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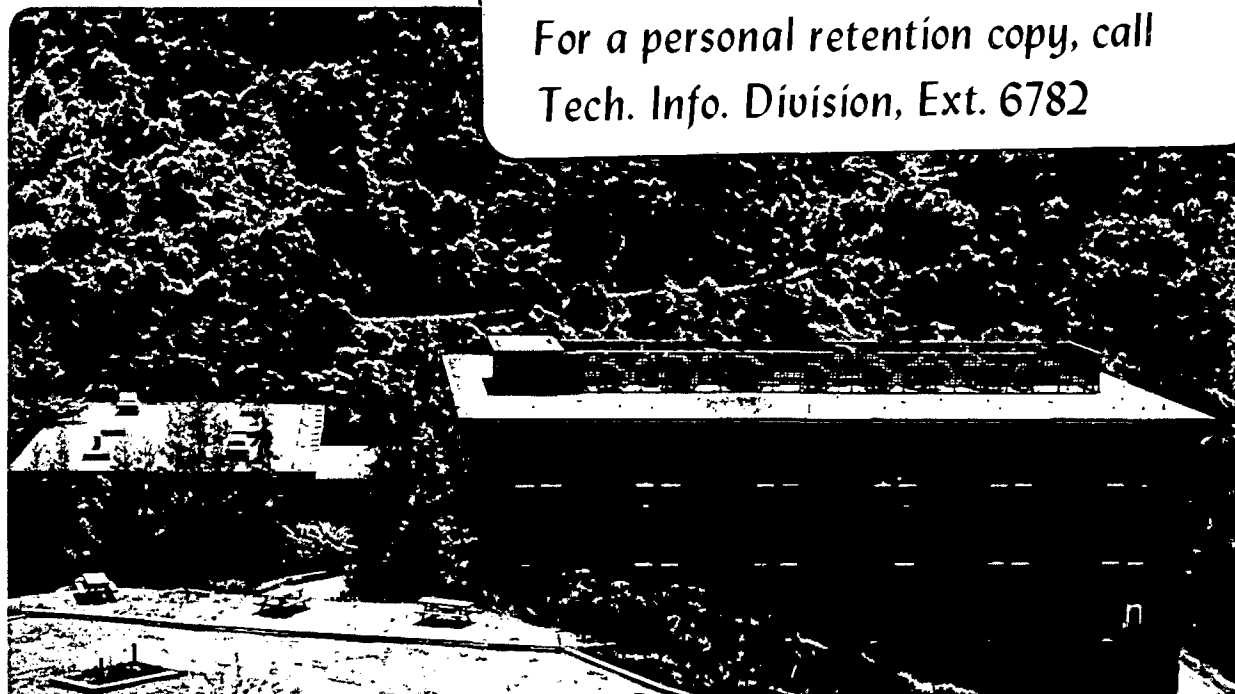
THE KINETICS OF THE REACTION OF Cl WITH ClNO AND
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H.H. Nelson and H.S. Johnston

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The Kinetics of the Reaction of Cl with ClNO and
ClNO₂ and the Photochemistry of ClNO₂

By

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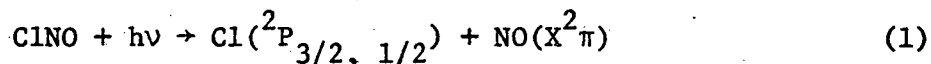
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Abstract

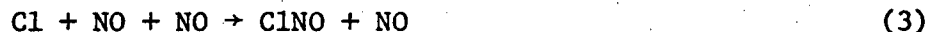
The room temperature rate constants for the reactions $\text{Cl} + \text{ClNO}$ (2) and $\text{Cl} + \text{ClNO}_2$ (4) have been measured by the method of laser flash photolysis/resonance fluorescence. The rate constants obtained are $(k_2 \pm 2\sigma) = (1.65 \pm 0.32) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ and $k_4 = (5.50 \pm 0.75) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$. The absorption spectrum of ClNO_2 was measured in the region 270 - 370 nm and the photodissociation channels $\text{ClNO}_2 + h\nu \rightarrow \text{Cl} + \text{NO}_2$ and $\text{ClNO}_2 + h\nu \rightarrow \text{ClNO} + \text{O}$ were investigated by resonance fluorescence detection of Cl or O atoms. The quantum yields derived are $\phi_{\text{Cl}} = 0.93 \pm 0.15$ and $\phi_{\text{O}} < 0.02$.

Introduction

The photochemistry of ClNO has been studied since 1930 when Kistiakowsky¹ showed that the quantum yield for NO production was approximately equal to 2. More recent work² shows that the primary process is photolysis to Cl atoms followed by the reaction of Cl with ClNO:



The reaction of Cl with ClNO is also important in the recombination of Cl atoms catalyzed by NO.³ This process goes through the mechanism of reactions (3) and (2)



The large affinity of Cl for both NO and ClNO explains the efficiency of the process. Reaction (2) has also been used as a titration reaction for the determination of Cl concentrations in flow experiments.⁴⁻⁶

In 1952, Burns and Dainton⁷ were able to derive a room temperature value for k_2 of $3.2 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$. Their study involved measurements of the retardation of the photochemical production of phosgene (from Cl_2 and CO) by added ClNO. The course of the reaction was followed by the pressure drop as phosgene was formed. Twenty years later, while investigating reaction (2) in connection with Cl titration, Clyne and Cruse⁸ used a discharge flow/resonance fluorescence system to obtain a room temperature value of $3.0 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$. Most recently, Grimley and Houston⁹ measured k_2 to be $5.4 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, and the rate constant

for the analogous $\text{Br} + \text{BrNO}$ reaction was $5.16 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$. This study used flash photolysis of XNO ($\text{X} = \text{Cl}, \text{Br}$) to produce X atoms and monitored the production of vibrationally excited NO from reaction (2).

The reaction of atomic chlorine with nitryl chloride has been shown



to be fast in preliminary work by Clyne referenced by Watson.¹⁰ In a discharge flow experiment at 1 Torr total pressure, Clyne found that $k_4 \gg k_5 [\text{M}]$ where reaction 5 is the recombination of atomic chlorine with nitrogen dioxide



Using the recommended value for k_5 ,¹¹ this means $k_4 \gg 4 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$.

The absorption spectrum of gaseous nitryl chloride in the ultra-violet has been reported by Illies and Takacs.¹² No work on the photolysis products or quantum yields has been reported although the continuous nature of the absorption spectrum suggests a photodissociation quantum yield of one in this region.

