BULLETIN OF THE

KOREAN CHEMICAL SOCEITY

Kinetics of Cl Atom Reactions. Anormalous Fluorescence Behavior of Some Cl Atomic Transitions

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(Received June 30,, 1979)

During the study of the kinetics of Cl atom reactions by atomic fluorescence method we observed anormalous fluorescence emission for some atomic transitions. Instead of usual decrease of the fluorescence intensity by adding substrate, 1363 Å transition ($^2P_{3/2} \rightarrow ^2P_{1/2}$) intensity increased by adding substrate. From the normally behaved fluorescence lines the absolute rate constant for the reaction, $Cl + CH_3Cl \rightarrow$, was found to be 4.2×10^{-13} cc/molecule sec at 20°C.

1. Introduction

Chlorine atoms ($^2P_{1/2}$, and $^2P^{3/2}$ state) have been detected directly by vacuum ultraviolet atomic absorption[1], atomic fluorescence,[2] and gas phase ESR techniques.[3] Kinetics of atomic species were usually carried out by using the flash photolysis[4] or flow discharge method.[5] The important advantage of atomic fluorescence method of the detection of free atoms has been claimed to be the sensitivity increase by increasing the emission line intensity. Furthermore the atomic transitions can be clearly seen without any interference from molecular species. These advantages of atomic fluorescence method over atomic absorption prompted us to carry out the kinetics of Cl atom reaction by the flow discharge-atomic fluorescence method.

In an atomic fluorescence experiment, the fluorescence intensity is given by,[6]

$$I_f = I_0 B_z A_x B_z \varPhi \frac{\Omega}{4\pi} \qquad (1)$$

where I_0 is the intensity of radiation of the emission lamp, A_x is the absorption factor, B_z is the factor which accounts for the decrease in fluorescence intensity due to the absorption from emission region to entrance slit, B_x is the factor which accounts for the decrease in intensity of the exciting radiation

by absorbing atoms in the region between the emitting area and the lamp window, Ω is the steric factor for the observation of the fluorescence, and $\varPhi$ is the fluorescence efficiency. For the work in atomic absorption spectroscopy an excitation source of moderate intensity with narrow emission line is needed. In atomic fluorescence, however, the intensity of the excitation source is of primary importance as shown in equation (1).

In this paper we wish to report the kinetics of Cl atom reaction with CH_3Cl by atomic fluorescence measurements of various Cl atom transitions. We observed anormalous behavior of some atomic flurescence signals, which indicates that kinetic-atomic fluorescence experiments should be carried out with caution, especially when the excited state energy levels are so closely spaced as Cl atoms. The possible reasons of the anormalous behavior are also discussed.

2. Experimental

Materials. Cl_2: Matheson Gas Products, Research Grade, 99.96 %; Ethylene: Phyllips Petr, Co. Research Grade, 99.98 %; Hydrogen: Matheson Gas Products, 99.95% min; Deuterium: Bio-Rad Lab., Research Grade, 99.65% min; Cyclopropane: Matheson Gas Products, 99% min. Possible impurities were eliminated by several freeze-pump-thaw cycles with appropriate coolants before use.

Procedure. The main flow line was made of 12 mm I.D. glass tubing, and the reaction zone (from injec:io1 port to the monochromator slit) was treated with orthophosphoric acid to reduce the wall recombination of atomic chlorine. The pressures in the flow line and the substrate reservoir were measured with the Statham Gauge Transducers that were precalibrated with a fused quartz pressure guage (Texas Ins. model 140), and the uncertainty in the pressure measurement was less than 0.5 torr in the range from 1 to 100 torr. The helium flow rate in the main flow line was measured with a precalibrated ball type flow meter (Manostat Co.) and the flow rates of the substrate were calculated by monitoring the pressure drop of the substrate reservoir. The constant flow of substrate was monitored with a ball type flow meter during the kinetic experiments. 2450 MHz microwave discharges with Evanson type aircooled electrodeless microwave discharge cavities were used for both main flow line and the emission lamp to generate chlorine atoms and the Cl atom emission line respectively.

