Cross Sections for the Collisions of Alkaline Earth Atoms in the ^3P Excited State with Chlorine Molecule *

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Z. Naturforsch. **34 a**, 459–463 (1979) ; received September 30, 1978

The total attenuation cross sections, σ^*, were measured for collisions of an excited atomic beam of Mg, Ca or Sr with a target of Cl_2 molecules. The experimental σ^* values equal: 85 Å², 100 Å² and 180 Å² for Mg*, Ca* and Sr*, respectively. Moreover, the reactive cross sections, $\sigma_{\hat{R}}$ were calculated, assuming the "harpoon mechanism" for the reactions in question. The obtained values are: $\sigma_{\hat{R}}^*(Mg^* + Cl_2) \leqq 61$ Å², $\sigma_{\hat{R}}^*(Ca^* + Cl_2) \leqq 102$ Å², $\sigma_{\hat{R}}^*(Sr^* + Cl_2) \leqq 130$ Å². The good agreement between the experimental and theoretical values shows that for this type of reaction the "harpoon mechanism" takes place.

The increasing number of chemical reaction studies is motivated by the search for chemical systems suitable for electronic transition chemical lasers. Experiments under single collision conditions are a useful tool for understanding the detailed dynamics of highly exothermic chemical reactions. Many studies of the reactions of alkaline earth atoms in the ground state with halogens have already been performed [1–7]. Brinkmann and Telle [8] for the first time used a beam of excited Ca atoms as the reactants in reactive systems including Cl_2 or HCl:

$$Ca^*(^3P, {}^1D) + Cl_2(HCl) \rightarrow CaCl^*(A^2\Pi, B^2\Sigma) + Cl(H). \quad (1)$$

Based on this technique, the reactions of other elements of the II a group of the periodic system, namely Mg and Sr, have been investigated. In our earlier work [9] we presented the chemiluminescent spectra of MgCl and SrCl radicals obtained in the reactions

$$Mg^*(^3P) + Cl_2 \rightarrow MgCl^*(A^2\Pi) + Cl\,; \quad (2)$$

$$Sr^*(^3P) + Cl_2 \rightarrow SrCl^*(A^2\Pi, B^2\Sigma, C^2\Pi) + Cl\,. \quad (3)$$

The present work contains pressure dependences of the chemiluminescent light for the reactions of excited $Mg^*(^3P)$, $Ca^*(^3P)$ and $Sr^*(^3P)$ atoms with Cl_2. From these measurements, values of attenuation cross sections, σ^*, were determined and compared with values calculated on the basis of the "harpoon model" for the reactions in question.

* This work was carried on under the research project MR.I.5.1.05.

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0340-4811 / 79 / 0400-0459 $ 01.00/0

Experimental

The experimental set up had been described previously [10]. The excited metal beam was produced by a source similar to that described by Walther [11] and Brinkmannn et al. [12]. The schematic diagram of the beam – gas arrangement is shown in Figure 1. The atomic beam crosses an uncollimated beam of Cl_2 molecules. The chlorine gas was proportioned by means of a calibrated inlet valve. The inlet valve was calibrated before measurements, using a resistance microgauge (placed at G; see Figure 1). Simultaneously, the pressure at the top of the vacuum chamber was measured, where it was significantly lower. In this way we obtained the dependences of both pressures on the scale of the inlet valve. During measurements, because of the corrosivity of chlorine gas, we measured the pressure at the top of the vacuum chamber only. The readings were used as mark points to test the scale of the inlet valve. The reaction zone was monitored

