The energetics of isomerisation in the Keggin-series of aluminate cations
Supporting information

C. A. Ohlin, James R. Rustad, William H. Casey

Contents

List of Tables

List of Figures

1 Computational methods

Computations were carried out using Kohn-Sham density functional theory as implemented in the Gaussian '09 (G09) and NWChem v6.4 packages.[1, 2] Structures were optimised using the 6-31+G(d,p)[3, 4, 5, 6] and 6-311++G(2d,2p)[6, 7, 8, 9] basis set using the PBE0,[10] B3PW91,[11] and X3LYP[12] exchange and correlation functionals. Analytical normal mode analyses were carried out using G09 with the 6-31+G(d,p) basis set and the B3PW91 and PBE0 exchange and correlation functionals. Nudged elastic band[13] calculations were carried out in NWChem at the B3PW91/6-31+G(d,p) level of theory using 10 beads, a step size of 1.0 and a spring constant of 1.0. Energies for the intermediates were recalculated in G09 to compensate for the slightly different implementations of B3PW91 in the two software packages.

References

[1] M. J. Frisch, G. W. Trucks, H. B. Schlegel, et al., *Gaussian 09 Revision D.01*, Gaussian Inc. Wallingford CT 2009.

[2] M. Valiev, E. J. Bylaska, N. Govind, K. Kowalski, T. P. Straatsma, H. J. J. van Dam, D. Wang, J. Nieplocha, E. Apra, T. L. Windus, W. A. de Jong, *Comput. Phys. Commun.* **2010**, *181*, 1477–1489.

[3] W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.* **1972**, *56*, 2257–2261.

[4] P. C. Hariharan, J. A. Pople, *Theoret. Chimica Acta* **1973**, *28*, 213–222.

[5] M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees, J. A. Pople, *J. Chem. Phys.* **1982**, *77*, 3654–3665.

[6] T. Clark, J. Chandrasekhar, G. W. Spitznagel, P. V. R. Schleyer, *J. Comp. Chem.* **1983**, *4*, 294–301.

[7] R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.* **1980**, *72*, 650–654.

[8] A. D. McLean, G. S. Chandler, *J. Chem. Phys.* **1980**, *72*, 5639–5648.

[9] M. J. Frisch, J. A. Pople, J. S. Binkley, *J. Chem. Phys.* **1984**, *80*, 3265–3269.

[10] C. Adamo, V. Barone, *J. Chem. Phys.* **1999**, *110*, 6158–6170.

[11] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652.

[12] X. Xu, W. A. Goddard III, *Proc. Nat. Acad. Sci.* **2004**, *101*, 2673–2677.

[13] G. Mills, H. Jónsson, *Phys. Rev. Letters* **1995**, *72*, 1124.

2 Implementation of B3PW91 in NWChem

```
xc HFexch 0.20 slater 0.80 becke88 nonlocal 0.72 perdew91 0.81 pw91lda 1.00
```

Listing 1: Implementation of B3PW91 in NWChem.

3 Gas phase and polarizable continuum energies

Table 1: Energies at the B3PW91/6-31+G(d,p) level of theory. $\Delta\epsilon$ and ΔH are given relative to ϵ_0 of the α isomer.

Entry	Compound	ϵ_0 (au)	H_{corr} (au)	S $(J \cdot mol^{-1} \cdot K^{-1})$	$\Delta\epsilon$ $(kcal \cdot mol^{-1})$	ΔH $(kcal \cdot mol^{-1})$
1	α	-6187.75427966	0.785501	373.677	0	0
2	β	-6187.75658974	0.787507	366.651	-1.4496	-0.19081
3	γ	-6187.75154762	0.786674	366.124	1.7143	2.4504
4	δ	-6187.76044999	0.786352	368.395	-3.8719	-3.3379
5	ϵ	-6187.76809424	0.783807	382.694	-8.6690	-9.7317

Table 2: PCM solvation energies at the B3PW91/6-31+G(d,p) level of theory. $\Delta\epsilon$ are given relative to ϵ_0^{PCM} of the α isomer. $\epsilon_{solv.}$ is defined as ϵ_0^{PCM}-ϵ_0(gas phase).