The calculated wavelength limits for two sets of photolysis products are



The present study was designed to obtain new experimental data on reactions 2, 4, and 6.

Experimental

The apparatus used in these experiments is shown in Figure 1. Chlorine atoms were produced by photolysis of ClNO or ClNO₂ with the output pulse of a Lumonics 860-01 Excimer Laser operating at 350 nm (XeF). The repetition rate was typically 30 Hz and the pulse energy 10-20 mJ. The average laser energy was measured with a Scientech Surface Absorbing Power Meter.

Atomic Cl and O were measured by the technique of resonance fluorescence. Chlorine atom fluorescence in the region 135-140 nm was excited by the output of a microwave driven resonance lamp operating with a 0.1% Cl₂ in He mixture at a total pressure of ~ 600 m Torr. The lamp, which was equipped with a MgF₂ window, was attached to the cell at a port perpendicular to the laser axis and the resonantly scattered photons were detected on the third axis by a photomultiplier tube with a CsTe photocathode. The Cl detection system was calibrated by means of Cl₂ photolysis using the 350 nm output of the laser. Chlorine atom concentrations were calculated using the measured Cl₂ concentration, the measured laser energy, and Seery and Britton's ¹³Cl₂ absorption cross section, $1.89 \times 10^{-19} \text{ cm}^2$. The fluorescence signal was linear to at least $1.5 \times 10^{11} \text{ Cl atoms/cm}^3$ and the detection sensitivity was approximately $4 \times 10^5 \text{ (atoms cm}^{-3}\text{)/Hz}$. The detection sensitivity was periodically measured throughout the course of the experiment and was found to decrease with time. Later experiments showed that this was due to a decrease in the transmission of the MgF₂ window of the lamp; replacement of the window restored the original sensitivity. The quantum yield measurements were performed with this new window for maximum sensitivity.

Oxygen atom measurements were performed using the same lamp, detection system, and flow of extra pure helium as described by Magnotta and Johnston.¹⁴ The lamp was operated for 24 hours after the change to insure that all residual Cl_2 was eliminated.

The photolytic precursors (ClNO or ClNO_2) were contained in a Pyrex saturator maintained at 157 K. A slow flow (~ 0.3 l/min) of either Ar or N_2 was split into two streams; the flow rate of each was controlled by stainless steel needle valves. One stream passed over the precursor resulting in partial saturation. The two streams were combined and directed through a 1 m Pyrex cell with fused silica windows where the precursor concentration was continuously measured by ultraviolet absorption. Radiation from a Beckman deuterium lamp was chopped and directed through the absorption cell from where it entered a McPherson model 218, 0.3 m monochromator operating with a 0.3 nm band pass. After exiting the monochromator the light was detected by an RCA 1P-28 photomultiplier tube and then a lock-in amplifier whose output was displayed on a digital voltmeter. The saturator containing the precursor was equipped with a bypass manifold so that I_0 was easily measured before and after each run. The concentration of precursor stabilized within 5 minutes in this system and typically drifted less than 3% during a run.

The nitrosyl chloride concentration was measured at 196 nm which is the peak of the absorption curve measured by Ballash and Armstrong.¹⁵ They report on absorption cross section of $8.00 \times 10^{-17} \text{ cm}^2$ which agrees with that of Illies and Takacs¹² within 4%. The ClNO_2 was monitored at 210 nm which corresponds to a flat part of the spectrum recorded by

Illies and Takacs. Their cross section, which was confirmed during this work, is $3.39 \times 10^{-18} \text{ cm}^2$.

After precursor concentration measurements, the gas stream entered the photolysis cell and then out through a glass vacuum manifold to a rotary mechanical pump. The photolysis cell consisted of a tube (3.8 cm diameter by 10 cm) sealed with CaF_2 windows and with two large Wood's horns facing the resonance lamp and photomultiplier tube. The total pressure in the photolysis cell was measured by an MKS Baratron capacitance manometer. The total pressure and precursor concentration in the UV absorption cell and photolysis cell were observed to be identical.¹⁶

Reagents

Nitrosyl chloride of 97% minimum purity was obtained from Matheson Gas Company. Following the purification scheme of Illies and Takacs,¹² samples of this product were degassed repeatedly at 77 K and then distilled twice from 196 to 77 K with the first and last portions of the distillate discarded. This procedure resulted in ClNO with $< 0.01\%$ NO_2 impurity (measured by UV absorption) and a small Cl_2 impurity, which did not affect the kinetic measurements.

Nitryl chloride was prepared by the method of Volpe and Johnston.^{17,18} Anhydrous HCl was dried further by passage through a trap maintained at 196 K. It then bubbled through a solution containing 25 ml 90% HNO_3 , 60 ml 95% H_2SO_4 and 70 ml 30% fuming H_2SO_4 . The product ClNO_2 was trapped at 196 K in a bulb isolated from the atmosphere by a calcium chloride drying tube. The synthesis was always stopped after $\sim 30\%$

conversion of the initial HNO_3 to avoid production of ClNO . Molecular chlorine impurity was removed by partial evaporation at 175 K leaving a product which was a pale yellow, almost colorless liquid and a white solid. Possible traces of NO_2 were removed by distilling the remaining ClNO_2 from 196 to 77 K.

Chlorine and nitrogen dioxide were obtained from Matheson Gas Company and distilled before use. Argon (99.999%) and nitrogen (99.999%), which were used as carrier gases, were supplied by Lawrence Berkeley Laboratory and were used without further purification.

Results

All experiments were performed using pseudo-first order conditions with the reactant precursor in large excess over Cl atoms. Initial Cl concentrations were typically less than 10^{11} atoms/cm³ and the precursor concentration ranged from 0.5 to 8×10^{14} cm⁻³ for ClNO_2 and 0.6 to 12×10^{13} cm⁻³ for ClNO . With these conditions, the Cl concentration temporal profile is described by

$$\ln([\text{Cl}]_t/[\text{Cl}]_0) = -(k_r[\text{reactant}] + k_d)t \equiv -k't \quad (7)$$

where k_r is the rate constant for the reaction of interest and k_d is a rate constant for any processes not proportional to the precursor concentration. This is primarily Cl diffusion out of the product viewing region but may also include reactions with the carrier gas or impurities in it.

Typical laser intensities of less than 1.5×10^{16} photons cm⁻² shot⁻¹ and the ClNO_2 absorption cross section at 350 nm measured in

this work ($1.78 \times 10^{-20} \text{ cm}^2$, see below) result in the photolysis of less than 0.03% of the ClNO_2 per shot. The residence time in the photolysis region was $\leq 0.1 \text{ s}$ (~ 3 shots) so the concentration perturbation due to photolysis or reaction was negligible.

