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

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Abstract

Ketene and HBr were generated by photolysis of acetyl bromide in an argon matrix. Of the photolysis products, ketene and HBr were trapped in the same matrix cage to form a 1 : 1 molecular complex. The HBr stretching mode in the complex was observed at 2396 cm^{-1}, which was displaced to 160 cm^{-1} below the frequency of the monomer HBr fundamental in solid argon. The DBr stretching frequency in the ketene-d_2–DBr complex produced on photolysis of acetyl bromide-d_3 was observed at 1717 cm^{-1}, which was displaced to 120 cm^{-1} below the frequency of the monomer DBr fundamental in solid argon. After the matrices were annealed, these absorptions were shifted to 2383 and 1708 cm^{-1}, respectively.

Introduction

Numerous infrared (IR) studies have recently been made of hydrogen-bonded complexes of hydrogen halides (HX) in low-temperature matrices [1]. The complexes were characterized by the displacement of the HX stretching frequency in the complex to a lower frequency than the monomer HX fundamental frequency. The red shift from the free HX frequency is a measure of the hydrogen-bond strength.

In a previous paper [2], we reported that acetyl chloride was decomposed by photolysis in solid argon to produce ketene and hydrogen chloride, which formed a 1 : 1 molecular complex. The HCl frequency in the complex has been observed at 2679 cm^{-1}, which is displaced to 191 cm^{-1} below the frequency of the monomer HCl fundamental.

In this paper, as an extension of a similar study, we report the photolysis of acetyl bromide and acetyl bromide-d_3 in argon matrices and the IR spectra of the complexes formed between HBr (DBr) and ketene (ketene-d_2).

Experimental

Acetyl bromide was prepared by reacting acetic acid with phosphorous tribromide. Acetyl bromide-d_3 was prepared from acetic acid-d_4 (MSD Isotopes, Montreal) in a similar manner. Argon matrix gas (Nihon Sanso) was used without further purification.

A sample was diluted with argon to form an argon/sample (200 : 1) mixture by using standard manometric procedures. The mixture was deposited for 3 h on a CsI window cooled to 20 K using a CTI model 21 closed-cycle refrigerator. The cryogenic apparatus and

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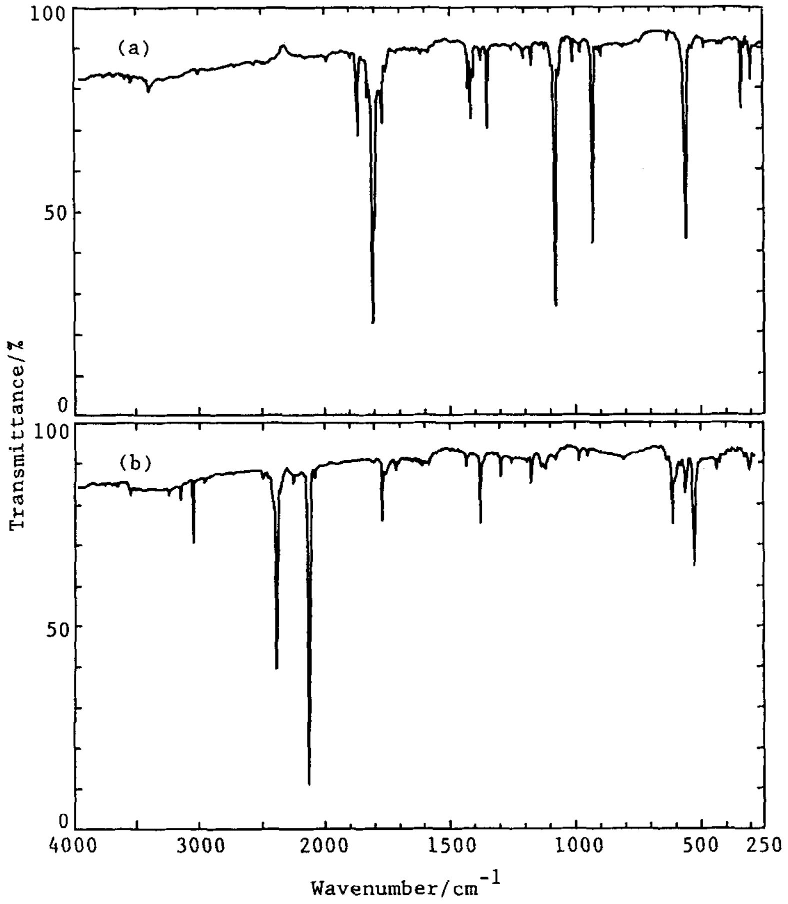

Fig. 1. IR spectra of (a) a matrix prepared by depositing an Ar/CH_3COBr (200 : 1) sample for 3 h and (b) the matrix after 40 min irradiation.

experimental techniques have been described in a previous paper [2].

