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Kinetic Study of the Reactions of Ca(^{1}S) and Sr(^{1}S) Atoms with Cl$_2$ in the Temperature Ranges from Respectively 303−1038 K and 303−991 K

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A kinetic investigation of the second-order reactions Ca(^{1}S) + Cl$_2$($^1\Sigma_g^+$) $\rightarrow$($k_{1_{\mathrm{Ca}}}$) CaCl + Cl and Sr(^{1}S) + Cl$_2$($^1\Sigma_g^+$) $\rightarrow$($k_{1_{\mathrm{Sr}}}$) SrCl + Cl was carried out in a fast-flow reactor in the temperature ranges of respectively 303−1038 K and 303−991 K. The calcium and strontium atoms in the gas phase were generated by thermal evaporation of the solid metal pellets. The concentration of the gas-phase metal atoms was followed by means of atomic absorption spectroscopy (AAS) at wavelengths of 422.7 nm for calcium and 460.7 nm for strontium atoms. Both reactions show an Arrhenius behavior and the rate constants are given by $k_{1_{\mathrm{Ca}}} = [(6.0 \pm 0.8) \times 10^{-10}]\exp(-0.2 \pm 0.5\ \mathrm{kJ\ mol^{-1}}/RT)\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ and $k_{1_{\mathrm{Sr}}} = [(7.3 \pm 0.6) \times 10^{-10}]\exp(-0.4 \pm 0.4\ \mathrm{kJ\ mol^{-1}}/RT)\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$. The results are interpreted in terms of the electron-jump mechanism. For both the Ca/Cl$_2$ and the Sr/Cl$_2$ reactions, the experimental rate constants are too high to be quantitatively explained by the classical electron-jump mechanism. However, the modified electron-jump mechanism which takes into account long distance forces between the reagents gives a better agreement with the experimental values.

Introduction

The classic collision theory states that a reaction can only occur when the solid sphere of reagent A with a diameter σ_A collides with the solid sphere of reaction partner B with a diameter σ_B. A necessary condition for having a reactive collision is that the centers of gravity of both reacting species approach to each other until a distance r_{A-B} equal to $(\sigma_A + \sigma_B)/2$ is reached. The maximum cross-section Q$_r$ for this reactive process can be expressed as $\pi(r_{A-B})^2$. However, for the alkaline-metal atom/halogen reactions extremely high values for Q_r were experimentally determined, which could not be explained on the basis of the classic collision theory. Indeed gas collision cross sections in the range of 30−50 Å^2 can be expected while for the alkaline-metal atom reactions cross sections with Cl$_2$, Br$_2$ and I$_2$ between 100 and 200 Å^2 have been measured.[1−5] Apparently such reactions do not require a classic collision between both reaction partners and they could better be treated by the so-called electron-jump or harpooning mechanism.[6−7]

It needs to be pointed out that the closed-shell character of the alkaline-earth-metal atoms may result in a potential energy barrier when the reagents approach each other under a number of geometrical configurations. Honjou and Yarkony[8] indeed calculated a maximum energy barrier of 28.5 kJ mol^{-1} for the perpendicular C_{2v} approach of the Ca atom toward the Cl$_2$ molecule. They also demonstrated that in contrast to the C_{2v} approach a collinear $C_{\infty v}$ approach does not show an energy barrier. Up until now the reaction dynamics of a C_s approach have not been looked at, but one may assume that this reaction geometry will give an energy barrier intermediate between the two extreme situations (C_{2v} and $C_{\infty v}$).

In this paper a kinetic study will be presented on the Ca(Sr)/Cl$_2$ reactions. The only kinetic measurements available were obtained in atomic diffusion flames in the narrow temperature ranges between 933 and 1083 K.[9] Both rate constants show a negative temperature dependence as can be seen from the following expressions:

$$k_{1_{\mathrm{Ca}}} = [(2.0 \pm 0.5) \times 10^{-5}]T^{-1.91\pm0.03}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}} \tag{1}$$

$$k_{1_{\mathrm{Sr}}} = [(9.1 \pm 0.3) \times 10^{-14}]T^{-0.50\pm0.02}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}} \tag{2}$$