Chlorine resonance-fluorescence signals were collected with channel times of 5, 10, or 20 μs and the data reduced in accordance with Eq. 7. A plot of $\ln(\text{fluorescence signal-background})$ is shown in Figure 2 for a typical experiment in this series. The channel width in this instance was 20 μs . Note the contribution in the first five channels after the laser pulse of cell fluorescence excited by the laser. The limits of the straight-line fit are denoted by arrows in the figure. These limits represent decay of an order of magnitude in Cl atom concentration and are representative of the number of channels fit for all runs in this system.

Pseudo-first order rate constants were measured for total pressures of 10 and 25 Torr and using Ar as the carrier gas, and two experiments at 10 Torr used N_2 as carrier gas. The results of these experiments are shown plotted in Figure 3. A linear least squares fit to the data at both pressures results in the line shown in Figure 3. The rate constant derived (2 σ limits) is $k_4 = (5.05 \pm 0.24) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$. The intercept of the fitted line is $226 \pm 100 \text{ s}^{-1}$ which is equal to the Cl diffusion rate measured in the calibration runs within the experimental uncertainty.

Measurements of the reaction of Cl with ClNO (Reaction 2) were carried out with two different experimental configurations. Initial experiments employed dye laser photolysis of ClNO at 500 nm as the Cl atom source. In these experiments however, only relative ClNO concentrations

were measured. These experiments were designed to measure the contribution of third order reactions to the experimental rate constant and check for any enhanced reactivity of the $\text{Cl}(^2\text{P}_{1/2})$ state.

The pseudo-first order rate constants measured in this phase of the work are shown plotted in Figure 4. The uncertainties of the points with added CCl_4 are much higher than for the points measured in pure nitrogen. Carbon tetrachloride was chosen for its efficiency for quenching $\text{Cl}(^2\text{P}_{1/2})$,¹⁹ but it also has a very large absorption cross section in the region of the Cl resonance lamp. Sufficient quantities of CCl_4 to quench completely any possible $\text{Cl}(^2\text{P}_{1/2})$ also absorbed a large fraction of the resonance radiation and correspondingly reduced the experimental ratio of signal-to-noise.

After substituting the excimer laser for the dye laser as photolysis source and obtaining absolute ClNO measurements, quantitative experiments were performed at a total pressure of 10 Torr Ar. These data are shown plotted in Figure 5. The rate constant calculated from these data is $1.65 \pm 0.12 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ where the error limits quoted are twice the standard deviation.

The nitryl chloride absorption cross sections were determined in the region 270-370 nm as a prelude to the quantum yield measurements. Samples of the purified ClNO_2 described above were added to a 10 cm long quartz absorption cell and the spectrum recorded on a Cary 118C spectrometer. Nitryl chloride concentrations were determined from pressure measurements. The absorption cross section σ , defined as

$$\sigma = \ln\left(\frac{I_0}{I}\right)/N\ell$$

where N is the ClNO_2 concentration in molecules/cm³, was determined at 10 nm intervals. The cross sections determined in this work along with those reported by Illies and Takacs¹² are listed in Table 1 and shown plotted along with the Cl_2 spectrum in Figure 6. Below 300 nm, the cross sections obtained in this work agree well with those reported earlier but in the Cl_2 absorption region they are significantly lower. In Figure 7, the difference between the cross sections of Illies and Takacs and those obtained in this work is plotted with the Cl_2 spectrum for reference. As can be seen from this figure, a 6% Cl_2 impurity in the ClNO_2 used in the earlier work would be sufficient to explain the difference.

Having obtained the ClNO_2 absorption cross section at the photolysis wavelength (350 nm) the photodissociation quantum yield in both the Cl and O atom channels was investigated. As stated above, the Cl detection system was calibrated using Cl_2 photolysis. Busch *et al.*²⁰ have shown that Cl_2 photolysis at 347.1 nm leads to two ground state, $^2\text{P}_{3/2}$, atoms.

After installation of a new resonance lamp window a series of photolysis experiments was performed which alternated Cl_2 and ClNO_2 as the precursor. After normalizing the Cl signal obtained in each case by the appropriate absorption cross section, the average quantum yield measured for Cl atom production in ClNO_2 photolysis was 0.93.

The O atom detection system was calibrated by means of NO_2 photolysis. As in the Cl case, O atom quantum yields were determined by alternate photolysis of NO_2 and ClNO_2 . The result obtained corresponds to an apparent oxygen atom quantum yield of 0.02 which is a signal four times the detection limit.

Discussion

Both of the reactions under discussion were studied as a function of total pressure to insure that third order reactions were not contributing to the observed rate constant. Both NO and NO₂ can be expected to be present in the ClNO and ClNO₂ used in this work as residual synthetic material or products of thermal decomposition. The impurity levels were measured and the rate constants for the reactions of Cl with NO and NO₂ are well known²¹ so that any contribution from these reactions can be neglected. The observed independence of the measured rate constants on total pressure confirms that any contribution from other third order reactions can likewise be neglected.

The various literature reports of the rate constant for the reaction Cl + ClNO are listed in Table 2. The rate constants reported span a range of about a factor of ten and the value measured in this work is at the upper end of the range. An attempt was made to determine if possible enhanced reactivity of the metastable Cl ²P_{1/2} state was responsible for some of the variance. Production of Cl ²P_{1/2} only requires an additional 811 cm⁻¹ compared to the ²P_{3/2} ground state. At the dye laser photolysis wavelength of 500 nm, there is about 7000 cm⁻¹ of excess energy available. Grimley and Houston⁹ have shown that for photolysis wavelengths greater than 480 nm, there is little if any vibrational excitation of the NO fragment. Although the majority of the excess energy is probably in the form of product translational energy²² there is still a possibility for Cl ²P_{1/2} production. Sufficient CCl₄ to completely quench any Cl ²P_{1/2} within one channel¹⁹ was added to the reaction mixture in several cases and as reference to Figure 4 shows,

there is no decrease in the observed reaction rate indicating that $\text{Cl } ^2\text{P}_{1/2}$ either reacts at the same rate as ground state $\text{Cl } ^2\text{P}_{3/2}$ or is not present in the system originally.

