

염소원자의 반응속도 연구

朱 光 烈

서울대학교 자연과학대학 화학과

(1979. 5. 27 접수)

A Direct Kinetic Study of Cl Atom Reactions

Kwang Yul Choo

Department of Chemistry, College of Natural Sciences, Seoul National University,
Seoul 151, Korea

(Received May 27, 1979)

요 약. Flow-discharge-원자흡수선 측정법으로 $\text{Cl}(^2P_{1/2})$ 원자의 존재를 확인하였고 $\text{Cl}(^2P_{3/2})$ 원자의 여러 물질과의 반응속도를 직접적으로 측정하였다. 본 실험에서 얻은 결과는 간접적인 방법으로 얻은 반응속도와 거의 같음을 보였다. $\text{Cl}(^2P_{3/2})$ 원자와 $\text{Cl}(^2P_{1/2})$ 원자는 거의 같은 반응성을 가지며, 이러한 반응의 유사성 때문에 $\text{Cl}(^2P_{1/2})$ 원자가 Cl 원자의 반응속도에는 그다지 큰 영향을 주지 않음을 보인다.

ABSTRACT. A non-Boltzman equilibrium population of $\text{Cl}(^2P_{1/2})$ atoms has been observed in a flow discharge-atomic absorption experiment. The rates of reactions of $\text{Cl}(^2P_{3/2})$ atoms with various substrates are in reasonable agreement with reported values determined by competition methods. The similar reactivities of both $\text{Cl}(^2P_{1/2})$ and $\text{Cl}(^2P_{3/2})$ atoms indicate that the contribution of $\text{Cl}(^2P_{1/2})$ atoms to the rate measurements in the competition experiment is small, and this negligible contribution may be the reason why the rate constants obtained by assuming single reactive species (in competition method) agree well with our direct measurement.

INTRODUCTION

The reaction of atomic chlorine with various hydrocarbons is one of the most extensively studied areas in reaction kinetics, as indicated in the reviews of Fettis and Knox.¹ Most of the reaction rates have been obtained by competition methods, in which two or more substances are made to react simultaneously with chlorine atoms. The chlorine atoms are conveniently generated by irradiating chlorine molecules by ultraviolet or visible light. The absorption spectrum of the chlorine molecule in

the ultraviolet and visible regions is quite well known. A strong continuum runs from about 2500 to 4,200 Å, a weak continuum is found between 4,300 and 4,800 Å, banded absorption between 4,800 and 5,800 Å.² The strong continuum is customarily attributed to transitions to a repulsive $^1\pi_u$ state, while the bands and the weak adjoining continuum are attributed to transitions to a stable $^3\pi_{0,u}$ state. An approximate potential energy diagram is shown in Fig. 1.

As one may notice from the diagram, the

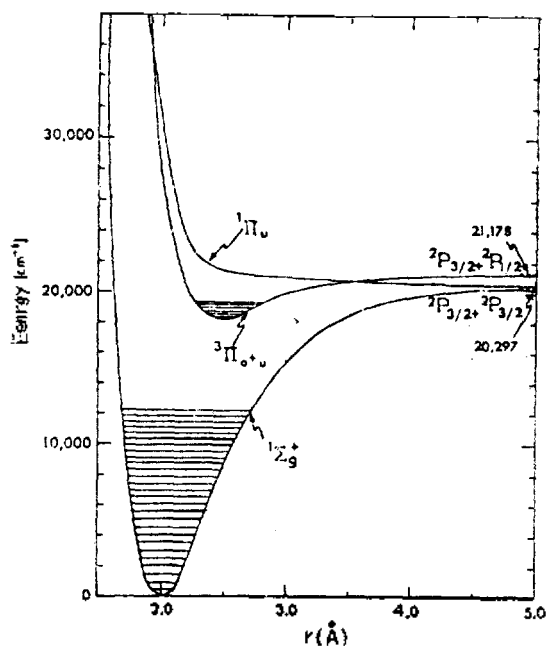


Fig. 1. Approximate energy diagram for Cl_2 .²

irradiation of chlorine molecules with wavelengths shorter than 5,000 Å can produce considerable amounts of electronically excited $\text{Cl}(^2P_{1/2})$ atoms as well as ground state $\text{Cl}(^2P_{3/2})$ atoms. The mean radiative lifetime for the spontaneous emission of $\text{Cl}(^2P_{1/2})$ atoms was estimated to be about 83 sec,³ so the contribution from emission to the overall decay of $\text{Cl}(^2P_{1/2})$ atom can usually be neglected. If the concentration of $\text{Cl}(^2P_{1/2})$ atoms is not negligible, and the chemical reactivity of $\text{Cl}(^2P_{1/2})$ atoms is quite different from that of $\text{Cl}(^2P_{3/2})$ atoms, the results obtained from the competition method may not be reliable, since only a single reactive species, namely the Cl atoms in the ground electronic state, was assumed to be present in the competitive kinetic studies.