Another source of information on the Ca(Sr)/Cl$_2$ reactions is coming from molecular beam experiments.[10] From the angle dependence of the MeX product formation, it has been concluded that the reactions proceed through the formation of a very short-living intermediate complex, with a lifetime which is several times lower than its rotational period. More recently Gole et al.[11] investigated the emission arising from the mixed halogen Sr/(Cl$_2$,Br$_2$) reactions using both chemiluminescent and LIF techniques.

$$\mathrm{Sr} + (\mathrm{Cl_2}, \mathrm{Br_2}) \rightarrow \mathrm{SrCl} + \mathrm{SrBr} \tag{3}$$

$$\mathrm{Sr} + (\mathrm{Cl_2}, \mathrm{Br_2}) \rightarrow \mathrm{SrCl_2^{*\dagger}} + \mathrm{SrBr_2^{*\dagger}} \tag{4a}$$

$$\mathrm{SrCl_2^{*\dagger}} + \mathrm{M} \rightarrow \mathrm{SrCl_2^{*}} \rightarrow \mathrm{SrCl_2} + h\nu \tag{4b}$$

$$\mathrm{SrCl_2^{*}} + \mathrm{SrCl} \rightarrow \mathrm{SrCl_2} + \mathrm{SrCl^{*}} \rightarrow \mathrm{SrCl_2} + \mathrm{SrCl} + h\nu \tag{4c}$$

$$\mathrm{SrBr_2^{*\dagger}} + \mathrm{M} \rightarrow \mathrm{SrBr_2^{*}} \rightarrow \mathrm{SrBr_2} + h\nu \tag{4d}$$

$$\mathrm{SrBr_2^{*}} + \mathrm{SrBr} \rightarrow \mathrm{SrBr_2} + \mathrm{SrBr^{*}} \rightarrow \mathrm{SrBr_2} + \mathrm{SrBr} + h\nu \tag{4e}$$

The main reaction leads to nascent electronically excited SrCl$_2^{*\dagger}$ and SrBr$_2^{*\dagger}$ dihalide products (4a). In a further step one gets collisional stabilization (M = bath gas or so-called third body) to form the long-living SrCl$_2^{*}$ and SrBr$_2^{*}$ molecules (4b and 4d). Also the SrCl and SrBr monohalides were formed in the ground-state (3), which is not surprising since the reaction

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to electronically excited states of SrCl and SrBr are endothermic for respectively 10.8 and 34.7 kJ mol^{-1}.[12] However, emission from SrCl* and SrBr* has also been seen (4c and 4e), and this was explained by assuming an energy transfer in (4c) and (4e) from the electronically excited $SrCl_2^*$ and $SrBr_2^*$ to the ground-state monohalides formed in (3).

Kinetic measurements on the Ca(^{1}S) and Sr(^{1}S) atom/Cl_2 reactions will now be presented covering the temperature ranges from respectively 303−1038 K and 303−991 K. The experiments were carried out in a fast-flow reactor using AAS as the detection technique for the thermally evaporated alkaline-earth-metal atoms. The results will be discussed in terms of the electron-jump mechanism.

Experimental Technique

The experimental setup has been amply described in earlier publications,[13−17] and only a brief summary will be presented here. It consists of two major parts: a fast-flow reactor under low pressure and an AAS detection technique. The fast-flow reactor consists of a quartz tube with an internal diameter of 5.7 cm and a length of 100 cm. At the upstream end a sample holder carried the metal pellets which were thermally evaporated at 600−700 K by means of a kanthal resistance wire. By means of the carrier gas helium, the alkaline-earth-metal atoms were transported downstream in the kinetic zone where they were mixed with an excess of Cl_2. In the pressure range from 6 to 12 Torr, the flow velocity v_g of the carrier gas helium has a constant value of 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 electrical oven and the temperature was monitored by a shielded chromel−alumel thermocouple. Calcium and strontium atoms were detected by AAS at respectively 422.7 and 460.7 nm.

