Higher Level Theoretical Binding Energies of Methyldiazonium Ion. Is an Experimental Reinvestigation Warranted?

Christopher J. Horan and Rainer Glaser*

Department of Chemistry, University of Missouri—Columbia, Columbia, Missouri 65211

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Several experimental values were reported for the binding energy of methyldiazonium ion, and they differ by 13 kcal/mol. Previous theoretical investigations also were associated with considerable uncertainty. The methyl cation affinity (MCA) of N_2 plays a crucial role as the anchor point for the absolute gas phase methyl cation affinity scale, and an accurate value is thus especially pertinent. To resolve this longstanding controversy, the reaction energy for the process $CH_3^+ + N_2 \rightarrow CH_3N_2^+$ has been determined using full fourth-order Møller–Plesset perturbation theory, CI theory (CID, CISD), quadratic CI theory (QCISD, QCISD(T)), Gaussian-1 (G1) and Gaussian-2 (G2) theory, and coupled cluster methods (CCD, CCSD, ST4CCD, CCSD(T)) with large basis sets. The proton affinity (PA) of diazomethane, $CH_2N_2 + H^+ \rightarrow CH_3N_2^+$, also was determined at these theoretical levels. The best calculations all point to an $MCA(N_2)$ of 44.1 kcal/mol and to a $PA(CH_2N_2) = 211.4$ kcal/mol. While the $PA(CH_2N_2)$ value falls within the experimental range, the calculated binding energy of methyldiazonium ion is more than 4.2 kcal/mol lower than the latest experimental value and 5.3 kcal/mol above the earliest experimental value. These results strongly reaffirm that an experimental reevaluation of the methyl cation affinity is warranted.

Introduction

The binding energy, E_b, of methyldiazonium ion, that is, the methyl cation affinity (MCA) of dinitrogen, has long been a matter of controversy. Two independent measurements of MCA(N_2) were reported, and, with different data for reference compounds, the resulting MCA values vary in the wide range of 38.2–51.2 kcal/mol. Foster and Beauchamp first measured the heat of formation of methyldiazonium ion, $\Delta H_f(CH_3N_2^+) = 223$ kcal/mol, by ion cyclotron resonance spectroscopy.[2] Subsequently, these workers and Williamson measured the photoionization appearance potential of $CH_3N_2^+$ from $CH_3N_2CH_3$ and obtained $\Delta H_f(CH_3N_2^+) = 209.4$ kcal/mol.[3] The combination with the latest value for the heat of formation of $CH_3N_2CH_3$,[4] $\Delta H_f(CH_3N_2CH_3) = 35.5$ kcal/mol, gave $\Delta H_f(CH_3N_2^+) = 212.9$ kcal/mol.[5] With $\Delta H_f(CH_3^+) = 261.2$ kcal/mol,[6] these three $\Delta H_f(CH_3N_2^+)$ values yield methyl cation affinities for N_2 of 38.2,[2] 51.2,[3] and 48.3[5] kcal/mol, respectively.
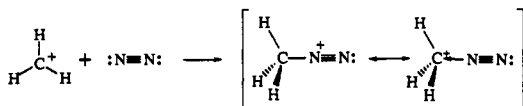
Previous theoretical estimates of MCA(N_2) also are associated with considerable uncertainty. At the STO-3G level, Radom[7] obtained a value of 51.6 kcal/mol which seemed to support the higher experimental value but it was recognized that this apparently good agreement might be fortuitous. Indeed, better Hartree–Fock level calculations with split-valence basis sets all tend to underestimate MCA(N_2) greatly and they also are rather basis set dependent. At the RHF/4-31G level, Radom[7] obtained $E_b = 28.5$ kcal/mol and Simonetta *et al.*[8] and Ford[9] calculated even lower values of 18.4 and 26.0 kcal/mol using more flexible DZ+P and 6-31G* basis sets, respectively. The inclusion of vibrational zero-point energies further reduces these theoretical binding energies.[9-12] At the RHF/6-31G* level and including the scaled vibrational zero-point energy corrections, for example, a value of 21.0 kcal/mol results for the binding energy.[10] Clearly, correlation effects cannot be neglected to even approximate the

