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Scandium ionization mechanisms in H_2–O_2–N_2 flames supported by calculated thermodynamic data

Jingzhong Guo, John M. Goodings*

Department of Chemistry and Centre for Research in Mass Spectrometry, York University,
4700 Keele Street, Toronto, Ont., Canada M3J 1P3

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Abstract

For 11 scandium neutrals and 20 positive ions containing hydrogen and oxygen in the gas phase, standard enthalpies and free energies of formation and entropies are tabulated at three temperatures of 0, 298.15 and 2400 K using energies and structural data from density functional calculations. These data are first employed to calculate bond dissociation energies, some of which can be compared with experimental and other calculated values. They are then used to determine the composition of scandium neutral species and also ions in an experimental flame at 2400 K, and to assess possible flame-ion production reactions involving chemi-ionization and thermal (collisional) ionization. The only viable mechanism appears to be the exothermic reaction of atomic Sc with O to yield ScO^+ and free electrons in the flame reaction zone. Further details of the flame-ion chemistry of scandium are discussed. In particular, a theoretical calculation shows that the formation of the stable dihydroxide ion $Sc(OH)_2{}^+$ from ScO^+ proceeds via the hydrate intermediate $ScO^+{\cdot}H_2O$ through a cyclic transition state. (Int J Mass Spectrom 214 (2002) 339–348) © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

When metals from the first row of 10 transition elements were introduced into a methane–oxygen flame, a considerable variety of metallic ions was observed [1]. For scandium, the ions could be represented by an oxide-ion series $ScO^+{\cdot}nH_2O$ ($n = 0$–3). Any such hydrocarbon flame contains a high concentration of natural ionization in the form of H_3O^+, an effective reagent for the chemical ionization (CI) of scandium neutral species by proton transfer. Shortly after this work was done, Dyke and coworkers reported the observation of chemi-ionization reactions of lanthanide metal atoms Ln (La, Ce, Pr, Nd, Sm, Eu, Gd) with O atoms to give LnO^+ ions and free electrons e^- [2–4]. Metal atoms from an oven were crossed with oxygen, and the products interpreted by chemi-electron and chemi-ion spectroscopy with mass analysis for the ions. These reactions are exothermic when the very strong LnO bond energy exceeds the low ionization energy of LnO. Subsequently, Armentrout and coworkers studied the ion and neutral thermochemistry of La, but also of the other group 3 metals Y and Sc for which a similar chemi-ionization reaction is expected. Specifically for Sc in the present context [5–9], some thermochemical information has been obtained from measurements using a guided ion beam mass spectrometer.

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* Corresponding author. E-mail: goodings@yorku.ca.

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With this background, it was of obvious interest to consider the ionization of the group 3 metals in a series of hydrogen–oxygen flames of both fuel-rich and fuel-lean (oxygen-rich) composition [10]. With no hydrocarbon present, such flames contain very little natural ionization such that CI of metallic species by H_3O^+ is very minor. Nevertheless, very large signals of La ions [10,11] were observed, with Y ions considerably smaller [10,12] and Sc ions smaller still. For each metal, the ion signals were always a factor of 2–4 higher in the fuel-rich flame compared with the fuel-lean one at the same temperature. It was clear that the ions must be produced by chemi-ionization reactions; the other possibility was thermal (collisional) ionization of the metallic oxides AO which are odd-electron species of low ionization energy. However, there is a difficulty in ascribing the ionization to the chemi-ionization reaction of $A + O$ to form AO^+ because O is a very minor species downstream in fuel-rich flames and atomic A should not be present. Thus, it was necessary to invoke other seemingly reasonable chemi-ionization reactions based on very crude estimates of the metallic species present in the flames because the necessary thermodynamic data were not available. This situation is far from satisfactory since the ionization mechanism is left in doubt. Accordingly, it was decided to remedy the situation, at least for Sc, because reasonably good thermodynamic data can be calculated.

Density functional calculations have been carried out successfully for scandium neutrals and positive ions containing hydrogen and oxygen in the gas phase giving equilibrium structures, vibrational frequencies, ionization energies [13], and also hydration energies and proton affinities [14]. These data provide the raw material needed to calculate thermodynamic functions for an ideal gas at any temperature with standard methods of statistical mechanics. From these calculations, values of the standard enthalpies of formation $\Delta_f H^\circ(T)$, standard free energies of formation $\Delta_f G^\circ(T)$ and entropies $S^\circ(T)$ for these species can be obtained. These numbers are of interest for many simple thermochemical calculations but most of them are not available in other compilations. They are listed here in tables at three temperatures T of 0, 298.15 and 2400 K. The high temperature is applicable to a particular experimental “flame 2” which we shall use for illustrative purposes; it has been employed in many previous studies. The format of the NIST-JANAF Thermochemical Tables [15] has been adopted to facilitate estimates of quantities such as bond dissociation energies, reaction enthalpies and equilibrium constants for proton transfer, electron transfer, chemi-ionization reactions, etc. In particular, our values are employed to calculate bond dissociation energies for comparison with experiment. The good agreement obtained lends credibility to the use of the numbers in the context of the proposed reaction mechanisms.

