Supplementary Information

Activation of X-H and X-D Bonds (X = O, N, C) by alkaline-earth metal monoxide cations: experiment and theory

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1. Ammonia Oxide, H_3NO

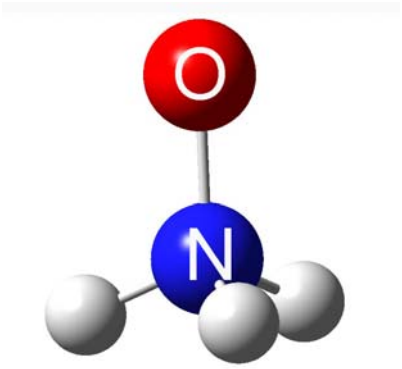

Figure 1. Structure of ammonia oxide optimized at B3LYP/6-311++G(2df,p) level of theory

Optimized geometry

0	1		
N	0.537976	0.000015	0.000020
H	0.939029	-0.471844	0.828172

H	0.938950	0.953173	-0.005495
H	0.939158	-0.481334	-0.822727
O	-0.822871	-0.000013	-0.000012

Thermochemistry

Sum of electronic and zero-point Energies=	-131.694178
Sum of electronic and thermal Energies=	-131.691252
Sum of electronic and thermal Enthalpies=	-131.690308
Sum of electronic and thermal Free Energies=	-131.716473

2. Reactions of MO^+ (M = Ca, Sr, Ba) with NH_3.

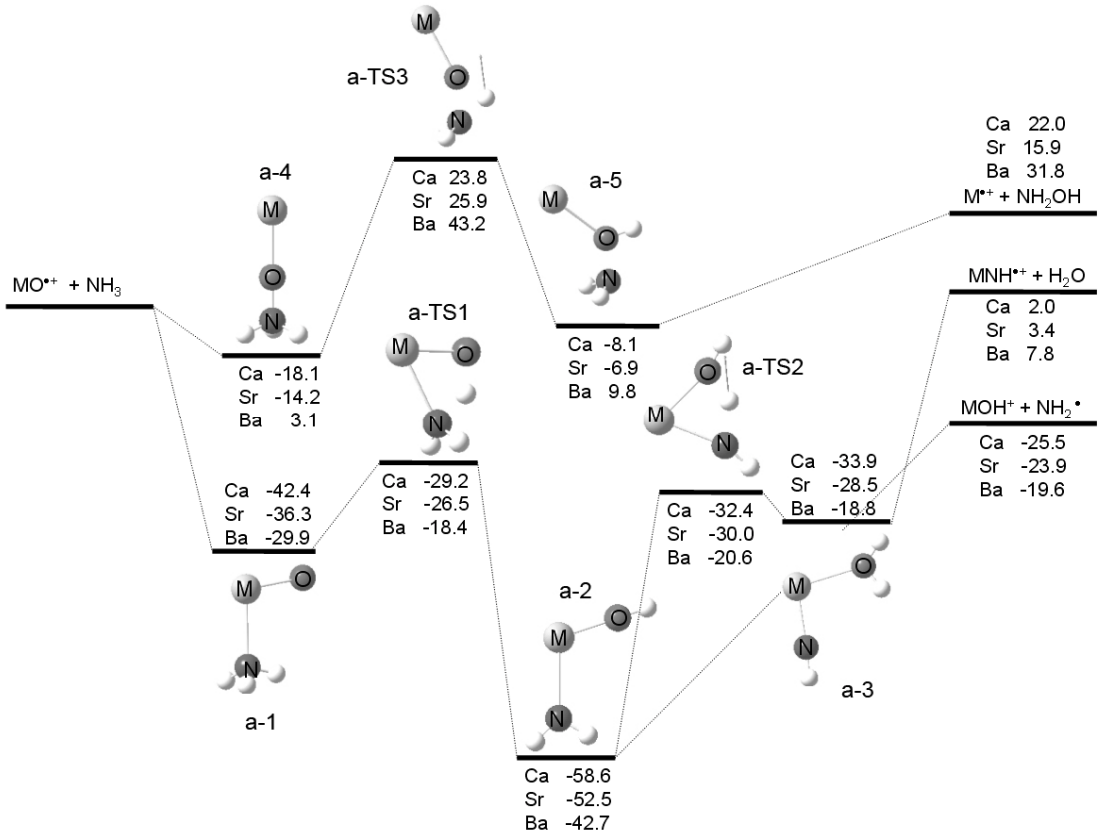

Figure 2. Enthalpy profile for the reactions of $MO^{\bullet+}$ (M = Ca, Sr, Ba) with ammonia based on the relative enthalpies computed at the B3LYP/SDD/6-31G(d) level of theory.

Figure 2 illustrates the potential enthalpy surface for reaction pathways considered in the reaction of $MO^{\bullet+}$ and NH_3, where M is a heavy alkaline earth metal Ca, Sr or Ba. All species are calculated at the B3LYP/SDD/6-31G(d) level of theory. The geometries of the structures change as the size of the metal cation increases. The Cartesian coordinates of all optimized minima and maxima are listed below. The numbers shown on the surface represent the change in the enthalpy with respect to the reactants, and are indicated for all intermediates and transition structures for all three metals.