This possible high chemical reactivity of electronically excited halogen atoms was experimentally observed by Callear and Broadbent,⁴

Table 1. $\Delta E(^2P_{3/2}-^2P_{1/2})$ for halogen atoms.

	F	Cl	Br	I
$E(\text{kcal})$	1.555	2.518	10.533	21.733

Table 2. Properties of $\text{Cl}(^2P_{1/2})$ atoms.

$\Delta E(^2P_{1/2}-^2P_{3/2})$	2.518 kcal (881 cm^{-1})
Boltzman fraction	7.3×10^{-3} at 300°K
τ (mean radiative life time)	83 seconds

and Callear and Wilson⁵. They observed various reaction products by irradiating iodine-hydrocarbon mixtures with visible light. Since ground state iodine atoms do not react with hydrocarbon C-H bonds, these products were attributed to the reactions of electronically excited ($^2P_{1/2}$) iodine atoms with hydrocarbon C-H bonds. However the energy separation of the first excited from the ground electronic state of the halogen atoms increases with atomic number as shown in Table 1.

The direct kinetic study of ground ($^2P_{3/2}$) halogen atoms was carried out by using flow discharge-ESR⁶ and flash photolysis-atomic fluorescence methods⁷. The results were in relatively good agreement with those obtained from competition methods.

The chemistry of electronically excited halogen atoms has been reviewed by Donovan and Husain.⁸ Table 2 shows the properties of electronically excited chlorine atoms.⁸

Carrington and coworkers⁹ first detected electronically excited $\text{Cl}(^2P_{1/2})$ atoms by a flow discharge-ESR technique. Gases such as CF_3Cl or a $\text{CF}_3\text{Cl}-\text{Cl}_2$ mixture were subjected to a microwave discharge to produce Cl atoms and the products were rapidly pumped into an ESR spectrometer. From the analysis of the relative intensities of signals from both ground and electronically excited Cl atoms, the population ratio of $\text{Cl}(^2P_{1/2})$ to $\text{Cl}(^2P_{3/2})$ was found to

be much larger than the expected Boltzman equilibrium ratio. This finding was explained as being due to the inefficient quenching of the $\text{Cl}(^2P_{1/2})$ atoms by Cl_2 or CF_3Cl molecules, a noticeable difference from the reaction of $(^2P_{1/2})$ atoms whose lifetimes were known to be considerably shortened by addition of molecular iodine.¹⁰

Electronically excited chlorine atoms were also detected in a discharge flow system with an atomic absorption detection technique.^{11a} However no reactions of this atom were studied.

By a flash photolysis-vacuum ultraviolet absorption technique^{11b}, a few rate constants were obtained for the decay of $\text{Cl}(^2P_{1/2})$ atoms in the presence of CCl_4 , CF_3Cl and HCl , which were the precursors of the Cl atoms.

The purpose of this research is twofold: first, we want to measure absolute rate constants for reactions of $\text{Cl}(^2P_{3/2})$ atoms with various substrates to compare our values with the rate constants obtained by competition methods. Especially the addition reactions of Cl atoms to double-bonded compounds have not yet been studied directly. Second, the reactions of $\text{Cl}(^2P_{1/2})$ atoms with various substrates will be studied to compare the reactivities of $\text{Cl}(^2P_{1/2})$ atoms and $\text{Cl}(^2P_{3/2})$ atoms. This study will give us some information about the possible contribution of $\text{Cl}(^2P_{1/2})$ atoms to the chemistry of chlorine molecules in a photochemical reaction system.

EXPERIMENTAL PROCEDURES

1. Materials

Cl_2 : Matheson Gas Products, Research grade, 99.96 % or high purity gas, 99.5 %, vacuum distilled before use.