Since the concentration of the generated chlorine atoms in the main flow line and also the emission intensity of the lamp were dependent on the power input of the discharge, pressure and the concentration of chlorine. as well as on other paramters, all the conditions were kept constant during each experiment. The actual power input of the discharge was measured with a bidirectional power meter (Opthos Instruments) which was located between the microwave generator and the coaxial cable leading to the cavity. The stability of the emission lines was found to be better than 2 % fluctuation. Five capillary substrate inlets were located 5 cm apart from each other in the middle of the flow tube for complete mixing with atomic chlorine, and the distance from the first (farthest) inlet to the detec-

tion point was about 35 cm.

Emission lamp. A flow discharge in molecular chlorine diluted with an excess of helium (less than 2% of hydrogen in helium) was used as the Cl atomic line source. This flow discharge lamp gave a very stable line for as long as we kept the conditions of the discharge constant. Although prolonged use of LiF window causes color centers, no change of transmission of LiF window was observed during a set of experiment.

Monochromator and detector. The vacuum inside the monochromator (1/2m) was always less than 10 torr. At the exit slit (slit width 100 to 150 μ) a model 650 McPherson photomultiplier assembly containing an EMI type 9514 photomultiplier tube was attached with a vacuum tight window which was coated with sodium salicylate which acted as a scintillator. The detector response was linear from 1,000 to 3,000 A. The photomultiplier output was pre-amplified and tuned to the frequency (100 Hz) of the electrical chopper (Type L40C, Bulova Co.) which was positioned just inside the entrance slit of the monochromator. The tuned signal was selectively amplified (PAR model 213 preamplifier $\rightarrow$ PAR model 210 selective amplifier $\rightarrow$ PAR 270 lock-in amplifier) and the output of the Lock-in amplifier was recorded by a strip chart recorder.[7]

The fluorescence cell and optical arrangements are shown in Figure 1. The reflection mirrors were coated with platinum and the outside surface of the cell was blackened to prevent any light interference. A Wood's horn was employed to prevent the possible interference of the radiation directly from the microwave discharge in the main flow line.

For the kinetic experiment, one first turns on the microwave discharge in the main flow line and slowly injects Cl_2 upstream from the discharge to make atomic chlorine, and
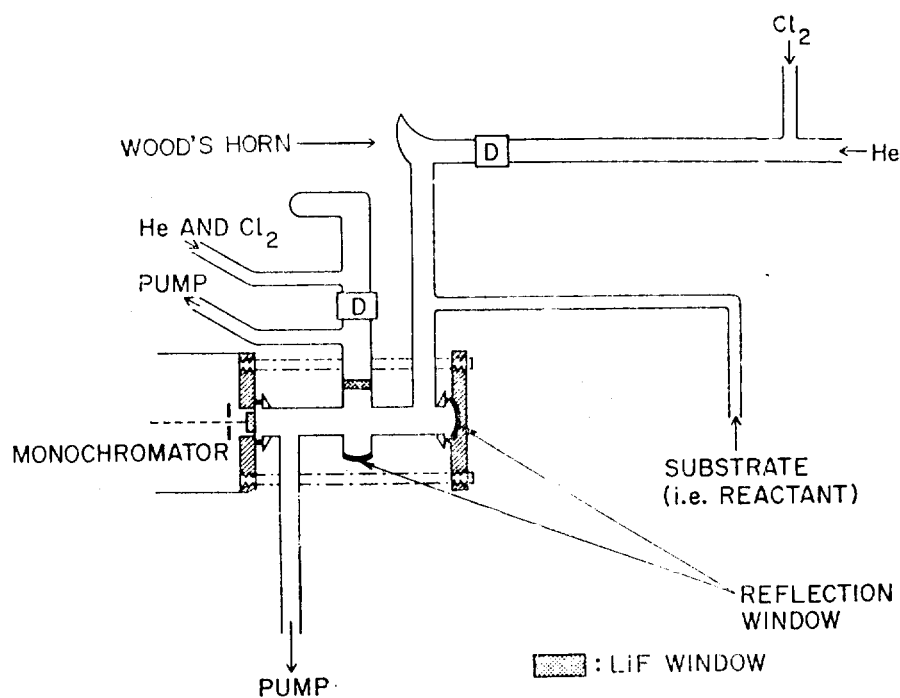