Assuming that the detection limit corresponds to an absorbance of $A = 0.005$, one can calculate the detection limit for the Ca(Sr) atoms by using a formalism explained in an earlier paper:[18] $[\mathrm{Ca(Sr)}] = C_1AL^{-1}T_g^{1/2}$ in which C_1 is a proportionality constant, L the optical path length (5.7 cm), and T_g the gas temperature. With values for $C_1(\mathrm{Ca}) = 0.663 \times 10^{10}$ cm^{-2} K$^{-1/2}$ and $C_1(\mathrm{Sr}) = 0.428 \times 10^{10}$ cm^{-2} K$^{-1/2}$ at 500 K,[19] one can calculate the detection limits for calcium to be 1.3×10^8 atoms cm^{-3} or 1.12 ppb and for strontium: 8.4×10^7 atoms cm^{-3} or 0.72 ppb at 6 Torr and 500 K.

Minimum distances between the metal atom source, the Cl_2 inlet, and the kinetic zone were maintained to allow for sufficient mixing of the reagents as explained in earlier publications.[16,17] Kinetic measurements were made by following the decay of the alkaline-earth-metal atom absorbance 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. Decays of the absorbances as a function of the distance can easily be transformed into decays as a function of the reaction time t using the expression $t = z_d/v_g$. An advantage of this technique is that relative positions of the metal atom source and the Cl_2 inlet remain constant during the experiments. Reproducible absorbances could be maintained within 10% when the temperature T_s of the metal pellets was stabilized within ± 1%.

For all the investigated reactions helium (L'Air Liquide) with a purity of 99.995% was used as a carrier gas as well as in the gas mixtures. The Cl_2 concentration was equal to 0.075% of Cl_2 for both the Ca/Cl_2 and the Sr/Cl_2 reactions. The calcium pellets (Fluka) and the strontium pellets (Aldrich) respectively had a purity of about 99.5% and 99.0%.

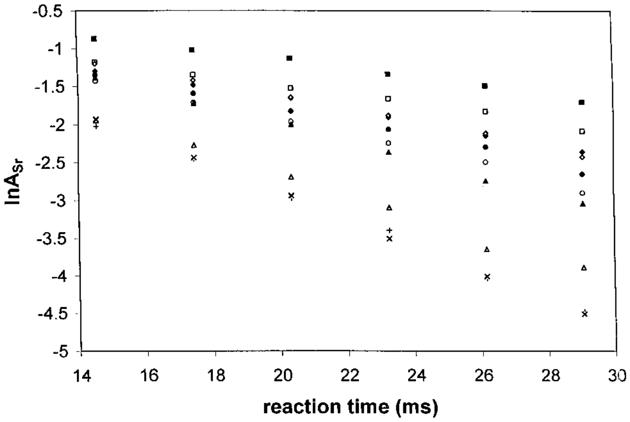

Figure 1. The natural logarithm of the Sr atom absorbance as a function of the reaction time t at various amounts of added Cl_2. The experimental conditions are $T_g = 651$ K, $P_r = 10$ Torr. He as carrier gas. [Cl_2] (■) 0, (□) 0, (◆) 1.9, (◇) 3.8, (●) 6.3, (○) 8.7, (▲) 11.0, (△) 14.0, (+) 21.0, and (×) 23.0 expressed in units of 10^{10} molecules cm^{-3}.

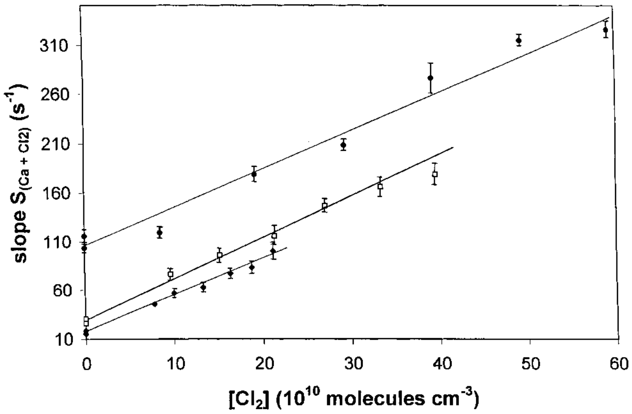

Figure 2. The slopes S of eq 5 for the Ca/Cl_2 reaction as a function of the added Cl_2 concentration. The experimental conditions are T_g = 303 K (◆) (P_r = 8 Torr), 489 K (□) (P_r = 10 Torr), and 930 K (●) (P_r = 10 Torr). He as carrier gas, [Cl_2] is expressed in units of 10^{10} molecules cm^{-3}.