Ethylene: Phillips Petroleum Co., Research grade, 99.98 %

cis 1, 2-Dichloroethylene: Matheson Coleman

& Bell, less than 2 % *trans*-isomer was detected by gas chromatography.

trans 1, 2-Dichloroethylene: Eastman Organic Chemicals, less than 1 % *cis*-isomer impurity was detected.

Vinyl chloride: Matheson Gas Products, 99.9 % min.

Hydrogen: Matheson Gas Products, 99.95 % min.

Deuterium: Bio-Rad Lab., Research Grade, 99.65 % min.

Methane: Phillips Petroleum Co., Research grade, 99.99 %

Methyl chloride: Matheson Gas Products, 99.5 % min.

Methyl fluoride: Peninsular Chemical Research, Research grade, no impurities given.

Cyclopropane: Matheson Gas Products, 99.0 % min.

2. Procedures

(1) Atomic Absorption Method

Cl atoms (both $^2P_{1/2}$ and $^2P_{3/2}$) were generated by microwave discharge in chlorine molecules diluted with helium (less than 0.5 % of Cl_2 in helium), and the emission lines of Cl atomic transitions were also obtained in the same way. Detailed apparatus and optical components were the same as those described in the previous publications.¹²

Minor changes in the flow system were made as follows: the pressure in the main line was measured with a Barocel Electric Manometer (Datametric Co.) which was coated with nickel to prevent corrosion. The molecular sieve trap for the purification of helium was replaced with a Titanium Inert Gas Purifier (R. D. Mathis Co.). The reaction zone was treated with orthophosphoric acid as suggested by Ashmore and coworkers.¹³ Most of the stopcocks and joints were sealed with silicon "O" rings, and "Kel-F" grease was used when necessary. Since

Cl_2 itself has molecular absorption bands in the region of the atomic transitions, always the minimum amount of Cl_2 was subjected to the

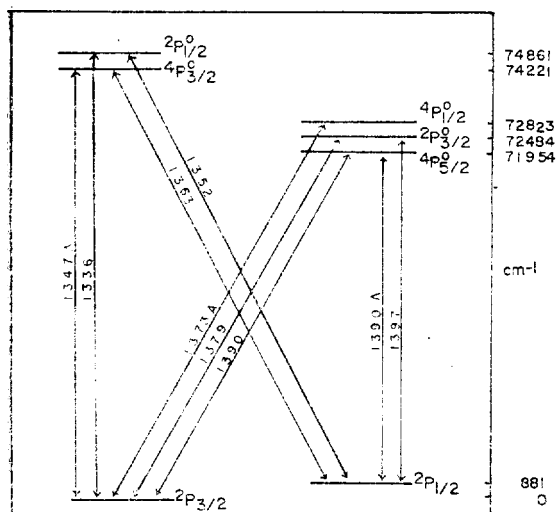


Fig. 2. Energy diagram for Cl.

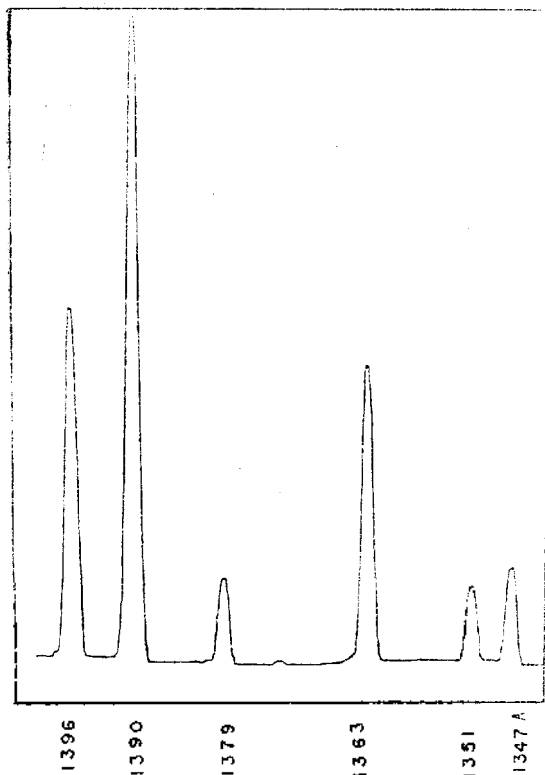


Fig. 3. Emission spectrum of Cl atom.

discharge so that nearly all the Cl_2 molecules were dissociated into atomic species. Under the usual conditions absorption by Cl_2 was less than 10 % of the total absorption by atomic chlorine. The 10 % maximum possible absorption by molecular chlorine was estimated by assuming no breakdown of molecular chlorine by microwave discharge. Since we expect that at least 80~90 % of the chlorine molecules can be dissociated into atoms by the powerful discharge, and also that most of the generated atoms can survive downstream of the plasma in a treated glass wall, actual Cl_2 absorption must be less than 1 or 2 % of the total absorption by atomic chlorines.

