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Gas-Phase Reaction of Trimethylgallium and Ammonia: Experimental Determination of the Equilibrium Constant and ab Initio Calculations

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The equilibrium constant for the reaction of trimethylgallium and ammonia has been determined at 40−100 °C via direct pressure measurements. The reaction enthalpy found from experimental data (−15.2 ± 1.5 kcal/mol) is in good agreement with the value obtained from ab initio calculations (−15.9 kcal/mol) using a series of Dunning's basis sets. Presented data should be useful for modeling of gallium nitride chemical vapor deposition reactors as well as for further theoretical analysis of thermodynamic and kinetic processes in gallium chemistry.

I. Introduction

Gallium nitride is a wide band gap (3.4 eV) semiconductor in which there has been significant interest for fabrication of blue light-emitting diodes and lasers.[1] Films of GaN are typically synthesized by chemical vapor deposition (CVD) from trimethylgallium (TMG) and ammonia at temperatures reaching 1000 °C. Because of the complexity of the reaction mechanism which involves both gas phase and surface chemistry, with the latter being considered a more important factor in determining the quality of semiconductor films along with the properties of a substrate, advances in GaN growth techniques have been made largely empirically and there is a lack of knowledge of fundamentals of the deposition process.

Apparently, the first reaction occurring during CVD of gallium nitride is the reversible formation of the Lewis acid−base adduct upon mixing of TMG and ammonia:

$$Ga(CH_3)_3 + NH_3 \leftrightarrow (CH_3)_3Ga{:}NH_3 \qquad (1)$$

Although this reaction seems to be important in the process of GaN deposition, its enthalpy and equilibrium constant have not been experimentally determined so far. The adduct of reaction 1 is reported to irreversibly decompose at temperatures higher than 70 °C with the loss of methane[2]

$$(CH_3)_3Ga{:}NH_3 \rightarrow [(CH_3)_2GaNH_2]_n + CH_4 \qquad (2)$$

The formation of gas phase adducts between group III and group IV precursors is generally considered to be a "parasitic" reaction that affects film growth uniformity and efficiency.[3] However, some researchers believe that this reaction is not important during the growth of gallium nitride from TMG and ammonia.[4] Determination of thermodynamic properties of reaction 1 should help in resolving this issue.

In this work, equilibrium constants for reaction 1 have been measured at 40−100 °C. The reaction enthalpy was found from experimental data and also calculated using molecular orbital quantum chemistry methods at different levels of theory and with various basis sets. Obtained data should be useful for the modeling of gallium nitride CVD reactors as well as for further theoretical analysis of thermodynamic and kinetic processes in gallium chemistry.

II. Experiment

Equilibrium constants of the association reaction of TMG with ammonia at different temperatures were determined by measuring the absolute pressure of a known amount of reactants contained in a vessel. A standard high-vacuum glass manifold was used to handle gases. A Pyrex bulb (approximately 250 cm^3) was connected to a MKS Baratron type 122A absolute pressure transducer through a Cajon fitting equipped with a Chemraz O ring and was sealed from the atmosphere with a Teflon stopcock. The leak-up rate was assessed not to exceed 1×10^{-3} Torr/h which is small compared to the observed pressure changes. The vessel with reactants was immersed in a 2 L ethyleneglycol bath equipped with a magnetic stirrer and coiled Aerorod BXX-09B-53−4T heater (ARI Industries). Using an immersion heater with high power (500 W at 115 V), low thermal mass, and high surface area allowed fast heating and efficient temperature control. The temperature was measured with a T-type thermocouple and regulated by an Omega CN773354 controller within 0.2 °C. The pressure transducer was kept at 45 °C (5 degrees below its maximum operating temperature) to minimize condensation and adsorption of reaction species. The transducer was calibrated at 45 °C using a more accurate MKS Baratron, model 622A11TAD, as a reference. No forced mixing inside the reaction vessel was applied because a stirring bar inside the bulb affected measurements dramatically because of its poor thermal contact with the vessel walls. It was shown in experiments with nonreacting gases at pressures of a few Torr that, upon rapid heating of the vessel by 10 degrees, the pressure stabilized within 1 mTorr in less than 2 min. This indicated that temperature uniformity was achieved fast, probably because of the natural convection of the gas inside the bulb.

