Gas-phase Metal Oxidation Reactions studied by Chemielectron Spectroscopy and Chemiion Mass Spectrometry: Reactions of Cerium and Lanthanum with $O_2(X^{3}\Sigma_g^{-})$, $O_2(a^{-1}\Delta_g)$ and $O(^{3}P)$

Martin C. R. Cockett,[†] John M. Dyke,^{*} Andrew M. Ellis[‡] and Timothy G. Wright Department of Chemistry, The University, Southampton, SO9 5NH, UK

The gas-phase reactions $M + O_2(X {}^{3}\Sigma_{g}^{-})$, $M + O_2(a {}^{1}\Delta_g)$ and $M + O({}^{3}P)$ have been studied with chemielectron spectroscopy, where M represents one of the lanthanide metals, cerium or lanthanum. Assignment of the observed bands has been assisted by mass analysis of the ions produced and by approximate kinetic modelling calculations. For the $M + O_2(X {}^{3}\Sigma_g^{-})$ and $M + O_2(a {}^{1}\Delta_g)$ associative ionization reactions, most of the excess energy appears as electron kinetic energy, whereas for the $M + O({}^{3}P)$ reactions a larger fraction of the reaction energy is retained in the positive ion.

In recent years, a number of gas-phase chemiionization reactions have been studied experimentally by various methods.¹⁻⁷ Some of these reactions, mainly involving metals and oxidants such as O_2 , O, O_3 , N_2O and OH, have been investigated under crossed molecular beam conditions using mass spectrometry and, in some cases, relative and absolute reaction cross-sections have been determined.^{3,5-7} Optical emission experiments have also been used to probe the excited-state population of ions formed in such processes.⁸ However, in spite of the interest and activity in this field, few experiments have been performed to measure the kineticenergy distribution of the electrons produced by these reactions.

Chemielectron spectroscopy, the measurement of the energy distribution of electrons arising from chemiionization reactions, has the ability to provide detailed information relating to the energetics and reaction dynamics of such processes.⁹ A small number of chemiionization reactions have already been studied with electron spectroscopy,⁹⁻¹² and they serve to demonstrate the potential of the method.

This paper describes the use of chemielectron spectroscopy to investigate a number of chemiionization reactions involving cerium or lanthanum, with an oxidant $[O(^{3}P), O_{2}(X \ ^{3}\Sigma_{g}^{-})$ or $O_{2}(a \ ^{1}\Delta_{g})]$. Reactions of this type have been studied in some detail previously using mass spectrometry, and in some cases reaction cross-sections have been measured.¹³⁻¹⁵ The associative ionization cross-sections determined in ref. (13)-(15) have proved useful in this present work in that they have been used to calculate approximate rate constants at a particular reaction temperature. These have been used in approximate kinetic simulations of the reactions of interest and provide insight into the $M + O_{2}$ reaction scheme.

One of the requirements necessary for a metal to undergo an oxidation chemiionization reaction is its ability to form a strong metal-oxygen bond and for the oxide to have a low first ionization energy. For example, if the simple associative ionization reaction between a metal atom and an oxygen atom, $O(^{3}P)$, is considered:

$$M + O(^{3}P) \rightarrow MO^{+} + e^{-}$$
(1)

the reaction enthalpy for this reaction can be written as

$$\Delta H_1 = -D_0^0(\mathrm{MO}) + E_{\mathrm{ia}}(\mathrm{MO})$$

where $D_0^0(MO)$ is the dissociation energy of the metal oxide and E_{ia} is its first adiabatic ionization energy. Clearly, ΔH_1 will only be negative if $D_0^0(MO) > E_{ia}(MO)$. In the case of cerium and lanthanum, which are studied in this work, and some of the other lanthanides, this requirement is satisfied.

Similarly, for the associative ionization reaction between a metal and ground-state molecular oxygen:

$$M + O_2(X^{3}\Sigma_g^{-}) \to MO_2^{+} + e^{-}$$
 (2)

the reaction enthalpy can be written as,

$$\Delta H_2 = -D_0^0(\mathrm{MO}_2) + E_{\mathrm{ia}}(\mathrm{MO}_2)$$

where $D_0(MO_2)$ represents the dissociation energy of MO_2 to give M and O_2 .

As $O_2(a \ ^1\Delta_g)$, as well as $O(^3P)$ and $O_2(X \ ^3\Sigma_g)$, has been used as an oxidant in this work, reaction (3) must also be considered:

$$M + O_2(a^{-1}\Delta_e) \rightarrow MO_2^+ + e^-$$
(3)

If the same ionic states are accessed in reactions (2) and (3), the reaction enthalpy, ΔH_3 , can be written as

$$\Delta H_3 = \Delta H_2 - T_0 (X^{-3} \Sigma_g^- - a^{-1} \Delta_g)$$

where $T_0(X \ {}^{3}\Sigma_{g}^{-}-a \ {}^{1}\Delta_{g})$ is the energy of $O_2(a \ {}^{1}\Delta_{g})$ relative to $O_2(X \ {}^{3}\Sigma_{g}^{-})$.

In principle, for a given reaction, if the energy distribution of the emitted electrons is measured, and if ΔH is known, then the distribution of the available energy between the product ion and the chemielectron can be determined. Furthermore, the shape, position and structure of the chemielectron band can be used to provide information concerning the mechanism of the chemiionization process.

The purpose of this study is to investigate the chemiionization reactions $M + O({}^{3}P)$, $M + O_{2}(X {}^{3}\Sigma_{g}^{-})$ and $M + O_{2}$ (a ${}^{1}\Delta_{g}$) using chemielectron spectroscopy. The gas-phase chemiionization reactions of atomic cerium with $O({}^{3}P)$ and $O_{2}(X {}^{3}\Sigma_{g}^{-})$ have been studied previously by mass spectrometry using both accelerated cerium beams¹⁶ and thermal reactants.^{15,17} For the reaction of cerium with $O_{2}(X {}^{3}\Sigma_{g}^{-})$, two different chemiionization channels were observed, leading to the formation of CeO⁺ and CeO⁺₂, with the measured relative cross-sections for these channels being *ca*. $1:30.^{17}$ It is somewhat surprising that any reaction was observed at all since the chemiionization channels yielding CeO⁺ + O + e⁻ and CeO⁺₂ + e⁻ for the reaction of cerium with $O_{2}(X {}^{3}\Sigma_{g}^{-})$ can be calculated as being endothermic using currently available thermodynamic data (although the error on some of the calculated reaction enthalpies is large). The

[†] Present address: Institute of Molecular Sciences, Okazaki, Japan.

