Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting information

Stability and structures of gaseous In_2MoO_4, In_2WO_4 and $In_2W_2O_7$

S. I. Lopatin, A.I. Panin and S. M. Shugurov*

Department of Chemistry, St. Petersburg State University, 198504 St. Petersburg, Russia.

Table S1 Equilibrium data for the gas-phase reaction (2) for the In_2O_3 – Mo system

T (K)	p_i (atm)			$-\Delta_r H^0(0)$ (kJ)
	In_2O $\times 10^8$	MoO_3 $\times 10^5$	In_2MoO_4 $\times 10^7$	
1769	1.7	1.1	90.3	485.7
1770	1.5	0.51	23.6	479.9
1781	1.9	0.47	14.2	473.0
1772	1.5	0.38	5.9	464.2
1839	2.8	0.92	15.9	473.3
1838	1.8	0.83	9.8	473.9
1885	3.2	1.8	26.4	479.8
1889	2.7	1.6	16.4	477.7
1885	2.4	1.3	16.3	481.4
1930	4.9	1.4	47.1	496.8
1933	4.9	3.0	34.8	480.4
1932	4.9	2.1	16.7	474.3
1965	9.9	3.7	19.6	464.0
1725	5.8	1.1	10.9	426.5
1745	3.7	0.83	5.6	432.7
1743	2.9	1.1	5.8	432.3
1744	4.4	1.0	5.4	426.6
1729	2.7	0.61	6.0	438.7
1724	3.1	0.63	6.2	435.9
1764	5.6	1.4	10.3	432.1
1766	5.2	1.2	10.5	436.4
1764	4.9	1.2	10.7	436.8
1763	4.8	1.2	10.5	436.5
1763	3.4	1.2	10.5	442.2
1804	1.7	1.0	12.1	466.5
2038	125.0	8.6	22.7	425.1
2043	32.4	8.6	9.9	434.8
2037	14.2	2.0	9.6	472.2
2046	6.9	12.7	4.1	439.9

1651	0.13	0.016	0.071	450.9
1711	0.13	0.024	0.020	441.9
1791	0.65	0.069	0.098	446.0
1786	0.54	0.065	0.086	446.4
1787	0.56	0.068	0.086	445.5
1804	0.59	0.093	0.11	434.2
1815	0.57	0.094	0.087	433.3
1806	0.55	0.089	0.087	432.7
1835	0.64	0.11	0.10	4347.
1843	0.62	0.17	0.10	431.8
1838	0.80	0.17	0.13	430.0
			Average value	451±21

Table S2 Equilibrium data for the gas-phase reaction (3) for the In_2O_3 – W system

T (K)	p_i (atm)			$-\Delta_r H^0(0)$ (kJ)
	In_2O $\times 10^7$	WO_3 $\times 10^7$	In_2WO_4 $\times 10^5$	
1457	3100	0.56	5.7	370.8
1449	226	0.64	2.4	388.6
1465	200	0.24	1.0	395.2
1514	198	0.34	1.3	407.4
1563	11.9	0.52	0.22	427.4
1558	3.2	0.26	0.11	442.5
1664	1.7	1.5	0.041	441.7
1717	0.59	5.1	0.0084	430.7
1548	0.42	3.3	0.050	423.6
1544	0.65	3.8	0.053	415.9
1553	0.62	3.5	0.065	422.6
1553	0.99	3.3	0.069	418.0
1547	2.0	2.9	0.24	425.0
1550	1.5	2.7	0.28	431.8
1548	8.9	2.2	0.69	423.4
1543	20.4	22.3	0.75	382.7
1548	30.7	26.7	0.89	378.4
1449	10.4	2.1	1.5	405.4
1446	10.9	1.3	1.2	407.2
1453	8.7	0.75	0.92	415.3
1452	9.3	0.90	1.1	414.4
1447	7.8	0.75	0.91	414.9
1489	16.4	4.1	1.4	401.5
1484	13.8	2.8	1.3	405.9
1486	12.9	2.4	1.2	407.8
1480	11.2	1.7	1.1	411.3
1493	11.3	1.8	0.98	412.6
1494	10.4	1.5	0.82	413.8
1492	9.8	1.4	0.82	415.3
1496	8.4	1.1	0.70	419.4
1493	8.1	0.65	0.45	420.0

