Absolute Cross Sections for the Chemiluminescent and Chemiionizing Reactions $Mg^*(^3P)$, $Ca^*(^3P) + SOCl_2$

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The absolute cross sections for different electronic exit channels for the reactions $Mg^*(^3P)$, $Ca^*(^3P) + SOCl_2$ were measured in a beam-gas experiment. The chemiluminescence and chemiionization yields measured are low (total 2%) but equal or are even higher for some channels than those calculated from a statistical model.

Introduction

A method developed by Dagdigian [1], and independently by Telle and Brinkmann [2], enables the measurement of chemiluminescence yields in excited atomic beam reactions. The method applied for all chemiluminescence channels and combined with chemiionization yield measurements [3, 4] gives a complete information on the electronic branching ratios.

The reactions of ground state Mg and Ca-atoms with $SOCl_2$ are dark and give no measurable ion signal while excitation of the metal atoms leads to production of light and chemiions. In this report we give absolute cross sections for the product electronic channels

$$M^*(^3P) + RCl \xrightarrow{\approx\sigma_{tot}^*} MCl(X^2\Sigma) + R, \quad (1)$$

$$\xrightarrow{\sigma_{CL}^*(i)} MCl(A^2\Pi, B^2\Sigma, C^2\Pi) + R, \quad (2)$$

$$\xrightarrow{\sigma_{CI}^*} MCl^+ + R^-, \quad (3)$$

where M = Mg, Ca; R stands for SOCl, and σ_{tot}^*, $\sigma_{CL}^*(i)$ and σ_{CI}^* are absolute cross sections for ground state, excited i-th state, and ion formation, respectively. To explain part of the results we postulate certain limits on the electron affinity of the SOCl-molecule.

A comparison of the experimental electronic branching with the statistical model [5, 6] shows that energetically lower electronic exit channels are statistically populated whereas channels for which almost the whole available energy is transferred into electronic excitation are highly overpopulated. Similar surprisals were also observed for some other reactions reported previously [4, 7].

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Experiment

The excited metal beam source and vacuum chamber have been described in details elsewhere [8]. To measure absolute cross sections we followed known methods [1, 2, 4]. We assumed that 20% of the metal atoms in the beam are in the metastable ^3P_J states (after Brinkmann et al. [9]). Pressures of $SOCl_2$ were measured with a capacitance manometer (sensitivity 10^{-4} Torr) in the range $10^{-4} = 3 \cdot 10^{-3}$ Torr.

The excited beam of Ca contained also a small fraction of atoms in the metastable $^1D_2$ state, however the role of these atoms in the reaction have been neglected since they amounted to only one hundreth of the excited reactants. Nevertheless, we took the opportunity to measure the attenuation cross section for $^1D_2$-atoms also.

Results and Discussion

The total cross sections measured are given in Table 1. The values obtained from the $^3P_1$-metastable decay and from the chemiluminescence agree very well for both metal reactants. In the case of Ca* the agreement confirms that the main part of the chemiluminescence arises from the reactive collision in which $Ca^*(^3P)$ takes place, while $Ca^*(^1D)$ gives a possible small contribution to the light observed.

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Table 1. Total attenuation cross sections σ^*_{tot} [in Å^2].

	a	b	c
Mg* + $SOCl_2$	58 ± 9	—	58 ± 12
Ca* + $SOCl_2$	43 ± 6	60 ± 6	47 ± 6

Results obtained: a from the attenuation of the $^3P_1-{}^1S_0$ spectral line. b from the attenuation of the $^1D_2-{}^1S_0$ spectral line. c from chemiluminescence.

