THERMAL DECOMPOSITION OF THE ALKALINE SALTS OF DIFLUOROCHLORO- AND DIFLUOROBROMOACETIC ACIDS

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ABSTRACT

The thermal properties of $CF_2ClCOOMe$ and $CF_2BrCOOMe$ (with Me = Li, Na, K, Rb Cs) have been studied by thermogravimetry and differential thermal analysis. Analysis of the evolved gases and the residue by gas chromatography, mass spectrometry and X-ray shows the formation of CO_2, CO, the acid halogenide and alkaline halogenide. The nature of the metal and the halogen contained in the salt influence the decomposition reaction. A two-step decomposition is observed for most of the salts studied.

INTRODUCTION

Since the work of Swarts [1] in 1895 on difluorochloroacetic acid some publications have appeared concerning the thermal decomposition of its sodium salt, in aqueous solution [2] and in di- or triglyme [3]. In both cases it was shown that the rate determining step of the decomposition is a single concerted process leading directly to carbon dioxide, alkaline chloride and difluoromethylene

$$CF_2ClCOONa \rightarrow CO_2 + NaCl + :CF_2$$

This reaction is widely used for the preparation of difluorocarbene with a view to adding CF_2 onto double bonds [4–6]. The electrochemical decarboxylation of several difluorohaloacetic salts in acetonitrile has also been studied [7] in order to obtain carbene at room temperature. In the present work the thermal decomposition of the pure alkaline salts of $CF_2ClCOOH$ and $CF_2BrCOOH$ are described in order to compare the behaviour of these salts with the trifluoroacetates studied previously [8].

EXPERIMENTAL

The salts of $CF_2ClCOOH$ (Koch-Light Lab) were prepared by neutralization with the carbonates. The solutions were then evaporated under vacuum

and the salts recrystallized three times in ethanol, and dried under vacuum at 50°C. Difluorobromoacetic acid was prepared from 1,1-difluoroethylene, as described in ref. 9. The salts were then prepared as above, and dried without recrystallization.

Differential thermal analysis and thermogravimetry were performed using a Mettler TA1 apparatus equipped with a quadrupolar mass spectrometer (Balzer QMG 311). Enthalpy measurements were made with a Mettler TA 2000 apparatus, and a Guinier–De Wulff camera (Nonius) was used for X-ray analysis.

RESULTS AND DISCUSSION

The temperatures of transition, melting and onset of decomposition are reported in Table 1. None of these salts is stable enough in the liquid state to be studied; thus, among the halogenoacetates, the trifluoroacetates of K, Rb and Cs are the only salts stable in the fused state [8]. Most of the salts studied here show a two-step exothermic decomposition. As an example, Fig. 1 shows the DTA and TG curves obtained with $CF_2ClCOONa$. The salt decomposes immediately after melting; a stable form is observed between 210 and 240°C, and then the salt decomposes again. The weight loss and composition of the residue are reported in Table 2. The small difference between the observed and the calculated weight loss is probably due to some halogeno-compounds formed by secondary reactions; in fact, the residues show a slightly brown colour.

The intermediate residue obtained after the first step has the same composition as the final one. An attempt to differentiate the two steps was