methyl cation affinity of N_2 as was shown by Ford,[9] Ikuta,[11] and us.[12] Ford[9] reported a dissociation energy of 42.3 at MP3/6-31G**//RHF/6-31G* without correction for internal motion and a value of 38 kcal/mol for the reaction enthalpy, and he pointed out that the binding energy change between the MP3/6-31G** and MP4(SDQ)/6-31G** was only 0.1 kcal/mol. Thus, Ford's value was in close agreement with the earlier experimental value. Ikuta[11] determined the methyl cation affinity at higher basis set levels using correlated methods and found 44.0 ± 1.0 kcal/mol as the most probable dissociation reaction enthalpy based on MP2/6-311G(3df,2pd)//MP2/6-31G** energies, an empirical estimate for the effects of higher order perturbations, and inclusion of a thermochemical correction term. We studied the dissociation of $CH_3N_2^+$ with Møller–Plesset theory employing more extended basis sets and reported[12] our best previous value of 43.3 kcal/mol determined at MP4(SDTQ=fc)/6-311++G-(df,p)//MP2(full)/6-311G** and including unscaled MP2(full)/6-31G* zero-point energy corrections. This value still remained a few kilocalories per mole lower than the latest experimental value.

Recent advances in the development of advanced modern theoretical methods for the accurate evaluation of electron correlation effects as well as in available hardware have made it possible to reexamine the methyl cation affinity of N_2. A reliable value for the binding energy of the methyldiazonium ion is of special significance since the absolute methyl cation affinity scale constructed by Kebarle *et al.*[5] employs the MCA of N_2 as their primary standard. Here, we report higher level ab initio calculations on the binding energy of methyldiazonium ion to resolve the controversy as to which experimental value is correct. The association of CH_3^+ and N_2 to methyldiazonium ion has been examined using full fourth-order Møller–Plesset perturbation theory, CI theory (CID, CISD), quadratic CI theory (QCISD, QCISD(T)), Gaussian-1 (G1) and Gaussian-2 (G2) theory, and coupled cluster methods (CCD, CCSD, ST4CCD, CCSD(T)). These calculations were based on geometries optimized at correlated levels (MP2(full)/6-31G*), and large and well-polarized basis sets up to 6-311+G(2df,p) were employed. With these higher level energies for the methyldiazonium ion, we have also determined an accurate theoretical estimate for the proton affinity of diazomethane.[13] The experimental PA(CH_2N_2) value

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has been bracketed by Foster and Beauchamp[2] via the gas phase proton exchange equilibrium between methyldiazonium ion and ammonia (PA(NH$_3$) = 207.0 kcal/mol),[14] azomethane (PA-(CH$_3$N=NCH$_3$) = 212 ± 5 kcal/mol), and methylamine (PA(CH$_3$NH$_2$) = 216 kcal/mol).[15] It was found that the proton affinity of diazomethane falls in the range 207.0–212(±5) kcal/mol; however, the upper limit is associated with considerable experimental uncertainty.
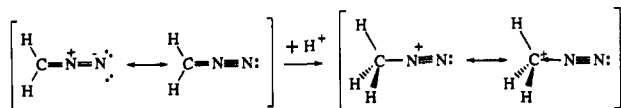
Results and Discussion

Gaussian-1 and Gaussian-2 Binding Energies. In G1 theory,[16] it is the general objective to approximate the total energy of a high-level QCISD(T)/6-311+G(2df,p) calculation through computation of correction terms at lower levels.

$$E_{tot} = E(combined) + \Delta E(HLC) + \Delta E(ZPE)$$

In the first step, the equilibrium geometries are determined at the RHF/6-31G* and MP2(full)/6-31G* levels. The zero-point energy correction ΔE(ZPE) is determined at the RHF/6-31G* level and scaled by the factor of 0.8929.[17] The total energy E(combined) results as the accumulation of various frozen core single-point calculations with the MP2(full)/6-31G* geometry.

