Journal of Fluorine Chemistry, *44* (1989) 267–273

Received: November 15, 1988; accepted: December 29, 1988

CARBONYL FLUORIDE INFRARED SPECTROPHOTOMETRIC DETERMINATION

A.E. CROCE and E. CASTELLANO

Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas
(INIFTA), Facultad de Ciencias Exactas, Universidad Nacional de
La Plata, Casilla de Correo 16, Sucursal 4, (1900) La Plata,
(Argentina)

SUMMARY

An infrared spectrophotometric method for carbonyl fluoride quantitative determination is presented. The gas phase thermal reactions between bis(fluoroxy)difluoromethane, $CF_2(OF)_2$ and CO in the temperature range 383-413 K, and between F_2O and CO in the range 423-453 K provide gas mixtures of known CF_2O concentration. The absorption cross sections of CF_2O at 1944 cm^{-1} band

$\sigma(1925\ cm^{-1}) = (4.8\pm0.3)\times10^{-19}\ cm^2\ molecule^{-1}$

$\sigma(1944\ cm^{-1}) = (4.7\pm0.3)\times10^{-19}\ cm^2\ molecule^{-1}$

$\sigma(1960\ cm^{-1}) = (4.1\pm0.3)\times10^{-19}\ cm^2\ molecule^{-1}$

were determined.

INTRODUCTION

Carbonyl fluoride appears as a reaction product in many kinetic studies on fluorine compounds [1-3]. In most cases, CF_2O can be easily identified by its infrared spectrum [4]. However, CF_2O quantitative determination offers a good deal of difficulty.

It is widely acknowledged that CF_2O samples are hard to manipulate because of its instability [5]. CF_2O readily reacts with traces of water [6]

$$CF_2O + H_2O \rightarrow CO_2 + 2\ HF \qquad (1)$$

such that it is usually accompanied by variable quantities of

0022-1139/89/$3.50

CO_2, unless special care is taken. Unfortunately, CO_2 cannot be quantitatively removed from a CF_2O/CO_2 mixture by fractional codistillation or by filtration at low temperatures, particularly at low CF_2O concentrations [7,8]. Heicklen and co-workers [9] have determined CF_2O in gas mixtures by quantitatively converting this substance to CO_2 and HF on a silica gel column. The HF does not pass through the column and CO_2 is measured in the effluent gas. Other chromatographic columns [10,11] have been used to determine CF_2O in the presence of fluorine containing compounds.

On the other hand, CF_2O is produced even together with CO_2 in a number of chemical reactions [12-14]. Therefore, several analytical methods have been proposed in order to establish the actual CF_2O concentration in a CF_2O/CO_2 mixture. Drennan and Matula [15] have described a gas chromatographic technique for the simultaneous quantitative determination of both CF_2O and CO_2. The alkaline hydrolysis of CF_2O/CO_2 mixtures, followed by fluoride ion determination can be also carried out. However, the volumetric methods for fluoride are unsatisfactory [16]. Heicklen and co-workers have also reported an absorption coefficient (base 10) of CF_2O at 5.10 μ (1960 cm^{-1}) of 0.013 $Torr^{-1} cm^{-1}$, but neither the slit width used in the measurements nor the temperature were indicated, though presumably the temperature was near 296 K [17].

In the course of the kinetic study of the gas phase thermal reaction between bis(fluoroxy)difluoromethane, $CF_2(OF)_2$ and CO in the temperature range 383-413 K, it was clearly established that CO_2 and CF_2O were the only reaction products [18]. Besides, the amount of CF_2O formed in the reaction can be easily determined. Because CF_2O infrared absorption at 1944 cm^{-1} band is not interferred by the other present species [19,20], CF_2O absorption cross section at this frequency has been determined from a Lambert-Beer plot.

The gas phase thermal reaction between F_2O and CO in the temperature range 423-453 K [13] constitutes another CF_2O source. This system has proved to be a reliable method to obtain CF_2O/CO_2 mixtures of exactly known concentration, with the advantage that F_2O is commercially available and easily purified. The results employing this reaction as CF_2O source are also presented.

EXPERIMENTAL

Gas mixtures of known CF_2O concentration were prepared in a conventional static system used in kinetic studies, which has been described elsewhere [18]. A quartz reaction vessel, 45 mm outer diameter and 100 mm long, was housed in a thermally isolated furnace made from an electrically heated aluminium block. The temperature was controlled to better than ±0.1°C by a Lauda R-10 electronic regulator. The reaction vessel was connected to a Bodenstein quartz spiral manometer used as a null instrument in connection with a mercury manometer. The furnace could be moved up and down the vessel, which was also connected through a low volume spiral trap to a standard vacuum line used for gas handling.