TABLE 1

Transition, melting and decomposition temperature

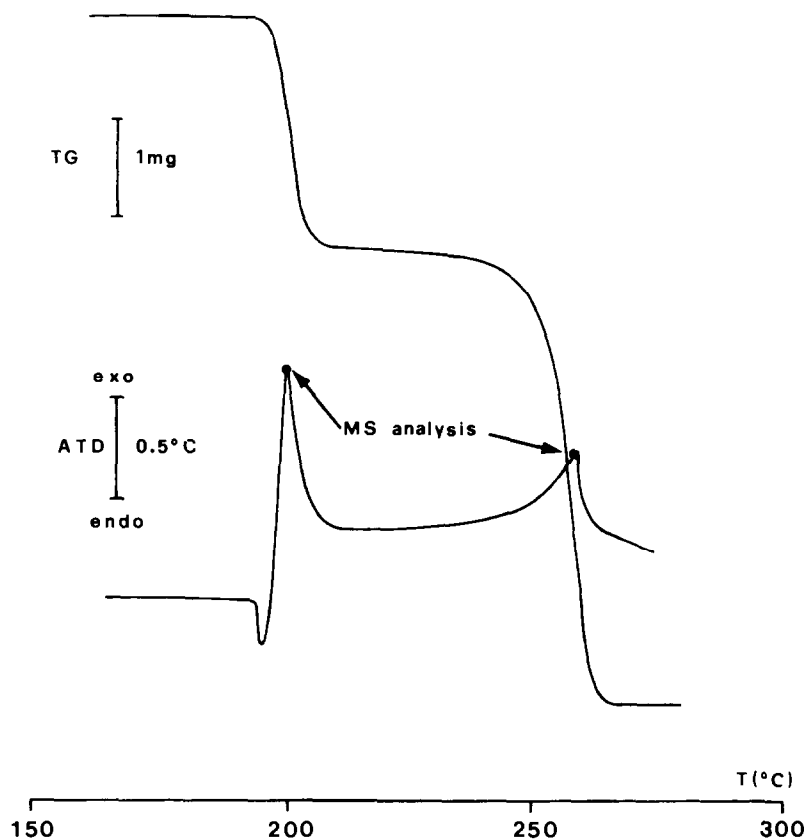| | Solid state Transition | | Melting | Onset of decomposition | |
| | | | | First step | Second step |
	$T(°C)$	ΔH^0(kJ mole^{-1})	$T(°C)$	$T(°C)$	$T(°C)$
$CF_2BrCOOLi$			212	215	no
Na			183	185	225
K	125	13.8	dec	148	185
Rb	110	24.7	128	131	no
Cs	83	21.1	127	135	no
$CF_2ClCOOLi$			252	255	no
Na			194	197	250
K	47/78	36.8/9.8	167	170	190
Rb	52	15.0	dec	162	170
Cs	58	11.0	dec	145	195

Fig. 1. DTA and TG curves for $CF_2ClCOONa$. Sample mass 11.15 mg; crucible: Pt; atmosphere: N_2, 5 l h^{-1}; heating rate: 2°C min^{-1}.

made by analyzing the gaseous products evolved at different temperatures. Figure 2 and Table 3 show the results obtained by mass spectrometric analysis performed at 201 and 259°C, as indicated in Fig. 1. The difference between the two temperatures is negligible (peak $m/e = 75,81$ and 94 are present only at 259°C). Analysis of the two steps by gas chromatography gave similar results. No explanation for this behaviour was found. Concerning the influence of the nature of the alkaline metal, analysis of the residue shows (Table 2) that the lithium salt gives LiF, the sodium salt a mixture of NaF–NaCl or NaF–NaBr, and the potassium, rubidium and caesium salts give the chloride or the bromide. Analysis of the gases evolved during the decomposition (Table 4) corroborate these results; in fact, the sodium salts give interhalogenated compounds, whereas the potassium salts give only fluorinated compounds; in this case all the other halogens are converted into the alkaline halogenide.

By analogy with the results obtained by different authors for other salts or using different conditions [2,3,10], two single concerted processes leading to

TABLE 2

Weight loss and composition of the residue

		Wt. loss(%)			Calcd. total wt. loss(%)	Composition of the residue [a]	
		First step	Second step	Total		Intermediate [b]	Final
$CF_2BrCOOLi$		83	no	83	86		LiF
	Na	21	37	58	55	$NaBr + NaF$	$NaBr + NaF$ (68 + 32%)
	K	40	7	47	44	KBr	KBr
	Rb	36	None	36	36		RbBr
	Cs	43	None	43	31		CsBr
$CF_2ClCOOLi$		77	None	77	81		LiF
	Na	21	42	63	63	$NaCl + NaF$	$NaCl + NaF$ (85 + 15%)
	K	44	9	53	56	KCl	KCl
	Rb	42	2	44	44	RbCl	RbCl
	Cs	29	5	34	36	CsCl	CsCl

[a] By X-ray analysis.
[b] The X-ray diagram of the intermediate residue shows in addition the lines of the starting material.