Entry	Compound	ϵ_0^{PCM} (au)	$\epsilon_{solv.}$ ($kcal \cdot mol^{-1}$)	$\Delta\epsilon$ ($kcal \cdot mol^{-1}$)
1	α	-6189.74616999	-1249.9	0
2	β	-6189.75246865	-1252.4	-3.9524
3	γ	-6189.74895302	-1253.4	-1.7464
4	δ	-6189.74878699	-1247.7	-1.6422
5	ϵ	-6189.73625462	-1235.0	6.2219

Table 3: Energies at the PBE0/6-31+G(d,p) level of theory. $\Delta\epsilon$ and ΔH are given relative to ϵ_0 of the α isomer.

Entry	Compound	ϵ_0 (au)	H$_{corr}$ (au)	S ($J \cdot mol^{-1} \cdot K^{-1}$)	$\Delta\epsilon$ ($kcal \cdot mol^{-1}$)	ΔH ($kcal \cdot mol^{-1}$)
1	α	-6184.77152072	0.790118	372.434	0	0
2	β	-6184.77360508	0.790989	364.256	-1.3079	-0.76139
3	γ	-6184.76886270	0.790698	360.162	1.6679	2.0319
4	δ	-6184.77593884	0.789840	365.850	-2.7724	-2.9468
5	ϵ	-6184.78042898	0.786974	380.012	-5.5900	-7.5628

Table 4: PCM solvation energies at the PBE0/6-31+G(d,p) level of theory. $\Delta\epsilon$ are given relative to ϵ_0^{PCM} of the α isomer. $\epsilon_{solv.}$ is defined as ϵ_0^{PCM}-ϵ_0(gas phase).

Entry	Compound	ϵ_0^{PCM} (au)	$\epsilon_{solv.}$ ($kcal \cdot mol^{-1}$)	$\Delta\epsilon$ ($kcal \cdot mol^{-1}$)
1	α	-6186.76792150	-1252.7	0
2	β	-6186.77507616	-1255.9	-4.4896
3	γ	-6186.77117525	-1256.5	-2.0417
4	δ	-6186.76983047	-1251.2	-1.1979
5	ϵ	-6186.75462859	-1238.8	8.3413

Table 5: Energies at the X3LYP/6-31+G(d,p) level of theory. $\Delta\epsilon$ are given relative to ϵ_0 of the α isomer.

Entry	Compound	ϵ_0 (au)	$\Delta\epsilon$ ($kcal \cdot mol^{-1}$)
1	α	-6188.09774395	0
2	β	-6188.09891706	-0.73613
3	γ	-6188.09339464	2.7292
4	δ	-6188.10167812	-2.4687
5	ϵ	-6188.11194453	-8.9109

Table 6: PCM solvation energies at the X3LYP/6-31+G(d,p) level of theory. $\Delta\epsilon$ are given relative to ϵ_0^{PCM} of the α isomer. $\epsilon_{solv.}$ is defined as ϵ_0^{PCM}-ϵ_0(gas phase).

Entry	Compound	ϵ_0^{PCM} (au)	$\epsilon_{solv.}$ ($kcal \cdot mol^{-1}$)	$\Delta\epsilon$ ($kcal \cdot mol^{-1}$)
1	α	-6190.08838892	-1249.1	0
2	β	-6190.09385711	-1251.8	-3.4313
3	γ	-6190.08952944	-1252.6	-0.71568
4	δ	-6190.08886718	-1247.0	-0.30011
5	ϵ	-6190.07866893	-1234.1	6.0993

Table 7: Energies at the B3PW91/6-311++g(2d,2p) level of theory. $\Delta\epsilon$ is given relative to ϵ_0^{PCM} of the α isomer.

Entry	Compound	ϵ_0 (au)	$\Delta\epsilon$ ($kcal \cdot mol^{-1}$)
1	α	-6189.29168362	0
2	β	-6189.29421940	-1.5913
3	γ	-6189.28982529	1.1659
4	δ	-6189.30280402	-6.9778
5	ϵ	-6189.31544408	-14.909

Table 8: PCM solvation energies at the B3PW91/6-311++g(2d,2p) level of theory. $\Delta\epsilon$ are given relative to ϵ_0^{PCM} of the α isomer. $\epsilon_{solv.}$ is defined as ϵ_0^{PCM}-ϵ_0(gas phase).