[‡] Present address: Laser Spectroscopy Facility, Department of Chemistry, Ohio State University, Columbus, Ohio, USA.

chemiionization cross-section at thermal energies for the reaction of cerium with atomic oxygen to give CeO⁺ + e⁻, has been measured to be *ca*. 300 times that of the associative ionization reaction between cerium and $O_2(X \ ^3\Sigma_g)$ to give CeO⁺₂ + e⁻.¹⁵

The gas-phase chemiionization reactions $La + O_2(X \ {}^{3}\Sigma_{g}^{-})$ and $La + O({}^{3}P)$ have also been studied by mass spectrometry using both accelerated lanthanum beams¹⁶ and crossed beams of thermal reactants.¹⁵ A number of cross-sections for the La + $O_2(X \ {}^{3}\Sigma_{g}^{-})$ reaction scheme have been measured¹⁵ under thermal conditions and it has been found that the cross-section for the associative ionization reaction producing $LaO_{2}^{+} + e^{-}$ [reaction (2)] is *ca.* two orders of magnitude larger than that of the corresponding cerium reaction. Additionally, the measured cross-section for the La + $O({}^{3}P)$ associative ionization reaction [reaction (1)] at thermal energies is *ca.* 300 times larger than that for the La + $O_2(X \ {}^{3}\Sigma_{g}^{-})$ associative ionization reaction.

Experimental

All of the chemielectron spectroscopic studies described in this work were performed on a single-detector, hightemperature photoelectron spectrometer, described elsewhere.¹⁸⁻²⁰ The metals (Cerac Inc., 99.9%) were evaporated using a radiofrequency induction heating system²⁰ and the metal vapour was reacted with the oxidant gas in a reaction cell which allowed partial pressures of 10^{-5} – 10^{-3} Torr to be used. Electrons produced from the reaction were energyanalysed and then detected using a channeltron electron multiplier. As described previously,¹⁰⁻¹² an He I photon source was used to produce photoelectron spectra in order to calibrate the kinetic energy scale of the chemielectron spectra obtained. The photon beam was blocked using a shutter arrangement, which could be operated from outside the vacuum system, when a chemielectron band was scanned. This enabled calibrated chemielectron spectra to be recorded without contributions from photoelectrons.

Cylindrical furnaces were used for the evaporation of the metals and these were machined from either molybdenum or tungsten. They were fitted with a molybdenum extension piece and supported by an alumina rod.²⁰ The extension

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pieces were used to keep the alumina/molybdenum or alumina/tungsten junction away from the high temperatures experienced inside the r.f. coil region, thus preventing reaction between the molybdenum or tungsten with the alumina.²⁰ The only other component in the furnace region was a molybdenum or tantalum radiator, which was supported from the extension piece.^{20,21} No ceramic components or insulating carbon felt were used anywhere in the furnace region, thus ensuring that reactive gases such as CO or CO₂ were not generated within the reaction environment.

Oxygen atoms were generated by a microwave discharge of pure molecular oxygen flowing in a boric-acid-coated glass inlet tube. This resulted in a mixture of O(³P), O₂(X ${}^{3}\Sigma_{g}^{-}$) and $O_2(a^{-1}\Delta_e)$ being present. In order to distinguish between contributions to the product electron and ion signal intensities arising from reaction of O atoms and $O_2(a^{-1}\Delta_e)$ with the reactant metal, the O atoms were deactivated, with little change in the $O_2(a \ ^1\Delta_g)$ partial pressure, using glass wool placed in the discharge tube. Any resulting change in either the chemielectron spectrum or the chemiion mass spectrum could then be attributed to the loss of the O atoms in the reactant beam. The $O_2(a^{-1}\Delta_g)$ and O atom yield under a given set of discharge conditions could be determined by recording the He I photoelectron spectra of molecular oxygen, discharged oxygen, and discharged oxygen passed through glass wool present in the inlet tube (see Fig. 1). From the known He I photoionization cross-sections at right angles to the photon beam,²² the experimental band intensities could be used to yield relative partial pressures of $O_2(X^{3}\Sigma_g^{-})$, $O_2(a^{1}\Delta_g)$ and $O({}^{3}P)$ under a given set of conditions.

In order to assist in the assignment of an experimental chemielectron spectrum, it was valuable to identify the ionic products of the chemiionization reaction. This was achieved by fitting an independently pumped quadrupole mass spectrometer to the front of the ionization chamber of a multi-detector photoelectron spectrometer.²¹ In these experiments the electron-impact source of the mass spectrometer was switched off, enabling the exclusive detection of ions produced by chemical reactions. In order to prevent the reactants from contaminating the quadrupole rods, they were mixed in a reaction cell outside the mass spectrometer housing and the



Fig. 1 He I photoelectron spectra recorded in the 11.0–14.0 eV ionization energy region for (a) $O_2(X^{3}\Sigma_{g}^{-})$, (b) $O_2(X^{3}\Sigma_{g}^{-})$, $O_2(a^{1}\Delta_{g})$ and $O(^{3}P)$ and (c) $O_2(X^{3}\Sigma_{g}^{-})$ and $O_2(a^{1}\Delta_{g})$

product ions were focused into the ion source of the mass spectrometer using an ion lens.

A typical 'chemiion' experiment is carried out in much the same way as a chemielectron experiment: the metal is evaporated from an r.f. inductively heated molybdenum or tungsten furnace and is then crossed with a beam of oxidant at right angles, in the reaction cell. The three oxidants used, $O_2(X^{3}\Sigma_g^{-}), O_2(a^{1}\Delta_g)$ and $O(^{3}P)$, were prepared as described above and again introduced into the reaction cell via a boricacid-coated glass discharge tube. In contrast to the chemielectron experiments, where the geometry of the discharge tube required that separate experiments be performed with and without the glass wool present in the discharge tube, in a chemiion experiment all three oxidant mixtures could be produced during the course of a single experiment by running the discharge either on the side of the glass wool furthest from the ionization chamber or on the side closest to the ionization chamber to obtain mixtures of $O_2(X^{3}\Sigma_{g})$ and $O_2(a \ ^1\Delta_g)$, or $O_2(X \ ^3\Sigma_g^-)$, $O_2(a \ ^1\Delta_g)$ and $O(^3P)$, respectively [see Fig. 1(c) and (b), respectively]. Pure $O_2(X \ ^3\Sigma_g^-)$ could obviously be obtained by simply switching off the discharge [see Fig. 1(a)]. Unfortunately, the relative yields of $O_2(X\ ^3\Sigma_g^-),\ O_2(a\ ^1\Delta_g)$ and $O(^3P)$ could be monitored for a chemiion experiment only by performing a separate photoelectron experiment on the multidetector instrument without the ion lens assembly in place, whereas for the chemielectron experiments, which were performed on the single-detector instrument, the relative yields of the three oxidants could be continually monitored during the course of a particular experiment. With the above procedure, the relative partial pressures of the three oxidants for a given discharge configuration could be calculated in a chemiion experiment in the same way as in the chemielectron experiments from the known photionization cross-sections of $O_2(X^{-3}\Sigma_{g}^{-})$, $O_2(a^{-1}\Delta_{g})$ and $O(^{3}P)$ at the He I photon energy.²²

From both the chemielectron and chemiion spectra obtained, the relative reaction cross-sections can be calculated, once the relative partial pressures of $O_2(X \ ^3\Sigma_g^-)$, $O_2(a^1\Delta_g)$ and $O(^3P)$ are known, by measuring the relative chemielectron band and chemiion signal intensities under the discharge on and discharge off conditions (see Fig. 1). The method used to obtain relative cross-sections will be described later.

