行政院國家科學委員會專題研究計劃成果報告

以雷射技術研究大氣化學之重要分子--氟氯烷取代物研究—與 Cl 之反應速率

Application of Laser Techniques to Study Important Species in Atmospheric Chemistry-- Freon substitutes — reaction rate with Cl

計劃編號：NSC 88-2113-M-009-007-L1
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一、中文摘要

本計劃爲「以雷射技術研究大氣化學之重要分子」整合型研究計劃之子計劃三，研究氟氯烷取代物之氧化。

我們利用雷射光解/原子共振螢光法以研究 Cl 原子與 CF_3CH_2Cl(133a) 之反應速率。

關鍵詞：動力學、 氟氯烷取代物、Cl 、CF_3CH_2Cl(133a)。

Abstract

This report covers reaction kinetics of Freon substitutes (HCFC) with Cl atoms. We have studied the reaction kinetics of Cl with HCFC-CF_3CH_2Cl(133a) using laser photolysis -atomic resonance fluorescence system.

Keywords: kinetics, Cl, HCFC, CH_3S, NO_2

二、緣由與目的

本計劃係整合型計劃「以雷射技術研究大氣化學之重要分子」中之子計劃三，內含子題屬於整合計劃四大方向中的(1)氟氯烷取代物。

以雷射光解/原子共振螢光法測量 Cl 原子與 CF_3CH_2Cl(133a) 之反應速率

Reaction Rate of Cl + CF_3CH_2Cl(133a)

INTRODUCTION

The major atmospheric removal process for hydrofluorocarbons (HCFCs) is their reactions with OH radicals in the troposphere. However, the concentrations of Cl atoms may be significant in the troposphere due to photodissociation of NOCl, from the heterogeneous reaction of N_2O_5 with NaCl, or the reaction of OH with HCl. It is of interest to study the kinetics of the reactions of Cl and HCFCs.

In this work, we have studied the kinetics of the reaction of Cl with HCFC-133a (CF_3CH_2Cl)

$$Cl + CF_3CH_2Cl \rightarrow \text{products} \quad (1)$$

in a laser photolysis-atomic resonance fluorescence (LP-ARF) system over the temperature range 297 – 550 K.

EXPERIMENTAL

Figure 1 shows the schematic of the LP-ARF system. Cl atoms were produced by photolying Cl_2 at 532 nm, from the second harmonic of a Nd-YAG laser. Cl atoms were excited with the 135 nm radiation from a microwave lamp. The resonance fluorescence was detected by a solar blind photomultiplier tube mounted perpendicular to each of the laser and excitation beams. The signals were

amplified with a current amplifier before being sent to a digital storage oscilloscope. The concentration of the reactants were calculated from the flow rates, pressure, and temperature.

RESULTS AND DISCUSSION

All kinetic measurements were carried out under pseudo-first-order conditions with [CF_3CH_2Cl] in large excess. The temporal profiles of Cl fluorescence followed a first-order rate law,

$$[Cl]_t=[Cl]_0\exp-(k[CF_3CH_2Cl]+k_d)t \quad (2)$$

where k_d is the rate coefficient for Cl loss in the absence of [HCFC]; k is the bimolecular rate coefficient of interest.

Figure 2 shows a typical set of Cl decay plots whose slopes are used to determine the first-order rate coefficients k^I. From these slopes we derived the second-order rate coefficients, k_1. We obtained a value $(1.07\pm0.04) \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} at 297 K and 10-100 Torr of Ar(Figure 3). In addition, k_1 have been determined at 325, 338, 350, 373, 400, 450, 500, and 550 K in 40-50 Torr of Ar. As shown in Figure 4, we obtained rate coefficients(in 10^{-14} cm^3 $molecule^{-1}$ s^{-1}) (1.38 ± 0.05), (2.23 ± 0.07), (2.04 ± 0.26), (2.90 ± 0.09), (4.49 ± 0.11), (8.15 ± 0.38), (13.04 ± 1.11), and (19.62 ± 0.52), respectively. Arrhenius expression for reaction 1, yielded from Figure 5, is k_1 = $(6.31 \pm 3.1) \times 10^{-12}$ $\exp[-(1940 \pm 190)]$ cm^3 $molecule^{-1}$ s^{-1}.

In the study of the title reaction, two problems may introduce errors to our measurements. CF_3CH_2Cl molecules quench the fluorescence of Cl significantly, hence, the concentration of Cl was maintained high to obtain reasonable fluorescence signal. Since the title reaction is slow, impurities in the reactant with high reactivity towards Cl atoms would introduce error in the measurements. Although the reactant was purified in low temperature trap-to-trap distillation, certain species, such as, CH_2CCl_2, may still remain. Cl reacts with CH_2CCl_2 rapidly; k = 1.3×10^{-10} cm^3 $molecule^{-1}$ s^{-1} at 298 K, a factor of ~50000 faster than the reaction under investigation. The measured rate coefficient will be doubled in the presence of about 50 ppm CH_2CCl_2. Lack of proper technique to identify the impurities qualitatively and quantitatively would decrease the accuracy of the measurements. Our results show that the rate coefficient for the title reaction at room temperature is about 47-65% faster than the published values.[2,3] As discussed before, the discrepancy may due to the presence of impurities. Currently, we are looking for suitable method to purify the reactant and identify the impurities.