Weighted regressions on all plots were made using the statistical SAS package.[20] The quoted errors σ were the standard deviations.

Results

Determination of the Rate Constants $k_{1_{Ca}}$ and $k_{1_{Sr}}$. The kinetic formalism used in the derivation of the rate constants of the Ca(Sr)/Cl_2 reactions has already been described in previous papers[16,17]

$$\ln A_{\mathrm{Ca(Sr)}} = -\left\{\frac{k_{1_{\mathrm{Ca(Sr)}}}[\mathrm{Cl_2}]}{\eta} + \frac{7.34D_{\mathrm{Ca(Sr)/He}}}{2r^2}\right\}t + B \qquad (5)$$

in which $\ln A_{\mathrm{Ca(Sr)}}$ is the natural logarithm of respectively the calcium and strontium absorbance, η a correction factor depending on the flow characteristics, $D_{\mathrm{Ca(Sr)/He}}$ the binary diffusion coefficients of the Ca and 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.[21]

The use of eq 5 for obtaining kinetic parameters has been well-illustrated in our earlier work[16,22] and will only briefly be summarized here. The values of the rate constants $k_{1_{\mathrm{Ca(Sr)}}}$ were

TABLE 1: The Rate Constants $k_{1_{\mathrm{Ca(Sr)}}}$ of the Reactions Ca(^{1}S) + Cl_2 and Sr(^{1}S) + Cl_2 as a Function of the Temperature T_g[a]

T_g (K)	P_r (Torr)	A^i_{Ca}	$k_{1_{\mathrm{Ca}}}$ ($\times 10^{-10}$ cm^3 molecule^{-1} s^{-1})	T_g (K)	P_r (Torr)	A^i_{Sr}	k_1Sr ($\times 10^{-10}$ cm^3 molecule^{-1} s^{-1})
303	6	0.55	5.6 ± 0.5	303	6	0.29	6.8 ± 1.1
303	8	0.75	4.9 ± 0.6	303	6	0.33	6.6 ± 0.9
303	8	0.93	4.9 ± 0.3	303	8	0.47	4.4 ± 1.0
303	10	0.84	5.9 ± 0.3	303	8	0.36	6.7 ± 0.9
303	12	0.41	5.6 ± 0.5	303	10	0.46	5.7 ± 0.9
356	10	0.76	5.3 ± 0.7	303	12	0.52	4.7 ± 0.6
398	8	1.20	4.1 ± 0.6	352	8	0.31	6.4 ± 0.3
398	8	0.56	5.3 ± 1.0	393	8	0.13	6.4 ± 0.9
489	10	1.10	5.5 ± 0.7	449	8	0.27	5.3 ± 0.7
544	8	0.72	4.5 ± 0.6	507	8	0.33	6.5 ± 0.4
544	8	0.33	5.4 ± 0.7	554	8	0.19	6.0 ± 0.9
603	10	1.01	7.7 ± 0.3	598	8	0.18	5.8 ± 0.2
700	8	0.40	8.2 ± 1.1	651	6	0.16	8.1 ± 1.4
790	10	1.00	5.7 ± 0.4	651	8	0.15	8.0 ± 0.4
790	10	0.34	8.3 ± 0.4	651	10	0.36	8.4 ± 0.3
930	10	0.80	6.4 ± 0.4	651	11	0.19	8.0 ± 0.4
1038	10	0.40	3.8 ± 0.3	651	12	0.10	7.4 ± 0.3
1038	10	0.52	4.5 ± 0.5	707	8	0.07	5.7 ± 0.4
				753	8	0.15	7.8 ± 0.4
				791	8	0.49	5.9 ± 0.9
				822	8	0.12	8.2 ± 0.3
				822	8	0.40	7.1 ± 1.0
				888	8	0.13	5.7 ± 0.2
				991	8	0.10	6.7 ± 0.2

[a] P_r is the reactor pressure, and $A^i_{\mathrm{Ca(Sr)}}$ is the initial absorbance.

determined by following first ln $A_{\mathrm{Ca(Sr)}}$ as a function of the reaction time t at various amounts of Cl_2 added. Then a weighted linear regression of ln $A_{\mathrm{Ca(Sr)}}$ versus t was performed, in which each value of ln $A_{\mathrm{Ca(Sr)}}$ had a weighting factor equal to $1/\sigma^2_{\ln A}$. As an example, the pseudo-first-order decays of Sr(^{1}S) atoms as a function of the reaction time t for various initial Cl_2 concentrations at a temperature T_g = 651 K and a pressure P_r equal to 10 Torr are shown in Figure 1.

