On the Thermal Analysis of the Phase Transition of $[(C_6H_5)_3PCH_3]^+(TCNQ)_2^-$

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In a previous paper,[1] we presented the temperature dependences of the electrical conductivity and ESR absorption of the TCNQ anion radical salt of triphenylmethylphosphonium, $[(C_6H_5)_3PCH_3]^+(TCNQ)_2^-$. The magnetic behavior of this salt has been known to show a singlet-triplet nature in the lower temperature range.[2,3] However, the ESR absorption intensity increased abruptly at about 40°C with an increase in the temperature. The discontinuity was also found in the electrical conductivity at 40°C. It was suggested that this discontinuity might be ascribed to a phase transition of the crystal.[1] Our preliminary X-ray study showed that there was a slight but clear difference between the crystal structures above and below 40°C. In this paper we will present other evidence on the phase transition obtained by the method of a differential thermal analysis.

The measurements were performed by means of a Shimadzu DT-10 differential thermal analysis apparatus, using powdered fused silica as a standard substance. One of the thermograms of $[(C_6H_5)_3PCH_3]^+(TCNQ)_2^-$ is shown in Fig. 1, in which the rates of raising and lowering the temperature were 3.0°C/min. and 2.8°C/min. respectively. Evidently the endothermic phase transition occurs at 40.4±0.25°C with an increase in the temperature. In order to determine the heat associated with this phase transition, the area of the signal line of $[(C_6H_5)_3PCH_3]^+(TCNQ)_2^-$ was compared with that of hexachloroethane. The phase transition of hexachloroethane, C_2Cl_6, occurs at 318.1°K with $\Delta H=0.613$ kcal./mol.[4] By using the molecular weight (686) of $[(C_6H_5)_3PCH_3]^+\cdot(TCNQ)_2^-$, the heat of transition, ΔH, was calculated as 0.558 kcal./mol., and the associated entropy change was estimated as $\Delta S=1.78$ e. u. These small values indicate that the phase transition observed is slight in its nature, which is quite in accordance with our preliminary X-ray study. It is interesting to see that this slight change in the crystal structure results in a fairly large change in its physical properties, such as electrical conductivity and magnetic susceptibility.

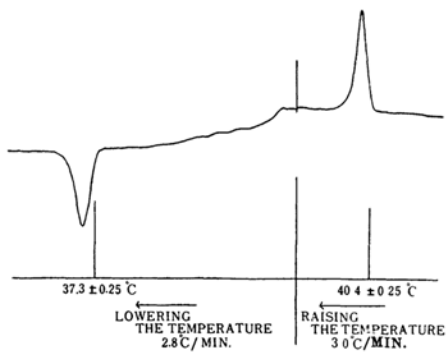

Fig. 1. One of the thermograms of $[(C_6H_5)_3PCH_3]^+(TCNQ)_2^-$.

On the other hand, a similar result of thermal analysis has been already obtained with Wurster's blue perchlorate crystals by two of the present authors (A. K. and K. S.).[5] McConnell et al.[6] have shown recently that the discontinuity observed in the temperature dependence of the paramagnetic susceptibility of Wurster's blue perchlorate is due to the formation of the dimeric structure below 187°K as a result of the change in the crystal structure. These phenomena appear to be quite analogous to our results.

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1) Y. Iida, M. Kinoshita, M. Sano and H. Akamatu, This Bulletin, 37, 428 (1964),
2) D. B. Chesnut and W. D. Phillips, *J. Chem. Phys.*, 35, 1002 (1961).
3) R. G. Kepler, ibid., 39, 3528 (1963).
4) Landort-Börnstein, "Zahlenwerte und Funkutionen aus Physik, Chemie, Astronomie, Geophysik, Tchnik," II Band, 4 Teil, 6 Auflage, Springer-Verlag, Berlin-Göttingen-Heidelberg (1961); Nippon Kagaku-kai, "Kagaku Benran," Maruzen, Tokyo (1958).
5) H. Suzuki, H. Mitsudo and A. Kawamori, The 16th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1963.
6) D. D. Thomas, H. Keller and H. M. McConnell, *J. Chem. Phys.*, 39, 2321 (1963).