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PROPERTIES OF MOLTEN ALKALI METAL TRIFLUORACETATES

PART II. THERMAL PROPERTIES AND KINETICS OF THERMAL DECOMPOSITION

R. DALLENBACH* and P. TISSOT

Université de Genève, Département de Chimie Minérale, Analytique et Appliquée, 30 quai Ernest Ansermet, 1211 Genève 4, Switzerland

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We have studied the thermal stabilities of the alkali metal trifluoroacetates by means of DTA and TG, and shown that they are stable in the solid form, with the exception of the lithium salt. We have determined the enthalpies of melting of these five salts. We have also studied the kinetics of decomposition of CF_3COONa, of CF_3COOK and of their mixture. This decomposition is in all cases of the first order. The mixture decomposes in two steps, the first one corresponding to the decomposition of the sodium salt.

In a previous paper [1] we studied the thermal properties of sodium and potassium trifluoroacetates and the binary phase diagram CF_3COOK-CF_3COONa. This mixture presents a compound and two eutectics; the stability of the mixture containing 62 wt.% of CF_3COOK is sufficient in the molten state to allow its use as an electrolytic medium [2, 3]. By means of DTA and TG, we have now investigated the thermal properties of the trifluoroacetates of Li, Na, K, Rb and Cs, and the kinetics of decomposition of the sodium and the potassium salts as well as their mixture.

Experimental

We have used the same techniques as described previously [1] for preparing the salts and the X-ray analysis. We have analyzed the gases evolved during the decomposition by gas-chromatography (Helwett Packard 5750 B; column: Porapak Q, 10 feet; temperature: 80 – 170°) and by mass-spectrometry (Varian Mat-SM1-BH). DTA and TG measurements have been made with a TA installation (Mettler) under the following conditions: sample and reference (Al_2O_3) weight: 12 – 15 mg; crucible: platinum; heating rate: 2° min^{-1}; atmosphere: N_2, 5 lh^{-1}. The enthalpies have been determined with a TA2000 device (Mettler) connected with a micro-computer (Tektronix 4051).

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[*] Present address: Union Carbide Europe SA, 43 rue L. Chevrolet, 2300 La-Chaux-de-Fond, Switzerland.

Results

Properties of pure salts. Figure 1 shows the DTA and TG curves obtained for the five alkali metal trifluoroacetates. Allotropic transformations observed with CF_3COORb (33 and 42°) and CF_3COOCs (91°) are not shown in this Figure. Moreover, CF_3COOLi often presents an exothermic peak at 127°, which we have attributed to the crystallization of this salt; as a matter of fact, the X-ray pattern obtained with the product heated near 140° shows some lines which are missing when the salt is not heated after its preparation. The small peak preceding the melting of CF_3COOLi could be attributed to a phase transition.

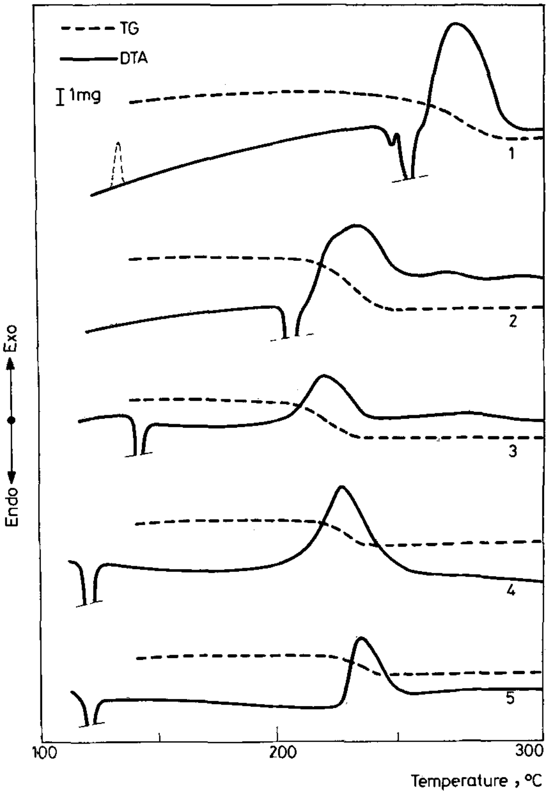

Fig. 1. DTA and TG curves for alkali-trifluoroacetates. (1) CF_3COOLi (12.4 mg); (2) CF_3COONa (15.9 mg); (3) CF_3COOK (13.4 mg); (4) CF_3COORb (13.6 mg); (5) CF_3COOCs (13.7 mg)

In Table 1 we present the interreticular distances; these results confirm those obtained previously for CF_3COONa and CF_3COOK [1, 4].