Bis(fluoroxy)difluoromethane was prepared by the method of Cauble and Cady [21]. It was purified by filtration [22] at the liquid oxygen temperature, trap-to-trap distilled at low temperature and kept in a trap cooled with liquid air.

Oxygen difluoride from Matheson Gas Products (USA), previously degassed at 77 K was kept stored as a gas in a Pyrex flask protected from light. Periodically it was condensed at 77 K and degassed.

Carbon monoxide 99.9% from Matheson Gas Products (USA) and high purity nitrogen from La Oxígena (Buenos Aires) were passed through a trap cooled at 153 K and stored in Pyrex flasks.

The infrared spectra were recorded in a Perkin Elmer 325 spectrophotometer. A 10 cm long (l) Pyrex cell, 30 mm outer diameter, fitted with NaCl windows, was employed in the spectrophotometric determinations.

Special care was taken to avoid moisture in the vacuum line, reaction vessel and infrared cell.

RESULTS AND DISCUSSION

The reaction [18] occurs without variation in the total number of moles

$$CF_2(OF)_2 + 2\ CO \rightarrow 2\ CF_2O + CO_2 \qquad \Delta n = 0 \qquad (2)$$

and follows a second order kinetics. In a typical experiment, 100 Torr of $CF_2(OF)_2$ and 100 Torr of CO were allowed to react at 403 K. After approximately 40 minutes ($\sim$ 30% CO consumption) the furnace was moved down, the reaction vessel and spiral trap placed into liquid oxygen baths and the unreacted CO pumped off. The pressure of the condensed mixture was then measured at 403 K and the distillation repeated until no pressure change was observed (within ±0.2 Torr). According to equation (2), the amount of CF_2O formed equals the CO consumption. This can be calculated as the difference between CO initial pressure and the pressure of the volatile fraction at 77 K. After this, the reaction vessel was kept at 298 K, the infrared cell was flushed two or three times with the $CF_2(OF)_2/CF_2O/CO_2$ mixture, an appropriate pressure equilibrated at this temperature and the infrared absorption measurement carried out. These operations were repeated to cover the whole pressure range. Low concentration mixtures (below 1 Torr CF_2O) were obtained by diluting the original with nitrogen. The absorption measurements were carried out at pressures up to 60 Torr.

In other series of experiments, the reaction between F_2O and CO at 423 K was employed as CF_2O source. This reaction occurs with a decrease in the total number of moles [13]

$$F_2O + 2\ CO \rightarrow CF_2O + CO_2 \qquad \Delta n = -1 \qquad (3)$$

The amount of CF_2O formed by reaction (3) equals the total pressure change at constant volume and temperature. These experiments were carried out in a similar way as the one described above for reaction (2). However, in this case, the condensed residue at 77 K corresponds to an equimolar mixture of CF_2O and CO_2.

As for the spectrophotometric measurement itself, the whole 1925-1944-1960 cm^{-1} band [8] was firstly scanned while reducing the slit width until the band was resolved. Then, the absorbance was recorded at the fixed frequency of the band center, 1944 cm^{-1}, at 1925 cm^{-1} and at 1960 cm^{-1} with a spectral slit width of 1 cm^{-1}. The absorption cross sections derived from these spectra were found to be independent of pressure in the range 4-60 Torr. This band therefore obeys the Lambert-Beer law over

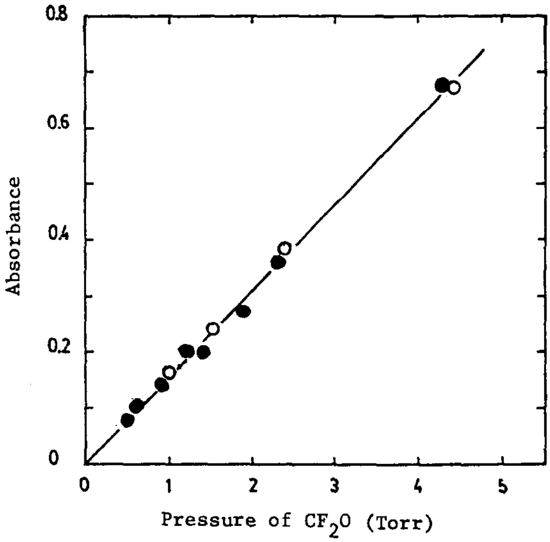

Fig. 1. Plot of absorbance at 1944 cm^{-1} against CF_2O pressure. CF_2O source: ● reaction (2), o reaction (3).

