	2234	2335	2237	$C \equiv N$ stretching	
_	2241			$C \equiv N$ stretching in BN?	
-	2516			-	
_	2547				
_	2580				
_	2834			CH_3 symmetric stretching (-N(CH_3) ₂ ; aromatics)	
BN	3077	3142	3079	C–H asymmetric stretching	
BN	3128	3192	3128	C–H asymmetric stretching	
BN	3175	3238	3173		
9	3377			NH stretching	
14	3426			NH stretching	

the aerosol can be assumed to be sufficiently evaporated and thus not affect the measurement.

To investigate the homogeneity of the introduced precursor, a model for droplet formation and evaporation was used to estimate the droplet distribution and time for evaporation. The results were then compared to experiment. The initial droplet size produced by the nebulizer was first estimated using Lang's correlation.⁴⁸ This model assumes each droplet generated by the ultrasonic nebulizer is a homogeneous sphere. The droplet diameter estimated for the system used in this study is ca. $2.7 \,\mu$ m. Next, the rate of evaporation was estimated by modeling the evaporation process for a droplet of pure benzonitrile in a laminar carrier gas. Briefly, the energy balance equation for a benzonitrile droplet gives:

$$N_c = \frac{h_c A \Delta T}{\lambda} \tag{1}$$

where N_c , h_c , A, ΔT and λ denote the solvent evaporation rate, heat transfer coefficient across the liquid-gas, total droplet surface area introduced to the reactor (6.18×10^{-4} m²), temperature difference between droplet surface and ambient, and latent heat of vaporization (3.67×10^2 J/g), respectively. To estimate the value of the heat transfer coefficient, the Nusselt number, Nu, is calculated for a liquid droplet in a flowing gas, using the empirical relation:

$$Nu = 2.0 + 0.6 \text{Re}^{0.5} \text{Pr}^{0.33}$$
[2]

where Re is the Reynolds number and Pr is the Prandtl number. Using this equation, the heat transfer coefficient, h_c is estimated as:

$$\frac{h_c D}{\kappa_d} = 2.0 + 0.6 \left(\frac{D \nu \rho}{\mu}\right)^{0.5} \left(\frac{C_p \mu}{\kappa_d}\right)^{0.33}$$
[3]

where *D* and κ_d are the droplet diameter and liquid thermal conductivity (0.1317 W/mK at 366.5 K). In addition, ν , ρ , μ , and C_p denote mean fluid velocity (2.5 cm/s), density (1.03 g/cm³), viscosity (1.25 × 10⁻³ Pa · s), and specific heat capacity at constant pressure (0.4369 J/kg K), respectively. With the property values mentioned above, Re and Pr have the value of 5.45 × 10⁻⁵ and 3.81, respectively. From Eq. 3, the heat transfer coefficient is calculated as 9.79 × 10⁴ J/sm²K.

The value of the temperature difference between the injected droplet and the gas ambient was assumed to be 10 K since the drop size is relatively small. Eq. 1 gives the value of the solvent evaporation rate as 1.65 g/s and applying this model to the reaction conditions gives a drop evaporation time of only 17 ms for a droplet of mean diameter 2.7 μ m. Using the inlet velocity of 2.5 cm/s velocity, the distance traveled by this droplet for full evaporation is 0.43 mm, which is well before the measurement zone.

The droplet diameter is predicted to show a normal distribution with standard deviation, σ , as follows:⁴⁹

$$\sigma = 4.6 \times 10^{-5} \frac{\rho^{0.1}}{f^{0.41} \tau^{0.50} \mu^{0.18}}$$
[4]

where f is the nebulizer frequency (1.44 MHz), τ is the surface tension (0.041 N/m) and μ is the dynamic viscosity (1.25 × 10⁻³ Pa · s). Using these values the standard deviation of drop diameter, σ , is 5.0 μ m. This implies that for a droplet at 2σ diameter (17.7 μ m) only 1.8 particles are present in the reactor volume and will be evaporated at 2.0 mm position in the reactor.

There is experimental evidence to support this conclusion. Frolov et al.⁴⁹ reported experimental results supported by calculations that show 70 μ m n-tetradecane droplets vaporize in 70 ms at a liquid surface temperature of 293.15 K and a gas temperature of 573.15 K. It is noted that n-tetradecane has a higher boiling temperature (526 K) than benzonitrile (464 K) and their droplet diameter was approximately 4 times larger than that in this study. As further evidence, the spectral positions of the strongest phenyl ring breathing mode of benzonitrile were carefully measured. No displacement of peak positions, as would be expected between liquid and gas phase samples, was detected along the reactor centerline as shown in Figure 11. Based on the modeling results, comparison to experiment using a less volatile solvent, and



Figure 11. Detected Raman spectra along the center line for injected benzonitrile. The observed wavenumber 1003 cm⁻¹ was assigned to the phenyl breathing mode of benzonitrile. Raman spectra are shifted for clarity. Black bottom signal was recorded at the gas inlet (cold region) and top signal just below the heated susceptor.

the lack of a measurable peak shift in the phenyl ring breathing mode, the assumption of homogeneous gas-phase reaction in the whole CVD reactor is substantiated.

Conclusions

The decomposition pathways of the dimethylhydrazido tungsten complexes (RCN)Cl₄W(NNMe₂) (**1a**: $R = CH_3$; **1b**: R = Ph) were investigated using Raman spectroscopy, NMR kinetics, ion cyclotron resonance and DFT calculations at the B3LYP/LanL2DZ level of theory. The rate of loss of acetonitrile from 1a was determined via variable temperature NMR spectroscopy to yield an activation enthalpy of 23.0 ± 0.2 kcal/mol and an activation entropy of 28.8 ± 0.6 cal/mol · K in the temperature range 50 to 84°C. These results indicate that acetonitrile dissociation is rapid and the precursor injected from benzonitrile solutions of 1a is thus predominantly 1b, which rapidly dissociates to 2. Raman scattering experiments in the up-flow, cold-wall aerosol-assisted CVD reactor identified peaks consistent with methylmethyleneimine (8), dimethylamine (9), and HNWCl₄ (14). These frequencies were assigned using gas-phase DFT calculations and literature data. The bond cleavages of both W-N¹ and N¹–N² are possible, although the calculated bond strength of W–N¹ is higher than that of N^1-N^2 . Detection of methylmethyleneimine (8) and dimethylamine (9) is consistent with homolysis of the N^1-N^2 bond followed by disproportionation of radical 3, however, this radical can also be produced by $W-N^1$ dissociation. DFT calculations suggested that homolysis of the N^1-N^2 bond can lead to HNWCl₄ (14) after disproportionation of the resulting radicals. Tentative assignment of the peak at 3426 cm⁻¹ to the N–H stretching mode of HNWCl₄ (14) evidences N1-N2 bond homolysis, consistent with experimental evidence on the deposition of films from the related tungsten imido complexes $Cl_4(CH_3CN)W(NR)$ where $R = {}^{i}Pr$, Ph and allyl.^{3,24,25} Finally, homogeneity of introduced precursor was confirmed by conducting droplet evaporation analysis based on the analytical and spectroscopic evidences.

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