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# ANOMALOUS BEHAVIORS IN SODIUM-CHLORANIL ION RADICAL SALT AROUND 110°C

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The electronic spectrum and the electrical conductivity of $Na^+(CA)^-$ abruptly change around 110°C. The X-ray studies show that the crystalline nature of the salt changes around this temperature. The results of the DSC measurement and the vibrational spectrum suggest that the above anomaly may be induced by release of water in the salt.

Phase transitions have been observed in alkali metal-TCNQ ion radical salts in the temperature range -150° to +230°C.[1),2)] In these salts the pressure induced phase transition has been found at room temperature. Alkali metal-chloranil ion radical salts show the electronic absorption spectra which are affected by the kind of the alkali metal cations. The chloranil anions, $(CA)^-$, seem to be dimeric in $Li^+(CA)^-$ and $Na^+(CA)^-$ and to be monomeric with a weak interaction between the anion radicals in $K^+(CA)^-$ and $Rb^+(CA)^-$ in the crystalline state.[3)]

The phase transition in $K^+(CA)^-$ occurs at 210°K and at 250°K on cooling and on heating respectively.[4)] In the case of $Rb^+(CA)^-$, the anomaly in the magnetic susceptibility has been observed at about 10°K. The magnetic susceptibility in $Li^+(CA)^-$ and $Na^+(CA)^-$ has been found to change monotonously at low temperatures.[5)] In this paper, the anomalous behaviors in the electronic absorption spectrum, the electrical conductivity and the differential scanning calorimetry (DSC) of $Na^+(CA)^-$ found around 110°C will be discussed.

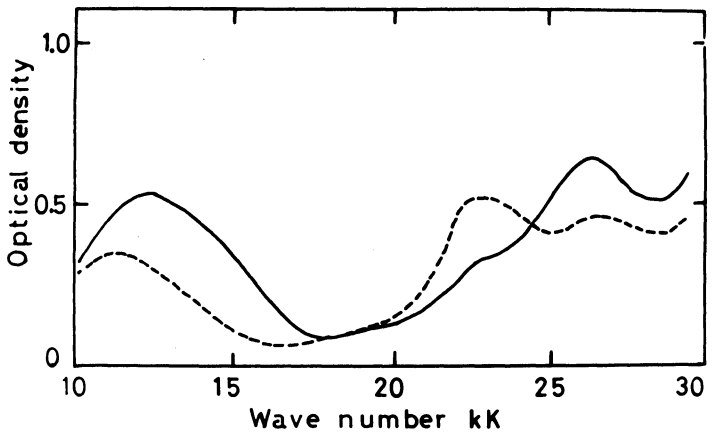


Fig. 1 Temperature dependence of the electronic absorption spectrum of the crystalline $Na^{+}(CA)^{-}$ salt.
——: room temperature,
---: at 145°C.

EXPERIMENTAL

Commercially available p-chloranil was purified by recrystallization from benzene and then by sublimation in vacuo. Its sodium salt was synthesized according to the method of Torry and Hunter.[6] The electronic absorption spectra were recorded on a Hitachi EPS-3T spectrophotometer and the vibrational spectra, as Nujol mineral oil nulls, on a Jasco IR-G infrared spectrophotometer. The electrical measurement was carried out by means of the direct current method with two electrode probes in $10^{-2}$ torr. The DSC measurements were performed by means of a Rigaku-denki Thermoflex apparatus. The X-ray measurements were made with a Toshiba recording X-ray diffractometer, Model ADG 301, using filtered copper radiation.

RESULTS AND DISCUSSION

The absorption spectra of crystalline powder of sodium salt rubbed on a glass plate were measured at room temperature and at 145°C as shown in Fig. 1. The bands around 26 kK and 12 kK and band at 23 kK were assigned to the absorption bands in dimeric crystalline state and in monomeric crystalline state respectively.[3]

Figure 2 shows the disappearance of dimer band at 26 kK as a function of the temperature. The absorbance varied gradually from about 80°C and suddenly changed around 110°-120°C and then varied more showly. Upon cooling the salt down to room temperature, absorbance recovered gradually, but the sudden change could not be

observed. The spectrum of this sample fairly recovered the initial aspect after a few days meanwhile standing at room temperature in air.

