Kinetic Investigation of the Reaction $Sr(^1S) + O_2 + He$ in the Temperature Range from 303 to 968 K

C. Vinckier* and J. Helaers

Department of Chemistry, KU Leuven, Celestijnenlaan 200F, 3001 Heverlee, Belgium

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A kinetic study of the third-order recombination reaction $Sr(^1S) + O_2 + He \xrightarrow{k_1(He)} SrO_2 + He$ has been carried out in a fast-flow reactor in the temperature and pressure range of respectively 303−968 K and 6−12 Torr. Strontium atoms were generated by thermal evaporation of strontium metal pellets and then monitored by atomic absorption spectroscopy (AAS). The Arrhenius plot shows a departure from linearity above 500 K. The modified Arrhenius expression taking into account a temperature dependence of the preexponential factor for the entire temperature range results in the expression $k_{1_{Sr}}(He) = [(1.9 \pm 0.3) \times 10^{-23}]T^{-1.7}$ exp-$[(-12.1 \pm 0.8 \text{ kJ mol}^{-1})/RT]$ cm^6 molecule^{-2} s^{-1}. The best representation of the temperature dependence is given by the polynomial fit $\log k_{1_{Sr}}(He) = -60.83 + 22.44(\log T) - 3.89(\log T)^2$. A lower limit to the bond energy of the $SrO_2(^3A_2)$ reaction product is estimated by means of the method based on the expression of the equilibrium constant and the theory of statistical mechanics. A value of $D_0 > 244$ kJ mol^{-1} was obtained, which is in the range of the values derived from ab initio calculations.

Introduction

Oxidation reactions of gaseous metal atoms have gained considerable attention over the past few decades because of a large variety of possible applications. One of these is situated in the field of combustion, where metals are added as fuel additives for the propulsion of rocket engines. It has been proven that they increase the flame temperature and also the efficiency.[1,2] Recently it has been mentioned that metal/N_2O reactions in incinerators may reduce the emission of the greenhouse gas N_2O.[3] Atmospheric chemists are also interested in metal atom reactions with molecular oxygen. Different studies have indicated that in the mesosphere, i.e., at a height of approximately 90 km, quite high concentrations of neutral metal atoms are present. Their most important source is the evaporation of meteoroids.[4−6] However, the abundance of the atoms observed in the mesosphere is quite different from the relative concentrations present in the meteoroids[6] and their concentrations also show a totally different seasonal dependence.

The simulation of combustion processes and atmospheric chemistry requires detailed reaction mechanisms, including the rate constants of a large number of elementary reactions.[3,7] A survey of much of the research work in metal atom kinetics carried out during the last years has been described in ref 8. While the alkali- and transition-metal atom/O_2 reactions have been studied extensively over a wide temperature range,[4,7,9−16] much less kinetic information is available on the alkaline-earth-metal atom/O_2 reactions.

Up till now, kinetic measurements for both magnesium and calcium atom reactions with molecular oxygen in the temperature range from 303 to 1000 K have been carried out by means of different experimental techniques.[9,17,18] The $Mg(^1S) + O_2 + N_2$ reaction has been investigated by means of a static-flow technique, in which the Mg atoms were produced by heating metal chips to 600−700 K and were detected by time-resolved laser-induced fluorescence (LIF).[9] The $Ca(^1S) + O_2 + M$ ($M = N_2$, He) reaction was studied by the same group of workers, using the pulsed laser photolysis of a Ca atom precursor, also followed by time-resolved LIF of the resulting Ca atoms.[9]

Vinckier at al.[17,18] used a fast-flow reactor technique with thermal vaporization of the metal as the source of the Mg and Ca atoms in the gas phase with atomic absorption spectroscopy as the detection technique. Excellent agreement has been observed between both techniques for the determination of the rate constant of the Mg/O_2 reaction.

While the results of the Ca/O_2 reaction matched in the temperature range from 230 to 330 K, a large discrepancy showed up at higher temperatures. The fast-flow-tube work[18] yielded a value for $k_{1_{Ca}}(He)$ which was about a factor of 100 larger at 1100 K than $k_{1_{Ca}}(He)$ derived from the photolysis−LIF measurements.[9] This was mainly due to the fact that the activation energy E_a, derived on the basis of the fast-flow-tube results, was higher than the value derived by means of the photolysis−LIF method.

The alkaline-earth-metal/O_2 reactions will now be extended with the reaction of strontium atoms. Kinetic data on the Sr/O_2 reaction will be presented covering the temperature range from 303 to 968 K:

$$Sr(^1S) + O_2 + He \rightarrow SrO_2 + He \tag{1}$$

In the case of the Sr/O_2 reaction it needs to be pointed out that the bimolecular reaction path $Sr(^1S) + O_2 \rightarrow SrO + O$ is too endothermic ($\Delta H = 71.6$ kJ mol^{-1})[19] to compete with the third-order reaction in the temperature range from 303 to 1000 K.