Results and Discussion

$Ce + O_2(X^{3}\Sigma_{\bullet})$

Previously we have described¹² the study of the Ce + O₂ $(X \, {}^{3}\Sigma_{g}^{-})$ reaction with chemielectron spectroscopy in some detail. The band shown in Fig. 2, reproduced from ref. (12) for comparison with Fig. 3, was attributed to electrons arising from the associative ionization reaction of cerium with O₂(X ${}^{3}\Sigma_{g}^{-})$ [*i.e.* reaction (2) with M = Ce]. This assignment was achieved on the basis of evidence from a number of sources: (a) mass analysis of the ions, (b) approximate kinetic modelling calculations and (c) measurement of the electron and positive ion concentrations as a function of oxygen pressure in the reaction region.

Ce + O(³P); Ce + O₂(a $^{1}\Delta_{s}$)

The chemielectron spectrum recorded at a furnace temperature of 1300 K, for the reaction between Ce and a mixture of $O_2(X \ ^3\Sigma_g)$, $O_2(a \ ^1\Delta_g)$ and $O(^3P)$, generated in a microwave discharge in flowing oxygen gas, is shown in Fig. 3(a). With the microwave discharge on, a sharp band was recorded, with the photon source off, having a maximum at



Fig. 2 Chemielectron spectrum recorded for the Ce + $O_2(X^{3}\Sigma_{g}^{-})$ reaction

 0.13 ± 0.06 eV and a tail extending to higher kinetic energy. At higher temperatures in the range 1350-1450 K, a second band with a maximum at 1.83 ± 0.10 eV electron kinetic energy was observed which was much broader than that of the low-kinetic-energy band (Fig. 3). When the microwave discharge was switched off at furnace temperatures > 1450 K, both bands disappeared to reveal the band due to the reaction between cerium and ground state molecular oxygen (Fig. 2), having an intensity at least two orders of magnitude smaller than the bands recorded with the discharge on. However, when the microwave discharge was switched off at lower furnace temperatures, the intensity of the chemielectron band due to the Ce + O₂(X ${}^{3}\Sigma_{g}^{-}$) reaction was below the detection limits of the spectrometer. This band was observed only when the furnace temperature was increased to 1450-1600 K. Unfortunately, no reliable band intensity ratios could be calculated from the observed band intensity changes because of the small number of data points available However, the qualitative changes observed in the chemielectron band intensities can be compared with the behaviour observed in the corresponding ion spectra. When the discharge was switched on, the chemiion mass spectrum showed a large increase in the intensity of the CeO⁺ signal together with a smaller increase in the intensity of the CeO_2^+ signal. The actual intensity changes will be presented later together with a description of the method used to calculate relative reaction cross-sections from the chemiion intensity changes. It is clear that the two chemielectron bands observed with the discharge on must be due to chemiionization reactions between Ce and O(³P), and Ce and O₂(a ${}^{1}\Delta_{g}$). However, with oxygen atoms deactivated only the feature centred at 1.83 ± 0.10 eV was present, thus enabling assignment of this band to a chemiionization reaction between Ce and O₂(a $^{1}\Delta_{e}$). Consequently, the band at 0.13 ± 0.06 eV can be

assigned to the associative ionization reaction between Ce and $O(^{3}P)$, producing CeO⁺ (see Fig. 3). It seems, from the

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Fig. 3 Chemielectron spectra recorded for the reactions Ce + O(³P) and Ce + O₂(a ${}^{1}\Delta_{g}$) at furnace temperatures of (a) 1300 K, (b) 1370 K and (c) 1450 K

dependence of the intensity ratio of the two chemielectron bands seen in Fig. 3 on temperature, that the Ce + $O_2(a \ ^1\Delta_g)$ and Ce + $O_2(X \ ^3\Sigma_g)$ reactions have significant activation energies whereas the Ce + O(³P) reaction does not. This point will be discussed later.

Neither of the two bands assigned as arising from the $Ce + O_2(a^{-1}\Delta_o)$ and $Ce + O(^{3}P)$ reactions exhibited vibrational structure. The associative ionization reaction [reaction (1)] between cerium and O(³P) is exothermic by 2.86 ± 1.78 eV and consequently this amount of energy should be available to the products of the reaction in the form of internal excitation energy and kinetic energy. Clearly, if the product electrons are emerging from reaction (1) (with M = Ce) with a kinetic energy of only 0.13 ± 0.06 eV (at the band maximum), then the CeO⁺ ion must be taking up the excess $2.73 \pm 1.84 \mbox{ eV}$ of energy in the form of either electronic or vibrational excitation energy at this point on the chemielectron band. Since no vibrational structure is resolved in the chemielectron spectrum for the $Ce + O(^{3}P)$ reaction, it seems likely that the product ion CeO⁺ is formed in a highly vibrationally excited state, resulting in transitions from an autoionizing state, CeO*, to the closely spaced vibrational levels on the ionic state potential curve (Fig. 4).