CO_2, CF_2 and the alkaline halogenide can explain the results obtained

$$CF_2XCOOMe \begin{cases} CO_2 + :CFX + MeF(Li,Na) & (1) \\ CO_2 + :CF_2 + MeX(Na,K,Rb,Cs) & (2) \end{cases}$$
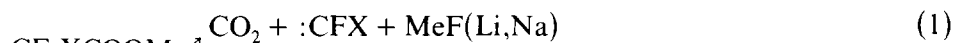
In solution, only reaction (2) occurs for $CF_2ClCOONa$ [2,3]. The difference observed between the various salts during the thermal decomposition in the molten state could be due to the decreasing ionization potential from Li to

TABLE 3

Mass observed in the mass spectrometric analysis of $CF_2ClCOONa$

m/e	Ion	m/e	Ion
12	C^+	47	COF^+
16	CH_4^+	50	CF_2^+
19	F^+	66	COF_2^+
20	HF^+	69	CF_3^+
28	CO^+	75	$CFCOO^+$
31	CF^+	78	CF_2CO^+
35	Cl^+	85	CF_2Cl^+
36	HCl^+	87	CF_2Cl^+
37	Cl^+	94	CF_2COO^+
44	CO_2^+	97	CF_2COF^+
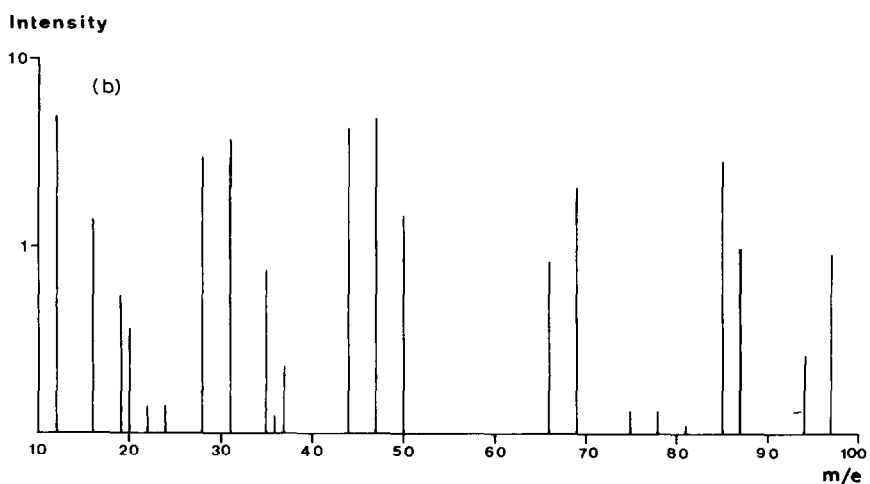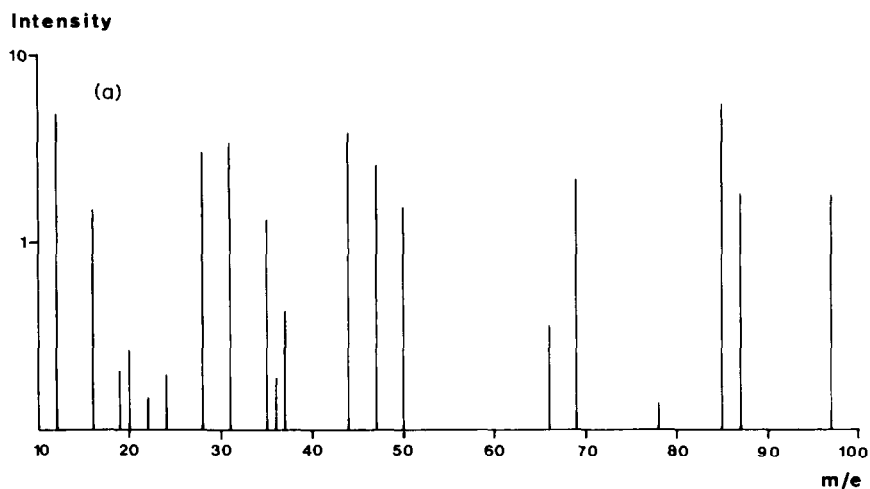
Fig. 2. Mass spectra for the decomposition of $CF_2ClCOONa$ at (a) 201°C; and (b) 259°C.
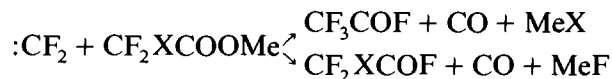
Cs. Reaction (1) probably proceeds through radical intermediates $[CF_2XCOO^{\cdot} + Me^{\cdot}]$, and reaction (2) through ionic intermediates $[CF_2XCOO^- + Me^+]$. Moreover, the C–Br bond being weaker than the C–Cl bond, the ratio NaF/NaX is greater for $CF_2ClCOONa$ (32/68) than for