E(combined) =
$$(MP4STDQ(fc)/6\text{-}311G^{**}//MP2(fu)/6\text{-}31G^*) +$$
$$\Delta E(+) + \Delta E(2df) + \Delta E(QCI)$$

where

$$\Delta E(+) = (MP4STDQ(fc)/6\text{-}311+G^{**}) -$$
$$E(MP4STDQ(fc)/6\text{-}311G^{**})$$

$$\Delta E(2df) = E[MP4STDQ(fc)/6\text{-}311G(2df,p)] -$$
$$E(MP4STDQ(fc)/6\text{-}311G^{**})$$

$$\Delta E(QCI) = (QCISD(T)(fc)/6\text{-}311G^{**}) -$$
$$E(MP4STDQ(fc)/6\text{-}311G^{**})$$

To better approximate experimental values, the ΔE(HLC) is a "higher level correction" due to remaining basis set deficiencies and it is described by the equation

$$\Delta E(HLC) = -0.19 n_\alpha - 5.95 n_\beta$$

where n_α is the number of α valence electrons and n_β is the number of β valence electrons. For G1 theory, the values determined in most cases are within 2 kcal/mol of known experimental data.

The general objective of G2 theory[18] is the same as with G1 with a few added corrections for basis set extensions and modifications of the higher level correlation. Therefore, the equation for the total electronic energy becomes

$$E_{tot}(G2) = E_{tot}(G1) + \Delta + 1.14 n pair$$

where Δ is the summation of the following terms.

$$\Delta(+2df) = E[MP2/6\text{-}311+G(2df,p)] -$$
$$E[MP2/6\text{-}311G^{**}]$$

$$\Delta(+) = E[MP2/6\text{-}311+G^{**}] - E[MP2/6\text{-}311G^{**}]$$

$$\Delta(2df) = E[MP2/6\text{-}311G(2df,p)] - E[MP2/6\text{-}311G^{**}]$$

$$\Delta_2 = E[MP2/6\text{-}311+G(3df,2p)] -$$
$$E[MP2/6\text{-}311+G(2df,p)]$$

The last term, 1.14$n$pair, where $n$pair is the number of valence pairs, is an added correction which lowers the E(HLC) in G1 theory by 1.14 millihartrees to closer approximate experiment.

The values required for the G1 and G2 evaluations were computed and are summarized in Table 1, and binding energies are summarized in Table 2. Table 2 also contains total energies and derived binding energies computed at other higher theoretical levels for comparison. All of these higher level calculations were carried out with the 6-311+G(2df,p) basis set, that is, the same basis set employed in the QCISD(T) calculation G1 theory approximates. Geometry optimizations were performed within D_{3h} symmetry for CH$_3^+$, in $D_{\infty h}$ symmetry for N$_2$, in C_{3v} symmetry for CH$_3$N$_2^+$, and in C_{2v} symmetry for CH$_2$N$_2$[13,19,20] at the RHF level and with the inclusion of the perturbational effects of electron correlation at the second-order Møller–Plesset[21] level with the 6-31G* basis set, MP2(full)/6-31G*, using Gaussian92.[22] The Hessian matrix was computed analytically at the RHF/6-31G* level for each structure to confirm that an extremum on the potential energy surface had indeed been located and to determine the vibrational zero-point energies (VZPEs).[12] VZPE corrections to relative energies were scaled as described.

The binding energies for G1 and G2 theory are 40.79 and 41.39 kcal/mol, respectively. G2 theory accounts for basis set effects associated with the additions of a third set of d functions and a second set of p functions, and it also incorporates a correction for the nonadditivity of energetic effects due to diffuse-sp and 2df basis set extensions. The third factor responsible for the difference in the G1 and G2 values is the modification to the "higher level correction". The combination of all these contributions results only in a minor increase of the G2 value compared to the G1 theoretical estimate. Most importantly, both values are about 2 kcal/mol *below* our best previously calculated value and 7 kcal/mol lower than the latest experimental value.

CI and QCISD Binding Energies. Since G1 theory approximates the full size-consistent QCISD(T)/6-311+G(2df,p)[23] level results, we examined the methyldiazonium ion dissociation with directly computed QCISD(T)/6-311+G(2df,p) energies using the MP2-(full)/6-31G* geometries. At this level and including VZPE-(RHF/6-31G*) corrections, we obtained E_b = 40.71 kcal/mol (Table 2), which is in excellent agreement with the G1 approximation. The consideration of the triples excitations has significant effects. Quadratic configurational interaction neglecting the triples excitations results in a QCISD/6-311+G(2df,p)//MP2/6-31G* + ΔVZPE(RHF/6-31G*) binding energy of 38.15 kcal/mol, more than 2 kcal/mol lower than the G1 value.