Figure 1. Fluorescence cell. D:Microwave discharge.

then, after assuring oneself that no stray light from the plasma in the main flow line reaches the detection point by scanning the spectrum, one turns on the discharge of the emission lamp with proper lamp conditions (pressure, flow rate and microwave power) which were predetermined by a separate experiment. Under the usual conditions, scattered light from the emission lamp itself is always less than 1% of the total intensity of the fluorescence emission by Cl atoms in the cell. If one assumes that the fluorescence intensity is directly proportional to the atomic concentrations, the fluorescence intensity is related to

$$\ln(I_0/I_m) = k_b[M]t \qquad (2)$$

$t = x/V$,   x: distance from injection to the detection point
V: linear velocity of the flow
k_b = bimolecular rate constant
$[M]$ = substrate concentration
I_0 = fluorescence intensity without M
I = fluorescence intensity with M

so k_b can be obtained from the slope of the $\ln(I_0/I_m)$ vs. t plot.

3. Results and Discussion

Table 1 includes the dependence of the fluorescence intensities on the concentration of substrate, in this case, CH₃Cl. As shown in the table the fluorescence intensities of 1390 A and 1396 A lines were reduced by increasing substrate concentrations, but the intensity of 1363 A line apparently increased at first (i.e., lower substrate concentration), then decreased as we increased the CH₃Cl concentrations. The same effect was observed with other substrates, such as ethylene, H₂, D and cyclopropane. This unexpected result (i.e., the increase of the fluorescence intensity by adding substrates) may be caused by several factors: (1) The most simple case, the oscillator strength of the 1363 A line has been changed by adding substrate, (2) The population of the Cl($^2P_{1/2}$) or Cl($^2P_{3/2}$) atoms were increased rather than decreased by the reaction with substrate, e.g., the Cl ($^2P_{1/2}$) or Cl($^2P_{3/2}$) atoms were generated by a chain reaction such as,

$$Cl + PH \longrightarrow HCl + R$$
$$R + Cl_2 \longrightarrow Cl(^2P_{1/2}) \text{ or } Cl(^2P_{3/2}) + RCl$$
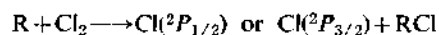
(3) The 1363 A line has much stronger absorption by C′₂ itself compared to the 1389 and 1396 A lines, and so, this stronger absorption by Cl₂ makes the original emission of the 1363 A line appear weaker than its actual intensity (i.e., radiation imprisonment by Cl₂). (4) The population of the excited state (the state from which the 1363 A line originates) was increased by substrates some way. Case (1) must not be important because we did not detect any unusual behavior in the absorption experiment for the 1363 A line. If the oscillator strength was changed by adding substrates the same effect should have been observed in the absorption experiment. Case (2) was also discarded from the following reasoning: if the concentration of Cl($^2P_{1/2}$) or Cl($^2P_{3/2}$) atoms increased during the reaction, we should have observed

the same effect for all the fluorescence lines. Furthermore under our usual conditions, most of the Cl₂ were dissociated and only a very small amount of molecular Cl₂ could exist in the reaction zone. Case (3) is also ignorable under our experimental conditions. Table 2 shows the absorption of Cl₂ on the emission lines of atomic chlorine.

Apparently the 1363 A line has less absorption than the 1390 and 1396 A lines. So, if the molecular absorption affected the measurements, the 1390 and 1396 A lines should show larger effects than the 1363 A line.

Therefore we believe that case (4) is the reason for the unexpected observation of the enhanced emission of the 1363 A line: in some way the population of the excited ($^2P^o_{1/2}$) state was increased by the reaction with substrate. A similar effect was also observed by Connor, Young and Strausz[8] in the flash photolysis study of excited antimony and bismuth atoms. In some cases the emission intensity from the excited bismuth or antimony atom was increased as the pressure of of the substrates was increased. At the present time we do not have reasonable explanations of how the excited state population could be increased by adding substrates.