The experiments were carried out in a fast-flow reactor using atomic absorption spectroscopy (AAS) as the detection technique for the thermally evaporated strontium atoms.

This work aims to explore the trend in the activation energies of the recombination reactions with molecular oxygen, which appear to decrease according to the series $E_a(Mg/O_2) > E_a(Ca/O_2) > E_a(Sr/O_2)$. This trend can be understood in relation to the ionization energy of the metal, since a metal−O_2 complex is formed with a partial ionic character.[20,21]

These activation energies leading to a positive temperature dependence of the rate constant are rather unusual for third-

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order reactions, but they are related to the closed-shell configuration of the alkaline-earth-metal atom. This has also been seen for the $Fe + O_2 + N_2$ reaction, in which the iron atom has a $3d^6 4s^2$ configuration and which shows an activation energy of (16.94 ± 0.67) kJ mol^{-1}.[16] Finally the occurrence of activation energies has been confirmed by ab initio calculations.[9,16,20]

It will be pointed out that the $Sr(^1S) + O_2 + He$ reaction follows an Arrhenius behavior up to about 500 K, after which the curve flattens out. The bond energy of SrO_2 will be estimated using a method based on the expression of the equilibrium constant in combination with the theory of statistical mechanics. This experimentally obtained value will be compared with the values derived by means of ab initio calculations.[22]

Experimental Technique

The experimental setup has been amply described in earlier publications,[18,20,23,24] and only a brief summary will be presented here. It contains two major parts: a fast-flow reactor under low pressure and an atomic absorption detection technique (AAS). The reactor consists of a quartz tube with an internal diameter L of 5.7 cm and a length of 100 cm. At the upstream end a sample holder contained strontium pellets, which were thermally evaporated at 600−700 K by means of a kanthal resistance wire. By means of the carrier gas helium, strontium atoms were transported downstream in the kinetic zone, where they were mixed with an excess of molecular oxygen. The flow velocity v_g of the carrier gas helium is 320 ± 10 cm s^{-1} at 303 K. The temperature in the kinetic zone could be varied between 303 and 1000 K by means of an oven, and the temperature was monitored by a chromel−alumel thermocouple. Strontium atoms were detected by atomic absorption spectroscopy (AAS) at 460.7 nm.

Assuming that the detection limit corresponds to an absorbance of $A = 0.005$, one can calculate the detection limit for strontium atoms on the basis of a formalism explained in our earlier work:[25] $[Sr] = C_1 A L^{-1} T_g^{1/2}$, in which C_1 is a proportionality constant, L the optical path length (5.7 cm), and T_g the gas temperature. With a value for $C_1 = 0.428 \times 10^{10}$ cm^{-2} $K^{-1/2}$ at 500 K,[26] one can calculate the detection limit for strontium atoms as equal to 8.4×10^7 atoms cm^{-3} or 0.72 ppb at 6 Torr and 500 K.

Minimum distances between the Sr atom source, the oxygen inlet, and the kinetic zone were maintained to allow for sufficient mixing of the reagents.[23,24] In the kinetic measurements the decay of the strontium absorbance was followed as a function of the axial distance along the fast-flow reactor. This was realized by moving the entire reactor assembly along its axis relative to the detection equipment, which remained at a fixed position. An advantage of this technique is that relative positions of the Sr atom source and the O_2 inlet remain constant during the experiments. Reproducible absorbances could be maintained within 10% when the temperature T_s of the strontium pellets was stabilized within ±1%.

The gases used were helium N4.5, a 1.00% mixture of oxygen in argon N5.0 and a 5.04% mixture of oxygen in helium N4.5 from UCAR. The strontium pellets (Aldrich) had a purity of about 99.0%.

The statistical analysis of the plots, i.e., weighted regressions, were made using the statistical SAS package.[27] The quoted errors σ were the standard deviations.

Results and Discussion

Determination of the Rate Constant k_1(He) of the Sr (^{1}S) + O_2 + He Reaction. The kinetic formalism used in the derivation of the rate constant of the $Sr(^1S) + O_2 + He$ reaction has already been described in previous papers:[23,24]

