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# Photolysis of matrix-isolated acetyl chloride and infrared spectrum of the 1:1 molecular complex of hydrogen chloride with ketene in solid argon

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## Abstract

Acetyl chloride in an argon matrix decomposed on irradiation to generate ketene and hydrogen chloride, which formed the ketene···HCl complex. The fundamental vibrational frequency of HCl in the complex was observed at 2679 cm$^{-1}$, i.e. 191 cm$^{-1}$ below the frequency of the corresponding HCl monomer in solid argon. The fundamental frequency of DCl in the ketene-$d_2$···DCl complex formed by photolysis of acetyl chloride-$d_3$ was observed at 1939 cm$^{-1}$, i.e. 140 cm$^{-1}$ below the frequency of the corresponding DCl monomer in solid argon.

## Introduction

Since the hydrogen-bonded complex of HCl with nitrogen was studied by matrix isolation infrared (IR) spectroscopy [1], the complexes of HCl with various bases of $\pi$-electron donors and lone-pair electron donors have been studied in low-temperature matrices [2]. The HCl stretching frequencies in the complexes were found to be spread over a wide range, from a complex with a weak base to one with a strong base. The HCl complexes with very weak bases such as CO and $CO_2$ [1] gave bands at 2816 cm$^{-1}$ for CO, and at 2854 cm$^{-1}$ for $CO_2$, and the complexes with very strong bases such as trimethylamine [3] and ammonia [4] gave bands at 1486 cm$^{-1}$ and 1371 cm$^{-1}$, respectively, in argon matrices. The HCl complex with ethylene (a $\pi$-electron donor base) gave a band at 2753 cm$^{-1}$ [1] and the complex with acetone (a lone-pair donor) gave a band at 2392 cm$^{-1}$ [5] in solid argon.

Matrix-isolated acetyl chloride decomposed on irradiation ($\lambda > 270$ nm) to form ketene and HCl [6]. In examining the photolysis of acetyl chloride in an argon matrix, we found that the HCl absorption shifted to a lower frequency. In this paper we report on the photolysis of acetyl chloride and acetyl chloride-$d_3$ in argon matrices, and a complex of HCl with ketene.

## Experimental

Acetyl chloride was prepared by reacting acetic acid with phosphorous trichloride. Acetyl chloride-$d_3$ was prepared from acetic acid-$d_4$ (MSD ISOTOPES, Montreal) in a similar manner. Ketene and ketene-$d_2$ were prepared by pyrolysis at 973 K of acetone and acetone-$d_6$ (MSD ISOTOPES, Montreal), respectively, and purified by trap-to-trap distillation under vacuum. Argon matrix gas (Nihon Sanso) was used without further purification.

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A sample was diluted with argon in an argon/sample (200 : 1) mixture using a standard manometric procedure. The mixture was deposited for 3 h at a rate of 2–3 mmol $h^{-1}$ onto a CsI window which was mounted on a rotatable cold head of a CTI Cryodyne model 21 closed-cycle cryocooler and maintained at 20 K. The matrix, cooled to 10 K, was irradiated through a quartz window fitted on a vacuum shroud set at right angles; CsI windows were used for IR measurement. Irradiation was performed using a 500 W high pressure mercury arc (Ushio Denki) through a water filter (10 cm) equipped with quartz windows.

IR spectra (4000–250 $cm^{-1}$) were recorded at 10 K on a Hitachi Model 260–50 grating spectrometer, which was calibrated using standard gases [7].

## Results and discussion

Irradiation of matrix-isolated acetyl chloride and acetyl chloride-$d_3$ for 3 h resulted in almost complete disappearance of the initial IR spectra (Figs. 1(a) and 2(a)) and the appearance of new absorptions (Figs. 1(b) and 2(b)). The observed frequencies of the photoproducts are collected in Table 1. A prominent absorption was observed at 2138 $cm^{-1}$ in the spectrum of the photolysis product of acetyl chloride (Fig. 1(b)). This absorption is in good agreement with the characteristic absorption of free ketene (2137 $cm^{-1}$) in solid argon (Table 1). Comparing the spectra of the photoproducts with those of free ketene and ketene-$d_2$ in solid argon, apart from slight frequency shifts, almost all absorptions of the photoproducts correspond well with those of ketene and ketene-$d_2$ (Table 1).