Table 1

Interreticular distances *d*,Å relating to alkali-trifluoroacetates

Salts	Strong I	Medium I	Weak I
CF_3COOLi	—	4.9 4.35 4.2	3.9 3.8 3.75 3.2 2.55 2.35
CF_3COONa	—	4.35 4.15 3.7	3.45 2.78 2.57 2.55
CF_3COOK	3.45*	5 3.78(2) 3.18 2.29 2.22 2.16 2.15	3.36 2.52 2.48 2.36 etc.
CF_3COORb	3.62* 2.98 2.48	3.2 3.04 2.64 2.4 etc.	
CF_3COOCs	3.84* 3.8 2.55	3.7 3.2 3.15 3.04 2.47 etc.	

* strongest line

The five salts each show an exothermic peak corresponding to decomposition according to the global Eq. (1):

$$2\,CF_3COOM_{(liq.)} \rightarrow CF_3COF_{(g)} + CO_{(g)} + CO_{2(g)} + 2\,MF_{(sol)} \qquad (1)$$

The results obtained by DTA and TG are collected in Tables 2 and 3; the temperature at the onset of decomposition is that read from the TG curve where it diverges from the base line. X-ray analysis of the residues obtained after the decomposition has confirmed that the thermolysis leaves alkali metal fluorides; the small difference between the observed and the calculated weight loss is probably due to some fluoro-compounds formed by secondary reactions. On the other hand, gas-chromatography and mass-spectrometry have confirmed the pres-

Table 2

Temperature and enthalpy of transformations

	Allotropic transformation		Melting		
	T, °C	ΔH, Jg^{-1}	T, °C	ΔH, Jg^{-1}	ΔS, $Jg^{-1}deg^{-1}$
CF_3COOLi	–	–	260	92.3	0.17
CF_3COONa	–	–	207	91.9	0.19
CF_3COOK	–	–	142	55.3	0,13
CF_3COORb	33	5.8	122	34.4	0.09
	42	4.2			
CF_3COOCs	91	15.1	124	23.2	0.06

ence of CO, CO_2 and CF_3COF in the decomposition gases; MS analysis shows peaks at m/e 47 (COF^+), m/e 78 (CF_2CO^+), m/e 97 (CF_3CO^+) and m/e 116 (CF_3COF^+), which are certainly fragments resulting from the breaking-up of CF_3COF [5]. The values of ΔH and ΔS connected with the melting of the lithium salt are probably too small, as decomposition occurs simultaneously with the melting. Figure 2 shows the linear relationship obtained between the cationic radii of the metals and the ΔH of melting of the trifluoroacetates; the extrapolated values for CF_3COOLi are $\Delta H = 122 \text{ J} \cdot \text{g}^{-1}$ and $\Delta S = 0.23 \text{ J} \cdot \text{g}^{-1} \text{deg}^{-1}$.

Thermal stability of the mixture $CF_3COOK - CF_3COONa$. The DTA curves of the mixtures (Fig. 3) show a small exxothermic peak superposed upon the decomposition; at the same temperature, the weight loss slows down. In Table 4 we list the R values calculated according to the equation

$$R = \frac{\text{weight loss at the inflexion point}}{\text{total weight loss}} \cdot 100.$$

Table 3

Decomposition temperature and weight loss

Salts	Onset of decomposition,	Field of stability in molten state,	Weight loss, %	
	°C	°C	observed	calculated acc. eq. (1)
CF_3COOLi	250	0	76	78.4
CF_3COONa	210	0	68	69.1
CF_3COOK	150	8	60.5	61.8
CF_3COORb	162	40	40.2	47.5
CF_3COOCs	154	30	37.1	38.2

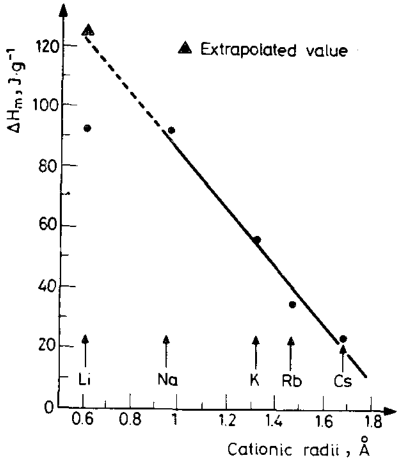

Fig. 2. $\Delta H_{(m)}$ of alkali-trifluoroacetates as a function of cationic radii of the metals