The separation of the zeroth vibrational levels in $O_2(a \ ^1\Delta_g)$ and $O_2(X \ ^3\Sigma_g^-)$ is 0.98 eV.²³ Assuming that the band maximum of the electron kinetic energy distribution measured for the Ce + $O_2(X \ ^3\Sigma_g^-)$ associative ionization reaction [reaction (2)] of 0.90 \pm 0.04 eV is a lower limit of the exothermicity of this reaction, then the energy available to the products of the Ce + $O_2(a \ ^1\Delta_g)$ associative ionization reaction [reaction (3)] must be at least 1.88 \pm 0.04 eV. Clearly then, the measured value for the band maximum of 1.83 \pm 0.10 eV electron kinetic energy for this reaction indicates that the product CeO₂⁺ ion is in the same electronic state as that of the CeO₂⁺ formed from the Ce + $O_2(X \ ^3\Sigma_g^-)$ reaction. A schematic potential-energy diagram describing the Ce + $O_2(a \ ^1\Delta_g)$ reaction is presented in Fig. 5. In practice, although qualitative information could be obtained from the chemielectron spectral intensity changes, relative reaction cross-sections could be calculated only for the chemiion experiments. Nevertheless, it was evident from the measured differences in the chemielectron band intensities at the highest experimental furnace temperatures, that the cross-section for the Ce + O(³P) reaction [reaction (1)] was several hundred times larger than the cross-section for the Ce + O₂(X ${}^{3}\Sigma_{e}^{-}$) reaction [reaction (2)] (consistent with the cross-section ratio measured in a molecular-beam study of *ca*. 330 : 1¹⁵) and was of the same order of magnitude as the cross-section for the Ce + O₂(a ${}^{1}\Delta_{e}$) reaction [reaction (3)].



reaction coordinate

Fig. 4 Schematic potential-energy diagram for the $Ce + O_2(^{3}P)$ reaction



Fig. 5 A schematic potential-energy diagram for the Ce + O₂(a ${}^{1}\Delta_{g})$ reaction. The dotted curve represents schematically the position of the excited state obtained from the Ce + O₂(X ${}^{3}\Sigma_{g}^{-1}$ reaction

In order to relate the chemiion signals with the chemielectron signals, the relative reaction cross-sections for production of a particular ionic product (in this case either CeO^+ or CeO_2^+) were calculated from the chemilon signal intensity changes as a function of discharge conditions (i.e. discharge off or discharge on, with and without glass wool). Representative chemiion mass spectra for the three experimental conditions are shown in Fig. 6. In Fig. 6(a) the discharge is off and the ratio CeO_2^+ : CeO^+ recorded from spectra of this type averaged from all the recorded experimental mass spectra, is (6 ± 1) : 1. A chemiion mass spectrum obtained with the discharge on is shown in Fig. 6(b). The intensity of the CeO⁺ signal is now greater than that of the CeO_2^+ signal. In fact, the measured ratio CeO_2^+ : CeO^+ , averaged from a large number of experimental mass spectra of which Fig. 6(b) is representative, is $1 : (3 \pm 1)$, corresponding to a ca. two-fold increase in the CeO_2^+ intensity and a ca. 40-fold increase in the CeO⁺ intensity over the respective CeO₂⁺ and CeO⁺ intensities measured with the discharge off. In Fig. 6(c), glass wool is present in the discharge tube to deactivate the O(³P). The average CeO₂⁺ : CeO⁺ intensity ratio measured under these conditions is (1.4 ± 0.5) :1. This arises as a consequence of a *ca*. two-fold increase in the CeO₂⁺ intensity and a *ca*. 10-fold increase in the CeO⁺ intensities measured with the discharge off.

In order to calculate the relative reaction cross-sections for these reactions, the intensity changes described above must be combined with the relative partial pressures of $O_2(X^{3}\Sigma_{g}^{-})$, $O_2(a^{1}\Delta_{g})$ and $O(^{3}P)$ present in the reaction region for each of the discharge configurations. This may be accomplished by application of the following expression to a particular set of experimental data:

$$\sum_{i} \sigma_{i}^{a} P_{ij} = I_{j}^{a}$$

where σ_i^a denotes the relative cross-section for the chemiionization channel involving reactant *i* and resulting in the production of ion *a*; P_{ij} is the relative partial pressure of oxidant *i*, under the discharge configuration *j*; and I_j^a is the normalized intensity of the signal due to ion *a*, under the discharge configuration *j*.

Use of this expression yields a chemiionization crosssection for production of CeO_2^+ from the $Ce + O_2(a^{-1}\Delta_e)$ reaction of (15 ± 7) : 1, relative to Ce + O₂(X ${}^{3}\Sigma_{g}^{-}$). Similarly, the chemiionization cross-section for production of CeO⁺ from the Ce + O(³P) reaction is (170 ± 60) : 1, relative to CeO⁺ produced from Ce + $O_2(X^{-3}\Sigma_g^{-})$. Additionally, the Ce + $O_2(a \ ^1\Delta_g)$ reaction was found to produce a significant amount of CeO⁺ and the corresponding relative crosssection for this reaction route was calculated as (60 ± 20) : 1. As the data were obtained at furnace temperatures of 1450 + 50 K, these results compare well with the general behaviour exhibited in the chemielectron experiments at a furnace temperature of 1450 ± 50 K, although it was not possible to quantify the chemielectron data in terms of relative reaction cross-sections for the reasons mentioned earlier. However, the chemiion intensity ratios for production of CeO^+ and CeO^+_2 do not compare well with the observed behaviour in the chemielectron experiment performed at the



Fig. 6 Chemiion mass spectra recorded for the reactions (a) Ce + $O_2(X^{3}\Sigma_{g}^{-})$, (b) Ce + $O_2(X^{3}\Sigma_{g}^{-})$, Ce + $O_2(a^{1}\Delta_{g})$ and Ce + $O(^{3}P)$ and (c) Ce + $O_2(X^{3}\Sigma_{g}^{-})$ and Ce + $O_2(a^{1}\Delta_{g})$

lower furnace temperature of 1300 ± 50 K. At this temperature it was not possible to measure the intensity ratio of the chemielectron bands assigned to the associative ionization reactions Ce + O(³P) and Ce + O₂(X ${}^{3}\Sigma_{g}^{-})$ because no electrons were observed when the discharge was switched off, although the ratio is expected to be high. Clearly, at the lowest temperatures at which chemielectron spectra were recorded (1300 K), a significant difference exists between the results obtained from the chemielectron spectra and those obtained from the chemiion mass spectra. This can be explained by considering the effect of the activation energies for the Ce + O₂(X ${}^{3}\Sigma_{g}^{-}$) and Ce + O₂(a ${}^{1}\Delta_{g}$) reactions on the reaction cross-section evaluated from experimental signal intensities obtained at different temperatures. At the lowest temperatures that reasonable chemielectron spectra could be recorded for the Ce + O(³P) reaction [see Fig. 3(a)], the available thermal energy would be insufficient to overcome the activation energy barrier of the Ce + $O_2(X^{3}\Sigma_{g}^{-})$ and the $Ce + O_2(a^{-1}\Delta_g)$ reactions. This would result in only one band being observed in the chemielectron spectrum, assignable to electrons emerging from the Ce + $O(\bar{}^{3}P)$ associative ionization reaction. At higher temperatures [Fig. 3(b) and (c)], the activation energy barriers for the Ce + $O_2(X^{3}\Sigma_{g}^{-})$ and Ce + $O_2(a^{-1}\Delta_e)$ reactions are overcome and three chemielectron bands would become evident in the chemielectron spectrum [although the band due to Ce + O₂(X ${}^{3}\Sigma_{g}^{-})$ is still at least one order of magnitude weaker than the bands arising from the Ce + $O_2(a^{-1}\Delta_g)$ and Ce + $O(^{3}P)$ reactions].

