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Note

THERMAL DECOMPOSITION OF TRIFLUOROACETATES

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In a previous paper [1] we studied the thermal decomposition of CF_3COONa and CF_3COOK from the weight loss curves at constant temperature. It was not possible to use an inert dry atmosphere with the apparatus used. Later on we observed that the mass spectra of the gaseous products obtained in dry nitrogen and static air were different. We than modified the thermobalance and studied the kinetics of decomposition of five alkali trifluoroacetates in dry nitrogen. All other experimental conditions are the same as in ref. 1.

The results obtained confirm that the reaction of decomposition is a first-order reaction at temperature close to onset of decomposition. Figure 1 shows the curve-fitting between the theoretical curve corresponding to a first-order reaction and the experimental results at one temperature. CF_3COOCs presents a two-step reaction which cannot be explained and interpreted. At higher temperature as well as at degrees of decomposition

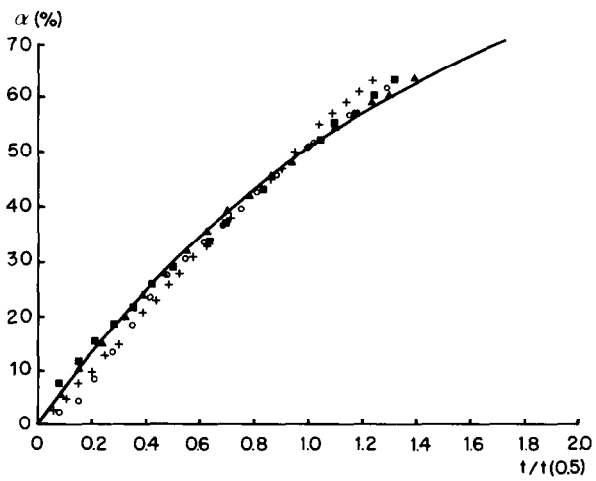

Fig. 1. Degree of decomposition as a function of reduced time: (———) theoretical curve, first-order reaction; (+) CF_3COOLi at 256°C; (○) CF_3COONa at 203°C; (▲) CF_3COOK at 182°C; (■) CF_3COORb at 191°C.

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TABLE 1

Kinetic parameters of thermal decomposition

Sample	Activation energy (kJ mol^{-1})	Pre-exponential factor (min^{-1})
CF_3COOLi	176	1.7×10^{20}
CF_3COONa	166	2.4×10^{16}
CF_3COOK	146	2.1×10^{14}
CF_3COORb	120	3.6×10^{11}

higher than 50, the first-order mechanism is not followed. In Table 1 are given the kinetic parameters calculated from the curves obtained at five temperatures between T_{onset} and $T_{onset} + 20\,°C$. The values obtained decrease with the increase of the ionic radius of the cation; this observation is in good agreement with the rate-determining step proposed [1], i.e. the break of the C–C bond, this bond becoming weaker as the radius of the cation increases.

The limitation of the interpretation of the curves at high temperature and at high α can be explained by a continuous modification of the chemical reactions as a function of T and α. Indeed the mass spectra obtained at 170 and 220 °C for CF_3COOK show a great difference of the relative intensity of several peaks. Differences are also observed at constant temperature but at different degrees of decomposition. All these observations allow us to conclude that several chemical reactions occur during the decomposition of the trifluoroacetates:

$$2\ CF_3COOMe \rightarrow CF_3COF + CO + CO_2 + 2\ MeF \quad (1)$$

$$2\ CF_3COOMe \rightarrow CF_3COCF_3 + Me_2CO_3 \quad (2)$$

$$X\ CF_3COOMe \rightarrow C_xF_{2x} + X\ CO_2 + X\ MeF \quad (3)$$

Reaction (1) is the main one which occurs at low temperature and low α. The kinetic parameters shown in Table 1 correspond to this reaction and to the mechanism proposed previously [1]. However, the temperature of the sample during dynamic experiments at low heating rates is too high, so that reactions (2) and (3) become important even at low α, and the kinetic parameters determined by this method have no significance.

REFERENCE

1 R. Dallenbach and P. Tissot, J. Therm. Anal., 20 (1981) 409.