Fig. 2 shows the energy diagram for the transitions between low-lying electronic states of chlorine atoms, and the emission lamp output in our experiment is shown in Fig. 3.

The kinetic analysis of the reactions of Cl atoms was done in the same way as described for the reactions of hydrogen atoms with silane and germane.¹²

RESULTS AND DISCUSSION

1. Detection of $\text{Cl}(^2P_{3/2})$ and $\text{Cl}(^2P_{1/2})$ Atoms

$\text{Cl}(^2P_{3/2})$ atoms were detected by the absorption of the 1379, 1347, 1336, and 1379 Å chlorine atomic emission lines. The 1363, 1351, and 1397 Å lines were monitored for the detection of $\text{Cl}(^2P_{1/2})$ atoms. Table 3 shows the observed absorption transitions for the Cl atoms.

For most kinetic experiments the 1379 Å line was monitored for the decay of $\text{Cl}(^2P_{3/2})$ atoms and 1363 Å line for the decay of $\text{Cl}(^2P_{1/2})$ atoms. The 1347 Å and 1351 Å lines were also used occasionally for independently checking the rate constants for the decay of $\text{Cl}(^2P_{3/2})$ and $\text{Cl}(^2P_{1/2})$ atoms respectively. Under our usual experimental conditions (linear velocity of about

Table 3. Observed transitions for Cl atoms.

Transition	$\Delta E(\text{cm}^{-1})$	Wavelength (Å)
4s $^4P_{5/2} \rightarrow 3P^5 \ ^2P_{3/2}$	71954	1390
4s $^4P_{3/2} \rightarrow 3P^5 \ ^2P_{3/2}$	72484	1379
4s $^4P_{3/2} \rightarrow 3P^5 \ ^2P_{1/2}$	71603	1397
4s $^4P_{1/2} \rightarrow 3P^5 \ ^2P_{3/2}$	72823	1373
4s $^4P_{1/2} \rightarrow 3P^5 \ ^2P_{1/2}$	71942	1390
4s $^2P_{3/2} \rightarrow 3P^5 \ ^2P_{3/2}$	74221	1347
4s $^2P_{1/2} \rightarrow 3P^5 \ ^2P_{3/2}$	74861	1336
4s $^2P_{3/2} \rightarrow 3P^5 \ ^2P_{1/2}$	73340	1363
4s $^2P_{1/2} \rightarrow 3P^5 \ ^2P_{1/2}$	73980	1351

1,000 cm/sec., distance from the discharge to the detection point of about 30 cm, and 20 Torr pressure), the absorption of the 1363 Å line was found to be about one third of the absorption of the 1379 Å line. If the $\text{Cl}(^2P_{1/2})$ atoms are in Boltzman equilibrium with $\text{Cl}(^2P_{3/2})$ atoms, the ratio of atomic concentrations at 300 °K is:

$$\text{Cl}(^2P_{1/2})/\text{Cl}(^2P_{3/2}) = g_{1/2}/g_{3/2} \exp(\Delta E/kT) \quad (3)$$

By substituting $T=3000$, $g_{1/2}=2$, $g_{3/2}=4$ and $\Delta E=881 \text{ cm}^{-1}$, one can obtain the ratio, $\text{Cl}(^2P_{1/2})/\text{Cl}(^2P_{3/2})=7 \times 10^{-3}$ at 300 °K. With reported oscillator strengths for the 1379 and 1363 Å lines ($A=0.11$ for 1379 Å line and $A=0.75$ for the 1363 Å line),¹⁴ the observed population ratio, $\text{Cl}(^2P_{1/2})/\text{Cl}(^2P_{3/2})$, was estimated to be in the range of 3×10^{-2} to 10×10^{-2} under our conditions. This ratio is about 5 to 14 times larger than the expected Boltzman population ratio at 300 °K.

Since the temperature in the microwave discharge plasma is expected to be several thousand degrees¹⁵ the temperature at the detection point can be higher than 300 °K. To find out whether $\text{Cl}(^2P_{1/2})$ atoms are in non-Boltzman population one has to make sure that the temperature is not higher than expected, since the ratio increases exponentially with temperature as

shown in equation (3).