Clyne and Cruse⁸ have pointed out several factors in the experiments of Burns and Dainton⁷ that might lead to an error in the interpretation of their data. These include: 1) cumulative errors in the equilibrium constant and rate constants used to derive k_2 ; 2) possible systematic errors in the thermopile actinometry used in the calculation of k_2 ; or 3) adsorption of ClNO on the walls of the vessel used. The static experiment of Grimley and Houston⁹ is also susceptible to this last problem. Clyne, Cruse, and Watson²³ have shown that ClNO adsorption on Pyrex walls can be considerable. In a static system with low ClNO concentrations, the measured rate constant would underestimate the true value by the percentage adsorption. The rate constant measured in this work in a flowing system is in much better agreement with the lower limit of Clyne, Cruse, and Watson²³ and the rate constant of Clyne and Cruse⁸, both measured in flow tube studies. This agreement (plus the fact that contributions to the measured rate due to NO , NO_2 , or $\text{Cl } ^2\text{P}_{1/2}$ have been shown to be negligible) increases the concern that ClNO wall absorption may be significant in static systems. The rate constant measured in this study is $k_2 = 1.65 \pm 0.32 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ where the error limits reflect twice the standard deviation of the data and an estimate of possible systematic error in each component of the experiment.

There has been no report of a direct measurement of the rate constant for the reaction of Cl with ClNO_2 . In his review of Cl chemistry, Watson¹⁰ refers to unpublished, provisional data of Clyne and White

that shows $k_4 \gg 3 \times 10^{-14}$. The value obtained in this work, $5.05 \pm 0.75 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, is in agreement with this limit and in accord with the rate constants observed for analogous reactions.¹⁰

In determining the quantum yield for production of atomic chlorine from photolysis of nitryl chloride at 350 nm, the ClNO_2 cross-sections were taken to be $3.4 \times 10^{-18} \text{ cm}^2$ at 210 nm (used to monitor ClNO_2 concentration) and $1.78 \times 10^{-20} \text{ cm}^2$ at 350 nm. The average observed quantum yield was 0.93. Consideration¹⁶ of possible errors in ClNO_2 cross sections, sample purity, flow rates, and pressure measurements led to an estimated error of about 0.15 quantum yield units. From these considerations the quantum yield and its error are $\phi_{\text{Cl}} = 0.93 \pm 0.15$.

The O atom quantum yield measured in this study should be regarded as an upper limit to the true value. The O atom signal could also be explained by an 0.15% NO_2 impurity in the ClNO_2 sample. The procedure for removing Cl_2 from the product ClNO_2 has the effect of concentrating any NO_2 present. The produce was redistilled after this, but a residue of 0.15% NO_2 is not impossible.

Acknowledgments

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Table 1. Nitryl chloride absorption cross sections.

$\lambda(\text{nm})$	$\sigma_{\text{this work}} (\text{cm}^2)$	$\sigma_{\text{Illies and Takacs}}^{12} (\text{cm}^2)$
270	3.72×10^{-19}	3.73×10^{-19}
280	2.23×10^{-19}	2.31×10^{-19}
290	1.81×10^{-19}	1.80×10^{-19}
300	1.55×10^{-19}	1.54×10^{-19}
310	1.25×10^{-19}	1.32×10^{-19}
320	8.70×10^{-20}	1.02×10^{-19}
330	5.58×10^{-20}	7.11×10^{-20}
340	3.33×10^{-20}	4.81×10^{-20}
350	1.78×10^{-20}	3.06×10^{-20}
360	1.14×10^{-20}	1.82×10^{-20}
370	7.20×10^{-21}	1.07×10^{-20}

Table 2. Summary of the measurements of $k_{Cl+ClNO}$.

Method	k_7 ($\text{cm}^3 \text{s}^{-1}$)	Ref.
ClNO Retardation of Photochemical Phosgene Production	$1.91 \times 10^{-11} \exp(-530/T)$ $k_{298} = 3.2 \times 10^{-12}$	7
Discharge Flow/Resonance Absorption	$\geq 8.0 \times 10^{-12}$	23
Discharge Flow/Resonance Fluorescence	3.0×10^{-11}	8
Flash Photolysis/NO IR Emission	5.4×10^{-12}	9
Flash Photolysis/Resonance Fluorescence	1.62×10^{-11}	16*

* This work.

Figure Captions

Figure 1. Schematic diagram of the experimental apparatus.

Figure 2. Typical pseudo-first-order decay plot for the reaction $\text{Cl} + \text{ClNO}_2$, showing the cell fluorescence at short times and the limits of the computer fit.

Figure 3. Pseudo-first-order rate constant (k') vs ClNO_2 concentration at both 10 and 25 Torr total pressure. The bimolecular rate constant derived is $5.05 \pm 0.24 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$. Argon is carrier gas in all cases except the two solid circles, for which N_2 is the carrier gas.

Figure 4. Pseudo-first-order rate constant (k') vs relative ClNO concentration for the reaction $\text{Cl} + \text{ClNO}$ showing the effect of total pressure and $\text{Cl}(^2\text{P}_{1/2})$ quenching by added CCl_4 .

Figure 5. Pseudo-first-order rate constant (k') vs ClNO concentration at a total pressure of 10 Torr.

Figure 6. Comparison of the measured ClNO_2 absorption cross sections with the Cl_2 spectrum for comparison. (a) Illies and Takacs.¹²
(b) This work.

Figure 7. The difference between the ClNO_2 absorption cross sections measured by Illies and Takacs and in this work with the Cl_2 spectrum for comparison.

