Supporting Information

Theoretical Investigation of *N*-Nitrosodimethylamine Formation from Nitrosation of Trimethylamine

Zhi Sun, Yong Dong Liu, Ru Gang Zhong*

Content

* Corresponding author. Fax: +86-10-6739-2001. E-mail: ydliu@bjut.edu.cn.

level in the Gas Phase

Table S8. Energies (E_{sol}) of each Stationary Point involved in Scheme 4 in Aqueous Solution at the CPCM-CCSD(T)/6-311+G(d,p)//B3LYP/CBSB7 level

Table S9. Energies (E, 0K / 298K), Enthalpies (H, at 298K and 1 atm), and Gibbs Free Energies (G, at 298K and 1 atm) as well as the Lowest Harmonic Vibrational Frequency (LHVF) of each Stationary Point involved in Scheme 5 at the CBS-QB3 level in the Gas Phase

Table S10. Energies (E_{sol}) of each Stationary Point involved in Scheme 5 in Aqueous Solution at the CPCM-CCSD(T)/6-311+G(d,p)//B3LYP/CBSB7 level

Table S11. Energies (E, 0K / 298K), Enthalpies (H, at 298K and 1 atm), and Gibbs Free Energies (G, at 298K and 1 atm) as well as the Lowest Harmonic Vibrational Frequency (LHVF) of each Stationary Point involved in Scheme 6 at the CBS-QB3 level in the Gas Phase

Table S12. Energies (E_{sol}) of each Stationary Point involved in Scheme 6 in Aqueous Solution at the CPCM-CCSD(T)/6-311+G(d,p)//B3LYP/CBSB7 level

Table S13. Energies (E, 0K / 298K), Enthalpies (H, at 298K and 1 atm), and Gibbs Free Energies (G, at 298K and 1 atm) as well as the Lowest Harmonic Vibrational Frequency (LHVF) of each Stationary Point involved in the Hydrolysis Mechanisms involving TS2-A′ and TS2-B′ at the PBE1W/CBSB7 level in the Gas Phase

Table S14. Energies (E_{sol}) of each Stationary Point involved in the Hydrolysis Mechanisms involving TS2-A′ and TS2-B′ in Aqueous Solution at the CPCM-CCSD(T)/6-311+G(d,p)//PBE1W/CBSB7 level

Table S1 Energies (E, 0K / 298K), Enthalpies (H, at 298K and 1 atm), and Gibbs Free Energies (G, at 298K and 1 atm) as well as the Lowest Harmonic Vibrational Frequency (LHVF) of each Stationary Point involved in Scheme 1 at the CBS-QB3 level in the Gas Phase [a]

Species	$E^{(0K)}$ [b]	$E^{(298K)}$	$H^{(298K)}$	$G^{(298K)}$	LHVF
TMA	-174.106383	-174.100885	-174.099940	-174.132700	252.3
NO^+	-129.405990	-129.403629	-129.402685	-129.425172	2494.4
CR1-A	-303.605823	-303.597545	-303.596600	-303.638074	43.9
TS1-A	-303.518428	-303.509877	-303.508933	-303.551590	137.7i
CP1-A	-303.529050	-303.519726	-303.518782	-303.564002	55.7
NOH	-130.255689	-130.252837	-130.251893	-130.276946	1273.3
Iminium Ion	-173.259908	-173.254611	-173.253667	-173.286719	128.5

[a] Energies, Enthalpies, and Gibbs Free Energies in hartree, lowest harmonic vibrational frequency in cm^{-1}; CR, TS, and CP correspond to Reactant Complex, Transition State, and Product Complex, respectively.

[b] Energies at 0K was corrected with Zero Point Energies (ZPE).

Table S2 Energies (E_{sol}) of each Stationary Point involved in Scheme 1 in Aqueous Solution at the CPCM-CCSD(T)/6-311+G(d,p)//B3LYP/CBSB7 level

Species	E_{sol} (hartree)
TMA	-174.047921
NO^+	-129.457976
CR1-A	-303.538799
TS1-A	-303.453356
CP1-A	-303.461817
NOH	-130.171622
Iminium Ion	-173.286665

Table S3 Energies (E, 0K / 298K), Enthalpies (H, at 298K and 1 atm), and Gibbs Free Energies (G, at 298K and 1 atm) as well as the Lowest Harmonic Vibrational Frequency (LHVF) of each Stationary Point involved in Scheme 2 at the CBS-QB3 level in the Gas Phase [a]

Species	$E^{(0K)}$ [b]	$E^{(298K)}$	$H^{(298K)}$	$G^{(298K)}$	LHVF
TMA^+	-173.817304	-173.810822	-173.809878	-173.846557	78.1
NO_2	-204.852546	-204.849612	-204.848668	-204.87656	766.7
CR1-B	-378.714002	-378.702828	-378.701884	-378.755062	15.4
TS1-B	-378.642342	-378.632746	-378.631802	-378.679586	834.7i
CP1-B	-378.746274	-378.735957	-378.735013	-378.785389	10.8
HNO_2	-205.475014	-205.471773	-205.470829	-205.499020	588.6
Iminium Ion	-173.259908	-173.254611	-173.253667	-173.286719	128.5

[a] Energies, Enthalpies, and Gibbs Free Energies in hartree, lowest harmonic vibrational frequency in cm^{-1}; CR, TS, and CP correspond to Reactant Complex, Transition State, and Product Complex, respectively.