A comparison of the values of the attenuation cross sections shows that

$$\sigma^*_{tot}(Mg^*(^3P)) \geqq \sigma^*_{tot}(Ca^*(^3P)) .$$

It disagrees with the electron-jump model ("harpooning"), usually applied for this type of reaction. According to the model, the Ca*(^{3}P)-atom with its ionization potential I.P.(Ca*(^{3}P)) = 97 kcal/mole should be more strongly attenuated than the Mg*(^{3}P)-atom which has I.P.(Mg*/^{3}P) = 113 kcal/mole. A quantitative comparison of our data with the electron-jump model is impossible, because the value of the vertical electron affinity of the $SOCl_2$ molecule is not available in literature, so we can not calculate the total cross sections for "harpooning".

Absolute cross sections for chemiluminescence from an electronic state i, $\sigma^*_{CL}(i)$, and for chemiionization σ^*_{CI}, together with corresponding photon yields defined as $\Phi^*_{CL}(i) = \sigma^*_{CL}(i)/\sigma^*_{tot}$ and $\Phi^*_{CI} = \sigma^*_{CI}/\sigma^*_{tot}$, are collected in Table 2. The photon yields for chemiluminescence and chemiionization total 2% for both metals, despite the fact that electronic excitation consumes rather different amounts of energy released in the reactions ($\approx 90\%$ for Mg and $\approx 50\%$ for Ca, respectively). Compared to the efficient reaction Ca* + Cl_2, where $\Phi^*_{CL} = (39.0 \pm 6.3)\%$ [2], the photon yields for chemiluminescence in the $SOCl_2$ reactions can be considered as low.

A close look at Table 2 reveals an interesting situation in the CI- and CL-photon yields. For magnesium Φ^*_{CI}(Mg) is higher than Φ^*_{CL}(Mg) by an order of magnitude; on the contrary $\Phi^*_{CI}(Ca) < \Phi^*_{CL}(Ca)$, and moreover $\Phi^*_{CI}(Mg) > \Phi^*_{CI}(Ca)$. These results can be explained as due to specific energetics of the chemiluminescence and chemiionization channels. A schematic energy diagram is given in Figure 1. It is based on dissociation energies taken from Rosen [10], excitation energies from Moore [11], and ionization potentials

$$\text{I.P.(MgCl)} = (154 \pm 7)\ \text{kcal/mole},$$
$$\text{I.P.(CaCl)} = (128 \pm 7)\ \text{kcal/mole}$$

after Wren [12]. Because of the lack of literature data on the electron affinity of the SOCl molecule, E.A.(SOCl), we can not place definitely the chemiionization levels for both reactions. However, ruling chemiionization levels like in Fig. 1 (dashed lines) clears the situation in Table 2, if we remember that in all known reactions the photon yield of a lower electronic state is higher than that of an

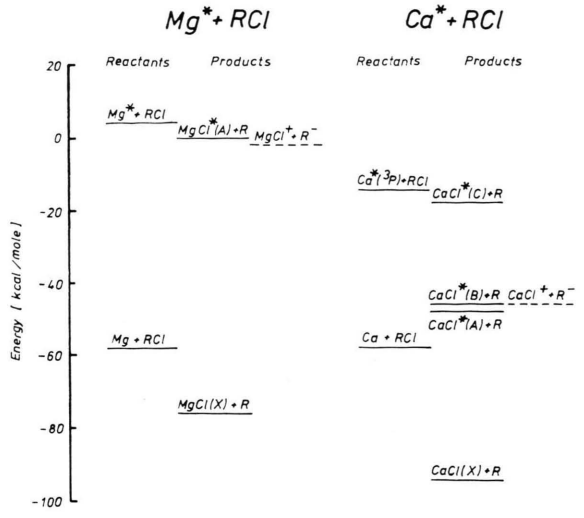

Fig. 1. Energy diagram for the reactions studied (R stands for SOCl). Zero on the energy scale corresponds to dissociation into M + R + Cl. Solid lines represent well known energy levels of the reactants and products, dashed lines mark the postulated energies of chemiionization levels.

Table 2. Absolute cross sections for chemiluminescence[a] σ^*_{CL}(i) and chemiionization[b] σ^*_{CI} [in Å^2] and corresponding photon yields Φ^*_{CL}(i) and Φ^*_{CI} [in %].