Obviously, much of this discussion is qualitative. Nevertheless, the chemiion spectra are consistent with the assignment of the chemielectron spectra and assist in the understanding of secondary reactions that occur in the reaction cell under the reaction conditions.¹²

La + O₂(X ${}^{3}\Sigma_{g}^{-}$)

10³

counts s⁻

The chemielectron spectrum obtained from the reaction between lanthanum and $O_2(X \ ^3\Sigma_g)$ at a furnace temperature of 1600 \pm 50 K is shown in Fig. 7. A band of some structural complexity was recorded with the photon source off with a maximum measured as 1.03 ± 0.20 eV. The large error

 $O_2(b^4\Sigma_g)$

lamp

off on

Fig. 7 Chemielectron spectrum recorded for the reaction La $+ O_2(X^{-3}\Sigma_g^{-})$

E/eV

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quoted for the position of the band arose because the band maximum moved in position from 1.25 eV (at an estimated furnace temperature of 1500 K) to 0.80 eV (at a furnace temperature of *ca.* 1700 K). In all experiments, as the furnace temperature was increased, so the position of the chemielectron band maximum moved to lower kinetic energy. This point will be discussed later.

The band is more symmetrical in shape than the band obtained for the Ce + $O_2(X \ ^3\Sigma_g)$ reaction and vibrational structure attributable to two different series was resolved in this band (see Fig. 7). The average separations of the components of these two series (denoted X and Y in Fig. 7) were measured at 670 \pm 30 and 655 \pm 30 cm⁻¹.

The chemiion spectrum recorded for this reaction again showed signals due to the metal monoxide and metal dioxide ions (Fig. 8), but in contrast to the Ce + $O_2(X^{3}\Sigma_{g}^{-})$ chemiion spectrum,¹² the LaO⁺ signal was found to be more intense than the LaO_2^+ signal at oxygen partial pressures in the reaction region of between 10^{-4} and 10^{-3} Torr. The experimental variations of the LaO^+ and LaO^+_2 signal intensities with the oxygen partial pressure in the reaction region between 0 and 0.8×10^{-3} Torr are shown in Fig. 9(a) and (b), respectively. At oxygen pressures of $\leq 6 \times 10^{-4}$ Torr, LaO₂⁺ increases with oxygen pressure, but as the pressure is increased above this value a gradual levelling off is observed. Similar behaviour is also noted for the LaO⁺ pressure plot, although the scatter in the data makes it difficult to ascertain the precise point at which this levelling occurs (see Fig. 9). The oxygen pressure dependence plot for the chemielectron signal, presented in Fig. 9(c), exhibits approximately linear behaviour over the full range of oxygen pressures considered. At oxygen partial pressures in the range $(2.0-2.5) \times 10^{-3}$ Torr, the LaO_2^+ : LaO^+ ratio changes in favour of the dioxide ion. The experimental oxygen pressure dependence plot over this range is presented in Fig. 10. Unfortunately, it was not possible to measure chemielectron intensities at oxygen partial pressures $>1 \times 10^{-3}$ Torr. However, the combined effect of these results is that it is difficult to associate either LaO_2^+ or LaO^+ uniquely with the observed chemielectron signal and hence to identify the main chemiionization reaction responsible for the observed chemielectrons. Clearly, evidence from other sources is required to achieve an assignment of the La + $O_2(X^3\Sigma_8^-)$ chemielectron spectrum and this is presented later.

A kinetic model of the La + $O_2(X^{3}\Sigma_g^{-})$ system can be considered as it may provide some evidence towards identifying a dominant reaction channel.







Fig. 9 Experimental oxygen dependence plots of (a) [LaO⁺], (b) [LaO₂⁺] and (c) [e⁻], for the La + O₂(X ${}^{3}\Sigma_{g}^{-})$ reaction in the oxygen pressure range 0–0.8 mTorr. All points have been normalised to the largest value

As in the Ce + $O_2(X^{3}\Sigma_g^{-})$ case¹² eight possible reactions were considered in constructing a reaction scheme for the La + $O_2(X^{3}\Sigma_g^{-})$ system (Table 1).

Unfortunately, fewer thermochemical data are available for the La + $O_2(X \ ^3\Sigma_g^-)$ system than the Ce + $O_2(X \ ^3\Sigma_g^-)$ system. Nevertheless, use can be made of the data in ref. (12) and (24)-(31) together with a value of 9.5 ± 1.5 eV for the first ionization energy of LaO₂, estimated by comparison with the known value for CeO₂, ²⁸ to obtain reaction enthalpies for each of the reactions (4)-(11). Comparison of the reaction enthalpies obtained with those calculated for the Ce + $O_2(X \ ^3\Sigma_g^-)$ system¹² shows very similar trends. Reaction (4) would seem to be the favoured chemiionization channel for reaction of La with $O_2(X \ ^3\Sigma_g^-)$ since it is the only che-



Fig. 10 Experimental oxygen pressure dependence plots for $[LaO_2^+]$ (+) and $[LaO^+]$ (\bigcirc) for the La + $O_2(X \ ^3\Sigma_g^-)$ reaction, in the oxygen pressure range 0–2.5 mTorr

Table 1 Reactions considered in constructing a reaction scheme for the La + $O_2(X^3\Sigma_a^-)$ system^{*a*}

	$\frac{\Delta H_{r}}{/eV}$	k/cm^3 molecule ⁻¹ s ⁻¹	
$La + O_2 \rightarrow LaO_2^+ + e^-$	-1.08 ± 1.95	1.5×10^{-12}	(4)
$La + O_2 \rightarrow LaO^+ + O^-$	$+0.41 \pm 0.32$	9.0×10^{-14}	(5)
$La + O_2 \rightarrow LaO^+ + O + e^-$	$+1.87 \pm 0.40$	1.0×10^{-12}	(6)
$La + O_2^- \rightarrow La^+ + O_2^-$	$+5.11 \pm 0.10$	1.0×10^{-18}	(7)
$La + O_2 \rightarrow LaO + O$	-3.08 ± 1.18	1.0×10^{-11}	(8)
$La + O \rightarrow LaO^+ + e^-$	-3.29 ± 0.32	6.2×10^{-10}	(9)
$LaO^+ + O_2 \rightarrow LaO_2^+ + O$	$+2.00 \pm 0.68$	1.0×10^{-14}	(10)
$LaO_2^+ + La \rightarrow LaO^+ + LaO$	-5.29 ± 2.36	1.0×10^{-10}	(11)

" See text for further details.

miionization route which is sufficiently exothermic to produce electrons under thermal conditions. However, as in the Ce + $O_2(X \ ^3\Sigma_g^-)$ case, the neutral reaction (8) is highly exothermic and the O atoms produced would be expected to undergo an associative ionization reaction with La [reaction (9)], to produce LaO⁺ and e⁻.