2. Experimental

For discussion of the ionization mechanisms of Sc species, the calculated thermodynamic data are applied to our “flame 2” used frequently in the past [11,12]. It is a fairly hot, premixed, laminar, cylindrical, H_2–O_2–N_2 flame stabilized on a multi-tube flat-flame burner at atmospheric pressure with a measured flame temperature of 2400 K. In normal use, the burnt gas containing ions is sampled along the flame axis through a nozzle into a mass spectrometer [16]. This flame is of fuel-rich composition ($H_2/O_2/N_2 = 2.74/1/2.95$) with an equivalence ratio $\varphi = 1.37$, i.e., H_2/O_2 is 1.37 times the stoichiometric composition. The calculated composition (mole fractions) of the equilibrium burnt gas at 2400 K is H_2O (0.346), H_2 (0.129), O_2 (0.000106), H (0.0000602), OH (0.000308), O (0.0000947) and diluent N_2 (0.516). The flame was doped with scandium by spraying a 0.1 M aqueous solution of $ScCl_3$ as an aerosol into the premixed gas using a pneumatic atomizer [16]. This technique introduces approximately 10^{-6} mol fraction of total Sc into the burnt gas. A profile of the ion signal exhibited a rapid rise near the bright luminous reaction zone upstream close to the burner, and a fairly constant but slightly decreasing signal downstream throughout the burnt gas.

3. Computational methods

In our previous studies of Sc species [13,14], energies, equilibrium structures and vibrational frequencies were calculated using density functional methods. In this communication, standard methods of statistical mechanics have been used to predict thermodynamic properties of these species using the procedures employed by Pople et al. [17]. Details and evaluations of the ab initio calculations with density functional methods have already been given [13,14]. For each species, four calculations were carried out using two density functionals, B3LYP and BP86, with two basis sets, TZVP and 6-311++G(3df, 3pd). In nearly all cases, the results of the four methods were very similar. Although the BP86 functional performed consistently better for predicting frequencies and structures, the B3LYP functional was better for energy calculations; the effects of the different basis sets were minor but the larger basis set 6-311++G(3df, 3pd) is preferred. For calculations of all thermodynamic functions, total energy data are taken from the B3LYP/6-311++G(3df, 3pd) method, with structural data and frequencies from the BP86/6-311++G(3df, 3pd) method.

First, the total energies are used to determine the total atomization energy $\sum D_e$ by direct calculation of the energy of the dissociation reaction:

$$\mathrm{ScO}_m\mathrm{H}_n\,(\text{or } \mathrm{ScO}_m\mathrm{H}_n{}^+) \rightarrow \mathrm{Sc}(\text{or } \mathrm{Sc}^+) + m\mathrm{O} + n\mathrm{H} \tag{1}$$

where all species are in their electronic ground states. In most cases, this dissociation reaction has unequal spins on both sides. Using the exact dissociation energy D_e for the hydrogen molecule of 109.48 kcal mol^{-1}, an isogyric correction to the total atomization energy $\sum D_e$ can be made by calculation of the energy of the isogyric reaction:

$$\begin{aligned}&\mathrm{ScO}_m\mathrm{H}_n\,(\text{or } \mathrm{ScO}_m\mathrm{H}_n{}^+) + 2k\mathrm{H}\\ &\quad\rightarrow \mathrm{Sc}(\text{or } \mathrm{Sc}^+) + m\mathrm{O} + n\mathrm{H} + k\mathrm{H}_2\end{aligned} \tag{2}$$

This isogyric reaction has equal spins on both sides. Subtraction of the zero-point energies (calculated from the BP86/6-311++G(3df, 3pd) frequencies) then gives the vibrationally-corrected total atomization energy $\sum D_0$ for $\mathrm{ScO}_m\mathrm{H}_n$ (or $\mathrm{ScO}_m\mathrm{H}_n{}^+$).