[b] Energies at 0K was corrected with Zero Point Energies (ZPE).

Table S4 Energies (E_{sol}) of each Stationary Point involved in Scheme 2 in Aqueous Solution at the CPCM-CCSD(T)/6-311+G(d,p)//B3LYP/CBSB7 level

Species	E_{sol} (hartree)
TMA^+	-173.853720
NO_2	-204.686334
CR1-B	-378.462713
TS1-B	-378.477870
CP1-B	-378.613557
HNO_2	-205.325480
Iminium Ion	-173.286665

Table S5 Energies (E, 0K / 298K), Enthalpies (H, at 298K and 1 atm), and Gibbs Free Energies (G, at 298K and 1 atm) as well as the Lowest Harmonic Vibrational Frequency (LHVF) of each Stationary Point involved in Scheme 3 at the CBS-QB3 level in the Gas Phase [a]

Species	$E^{(0K)}$ [b]	$E^{(298K)}$	$H^{(298K)}$	$G^{(298K)}$	LHVF
Iminium Ion	-173.259908	-173.254611	-173.253667	-173.286719	128.5
H_2O	-76.337482	-76.334647	-76.333703	-76.355129	1637.9
CR2-A	-249.612255	-249.602993	-249.602049	-249.646644	49.7
TS2-A	-249.548175	-249.541775	-249.540831	-249.577565	1374.1i
CP2-A	-249.608532	-249.601442	-249.600498	-249.639165	58.1

[a] Energies, Enthalpies, and Gibbs Free Energies in hartree; CR, TS, and CP correspond to Reactant Complex, Transition State, and Product Complex, respectively.

[b] Energies at 0K was corrected with Zero Point Energies (ZPE).

Table S6 Energies (E_{sol}) of each Stationary Point involved in Scheme 3 in Aqueous Solution at the CPCM-CCSD(T)/6-311+G(d,p)//B3LYP/CBSB7 level

Species	E_{sol} (hartree)
Iminium Ion	-173.286665
H_2O	-76.297923
CR2-A	-249.589700
TS2-A	-249.537370
CP2-A	-249.607568

Table S7 Energies (E, 0K / 298K), Enthalpies (H, at 298K and 1 atm), and Gibbs Free Energies (G, at 298K and 1 atm) as well as the Lowest Harmonic Vibrational Frequency (LHVF) of each Stationary Point involved in Scheme 4 at the CBS-QB3 level in the Gas Phase [a]

Species	$E^{(0K)}$ [b]	$E^{(298K)}$	$H^{(298K)}$	$G^{(298K)}$	LHVF
Iminium Ion	-173.259908	-173.254611	-173.253667	-173.286719	128.5
H_2O	-76.337482	-76.334647	-76.333703	-76.355129	1637.9
CR2-B	-325.962657	-325.951055	-325.950111	-325.999951	33.9
TS2-B	-325.925357	-325.916748	-325.915804	-325.957707	276.5i
CP2-B	-325.969765	-325.959492	-325.958548	-326.004720	50.9

[a] Energies, Enthalpies, and Gibbs Free Energies in hartree; CR, TS, and CP correspond to Reactant Complex, Transition State, and Product Complex, respectively.

[b] Energies at 0K was corrected with Zero Point Energies (ZPE).

Table S8 Energies (E_{sol}) of each Stationary Point involved in Scheme 4 in Aqueous Solution at the CPCM-CCSD(T)/6-311+G(d,p)//B3LYP/CBSB7 level

Species	E_{sol} (hartree)
Iminium Ion	-173.286665
H_2O	-76.297923
CR2-B	-325.893402
TS2-B	-325.869018
CP2-B	-325.913364

Table S9 Energies (E, 0K / 298K), Enthalpies (H, at 298K and 1 atm), and Gibbs Free Energies (G, at 298K and 1 atm) as well as the Lowest Harmonic Vibrational Frequency (LHVF) of each Stationary Point involved in Scheme 5 at the CBS-QB3 level in the Gas Phase [a]

Species	$E^{(0K)}$ [b]	$E^{(298K)}$	$H^{(298K)}$	$G^{(298K)}$	LHVF
Iminium Ion	-173.259908	-173.254611	-173.253667	-173.286719	128.5
NO_2^-	-204.936076	-204.933143	-204.932199	-204.959105	803.2
PR3	-378.400254	-378.391976	-378.391031	-378.433198	69.7
TS3	-378.355724	-378.347317	-378.346373	-378.388084	383.5i
CP3	-378.408432	-378.398086	-378.397142	-378.445556	29.7
NDMA	-264.058460	-264.052232	-264.051288	-264.088541	34.6
CH_2O	-114.344172	-114.341303	-114.340359	-114.365173	1202.1

[a] Energies, Enthalpies, and Gibbs Free Energies in hartree; PR, TS, and CP correspond to Prereactant, Transition State, and Product Complex, respectively.