IR spectra (4000–250 cm^{-1}) were recorded at 10 K on a Hitachi Model 260–50 grating spectrometer, which was calibrated with standard gases [3].

Results and discussion

Irradiation of matrix-isolated acetyl bromide and acetyl bromide-d_3 for 40 min 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.

At about 1770 cm^{-1} in Figs. 1(a) and 2(a), weak absorptions due to the C=O stretch of acetic acids were observed and these remained unaffected by irradiation (Figs. 1(b) and 2(b)). In other regions, there were several weak absorptions which also remained insensitive to irradiation. These are due to acetic acids which were formed by the reaction of acetyl bromides with water adsorbed on the glass walls of the vacuum lines and sample containers.

Prominent absorptions were observed at 2137 cm^{-1} (Fig. 1b)) and 2115 cm^{-1} (Fig. 2(b)) in the spectra of the photolysis products of acetyl bromide and acetyl bromide-d_3, respectively, in accordance with the photolysis of acetyl chloride and acetyl chloride-d_3 [2]. This shows that ketene

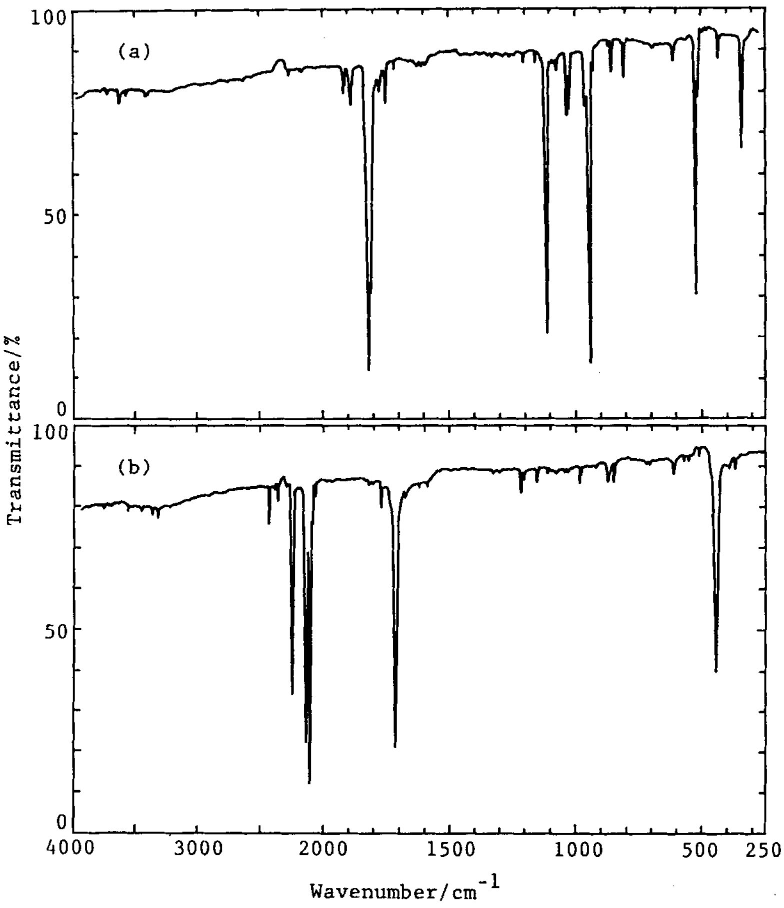

Fig. 2. IR spectra of (a) a matrix prepared by depositing an Ar/CD_3COBr (200 : 1) sample for 3 h and (b) the matrix after 40 min irradiation.

and ketene-d_2 were also formed by the photolysis of acetyl bromide and acetyl bromide-d_3. The observed frequencies of ketene and ketene-d_2 produced by the photolysis of acetyl bromide and acetyl bromide-d_3 are in good agreement with those generated by the photolysis of acetyl chloride and acetyl chloride-d_3 [2] (Table 1).