To obtain the standard enthalpy of formation $\Delta_f H^\circ(\mathrm{M/M^+},\ 0\,\mathrm{K})$ for a given scandium neutral M ($\mathrm{ScO}_m\mathrm{H}_n$) or ion M^+ ($\mathrm{ScO}_m\mathrm{H}_n{}^+$) at 0 K, the atomization energy $\sum D_0$ is subtracted from the well-established enthalpies of formation of the isolated atoms (or ions):

$$\begin{aligned}&\Delta_f H^\circ(\mathrm{M/M^+},\ 0\,\mathrm{K})\\ &\quad= \Delta_f H^\circ(\mathrm{Sc\ or\ Sc^+},\ 0\,\mathrm{K}) + m\Delta_f H^\circ(\mathrm{O}, 0\,\mathrm{K})\\ &\qquad + n\Delta_f H^\circ(\mathrm{H}, 0\,\mathrm{K}) - \sum D_0\end{aligned} \tag{3}$$

The atomic (ionic) $\Delta_f H^\circ(0\,\mathrm{K})$ values of 89.87 kcal mol^{-1} for Sc(g), 240.69 for Sc$^+$(g), 58.983 for O(g) and 51.626 kcal mol^{-1} for H(g) from [18] are used; these data do not appear in some later editions. Finally, thermal corrections to the desired temperatures T (298.15 and 2400 K) are made:

$$\begin{aligned}&\Delta_f H^\circ(\mathrm{M/M^+},\ T)\\ &\quad= \Delta_f H^\circ(0\,\mathrm{K}) + [H^\circ(\mathrm{M/M^+},\ T)\\ &\qquad - H^\circ(\mathrm{M/M^+},\ 0\,\mathrm{K})] - [H^\circ(\mathrm{Sc},\ T)\\ &\qquad - H^\circ(\mathrm{Sc},\ 0\,\mathrm{K})] - \tfrac{1}{2}m[H^\circ(\mathrm{O_2},\ T)\\ &\qquad - H^\circ(\mathrm{O_2},\ 0\,\mathrm{K})] - \tfrac{1}{2}n[H^\circ(\mathrm{H_2},\ T)\\ &\qquad - H^\circ(\mathrm{H_2},\ 0\,\mathrm{K})]\end{aligned} \tag{4}$$

The thermal corrections for M/M$^+$ are made using the calculated frequencies for vibrations and the classical approximation for translation and rotation, while the corrections for Sc, O and H refer to the standard state at 1 atm pressure, and are computed from heat capacities reported in [19]. The standard states for Sc are the solid α phase below 1608 K, the solid β phase between 1608 and 1812 K, liquid between 1812 and 3101 K and gas phase above 3101 K. The standard states for all other species refer to the gas phase at 1 atm pressure.

Entropies $S^\circ(T)$ for M/M$^+$ at temperature T (298.15 or 2400 K) are calculated theoretically using the structures, frequencies and moments of inertia determined previously [13,14]. Finally, standard-free energies of formation $\Delta_f G^\circ(\mathrm{M/M^+},\ T)$ are obtained from the usual definition:

$$\Delta_f G^\circ(\mathrm{M/M^+},\ T) = \Delta_f H^\circ(\mathrm{M/M^+},\ T) - T[S^\circ(\mathrm{M/M^+},\ T) - S^\circ(\mathrm{Sc},\ T) - \tfrac{1}{2}mS^\circ(\mathrm{O_2},\ T) - \tfrac{1}{2}nS^\circ(\mathrm{H_2},\ T)] \qquad (5)$$

The entropies for Sc, O_2 and H_2 in their standard states can be calculated from their heat capacities [19].

4. Results and discussion

Standard enthalpies of formation, free energies of formation and entropies at 0, 298.15 and 2400 K are given for neutral Sc species containing H and/or O in Table 1, and similarly for ions in Table 2. Table 3 presents selected bond dissociation energies D_0° at 0 K for the neutral species and the corresponding ions based on the ΔH_0° values in Tables 1 and 2 together with data from the NIST-JANAF Thermochemical Tables [15]. Nine bond energies for ion hydration can readily be calculated from Tables 1 and 2 but these values have been given previously [14]. All of the values in Tables 1–3 are thought to be accurate to $\pm 12.6\,\mathrm{kJ\,mol^{-1}}$ ($\pm 3\,\mathrm{kcal\,mol^{-1}}$) [13,14].