1493	7.8	0.32	0.41	427.9
1352	4.7	1.3	1.3	393.0
1355	3.5	0.64	1.0	403.2
1410	5.4	1.3	0.25	388.1
1412	1.0	0.67	0.17	411.1
1410	1.2	0.67	0.22	411.6
1421	2.0	0.76	0.30	410.5
1424	2.8	0.76	0.55	414.8
1427	4.5	0.68	0.68	413.7
1427	4.9	0.34	0.88	423.8
1430	6.4	0.85	0.95	411.7
1483	11.6	4.1	1.6	406.1
			Average value	412±15

Table S3 Equilibrium data for the Gas-Phase Reaction (4) for the In_2O_3 – W System

T (K)	p_i (atm)			$-\Delta_r H^0(0)$ (kJ)
	In_2O $\times 10^7$	WO_3 $\times 10^7$	$In_2W_2O_7$ $\times 10^8$	
1668	1.9	2.3	7.4	872.7
1708	2.1	2.6	10.1	894.5
1747	2.7	4.1	9.1	895.8
1749	2.9	3.8	9.1	898.7
1758	2.8	2.8	7.8	910.2
1821	6.9	7.7	13.5	907.6
1822	6.3	13.0	13.5	893.4
1832	5.3	5.3	9.5	922.8
1885	6.0	15.8	11.1	916.3
			Average value	901±15

Table S4 Equilibrium data for the gas-phase reaction (5) for the In_2O_3 – W system

T (K)	p_i (atm)			$-\Delta_r H^0(0)$ (kJ)
	WO_3 $\times 10^7$	In_2WO_4 $\times 10^7$	$In_2W_2O_7$ $\times 10^7$	
1665	3.1	2.4	2.8	458.1
1669	3.5	3.1	3.1	456.0
1669	3.1	3.5	3.8	458.6
1666	4.6	4.5	3.8	448.7
1660	3.3	2.4	4.3	461.8
1660	8.7	4.5	4.3	439.8
1661	10.9	5.2	4.4	435.4
1665	11.5	5.6	4.4	434.9
1659	2.2	2.1	1.8	457.0
1710	3.4	2.9	3.1	469.6
1709	3.2	5.0	2.6	459.6
1708	3.6	4.3	2.6	459.9
1703	6.2	2.5	1.2	447.0
1712	2.8	0.84	1.0	474.7
1642	2.3	2.1	0.97	442.9
1638	2.1	1.7	0.61	439.7
1668	2.3	1.7	0.74	449.6
1672	2.3	1.4	0.62	451.3
1708	2.6	1.5	1.0	466.0
1713	1.7	1.2	0.63	470.7
1713	2.0	0.82	0.51	469.8
1746	3.2	1.1	0.91	477.4
1747	4.1	1.3	0.91	471.1
1749	3.2	1.3	0.91	475.4
1748	3.6	1.4	0.91	472.2
1746	3.8	1.6	1.0	471.7
1749	3.8	1.3	0.91	473.0
1751	2.6	1.7	0.91	475.3
1761	3.0	1.7	1.0	478.1
1761	3.0	1.4	0.78	476.2
1758	2.8	1.3	0.78	477.5

1758	2.7	1.3	0.65	475.9
1760	2.8	0.96	0.65	480.1
1823	8.8	2.0	1.3	481.6
1821	7.7	2.0	1.3	483.2
1825	12.4	2.5	1.5	475.1
1825	11.2	1.9	1.5	481.0
1821	11.8	1.7	1.2	477.1
1822	13.0	1.7	1.3	477.5
1828	10.0	1.3	0.95	482.8
1832	11.3	1.5	0.95	479.5
1831	11.2	1.1	0.81	481.2
1832	5.3	1.4	0.95	492.2
1878	16.4	1.4	1.1	490.2
1885	15.8	1.5	1.1	491.3
1885	12.2	1.9	1.1	492.0
			Average value	468±15