One finds that R is approximately equal to the mole percent of sodium salt present in the mixture. To prove that the first part of the TG curve corresponds to the decomposition of CF_3COONa, we have analyzed, by X-rays, the residue obtained at the inflexion point; the X-ray patterns show that the residue consists

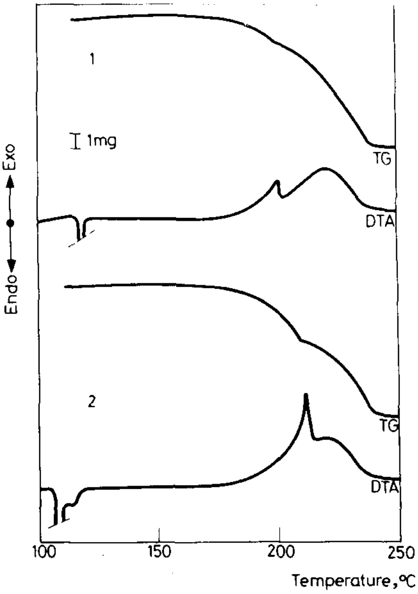

Fig. 3. DTA and TG curves of two $CF_3COOK-CF_3COONa$ mixtures.
(1) $CF_3COOK-CF_3COONa$ 78–22 mole%; (2) $CF_3COOK-CF_3COONa$ 54–46 mole%

Table 4

Mixture composition, mole % CF_3COONa	R, %
22	20
27	25
32	31
38	37
41	39
43	42
46	44
51	51

of NaF and CF_3COOK. The endothermic peaks shown near 120°in Fig. 3 correspond to the liquidus of the mixtures [1]. As the decomposition begins around 150° for all the compositions studied, it follows that the thermal stability in the molten state extends for 30 degrees and even up to 38 degrees in the case of the eutectic E_2 [1].

Kinetics of the decomposition of CF_3COOK, CF_3COONa *and their mixture.* The kinetics of the decomposition have been studied from the weight loss at constant temperature. The rate equation can be expressed as

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n$$

where k = rate constant

α = decomposed fraction (weight loss at time t divided by the total weight loss)

n = apparent order of the reaction.

In the case of the pure salts we obtain a linear relationship between $\ln(1 - \alpha)$ and the time, with a correlation coefficient better than 0.997. The apparent order of the decomposition reaction is then 1. The standard deviation of the rate constant calculated from these straight lines lies between 0.3 and 1%.

In the case of the mixture studied (62 mole % of CF_3COOK), the weight loss curves at constant temperature show a slope change when all the sodium salt is decomposed. If we define α_1 and α_2 as the decomposed fractions relating to the first and the second part of the curve, respectively, we obtain straight lines for $\ln(1 - \alpha_1)$ and for $\ln(1 - \alpha_2)$ as a function of the time (correlation coefficient > 0.995). However, this linear relationship in the case of α_1 is observed only between 0 and 0.6. Figure 4 and Table 5 show the kinetic results obtained.

Table 5

Kinetic parameters of thermal decomposition

Sample	Activation energy, kJm^{-1}	Preexponential factor, min^{-1}	Rate constant at 210 °C, min^{-1}
CF_3COONa	192.5 ± 2	$1.1 \quad 10^{19}$	$183.4 \quad 10^{-4}$
CF_3COOK	164.4 ± 2	$3.2 \quad 10^{16}$	$531.1 \quad 10^{-4}$
62–38 mole % (first part)	184.5 ± 2	$7 \quad 10^{19}$	$7585 \quad 10^{-4}$
62–38 mole % (second part)	170.7 ± 4	$2.2 \quad 10^{19}$	$770 \quad 10^{-4}$

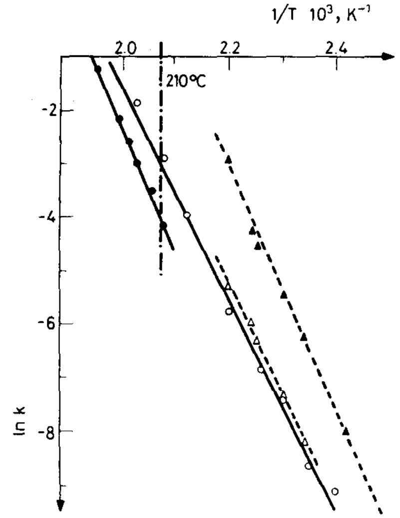

Fig. 4. Arrhenius plot for the thermal decomposition. ● CF_3COONa; ○ CF_3COOK; ▲ $CF_3COOK-CF_3COONa$ 62–38 mole% (First part); △ $CF_3COOK-CF_3COONa$ 62–38 mole% (Second part)