The bond energies in Table 3 provide a means of comparing our calculated values with experimental and computed values obtained by other workers. Good agreement within our stated accuracy of $\pm 3\,\mathrm{kcal\,mol^{-1}}$ is obtained for O–Sc, O–ScO, H–Sc^+, HO–$ScOH^+$ and HO–$Sc(OH)_2{}^+$; for HO–Sc^+, the literature results are somewhat scattered but three out of five show good agreement. Two exceptions occur for O–Sc^+ where our calculated values are 9–10 $\mathrm{kcal\,mol^{-1}}$ lower [7,9], and for O–ScO^+ where our results are 18 $\mathrm{kcal\,mol^{-1}}$ higher [8], compared with the experimental results of Armentrout's group. However, the values obtained by Armentrout's group for $D_0^\circ(\mathrm{O{-}Sc^+})$ of 164.7 ± 1.4 [7] and $165.1 \pm 2.1\,\mathrm{kcal\,mol^{-1}}$ [9] show some variance with other values in the literature. The ionic bond energy amounts to $D_0^\circ(\mathrm{O{-}Sc^+}) = D_0^\circ(\mathrm{Sc{-}O}) + \mathrm{IE}_0^\circ(\mathrm{Sc}) - \mathrm{IE}_0^\circ(\mathrm{ScO}) = 161.7$ [20] (or 160.5 [21]) + 151.3 (6.561 eV) [21] − 152.2 (6.6 eV) [7,9,13] = 160.8 (or 159.6 $\mathrm{kcal\,mol^{-1}}$); these latter values are roughly mid-way between our calculated value of 155.3 $\mathrm{kcal\,mol^{-1}}$ in Table 3 and those of Armentrout's group [7,9]. Also, our calculations for $ScO_2{}^+$ show that the ground state has a cyclic structure with a linear excited state above it [13]. The dissociation of O–ScO^+ from the cyclic structure cannot occur in one step because the breakage of two bonds is involved. It is very possible that the lower experimental bond energy [8] corresponds to dissociation from a non-cyclic excited state (or intermediate state) lying between the cyclic ground state and the products. In summary, there are reasons to question the experimental values for the bond energies of both O–Sc^+ and O–ScO^+ in comparison

Table 1
Neutral scandium species in the gas phase: energy values ($\mathrm{kJ\,mol^{-1}}$), with S° ($\mathrm{J\,K^{-1}\,mol^{-1}}$)

Species	$\Delta_f H^\circ$ (0 K)	$\Delta_f H^\circ$ (298 K)	$\Delta_f H^\circ$ (2400 K)	$\Delta_f G^\circ$ (298 K)	$\Delta_f G^\circ$ (2400 K)	S° (298 K)	S° (2400 K)
Sc	376.016	376.995	326.365	339.034	103.872	161.975	205.330
ScO	−44.522	−45.296	−101.069	−71.287	−214.120	224.388	297.562
ScH	362.033	361.267	306.562	332.950	175.502	194.970	264.680
ScOH	−55.802	−58.028	−115.349	−67.831	−92.889	235.434	338.548
HScO	−73.898	−76.827	−127.813	−90.161	−145.453	247.287	355.255
HScOH	−110.278	−114.763	−158.921	−115.529	−89.613	270.466	416.475
ScO_2	−188.795	−190.234	−239.781	−200.527	−244.162	274.303	390.120
OScOH	−455.838	−460.545	−506.126	−453.106	−370.108	280.173	429.069
$Sc(OH)_2$	−519.293	−525.293	−563.811	−503.904	−330.754	298.725	486.085
$HSc(OH)_2$	−593.835	−601.329	−627.027	−564.727	−296.332	313.051	542.849
$Sc(OH)_3$	−990.277	−997.963	−1017.273	−940.467	−536.322	345.523	618.081

Table 2
Scandium ions in the gas phase: energy values (kJ mol^{-1}), with S° (J K^{-1} mol^{-1})

Species	$\Delta_f H^\circ$ (0 K)	$\Delta_f H^\circ$ (298 K)	$\Delta_f H^\circ$ (2400 K)	$\Delta_f G^\circ$ (298 K)	$\Delta_f G^\circ$ (2400 K)	S° (298 K)	S° (2400 K)
Sc^+	1000.269	1001.248	950.617	962.278	720.037	165.347	208.698
ScO^+	597.291	596.496	540.422	572.384	443.563	218.078	290.817
ScH^+	978.387	977.621	922.677	947.538	778.078	200.882	270.320
$ScOH^+$	546.522	543.255	493.750	533.456	500.059	235.417	345.280
$HScO^+$	797.952	797.073	758.777	781.651	689.218	254.287	376.891
$Sc^+\cdot H_2O$	620.307	614.935	559.928	616.684	678.812	262.019	395.823
$HScOH^+$	521.908	516.335	470.173	519.502	578.999	257.266	400.011
$ScO_2{}^+$	603.927	600.781	548.610	596.203	600.919	255.136	366.502
$OscOH^+$	406.492	402.308	357.950	406.609	464.286	290.696	441.437
$Sc(OH)_2{}^+$	82.404	74.877	34.551	101.115	315.118	282.466	466.290
$ScO^+\cdot H_2O$	206.041	198.819	154.904	221.915	422.036	293.006	471.884
$ScOH^+\cdot H_2O$	166.557	158.260	121.583	192.171	460.512	322.063	539.418
$HSc(OH)_2{}^+$	303.520	295.328	258.948	328.791	593.438	323.570	541.267
$Sc^+\cdot 2H_2O$	256.429	247.730	214.974	295.219	659.511	341.870	592.864
$Sc(OH)_3{}^+$	−26.338	−34.020	−51.229	20.347	398.133	356.025	631.240
$ScO^+\cdot 2H_2O$	−168.427	−180.523	−203.213	−108.370	420.325	361.724	656.114
$Sc(OH)_2{}^+\cdot H_2O$	−310.972	−323.176	−342.159	−249.638	280.014	357.071	656.683
$ScOH^+\cdot 2H_2O$	−204.104	−215.827	−229.982	−136.536	431.006	403.112	737.957
$Sc(OH)_2{}^+\cdot 2H_2O$	−682.766	−699.494	−696.933	−573.405	307.963	414.065	829.947
$ScO^+\cdot 3H_2O$	−527.393	−543.845	−544.744	−418.212	468.273	415.597	826.566