In the next step, the slopes S of these lines were plotted versus the added [Cl_2] and a weighted linear regression resulted in a straight line with a slope equal to $k_{1_{\mathrm{Ca(Sr)}}}/\eta$ as is illustrated in Figure 2 for three different temperatures: 303, 489, and 930 K for the Ca/Cl_2 reaction.

Finally the observed slopes in Figure 2 need to be multiplied by η to obtain the correct second-order rate constants $k_{1_{\mathrm{Ca(Sr)}}}$. The value of η depends on the magnitude of the intercept and the procedure to determine its value is the same as in a previous paper on the Mg(Ca,Sr)/NO_2 reactions.[23] In the given examples for the Ca/Cl_2 reaction values for the second-order rate constants $k_{1_{\mathrm{Ca}}}$ = 4.9 ± 0.6 (303 K), 5.5 ± 0.7 (489 K) and 6.4 ± 0.4 (930 K) in units of 10^{-10} cm^3 molecule^{-1} s^{-1} were obtained.

To confirm the second-order behavior of the reactions, the pressure dependence of the rate constants $k_{1_{\mathrm{Ca(Sr)}}}$ was examined in the pressure range between 6 and 12 Torr and this at various temperatures between 303 and 651 K. It was indeed found that the obtained values of $k_{1_{\mathrm{Ca(Sr)}}}$ were independent of the pressure. This also confirms that hydrodynamic effects, as there are the mixing of the reagents or the wall-loss of Ca(Sr) atoms, have no systematic effect on the derived values of $k_{1_{\mathrm{Ca(Sr)}}}$.

The influence of the initial alkaline-earth-metal atom concentration on the value of $k_{1_{\mathrm{Ca(Sr)}}}$ has been checked. For this purpose, $A^i_{\mathrm{Ca(Sr)}}$ was varied with a factor of 2 to 3.5 and in none of the cases any systematic effect on $k_{1_{\mathrm{Ca(Sr)}}}$ was noticed. This proves that, as expected at these low initial metal atom concentrations, mutual reactions between the metal atoms or consecutive reaction steps involving these metal atoms could be neglected.

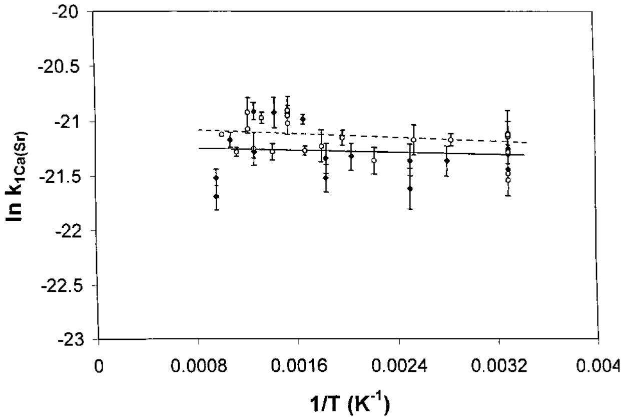

Figure 3. Plot of ln $k_{1_{\mathrm{Ca(Sr)}}}$ versus 1/T according to the weighted nonlinear regression method: Ca/Cl_2 (◆) (—) (eq 7) and Sr/Cl_2 (○) (— —) (eq 8).