We also studied the dissociation of methyldiazonium ion with this same large basis set, 6-311+G(2df,p), and employing CI methods with double (CID) and both single and double substitutions included (CISD)[24] as well as Møller–Plesset perturbation theory up to full fourth-order (Table 2) in the frozen core approximation. The CID and CISD values were also lower than the G1 and G2 values by about 3.5–4 kcal/mol and gave similar binding energies of 37.25 and 37.65 kcal/mol, respectively. Møller–Plesset perturbation theory up to the fourth-order level showed fluctuations with binding energies ranging from an overestimated MP2 value of 43.48 kcal/mol, to a low value of 38.72 kcal/mol for MP3, to an MP4 value of 41.57 kcal/mol. The best MP4 level calculations are in excellent agreement with the G1 and G2 calculations and with the directly computed QCISD(T) binding energy.

Coupled Cluster Binding Energies. The binding energies were also determined using coupled cluster theory with double substitutions (CCD),[25] with single and double substitutions

TABLE 1: Energies and Parameter Values for Gaussian-1 and Gaussian-2 Evaluations[a,b]

theoretical level	$CH_3N_2^+$	CH_2N_2	CH_3^+	N_2
RHF/6-31G	-148.216056	-147.843784	-39.230640	-108.943949
RHF/6-31G* VZPE	30.70	21.56	21.15	3.94
MP2(full)/6-31G*	-148.666119	-148.310594	-39.329435	-109.261574
MP2(fc)/6-311G**	-148.728552	-148.369869	-39.356178	-109.296781
MP4(fc)/6-311G**	-148.769011	-148.408963	-39.379697	-109.316156
QCISD(T)(fc)/6-311G**	-148.763342	-148.404377	-39.381068	-109.310209
MP2(fc)/6-311+G**	-148.730937	-148.375696	-39.356306	-109.301350
MP4(fc)6-311+G**	-148.771601	-148.414914	-39.379833	-109.320914
MP2(fc)/6-311G(2df,p)	-148.796338	-148.446610	-39.369400	-109.374505
MP4(fc)/6-311G(2df,p)	-148.839782	-148.489061	-39.393570	-109.369833
MP2(fc)/6-311+G(3df,2p)	-148.809878	-148.462376	-39.375143	-109.356661

parameter	$CH_3N_2^+$	CH_2N_2	CH_3^+	N_2
		G1 Theory		
MP4(fc)/6-311G**	-148.769011	-148.408963	-39.379697	-109.316156
$\Delta E(+)$	-0.002590	-0.005951	-0.000136	-0.004758
ΔE(2df)	-0.070771	-0.080098	-0.013873	-0.053677
ΔE(QCI)	0.005669	0.004586	-0.001371	0.005947
ΔE(HLC)	-0.049120	-0.049120	-0.018420	-0.030700
ΔE(ZPE)	0.043688	0.030686	0.030102	0.005610
total G1 energy	-148.842135	-148.508860	-39.383395	-109.393734
		G2 Theory		
E_{tot}(G1)	-148.842135	-148.508860	-39.383395	-109.393734
Δ	-0.011155	-0.009939	-0.005615	-0.004587
1.14$n$pair	0.009120	0.009120	0.003420	0.005700
total G2 energy	-148.844170	-148.509679	-39.385589	-109.392621

[a] All single-point calculations with the geometry determined at the MP2(full)/6-31G* level. [b] Total energies in atomic units. VZPE values in kcal/mol.