Discussion

Swarts [6] first noticed that CF_3COONa does not decompose in the same manner as the alkali metal carbonates; as a matter of fact, he observed that the main products of the thermolysis of CF_3COONa were CF_3COF, CO_2, CO and NaF. Since then, many trifluoroacetates have been shown to decompose in the same manner: $(CF_3COO)_2Ba$ [7], CF_3COONa [8, 9], CF_3COOLi and $(CF_3COO)_2Ca$ [10], CF_3COOK [11], trifluoroacetates of rare earths [12, 13], $(CF_3COO)_2Pb$ and $(CF_3COO)_2Sn$ [14].

In this study we have established that CF_3COORb and CF_3COOCs behave in the same manner. The trifluoroacetate of lithium is the only compound in this group which decomposes slightly before its melting point; all the other alkali metal salts are stable in the solid state.

The mixture $CF_3COOK-CF_3COONa$ decomposes in two successive steps; although in the pure state the sodium salt is stable until 210°, it decomposes in the mixture at as low as 150°, because at that temperature the mixture has melted. The same observation has been made by Auerbach [15] during a study on the kinetics of the decomposition of CF_3COONa dissolved in glycol-diethylene; he observed a first-order decomposition reaction, with an activation energy of 10 $kJmol^{-1}$ at 180°.

We have extrapolated the Arrhenius plots shown in Fig. 4 to compare the rate constant at 210° for the salts in the pure state and in the mixture. One can see (Table 5) that the rate constant is 40 times greater for CF_3COONa in the mixture, whereas the values for the pure salt and the mixture are similar in the case of CF_3COOK. In all cases the apparent order of the decomposition reaction is unity.

According to these results and by analogy with the works of Auerbach [15] and Kirmse [16] dealing with the thermolysis of acetates and trifluoroacetates in solution, one can propose that the step determining this very complicated mechanism is the decarboxylation of the trifluoroacetate ion:

$$CF_3COO^- \rightarrow CF_3^- + CO_2. \tag{2}$$

The formation of the products indicated in reaction (1) could be explained by the following reactions:

$$CF_3^- \rightarrow CF_2: + F^- \tag{3}$$

$$CF_2: + CF_3COO^- \rightarrow CF_3COF + CO + F^- \tag{4}$$

It must be mentioned, however, that we have not succeeded in detecting intermediate difluorocarbene by reaction with an olefinic compound.

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RÉSUMÉ — Nous avons étudié la stabilité thermique des trifluoroacétates alcalins par ATD et TG, et montré que seul le sel de lithium se décompose avant la fusion. Nous avons déterminé les enthalpies de fusion de ces cinq sels. Nous avons également étudié la cinétique de décomposition de CF_3COONa, CF_3COOK et de leurs mélanges. Cette décomposition est dans tous les cas d'ordre 1. Les mélanges se décomposent en deux étapes, la première correspondant à la thermolyse complète du sel de sodium.

ZUSAMMENFASSUNG — Die Thermostabilität der Alkalitrifluoracetate wurde durch DTA und TG untersucht und festgestellt, daß diese in der festen Form mit Ausnahme des Lithiumsalzes stabil sind. Die Schmelzenthalpie dieser fünf Salze wurde bestimmt. Die Kinetik der Zersetzung von CF_3COONa, CF_3COOK und ihrer Gemische wurde ebenfalls untersucht. Diese Zersetzung ist in allen Fällen ein Vorgang erster Ordnung. Die Gemische werden in zwei Stufen zersetzt, wobei die erste Stufe der Thermolyse des Natriumsalzes entspricht.

Резюме — С помощью ДТА и ТГ изучена термическая стабильность трифторацетатов щелочных металлов. Установлено, что все они устойчивы в твердой фазе. За исключением литиевой соли, определена энтальпия плавления этих солей. Изучена кинетика разложения CF_3COOK, CF_3COONa и их смесей. Во всех случаях разложение является реакцией первого порядка. Смеси солей разлатаются в две стадии, первая из которых соответствует термолизу натриевой соли.