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Infrared Studies of γ-Irradiated HCOOH Isolated in CO_2 Matrix[*1)]

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Synopsis

HCOOH in CO_2 matrix was γ-irradiated at 74–77°K. The infrared spectra of irradiated samples showed that a small fraction of formic acid was crystallized during the irradiation. The structure of the crystal was assigned to α-form. The crystallization was ascribed to the thermal effect of γ-ray.

1. Introduction

Infrared spectroscopy with the matrix isolation technique was applied in the field of radiation chemistry. The technique has been frequently applied in the field of photochemistry and valuable information with respect to the molecular structure of unstable species trapped in cold matrices have been obtained[1)]. We have applied this method to the γ-ray irradiated systems at 77°K. In this report, the effect of γ-irradiation on HCOOH isolated in CO_2 matrix was studied. The infrared spectra of HCOOH has been well interpreted[2)], and the absorption band due to C=0 stretching vibration has a high absorption coefficient which enables us to detect a small amount of the compound. The CO_2 was chosen as matrix in this experiment because of i) its inertness and transparency in infrared region except for 3,800–3,600 cm^{-1}, 2,500–2,200 cm^{-1} and 700–500 cm^{-1}, and ii) its low vapor pressure, 10^{-7} torr, at 77°K.

2. Experimental

The Special Grade formic acid from Wako Pure Chemicals was used without further purification. 99.5% CO_2 was used as the matrix gas after purifying by freeze, pump and thaw technique at temperatures of liquid nitrogen and dry ice-acetone. Then, HCOOH was mixed with the CO_2 in a conventional vacuum system at room temperature. The concentrations of HCOOH were 0.2, 0.6 and 1.0%. The metal infrared cell designed for matrix isolation is shown in Fig. 1 and Fig. 2. The vacuum system for pumping out of the cell and sample gas supply is shown in Fig. 3. The plate (A) on which the sample was deposited was a KBr disk. It was fixed in a copper holder with thin indium gaskets. The tempereture of the plate was measured with Cu-Constantan thermocouples. The plate can be cooled down to 82–85°K when the liquid nitrogen was filled in the dewar (D). 68–71°K was achieved by reducing the vapor pressure of liquid nitrogen down to 93 torr which can be maintained by use of a manostat (G).

After the cell was evacuated for 16 hours at 10^{-7} torr or less, the plate was cooled down introduction of liquid nitrogen in the dewar. Then, the sample gas was deposited on the plate for 1.5–2 hours through nozzle I. The flow rate is

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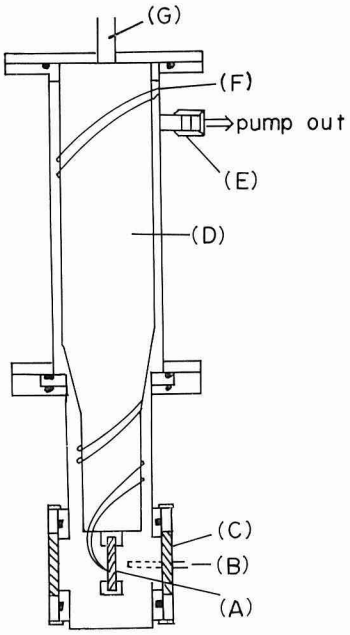


Fig. 1 Infrared cell for matrix isolation. (A): KBr plate for sample deposition and copper holder, (B); nozzle, (C); KRS-5 window for optical pass, (D); dewar, (E); seal of valve, (F); thermocouples lead out, (G); outlet for pumping out the dewar