In each of the photoproduct spectra, other sharp and strong absorptions were observed at 2679 $cm^{-1}$ (Fig. 1(b)) and 1939 $cm^{-1}$ (Fig. 2(b)).

A matrix IR spectrum of HCl has been thoroughly investigated and, even at high dilution, the vibration due to HCl has been observed as a multiplet in the 2900 $cm^{-1}$ region [9]. In Fig. 1(b), there are no absorptions in this

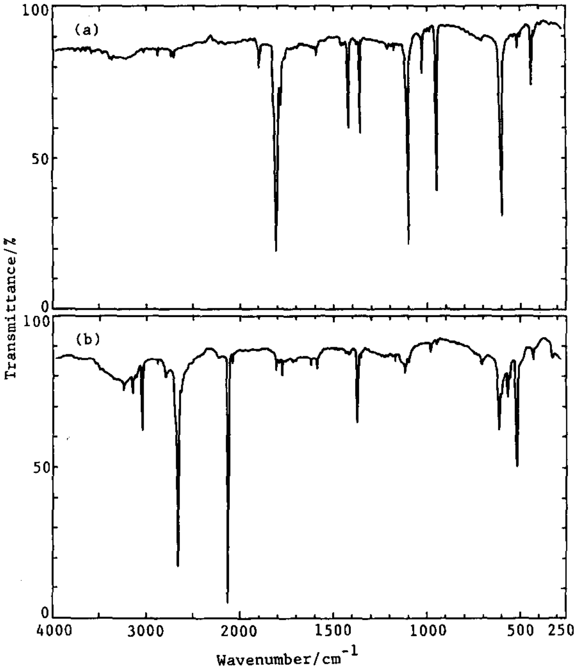

Fig. 1. IR spectra of (a) a matrix prepared by depositing an Ar/$CH_3COCl$ (200 : 1) sample for 3 h and (b) the matrix after subsequent 3 h irradiation.

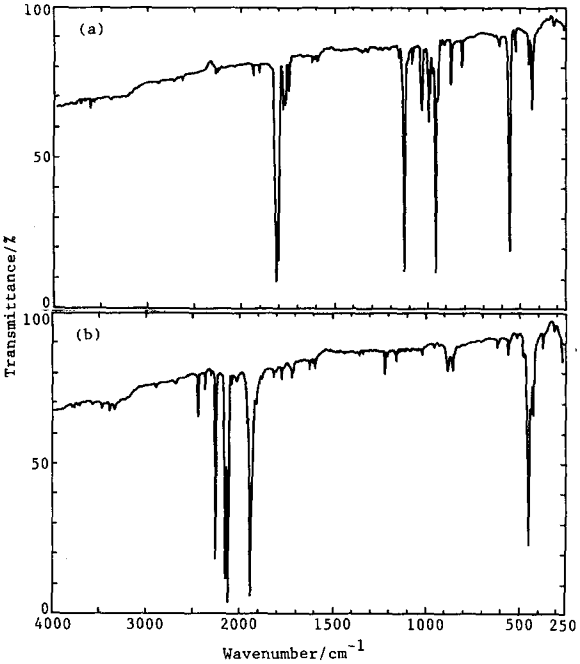

Fig. 2. IR spectra of (a) a matrix prepared by depositing an Ar/$CD_3COCl$ (200 : 1) sample for 3 h and (b) the matrix after subsequent 3 h irradiation.