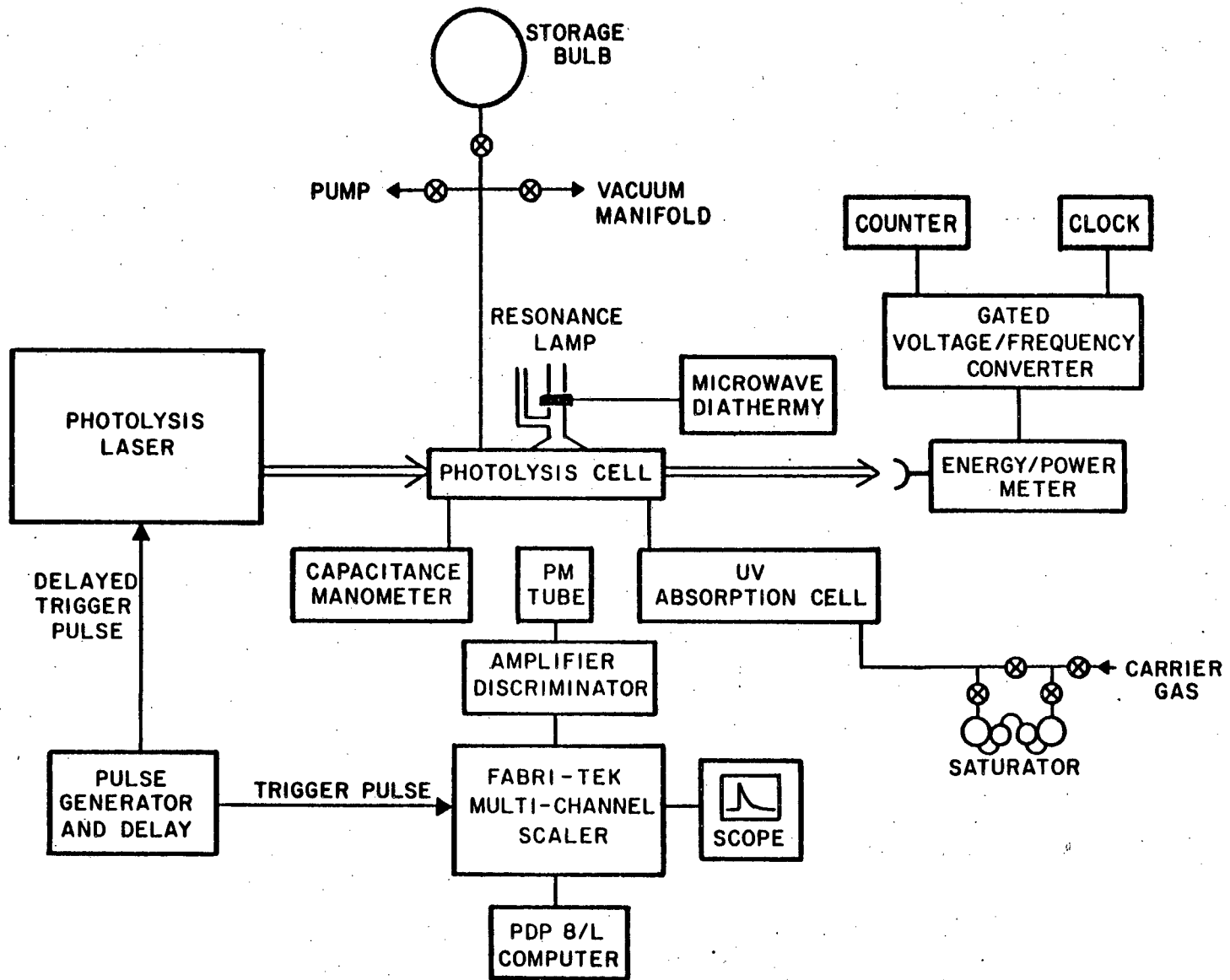


Figure 1

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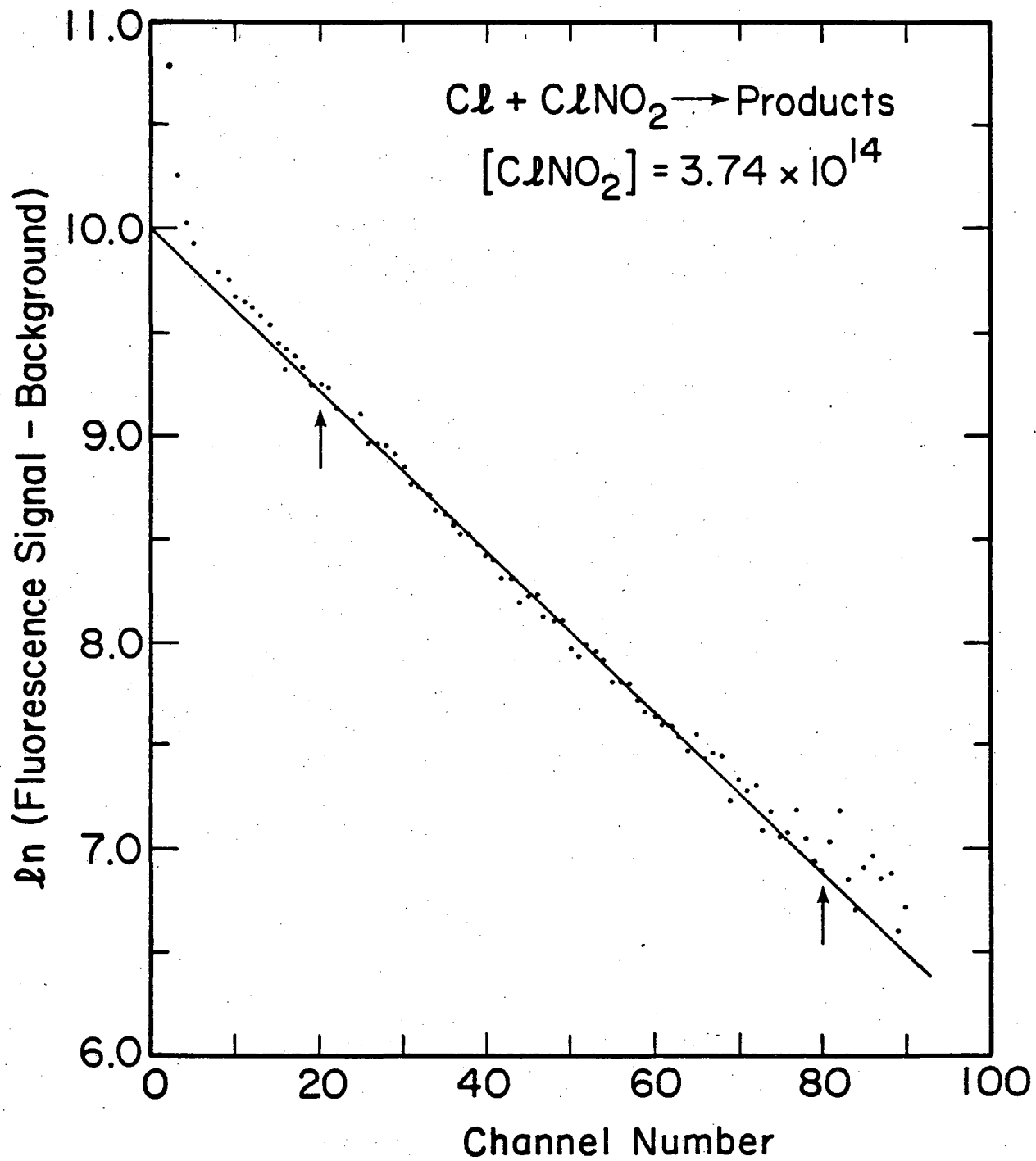