The fluorescence decay of 1396 and 1390 A lines follows the kinetic equation, and Figure 2 shows the kinetic plot for the reaction of Cl atoms with CH₃Cl. The rate constants obtained from the fluorescence experiment by monitoring 1396 and 1390 A lines are in reasonable agreement with the values from the atomic absorption measurements, indicating the similar chemical reactivities of Cl($^2P_{1/2}$) and Cl($^2P_{3/2}$)

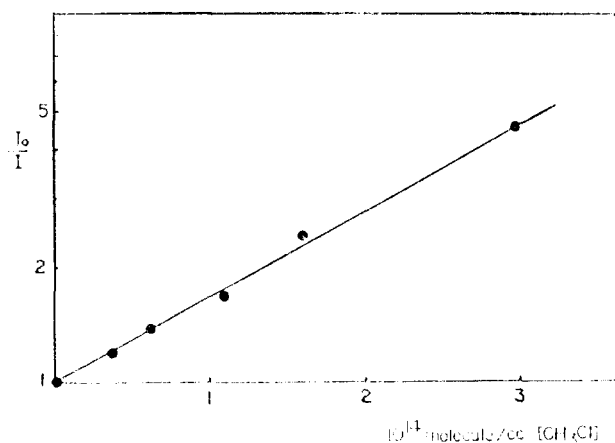**Figure 2.** I_{OF}/I_F vs. [CH_3Cl] for the 1396 A fluorescence line. $k=4.2\times10^{-13}$ cc/molecule sec.

atoms. If the reactivity of the $Cl(^2P_{1/2})$ atom is more than two orders of magnitude faster than $Cl(^2P_{3/2})$, as reported by Donovan and coworkers, the rate constant obtained by the fluorescence method will be larger than the rate constant obtained by the absorption method since the fluorescence signal intensity is proportional to the mixed concentration of both $Cl(^2P_{1/2})$ and $Cl(^2P_{3/2})$ atoms, and the concentration of $Cl(^2P_{1/2})$ atoms in our experiment is about 5 to 10 % of the $Cl(^2P_{3/2})$ atom concentration.

The fluorescence method is less specific for the study of the individual reactivity of $Cl(^2P_{1/2})$ and $Cl(^2P_{3/2})$ atoms because of the fact that both transitions to $Cl(^2P_{1/2})$ and $Cl(^2P_{3/2})$ are from identical excited energy levels, and also because the fluorescence of Cl atoms apparently involves many unknown interferences. The 1363 A line does not follow

the simple assumption that the fluorescence emission is not perturbed by the reaction. We think that the mechanism of atomic fluorescence is much more complicated when the upper (excited) states are very closely stpaced, as in the case of Cl atomic transitions, so great care should be made to get reasonable results.

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MO Studies on Configuration and Conformation (VI). FMO Interpretation of Nonbonded Interactions

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Simple rules for predicting nonbonded interactions have been proposed. It was found that an end-to-end nonbonded interaction is either attractive or repulsive depending on the sign of the product of AO coefficients of two end atoms in the HOMO of a closed shell conjugated system with a crowded structure. The nonbonded attraction becomes the greatest in a 4N+2 electron conjugated system, while it is repulsive in a 4N electron system. For 4N+1 and 4N−1 electron systems, it is attractive but the effect is less than that in 4N+2 system. As a result of the attractive interaction, the overlap population of an atom pair increases (decreases) if the HOMO is antibonding (bonding) for the atom pair. The rules were illustrated with some examples.

Introduction

In the Hartree-Fock SCF method, an orbital energy ϵ_i is an eigenvalue of the effective one-electron operator

(Fock operator) $\hat{F}$ associated with eigenfunction Ψ_i.

$$\hat{F}\Psi_i=\epsilon_i\phi_i \tag{1}$$

The total Hartree-Fock energy, E_T, is however not a simple