As in the Ce + $O_2(X^{3}\Sigma_{g}^{-})$ case,¹² the rate constants for reactions (4), (5), (6) and (9) were calculated from the available cross-sections measured by Fite *et al.*,¹⁵ assuming a reaction temperature of 1000 K. Also as in ref. 12, the remaining rate constants were estimated by using the calculated reaction enthalpies as an approximate guide. The reaction time after which ion and electron intensities were measured was estimated as 4 ms, from flow-rate measurements. Simulations were therefore carried out for reaction times in the range 1–8 ms.

A plot of the computed concentrations of LaO_2^+ , LaO^+ and e⁻ as a function of reaction time in the range 1-8 ms and at initial partial pressures of the reactants, La and O₂, of 1×10^{-4} Torr is shown in Fig. 11(a). The vapour pressure of lanthanum at 1600 K was obtained from ref. 29. For reaction times of up to 8 ms, the LaO⁺ concentration was found to be substantially greater than the LaO_2^+ concentration, which at least qualitatively agrees with the relative intensities of the two ions observed in the experimental chemiion spectrum recorded for pressures $< 8 \times 10^{-4}$ Torr in the reaction region (Fig. 10). Plots of the individual contributions of reactions (9) and (11) to the total LaO^+ concentration and of reactions (4) and (9) to the total electron concentrations are presented in Fig. 11(b). No plot for the contributions of individual reactions to the LaO_2^+ concentration is presented because reaction (4) is the only reaction to contribute significantly to the production of LaO_2^+ . These plots indicate that one of the major sources of both LaO^+ and electrons is reaction (9). Note that reaction (5) also contributes to the total LaO⁺ concentration but to a far smaller extent than reactions (9) and (11) and for this reason has been excluded from Fig. 11(b). Additionally, although reaction (6) will in principle contribute to the LaO⁺ and electron concentrations, it has been excluded from Fig. 11(b) because its contributions were found to be small [although it has been included in the full kinetic scheme used to obtain the results presented in Fig. 11(a)].

The simulated dependence of the product ion and electron concentrations on the initial partial pressure of oxygen proved to be more revealing. The computed pressure dependence plot of the LaO_2^+ , LaO^+ and e^- concentrations over the oxygen pressure range 0–0.1 Torr is shown in Fig. 11(c). Clearly, the dominant ion is the monoxide ion up to 0.01 Torr. Thereafter the LaO^+ concentration decreases, while the LaO_2^+ concentration continues to increase until the LaO_2^+ : LaO^+ concentration ratio changes in favour of the dioxide ion at 0.06 Torr. This behaviour is in good qualitative agreement with the behaviour seen in the experimental pressure plots (see Fig. 10).



Fig. 11 (a) Computed plots of $[LaO_2^+](\times)$, $[LaO^+](+)$ and $[e^-](\bigcirc)$ as a function of reaction time, for the La + $O_2(X^{3}\Sigma_{g}^{-})$ reaction. (b) Computed plots of the contributions of the reactions involved in the La + $O_2(X^{3}\Sigma_{g}^{-})$ reaction to production of $[LaO^+]$ and $[e^-]$, as a function of reaction time. (c) Computed oxygen pressure dependence plots for $[LaO_2^+]$, $[LaO^+]$ and $[e^-]$ for the La + $O_2(X^{3}\Sigma_{g}^{-})$ reaction in the oxygen pressure range 0–100 mTorr. See text for details of the method used

It would be sensible at this stage not to draw any firm conclusions from the results of the kinetic model discussed above. Nevertheless, it does prove to be a useful exercise in building up to a qualitative picture of the overall reaction scheme. For example, it seems reasonable to conclude that the chemielectron band in Fig. 7 is due to electrons from the two competing associative ionization processes (4) and (9), since neither reaction has been shown to be sufficiently dominant under the reaction conditions used, to enable an assignment of the chemielectron spectrum exclusively to one reaction.

Since reaction (9) is almost certainly contributing to the chemielectron band shown in Fig. 7, the obvious way of investigating this is to record the chemielectron spectrum for the reaction between lanthanum and oxygen atoms by producing the latter using a microwave discharge in molecular oxygen.

La + O(³P); La + O₂(a ${}^{1}\Delta_{s}$)

The chemielectron spectrum recorded for the reaction between La and a mixture of $O_2(X^{3}\Sigma_{g}^{-})$, $O_2(a^{1}\Delta_{g})$ and $O(^{3}P)$, is shown in Fig. 12. With the microwave discharge on, two chemielectron bands were recorded, with the photon source off, having band maxima at 0.67 ± 0.06 and 2.41 ± 0.06 eV electron kinetic energy. No vibrational structure was observed on either band and the average intensity ratio of these bands was measured as (3.2 ± 0.5) : 1, respectively. No correction for the transmission function of the spectrometer has been made in the relative band intensity ratio quoted. When the discharge was switched off, both bands disappeared to reveal the chemielectron band at 1.03 ± 0.20 eV. The band at 0.67 ± 0.06 eV has a measured signal intensity ca. 100 times greater than that of the band observed with the discharge off, whilst the band at 2.41 ± 0.06 eV is ca. 30 times more intense than the band observed with the discharge off. All intensities quoted were measured at oxygen partial pressures in the reaction region of up to 10^{-3} Torr.

The ion spectrum recorded with the discharge on shows an increase in the LaO⁺ signal intensity compared with that observed with the discharge off, but no apparent increase in the LaO⁺₂ signal intensity was observed. This is somewhat surprising, as it might be expected that a reaction between La and $O_2(a \ ^1\Delta_g)$ would produce a significant increase in the dioxide ion partial pressure, as was observed in the cerium case, owing to an associative ionization reaction between the two reactants. Secondary reactions (9)-(11) will, however, affect the observed LaO⁺₂ and LaO⁺ signal intensities.