Figure 2

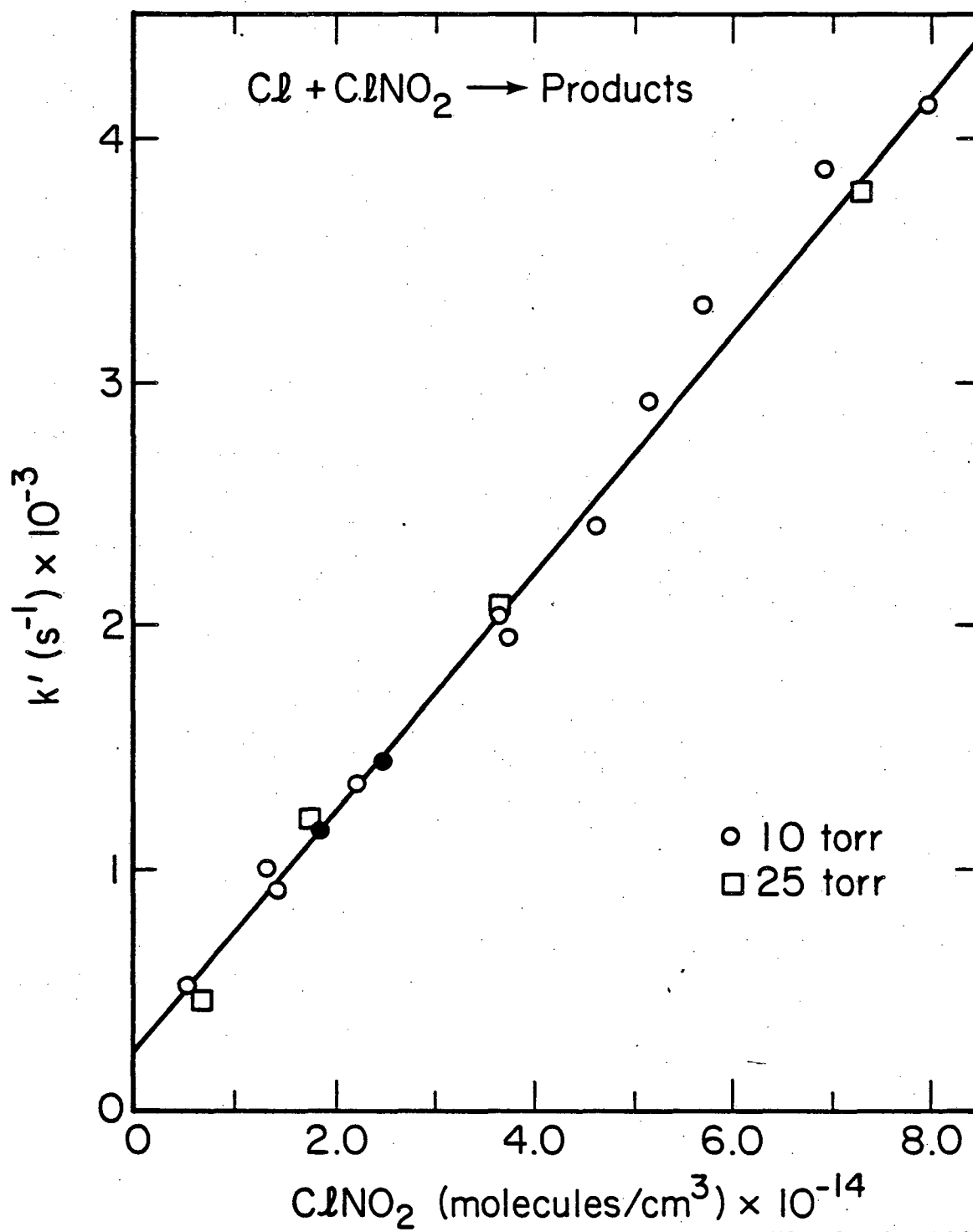


Figure 3

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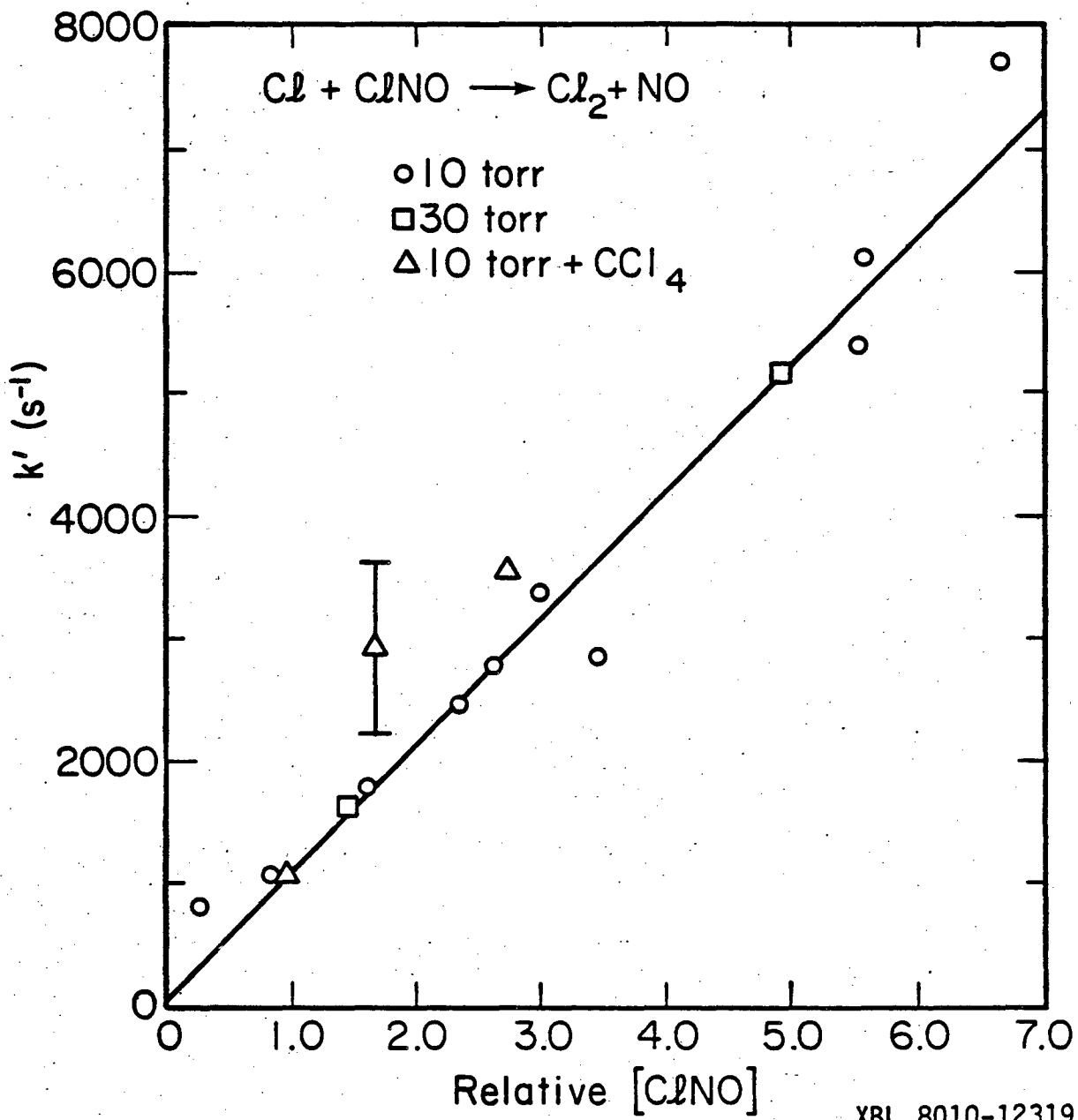