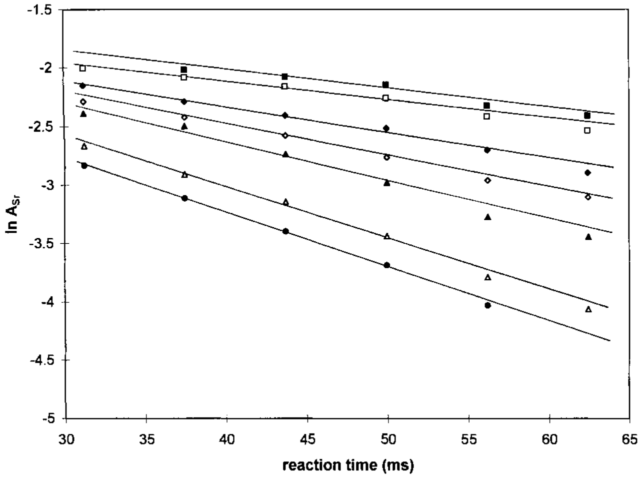

Figure 1. Natural logarithm of the Sr atom absorbance as a function of the reaction time t with various amounts of molecular oxygen added: The experimental conditions are $T_g = 303$ K, $P_r = 9$ Torr, He as carrier gas. $[O_2]$ (10^{12} molecules cm^{-3}): (■) 0; (□) 0; (◆) 3.5; (◇) 6.3; (▲) 9.1; (△) 15.0; (●) 17.0.

$$\ln A_{Sr} = -\left\{\frac{k_1(\mathrm{He})[\mathrm{O_2}][\mathrm{He}]}{\eta} + \frac{7.34 D_{Sr/He}}{2r^2}\right\} t + B \qquad (2)$$

in which ln A_{Sr} is the natural logarithm of the strontium absorbance, η a correction factor depending on the flow characteristics, $D_{Sr/He}$ the binary diffusion coefficient of Sr atoms in the carrier gas helium, r the reactor radius, t the reaction time, and B an integration constant. The correction factor η is related to the flow characteristics, and the determination of its magnitude has been amply discussed elsewhere.[28]

The use of eq 2 for obtaining kinetic parameters has been well-illustrated in our earlier work[10,24] and will only briefly be summarized here. The value of k_1(He) is determined by following first ln A_{Sr} as a function of the reaction time t at various amounts of O_2 added. A weighted linear regression of ln A_{Sr} versus t is carried out, taking into account a statistical error for ln A_{Sr}, which at average varies between 10.7 and 13.3% as one goes from the highest to the lowest value of ln A_{Sr}. Figure 1 shows an example of the pseudo-first-order decays of $Sr(^1S)$ atoms as a function of the reaction time at a temperature $T_g =$ 303 K and a pressure P_r of 9 Torr for various initial O_2 concentrations. In the next step the slopes S of these lines are plotted versus the added $[O_2]$ and a weighted linear regression results in a straight line with a slope equal to the pseudo-second-order rate constant $k'_1 = k_1(\mathrm{He})[\mathrm{He}]/\eta$, as is illustrated in Figure 2 for three different temperatures: 303, 600, and 839 K. In some cases the magnitude of the intercept of this graph is larger than 2 times its standard deviation, which implies that plug flow conditions do not prevail. In these cases the factor η is set equal to 1.3 with an associated systematic error of 10%.[28] In other cases the magnitude of the intercept is about equal to $7.34 D_{Sr/He}/2r^2$ and a correction factor of 1.6 will be used. The uncertainties σ_S and σ_k for the calculated values of the slope S and the rate constant k_1(He) are calculated by combining the uncertainties of several variables such as temperature, flow velocity, reactor radius, and total pressure according to the method explained by Howard.[29] Finally, in the case where the correction factor 1.3 was used, the systematic error of 10% was

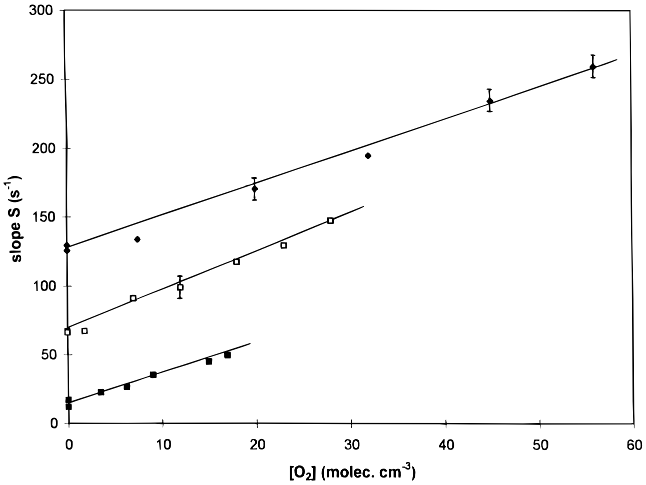

Figure 2. Slopes S (Figure 1) as a function of the added O_2 concentration. The experimental conditions are $P_r = 9$ Torr, He as carrier gas, T_g: (■) 303 K; (□) 600 K; (◆) 839 K. [O_2] is expressed in units of 10^{12} molecules cm^{-3}.