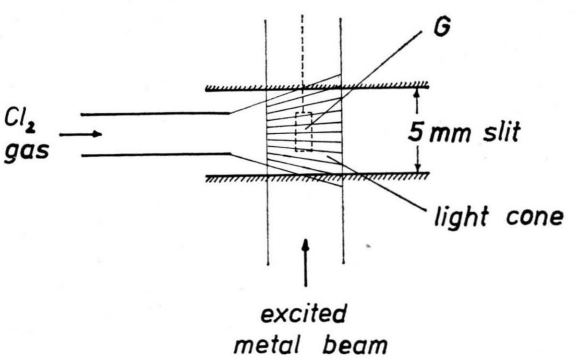

Fig. 1. Schematic diagram of the beam – gas arrangement for total attenuation cross section measurements. Localisation of the pressure microgauge (G) during the calibration of inlet valve is marked by dashed lines.

through a 5 mm slit mounted parallel to the Cl_2-molecular beam orifice at a distance of 2 cm from the center of the beam crossing. In our molecular beam apparatus we did not observe any influence of Cl_2 (or air) flow on the production rate of ^3P-excited atoms in the mTorr range.

The spectra in the $\lambda = 3000 \div 4000$ Å region were recorded using a scanning monochromator (typical scan rate 100 Å/min) equipped with a Jobin-Yvon diffraction grating (1800 grooves/mm; blaze wavelength 3500 Å) and a Carl Zeiss Jena M 12 FQS 35 photomultiplier (S-13 cathode). In the $\lambda = 4000 \div 7000$ Å region we used a scanning Carl Zeiss Jena SPM-2 grating monochromator (typical scan rate 50 Å/min; grating 650 grooves/mm; 5700 Å blaze wavelength) and FEU-51 photomultiplier (S-20 cathode). The typical value of the spectral slitwidth was 8 Å. The chemiluminescence spectra are uncorrected for the spectral response of the photocathodes.

Atomic beams of Ca and Sr contain a small fraction of atoms excited to the ^1D state also. Since the radiative lifetimes of the ^3P and ^1D levels of Ca are known [13, 14], the relative ^1D to the ^3P-state population can be obtained from the measurements of the intensities of both $^3P_1$-^1S and ^1D-^1S lines. The ratio of ^1D to $^3P_1$ populations was obtained to be 0.028. That value gives a ratio of ^1D to total ^3P population of about 1%, which is in good agreement with the value determined by Dagdigian [14]. We assumed that this small ^1D component in the Ca-beam (and in Sr-beam) and its influence on the chemiluminescence spectra can be neglected.

Experimental Results

The chemiluminescent spectra recorded at several pressures of Cl_2 are presented in Figs. 2, 3, 4 for Mg^*, Ca^*, $Sr^* + Cl_2$, respectively.

It results from the Figs. 2, 3, 4 that the contours of the chemiluminescence spectra do not depend on the Cl_2 pressure.

As shown by Jonah et al. [2] and Yokozeki et al. [15], the variation of the chemiluminescent light intensity I with Cl_2 pressure is described by

$$I = C \cdot [Cl_2] \exp\{-\sigma^* l [Cl_2]\}, \quad (4)$$

where C is a constant, $[Cl_2]$ the Cl_2 concentration, l the effective path length of the atomic beam in the