Figure 4

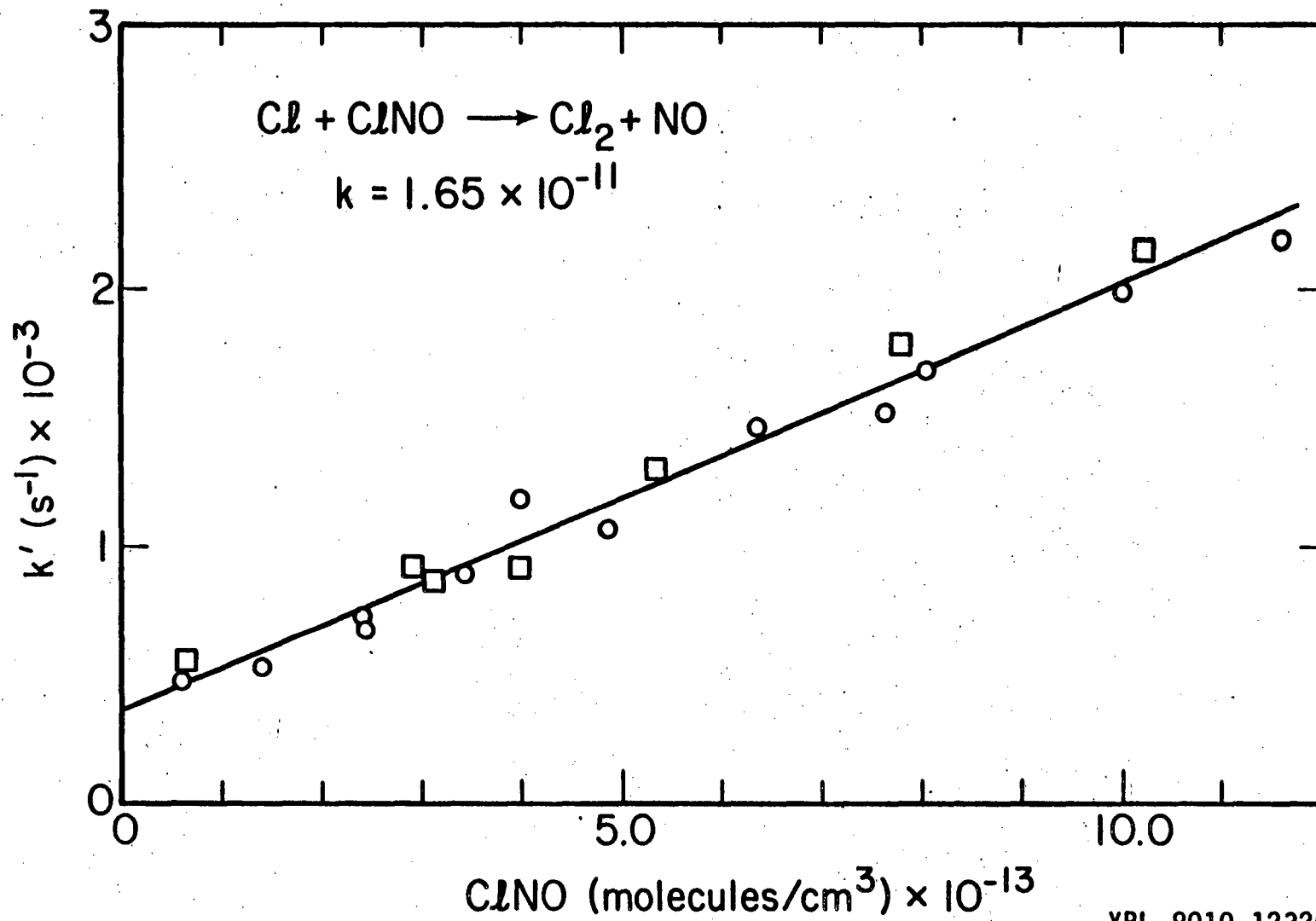


Figure 5

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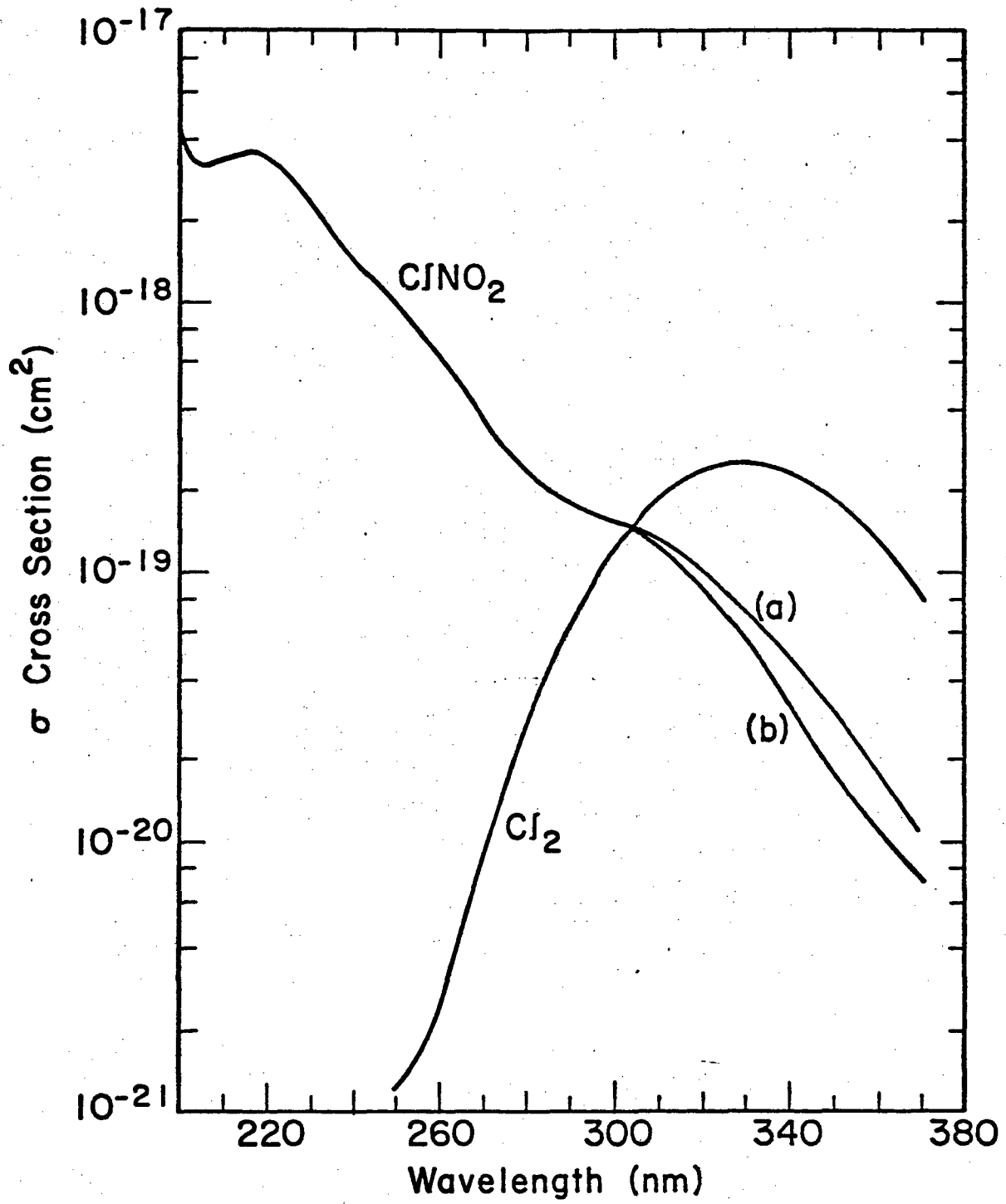


Figure 6