Table 3
Selected bond dissociation energies of scandium neutral and ionic species at 0 K; comparisons with other work, both experimental and theoretical are given in the footnotes (kcal mol^{-1})

Neutrals	D_0° (kJ mol^{-1})	D_0° (kcal mol^{-1})	Ions	D_0° (kJ mol^{-1})	D_0° (kcal mol^{-1})
O–Sc	667.3	159.5[a]	O–Sc^+	649.8	155.3[b]
H–Sc	230.0	55.0	H–Sc^+	237.9	56.9[c]
HO–Sc	470.2	112.4	HO–Sc^+	492.1	117.6[d]
HSc–O	682.7	163.2	–	–	
H–ScO	245.4	58.7	–	–	
HO–ScH	510.7	122.1	HO–ScH^+	494.9	118.3
H–ScOH	270.5	64.7	H–$ScOH^+$	240.6	57.5
O–ScO	391.1	93.5[e]	O–ScO^+	240.2	57.4[f]
O–ScOH	646.8	154.6	O–$ScOH^+$	386.8	92.5
HO–ScO	449.7	107.5	HO–ScO^+	229.2	54.8
HO–ScOH	501.9	120.0	HO–$ScOH^+$	502.5	120.1[g]
H–$Sc(OH)_2$	290.6	69.5	–	–	
HSc(OH)–OH	521.9	124.7	–	–	
HO–$Sc(OH)_2$	509.4	121.7	HO–$Sc(OH)_2{}^+$	147.1	35.2[h]

[a] 161.7 [20], 160.5 [21], experimental.

[b] 165.1 ± 2.1 [9], 164.7 ± 1.4 [7], both experimental.

[c] 57.2 ± 2.1 [6,22], 56.2 ± 2 [5], both experimental.

[d] 107.9 [22], computed, 87.9 ± 3.0 [23], experimental; $D_0^\circ(\text{HO–Sc}^+) = 119.2 \pm 2.1$ [9], experimental; 118.8 [24], computed by density functional B3LYP method; 117.6 [24], computed by coupled-cluster CCSD(T) method.

[e] 91.1 ± 7.6 [8], experimental.

[f] 39.7 ± 4.4 [8], experimental.

[g] 117.6 [24], computed by density functional B3LYP method; 117.1 [24], computed by coupled-cluster CCSD(T) method.

[h] 32.5 [24], computed by density functional B3LYP method.

with our calculated values. Although the other checks on our calculated numbers are relatively few, our overall agreement with available experimental and other calculated values is an encouraging basis for a consideration of the flame-ion chemistry of scandium.

The first step in the discussion of the ionization mechanisms for scandium in a flame is the determination of the Sc neutrals present in the flame; "flame 2" [11,12] described in the experimental section provides an excellent practical example. Equilibrium constants $K = \exp[-\Delta G^\circ(\text{reaction})/RT]$ at the flame temperature of 2400 K involving 10 ratios of Sc neutral species can be determined by setting up a series of 10 simple reactions such as

$$\mathrm{Sc} + \mathrm{H_2O} = \mathrm{ScO} + \mathrm{H_2},\quad [\mathrm{ScO}]/[\mathrm{Sc}] = K_6[\mathrm{H_2O}]/[\mathrm{H_2}] \tag{6}$$

$$\mathrm{ScO} + \mathrm{H_2O} = \mathrm{OScOH} + \mathrm{H},\quad [\mathrm{OScOH}]/[\mathrm{ScO}] = K_7[\mathrm{H_2O}]/[\mathrm{H}] \tag{7}$$

