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THE THERMAL PHASE TRANSFORMATIONS OF LITHIUM, SODIUM AND POTASSIUM FORMATES.

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SUMMARY

The existence of thermal phase transformations of lithium, sodium and potassium formates was shown by means of thermal analysis and X-ray powder diffraction analysis. A monoclinic phase of HCO_2Na transformed into a triclinic phase at 237 °C, and an orthorhombic phase of HCO_2K into a monoclinic phase at 135 °C. The phase transformation of HCO_2Li was also observed at 230 °C. The lattice parameters for these phases before and after transformations were estimated from the X-ray diffraction lines. The transformed phases scarcely returned to the original phases by standing at room temperature for 12 hours in vacuum, but reversed easily in humid air. Therefore, the reverse transformation seems to be accelerated by the water molecule of atmosphere.

INTRODUCTION

Although a number of studies have been carried out on the thermal decompositions of various formates (refs.1-9), only a few papers have been reported on the thermal phase transition of them. In the course of thermal analysis of alkali metal formates, we found (ref. 10) that the phases of anhydrous lithium, sodium and potassium formates transformed immediately before melting. In the present paper, to obtain further detailed informations on these phase transformations, their thermal behavior was investigated by means of thermogravimetry, differential thermal analysis, differential scanning calorimetry and the X-ray powder diffrac-

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tion analysis.

EXPERIMENTAL

Material

Lithium formate monohydrate, and sodium and potassium formates (guaranteed reagents) were purchased from Kishida Chemicals Co. Ltd. (Osaka, Japan). These reagents were recrystallized from redistilled water. The anhydrous lithium formate was obtained from its monohydrate by means of thermal dehydration in the temperature range from 40 to 70 °C, referred to the thermogravimetric (TG) curve.

Apparatus

Thermogravimetric (TG) and differential thermal analysis (DTA) curves were obtained simultaneously with differential thermal microbalance, Rigaku-Thermoflex TG-DTA M 8075. About 10 mg of powder specimen was weighed into a platinum crucible, and α-alumina was used as a reference material. The enthalpy change for phase transformation was obtained from differential scanning calorimetric (DSC) curve recorded on a Shinku Richo DSC-1500 M/L. About 5mg of specimen was placed in an aluminum crucible, and α-alumina was used as a reference material. This instrument was calibrated with the heat of melting of indium (ΔH = 3.27 kJ mol^{-1}, 156.5°C) and zinc (ΔH = 6.57 kJ mol^{-1}, 419.6°C) and the enthalpy change for the phase transition of potassium perchlorate (ΔH = 13.8 kJ mol^{-1}, 299.6°C) (ref. 11). Powder X-ray diffraction patterns were obtained at various temperatures on a Rigaku-Diffractometer RAD-rA equipped with a standard high temperature sample holder. Cu Kα radiation, nickel filter and a graphite monochromator were used in all measurements. The specimen was heated at a rate of 2°C min^{-1} and cooled at a rate of -2°C min^{-1}. Diffraction data were taken at a step of 0.02 deg width, and the diffraction peaks were indexed by use of a microcomputer, Epson PC-286 VE.

RESULTS AND DISCUSSION

The DTA curves of alkali metal formates are shown in Fig.1. In the DTA curves of HCO_2Li, HCO_2Na and HCO_2K, small endothermic peaks without any weight change were observed at 230, 237 and 135 °C, respectively, just before their melting points.

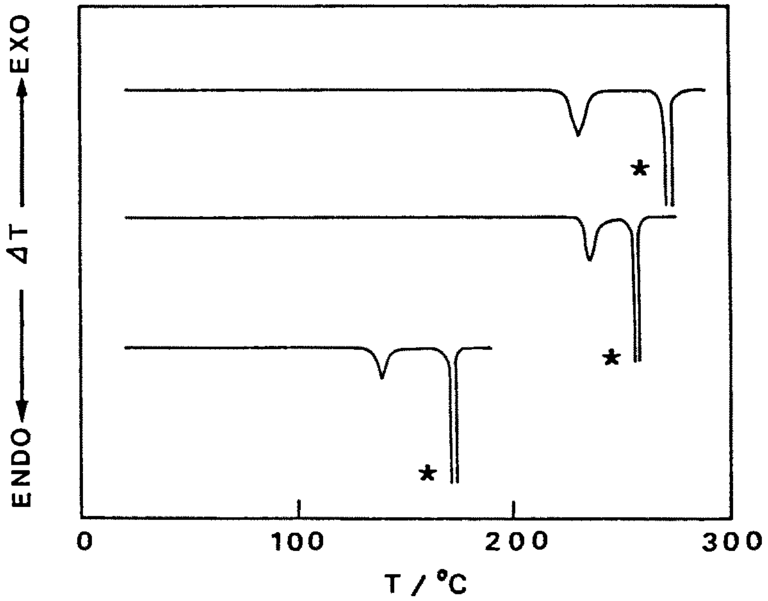

Fig.1. DTA curves of HCO_2Li, HCO_2Na and HCO_2K.
The peaks marked with * correspond to the melting of specimens.