TABLE 2: Total Energies Calculated with MP2(full)/6-31G* Geometries, Relative Binding Energies, and Proton Affinities[a,b]

theoretical level	$CH_3N_2^+$	CH_2N_2	CH_3^+	N_2	E_b'	E_b	PA'	PA
RHF/6-311+G(2df,p)	-148.255508	-147.892254	-39.244685	-108.971488	24.68	19.68	227.95	219.79
MP2(fc)/6-311+G(2df,p)	-148.798427	-148.452081	-39.369533	-109.351623	48.49	43.48	217.34	209.18
MP3(fc)/6-311+G(2df,p)	-148.797822	-148.450055	-39.388544	-109.339597	43.73	38.72	218.23	210.07
MP4(fc)/6-311+G(2df,p)	-148.841988	-148.494479	-39.393707	-109.374066	46.57	41.57	218.07	209.91
CID(fc)/6-311+G(2df,p)	-148.805930	-148.453834	-39.392588	-109.346005	42.25	37.25	220.94	212.78
CISD(fc)/6-311+G(2df,p)	-148.812504	-148.462150	-39.393206	-109.351317	42.66	37.65	219.85	211.69
QCISD(fc)/6-311+G(2df,p)	-148.809709	-148.458938	-39.392265	-109.348676	43.15	38.15	220.11	211.95
QCISD(T)(fc)/6-311+G(2df,p)	-148.835302	-148.488434	-39.395037	-109.367410	45.72	40.71	217.66	209.50
CCD(fc)/6-311+G(2df,p)	-148.802655	-148.449518	-39.391656	-109.343153	42.57	37.57	221.60	213.44
ST4CCD(fc)/6-311+G(2df,p)	-148.834900	-148.486128	-39.395011	-109.367382	45.50	40.49	218.86	210.70
CCSD(fc)/6-311+G(2df,p)	-148.807991	-148.456799	-39.392181	-109.347263	43.01	38.01	220.38	212.22
CCSD(T)(fc)/6-311+G(2df,p)	-148.834529	-148.487448	-39.395003	-109.366785	45.65	40.64	217.80	209.64
Gaussian-1 theory	-148.842135	-148.508860	-39.383395	-109.393734		40.79		209.13
Gaussian-2 theory	-148.844170	-148.509679	-39.385589	-109.392621		41.39		209.90

[a] Total energies (-E) in atomic units. CID and CISD energies are size-consistency corrected. [b] Binding energies (E_b) of $CH_3N_2^+$ and proton affinities (PA) of CH_2N_2 are given in kcal/mol. E_b' and PA' values do not contain VZPE corrections and E_b and PA values do include the scaled RHF/6-31G* vibrational zero-point energy corrections.

(CCSD),[26] with double substitutions and including single and triple contributions evaluated through fourth order using the CCD wave function (ST4CCD),[27] and with single and double excitations with noniterative inclusion of triple excitations (CCSD(T)).[23,28] Both calculations with the triple substitutions included give binding energies over 40 kcal/mol and close to the G1 and G2 values. The two coupled cluster calculations excluding the triples contributions predict E_b values of 37.57 and 38.01 kcal/mol for the CCD and CCSD levels, respectively, and they are 2–3 kcal/mol lower.

Proton Affinity of Diazomethane. Diazomethane may be C- or N_β-protonated. Berner and McGarrity[29] showed that the protonation of CH_2N_2 in superacid media yields the methyldiazonium ion and the methylenediazenium ion in a ratio of 4:1, and calculations indicate that the former ion is more stable in the gas phase.[30] We thus report the reaction energy for methyldiazonium ion formation as the proton affinity of CH_2N_2.

With the data in Tables 1 and 2 for methyldiazonium ion and diazomethane, we find that the proton affinity values of diazomethane determined at our highest levels (MP4, QCISD(T), CCSD(T), G1, and G2) all fall within the narrow range of PA-(CH_2N_2) = 209.5 ± 0.5 kcal/mol.[31] Thus, the predicted proton

affinity falls within the experimental range of 207–212(±5) kcal/mol and it is substantially lower than the previous best theoretical value.[19c]