Entry	Compound	ϵ_0^{PCM} (au)	$\epsilon_{solv.}$ $(kcal \cdot mol^{-1})$	$\Delta\epsilon$ $(kcal \cdot mol^{-1})$
1	α	-6191.29054763	-1254.3	0
2	β	-6191.29727644	-1256.9	-4.2223
3	γ	-6191.29481702	-1258.1	-2.6791
4	δ	-6191.29688280	-1251.3	-3.9753
5	ϵ	-6191.28898131	-1238.4	0.98287

Table 9: Energies at the PBE0/6-311++g(2d,2p) level of theory. $\Delta\epsilon$ is given relative to ϵ_0^{PCM} of the α isomer.

Entry	Compound	ϵ_0 (au)	$\Delta\epsilon$ $(kcal \cdot mol^{-1})$
1	α	-6186.27886751	0
2	β	-6186.28126818	-1.5064
3	γ	-6186.27633220	1.5909
4	δ	-6186.28823889	-5.8806
5	ϵ	-6186.29827602	-12.179

Table 10: PCM solvation energies at the PBE0/6-311++g(2d,2p) level of theory. $\Delta\epsilon$ are given relative to ϵ_0^{PCM} of the α isomer. $\epsilon_{solv.}$ is defined as ϵ_0^{PCM}-ϵ_0(gas phase).

Entry	Compound	ϵ_0^{PCM} (au)	$\epsilon_{solv.}$ $(kcal \cdot mol^{-1})$	$\Delta\epsilon$ $(kcal \cdot mol^{-1})$
1	α	-6188.28233219	-1257.2	0
2	β	-6188.28992072	-1260.4	-4.7618
3	γ	-6188.28641324	-1261.3	-2.5609
4	δ	-6188.28793823	-1254.8	-3.5178
5	ϵ	-6188.27768075	-1242.1	2.9188

Table 11: Energies at the X3LYP/6-311++g(2d,2p) level of theory. $\Delta\epsilon$ is given relative to ϵ_0^{PCM} of the α isomer.

Entry	Compound	ϵ_0 (au)	$\Delta\epsilon$ $(kcal \cdot mol^{-1})$
1	α	-6189.68942254	0
2	β	-6189.69085146	-0.8967
3	γ	-6189.68614710	2.0553
4	δ	-6189.69869411	-5.8180
5	ϵ	-6189.71339336	-15.042

Table 12: PCM solvation energies at the X3LYP/6-311++g(2d,2p) level of theory. $\Delta\epsilon$ are given relative to ϵ_0^{PCM} of the α isomer. $\epsilon_{solv.}$ is defined as ϵ_0^{PCM}-ϵ_0(gas phase).

Entry	Isomer	ϵ_0^{PCM} (au)	$\epsilon_{solv.}$ $(kcal \cdot mol^{-1})$	$\Delta\epsilon$ $(kcal \cdot mol^{-1})$
1	α	-6191.68681257	-1253.4	0
2	β	-6191.69313719	-1256.4	-3.9687
3	γ	-6191.68945657	-1257.1	-1.6591
4	δ	-6191.6911025	-1250.2	-2.6919
5	ϵ	-6191.68501900	-1237.2	1.1255

Table 13: $\Delta\left(\epsilon^{isomer}_{solv.} - \epsilon^{\alpha}_{solv.}\right)$ given in kcal·mol^{-1} for different levels of theory.

Entry	Isomer	B3PW91/A[a]	B3PW91/B[a]	PBE0/A	PBE0/B	X3LYP/A	X3LYP/B
1	α	0	0	0	0	0	0
2	β	-2.5	-2.6	-3.2	-3.2	-2.7	-3.0
3	γ	-3.5	-3.8	-3.8	-4.1	-3.5	-3.7
4	δ	2.2	3.0	1.5	2.4	2.1	3.2
5	ϵ	14.9	15.9	13.9	14.9	15.0	16.2

[a] A=6-31+G(d,p). [b] B=6-311++G(2d,2p).

Table 14: Comparison of bond lengths in Ångström from crystallographic data[a,b] and from optimisation at B3PW91/6-311++G(2d,2p) for the γ and ϵ isomers. The nomenclature used in G. Johansson, *Acta Chem. Scand.*, **1960**, *14(3)*, 771-773 has been adopted and adapted.