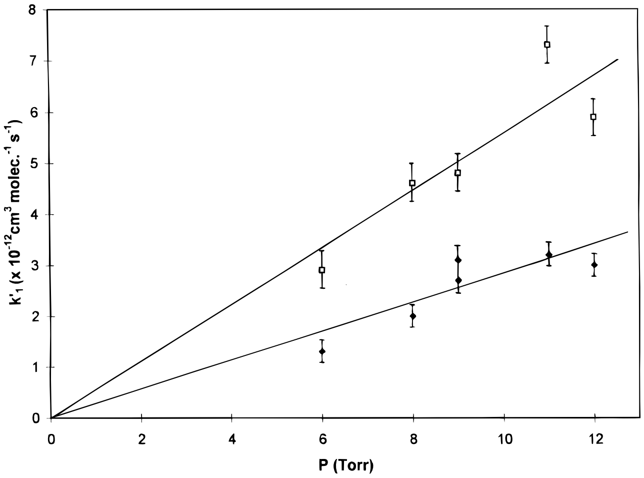

Figure 3. Pseudo-second-order rate constant k'_1 as a function of the pressure at $T_g = 303$ K (◆) and 600 K (□). k'_1 is expressed in units of 10^{-12} cm^3 molecule^{-1} s^{-1}.

taken intoaccount, resulting in the total standard deviation σ_k. The third-order rate constant k_1(He) is then obtained by dividing $k'_1\eta$ by the helium concentration. In the example mentioned above, at 9 Torr of He and with $\eta = 1.6$, third-order rate constants $k_1(\text{He}) = 10.8 \pm 0.7$, 33.1 ± 1.4, and 34.6 ± 1.9 in units of 10^{-30} cm^6 molecule^{-2} s^{-1} are derived at, respectively, 303, 600, and 839 K.

To illustrate the third-order behavior of the Sr/O_2 reaction, the pressure dependence between 6 and 12 Torr of the pseudo-second-order rate constant k'_1 is examined as shown in Figure 3. The lines were forced through the origin, because the values of the intercepts I are smaller than or of the same order as 2 times their standard deviations. It is clear that k'_1 indeed linearly increases when the pressure is raised, which confirms that $Sr(^1S) + O_2 + He$ is a third-order reaction and is still at its low-pressure limit.

Finally, the effect of the initial Sr atom concentration on the value of k_1(He) has been examined. For this purpose, A^i_{Sr} is varied by a factor of 6 and 2 at 303 and 511 K, respectively. Table 1 shows that A^i_{Sr} has no systematic effect on k_1(He), which proves that, as expected at these low Sr atom concentrations, complex reactions were unimportant.

TABLE 1: Effect of Initial Absorbance A^i_{Sr} on k_1(He)[a]

T_g (K)	P_r (Torr)	A^i_{Sr}	k_1(He) (10^{-30} cm^6 molecule^{-2} s^{-1})
303	11	0.04	9.1 ± 1.7
303	9	0.15	9.4 ± 0.7
303	8	0.26	7.8 ± 1.6
511	8	0.53	30.5 ± 1.3
511	8	1.11	36.4 ± 0.7

[a] T_g is the gas temperature and P_r the reactor pressure.

TABLE 2: Rate Constant k_1(He) of the Reaction $Sr(^1S) + O_2 + He$ as a Function of Temperature T_g[a]

T_g (K)	P_r (Torr)	A^i_{Sr}	k_1(He) (10^{-30} cm^6 molecule^{-2} s^{-1})
303	6	0.17	6.8 ± 1.0
303	8	0.26	7.8 ± 1.6
303	9	0.15	9.4 ± 0.7
303	9	0.13	10.8 ± 0.7
303	11	0.04	9.1 ± 1.7
303	12	0.14	7.8 ± 1.3
360	8	0.21	11.7 ± 0.9
401	8	0.25	16.7 ± 2.1
455	8	0.38	25.9 ± 1.8
511	8	1.11	36.4 ± 0.7
511	8	0.53	30.5 ± 1.3
541	8	0.52	28.7 ± 4.2
600	6	0.78	30.0 ± 4.1
600	8	0.62	35.7 ± 1.6
600	9	0.32	33.1 ± 1.4
600	11	0.69	41.2 ± 1.1
600	12	0.57	30.6 ± 1.0
662	9	0.48	35.1 ± 1.5
697	8	0.54	26.1 ± 3.6
738	8	0.34	34.3 ± 3.8
839	9	0.59	34.6 ± 1.9
899	9	0.89	33.1 ± 3.1
968	9	0.57	42.4 ± 2.2

[a] P_r is the reactor pressure and A^i_{Sr} the initial absorbance.