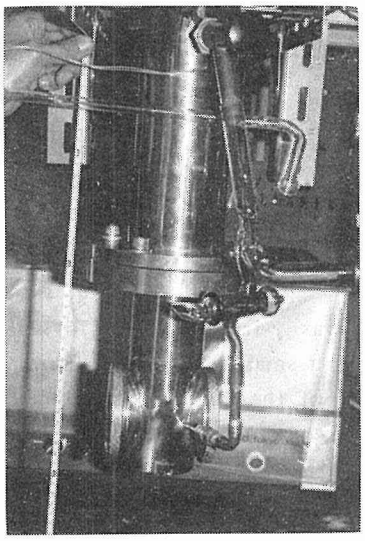


Fig. 2 Photogragh of the cell

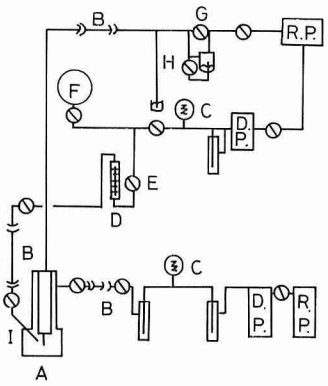


Fig. 3 Vacuum system. A; Infrared cell, B; ball joints, C; ion gauges, D; flow meter, E; needle valve, F; sample gas bulb, G; manostat, H; manometer, I; nozzle.

controlled by the needle valve E. In most experiments, the amounts of the deposit were estimated to be 0.8–0.3 g, which are calculated from the difference in the pressure of the sample gas bulb before and after the introduction. The thickness of the deposited film was estimated to be 0.5–0.2 mm which is calculated from the density of solid CO_2 as 1.6. Relative thickness can be also estimated by use of the intensity of CO_2 absorption bands.

After the deposition, the cell was removed from the vacuum system and was irradiated for 3.5–4.0 hours with γ-ray of Co-60. Dose rate was 2.6×10^{19} eV/g by Fricke dosimetry. The temperature of the plate was maintained below 77°K during irradiation. Infrared spectra were recorded at 85°K by Hitachi 285 Infrared Spectrometer before and after irradation. At each recording, the cell was set at the same position in the spectrometer as precisely as practical.

3. Results and Discussion

Pure CO_2 was studied first. The results are shown in Fig. 4. After the film of CO_2 was irradiated at 75°K, new bands appeared at 2,140, 1,880 and 980 cm^{-1}, as shown in the curve b. These bands are concluded to be due to CO_3 radical, since it is known that the infrared bands of CO_3 radical trapped in CO_2 are 2,040, 1,880, 1,075, 970, 590 and 570 cm^{-1} [3], and that 2,040 and 1,880 cm^{-1} bands due to C=0 stretching are most intense and the others are very weak. In the curve b,

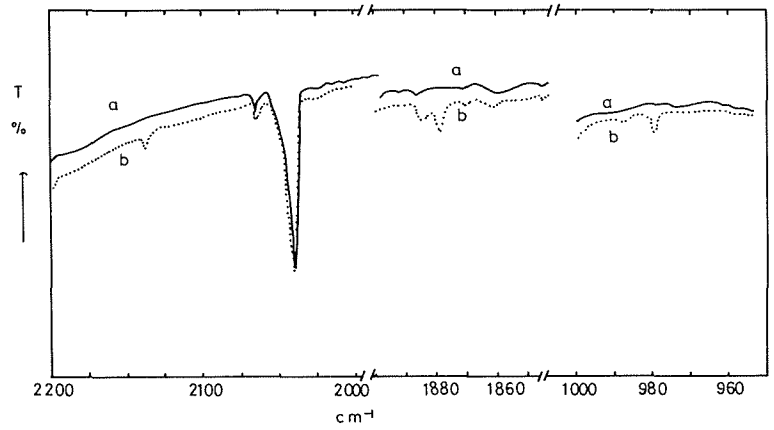


Fig. 4 Infrared spectra of irradiated CO_2. a; Before irradiation, b; after irradiation.