TMG (Strem Chemicals, 99%+ purity) and ammonia (Matheson, 99.995%) were additionally purified before every experiment by three freeze−pump−thaw cycles. The reaction vessel was preconditioned by filling it with TMG and heating with a

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heat gun to remove traces of water adsorbed on the surface followed by pump out.

The amount of methane released during decomposition of the TMG−ammonia adduct was determined by cooling the bulb with liquid nitrogen and measuring the residual pressure. Quantitative gas chromatography analysis showed that uncondensed gas was essentially pure methane. Indeed, among the species involved in reactions 1 and 2, only methane has an observable vapor pressure (8 Torr at −193 °C [5]), and its quantity could be obtained from the ideal gas law.

III. Results and Discussion

Experimental Determination of the Equilibrium Constant. Measuring the equilibrium constant of reaction 1 presents an experimental challenge because of the low vapor pressure of the adduct as well as its decomposition. The vapor pressure of the TMG:NH3 complex was reported to be about 4 Torr[2] at room temperature. Sywe et al.[6] reported values ranging from 0.46 to 1.37 Torr. The discrepancy probably resulted from uncontrollable partial decomposition of the complex. We have performed careful measurements which provided the value for vapor pressure of TMG:NH3 at 25 °C of 0.69 ± 0.05 Torr. Note that the latter value was corrected to take into account the dissociation of the complex. Consequently, our measurements of the equilibrium constant were conducted with small quantities of reactants (0.5−1.5 Torr at room temperature), so that the vapor pressure of the adduct was always lower than its saturation point. Also, data points were taken at temperatures higher than 40 °C to avoid condensation of the complex and minimize the effect of multilayer adsorption.

The TMG:NH3 complex decomposes quite easily, releasing methane. The second product of the reaction was long believed to be a cyclic dimer until it was proven that it was a trimer.[7] The decomposition was reported to start at 70 °C and to proceed rapidly at 90 °C.[2] It is believed that this process occurs through the low activation energy (approximately 10 kcal/mol) surface reaction.[8] We have observed that the adduct was decomposing even at room temperature, affecting determination of the equilibrium constant. It is worth to note that the rate of methane generation has not significantly changed when the bath temperature increased from 40 to 100 °C. This fact evidences that decomposition takes place on the stainless steel surface of the pressure transducer kept at a constant temperature, rather than on the glass.

Equilibrium constants, K_p, for reaction 1 were calculated from the total pressure in the vessel assuming ideal gas behavior, which should be a good approximation at the low pressures studied. Reactant concentrations were adjusted according to the amount of methane produced by the decomposition reaction. The contribution of the trimer to the total pressure was neglected. The resulting formula for the equilibrium constants obtained from the material balances is

$$K_p = \frac{(\nu^0_{\mathrm{TMG}} + \nu^0_{\mathrm{NH3}} - \nu - \nu_{\mathrm{CH4}})}{(\nu - \nu^0_{\mathrm{TMG}})(\nu - \nu^0_{\mathrm{NH3}})}\left(\frac{RT}{V}\right)^{-1} \qquad (3)$$

where $\nu = PV/RT$ is the total number of moles of gas-phase species in the vessel, ν^0_{TMG} and ν^0_{NH3} are the initial quantities of reactants, and ν_{CH4} is the amount of methane due to the adduct decomposition. Also, further correction was made to take into account the part of the reaction volume that was always kept at 45 °C. The average measured value of K_p at seven temperatures from 40 to 100 °C are presented in Table 1. The averages, as well as the average deviations, were calculated from replicate experiments at each temperature (see Figure 1).

TABLE 1: Equilibrium Constants for the Reaction of TMG with Ammonia at Different Temperatures

temperature, °C	K_p, atm^{-1}	fraction of adduct dissociated, %[a]
40	$1.5 \pm 0.5 \times 10^4$	22
50	$6.5 \pm 1.6 \times 10^3$	32
60	$3.1 \pm 0.7 \times 10^3$	44
70	$1.6 \pm 0.4 \times 10^3$	57
80	$8.8 \pm 2.5 \times 10^2$	68
90	$5.1 \pm 1.6 \times 10^2$	77
100	$3.1 \pm 0.8 \times 10^2$	84

[a] At a total pressure of 1 Torr.