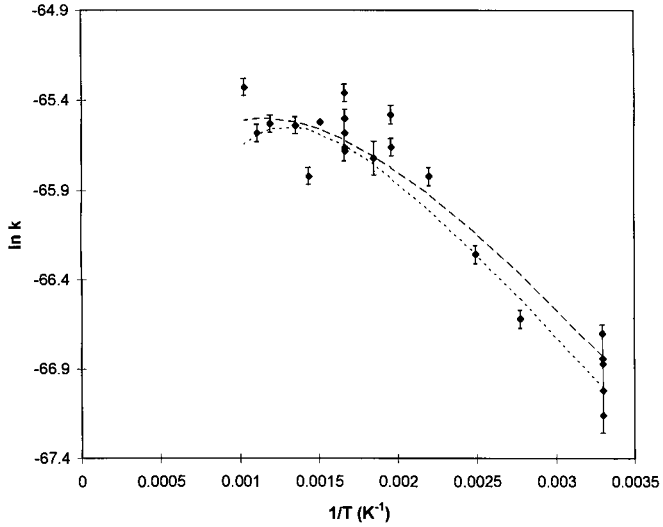

Figure 4. Plots of ln $k_{1_{Sr}}$(He) versus 1/T according to the $T^{-1.7}$ fit (— — —) (eq 5) and the polynomial fit (- - -) (eq 7).

Temperature Dependence of k_1(He). The experimental conditions together with the values of k_1(He) determined in the temperature range from 303 to 968 K are listed in Table 2.

As can be seen from Table 2, k_1(He) increases with increasing temperatures and analogous to the Mg/O_2 and Ca/O_2 reactions the Sr/O_2 reaction will be characterized by an activation energy.

The experimental values for k_1(He) are shown in Figure 4. One clearly sees that the points flatten out at temperatures above 500 K.

Below 500 K, the Arrhenius expression is given by

$$k_{1_{\mathrm{Sr}}}(\mathrm{He}) = [(2.7 \pm 0.5) \times 10^{-28}] \times \exp\left(\frac{-8.7 \pm 0.6\ \mathrm{kJ\ mol^{-1}}}{RT}\right)\ \mathrm{cm^6\ molecule^{-2}\ s^{-1}} \quad (3)$$

It should be mentioned here that eq 3 is slightly different from the Arrhenius expression when all the data over the entire temperature range are taken into account.[30]

To fit the rate constants k_1(He) over the entire temperature range, the following three-parameter expression was tried:

$$k = AT^n \exp\left(\frac{-E_a}{RT}\right) \quad (4)$$

with A being the preexponential factor, T the temperature, n the temperature dependence of A, E_a the activation barrier, and R the universal gas constant.

In the case of a plain bimolecular reaction, normal Arrhenius behavior is expected, giving positive values for n. In most cases third-order reactions will show a negative temperature dependence, and thus n becomes negative. The latter is not surprising in view of the RRKM theory, which predicts that the rate constant indeed decreases when the temperature is being raised.[31−33] To determine the best value for n, we allowed n to vary between −2.5 and −1.0 with increments of 0.1. The smallest residual sum of squares was obtained when n was set equal to −1.7. This results in the following expression for k_1(He):

$$k_{1_{\mathrm{Sr}}}(\mathrm{He}) = [(1.9 \pm 0.3) \times 10^{-23}]T^{-1.7} \times \exp\left(\frac{-12.1 \pm 0.8\ \mathrm{kJ\ mol^{-1}}}{RT}\right)\ \mathrm{cm^6\ molecule^{-2}\ s^{-1}} \quad (5)$$

This is also illustrated in Figure 4, which shows that eq 5 fits the experimental results reasonably well.

The behavior of k_1(He) observed in this work is quite different from the expression obtained by Kashireninov et al. by means of the diffusion flame technique.[34] These authors have proposed the following second-order rate constant for the Sr/O_2 reaction between 1040 and 1215 K:

$$k_{1_{\mathrm{Sr}}} = [(3.2 \pm 0.5) \times 10^{-10}] \times \exp\left(\frac{-59.8 \pm 7.9\ \mathrm{kJ\ mol^{-1}}}{RT}\right)\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}} \quad (6)$$

At the highest temperature at which we measured, i.e., 968 K, the value of $k_{1_{\mathrm{Sr}}}$ in eq 6 leads to a second-order rate constant of 1.9×10^{-13} cm^3 molecule^{-1} s^{-1}. This value is about 20 times lower than the pseudo-second-order rate constant measured in our work, which is 3.8×10^{-12} cm^3 molecule^{-1} s^{-1}. In that case the third-order recombination rate constant with He as a third body is more important than the second-order oxygen atom abstraction process.

Finally the experimental values for k_1(He) could also be fitted to the second-degree polynomial

$$\log k_{1_{\mathrm{Sr}}}(\mathrm{He}) = -60.83 + 22.44(\log T) - 3.89(\log T)^2 \quad (7)$$

Figure 4 shows that this fit is a very good representation of the temperature dependence. A polynomial, however, does not provide any kinetic information.