TABLE 1

CF_2O absorbance at 1925, 1944 and 1960 cm^{-1} (T = 298 K, l = 10 cm)

$[CF_2O]$/Torr	$A_{1925\ cm^{-1}}$	$A_{1944\ cm^{-1}}$	$A_{1960\ cm^{-1}}$
0.5	0.086	0.076	0.073
0.6	0.10	0.10	0.092
0.9	0.15	0.14	0.12
1.0	0.17	0.16	0.14
1.2	0.20	0.20	0.17
1.4	0.20	0.20	0.18
1.5	0.26	0.24	0.22
1.9	0.28	0.27	0.23
2.3	0.37	0.36	0.32
2.4	0.39	0.38	0.34
4.3	0.68	0.68	0.59
4.4	0.69	0.67	0.59

the range of pressures and absorber amounts and at the resolution and temperature used. This is illustrated in Fig. 1 in which the absorbance at the center of the band is plotted as a function of absorber amount. Table 1 shows the whole set of absorbance and CF_2O pressure data. From these results, the following absorption cross sections for CF_2O at 298 K can be calculated

$$\sigma(1925\ \mathrm{cm}^{-1}) = (4.8\pm0.3)\mathrm{x}10^{-19}\ \mathrm{cm}^2\ \mathrm{molecule}^{-1}$$

$$\sigma(1944\ \mathrm{cm}^{-1}) = (4.7\pm0.3)\mathrm{x}10^{-19}\ \mathrm{cm}^2\ \mathrm{molecule}^{-1}$$

$$\sigma(1960\ \mathrm{cm}^{-1}) = (4.1\pm0.3)\mathrm{x}10^{-19}\ \mathrm{cm}^2\ \mathrm{molecule}^{-1}$$

The error estimates represent three standard deviations. The 1960 cm^{-1} absorption cross section value is in excellent agreement with the previously reported value [17] which has been obtained from measurements performed at total pressures of up to 1 atm.

ACKNOWLEDGMENTS

This research project is supported by the CONICET and the CIC de la Provincia de Buenos Aires. Part of the equipment used in the present work was provided by the Cooperation Agreement between the University of Mainz (F.R.G.) and the University of La Plata (Argentina). We also thank the Stiftung Volkswagenwerk for a partnership project with Professor J. Troe.

REFERENCES

1 J.M. Heras, A.J. Arvia, P.J. Aymonino and H.J. Schumacher, Z.Phys.Chem.Neue Folge, 28, 250 (1961).

2 M. Dos Santos Afonso, E. Castellano and H.J. Schumacher, An. Asoc.Quím.Argent., 74, 465 (1986).

3 R.C. Kennedy and J.B. Levy, J.Phys.Chem., 76, 3480 (1972).

4 A.H. Nielsen, T.G. Burke, P.J.H. Woltz and E.A. Jones, J. Chem.Phys., 20, 596 (1952).

5 G.L. Workman and A.B.F. Duncan, J.Chem.Phys., 52, 3204 (1970).

6 M.W. Farlow, E.H. Man and C.W. Tullock, in W.L. Jolly, (ed.) 'Inorganic Synthesis,' Vol. 6, McGraw-Hill, New York, 1962, p. 155.

7 E.L. Pace and M.A. Reno, J.Chem.Phys., 48, 1231 (1968).
8 D.R. Stull, Ind.Eng.Chem., 39, 517 (1947).
9 J. Heicklen, V. Knight and S.A. Greene, J.Chem.Phys., 42, 221 (1965).
10 G.D. Foss and D.A. Pitt, J.Phys.Chem., 72, 3512 (1968).
11 R.L. Cauble and G.H. Cady, J.Am.Chem.Soc., 89, 5161 (1967).
12 A.E. Croce and E. Castellano, J.Photochem., 19, 303 (1982).
13 A.J. Arvia, P.J. Aymonino and H.J. Schumacher, Z.Phys.Chem. Neue Folge, 51, 170 (1966).
14 E. Vasini and H.J. Schumacher, Z.Phys.Chem.Neue Folge, 94, 39 (1975).
15 G.A. Drennan and R.A. Matula, J.Chromatog., 34, 77 (1968).
16 T.A. O'Donnell and D.R. Stewart, Anal.Chem., 33, 337 (1961).
17 D. Saunders and J. Heicklen, J.Am.Chem.Soc., 87, 2088 (1965).
18 A.E. Croce and E. Castellano, Int.J.Chem.Kinet., 14, 647 (1982).
19 R.W. Mitchell and J.A. Merritt, J.Mol.Spectrosc., 24, 128 (1967).
20 E.F. Barker and T.Y. Wu, Phys.Rev., 45, 1 (1934).
21 R.L. Cauble and G.H. Cady, J.Am.Chem.Soc., 89, 1962 (1967).
22 F.A. Hohorst and J.M. Shreeve, in W.L. Jolly, (ed.), 'Inorganic Synthesis,' Vol. 11, McGraw-Hill, New York, 1968, p. 143.