The conclusion that was drawn from these observations was that the two bands centred at 0.67 ± 0.06 eV and 2.41 ± 0.06 eV in Fig. 12 must arise from reactions between



Fig. 12 Chemielectron spectra recorded for the reactions (a) $La + O({}^{3}P) + O_{2}(a {}^{1}\Delta_{g}) and (b) La + O_{2}(X {}^{3}\Sigma_{g}^{-})$

La and O(³P), and La and O₂(a ¹ Δ_g). In order to assign these bands positively, the experiment was repeated with glass wool in the discharge tube. The result of this experiment was that only the band centred at 2.41 ± 0.06 eV was observed when the discharge was switched on (Fig. 13), thus allowing assignment of this band to a chemiionization reaction between lanthanum and O₂(a ¹ Δ_g). The band centred at 0.67 ± 0.06 eV electron kinetic energy in Fig. 12 can now be confidently assigned to reaction (9), and the band centred at 1.03 ± 0.20 eV in Fig. 7 can be assigned to reaction (4). In view of the fact the measured maximum of the band assigned to reaction (9) (0.67 ± 0.06 eV) lies within the lower kinetic energy side of the band in Fig. 7, it seems likely that reaction (9) is contributing to the chemielectron band recorded from



Fig. 13 The chemielectron spectrum recorded for the La + $O_2(a^{-1}\Delta_e)$ reaction

The ratios of the discharge on : discharge off chemielectron band intensities can provide approximate estimates for the relative chemiionization cross-sections for each of the reactions contributing to the observed chemielectron band envelopes recorded in Fig. 7, 12 and 13. The method used is identical to that described earlier for the calculation of the relative reaction cross-sections from chemiion spectral intensity changes for the analogous reactions involving cerium. In this way the relative chemielectron reaction cross-sections, σ , for each of the reactions La + O₂(X ${}^{3}\Sigma_{g}^{-}$), La + O₂(a ${}^{1}\Delta_{g}$) and La + O(${}^{3}P$) have been calculated as 1 : (80 ± 20) : (750 ± 180) at an oxygen pressure in the reaction cell of 10⁻³ Torr.

Some discrepancy occurs when the cross-sections are evaluated from the chemiion mass spectra. Representative chemiion mass spectra for the three discharge conditions are presented in Fig. 14. In Fig. 14(a) the discharge is off and the average intensity ratio of LaO_2^+ : LaO^+ is $1:(3 \pm 1)$ at a pressure in the reaction cell of *ca*. 10^{-3} Torr. A typical chemiion mass spectrum obtained with the discharge on [see Fig. 1(b)] is presented in Fig. 14(b). The intensity of the LaO⁺ signal has increased to the point where it is ca. 26 times more intense than the LaO_2^+ signal. This arises from a ca. nine-fold increase in the LaO⁺ signal intensity. In Fig. 14(c) glass wool is present in the discharge tube to deactivate the $O(^{3}P)$. The measured intensity ratio LaO_2^+ : LaO^+ averaged from a number of spectra of the type presented in Fig. 14(c) is 1 : (6 ± 4) which is accounted for by a *ca*. two-fold increase in the LaO⁺ intensity over that recorded with the discharge off. These intensities convert, using the method described previously, to relative reaction cross-sections for production of LaO⁺ from the three reaction routes, La + O₂(X ${}^{3}\Sigma_{o}$), La $+ O_2(a^{-1}\Delta_{e})$ and La + O(³P), of 1 : (6 ± 4) : (35 ± 15), respectively. For production of LaO_2^+ , relative cross-sections of 1: (1.0 \pm 0.1) for La + O₂(X ${}^{3}\Sigma_{g}^{-}$) and La + O₂(a ${}^{1}\Delta_{g}$) were obtained. Although these are qualitatively in agreement with



Fig. 14 Chemiion mass spectra recorded for the reactions (a) La + $O_2(X^3\Sigma_g^-)$, (b) La + $O_2(X^3\Sigma_g^-)$, La + $O_2(a^1\Delta_g)$ and La + $O(^3P)$ and (c) La + $O_2(X^3\Sigma_g^-)$ and La + $O_2(a^1\Delta_g)$

the chemielectron-derived values, they are quantitatively very different. One reason for this large difference may arise because the ions observed in the chemiion experiments are extracted from the reaction cell under relatively high pressure conditions and their concentrations will be affected by secondary reactions. For example, LaO₂⁺ produced by reaction (4) will react rapidly via reaction (11). This would reduce the observed LaO_2^+ signal relative to LaO^+ . Also, if the massspectrometric results were obtained at a temperature somewhat higher than that used to obtain the chemielectron spectra, as appears to be the case experimentally, then the effects of activation energy differences between the three associative ionization reactions, La + O₂(X ${}^{3}\Sigma_{g}^{-}$), La + O₂(a ${}^{1}\Delta_{g}$) and La + $O(^{3}P)$, would become evident on comparison of the derived cross-section values from the two experimental methods. At the higher temperatures, the activation energy of the La + $O_2(X^{3}\Sigma_{g}^{-})$ reaction is overcome and this reaction contributes more to the overall reaction scheme with the discharge on relative to the La + O(³P) and La + O₂(a ${}^{1}\Delta_{g}$) reactions. At lower temperatures, the La + $O_2(a^{-1}\Delta_g)$ and $La + O(^{3}P)$ reactions dominate to a much larger extent over the La + ${\rm O}_2(X~^3\Sigma_g^-)$ reaction and this is reflected in the calculated chemielectron reaction cross-sections. It should also be remembered that the two sets of data were recorded on two separate instruments and this potentially introduces a number of instrumental factors which may affect the validity of direct comparisons.

Comparison of the available reaction enthalpy and the product electron kinetic energy, measured from the chemielectron band maximum, for the reactions of lanthanum with $O_2(a \ \Delta_g)$ and $O(^3P)$ shows similar trends to that of the cerium case discussed earlier. The associative ionization reaction (9) between La and $O(^3P)$ is exothermic by 3.29 ± 0.32 eV and so this energy should be available to the products of the reaction. In this case, the observed chemielectrons are emerging from reaction (9) with a kinetic energy of 0.67 ± 0.06 eV at the band maximum, which leaves an excess of 2.62 ± 0.38 eV of energy to be taken up by the product LaO⁺ ion in the form of internal excitation energy, for the autoionizing transition corresponding to the band maximum.

The relationship between the reaction enthalpy (as calculated from available literature data) and the experimental electron kinetic energy can be investigated in more detail by measuring the onset on the high electron kinetic energy (e.k.e.) side of the chemielectron band as well as the band maximum. This has been done for the six reactions investigated and the values obtained are listed in Table 2.

The high e.k.e. onset, when reduced by the excitation energy in the reactant channel at the temperatures used (estimated for the reactions studied as 0.15 eV), will provide a lower limit for the exothermicity of the reaction studied, as the Franck-Condon factors in the region of the onset will be very low and the true high e.k.e. onset may not be observed.