Extrapolation of k_1(He) between 303 and 2000 K. A method to fit and extrapolate the experimental values of third-order rate constants as a function of the temperature is based on the so-called Troë formalism.[31−33] This formalism calculates the strong collision rate constant $k_{\mathrm{diss},0}^{\mathrm{sc}}$ for the reverse unimolecular decomposition reaction

$$\mathrm{Sr} + \mathrm{O_2} + \mathrm{M} \underset{k_{\mathrm{diss}}}{\overset{k_{\mathrm{rec}}}{\rightleftharpoons}} \mathrm{SrO_2} + \mathrm{M}:$$

$$k_{\mathrm{diss},0}^{\mathrm{sc}} = \frac{Z_{\mathrm{LJ}}\rho(E_0)RT\exp(-E_0/RT)F_{\mathrm{anh}}F_{\mathrm{E}}F_{\mathrm{rot}}F_{\mathrm{rot,int}}F_{\mathrm{corr}}}{Q_{\mathrm{vib}}} \quad (8)$$

in which Z_{LJ} is the collision frequency for a bimolecular collision between the complex SrO_2 and He, $\rho(E_0)$ is the density of harmonic vibrational energy levels of SrO_2 at the dissociation threshold energy E_0, Q_{vib} is the vibrational partition function of SrO_2 and F_{anh}, F_{E}, and F_{rot} are correction factors which are related to the anharmonicity, the energy, and the rotation dependence of ρ.

$F_{\mathrm{rot,int}}$ takes into account internal rotations, and F_{corr} is the correction factor to account for the coupling between different degrees of freedom and is usually taken as unity.[31,32]

To take into account the barrier in the entrance channel E_a, the following expression can be used:[9]

$$E_0 = D_0(\mathrm{Sr{-}O_2}) + E_a \quad (9)$$

where $D_0(\mathrm{Sr{-}O_2})$ represents the bond energy of SrO_2. In this calculation the value of $D_0(\mathrm{Sr{-}O_2})$ was respectively set equal to 190 and 255 kJ mol^{-1}, as determined by different ab initio calculation methods[22] (see further in the text). For E_a the value of 8.7 kJ mol^{-1} derived from the temperature dependence of $k_{1_{\mathrm{Sr}}}$(He) below 500 K was used (eq 3).

The rate constant for the strong collision recombination reaction is obtained by means of eq 10, in which K_{eq} is the equilibrium constant of the reaction.

$$k_{\mathrm{rec},0}^{\mathrm{sc}} = K_{\mathrm{eq}}k_{\mathrm{diss},0}^{\mathrm{sc}} \quad (10)$$

The weak collision rate constant $k_{\mathrm{rec},0}$ can be calculated by introducing the collision efficiency for energy transfer β_c

$$k_{\mathrm{rec},0} = \beta_c k_{\mathrm{rec},0}^{\mathrm{sc}} \quad (11)$$

in which β_c varies between 0 and 1. Its value as a function of the temperature is given by

$$\frac{\beta_c}{1-\sqrt{\beta_c}} = -\frac{\langle\Delta E\rangle}{F_{\mathrm{E}}RT} \quad (12)$$

in which $\langle\Delta E\rangle$ is the average energy transferred per collision which in this case was temperature-dependent according to $\langle\Delta E\rangle \approx T^{1.04\pm0.05}$.

The parameters for calculating $k_{\mathrm{diss},0}^{\mathrm{sc}}$ for the $SrO_2(^3A_2)$ molecule are listed in Table 3. The ground state $^1A_1$ of SrO_2 should not be used, because its formation in reaction 1 is spin-forbidden and such reactions are too slow within the time scale of these experiments. The second reason the $^1A_1$ state will not be formed is that its formation requires a second electron transfer from the metal toward the oxygen,[22] which is normally a step with a high energy barrier.

The interatomic distances $r_{\mathrm{Sr-O}}$ and $r_{\mathrm{O-O}}$[21] as well as the vibrational frequencies[22] were values obtained from ab initio calculations, since no experimental values are available. An estimation for the Lennard−Jones parameter $\epsilon(\mathrm{SrO_2{-}He})$ was based on the value for $\epsilon(\mathrm{CaO_2{-}He})$.[9] For the characterization

TABLE 3: Extrapolation of Rate Data for the Reaction $Sr(^1S) + O_2 + He$: Input Parameters Used in the Troë Formalism[31−33] [a]