Strong absorptions unassigned to ketene and ketene-d_2 were observed at 2396 cm^{-1} (Fig. 1(b)) and 1717 cm^{-1} (Fig. 2(b)). The frequency ratio (2396/1717 = 1.395) is in close agreement with that (2556/1837 = 1.391) for free HBr and DBr fundamental frequencies in argon matrices [5]. Consequently, it is concluded that the absorptions of the photoproducts of acetyl bromide and acetyl bromide-d_3 at 2396 and 1717 cm^{-1} are due to HBr and DBr stretches, respectively. These frequencies are lower by 160 and 120 cm^{-1} than the HBr and DBr fundamental frequencies in solid argon, respectively.

No absorptions of the free HBr fundamental around 2550 cm^{-1} (Fig. 1(b)) and the free DBr around 1830 cm^{-1} (Fig. 2(b)) were observed.

It is deduced from the above facts that HBr and ketene were produced by the photolysis of acetyl bromide and were trapped in the same matrix cage where the acetyl bromide was formerly trapped, and that they formed a 1 : 1 complex.

After the matrices were annealed at 30 K, these bands shifted to 2383 and 1708 cm^{-1}, respectively. Upon co-condensation of Ar/ketene (200 : 1) and Ar/HBr (200 : 1) samples, a new absorption

Table 1
Observed frequencies (cm^{-1}) of the photolysis products of CH_3COBr and CD_3COBr in argon matrices, and H_2CCO and D_2CCO produced by photolysis of CH_3COCl and CD_3COCl in argon matrices

CH_3COBr [a]	CH_3COCl [b]	Assignment[c]	CD_3COBr [a]	CD_3COCl [b]	Assignment[c]
3251	3251	$\nu_2 + \nu_4$	2437	2436	$2\nu_3$
3150	3151	ν_5 H_2CCO	2364	2364	ν_5 D_2CCO
3054	3053	ν_1 H_2CCO	2249	2249	ν_1 D_2CCO
2396		HBr	2149	2150	$\nu_3 + \nu_4$
2137	2138	ν_2 H_2CCO	2115	2118	ν_2 D_2CCO
2082	2084	ν_2 (C^{13})	2070	2074	$\nu_3 + \nu_6$
1435		CH_3Br	1717		DBr
1377	1378	ν_3 H_2CCO	1218	1217	ν_3 D_2CCO
1297		CH_3Br	1048		CD_3Br
1123	1122	$\nu_8 + \nu_9$	985		CD_3Br
986	984	ν_6 H_2CCO	875	880	$2\nu_9$
955		CH_3Br	852	854	ν_6 D_2CCO
615	618	ν_8 H_2CCO	712		CD_3Br
603		CH_3Br	568		CD_3Br
561		?	553	556	ν_8 D_2CCO
526	528	ν_9 H_2CCO	509		?
436	435	ν_7 H_2CCO	446	448	ν_9 D_2CCO
			370	370	ν_7 D_2CCO

[a] Precursor.
[b] Precursor, Ref. 2.
[c] The numbering and assignments for ketene and ketene-d_2 reported by Moore and Pimentel [4] were applied.

band was observed at 2383 cm^{-1}, and upon co-condensation of Ar/ketene-d_2 (200 : 1) and Ar/DBr (200 : 1) samples, a new band was found at 1708 cm^{-1} [6]. The frequencies observed in each experiment, on annealing after photolysis and co-condensation, are in good agreement. For acetyl chloride and acetyl chloride-d_3, no such shifts for HCl and DCl frequencies were observed on annealing. On photolysis at 10 K, an arrangement of argon atoms surrounding an acetyl bromide molecule will be subjected to slight strain by development of a ketene and an HBr molecule (the Br atom is larger than the Cl atom). On being annealed, the strain of the solid argon will be released and the conformation of the ketene–HBr complex initially formed will be adjusted to a more favourable structure. This will cause the HBr stretching frequency in the complex to be slightly shifted to a lower frequency.

Very weak absorptions in Fig. 1(b) were observed at 1435, 1297, 955 and 603 (shoulder) cm^{-1}. These are assigned to CH_3Br (Table 1), which is possibly produced by cleavage of the C=C bond of the ketene in the ketene–HBr complex by the action of light to form CO and carbene which then reacts with the HBr in the same matrix cage, or by the reaction of the excited ketene molecule perturbed by an HBr molecule as in the photo-oxidation of ketene in an O_2/Ar matrix or in solid O_2 [7]. The absorption of CO, which should be released from the ketene on the formation of CH_3Br, was overlapped with the strong absorption of the ν_2 mode of ketene. The corresponding CD_3Br absorptions were observed in Fig. 2(b) at 1048, 985, 712 and 568 cm^{-1} (Table 1).

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