The gas temperature inside the flow tube was measured by inserting copper-constantan thermocouple at the center of the flow tube at various distances from the discharge. The temperature was found to be 299 ± 3 °K throughout the reaction zone and about 10 cm from the discharge was found to be enough to cool the plasma temperature to room temperature at our ordinary experimental conditions (1000 cm/sec flow rate, 20 Torr pressure, and 50 watt microwave power input).

Another possibility for the unexpectedly large absorption for the 1363 Å line could be the self-reversal of the emission line source. The self-reversal of the 1379 Å line could be larger than that of the 1363 Å line, since the 1379 Å emission line is a transition to the ground state which certainly has a higher population than the $\text{Cl}(^2P_{1/2})$ state, whereas 1363 Å line is a transition to the $\text{Cl}(^2P_{1/2})$ state.

This possibility was also eliminated by the following experiment. In our experiment the distance from the lamp window to the discharge was relatively short (ca. 2 cm), and the Cl_2 concentration and the pressure were kept as low as practically possible to minimize the optical density between the discharge and the lamp window. Therefore the possibility of self-reversal of the emission lines was minimized.

To verify experimentally that the self-reversal of the emission lines is not important, we changed the external conditions for the generation of Cl atoms in the main flow line with the same emission lamp. If the larger absorption of the 1363 Å line compared to that of the 1379 Å line was due to the larger self-reversal of the 1379 Å emission line and not from non-Boltzman distribution of the population ratio, the ratio of absorption should be constant as

long as the temperature at the detection point and the emission lamp are kept constant. Whereas, if the large absorption of the 1363 Å line is due to the large concentration (non-Boltzman) of $\text{Cl}(^2P_{1/2})$ atoms which survived down-stream from the plasma, the ratio should be changed by the various parameters of the system such as pressure, flow rate and microwave power input, etc.

Table 4 shows that the ratio, absorption (%) of the 1363 Å line to that of the 1379 Å line, is indeed dependent on the conditions in the system.* The ratio is changed from about 0.5 to 6 by changing the pressure in the flow line from 3 Torr to 60 Torr with an exactly identical emission lamp.**

Therefore it is evident that the large absorption of 1363 Å line was due to the large concentration of $\text{Cl}(^2P_{1/2})$ atoms which survive at the detection point. This result is consistent with the results obtained by Carrington and coworkers.⁹ They also detected an unexpectedly large ($^2P_{1/2}/^2P_{3/2}=3.6 \times 10^{-2}$) concentration of electronically excited Cl atoms from the ESR intensity measurements in the flow discharge ESR experiment. However, our result does not agree with the flash-photolysis experiment¹² in which very fast decay of $\text{Cl}(^2P_{1/2})$ atoms was observed in most substrates.

2. Reactions of $\text{Cl}(^2P_{3/2})$ and $\text{Cl}(^2P_{1/2})$ Atoms

The rate of decay of $\text{Cl}(^2P_{3/2})$ and $\text{Cl}(^2P_{1/2})$ atoms in the presence of various substrates has

*The change of the pressure from 3 to 60 Torr had no effect on the temperature at the detection point under our experimental conditions.

**Since the pressure change also affects the actual microwave power input and the flow rate this change of the ratio should not be considered as purely a pressure effect. Whatever the causes of the effect are our argument about the non-Boltzman population of $\text{Cl}(^2P_{1/2})$ atoms is not affected.

Table 4. Dependence of % absorption on the pressure change.

Pressure ^b	% Absorption ^c		Ratio ^c
	1363 Å	1379 Å	
Torr			
1.0	49	24	0.5
6.0	29	25	0.9
16	17		
22	13	26	2.0
40	11	27	2.5
60	5	32	6.4

^a% absorption = $\{(I_0 - I)/I_0\} \times 100$.

^bA pressure change also changes the flow rate and the actual discharge input power; therefore these ratios do not represent directly the pressure effect.

^cRatio = (% absorption of 1379 Å line) / (% absorption of 1363 Å line).

been determined in the usual way and the experimentally determined rate constants along with reported values at 300 °K are included in Table 5.