Input Parameters for the $SrO_2(^3A_2)$ Molecule	
$D_0(Sr-O_2) = 190$ kJ mol^{-1} (B3LYP(RECP))[b]	$D_0(Sr-O_2) = 255$ kJ mol^{-1} (MP2)[b]
$r_{Sr-O} = 2.349$ Å; $r_{O-O} = 1.340$ Å	$r_{Sr-O} = 2.349$ Å; $r_{O-O} = 1.340$ Å
$I_A = 2.23 \times 10^{-45}$ kg m^2	$I_A = 2.23 \times 10^{-45}$ kg m^2
$I_B = 2.39 \times 10^{-46}$ kg m^2	$I_B = 2.39 \times 10^{-46}$ kg m^2
$I_C = 1.99 \times 10^{-45}$ kg m^2	$I_C = 1.99 \times 10^{-45}$ kg m^2
$\nu_1 = 339$ cm^{-1}	$\nu_1 = 1726$ cm^{-1}
$\nu_2 = 360$ cm^{-1}	$\nu_2 = 358$ cm^{-1}
$\nu_3 = 1182$ cm^{-1}	$\nu_3 = 1074$ cm^{-1}
$E_a = 8.7$ kJ mol^{-1}	$E_a = 8.7$ kJ mol^{-1}
$E_0 = 199$ kJ mol^{-1}	$E_0 = 264$ kJ mol^{-1}
Data for $Sr + O_2 + He$ at 303 K	
$\sigma(SrO_2-He) = 3.25$ Å; $\epsilon(SrO_2-He)/k = 350$ K	$\sigma(SrO_2-He) = 3.25$ Å; $\epsilon(SrO_2-He)/k = 350$ K
$Z_{LJ} = 7.12 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}	$Z_{LJ} = 7.12 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}
$s = 3$; $m = 2$; $r = 0$	$s = 3$; $m = 2$; $r = 0$
$Q_{vib} = 1.531$	$Q_{vib} = 1.231$
$F_E = 1.024$; $F_{anh} = 1.78$; $F_{rot} = 37.69$; $F_{corr} = 1$; $F_{elec} = 1$	$F_E = 1.018$; $F_{anh} = 1.78$; $F_{rot} = 50.30$; $F_{corr} = 1$; $F_{elec} = 1$
$K_{eq} = 2.0 \times 10^9$ cm^3 molecule^{-1}	$K_{eq} = 2.5 \times 10^{20}$ cm^3 molecule^{-1}
$k^{sc}_{diss,0} = 4.0 \times 10^{-40}$ cm^3 molecule^{-1} s^{-1}	$k^{sc}_{diss,0} = 1.6 \times 10^{-51}$ cm^3 molecule^{-1} s^{-1}
$k^{sc}_{rec,0} = 7.8 \times 10^{-31}$ cm^6 molecule^{-2} s^{-1}	$k^{sc}_{rec,0} = 4.1 \times 10^{-31}$ cm^6 molecule^{-2} s^{-1}
$k^{exp}_{rec,0} = 9.2 \times 10^{-30}$ cm^6 molecule^{-2} s^{-1} [c]	$k^{exp}_{rec,0} = 9.2 \times 10^{-30}$ cm^6 molecule^{-2} s^{-1} [c]
$\beta_c = 11.8$; $\langle \Delta E \rangle = 12.50$ kJ mol^{-1}	$\beta_c = 22.6$; $\langle \Delta E \rangle = 15.43$ kJ mol^{-1}

[a] For the definition of symbols not in the present text, see refs 31−33. [b] For the meaning of the symbols, see refs 21 and 22. [c] Weighted mean value at 303 K.

of the $SrO_2(^3A_2)$ state Andrews et al.[22] provided different values for both $D_0(Sr-O_2)$ as well as the vibrational frequencies depending on the ab initio method used. The various input parameters are shown in Table 3.

When this modified Troë formalism was used to calculate the rate constant $k_{rec,0}$ with the input parameters from Table 3, collision efficiencies β_c of about 13 were obtained when $D_0(Sr-O_2)$ was set equal to 190 kJ mol^{-1} (B3LYP(RECP) method). With a $D_0(Sr-O_2)$ value of 255 kJ mol^{-1} (MP2 method), together with the vibrational frequencies calculated with the same method, β_c values of the order of about 25 were obtained. With the helium atom as collision partner for the stabilization of the SrO_2 molecule one normally expects values for β_c of the order of 0.1. Lower values for β_c could only be obtained by increasing the bond energy $D_0(Sr-O_2)$ to values of about 1000 kJ mol^{-1}, which is not a realistic value. Another way to reduce β_c when keeping $D_0(Sr-O_2)$ at 190 or 255 kJ mol^{-1} is by introducing an additional correction factor F_{elec} into eq 8. This factor takes into account that several low-lying electronic excited states of the SrO_2 molecule might participate in the reaction. A similar procedure has also been followed by several authors[16,35,36] to fit the experimental data to the RRKM calculation. This led to values for F_{elec} between 75 and 100, which is of course completely out of range.

Using the molecular parameters of $SrO_2(^3A_2)$ taken from the various ab initio methods, one thus arrives at β_c values which are unrealistically high. When the calculations were performed with the other triplet state $SrO_2(^3B_2)$, β_c values in the same range were obtained. However, as can be seen from Table 3, the problem is that there are large uncertainties on the value of $D_0(Sr-O_2)$ ranging from 190 to 255 kJ mol^{-1}. In addition, one should notice a very large discrepancy between the calculated values of ν_1: 339 and 1726 cm^{-1} when, respectively, the B3LYP(RECP) or the MP2 method was used.[22]

In view of the foregoing, a fit based on the Troë formalism is inappropriate and thus the extrapolation over a broader temperature range should not be made.