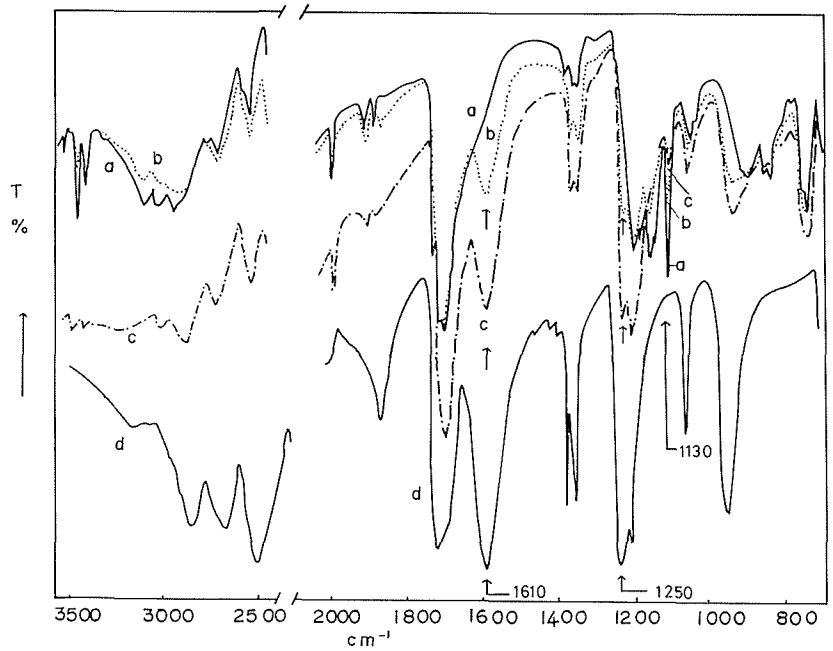


Fig. 5 Infrared spectra of CO_2-HCOOH (0.6%) experiment. a; Before irradiation, b; after irradiation for 4 hr, c; after warmed up to 100°K for 3 hr following to recording b, d; after warmed up to 140°K for 30 min following to recording c.

the 2,040 cm^{-1} band of CO_3 radical cannot be recognized because a combination band $\nu_1+\nu_2$ of CO_2 exists originally at 2,040 cm^{-1}. These new bands were stable until the plate was warmed up to 100°K. As CO_2 began to vaporize, these bands decreased. This phenomenon is also similar with that reported previously[3]. The results of irradiation of 0.6% HCOOH in CO_2 matrix are shown in Fig. 5. The curve a is the spectrum of freshly deposited HCOOH in CO_2. The assignment is listed in Table I, which is based on Millikan and Pitzer interpretation[2]. As shown in Table I, the state of formic acid was a mixture of monomer and dimer.

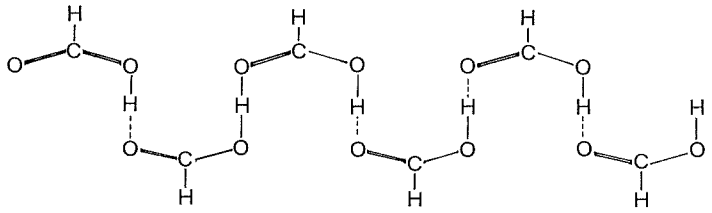
Table I Observed frequencies of HCOOH in CO_2 matrix at 85°K and assignment

ν obs. cm^{-1}		Assignment
3500	vs	OH strech, monomer
3450	s	OH strech, monomer
3150	m	OH strech, dimer
3050	m	
3000	m	
2750	m	
2600	m	
1750	s	C=O strech, monomer
1740	vs	C=O strech, monomer
1720	vs	C=O strech, dimer
1680	sh	
1390	w	CH bend, monomer
1380	w	CH bend, dimer
1220	s	C-O strech, dimer; OH bend, monomer
1170	s	
1130	vs	C-O strech, monomer
1020	w	CH bend (off plane), monomer
920	m	
880	m	

Table II Observed frequencies of solid HCOOH. Comparison with crystalline HCOOH of α-form

ν obs. cm^{-1}		crystalline HCOOH, cm^{-1} [4]	
2890	m		
2700	m		
2550	s	2532	OH strech
1880	m		
1730	s	1690	C=O strech
1610	s	1610	C=O strech
1400	m	1400	CH bend
1250	s	1255	C-O strech
1220	s	1215	C-O strech
1080	m	1098	CH bend (off plane)
970	s	975	OH bend (off plane)

The curve b is the spectrum after the irradiation for 4 hours. New bands are observed at 1,610 cm^{-1} and 1,250 cm^{-1}, and the intensity of the bands at 3,500 cm^{-1} and 1,130 cm^{-1} due to monomer and 3,150 cm^{-1} due to dimer decreased. When this sample was warmed up to 100°K for 3 hours and recooled to 85°K, it was observed that 1,610 cm^{-1} and 1,250 cm^{-1} bands were enhanced remarkably, and monomer bands almost disappeared. This shown in the curve c. The curve d was obtained after CO_2 was completely evacuated at 140°K. This spectrum is quite analogous to that of α-form crystalline HCOOH which was reported by Mikawa et al[4]. The frequencies are listed in Table II. α-Form structure proposed by Mikawa et al is described below.