REFERENCES

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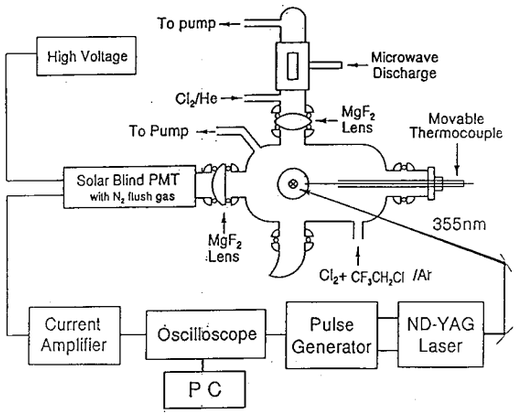

Figure 1. Schematic of the laser photolysis-resonance fluorescence system.

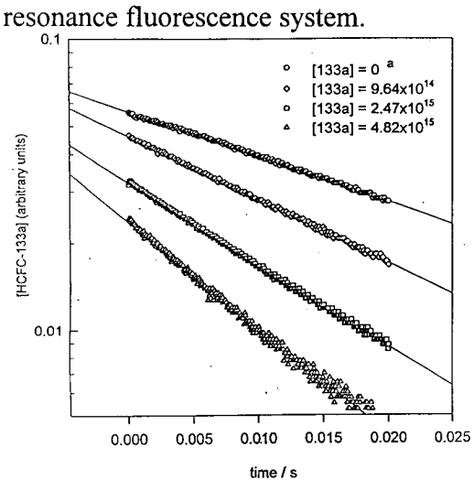

Figure 2. Decay plots of Cl with $[CF_3CH_2Cl]$ (10^{15} molecules cm^{-3}) = 0, (○); 0.96, (◇); 2.47, (□); 4.82, (△).

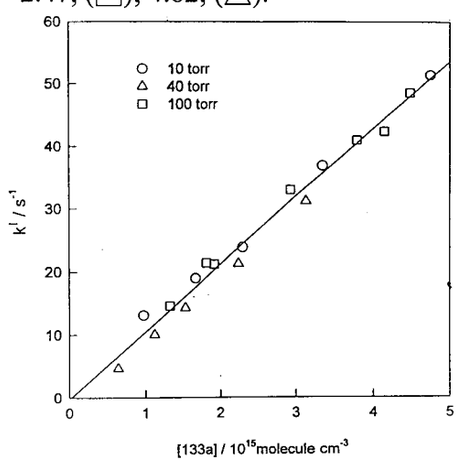

Figure 3. Plots of pseudo-first-order decay rate of Cl, k^I, vs. $[CF_3CH_2Cl]$ in 10, (○); 40, (△); and 100, (□) Torr Ar and 297 K.

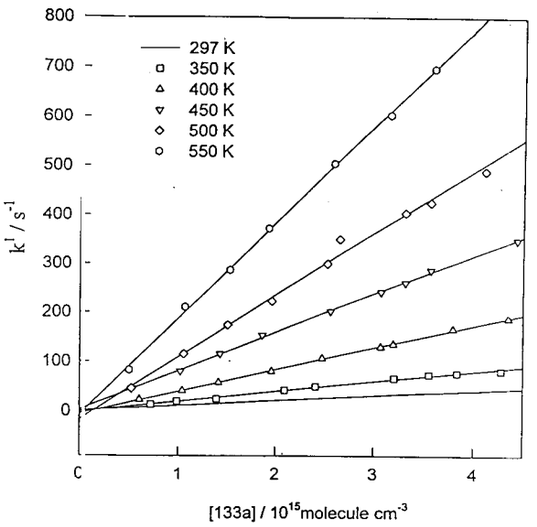

Figure 4. Plots of pseudo-first-order decay rate of Cl, k^I, vs. $[CF_3CH_2Cl]$ at 297 K, (—); 350 K, (□); 400 K, (△); 450 K, (▽); 500 K, (◇); and 550 K, ( ).

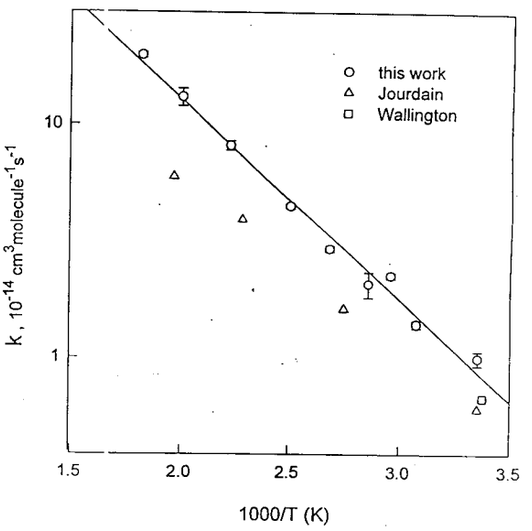

Figure 5. Arrhenius plot for reaction 1. (○) and solid line, this work; (△), ref.2; and (□), ref.3.