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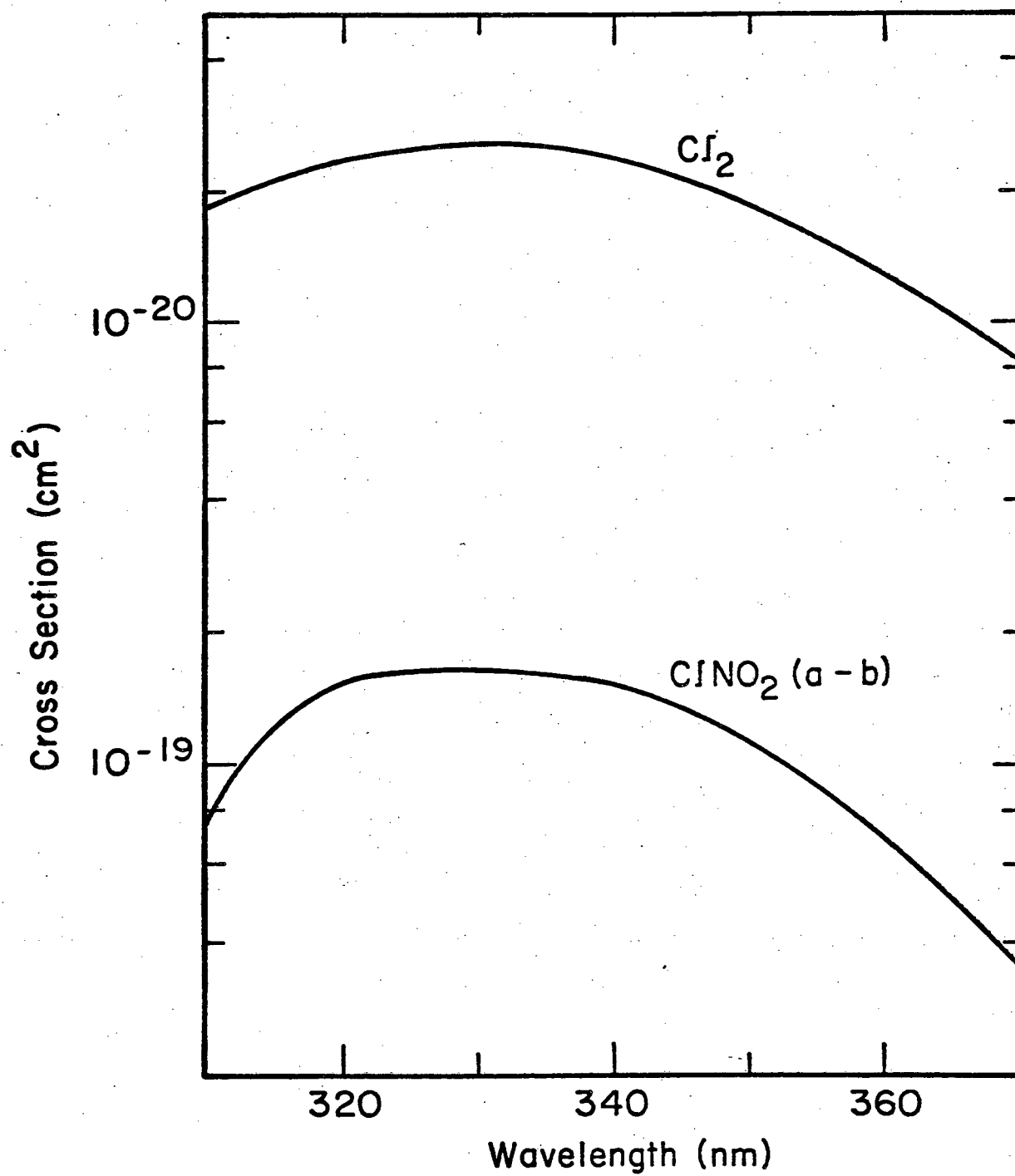


Figure 7

XBL 8010-7365

Figure 7

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