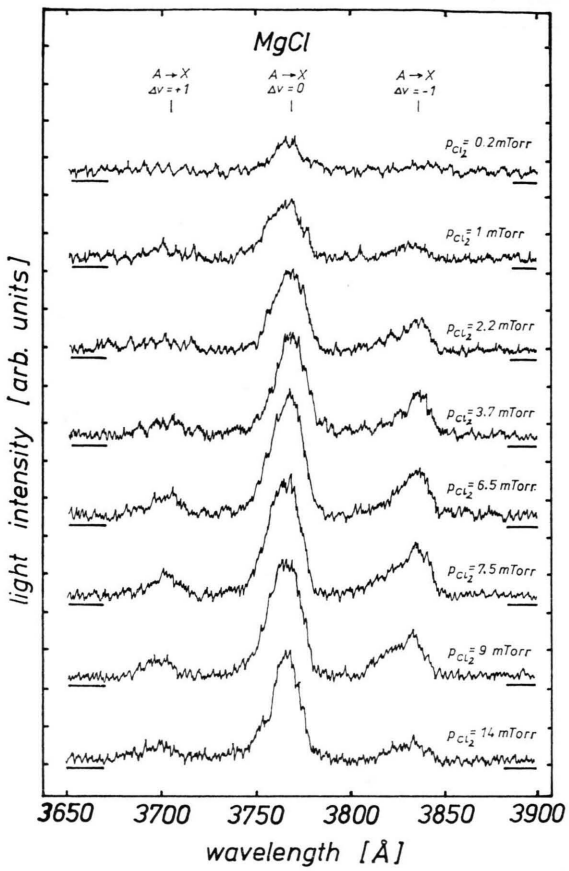

Fig. 2. Chemiluminescent spectra of MgCl from the reaction $Mg^* + Cl_2$ for several Cl_2 pressures. The spectra are given with different baselines.

chlorine gas and σ^* the total attenuation cross section for the collision process $M^* + Cl_2$ (where M = Mg, Ca, Sr). It follows from (4) that the attenuation cross section σ^* is related to the chlorine pressure $[Cl_2]_{max}$ at the intensity maximum of chemiluminescence light, by the equation

$$\sigma^* = 1/l[Cl_2]_{max}. \quad (5)$$

In Fig. 5 the pressure dependences of chemiluminescence light from $Mg^* + Cl_2$, $Ca^* + Cl_2$ and $Sr^* + Cl_2$ reactions for optimal atomic beam oven temperatures (870 K, 1020 K and 1070 K, respectively) are collected. The effective beam path length was assumed to be 5 mm. The diameter of the visible chemiluminiscent light cone at the position of pressure gauge (see Fig. 1) was about 5 mm, and the slit mounted near the beam-crossing point had the same width. The beam profile, and with it l,

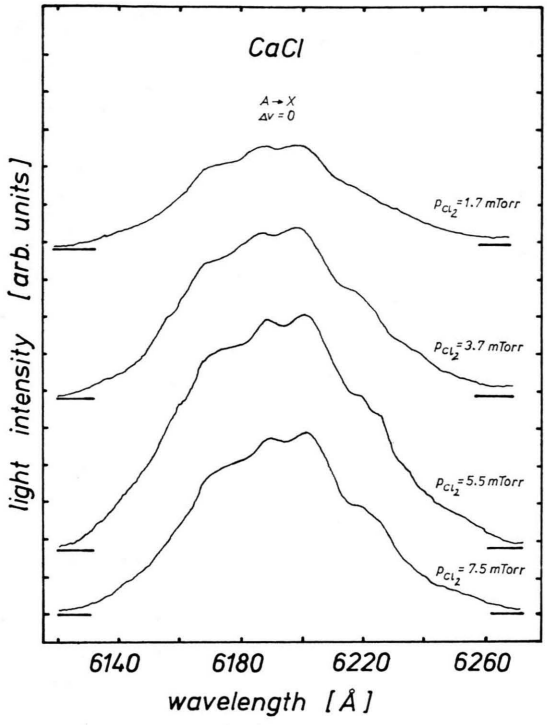

Fig. 3. Chemiluminescent spectra of CaCl from the reaction $Ca^* + Cl_2$ for several Cl_2 pressures. The spectra are given with different baselines.