Comparison between the Alkaline-Earth-Metal/O_2 Reactions. It is well-known that the third-order reaction of closed-shell metal atoms with molecular oxygen is characterized by an energy barrier. This barrier is located in the entrance channel at the crossing of the covalent and ionic potential energy surfaces.

As has already been mentioned, both the $Mg + O_2$ and the $Ca + O_2$ reactions previously studied at our laboratory[17,18] showed Arrhenius expressions for their rate constants:

$$k_{1_{Mg}}(He) = [(5.5 \pm 1.1) \times 10^{-31}] \times \exp\left(\frac{-16.8 \pm 0.8 \text{ kJ mol}^{-1}}{RT}\right) \text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \quad (13)$$

$$k_{1_{Ca}}(He) = [(1.5 \pm 0.2) \times 10^{-28}] \times \exp\left(\frac{-10.2 \pm 0.4 \text{ kJ mol}^{-1}}{RT}\right) \text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \quad (14)$$

While for both the Mg and Ca/O_2 reactions an Arrhenius behavior was observed over the entire temperature range between 303 and 1000 K, the rate constant of the Sr/O_2 reaction starts to level off at temperatures above 500 K and probably decreases from 1000 K and higher. When only the rate constants $k_{1_{Sr}}(He)$ below 500 K are considered (eq 3), one sees that the Arrhenius activation energies decrease according to the series $E_a(Mg) = 16.8$, $E_a(Ca) = 10.2$, and $E_a(Sr) = 8.7$ (each expressed in kJ mol^{-1}). Since the reaction most probably proceeds through a partial charge transfer between the metal atom and the oxygen molecule, it is logical to establish a qualitative correlation between the Arrhenius activation energy E_a and the ionization energy (IE) of the metal, which indeed shows the trend IE(Mg) = 7.64 eV > IE(Ca) = 6.11 eV > IE(Sr) = 5.69 eV.

The preexponential factor for the Mg/O_2 reaction is much lower than for the other two reactions. This implies that the probability for redissociation of the CaO_2 and SrO_2 transition states is much lower than for MgO_2. This can be understood in terms of the magnitudes of the dissociation energies for the ground-state metal−O_2 molecules. For MgO_2 in either the $^3A_2$ or the $^3\Sigma_g^-$ state dissociation energies in the range from 82 to 106 kJ mol^{-1} were derived, while for $CaO_2(^3A_2)$ and $SrO_2(^3A_2)$ ranges from respectively 156−204 kJ mol^{-1} and 190−255 kJ mol^{-1} were obtained, depending on the ab initio method used.[22]

Bond Energy of the SrO_2 ($^3A_2$) Molecule. Up until now no experimental values have been available for the bond energy of the SrO_2 molecule. Our results allow us to derive a minimal value for this bond energy, based on the expression for the equilibrium constant K_{eq} for the reaction $Sr + O_2 + He \rightleftharpoons SrO_2 + He$:

$$K_{eq} = \frac{[SrO_2]_t}{[Sr]_t[O_2]} = \frac{(A_0 - A_t)}{A_t[O_2]} \qquad (15)$$

with A_0 being the initial absorbance at a reaction time $t = 0$ ms and A_t the absorbance at time t. In this expression the SrO_2 concentration is set equal to the amount of Sr atoms which reacted.

Since the decay curves of $\ln A_{Sr}$ as a function of time at the highest temperature and lowest O_2 concentration still remain linear, the equilibrium is far from being reached and thus the calculated equilibrium constant is a lower limit. K_{min} is now calculated at 968 K and at an O_2 concentration of 4.3×10^{12} molecules cm^{-3}, resulting in the value $K_{min} = 7.4 \times 10^{-11}$ cm^3 $molecule^{-1}$.

On the other hand, the equilibrium constant can also be calculated on the basis of statistical mechanics, according to eq 16, with Q_{SrO_2}, Q_{Sr}, and Q_{O_2} being the partition functions of respectively $SrO_2(^3A_2)$, Sr, and O_2; D_0 is the bond energy of SrO_2. In the calculation of the partition function of $SrO_2(^3A_2)$ the vibrational frequencies from the B3LYP(RECP) method were used.[22]

$$K_{eq} = \frac{Q_{SrO_2}}{Q_{Sr}Q_{O_2}} \exp\left(\frac{D_0}{RT}\right) \qquad (16)$$

After K_{eq} was set equal to $K_{min} = 7.4 \times 10^{-11}$ cm^3 $molecule^{-1}$, a minimal value for the bond energy of the SrO_2 molecule $D_0 > 244$ kJ mol^{-1} was obtained. This result lies between the values of 190 and 255 kJ mol^{-1} obtained by means of the ab initio calculations mentioned above.[22] Incorporating the vibration frequencies from the MP2 method only resulted in a slightly higher minimal value for D_0 of 251 kJ mol^{-1}.

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