	MCl* (A state)		MCl* (B state)		MCl* (C state)		MCl^+ formation	
	σ^*_{CL}(A)	Φ^*_{CL}(A)	σ^*_{CL}(B)	Φ^*_{CL}(B)	σ^*_{CL}(C)	Φ^*_{CL}(C)	σ^*_{CI}	Φ^*_{CI}
Mg* + $SOCl_2$	0.10	0.18	—	—	—	—	0.86	1.5
Ca* + $SOCl_2$	0.86	1.9	0.10	0.23	0.010	0.023	0.20	0.47

[a] Experimental error: ±30%. [b] Experimental error: ±50%.

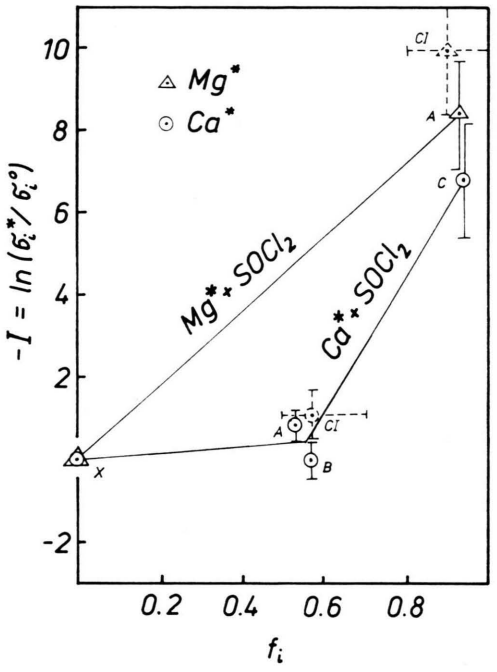

Fig. 2. Surprisal plot of electronic product state distributions (explanation see in text). The points found using the postulated energies of chemiionization channels are drawn with dashed lines.

upper one. Thereby we postulate certain limits on the value of the E.A.(SOCl). These limits, that can be written in the form

$$\text{E.A.(SOCl)} = (80.2 \pm 8.8)\,\text{kcal/mole}\,,$$

are calculated as the differences between ionization potentials of the product radical (MgCl or CaCl) and the postulated energy of a given chemiionization channel from Figure 1. The upper limit is probably overestimated, since we can expect E.A.(SOCl) to be lower than the electron affinity of the Cl atom, i.e. (83.3 ± 0.2) kcal/mole [13].

To compare the obtained branching ratios with the statistical model [5, 6] the negative surprisal plot is presented in Figure 2. Assuming reactive collisions only, we can write the negative surprisal as $-I = \ln \sigma_i^*/\sigma_i^0$, with RRHO-prior $\sigma_i^0 \approx g_i \cdot (E'_{\text{tot}} - E'_i)^7$ for the i-th electronic state with energy E'_i and degeneracy g_i, where E'_{tot} is the total energy available to products (σ_i^* above stands for both $\sigma_{\text{CL}}^*(i)$ and σ_{CI}^*). The negative surprisal is plotted against $f_i = E'_i/E'_{\text{tot}}$, i.e. the fraction of available energy present as product electronic excitation. As shown in Fig. 2, the production of the A and B excited states of CaCl agrees with that from the statistical model, while the production of CaCl*(C) and MgCl*(A) is faster than expected by a factor of 10^3. The dashed points on the surprisal plot were calculated for chemiionization channels in order to check the value of E.A.(SOCl) suggested above. As one can see from Fig. 2, they fit well to the solid points obtained from chemiluminescence.

At present we can not explain why the channels with higher f_i-values are overpopulated relative to the statistical model. The effect is probably due to reaction dynamics. A similar non-statistical "resonance" in electronic energy transfer was also observed in analogous reactions of Mg* and Ca* with hexafluorides [7] and some halogens [4].

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