Figure 3 shows the electrical conductivity of the $Na^+(CA)^-$ salt as a function of reciprocal temperature. The results show that the break point and the anomalous region were observed at 75°C and around 112°C respectively. The activation energy is 0.61 eV in the region from room temperature to 75°C and is 0.42 eV in the region from 75°C to 112°C. The conductivity changes slowly from 112°C up to 140°C, above which a linear behavior in the curve of $\log \sigma$ versus 1/T is obtained with the activation energy of 0.26 eV. Judging from these results, the anomalies in the conductivity and absorption spectra around 110°C seem to be due to a phase transition. In this paper, we denote the phase which is obtained by the method of Torrey and Hunter[6] as phase I and that produced by heating phase I above 110°C as phase II.

The DSC measurement for $Na^+(CA)^-$ was carried out above room temperature. Typical pattern of the DSC thermograms for the salt and hexamethylbenzene as reference sample is shown in Fig. 4. The result exhibited a transition temperature

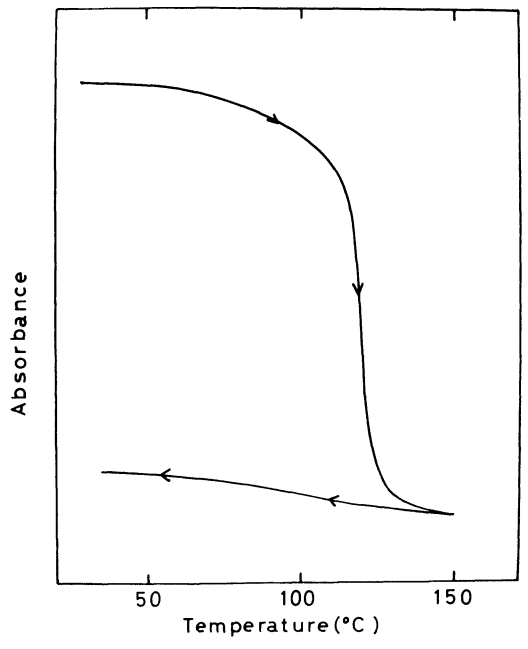


Fig. 2 Absorbance at 680 nm as a function of the temperature.

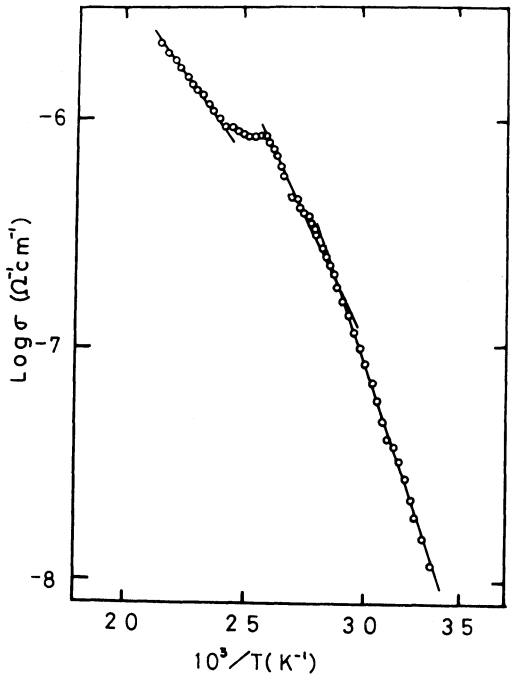


Fig. 3 Electrical conductivity as a function of reciprocal temperature of $Na^+(CA)^-$.

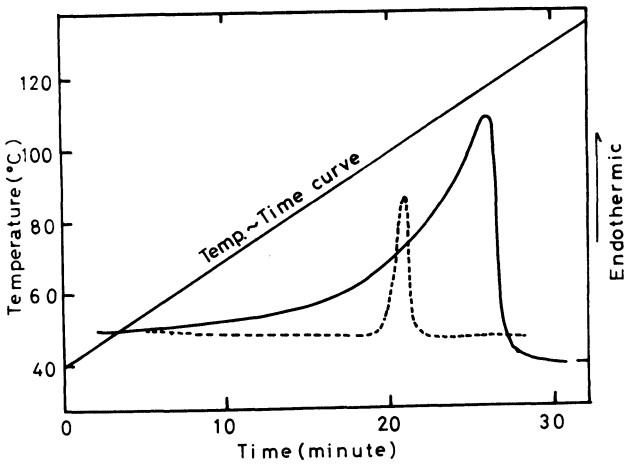


Fig. 4 DSC thermogram for $Na^+(CA)^-$ and hexamethylbenzene ——: $Na^+(CA)^-$ (11.8 mg), ---: hexamethylbenzene (18.0 mg).