Fig. 4 shows a typical kinetic plot for the decay of $\text{Cl}(^2P_{1/2})$ and $(^2P_{1/2})$ atoms with *cis*-1,2-dichloroethylene. To increase the accuracy of the experiment the reactions of $\text{Cl}(^2P_{1/2})$ and $\text{Cl}(^2P_{3/2})$ atoms were always carried out at the same time under identical conditions. Therefore the relative rate constants of $\text{Cl}(^2P_{1/2})$ and $\text{Cl}(^2P_{3/2})$ atoms with substrates may be accurate to $\pm 10\%$, although the error in the absolute values could be as high as $\pm 40\%$ because of the systematic errors in the rate measurements. For the reactions with CCl_4 and Cl_2 only lower limits for the rate constants were obtained because of the strong absorption of CCl_4 and Cl_2 in the vacuum ultraviolet region at the relatively high concentrations of CCl_4 and Cl_2 , which were inevitable due to the slowness of the reactions.

The rates of reactions of $\text{Cl}(^2P_{3/2})$ atoms with various substrates show close relation with those of the reactions of $\text{Cl}(^2P_{1/2})$ atoms.

Table 5. Rates of reactions of Cl atoms.

Substrate	Cl($^2P_{3/2}$) k (cc/molecule sec)		Cl($^2P_{1/2}$) k (cc/molecule, sec)	
	This work	Reference ^a	This work	Reference
H ₂	1.7×10^{-14}	1.2, ^a 1.4 ^b	2.7×10^{-14}	7×10^{-12d}
D ₂	1.7×10^{-16}	1.3 ^c	3.3×10^{-15}	
Cyclopropane	3.8×10^{-13}	0.8 ^c	6.5×10^{-13}	
CH ₂ Cl	4.9×10^{-13}	3.0 ^c	8.4×10^{-13}	
CH ₃ F	4.7×10^{-13}		7.8×10^{-13}	
CH ₄	2.6×10^{-13}	0.6, ^g 1.5 ^b	2.8×10^{-13}	
CH ₂ =CH ₂	2.6×10^{-12}	3.3 ^c	0.8×10^{-12}	
CH ₂ =CHCl	2.5×10^{-12}	3.3	0.4×10^{-12}	
<i>t</i> -CHCl=CHCl	3.9×10^{-12}	4.0	1.3×10^{-12}	
<i>c</i> -CHCl=CHCl	3.8×10^{-12}	6.0	1.1×10^{-12}	
Cl ₂	$<4 \times 10^{-13}$		$<4 \times 10^{-13}$	
CCl ₄	$<5 \times 10^{-13}$		$<5 \times 10^{-13}$	5×10^{-11d}

^aCalculated from "Tables of Bimolecular Gas Reactions," A. F. Trotman-Dickenson and G. S. Milne, NSRDS-NBS 9.

^bReference 7.

^cJ. Knox and K. C. Waugh, *Trans. Far. Soc.*, 65, 1585 (1969).

^dReference 11b.

^eAll the rate constants are of the same orders of magnitude as our values.

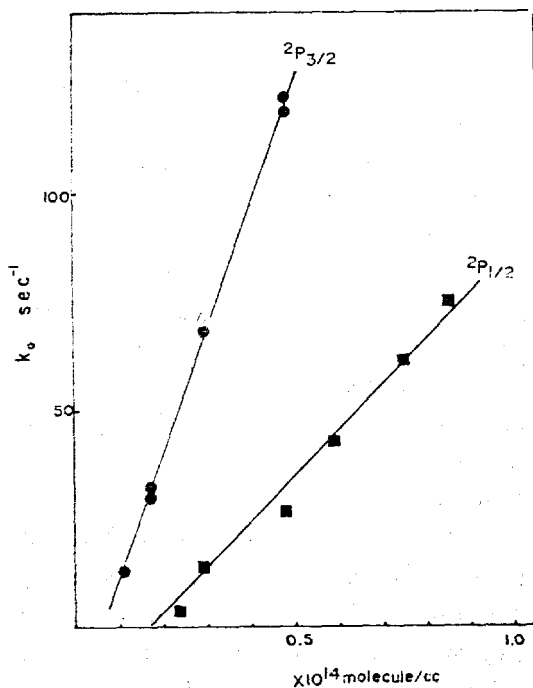
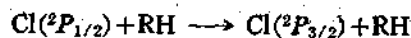


Fig. 4. Kinetic plot of Cl atom reactions with *cis*-1,2-dichloroethylene, Slope is $k_{\text{bin}}(\text{Cl} + \text{cis-CHCl}=\text{CHCl} \rightarrow)$