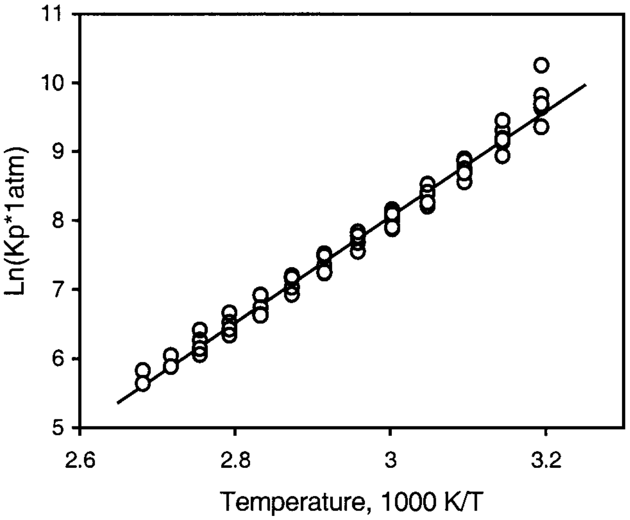

Figure 1. Equilibrium constant of the reaction of TMG and ammonia as a function of temperature in van't Hoff coordinates.

Figure 1 shows the measured values of K_p at temperatures from 40 to 100 °C on a van't Hoff plot. The reaction enthalpy obtained from the slope is $\Delta H = -15.2 \pm 1.5$ kcal/mol and $K_p(25\ °\mathrm{C}) = 4.7 \pm 1.2 \times 10^4$ atm^{-1}. The reproducibility of ΔH was good in separate experiments, whereas individual values of the equilibrium constant varied noticeably because of the high sensitivity of K_p to the uncertainty in pressure and temperature measurements. Experimentally determined reaction enthalpy agrees fairly well with the prediction from NMR chemical shifts of the methyl group[9] (−18.5 kcal/mol). Note, however, that this prediction is based on experimental data of mostly unknown accuracy[2] and should be viewed with caution.

Ab initio Calculations. A series of ab initio as well as density-functional theory molecular orbital calculations were carried out to obtain a purely theoretical estimation for the reaction enthalpy of TMG:NH3 formation. The Gaussian 98 set of programs[10] was used on an IBM SP supercomputer with some calculations being made in MOLPRO (ver. 2000.1).[11]

Geometry optimization was performed at different levels of theory using various basis sets (see Table 2). Subsequent calculations of single-point energies at different levels were carried out using high quality Danning's correlation-consistent all-electron basis sets. Geometries for these calculations were obtained at the MPW1PW91/aug-cc-pvdz level because it describes well the geometries of reactants, and the employed density functional has been proven to produce good results for both covalent and noncovalent interactions.[15] The optimized geometry of TMG has D_{3h} symmetry, similar to ab initio results from ref 16 and commonly used for the interpretation of IR spectra and calculation of thermodynamic functions.[17] Graves

TABLE 2: Optimized Bond Lengths (Å) and Angles (Degrees) for TMG, Ammonia, and Their Adduct

	$Ga(CH_3)_3$		NH_3		$(CH_3)_3Ga{:}NH_3$				
	Ga−C	C−Ga−C	N−H	H−N−H	Ga−N	Ga−C	C−Ga−C	N−H	H−N−H
B3LYP/LANL2DZ	1.985	120.0	1.009	117.2	2.170	2.007	117.3	1.022	110.5
MP2/LANL2DZ	2.005	120.0	1.016	114.7	2.187	2.025	117.4	1.026	109.9
MPW1PW91/LANL2DZ	1.983	120.0	1.004	117.6	2.158	2.005	117.3	1.018	110.7
MPW1PW91/LANL2DZP	1.987	120.0	1.014	107.2	2.184	2.007	117.7	1.016	108.0
B3LYP/6-31+G(d,p)	1.981	120.0	1.016	108.1	2.182	2.000	117.9	1.018	108.0
B3LYP/aug-cc-pvdz	1.993	120.0	1.018	106.7	2.241	2.010	118.1	1.018	107.5
MP2/aug-cc-pvdz	1.983	120.0	1.020	106.5	2.189	2.001	118.3	1.021	107.2
MPW1PW91/aug-cc-pvdz	1.977	120.0	1.016	106.5	2.202	1.996	118.0	1.016	107.5
experiment	1.967[a]	120.0	1.0124[b]	106.67[b]	2.161[c]	1.979[c]	115.9[c]		

[a] From ref 12. [b] From ref 13. [c] From ref 14.

