The Phase Transitions of the Anion-radical Salts Containing Mixed Cations; $[(C_6H_5)_3PCH_3]_{1-x}{}^+[(C_6H_5)_3AsCH_3]_x{}^+(TCNQ)_2{}^{\dot{-}}$, $(0\leq x\leq 1)$

Yôichi Iida

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo, Hokkaido

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Much attention has been paid to the solid anion-radical salts of 7,7,8,8-tetracyanoquinodimethane (TCNQ) because of their prominent electrical, magnetic, and optical properties.[1-3] In the course of our study of these salts, we found that the ESR absorption intensity of the salt of methyltriphenylphosphonium, $[(C_6H_5)_3PCH_3]^+(TCNQ)_2{}^{\dot{-}}$, increased abruptly at 40°C when the temperature was raised.[4] The discontinuity was also found in the electrical conductivity at that temperature.[4] This anomaly was ascribed to the phase transition of the crystal, as evidenced by the differential thermal analysis.[5] The methyltriphenylarsonium salt, $[(C_6H_5)_3AsCH_3]^+(TCNQ)_2{}^{\dot{-}}$, exhibits electronic properties almost identical with those of the phosphonium salt; on the other hand, the arsonium salt is known to have no such anomaly. It was suggested that one could prepare the salts containing mixed cations, which may be expressed as $[(C_6H_5)_3PCH_3]_{1-x}{}^+[(C_6H_5)_3AsCH_3]_x{}^+(TCNQ)_2{}^{\dot{-}}$, $(0\leq x\leq 1)$.[6] Therefore, it seemed that it would be interesting to investigate the effect of the composition upon the phase-transition phenomenon. The present investigation was performed by means of a differential scanning calorimeter (DSC).

The six salts with x=0.00, 0.20, 0.40, 0.60. 0.80, and 1.00 were prepared according to the method of Melby *et al.*[6] The DSC measurements were made by using powdered α-alumina as a standard substance, with the temperature raised at the rate of 3.0°C/min.

All the salts except for that with x=1.00 showed endothermic phase transitions when the temperature was raised. These phase transitions were found to be reversible. The relation of the transition temperature, T_c, to the composition parameter, x, is given in Fig. 1. In DSC measurements, the peak area of the signal line should be proportional to the magnitude of the heat, ΔH, associated with the phase transition. Therefore, in order to determine the heats associated with the phase transitions of these salts, the area of the signal line of $[(C_6H_5)_3PCH_3]_{1-x}{}^+[(C_6H_5)_3AsCH_3]_x{}^+(TCNQ)_2{}^{\dot{-}}$ was compared with that of hexachloroethane or hexamethylbenzene. The phase transition of hexachloroethane is known to take place at 318.1°K with ΔH=0.613 kcal/mol and at 344.4°K with ΔH=1.965 kcal/mol, and that of hexamethylbenzene, at 384.1°K with ΔH=0.42 kcal/mol.[7] The magnitudes of ΔH *versus* x obtained with the above six TCNQ salts are also illustrated in Fig. 1.

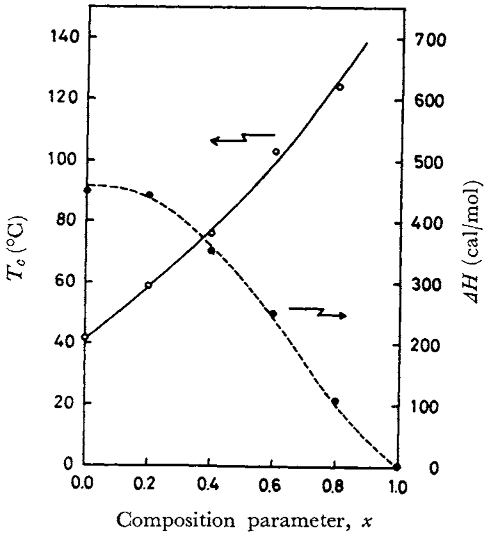

Fig. 1. The relations of the transition temperature, T_c, and of the magnitude of the heat, ΔH, associated with the phase transition, to the composition parameter, x, in $[(C_6H_5)_3PCH_3]_{1-x}{}^+[(C_6H_5)_3AsCH_3]_x{}^+(TCNQ)_2{}^{\dot{-}}$, $(0\leq x\leq 1)$.

It is noteworthy that T_c increases, and the value of ΔH decreases, monotonously with an increase in the value of x, and that the phase transition disappears with x=1.00.

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