TABLE 2: Reaction Enthalpy ΔH_R (kJ mol^{-1}) of the Ca(Sr)/Cl_2 Reactions Leading to Various Electronic States of the Corresponding Metal Chloride MeCl[12]

electronic states of the MeCl product	Ca	Sr
$X^2\Sigma^+$	−161.1	−166.6
$A^2\Pi$	+31.5	+10.8
$B^2\Sigma$	+40.6	+22.3

Temperature Dependence of $k_{1_{\mathrm{Ca}}}$ and $k_{1_{\mathrm{Sr}}}$. To establish the temperature dependence of the rate constants $k_{1_{\mathrm{Ca(Sr)}}}$, experiments were carried out in the temperature ranges of respectively 303−1038 K and 303−991 K. The experimental conditions together with all the values of $k_{1_{\mathrm{Ca}}}$ and $k_{1_{\mathrm{Sr}}}$ are listed in Table 1.

The results can be fitted to the classical Arrhenius formalism according to eq 6:

$$k_{1_{\mathrm{Ca(Sr)}}} = A \exp\left(\frac{-E_a}{RT}\right) \qquad (6)$$

in which A is the preexponential factor (cm^3 molecule^{-1} s^{-1}), E_a is the activation energy (kJ mol^{-1}), R is the universal gas constant (8.31441 J mol^{-1} K^{-1}), and T is the temperature (K).

The rate constants $k_{1_{\mathrm{Ca(Sr)}}}$ were fitted to eq 6 by means of a

TABLE 3: Comparison between the Calculated Values of r_c, k_{ej}, and k_{mej} (Equation 9) with the Value of r_c(exp) Derived from k_{exp} and the Experimental Value k_{exp} at Room Temperature

	r_c (Å)	k_{ej} (cm^3 molecule^{-1} s^{-1})	r_c(exp) (Å)	k_{exp} (cm^3 molecule^{-1} s^{-1})	k_{mej} (cm^3 molecule^{-1} s^{-1})
Ca/Cl_2 (303 K)	2.8	1.2×10^{-10}	5.9	5.4×10^{-10}	7.7×10^{-10}
Sr/Cl_2 (303 K)	3.1	1.2×10^{-10}	6.6	5.6×10^{-10}	6.6×10^{-10}

weighted nonlinear regression using the SAS package,[20] resulting in the following Arrhenius expressions:

$$k_{1_{Ca}} = [(6.0 \pm 0.8) \times 10^{-10}] \times \exp\left(\frac{-0.2 \pm 0.5\ \text{kJ mol}^{-1}}{RT}\right) \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \quad (7)$$

$$k_{1_{Sr}} = [(7.3 \pm 0.6) \times 10^{-10}] \times \exp\left(\frac{-0.4 \pm 0.4\ \text{kJ mol}^{-1}}{RT}\right) \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \quad (8)$$

The quoted error margins on both the preexponential factors and the Arrhenius activation energies are at the 1σ level.

Figure 3 represents the values of ln $k_{1_{Ca(Sr)}}$ from Table 1 versus 1/T.

One sees that the rate constants are almost independent of the temperature and both eqs 7 and 8 show that the reactions are characterized by a small or even negligible activation energy in the range between 0.2 and 0.4 kJ mol^{-1} with an associated error of the same magnitude.

Discussion

The reaction enthalpies of the possible Ca(Sr)/Cl_2 reactions are summarized in Table 2[12] and as one sees both reactions can only lead to ground-state CaCl and SrCl ($X^2\Sigma^+$) in view of the endothermicity of the other reactions.

As already said the rate constants derived in this work can only be compared with the results of Kashireninov et al., obtained in the narrow temperature ranges between 990 and 1083 K for the Ca/Cl_2 reaction and 933−1073 K for the Sr/Cl_2 reaction.[9] In both cases a small negative temperature dependence was observed (eqs 1 and 2). At the highest experimental temperatures covered in this work, i.e., 1038 K for the Ca/Cl_2 reaction and 991 K for the Sr/Cl_2 reaction, eqs 1 and 2 lead to values of $k_{1_{Ca(Sr)}}$ respectively equal to 3.5×10^{-11} cm^3 molecule^{-1} s^{-1} and 2.9×10^{-15} cm^3 molecule^{-1} s^{-1}. These values are respectively about 1 and 5 orders of magnitude lower than the second-order rate constants calculated from our data (eqs 7 and 8). In this context it should be mentioned that the derivation of kinetic data obtained by means of the TVDF (temperature variation of the diffusion flame) technique[9] is strongly complicated due to several interferences as there are the high temperature gradients in the reaction zone, the occurrence of secondary reactions, and the influence of condensation of the gas-phase products onto the thermocouples. Another point is that their results were obtained in the narrow temperature range of about 150 K, which certainly diminuishes the reliability of the derived kinetic parameters.