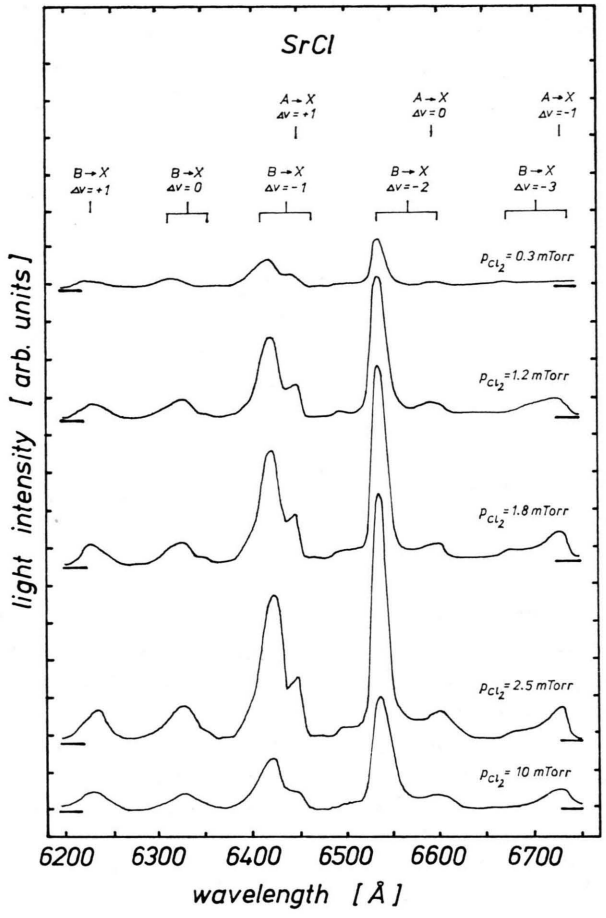

Fig. 4. Chemiluminescent spectra of SrCl from the reaction $Sr^* + Cl_2$ for several Cl_2 pressures. The spectra are given with different baselines.

slightly changes with pressure, but this variation is not taken into account in the σ^* values which we obtained.

From the experimental data presented in Fig. 5 and using (5) we found the attenuation cross sections σ^* (an asterisk denotes a process including an excited reactant). The results are summarized in Table 1.

The total cross sections σ^* are given without any experimental error, which can not be determined exactly. As one can expect, the error arises from the uncertainty of the effective beam path length, from the partial pressure of the reaction products, and from the fact that our assumption of uniform pressure in the observed region was not rigorously fulfilled.

Reactive system	σ^*[Å²]
$Mg^* + Cl_2$	85
$Ca^* + Cl_2$	100
$Sr^* + Cl_2$	180

Table 1. Experimental total attenuation cross sections.

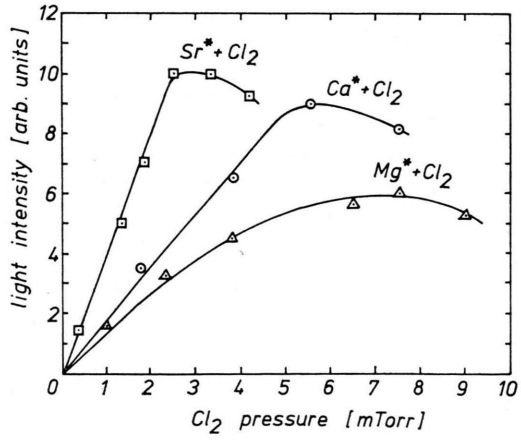

Fig. 5. Pressure dependences of the chemiluminescence from $Mg^* + Cl_2$, $Ca^* + Cl_2$ and $Sr^* + Cl_2$ reactions (see text).

Discussion

Experimentally determined values of the total (reactive and non-reactive) cross sections σ^* are the upper limits of the reactive cross sections. The relatively large magnitudes of the obtained attenuation cross sections suggest the "harpoon mechanism" for the reactions in question. The harpoon model for the reactions of group II a atoms with halogens was considered by many authors [2, 4, 16]. Since the excited alkaline earth atom has a lower ionization potential, it is more "alkali-like" than the unexcited one and an application of the "harpoon mechanism" as a first approximation is justified.