Table S5 Equilibrium geometry parameters and vibrational frequencies of diindium monoxide ground state (gas phase, $D_{\infty h}$, Σ_g^+)

Bond lengths (Å), valence angles (deg), frequencies (cm^{-1})	DFT B3LYP, (Def2-QZVP basis set) Present work	MP2(Full) (Def2-QZVP basis set) Present work	DFT B2LYP (LANL2DZ Basis set)[S1]	Expt[S2]	NIST Chemistry WebBook[S3]
R(In-O)	2.021	1.987	1.930	2.017	-
<(In-O-In)	180	180	180	180	180
InO s-stretch (Σ_g^+)	199	211	203	200	222
Bend (Π_u)	47	65	112	-	52
InO a-stretch (Σ_u^+)	718	771	765	-	735 (in Ar)

Table S6 Equilibrium geometry parameters and vibrational frequencies of molybdenum trioxide ground state (gas phase, C_{3v}, $^1A_1$)

Bond lengths (Å), valence angles(deg), frequencies (cm^{-1})	DFT B3LYP, (Def2-QZVP basis set) Present work	MP2(Full) (Def2-QZVP basis set) Present work	LCGTO-KS-MCP-DFT[S4]	NIST Chemistry WebBook[S3]
R(Mo-O)	1.703	1.742	1.74	-
<(O-Mo-O)	110.6	106.4	110.7	-
$\omega_1(A_1)$	248	275	-	-
$\omega_2(E)$	338	326	-	-
$\omega_3(E)$ (MoO stretch)	963	895	-	923 (in Ne)
$\omega_4(A_1)$ (MoO stretch)	1006	858	-	976 (in Ne)

Table S7 Equilibrium geometry parameters and vibrational frequencies of tungsten trioxide ground state (gas phase, C_{3v}, $^1A_1$)

Bond lengths (Å), valence angles (deg), frequencies (cm^{-1})	DFT B3LYP, (Def2-QZVP basis set) Present work	MP2(Full) (Def2-QZVP basis set) Present work	CCSD(T) (aug-cc-pVTZ basis set)[S5]	NIST Chemistry WebBook[S3]
R(W-O)	1.725	1.751	1.737	-
<(O-W-O)	107.6	104.6	108.3	-
$\omega_1(A_1)$	281	288	-	-
$\omega_2(E)$	343	332	-	-
$\omega_3(E)$ (WO stretch)	939	886	-	924 (in Ne)
$\omega_4(A_1)$ (WO stretch)	1022	907	-	-

Table S8. Equilibrium geometry parameters and vibrational frequencies of two isomers of In_2WO_4.

Geometric parameters (Å, deg)	Structure I (D_{2d})	Structure II (C_s)
r (In-O_1)	2.383	2.250
r (In-O_2)	2.383	2.606
r (W-O_1)	1.796	1.822
r (W-O_2)	1.796	1.820
r (W-O_3)	-	1.730
∠(O_1-In-O_2)	70.3	69.7
∠(In-O_1-W)	95.1	101.1
∠(O_1-W-O_2)	99.5	100.0
∠(O_1-W-O_3)	-	113.1
∠(O_2-W-O_3)	-	113.2
	48 (E)	34 (A"⊕ A')
	133 (A_1)	76 (A')
	149 (E)	105 (A")
	183 (B_2)	169 (A')

	282 (B_1)	188 (A")
Frequencies (cm^{-1})	292 (E)	280 (A')
	392 (B_2)	299 (A')
	396 (A_1)	304 (A")
	809 (E)	390 (A')
	835 (B_2)	391 (A")
	909 (A_1)	758 (A')
		777 (A")
		846 (A')
		979 (A')

Table S9. Equilibrium geometry parameters and vibrational frequencies of two isomers of In_2MoO_4.