TABLE 3: Total Energies (hartrees) for TMG, Ammonia, and Their Adduct; Interaction Energies (kcal/mol) for TMG and NH_3; and Counterpoise Correction (kcal/mol)

	NH_3	$Ga(CH_3)_3$	$(CH_3)_3Ga{:}NH_3$	ΔE	CP_{TMG}	CP_{NH3}	$\Delta E + CP$
CCSD(T)/cc-pvdz	−56.402 178	−2042.673 238	−2099.112 884	−23.51	2.15	6.34	−15.02
CCSD(T)/aug-cc-pvdz	−56.425 389	−2042.714 192	−2099.173 752	−21.44	4.07	1.49[a]	−15.87
CCSD/cc-pvdz	−56.398 358	−2042.655 829	−2099.090 425	−22.74	1.98	5.99	−14.77
CCSD/aug-cc-pvdz	−56.419 896	−2042.692 988	−2099.145 771	−20.64	3.67	1.39[a]	−15.58
MP4(SDQ)/cc-pvdz	−56.397 970	−2042.655 463	−2099.089 779	−22.81	2.00	6.02	−14.78
MP4(SDQ)/aug-cc-pvdz	−56.419 711	−2042.693 172	−2099.145 859	−20.69	3.86	1.40[a]	−15.43
MP3/cc-pvdz	−56.395 763	−2042.647 817	−2099.080 023	−22.87	1.96	5.94	−14.98
MP3/aug-cc-pvdz	−56.417 470	−2042.685 656	−2099.136 299	−20.82	3.73	1.42[a]	−15.67
MP2/cc-pvdz	−56.382 094	−2042.596 659	−2099.017 066	−24.04	1.99	6.42	−15.63
MP2/aug-cc-pvdz	−56.404 850	−2042.634 940	−2099.074 341	−21.68	3.94	1.48	−16.26
MP2/cc-pvtz	−56.452 908	−2042.887 363	−2099.375 622	−22.18	2.27	2.57	−17.34
MP2/aug-cc-pvtz	−56.460 507	−2042.910 564	−2099.406 808	−22.42	4.23	0.41	−17.79
MP2/cc-pvqz	−56.474 559	−2043.003 838	−2099.511 690	−20.89	1.94	1.00	−17.95
HF/cc-pvdz	−56.195 504	−2042.062 679	−2098.285 396	−17.08	0.39	3.59	−13.10
HF/aug-cc-pvdz	−56.205 200	−2042.069 544	−2098.297 737	−14.43	0.92	0.62	−12.89
HF/cc-pvtz	−56.217 567	−2042.173 489	−2098.414 936	−14.98	0.12	1.29	−13.58
HF/aug-cc-pvtz	−56.220 025	−2042.174 993	−2098.416 946	−13.76	0.04	0.04	−13.68
HF/cc-pvqz	−56.222 777	−2042.184 549	−2098.429 909	−14.17	0.02	0.44	−13.71
B3LYP/aug-cc-pvdz	−56.570 776	−2044.625 755	−2101.219 424	−14.37	0.85	0.73	−12.79
MPW1PW91/aug-cc-pvdz	−56.552 876	−2044.702 103	−2101.281 367	−16.56	0.81	0.67	−15.08
MPW1PW91/aug-cc-pvtz	−56.569 224	−2044.809 316	−2101.403 396	−15.60	0.13	0.07	−15.40
MPW1PW91/LANL2DZ	−56.526 967	−121.769 186	−178.335 721	−24.83	0.44	1.87	−22.52
MPW1PW91/LANL2DZP	−56.554 426	−121.803 596	−178.389 534	−19.77	0.32	1.64	−17.81

[a] Calculations made in MOLPRO.

and Scuseria[18] have found C_3 symmetry for this molecule with a small distortion from planarity (0.04−0.07 degrees for the Ga−C bond). This result, however, seems to stem from their choice of initial geometries, their optimization conversion criteria, and the inability of many quantum chemistry software packages to handle symmetry change on the fly. Indeed, starting the optimization with different initial geometries leads to very similar TMG structures in which total energies are within a few microhartrees. Optimization of the TMG:NH3 adduct resulted in C_{3v} geometry, in accord with available experimental data.[17]