Reactions with saturated hydrocarbons are slightly faster for Cl($^2P_{1/2}$) atoms than Cl($^2P_{3/2}$) atoms, while Cl($^2P_{3/2}$) atoms react faster with double bonded compounds, such as ethylene and chloroethylenes, than Cl($^2P_{1/2}$) atoms. The measured rate constants for the reactions of Cl($^2P_{3/2}$) atoms are in good agreement with reported values by both direct and competition methods in $\pm 40\%$ probable error range. But the rate constants for the reaction of Cl($^2P_{1/2}$) atoms are very different from the values published by Donovan and coworkers, which is the only work reported on the reactions of Cl($^2P_{1/2}$) atoms. Donovan and coworkers^{11b} reported $k(\text{Cl}(\text{}^2P_{1/2}) + \text{H}_2)$ was 7×10^{-12} cc/molecule sec, while our value is 2.7×10^{-14} cc/molecule sec.

The electronically excited chlorine atoms can disappear mainly by the following two mechanisms:

Physical relaxation (or spin-orbit relaxation)



or chemical reaction,

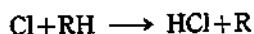


In the physical relaxation mechanism the excess electronic energy (2.5 kcal) of $\text{Cl}(^2P_{1/2})$ atoms may be transferred to the substrates as a rotational or vibrational energy, whereas in the chemical reaction the excess energy (or part of it) may be used as an activation energy for the reaction.

Husain and Donovan tried to explain their rate constant for the reaction of $\text{Cl}(^2P_{1/2})$ atoms with H_2 as a chemical reaction under the assumptions that *all* the electronic energy of $\text{Cl}(^2P_{1/2})$ atoms was used as the activation energy for the chemical reaction, and the frequency factors for the reactions of both $\text{Cl}(^2P_{1/2})$ and $\text{Cl}(^2P_{3/2})$ atoms were the same. Under these assumptions the predicted rate constant was estimated to be about 2.0×10^{-12} cc/molecule sec, still smaller than their reported experimental value, 7.0×10^{-12} . We believe the chemical reaction of $\text{Cl}(^2P_{1/2})$ atoms with H_2 could be much smaller than their estimation for the following reasons. First, *all* the electronic energy of $\text{Cl}(^2P_{1/2})$ atoms can not be used as the activation energy. The bond-energy-bond-order method, developed by Johnston¹⁶, has been accepted as a relatively simple and reliable method to predict activation energies for various atom transfer reactions. The potential energy of activation is given as

$$V = E_{\text{RH}}(1-n^p) - E_{\text{HCl}}(1-n)^q \\ + \text{repulsion term}(\alpha E_{\text{RCl}})$$

for the reaction



If we assume that all the electronic energy of $\text{Cl}(^2P_{1/2})$ atoms were used as a bonding energy of H-Cl or R-Cl bonds, *i. e.*, $E(\text{H-Cl}^*) = E$

$(\text{H-Cl}) + 2.5$ kcal and neglect the repulsive term, then calculation shows that the decrease in the activation energy by changing $\text{Cl}(^2P_{3/2})$ atoms to $\text{Cl}(^2P_{1/2})$ could be from 0 to 2.3 kcal depending on the position of the activated complex in the reaction coordinate. Since we ignored the repulsive term which has higher value for the $\text{Cl}(^2P_{1/2})$ atom reactions compared to the $\text{Cl}(^2P_{3/2})$ atom reactions, the decrease of activation energy may be even lower than 0 to 2.3 kcal, if the repulsive term is included. Therefore, the assumption that all the electronic energy can be used as an activation energy is not reasonable except in a very extreme case. Second, we do not think the frequency factors will be the same for the reactions of both $\text{Cl}(^2P_{3/2})$ and $\text{Cl}(^2P_{1/2})$ atoms. The chemical reactions of electronically excited iodine atoms with various hydrocarbons were studied by Callear and Wilson.⁵ They obtained unusually low frequency factors for the reactions of $\text{I}(^2P_{1/2})$ atoms with several hydrocarbons and attributed this to the lack of equilibrium between the reactants and transition state caused by relaxation to the lower surface. Therefore the frequency factor for the reactions of $\text{Cl}(^2P_{1/2})$ atoms may also be lower than that for the reactions of $\text{Cl}(^2P_{3/2})$ atoms. From the above arguments, *i. e.* the lower frequency factor and smaller contribution of the electronic energy to the activation energy, we believe that the *chemical* reaction of $\text{Cl}(^2P_{1/2})$ atoms with H_2 should be much smaller than the value reported by Donovan and coworkers. Since the electronic energy of $\text{Cl}(^2P_{1/2})$ atom is only 2.5 kcal, in some cases when the lowering of frequency factors exceeds the contribution of electronic energy to the activation energy, the rate of reaction of $\text{Cl}(^2P_{1/2})$ atoms could be slower than that of $\text{Cl}(^2P_{3/2})$ atoms, as observed in our experiment for the reactions with unsaturated