An attractive mechanism for interpretating the experimental results of the alkaline-earth-metal atom/Cl_2 reactions is the electron-jump mechanism. The electron-jump distance r_c with the corresponding rate constant k_{ej} can be calculated using the same expressions as given in our previous paper on the alkaline-earth-metal atom/NO_2 reactions.[23] With the ionization energy $IE_{Ca(Sr)}$ of the Ca or Sr atoms, which is respectively equal to 6.10 and 5.69 eV, and the vertical electron affinity $EA_v(Cl_2)$ of the Cl_2 molecule (1.0 eV),[3] one can calculate the values for r_c of the Ca(Sr)/Cl_2 reactions: see Table 3.

In the next step, the values of the electron-jump rate constants k_{ej} at, e.g., 303 K can be calculated and can then be compared with the experimental values at the same temperature. From Table 3 it is clear that for both reactions the electron-jump rate constant is about a factor of 5 lower than the experimental value. To explain these larger experimental values, long-range forces between the reacting species should be taken into account.[24] These forces are mainly attractive dispersion forces which are active at distances larger than the electron-jump distance. This mechanism leads to a so-called modified electron-jump rate constant k_{mej} which is given by eq 9: [25]

$$k_{m.e.j.} = \pi\left(\frac{2C_6}{RT}\right)^{1/3}\left(\frac{8RT}{\pi\mu}\right)^{1/2}\Gamma(^2/_3)\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \quad (9)$$

in which Γ ($^2/_3$) is the gamma function of $^2/_3$ (=1.354), T is the gas temperature, R is the universal gas constant (=1.38×10^{-23} J molecule^{-1} K^{-1}), and μ is the reduced mass of the reacting species. In eq 9 the factor C_6 only takes into account a dispersion interaction C_6^{disp}. The derived values for C_6^{disp} for the Ca/Cl_2 and the Sr/Cl_2 reactions are respectively equal 1.0×10^{-16} and 1.2×10^{-16} J Å^6 molecule^{-1}. Since Cl_2 has no permanent dipole moment, the dipole-induced component C_6^{ind} is equal to zero.

Values of the rate constant k_{mej} calculated at 303 K by means of eq 9 are also shown in Table 3. For the Ca(Sr)/Cl_2 reactions they are respectively equal to 7.7×10^{-10} and 6.6×10^{-10} cm^3 molecule^{-1} s^{-1}. One sees that the modified electron-jump formalism, although it slightly overestimates k_{exp}, better explains the magnitude of the rate constants than the classical electron-jump formalism.

In view of the very large value of the rate constants and the absence of any third-order character, one is allowed to estimate that chemiluminescence from the reaction sequence (4a−c) is unimportant for the overall destruction of the metal atoms in our experimental conditions.

In the past also the Mg/Cl_2 reaction has been investigated between 303 and 903 K using the same fast-flow reactor technique.[17] Since the electron-jump distance r_c (2.2 Å) at 303 K is about equal to the equilibrium bond length of the reaction product MgCl, a short distance charge-transfer rather than a clear electron-jump mechanism was postulated. In addition, at this short distance r_c a repulsion on the potential energy surface already occurs, resulting in a low energy barrier for the Mg/Cl_2 reaction of 3.6 ± 0.3 kJ mol^{-1}.

It needs to be pointed out that the observed activation energies of 0.2 ± 0.5 and 0.4 ± 0.4 kJ mol^{-1} for respectively the Ca and Sr reactions with Cl_2 should be considered as negligible in view of the errors which are of the same magnitude (eqs 7 and 8). This observation is in qualitative agreement with the modified electron-jump mechanism, which implies the absence of an energy barrier. The large distances r_c between 5.9 and 6.6 Å probably explains why the calculated reaction barriers on the basis of an approach of both reagents on a covalent potential energy surface will not be realistic.

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