		ϵ-Al$_{13}$		γ-Al$_{13}$	
Entry	Atoms	Crystals structure	B3PW91/6-311++G(2d,2p)	Crystal structure	B3PW91/6311++G(2d,2p
1	Al$_T$-O(2)	1.831(4)	1.853(3)	1.777(6)	1.789(4
2	Al$_o$-O(1)	1.857(6)	1.867(11)	1.884(37)	1.878(12
3	Al$_o$-O(2)	2.026(4)	2.049(15)	1.976(27)	2.002(44
4	Al$_o$-O(3)	1.961(4)	2.023(4)	1.899(30)	1.990(10
5	Al$_o$-O(4)	1.857(6)	1.867(5)	1.892(25)	1.884(15
6[c]	Al$_o$-O(5)	–	–	1.875(21)	1.905(20

[a] From Kiricsi *et al.*, *Inorg. Chem.*, **1997**, *36(4)*, 571-575. [b] Pan *et al.*, *Chem. Commun.*, **2013**, *49*, 11352-11354. [c] O(5) denotes hydroxide units connecting corner-sharing octahedra..

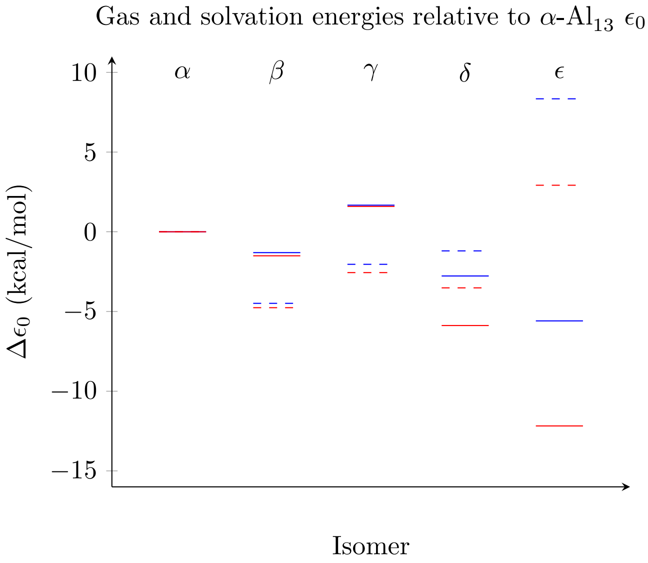

Figure 1: Relative gas phase energies ($\Delta\epsilon$) at PBE0/6-31+G(d,p) given in solid blue and relative solvated energies(PCM) given in dashed blue. Energies using 6-311++G(2d,2p) given in red. Energies are calculated relative to the corresponding energy for the α isomer.

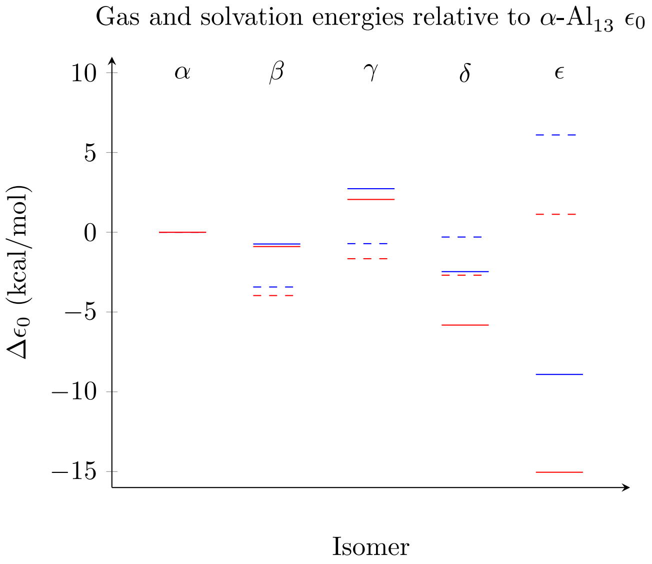

Figure 2: Relative gas phase energies ($\Delta\epsilon$) at X3LYP/6-31+G(d,p) given in solid blue and relative solvated energies(PCM) given in dashed blue. Energies using 6-311++G(2d,2p) given in red. Energies are calculated relative to the corresponding energy for the α isomer.