compounds.

Although we can not decide unequivocally whether the decay of $\text{Cl}(^2P_{1/2})$ atoms is physical relaxation or chemical reaction, we prefer the chemical reaction mechanism for the following reasons: If $\text{Cl}(^2P_{1/2})$ atoms decay by physical relaxation the decay of the $\text{Cl}(^2P_{1/2})$ atoms should not have any correlation with the decay of $\text{Cl}(^2P_{3/2})$ atoms whose decay depends on the bond dissociation energies of O-H bonds of hydrocarbons. Since $\text{Cl}(^2P_{3/2})$ atoms must be reacting chemically and since $\text{Cl}(^2P_{1/2})$ decays more slowly than $\text{Cl}(^2P_{3/2})$ with some substrates, it is very likely also reacting chemically. The relative rates of the spin-orbit relaxation of I ($^2P_{1/2}$) atoms with CH_4 , C_2H_2 and I_2 are 1.8, 2.6 and 280 respectively.^{8b} So apparently the rates do not depend strictly on the bond energy of substrates, but depend also on other factors such as the spin-orbit coupling constant. Unfortunately no reliable theoretical considerations have appeared for the physical relaxation or energy transfer mechanisms.

ACKNOWLEDGEMENT

An experimental work was carried out at Brookhaven National Laboratory. The author wishes to thank Drs. A. P. Wolf and P. P. Gaspar for helpful discussions and support during his stay there.

REFERENCES

1. G. C. Fettis and J. H. Knox, "Progress in Reaction Kinetics", Vol. 2, P. 1, Pergamon, London, 1964.
2. P. B. Pearce and A. G. Gaydon, "The Identification of Molecular Spectra," Chapman and Hall, Ltd., London, 1963.
3. R. H. Garstang, *J. Res. Nat. Bur. Stand.*, A **68**, 61 (1964).
4. T. W. Broadbent and A. B. Callear, *Trans. Far. Soc.*, **67**, 3030 (1971).
5. A. B. Callear and J. F. Wilson, *Trans. Far. Soc.* **63**, 1358 (1967); *idem.*, *ibid.*, **63**, 1983 (1967).
6. A. A. Westenberg and N. de Hass, *J. Chem. Phys.*, **48**, 4405 (1968).
7. D. D. Davis, W. Braun and A. M. Bass, *Int. J. Chem. Kinetics*, **2**, 101 (1970).
8. R. J. Donovan and D. Husain, *Chem. Revs.*, **70**, 489 (1970); D. Husain and R. J. Donovan, "Advances in Photochemistry", Vol. 8, Wiley & Sons, P. 1, 1971.
9. A. Carrington, D. H. Levy and T. A. Miller, *J. Chem. Phys.*, **45**, 4093 (1966).
10. R. J. Donovan and D. Husain, *Nature*, **206**, 171 (1965).
11. (a) R. J. Donovan *et al.*, *J. Chem. Phys.*, **50**, 4115 (1969); (b) M. A. A. Clyne and H. W. Cruse, *Trans. Far. Soc.*, **67**, 2869 (1971).
12. K. Y. Choo, P. P. Gaspar and A. P. Wolf, *J. Phys. Chem.*, **79**, 1752 (1975).
13. P. G. Ashmore, A. J. Parker and D. E. Sterne, *Trans. Far. Soc.*, **67**, 3081 (1971).
14. NSRDS-NBS 22, Vol. II, 1962.
15. W. L. Fite, "Chemical Reactions in Electrical Discharges", Advances in Chemistry Series 80. American Chemical Soc., Washington D. C., Washington D. C., 1969.
16. H. S. Johnston, "Gas Phase Reaction Rate Theory", Ronald Press, N. Y. 1966.