The powder X-ray diffraction profiles and Raman spectra measured before and after these endothermic peaks are shown in Fig.2 and Fig.3, respectively. The differences between the diffraction patterns measured before and after the endothermic peaks indicate that the peaks can be corresponding to the phase trans-

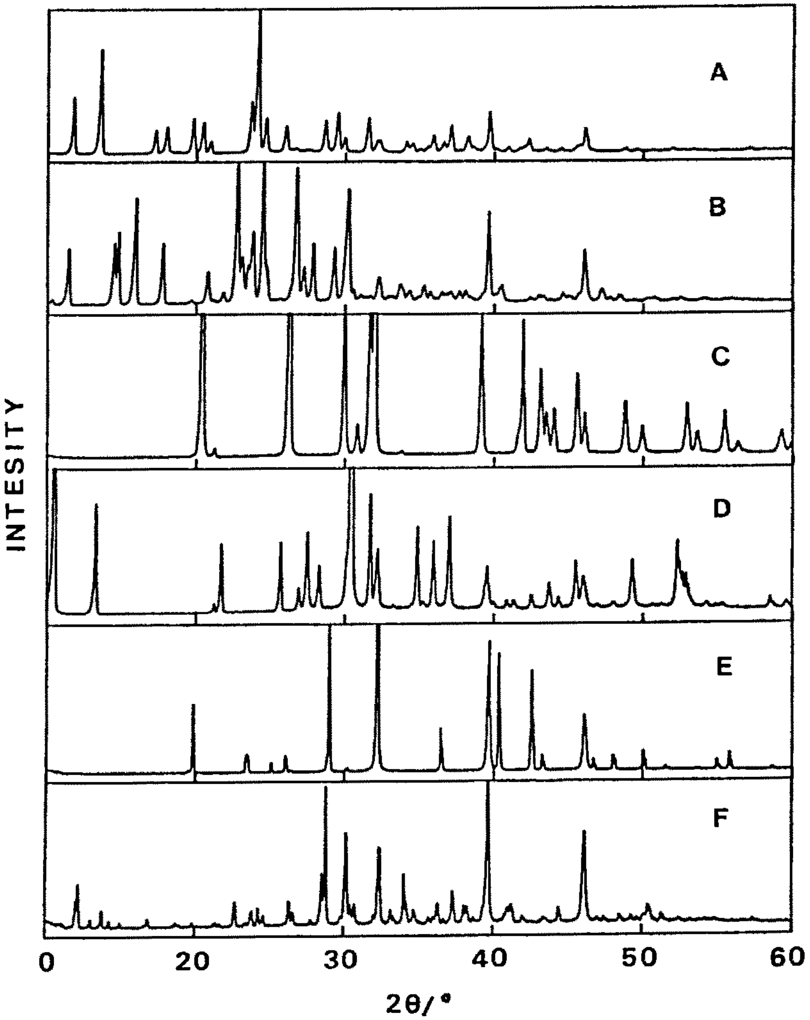

Fig.2. X-ray diffraction paterns measured before and after the thermal transformations of HCO_2Li,HCO_2Na and HCO_2K.
A;HCO_2Li (100°C), B;HCO_2Li (255°C), C;HCO_2Na (100°C), D;HCO_2Na (245°C), E;HCO_2K (100°C) and F;HCO_2K (150°C).

formations. The differences between the Raman spectra are also similar.

The X-ray diffraction lines of HCO_2Na before transformation (Fig.2C) were able to index on the assumption that the crystal has a monoclinic unit cell with lattice parameters a = 6.29, b = 6.76, c = 6.22 Å and β = 116.6°. The lattice parameters obtained