[b] Energies at 0K was corrected with Zero Point Energies (ZPE).

Table S10 Energies (E_{sol}) of each Stationary Point involved in Scheme 5 in Aqueous Solution at the CPCM-CCSD(T)/6-311+G(d,p)//B3LYP/CBSB7 level

Species	E_{sol} (hartree)
Iminium Ion	-173.286665
NO_2^-	-204.864008
PR3	-378.174904
TS3	-378.134346
CP3	-378.180870
NDMA	-263.906926
CH_2O	-114.271329

Table S11 Energies (E, 0K / 298K), Enthalpies (H, at 298K and 1 atm), and Gibbs Free Energies (G, at 298K and 1 atm) as well as the Lowest Harmonic Vibrational Frequency (LHVF) of each Stationary Point involved in Scheme 6 at the CBS-QB3 level in the Gas Phase [a]

Species	$E^{(0K)}$ [b]	$E^{(298K)}$	$H^{(298K)}$	$G^{(298K)}$	LHVF
Iminium Ion	-173.259908	-173.254611	-173.253667	-173.286719	128.5
N_2O_3	-334.613669	-334.608732	-334.607788	-334.641782	149.5
CR4	-507.890622	-507.878283	-507.877339	-507.932367	12.8
TS4-1	-507.844215	-507.833455	-507.832510	-507.881416	345.5i
IM	-507.890985	-507.879756	-507.878812	-507.928094	51.4
TS4-2	-507.866580	-507.855554	-507.854610	-507.903213	211.9i
CP4	-507.896296	-507.883458	-507.882513	-507.937756	27.3

[a] Energies, Enthalpies, and Gibbs Free Energies in hartree; CR, TS, and CP correspond to Reactant Complex, Transition State, and Product Complex, respectively.

[b] Energies at 0K was corrected with Zero Point Energies (ZPE).

Table S12 Energies (E_{sol}) of each Stationary Point involved in Scheme 6 in Aqueous Solution at the CPCM-CCSD(T)/6-311+G(d,p)//B3LYP/CBSB7 level

Species	E_{sol} (hartree)
Iminium Ion	-173.286665
N_2O_3	-334.350510
CR4	-507.640108
TS4-1	-507.613084
IM	-507.654014
TS4-2	-507.621957
CP4	-507.644638

Table S13 Energies (E, 0K / 298K), Enthalpies (H, at 298K and 1 atm), and Gibbs Free Energies (G, at 298K and 1 atm) as well as the Lowest Harmonic Vibrational Frequency (LHVF) of each Stationary Point in the Hydrolysis Mechanisms involving TS2-A′ and TS2-B′ at the PBE1W/CBSB7 level in the Gas Phase [a]

Species	$E^{(0K)}$ [b]	$E^{(298K)}$	$H^{(298K)}$	$G^{(298K)}$	LHVF
Iminium Ion	-173.317245	-173.311917	-173.310973	-173.344057	128.7
H_2O	-76.339568	-76.336732	-76.335788	-76.357241	1605.4
CR2-A′	-249.678360	-249.669825	-249.668881	-249.710494	59.7
TS2-A′	-249.554414	-249.547602	-249.546657	-249.583634	1268.4i
CP2-A′	-249.625403	-249.618722	-249.617778	-249.654357	185.9
CR2-B′	-326.038031	-326.026500	-326.025555	-326.075100	34.8
TS2-B′	-325.937748	-325.929397	-325.928453	-325.969490	1015.6i
CP2-B′	-325.985864	-325.975878	-325.974933	-326.019444	58.7

[a] Energies, Enthalpies, and Gibbs Free Energies in hartree; CR, TS, and CP correspond to Reactant Complex, Transition State, and Product Complex, respectively.

[b] Energies at 0K was corrected with Zero Point Energies (ZPE).

Table S14 Energies (E_{sol}) of each Stationary Point in the Hydrolysis Mechanisms involving TS2-A′ and TS2-B′ in Aqueous Solution at the CPCM-CCSD(T)/6-311+G(d,p)//PBE1W/CBSB7 level

Species	E_{sol} (hartree)
Iminium Ion	-173.286946
H_2O	-76.297988
CR2-A′	-249.587396
TS2-A′	-249.442926
CP2-A′	-249.544889
CR2-B′	-325.893087
TS2-B′	-325.762853
CP2-B′	-325.846442