Total electronic energies for the species involved in reaction 1 obtained at different levels of theory and with different basis sets are shown in Table 3. The interaction energy, ΔE, of the TMG:NH3 complex was computed as a difference between single-point energies of the adduct and its components. In assessing energies of noncovalent bonds, the basis set superposition error (BSSE) is known to play a significant role.[19] It stems from the unavoidable incompleteness of basis sets and causes binding forces to be more attractive. Ideally, BSSE can be suppressed by using very large basis sets; however, it is seldom a feasible approach for all but very small molecular systems. In practice, the counterpoise method (CP) by Boys and Bernardy[20] is considered to be the most useful scheme today to deal with BSSE.[19]

The CP correction was calculated as a difference in single-point energies of a monomer (TMG or NH_3) in its own basis set and in the dimer basis set where ghost orbitals were replacing atomic orbitals of the second fragment. In these calculations we used geometries of the fragments as they appear in the TMG:NH_3 complex. Both uncorrected and corrected values of binding energies are shown in Table 3 as well as in Figure 2. It may be seen that, at the HF level, increasing the size of the basis set quickly reduces BSSE to less than 1 kcal/mol and the interaction energy ΔE converges rather quickly. Adding diffuse functions to the cc-pvdz basis set increases BSSE associated with the Ga fragment of the molecule because diffuse functions on gallium reach further and interact more strongly with nitrogen orbitals. At the same time, diffuse functions decrease the BSSE of the ammonia fragment, probably because of a poorer description of nitrogen's lone pair electrons in the unaugmented basis sets.

Taking into account electron correlation effects at the MP2 level leads to increasing the computed interaction energy approximately by 7 kcal/mol. However, CP corrected values are only 2−3 kcal/mol more negative than the HF interaction energies. This is the result of the consistently larger magnitude of BSSE in correlated calculations. Moreover, even with increased basis set size, the BSSE remains substantial, furthermore justifying a necessity for CP correction. Higher correlation does not significantly change either the interaction energy of the TMG:NH_3 complex or the BSSE. The CP corrected ΔE at the CCSD(T)/aug-cc-pvdz level is only 0.4 kcal/mol lower than the corresponding MP2 value. Estimation of the basis set limit

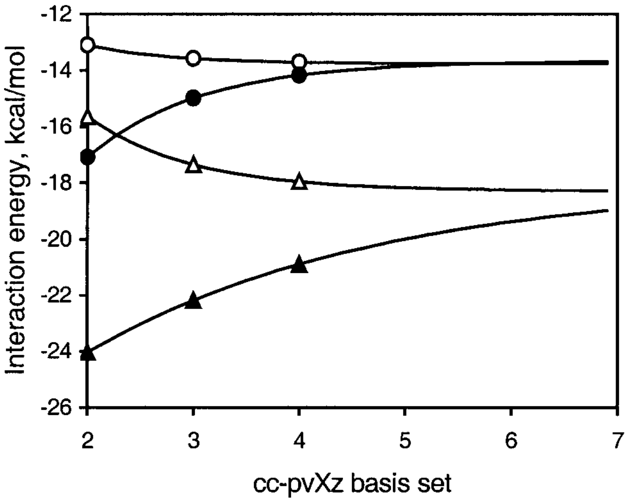

Figure 2. Dependence of calculated TMG−ammonia interaction energy on the size of the cc-ppXz basis set (circles, HF; triangles, MP2; open shapes, counterpoise correction included; the lines show the convergence of each series).

of the interaction energy was performed using convergence properties of cc-pvXz (X = d, t, q, 5, and 6) basis sets.[21] When the formula $E(n) = E(\infty) + B\exp(-Cn)$, with $n = 2$, 3, or 4, was applied to the series of HF and MP2 calculations, the extrapolated value of the energy, $E(\infty)$, was estimated to be −13.8 kcal/mol at the HF level (−13.7 kcal/mol for CP corrected energies) and for MP2 energies −18.0 and −18.3 kcal/mol, respectively (see Figure 2). Note that the counterpoise correction leads to faster convergence, especially at the correlated levels of theory and BSSE corrected energies obtained with aug-cc-pvdz and cc-pvtz basis sets are reasonably close to the extrapolated value. Using the MP2 extrapolated interaction energy (−18 kcal/mol) adjusted to account for higher-order electron correction at the CCSD(T)/aug-cc-pvdz level (0.4 kcal/mol) produces the value of −17.6 kcal/mol as the best theoretical estimate for the electronic binding energy in the TMG:NH3 complex.