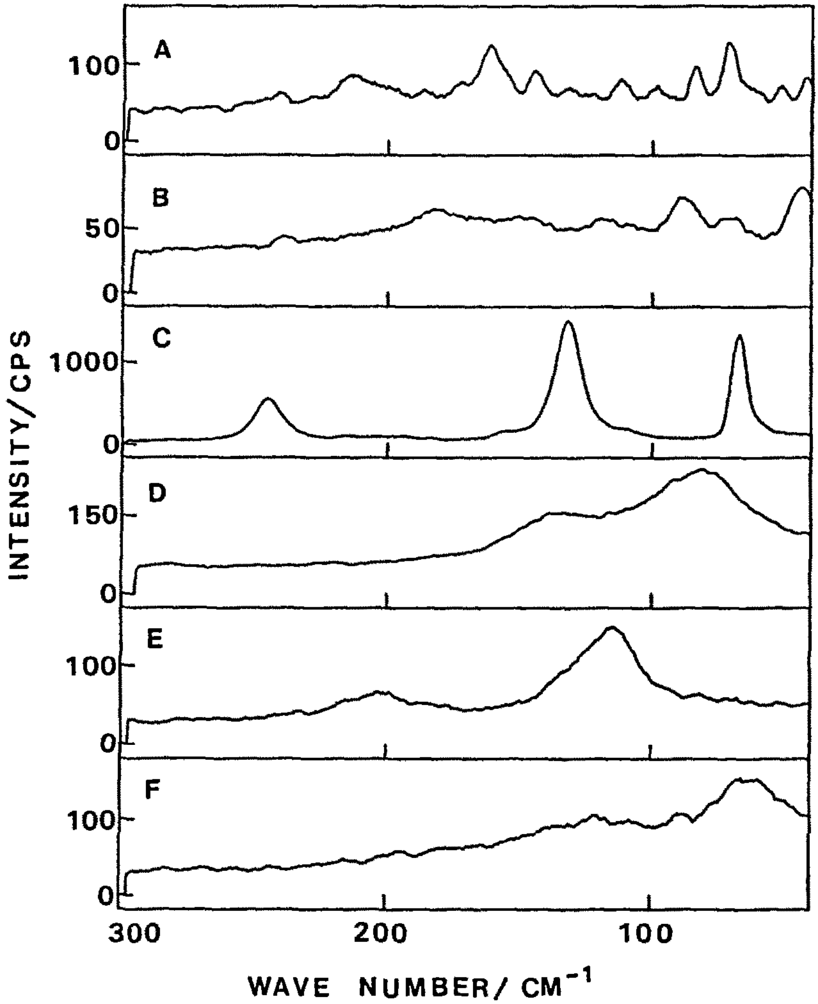

Fig.3. Raman spectra measured before and after the thermal transformations of HCO_2Li, HCO_2Na and HCO_2K.
A;HCO_2Li(25°C), B;HCO_2Li(250°C), C;HCO_2Na(25°C), D;HCO_2Na(248°C), E;HCO_2K(100°C) and F;HCO_2K(150°C).

are in satisfactory agreement with those reported in a literature (ref.12). The phase of transformed HCO_2Na (Fig.2D) was also identified as a triclinic crystal having the lattice parameters a = 6.92, b = 8.39, c = 8.96Å, α = 102.6, β = 107.2 and γ = 93.5°. Table 1 also shows the lattice parameters obtained for the crystal phases of HCO_2K. The parameters for the crystals of HCO_2Li are not shown because it is difficult at present to determine them. The parameters will be reported in a future work.

The enthalpy and entropy changes caused by these phase transformations are summarized in Table 2. The values of ΔH and ΔS decrease in the order of Li, Na and K.

TABLE 1

Lattice parameters of HCO_2Li, HCO_2Na and HCO_2K.

Formate	Phase before Transformation	Phase after Transformation
HCO_2Na	Monoclinic a = 6.29 Å (6.239 Å)[a] b = 6.76 Å (6.749 Å)[a] c = 6.22 Å (6.079 Å)[a] β = 116.6° (116.61°)[a] (100°C) (-153°C)[a]	Triclinic a = 6.92 Å b = 8.39 Å c = 8.96 Å, α = 102.6° β = 107.2°, γ = 93.5° (245°C)
HCO_2K	Orthorhombic a = 5.93 Å (5.887 Å)[b] b = 6.85 Å (6.791 Å)[b] c = 7.08 Å (7.042 Å)[b] (100°C) (22°C)[b]	Monoclinic a = 12.67 Å b = 7.36 Å c = 9.20 Å, β = 110.5° (158°C)

a) H.Fuess and J.W.Bats, Acta Cryst.,B38 (1982) 736-743 (ref.12)
b) J.W.Bats and H.Fuess, Acta Cryst.,B36 (1980) 1940-1942 (ref.13)

Table 2 shows that there are appreciable difference in the values between ΔH and ΔS of HCO_2Li and those of HCO_2Na and HCO_2K. However, further analysis of the relation between these values can not be given at present because the detailed crystal structures of these salts before and after the phase transformations have not been clarified.

The phases transformed by elevating temperature scarcely returned to the former phase by standing at room temperature for 12 hours in vacuum, but easily returned to the lower temperature phases in the atmosphere including moisture. Therefore, these reverse transformations seem to be accelerated by the water molecules included in the atmosphere.

TABLE 2

The values of enthalpy change and entoropy change for the thermal phase transitions of HCO_2Li, HCO_2Na and HCO_2K.

Formate	Temperature[a)] °C	ΔH kJ mol^{-1}	ΔS J $mol^{-1}K^{-1}$
HCO_2Li	230	2.40 ± 0.13	4.77 ± 0.26
HCO_2Na	237	1.20 ± 0.01	2.35 ± 0.02
HCO_2K	135	0.67 ± 0.02	1.64 ± 0.05

a) Phase transformation temperature measured at peak of DSC curve.

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