Geometric parameters (Å, deg)	Structure I (D_{2d})	Structure II (C_s)
r(In-O_1)	2.371	2.266
r (In-O_2)	2.371	2.524
r (Mo-O_1)	1.776	1.799
r (Mo-O_2)	1.776	1.820
r (Mo-O_3)	-	1.702
∠(O_1-In-O_2)	70.0	70.3
∠(In-O_1-Mo)	95.1	99.5
∠(O_1-Mo-O_2)	99.8	100.0
∠(O_1-Mo-O_3)	-	113.0
∠(O_2-Mo-O_3)	-	113.9
Frequencies (cm^{-1})	56 (E)	43 (A')
	132 (A_1)	92 (A'')
	153 (E)	97 (A')
	207 (B_2)	121 (A'')
	279 (B_1)	188 (A')
	309 (E)	190 (A'')
	399 (A_1)	282 (A')
	414 (B_2)	312 (A')
	817 (E)	321 (A'')
	854 (B_2)	389 (A')
	886 (A_1)	398 (A'')
		747 (A')
		800 (A'')
		838 (A')
		986 (A')

Table S10. Equilibrium geometry parameters, and vibrational frequencies of $In_2X_2O_7$(I) (X=W, Mo).

Geometric parameters (Å, deg)	$In_2W_2O_7$(I) (C_{2v})	$In_2Mo_2O_7$(I) (C_{2v})
r(In-O)	2.350	2.345
r (X-O)	1.783	1.763
r (X-O')	1.719	1.691
r (X-O'')	1.917	1.904
∠(O-In-O)	86.0	85.8
∠(In-O-X)	138.7	138.7
∠(O'-X-O'')	112.7	112.4
∠(X-O''-X)	119.6	119.7
∠(O-X-O)	109.8	110.3
Frequencies (cm^{-1})	33 (A_1)	34 (A_1)
	38 (A_2)	42 (A_2)
	75 (B_1)	72 (B_1)
	92 (B_2)	104 ($A_1 \oplus A_2$)
	97 (A_1)	106 (B_2)
	99 (A_2)	109 (B_1)
	107 (B_1)	164 (A_1)
	150 (A_1)	166 (B_1)
	165 (B_1)	191 (A_1)
	174 (A_1)	198 (B_2)
	190 (B_2)	205 (A_2)
	198 (A_2)	305 (B_2)
	292 (B_2)	306 (A_1)
	301 (A_1)	312 (B_1)
	304 (B_1)	316 (A_2)
	309 (B_2)	317 (B_2)
	310 (A_2)	344 (B_1)
	335 (A_1)	348 (A_1)
	340 (B_1)	575 (A_1)
	560 (A_1)	683 (B_2)
	700 (B_2)	801 (A_2)

793 (A_2)	872 (B_1)
857 (B_1)	891 (B_2)
895 (B_2)	904 (A_1)
902 (A_1)	1002 (B_2)
999 (B_2)	1011 (A_1)
1005 (A_1)	

References

S1 S. Mukhopadhyay, S. Gowtham, R. Pandey, and A. Costales, *Journal of Molecular Structure:THEOCHEM*, 2010, **948,** 31.

S2 N. M. Lakin, G. van der Hoek, I.R. Beattie, and J. M. Brown, *J.Chem.Phys.*, 1997, **107**(11), 4439.

S3 P.J. Linstrom and W.G. Mallard, Eds., *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, National Institute of Standards and Technology, Gaithersburg MD, 20899, http://webbook.nist.gov.

S4 J. A. Oliveira, W. B. De Almeida, and H .A. Duarte, *Chem. Phys. Lett.*, 2003, **372**, 650.

S5 H.-J. Zhai, B. Kiran, L.-F. Cui, X. Li, D. A. Dixon, and L.-S. Wang, *J.Am.Chem.Soc.*, 2004, **126**, 16134.