If the M + O values listed in Table 2 are considered first, it can be seen that for the both the La + O and Ce + O reactions, the high e.k.e. onset is less than the expected reaction

exothermicity by >1 eV. This indicates that even at the chemielectron band onset an appreciable fraction of the reaction exothermicity is retained in the ion.

For the La + O₂(X ${}^{3}\Sigma_{g}^{-}$) and La + O₂(a ${}^{1}\Delta_{g}$) reactions, although the errors on the calculated heats of reaction are larger, it appears that at the high e.k.e. band onset almost all of the reaction enthalpy is converted to electron kinetic energy. A similar situation is expected to occur in the analogous cerium reactions, although in this case the high e.k.e. onsets measured for the Ce + $O_2(X^{-3}\Sigma_g^{-1})$ and Ce + $O_2(a^{-1}\Delta_g)$ reactions are inconsistent with available reaction enthalpies (the ΔH values evaluated from available literature data are too positive by at least 1.5 eV). The only conclusion that can be drawn from these measurements is that the thermodynamic data used to calculate ΔH for the Ce + O₂(X ${}^{3}\Sigma_{e}^{-}$) and $Ce + O_2(a^{-1}\Delta_e)$ reactions listed in Table 2 are unreliable. In ref. 12, the atomization energy of CeO_2 and the first adiabatic ionization energy of CeO₂ was used to calculate ΔH for the Ce + O₂(X ${}^{3}\Sigma_{g}^{-}$) reaction.

Having assigned the main chemielectron band recorded for the reaction between lanthanum and $O_2(X^{3}\Sigma_{g}^{-})$ to the associative ionization process which produces LaO_2^+ , attention can now be given to the two vibrational series observed in this band which must be associated with vibrational modes in LaO₂⁺. If the LaO₂⁺ and LaO₂^{*} states involved in the autoionization process possess a C_{2v} or $D_{\infty h}$ equilibrium geometry, then the asymmetric stretching mode, v_3 , can be ruled out as a contributor to the structure seen in the band, as it will be forbidden in single-quantum transitions. To our knowledge, no experimental values for the two singlequantum-allowed modes, v_1 and v_2 , have been reported in the literature for either LaO_2^+ or LaO_2 . However, inspection of the results of matrix-isolation infrared spectroscopic studies on the dioxides of other lanthanide elements³⁰⁻³² suggests that the bending mode, v_2 , of LaO₂⁺ will be of the order of 200 cm⁻¹ or less. Since the average separations of the components in the two vibrational series (655 \pm 30 and 670 ± 30 cm⁻¹) are much larger than this value, the two series cannot be assigned to progressions in both the v_1 and v_2 modes. A more plausible explanation is that both series correspond to excitation in v_1 but that they differ by one quantum in the v_2 mode. This suggestion is supported by the fact that the two series are displaced from one another by 250 ± 50 cm⁻¹, which is in reasonable agreement with the estimate made above for the value of the v_2 mode in the ion of 200 cm⁻¹. Alternatively, if the LaO₂^{*} state has a C_s or $C_{\infty v}$ equilibrium geometry (i.e. an La-O-O structure), then all three vibrational modes would be expected to contribute to the observed chemielectron band.

As with the Ce + $O_2(X \ {}^3\Sigma_g^-)$ associative ionization reaction,¹² the classical turning-point mechanism may be invoked in order to explain the vibrational structure in terms of a potential-energy diagram and a schematic diagram for the lanthanum plus oxygen chemiionization reaction is shown in Fig. 15. A rather shallow potential-energy curve describing the autoionizing state of neutral LaO₂ can be used to explain

Table 2 Comparison of the high e.k.e. band onsets, band maxima and calculated heats of reaction for the reactions studied in this work

reaction	band maximum/eV	high e.k.e. band onset ^a /eV	heat of reaction ^{b} /kJ mol ⁻¹
$Ce + O_2(X^{3}\Sigma_g^{-}) \rightarrow CeO_2^{+} + e^{-}$ $Ce + O_2(a^{-1}\Delta_g) \rightarrow CeO_2^{+} + e^{-}$	0.90 ± 0.04 1.83 ± 0.10	$2.4 \pm 0.1 \\ 3.1 \pm 0.3 \\ 0.1 $	$+0.49 \pm 0.42$ -0.41 ± 0.42
$Ce + O(^{3}P) \rightarrow CeO^{+} + e^{-}$ $La + O_{2}(X \ ^{3}\Sigma_{g}^{-}) \rightarrow LaO_{2}^{+} + e^{-}$ $La + O_{3}(a \ ^{1}\Delta_{2}) \rightarrow LaO_{3}^{+} + e^{-}$	0.13 ± 0.06 1.03 ± 0.20 2.41 ± 0.06	$\begin{array}{c} 0.9 \pm 0.1 \\ 1.5 \pm 0.1 \\ 3.3 \pm 0.1 \end{array}$	-2.86 ± 1.78 -1.08 ± 1.95 -2.06 ± 1.95
$La + O(^{3}P) \rightarrow LaO^{+} + e^{-}$	0.67 ± 0.06	1.8 ± 0.1	-3.29 ± 0.32

" This work. ^b Calculated from available thermochemical data (see text).



Fig. 15 Schematic potential-energy diagram for the La + $O_2(X^{-3}\Sigma_g^{-})$ reaction

the shifts in band maximum of the electron kinetic energy distribution for small changes in $k_{\rm B}T$. As can be seen in the schematic diagram in Fig. 15, as the temperature increases, the turning point moves to a smaller reaction coordinate and the autoionization transition takes place to a point on the ionic potential-energy surface higher in energy. The result of this is that the band maximum of the electron distribution moves to lower kinetic energy as the temperature increases, as is observed experimentally.

As with cerium, it is clear that in order to achieve a more complete understanding of the overall reaction scheme involved in these chemiionization reactions, more precise kinetic and thermodynamic data are needed together with a temperature dependence study of the reaction cross-sections.

In conclusion, cerium and lanthanum show a number of similarities in the chemijonization reactions studied. From the measured onsets on the high-kinetic-energy side of the chemielectron bands for the M + O₂(X ${}^{3}\Sigma_{e}^{-}$) and M + O₂(a ${}^{1}\Delta_{g}$) reactions, most of the reaction exothermicity is converted into electron kinetic energy. Alternatively, for the $M + O(^{3}P)$ reactions studied, the electron carries away only a fraction of the available energy and most of the excess energy is retained in the product ion. Experiments are currently in progress on the reactions of other lanthanides (Pr, Nd, Sm, Eu and Gd) with the three oxidants used in this work. Available thermodynamic data show that on moving across the lanthanide series the heats of reaction of the associative ionization reactions become more positive. It will, therefore, be of interest to investigate how the excess energy is partitioned between the chemielectron and the product ion in each case.

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