encompassing the 11 neutrals in Table 1 using the $\Delta_f G^\circ(2400\,\mathrm{K})$ values, and those from the NIST-JANAF Thermochemical Tables [15] for H_2O, H, OH (which are major flame neutrals). From the equilibrium constants and the known mole fractions of $[H_2O]$, $[H_2]$, [H] and [OH] given in the experimental section, it is a simple matter to obtain numerical values for 10 ratios of Sc neutrals, all in terms of a common denominator such as [Sc]. By setting the sum of the 11 Sc neutral concentrations equal to the total Sc concentration present in the flame, the percentages of all 11 Sc neutrals can be determined. This assumes that the total concentration of Sc ions is much less than that of the Sc neutrals; the assumption has been verified. The spreadsheet calculations show that just four neutrals account for 99.83% of the total scandium present in the flame. They are $Sc(OH)_3$ (79.56%), OScOH (17.34%), ScO (2.12%) and $Sc(OH)_2$ (0.81%); the other seven Sc neutrals have negligible concentrations. In particular, atomic Sc is a very minor species because $[\mathrm{Sc}]/[\mathrm{ScO}] = 1.24 \times 10^{-5}$. It is also interesting to note that for similar flames at progressively lower temperatures, even fewer Sc neutrals have appreciable concentrations. For example, at 1820 K (our "flame 5" in previous publications [11,12]), $Sc(OH)_3$ alone accounts for 99.55% of the total Sc present.

With this knowledge, possible ionization reactions for scandium in "flame 2" can be considered. The likely candidates are three chemi-ionization reactions:

$$\mathrm{Sc} + \mathrm{O} \rightarrow \mathrm{ScO^+} + \mathrm{e^-},\quad \Delta H^\circ = -42\,\mathrm{kJ\,mol^{-1}} \tag{8}$$

$$\mathrm{Sc(OH)_3} + \mathrm{H} \rightarrow \mathrm{Sc(OH)_2}^+ \cdot \mathrm{H_2O} + \mathrm{e^-},\quad \Delta H^\circ = 447\,\mathrm{kJ\,mol^{-1}} \tag{9}$$

$$\mathrm{OScOH} + \mathrm{H} \rightarrow \mathrm{Sc(OH)_2}^+ + \mathrm{e^-},\quad \Delta H^\circ = 312\,\mathrm{kJ\,mol^{-1}} \tag{10}$$

and three thermal (collisional) ionization reactions involving the three Sc neutrals of lowest ionization energy similar to

$$\mathrm{ScO} + \mathrm{M} \rightarrow \mathrm{ScO^+} + \mathrm{e^-} + \mathrm{M},\quad \Delta H^\circ = 6.60\,\mathrm{eV} = 637\,\mathrm{kJ\,mol^{-1}} \tag{11}$$

where M is a third body [7,9,13]; the other two involve thermal ionization of atomic Sc and of $Sc(OH)_2$ having ionization energies (reaction endothermicities) of 6.561 eV (633 $\mathrm{kJ\,mol^{-1}}$) [22] and 6.2 eV (598 $\mathrm{kJ\,mol^{-1}}$) [13], respectively. All of the ΔH° (reaction) values refer to 2400 K. Reaction (8), the scandium counterpart to the lanthanide mechanism studied by Dyke and coworkers [2–4], is the only exothermic process we have been able to find. Reactions (9) and (10) involve major Sc neutrals but they are too endothermic to warrant serious consideration. The same criticism applies to the thermal ionization reactions involving ScO, Sc and $Sc(OH)_2$, the three neutrals of lowest ionization energy. We have hypothesized previously that thermal ionization can be a major mechanism in the case of LaO where the ionization energy is much lower (4.90 eV) [11], and even to a small extent for YO (5.85 eV) [12], but reactions like (11) with ScO (6.60 eV) or $Sc(OH)_2$ (6.2 eV) are too endothermic to make a significant contribution. Thus, we are forced to the conclusion that the chemi-ionization reaction (8) must be the major operative mechanism for scandium.

On first consideration, there might be a considerable difficulty with reaction (8) in the flame context. In the equilibrium burnt gas, Sc is a very minor species and also O, especially in a fuel-rich flame such as “flame 2” (9.5×10^{-5} mol fraction). However, the reaction rate in the flame reaction zone can be much higher. Scandium enters the flame as $ScCl_3$ salt which dissociates into atoms in the preheat zone before oxidizing to form $Sc(OH)_3$, OScOH, etc., further downstream. There must be a brief region in the reaction zone where [Sc] is considerably greater than its equilibrium concentration. The same is true for [O]. The radical concentrations of H and OH in a fuel-rich flame overshoot their equilibrium concentrations in the reaction zone by a factor $\gamma > 100$, where γ is Sugden’s disequilibrium parameter [25]. In the case of O, the factor is γ^2. A curve of γ as a function of axial distance has been measured by Butler and Hayhurst for “flame 2” [26]. Thus, there will be a short region or “window of opportunity” in the reaction zone where the rate of reaction (8) can, potentially, be very large. We believe that this must be the basic mechanism for the initial rapid boost of scandium ionization observed in flames.