The Figure shows that the relative stabilities of the species on the surface decrease with increasing size of the metal. In addition, the calculations at this level of theory suggest that the only exothermic, and therefore the thermodynamically favoured channel, is the H-atom abstraction. This is consistent with the experimental observations.

Structures optimized at B3LYP/SDD/6-31G(d) level of theory

Calcium

CaO^+

O	0.000000	0.000000	-1.414236
Ca	0.000000	0.000000	0.565695

NH_3

N	0.000000	0.000000	0.119357
H	0.000000	0.938797	-0.278500
H	-0.813022	-0.469398	-0.278500
H	0.813022	-0.469398	-0.278500

a-1-Ca

N	-1.855817	0.338054	-0.000156
H	-2.560768	-0.033924	-0.642650

H	-1.737528	1.320482	-0.270184
H	-2.321068	0.372779	0.911708
Ca	0.400318	-0.633409	0.000202
O	1.450466	1.080309	-0.000227

a-TS1-Ca

N	1.429459	-0.625432	0.000006
H	2.024140	-0.772023	0.821400
H	1.272176	0.665590	-0.000013
H	2.024137	-0.772047	-0.821387
Ca	-0.893985	-0.282717	0.000006
O	0.319130	1.363854	-0.000020

a-2-Ca

N	-2.045440	0.453319	-0.000002
H	-2.130888	1.479191	0.000026
H	2.320739	1.372370	0.000016
H	-3.008226	0.091848	-0.000018
Ca	0.212400	-0.593008	0.000002
O	1.611058	0.717939	-0.000006

a-TS2-Ca

N	0.673959	1.400028	-0.000003
H	1.815331	-1.630466	0.000154
H	1.121100	2.318475	-0.000007
Ca	-0.880698	-0.128132	-0.000049
O	1.076184	-1.003504	0.000097
H	1.350347	0.102477	0.000078

a-3-Ca

N	-1.702931	0.791646	0.000077
H	2.743104	0.212866	0.000180
H	-2.446872	1.491784	0.000080
Ca	-0.232262	-0.627437	-0.000014
O	1.807348	0.480832	-0.000047
H	1.810741	1.455912	-0.000140

a-4-Ca

N	-2.078712	0.000110	0.000261
H	-2.447137	0.962086	-0.058074
H	-2.446877	-0.430044	0.862798
H	-2.447953	-0.531492	-0.803233
O	-0.709635	-0.000266	-0.000667
Ca	1.378502	0.000040	0.000101

a-TS3-Ca

N	2.223171	-0.115699	-0.002420
O	0.754027	0.272968	0.001012
H	1.715163	0.987464	-0.064045
H	2.398520	-0.692722	-0.825115
H	2.429895	-0.580112	0.881949
Ca	-1.406899	-0.054424	0.000803

a-5-Ca

N	-2.100298	-0.276284	-0.000008
O	-0.859376	0.505841	-0.000037
H	-1.186207	1.424959	0.000064
H	-2.025645	-0.868651	0.828408
H	-2.025491	-0.868894	-0.828239
Ca	1.340722	-0.090008	0.000006

NH_2OH

N	0.011456	0.709274	0.000000
O	0.011456	-0.739187	0.000000
H	0.960972	-0.936179	0.000000
H	-0.566407	0.942378	0.810631
H	-0.566407	0.942378	-0.810631

$CaOH^+$

Ca	0.000000	0.000000	0.619784
O	0.000000	0.000000	-1.269871
H	0.000000	0.000000	-2.236715

$CaNH^{\cdot+}$

Ca	0.000042	-0.612935	0.000000
N	0.000042	1.404602	0.000000
H	-0.001121	2.426485	0.000000

H2O

O	0.000000	0.119720	0.000000
H	0.761563	-0.478878	0.000000
H	-0.761563	-0.478880	0.000000

$NH2^{\cdot}$

N	0.000000	0.000000	0.144489
H	0.000000	0.804400	-0.505711
H	0.000000	-0.804400	-0.505711

Strontium

SrO^+

O	0.000000	0.000000	-1.657662

Sr	0.000000	0.000000	0.348982

a-1-Sr

N	-2.180406	0.348618	-0.000385
H	-2.933758	-0.300628	-0.239557
H	-2.271856	1.126234	-0.660783
H	-2.451121	0.751778	0.901134
Sr	0.342627	-0.406189	0.000101
O	1.237470	1.427183	-0.000243

a-TS1-Sr

N	1.722662	-0.778308	0.000004
H	2.294908	-1.006902	0.818424
H	1.757425	0.525319	-0.000014
H	2.294901	-1.006925	-0.818415
Sr	-0.682432	-0.106309	0.000004
O	0.940821	1.372049	-0.000022