Thermochemistry. The experimental values refer to enthalpies measured at ambient temperatures, and the theoretical binding energies calculated for the motionless state at 0 K need to be corrected for the temperature dependence of the enthalpies. The binding energies in Table 2 only include the scaled (factor 0.8929) VZPE corrections calculated at the RHF/6-31G* level. We examined the effects of this approximation and the consideration of $\Delta\Delta H$ instead of $\Delta\Delta$VZPE, and in Table 3 we have summarized the pertinent data. Note that the values for methyldiazonium ion, methyl cation, and dinitrogen agree very closely with the respective values determined at the MP2(full)/6-31G* level.[12] For diazomethane, we also evaluated the thermodynamic functions using the CISD/6-31G* vibrational data. We scaled these frequencies by a factor of 0.92 to best match the experimental vibrational frequencies,[32] and the data thus obtained agree excellently with the RHF/6-31G* data. As can be seen from Table 3, the consideration of $\Delta\Delta H$, $\Delta\Delta H = \Delta\Delta E + \Delta(pV)$, instead of $\Delta\Delta$VZPE results in an increase in the binding energies of

TABLE 3: Thermochemical Data[a,b]

molecule	VZPE	ΔE	ΔS	ΔG
$H_3CN_2^+$	27.42	28.18	55.89	11.52
H_2CN_2	19.26	21.36	56.95	4.38
H_2CN_2 (CISD)[c]	19.16	20.77	57.44	3.65
H_3C^+	18.89	20.67	44.50	7.41
N_2	3.52	5.00	45.69	−8.62

reaction	ΔVZPE	$\Delta\Delta E$	$\Delta\Delta S$	$\Delta\Delta G$
$H_3CN_2^+ \rightarrow CH_3^+ + N_2$	−5.01	−1.91	34.30	−12.73
$CH_2N_2 + H^+ \rightarrow H_3CN_2^+$	8.16	6.23	−1.06	7.14

[a] RHF/6-31G* data. 298.15 K. VZPE values scaled by 0.8929. All numbers in kcal/mol except for ΔS and $\Delta\Delta S$, which are in cal/(K·mol). [b] The two lowest frequency vibrations were omitted for the computation of the state functions of methyldiazonium ion. [c] Using CISD/6-31G* frequencies; see text.

methyldiazonium ion of ~3.1 kcal/mol, which is more than 1 kcal/mol higher compared to the earlier estimates by Ikuta[11] and by us.[12] Similarly, the proton affinity of diazomethane is increased by ~1.9 kcal/mol when $\Delta\Delta H$ is considered.

Conclusion

At the highest level in our previous study, MP4[SDTQ]/6-311G**//MP2(full)/6-31G*+VZPE(MP2(full)/6-31G*), we reported an enthalpy of 43.3 kcal/mol for the binding energy of methyldiazonium ion. This value is well within the experimental range but it is a few kcal/mol lower than the latest experimental value of 48.3 kcal/mol. We pointed out that this latest experimental value might be too high by ~5 kcal/mol in light of our computations and considering that photoionization appearance potentials do not always provide reliable heats of formation for ionic species. The higher level binding energies reported here confirm our earlier work and support much more strongly our conclusion.

The best calculations described here all point to a binding energy of 41.0 ± 0.5 kcal/mol, more than 7.0 kcal/mol lower than the latest experimental value and 2.5 kcal/mol above the experimental value derived from ion cyclotron resonance spectroscopy. The inclusion of triples excitations is important as it increases the E_b value by ~2 kcal/mol. Temperature-dependent enthalpy changes certainly contribute to the difference between theory and experiment, and the above discussion shows that such effects are not negligible and that they increase the binding energy by ~3.1 kcal/mol. Note that the magnitude of the difference |ΔVZPE − $\Delta\Delta H$| slightly exceeds the usual precision of 2 kcal/mol for the calculated G1 and G2 data. With consideration of the |ΔVZPE − $\Delta\Delta H$| value, our best estimate for the methyl cation affinity of dinitrogen becomes 44.1 ± 0.5 kcal/mol. While Ford's computed MCA value agreed very closely with the earlier experimental value, our present higher level study strongly reaffirms the conclusion made earlier by us[12] and by Ikuta[11] that an experimental reevaluation of the methyl cation affinity is warranted. In addition, this conclusion has now been further supported by the results presented for the proton affinity of diazomethane; our best theoretical value, PA(CH_2N_2) = 211.4 ± 1.0 kcal/mol, lies within the experimental range.

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