The Difluorodioxocarbonate Ion, $CO_2F_2^{2-}$

By E. MARTINEAU and J. B. MILNE*

(*Department of Chemistry, University of Ottawa, Ottawa, Canada*)

Summary $Cs_2CO_2F_2$ and $[Me_4N]_2CO_2F_2$ have been prepared; Raman and i.r. spectra are reported and the X-ray powder pattern shows that the caesium compound is isomorphous with Cs_2BeF_4.

CAESIUM FLUORIDE is known to catalyse the reaction of fluorine with oxides and oxyfluorides of carbon and sulphur[1–4] to give fluoro-oxy derivatives. For instance the fluorination of carbonyl fluoride in the presence of alkali metal fluorides or silver fluoride gives CF_3OF in good yield.[2] The reaction is thought to proceed *via* the known trifluoromethoxides, $MOCF_3$.[5] The corresponding catalytic fluorination of carbon dioxide in the presence of caesium fluoride yields $CF_2(OF)_2$[3] and a possible intermediate for this reaction is the difluorodioxocarbonate, $Cs_2CO_2F_2$.

Caesium fluoride suspended in acetonitrile reacts with carbon dioxide at *ca.* 10 atm in a sealed tube to give $Cs_2CO_2F_2$ as indicated by caesium and fluorine analysis. Preliminary analytical results (fluorine only) indicate that $CsCO_2F$ is formed at higher CO_2 pressures (*ca.* 45 atm). Caesium difluorodioxocarbonate is stable at 25 °C and does not lose carbon dioxide under vacuum. Carbon dioxide, identified by mass spectrometry, is evolved when the compound is heated to 100 °C. Dry caesium fluoride shows no tendency to adsorb carbon dioxide but catalytic amounts of $Cs_2CO_2F_2$ may be formed in the fluorination. The potassium fluoride suspension appeared to react with carbon dioxide but after the product had been kept for several hours under reduced pressure to remove solvent only potassium fluoride was recovered. Apparently $K_2CO_2F_2$ loses carbon dioxide at 25 °C. Willis[5] has reported that $KOCF_3$ loses carbonyl fluoride similarly.

A solution of anhydrous tetramethylammonium fluoride in acetonitrile (0·4M) takes up carbon dioxide [initial $P(CO_2)$ = 648 mmHg] at 25 °C. After correction for the solubility of carbon dioxide in acetonitrile the molar ratio of Me_4NF to carbon dioxide absorbed was 1·92:1. After pumping off the solvent, analysis for fluorine showed the product to be $[Me_4N]_2CO_2F_2$.

All of the fluorocarbonates effervesce on contact with water. They are extremely deliquescent and for this reason good i.r. spectra are very difficult to obtain. The i.r. and Raman spectra for the $CO_2F_2^{2-}$ ion in the two compounds are given in the Table. The characteristic bands for CO_3^{2-} and HCO_3^-, both likely products of hydrolysis, do not appear in the spectra.

TABLE

I.r. and Raman spectra of the $CO_2F_2^{2-}$ *ion*

$Cs_2CO_2F_2$		$[Me_4N]_2CO_2F_2$	
I.r.	Raman	I.r.	
1008w,sh	1014s		C–O and C–F stretching vibrations
985m	973w	990m	
	919w		
850s		840s	
680s	671m	690m	deformations
656w,sh	647w		
	632m		
	610m		

The X-ray powder photograph of $Cs_2CO_2F_2$ has no lines which may be attributed to CsF. The pattern fits an orthorhombic unit cell with dimensions similar to those for the caesium salt of the tetrafluoroberyllate ion[6] which is iso-electronic with $CO_2F_2^{2-}$:

	a/Å	b/Å	c/Å
Cs_2BeF_4 ..	10·79	7·99	6·21
$Cs_2CO_2F_2$ ..	10·66	7·90	6·19

(*Received, July* 28*th*, 1971; *Com.* 1315.)

---

[1] J. K. Ruff and M. Lustig, *Inorg. Chem.*, 1964, 3, 1422.
[2] J. K. Ruff, A. R. Pitochelli, and M. Lustig, *J. Amer. Chem. Soc.*, 1966, 88, 4531.
[3] F. A. Hohorst and J. M. Shreeve, *J. Amer. Chem. Soc.*, 1967, 89, 1809.
[4] R. L. Cauble and G. H. Cady, *J. Amer. Chem. Soc.*, 1967, 89, 1962.
[5] M. E. Redwood and C. J. Willis, *Canad. J. Chem.*, 1965, 43, 1893.
[6] O. H. Breusov and Yu. P. Simanov, *Zhur. neorg. Khim.*, 1959, 4, 2582.