A further consideration involves the scandium ions actually present in the flame. The relative concentrations of 20 Sc cations in the equilibrium burnt gas can be calculated from the data in Table 2 in exactly the same way as was done for the Sc neutral species. In this case, 19 simple ion–molecule reactions were set up in a spreadsheet, ultimately to give 19 ion ratios. The calculations show that just five ions account for 99.91% of the total scandium flame ions; they are, in descending concentration, ScO^+ (57.78%), $Sc(OH)_2{}^+$ (40.52%), $ScOH^+$ (1.16%), $Sc(OH)_2{}^+\cdot H_2O$ (0.26%) and $ScO^+\cdot H_2O$ (0.19%). At first glance, these calculated relative concentrations would appear to be rather different from the measured relative concentrations in “flame 2”; the latter are ScO^+ (28.32%), $Sc(OH)_2{}^+$ including $ScO^+\cdot H_2O$ (47.85%, isomers with the same mass number of 79 u), $Sc(OH)_2{}^+\cdot H_2O$ (23.44%) and $Sc(OH)_2{}^+\cdot 2H_2O$ (0.39%). They were measured 30 mm downstream of the flame reaction zone by sampling the flame gas through a nozzle into a mass spectrometer [16]. The measured percentages depend to some extent on the actual nozzle and orifice size employed to make the measurements.

In fact, the measured ion signals are in good qualitative agreement with the calculated results. After the initial formation of ScO^+ by chemi-ionization via reaction (8), a sequence of three-body reactions takes place in the burnt gas region which are fast enough to be balanced in a flame at atmospheric pressure:

$$ScO^+ + H_2O + M \rightleftarrows M + ScO^+ \cdot H_2O, \quad \Delta H^\circ = -133\,kJ\,mol^{-1} \tag{12}$$

$$ScO^+ \cdot H_2O + M \rightleftarrows Sc(OH)_2{}^+ + M, \quad \Delta H^\circ = -123\,kJ\,mol^{-1} \tag{13}$$

$$Sc(OH)_2{}^+ + H_2O + M \rightleftarrows Sc(OH)_2{}^+ \cdot H_2O + M, \quad \Delta H^\circ = -124\,kJ\,mol^{-1} \tag{14}$$

Reaction (13) is an isomeric rearrangement from the hydrate to form the dihydroxide ion, and further discussion will be given. However, the hydration reactions (12) and (14) proceed without an energy barrier. When the flame is sampled through the nozzle, the sample cools in two regions: in the cold boundary layer covering the nozzle tip, and in the supersonic expansion downstream of the nozzle throat [27]. When these two equilibria are cooled during sampling, their reaction rates are fast enough to shift the equilibria in the exothermic direction such that the hydrate signals are enhanced. In general, hydrated ions are very minor species at the flame temperature but their signals are greatly enhanced due to cooling during sampling. This is the behavior shown very clearly by the measured percentages in comparison with the calculated percentages.

The isomeric rearrangement in reaction (13) of the hydrate $ScO^+\cdot H_2O$ to form the dihydroxide ion $Sc(OH)_2{}^+$, both at mass number 79 u, is interesting. The measured mass-spectrometric ion signal at 79 u is too large to be that of a simple hydrate; an ion of greater stability is indicated, and the requirement is fulfilled by the dihydroxide ion. It proved possible

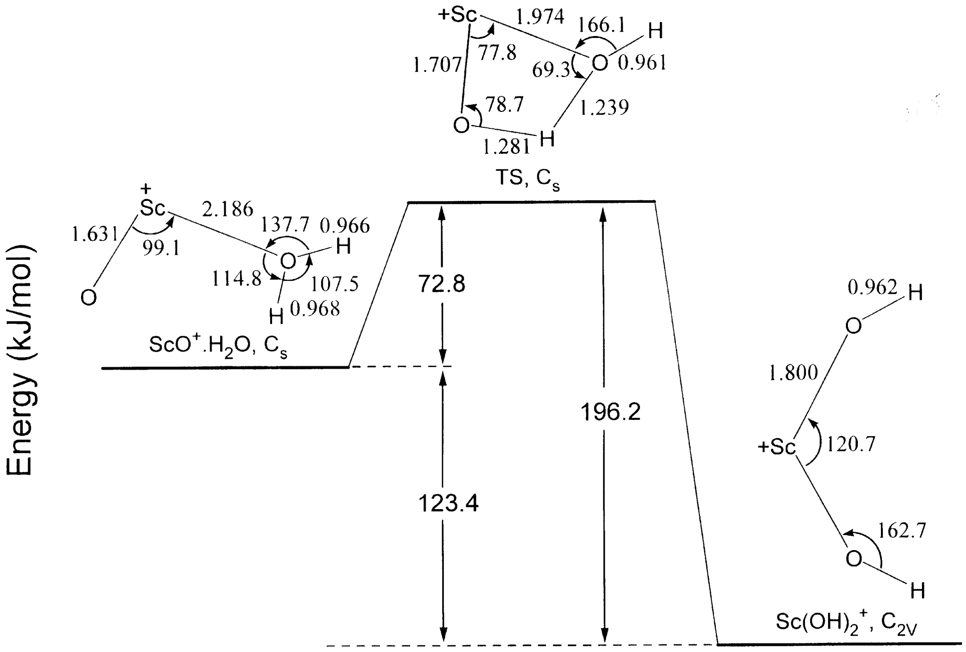

Fig. 1. Potential energy surface for the transformation of $ScO^+{\cdot}H_2O$ to $Sc(OH)_2{}^+$ via a transition state calculated at the B3LYP/6-311++G(3df, 3pd) level of theory, with energy values (kJ mol^{-1}), bond lengths (Å) and bond angles (°).