a-2-Sr

N	-2.218629	0.570040	-0.000363
H	-2.308375	1.583620	-0.155974
H	1.872569	2.056028	0.020308
H	-3.176281	0.230133	0.158209
Sr	0.223274	-0.471295	-0.002977
O	1.332262	1.256145	0.011640

a-TS2-Sr

N	1.233279	1.334507	0.000019
H	2.058341	-1.790817	0.000176
H	1.826919	2.166746	0.000021
Sr	-0.661427	-0.018847	-0.000036
O	1.360578	-1.118463	0.000119
H	1.731389	-0.053571	0.000100

a-3-Sr

N	1.421056	1.358344	0.000649
H	-2.931584	0.304999	0.015173
H	1.994868	2.204795	0.000921
Sr	0.237834	-0.482087	-0.000061
O	-2.002406	0.591901	-0.001888
H	-2.029121	1.565885	-0.003199

a-4-Sr

N	2.630636	-0.000006	-0.000298
H	3.000774	0.900668	-0.340583
H	3.000518	-0.744885	-0.610515

H	3.001599	-0.155883	0.949506
O	1.258676	0.000027	0.000721
Sr	-0.986494	-0.000002	-0.000055

a-TS3-Sr

N	2.795961	-0.113052	-0.001694
O	1.320487	0.259573	0.000515
H	2.287872	0.978878	-0.051442
H	2.982561	-0.676869	-0.830437
H	3.006433	-0.586142	0.876591
Sr	-1.010855	-0.026345	0.000343

a-5-Sr

N	-2.659381	-0.287453	-0.000459
O	-1.426903	0.504225	0.000022
H	-1.768756	1.417162	-0.001762
H	-2.580699	-0.877922	0.828666
H	-2.576769	-0.883625	-0.825057
Sr	0.972556	-0.044138	0.000031

$SrOH^+$

Sr	0.000000	0.000000	0.408511
O	0.000000	0.000000	-1.617440
H	0.000000	0.000000	-2.583884

$SrNH^{\cdot+}$

Sr	0.000000	0.000000	0.397821
N	0.000000	0.000000	-1.761826
H	0.000000	0.000000	-2.784411

Barium

BaO^+

O	0.000000	0.000000	-1.833249
Ba	0.000000	0.000000	0.261893

a-1-Ba

N	-2.451146	0.214975	-0.000246
H	-3.130040	-0.538472	-0.130205
H	-2.659081	0.897013	-0.734461
H	-2.731207	0.682875	0.865738
Ba	0.338338	-0.298014	0.000028
O	0.841424	1.767817	-0.000116

a-TS1-Ba

N	2.024053	-0.802925	0.000003

H	2.604020	-1.017457	0.817730
H	2.048262	0.492249	-0.000015
H	2.604013	-1.017479	-0.817724
Ba	-0.561969	-0.065549	0.000003
O	1.255696	1.354235	-0.000023

a-2-Ba

N	2.501358	0.439755	0.000467
H	2.716493	1.442667	0.088540
H	-1.355968	2.562741	-0.009721
H	3.415727	-0.023822	-0.087432
Ba	-0.255605	-0.363890	0.001014
O	-0.996487	1.664747	-0.006433

a-TS2-Ba

N	1.534186	1.327994	0.000023
H	2.361647	-1.783254	0.000181
H	2.160121	2.138216	0.000025
Ba	-0.543537	-0.010153	-0.000026
O	1.646883	-1.128067	0.000124
H	2.001949	-0.057840	0.000099

a-3-Ba

N	-0.855045	1.890352	-0.006932
H	3.161086	-0.098076	-0.103828
H	-1.137189	2.875681	-0.018835
Ba	-0.300207	-0.353952	0.001025
O	2.288698	0.318041	-0.001560
H	2.463404	1.266901	0.126288

a-4-Ba

N	-2.959117	0.000174	0.000260
H	-3.328053	0.957149	-0.113843
H	-3.327996	-0.379126	0.886256
H	-3.329021	-0.577120	-0.771010
O	-1.585699	-0.000408	-0.000622
Ba	0.774723	0.000020	0.000031

a-TS3-Ba

N	-3.133728	-0.119540	-0.000181
O	-1.672132	0.263341	0.000080
H	-2.646174	0.980546	-0.005417
H	-3.332197	-0.635870	0.856795
H	-3.329554	-0.645333	-0.851999
Ba	0.796805	-0.017309	0.000022

a-5-Ba

N	3.019983	-0.289737	-0.000005
O	1.786168	0.496684	0.000002
H	2.127682	1.409406	-0.000023
H	2.938743	-0.884838	-0.825631
H	2.938791	-0.884778	0.825669
Ba	-0.775615	-0.028305	0.000000

$BaOH^+$

Ba	0.000000	0.000000	0.310486
O	0.000000	0.000000	-1.824323
H	0.000000	0.000000	-2.792612

$BaNH^{\cdot+}$

Ba	0.000000	0.000000	0.301130
N	0.000000	0.000000	-1.979802
H	0.000000	0.000000	-3.004668