In the first step of the reaction the transfer of the valence electron to the halogen molecule occurs. A simple estimate of the range R_x of the "harpoon electron" can be made on the basis of the energy balance of the charge transfer [17]:

$$-e^2/R_x + \Delta E_0 = -C/R_x{}^6\,, \tag{7}$$

where the first term is the attractive Coulombic potential and ΔE_0 the difference between the ionization potential of the alkaline earth atom and the electron affinity of the halogen molecule. Since the covalent interaction $-C/R_x{}^6$ is neglegible compared to the Coulombic interaction at R_x, we obtain as an approximate formula for R_x:

$$R_x \approx \frac{e^2}{\Delta E_0} = \frac{14.35}{\Delta E_0[\mathrm{eV}]}\ [\mathrm{in\ \AA}]. \tag{8}$$

Since the reaction takes place after the electron transfer, we expect that the reactive cross section is

$$\sigma_R = \pi R_x{}^2\,. \tag{9}$$

The reaction energetics can be illustrated by the potential curves which are given in Fig. 6 for the

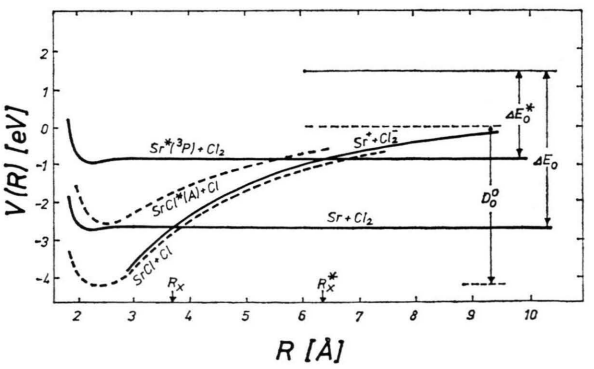

Fig. 6. Potential energy diagram for $Sr^* + Cl_2$ "harpoon reaction" (explanation — see text).

Table 2. Theoretical reactive cross sections calculated on the ground of the "harpoon model".

	Mg	Ca	Sr
ΔE_0 [eV]	6.0	4.4	4.0
R_x [Å]	2.4	3.3	3.6
σ_R [Å²]	18	33	40
	Mg* (^{3}P)	Ca* (^{3}P)	Sr* (^{3}P)
$\Delta E_0{}^*$ [eV]	3.2	2.5	2.2
$R_x{}^*$ [Å]	4.4	5.7	6.4
$\sigma_R{}^*$ [Å²]	61	102	130

$Sr + Cl_2$ system before (solid lines) and after (dashed lines) reaction. The ΔE_0 and R_x values for the reactant in the excited state are marked by an asterisk ($D_0{}^0$ is the dissociation energy of the SrCl molecule).

Table 2 summarize the calculated values of the reactive cross sections for the $M(^1S) + Cl_2$ and $M^*(^3P) + Cl_2$ reactive systems, obtained using (9). The calculations were performed with atomic energy levels taken from Moore's [18] tables, and taking the electron affinity of Cl_2 from Kikoin [19]. Since the electron affinity is $\leqq 1.7$ eV, the reactive cross sections given in Table 2 must be considered as upper limits of the real values.

The comparison of the experimental values of cross sections σ^* with the theoretical values $\sigma_R{}^*$ confirms that the "harpoon mechanism" is an adequate model for the reactive collisions of alkaline earth atoms in long-lived excited states with chlorine molecules. The observed discrepancies between σ^* and $\sigma_R{}^*$ may arise from experimental errors as discussed above. A systematic trend in the σ^* (experimental) and $\sigma_R{}^*$ (theoretical) values for Mg, Ca and Sr is evident (see Tables 1 and 2). It follows that $\sigma^*(Mg^* + Cl_2) < \sigma^*(Ca^* + Cl_2) < \sigma^*(Sr^* + Cl_2)$, and the calculated values show the same ordering. To conclude, one can say that, if the ionization potential from a given state of an element decreases, the reactive cross section increases. The cross sections obtained for excited reactants are of the same order of magnitude as the reactive cross sections for the collisions of alkali atoms with chlorine molecules [17].

Acknowledgements

We thank Docent Dr. Habil. Józef Heldt for helpful discussions. We are also grateful to Prof. Michael Menzinger for his comments on an initial draft of the manuscript.

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