TABLE 4

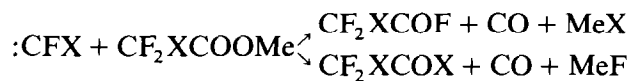Analysis of the evolved gases at 300°C by gas chromatography

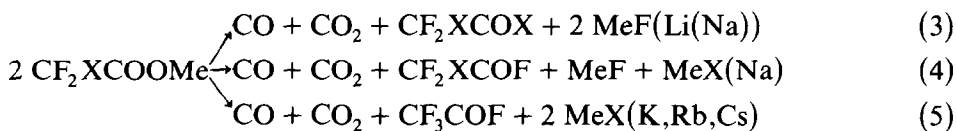| Sample	Gases detected
$CF_2ClCOONa$	CO, CO_2, CF_2Cl, C_2F_4, C_2F_3Cl, $C_2F_4Cl_2$, C_3F_6, C_4F_8
$CF_2ClCOOK$	CO, CO_2, C_2F_4, C_3F_6, C_4F_8
$CF_2BrCOONa$	CO, CO_2, CF_2Br_2, C_2F_4, C_2F_3Br, C_3F_6, C_4F_8
$CF_2BrCOONa$	CO, CO_2, C_2, C_2F_4, C_3F_6, C_4F_8

$CF_2BrCOONa$ (15/85). The carbene formed in the first step reacts with another salt molecule, leading to the formation of the halogenide of carboxylic acid

$$:CF_2 + CF_2XCOOMe \begin{cases} CF_3COF + CO + MeX \\ CF_2XCOF + CO + MeF \end{cases}$$

and

$$:CFX + CF_2XCOOMe \begin{cases} CF_2XCOF + CO + MeX \\ CF_2XCOX + CO + MeF \end{cases}$$

The overall reaction can be written as three bimolecular reactions

$$2\ CF_2XCOOMe \begin{cases} CO + CO_2 + CF_2XCOX + 2\ MeF(Li(Na)) & (3) \\ CO + CO_2 + CF_2XCOF + MeF + MeX(Na) & (4) \\ CO + CO_2 + CF_3COF + 2\ MeX(K,Rb,Cs) & (5) \end{cases}$$

The ions detected by mass spectrometry are in good agreement with the formation of the acid halogenide; on the other hand, these compounds cannot be detected by gas chromatography, due to their low stability.

CONCLUSION

Difluorochloro- and difluorobromoacetates probably decompose according to reaction (3), (4) or (5). The nature of the metal influences the rate determining step [reaction (1) or (2)]; this step is the same as that observed for the thermal decomposition of the trifluoroacetates [10] and trichloroacetates [11]. Most of the salts studied in this work decompose in two steps; no explanation was found for this phenomenon.

ACKNOWLEDGEMENTS

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