Table 1
Observed frequencies ($cm^{-1}$) of the products produced by photolysis of $CH_3COCl$ and $CD_3COCl$ in argon matrices, and of $H_2CCO$ and $D_2CCO$ in argon matrices

| $CH_3COCl$[a] | $H_2CCO$ | Assignment[b] | $CD_3COCl$[a] | $D_2CCO$ | Assignment[b] |
|---|---|---|---|---|---|
| 3251 | 3255 | $\nu_2 + \nu_4$ | 2436 | 2446 | $2\nu_3$ |
| 3145 | 3151 | $\nu_5$ $H_2CCO$ | 2364 | 2367 | $\nu_5$ $D_2CCO$ |
| 3053 | 3060 | $\nu_1$ $H_2CCO$ | 2300 | 2305 | CHDCCO |
| 2679 | | HCl | 2249 | 2256 | $\nu_1$ $D_2CCO$ |
| 2138 | 2137 | $\nu_2$ $H_2CCO$ | 2150 | 2146 | $\nu_3 + \nu_4$ |
| 2084 | 2083 | $\nu_2(^{13}C)$ | 2118 | 2110 | $\nu_2$ $D_2CCO$ |
| 1378 | 1377 | $\nu_3$ $H_2CCO$ | 2074 | 2064 | $\nu_3 + \nu_6$ |
| 1122 | 1122 | $\nu_8 + \nu_9$ | 1939 | | DCl |
| | 1110 | $\nu_4$ $H_2CCO$ | 1717 | | ? |
| 984 | 972 | $\nu_6$ $H_2CCO$ | 1217 | 1221 | $\nu_3$ $D_2CCO$ |
| 618 | 591 | $\nu_8$ $H_2CCO$ | 1021 | 1035 | CHDCCO |
| 569 | | ? | | 921 | $\nu_4$ $D_2CCO$ |
| 528 | 527 | $\nu_9 H_2CCO$ | 880 | 858 | $2\nu_9$ |
| 435 | 438 | $\nu_7$ $H_2CCO$ | 854 | 848 | $\nu_6$ $D_2CCO$ |
| | | | 556 | 543 | $\nu_8$ $D_2CCO$ |
| | | | 514 | | ? |
| | | | 448 | 434 | $\nu_9$ $D_2CCO$ |
| | | | 424 | | ? |
| | | | 370 | 371 | $\nu_7$ $D_2CCO$ |

[a] Precursor.
[b] The numbering and assignments for ketene and ketene-$d_2$ reported by Moore and Pimentel [8] were applied.

region. Upon co-deposition of argon/ketene (200 : 1) and argon/HCl (200 : 1) samples, a new absorption was observed at 2679 $cm^{-1}$ together with absorptions due to free HCl in the 2900 $cm^{-1}$ region. In addition, upon co-deposition of argon/ketene-$d_2$ and argon/DCl samples, free DCl absorptions were accompanied by a new absorption at 1938 $cm^{-1}$ [10]. The frequency ratio (2679/1939 = 1.381) is in good agreement with the ratio (2870/2079 = 1.380) for free HCl and DCl fundamental vibrations in argon matrices [11]. Consequently, it is concluded that the absorptions of the photolysis products of acetyl chloride and acetyl chloride-$d_3$ at 2679 and 1939 $cm^{-1}$ are due to HCl and DCl stretchings, respectively. These frequencies are 191 and 140 $cm^{-1}$ respectively, below the HCl and DCl fundamental frequencies in solid argon.

The absence of free HCl absorptions in Fig. 1(b) shows that the HCl generated by the photolysis of acetyl chloride in the argon matrix should be trapped, together with the ketene generated by the elimination of HCl from acetyl chloride in the same matrix cage, effectively forming a 1 : 1 complex. Formation of the complex weakens the HCl bond, and causes the stretching vibration of HCl to be shifted to a lower frequency.

In the complex of HCl with allene, which is isoelectronic with ketene, the HCl stretching mode has been observed at 2736 $cm^{-1}$ [12]. In the ketene–HCl system, the perturbed H–Cl stretching frequency is displaced to 57 $cm^{-1}$ below that of the allene···HCl complex. This implies that the strength of the interaction between HCl and ketene is more than that in the allene···HCl complex.

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