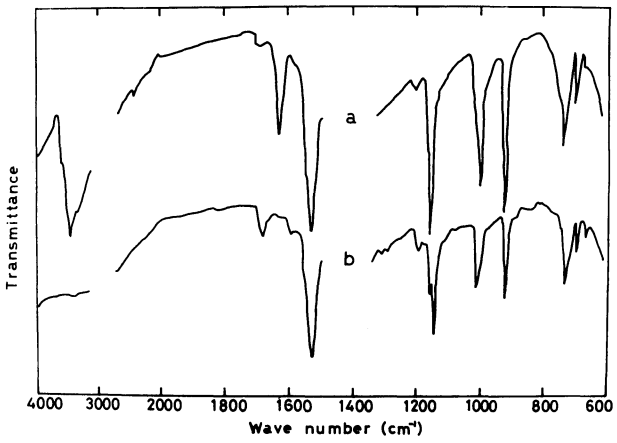


Fig. 5 Infrared spectra of $Na^+(CA)^-$ in phase I (a) and in phase II (b).

at 108°C and the value is almost consistent with those of the other measurements. The magnitude of the heat, $\Delta H$, of $Na^+(CA)^-$ was 13.3 x $10^3$ cal/mole. The value is extraordinarily large compared with that of heat of phase transition in other ion radical salts; e.g., $\Delta H$ = 408 cal/mole for Würster blue perchlorate,[7] 484 cal/mole for $[(C_6H_5)_3PCH]^+(TCNQ)_2^-$ [8] and 365 cal/mole for $K^+(CA)^-$.[9] This abnormally large value in $Na^+(CA)^-$ cannot be interpreted only with the heat of the phase transition.

Figure 5 illustrates the vibrational spectra of phase I and phase II of the sodium salt. Matsunaga[10] has assigned the band at 1525 $cm^{-1}$ to the CO stretching vibration in the chloranil anion (semiquinone ion). The vibrational bands of the chloranil anion were common to the both phases of $Na^+(CA)^-$. However, the strong absorption band near 3400 $cm^{-1}$ in phase I of the salt could not be observed at phase II. This band may be assigned to the OH stretching vibration in $H_2O$ included in the sodium salt. When the sample is heated up to 110°C, the water in $Na^+(CA)^-$ may be released. These results have been confirmed by Hiroma and Kuroda.[11]

Figure 6 gives the X-ray diffraction powder patterns of sodium salt in phase I and in phase II. The results show a remarkable difference in the crystalline

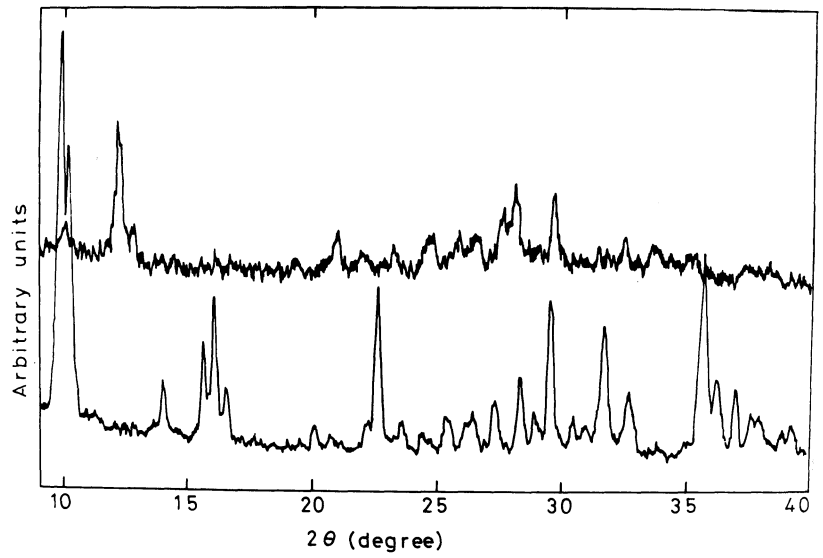


Fig. 6 X-ray diffraction powder patterns of $Na^{+}(CA)^{-}$ in phase I (top) and in phase II (bottom).

nature between the sample in the both phases. Our preliminary works show that the pattern of $Na^{+}(CA)^{-}$ in phase I was resemble that of $Li^{+}(CA)^{-}$ and the pattern of $Na^{+}(CA)^{-}$ in phase II was similar to those of $K^{+}(CA)^{-}$ and $Rb^{+}(CA)^{-}$. These results almost coincide with those of the electronic spectral studies; in other words, phase I is in the dimeric crystalline state and phase II is in the monomeric crystalline state.

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