Density-functional theory provides a computationally inexpensive route to the post-SCF methods. For our system, the commonly employed B3LYP potential showed no improvement over the HF level (see Table 3). MPW1PW91/aug-cc-pvdz did a better job, with its energies being close to CCSD(T)/aug-cc-pvdz and within 1 kcal/mol of the best estimate. Upon consideration that the magnitude of BSSE in DFT calculations is significantly lower than that for the electron correlation methods (1.5 kcal/mol vs 5.4 kcal/mol at MPW1PW91/aug-cc-pvdz and MP2/aug-cc-pvdz, respectively), MPW1PW91 becomes an attractive method for running inexpensive calculations without counterpoise corrections. Note, however, that improving the basis set from double- to triple-ζ quality failed to produce a better interaction energy for the TMG:NH3 complex at the MPW1PW91 level.

It is worth noting that the LANL2DZ effective core potential (ECP) basis set does not well reproduce molecular geometries for the species of interest (see Table 2) and noticeably overestimates the binding energy (Table 3) compared to the all-electron basis sets. The addition of one set of polarization functions (p exponent for H is 1.0, d exponent for C and N is 0.8, and d exponent for Ga is 0.16) significantly improves the descriptions of geometries as well as energies (see Tables 2 and 3), similar to other donor−acceptor complexes of Al, Ga, and In.[22] Therefore, the LANL2DZP basis set may be recommended for molecular orbital calculations of much bigger systems containing many gallium atoms, including surface chemistry.

Zero-point and thermal corrections to the interaction energy were made by conducting unscaled frequency analysis followed by calculation of thermodynamic functions in Gaussian 98. These calculations were complicated by the extreme floppiness of the TMG molecule which resulted in the appearance of three imaginary frequencies, corresponding to internal rotations of methyl groups, in some model chemistries including MPW1PW91/aug-cc-pvdz. We adjusted the thermodynamic functions computed by Gaussian by replacing appropriate vibrational terms in the thermal energy with $^1/_2RT$ and entropy terms with 5.8 cal/(mol K) (at 298.15 K) per each methyl rotor. Quantitatively similar results were obtained using the MPW1PW91/cc-pvdz model chemistry, which produced no imaginary frequencies, along with the hindered rotation analysis in Gaussian 98 (using keywords HindRot and ReadHind). The barrier for the methyl rotation in TMG was estimated to be 0.16 kcal/mol which warrants essentially free rotation at room temperature and above. This barrier increases to 0.72 kcal/mol in the adduct, whereas the NH_3 fragment rotates almost freely (0.08 kcal/mol).

The enthalpy of reaction 1 was computed using the best estimate for the electronic term (−17.6 kcal/mol) and thermal correction which included internal rotation analysis as described above. The obtained value, $\Delta H_{298} = -15.9$ kcal/mol, is in excellent agreement with the experimental data. However, the computed equilibrium constants are underestimated by a factor of 15−20. This probably results from errors in calculated values of both thermal and electronic contributions to the binding energy. The entropy change, ΔS, in the reaction of adduct formation at 25 °C obtained from presented experimental data is −29.6 cal/(mol K), whereas Gaussian predicts −37.5 cal/(mol K). Using entropies of TMG and the adduct from ref 17, calculated from experimental data, gives $\Delta S = -35.1$ cal/(mol K). With the latter value and with an arbitrary adjustment of the enthalpy change to $\Delta H = -16.8$ kcal/mol, the experimental values of K_p are reproduced. The adjustment in the computed ΔH, which is only 0.9 kcal/mol, is smaller than the absolute uncertainty in energy that is frequently found in state of the art ab initio calculations. It may be taken as an indication of the accuracy of the best calculations shown in Table 3. Anharmonicity of low frequency molecular vibrations in TMG and TMG:NH3 and unaccounted coupling of internal rotations may certainly contribute to the inaccuracy of the computed thermodynamic properties. Still, it is unlikely that these effects would account for the 8 cal/(mol K) difference between the experimental and theoretical reaction entropy. This suggests that the discrepancy in the calculated equilibrium constant results in part from the underestimation of the reaction enthalpy. Consequently, the experimental value of ΔH is probably near the upper limit of its predicted margins, but its absolute value is certainly lower than the prediction (18.5 kcal/mol) reported earlier.[9]

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