Thus, 1,610 and 1,250 cm^{-1} bands in the curve b are attributed to the crystalline HCOOH which formed from monomer and dimer during irradiation.

The crystallization and disappearance of dimer and monomer were observed on all four sample containing 0.5% and 1% HCOOH but were not on 0.2% HCOOH sample. The amounts of the crystallite formed were 15–20% of the initial formic acid, estimated from the intensity ratio of 1,610 cm^{-1} band just after the irradiation and of pure crystallite obtained from the same sample by the evaporation of CO_2. This amounts correspond to G (crystallization) of about 4.

A similar aggregation was also observed in 0.5% H_2O in CO_2 matrix which

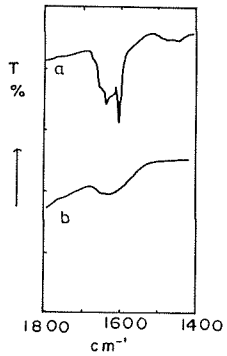


Fig. 6 Infrared spectra of irradiated H_2O in CO_2 matrix.
a; Before irradiation, b; after irradiation

was irradiated below 77°K. The results are shown in Fig. 6. The curve a is the spectrum of the freshly deposited H_2O in CO_2. The bands at 1,600 cm^{-1} and 1,650 cm^{-1} are due to the OH bending of the monomer and polymer, respectively. The curve b is the spectrum after irradiation, where the monomer band at 1,600 cm^{-1} disappeared.

These results seem to indicate that the diffusion of CO_2 occurred during the irradiation and it resulted in crystallization or aggregation of solutes. The matrix diffusion and then the crystallization of HCOOH were also seen when the plate was warmed up to 100°K. In this case, warming for 3 hours was required to obtain a crystallization comparable to the case of irradiation. No crystallization was found at 85°K, even when the sample was left for almost 20 hours at that temperature. Thus, the thermal effect of radiation is most likely to be the cause of matrix diffusion under irradiation. However, it is not likely that the whole sample film is warmed at 100°K by irradiation since the temperature of the plate was kept below 77°K. Although it is suspected that some localized effect would cause such crystallization, whether the effect is related to the "thermal spike" which is sometimes discussed in spur theory of liquid is not clear.

For elucidation of the effect of structure of the film, other matrices such as CCl_4 (m. p. 252°K) and SF_6 (m. p. 240°K) were examined with 0.5% of HCOOH content. Crystallization was not observed in either matrices.

The color centers formed on KBr plate do not seem to play an important role in this crystallization process, because the very thin deposit gave no informations of crystallization.

Fufther experiments are required to draw any quantitative conclusions.

References

*1) A part of present studies has been presented at 32nd Annual Meeting of Chemical Society of Japan, April 1975, Tokyo, by M. TANAKA, Y. KONDO and M. KATAYAMA.
1) Andrews, L.: *Ann. Rev. Phys. Chem.*, 22, 109 (1971).
2) a) Miyazawa, T.: *Nippon Kagaku Zasshi.* 74, 743, 915 (1953).
b) Millikan, R. C. and K. S. Pitzer: *J. Chem. Phys.*, 27, 1305 (1957).
c) Millikan, R. C. and K. S. Pitzer: *J. Am. Chem.* Soc., 80, 3515 (1958).
3) a) Moll, N. G., D. R. Clutter and W. E. Thompson: *J. Chem. Phys.*, 45, 4469 (1966).
b) Weissberger, E., W. H. Breckenridge and H. Taube: *ibid.*, 47, 1764 (1969).
c) Jacox, M. E. and D. E. Milligan: *ibid.*, 54, 919 (1971).
4) Mikawa, Y., R. J. Jakobsen and J. W. Brasch: *ibid.*, 45, 4750 (1966).