to locate and calculate the transition state shown in Fig. 1 which links the two ions. The energy barrier of 72.8 kJ mol^{-1} in the forward direction is sufficiently low that the dihydroxide ion can readily form at the flame temperature.

Of greatest significance is the fact that the major ions, both observed and calculated, are members of the same oxide ion series $ScO^+{\cdot}nH_2O$ ($n = 0$–3). The presence of $ScOH^+$ (1.16%) in the calculated values is the one minor exception. Its formation from ScO^+ in the flame would require a mechanism such as

$$ScO^+ + H_2, H_2O \rightleftarrows ScOH^+ + H, OH,$$
$$\Delta H^\circ = 182, 242\,\text{kJ mol}^{-1} \qquad (15)$$

but the reactions are endothermic and would probably involve an appreciable activation energy. Despite a determined effort, the $ScOH^+$ ion was never detected with the mass spectrometer. Also, it was mentioned in Section 1 that the measured total Sc ion signal was always a factor 2–4 higher in a fuel-rich flame than in a fuel-lean (oxygen-rich) flame at the same temperature. Although [O] is higher in the reaction zone of the fuel-lean flame, this observation can only mean that the "window of opportunity" for reaction (8) must be reduced by the more rapid oxidation of Sc atoms in the presence of excess O_2 for the oxygen-rich case.

5. Summary and conclusions

Thermodynamic data ($\Delta_f H^\circ$, $\Delta_f G^\circ$, S°) for ScH_mO_n species (11 neutrals and 20 cations) have been calculated at three temperatures of 0, 298.15 and 2400 K using standard methods of statistical mechanics. They are based on our prior density functional theory (DFT) calculations of structures, vibrational frequencies and ionization energies [13], and also hydration energies and proton affinities [14]. The data were employed to calculate selected bond dissociation energies (14 for neutrals and 10 for ions) for comparison with published values when available, both experimental and theoretical. The overall agreement is good except for D_0°(O–Sc$^+$) and D_0°(O–ScO$^+$), but there appear to be logical reasons for these two discrepancies.

When applied to an experimental fuel-rich H_2–O_2–N_2 flame at 2400 K, the thermodynamic data indicate the preponderance of just two major scandium neutrals ($Sc(OH)_3$ and OScOH) and two minor ones (ScO and $Sc(OH)_2$); all others were negligible. Experimentally, it is well-known that scandium ionizes readily in such flames. Accordingly, the data were then employed to investigate viable ionization mechanisms for Sc species. The only exothermic reaction we can find is the chemi-ionization of atomic Sc with O to form ScO^+; it is explained how the reaction might occur in the flame reaction zone. The data indicate that our previous hypothesis of a chemi-ionization reaction of OScOH with H giving $Sc(OH)_2{}^+$ [10] is too endothermic to make any appreciable contribution. Similarly, thermal (collisional) ionization of the minor neutrals ScO and $Sc(OH)_2$ is very endothermic although this mechanism might make a minor contribution to the ionization of Y [12] and a more major one for La [11]. It is also reasonable to speculate that Y + O and La + O are the only exothermic chemi-ionization reactions for these other group 3 metals as well.

Finally, the thermodynamic data were then used to predict which scandium ions should be present in the experimental flame at 2400 K. The calculations indicate the overwhelming predominance of ScO^+ and $Sc(OH)_2{}^+$. This is in excellent agreement with our experimental observation that the ions are members of the oxide ion series $ScO^+ \cdot nH_2O$ (n = 0–3). Experimentally, hydrate ions are emphasized when the flame gas is cooled in passing through the sampling nozzle into the mass spectrometer. Experimental measurements indicate a special stability for the scandium ion at 79 u. The ion appears to form as the hydrate $ScO^+ \cdot H_2O$ and then rearrange to the isomeric dihydroxide $Sc(OH)_2{}^+$ of greater stability. The calculated transition state indicates that this transformation has an energy barrier of 72.8 kJ mol^{-1}, supporting $Sc(OH)_2{}^+$ as a major flame-ion. The same dominance of the dihydroxide ion is observed in the mass spectra of Y and La in flames [10].

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