CHEMISTRY LETTERS, pp. 1859-1862, 1985.

SELF-DIFFUSION OF METHYLAMMONIUM CATIONS IN THE HIGHEST TEMPERATURE SOLID PHASE OF $(CH_3NH_3)_2SO_4$ AS REVEALED BY ^1H NMR TECHNIQUES

Hiroyuki ISHIDA, Noritoshi MATSUHASHI, Ryuichi IKEDA,
and Daiyu NAKAMURA*
Department of Chemistry, Faculty of Science,
Nagoya University, Chikusa, Nagoya 464

The ^1H NMR parameters of solid methylammonium sulfate were determined at various temperatures. A first-order phase transition was located at 428 K for this salt. Above this temperature, the cations were found to perform self-diffusion as well as overall rotation about their center of gravity.

The motion of methylammonium (MA) cations in ionic crystals and its participation in structural phase transitions usually found in various MA salts have been extensively studied by employing ^1H NMR experiments.[1-14] Among these studies, it has recently attracted much attention from the viewpoint of new electrically conductive materials that the existance of a novel solid phase named the liquid-like phase showing large transition entropies to transform from a normal phase was found in $(MA)NO_3$,[10,12] $(MA)I$,[11,14] and $(MA)ClO_4$.[10,13] In this phase of the crystals, the cations undergo translational self-diffusion as well as overall rotation about their center of gravity. The former results in a high electrical conductivity. This unusual phase may be classified as the plastic phase of ionic crystals.

Methylammonium sulfate, $(MA)_2SO_4$ forms monoclinic crystals at room temperature belonging to the space group $P2_1/c$, but its physical properties are almost unknown. In a series of our studies of MA salts, we took up this salt because of its known crystal structure at room temperature, and found a new solid phase similar to the liquid-like phase at higher temperatures.

^1H NMR absorptions were recorded by use of a JEOL-MW-40S spectrometer. The ^1H spin-lattice relaxation time, T_1 was measured at the Larmor frequencies of 8.8, 11.8, and 45.7 MHz, while the ^1H spin-spin relaxation time, T_2 was observed at 8.8 and 45.7 MHz. Experimental methods and apparatus employed for the measurements of T_1, T_2, the second moment, M_2 of ^1H NMR spectra, and differential thermal analysis (DTA) were already described elsewhere.[16-18] $(MA)_2SO_4$ procured from commerical sources was purified by recrystallizations from methanol carried out two times. Partially deuterated analog, $(CH_3ND_3)_2SO_4$ (abbreviated as $(MA\text{-}d)_2SO_4$) was prepared from purified $(MA)_2SO_4$ by crystallizations repeatedly carried out from heavy water and, then, finally recrystallized from a solution of CH_3OD. Because the samples are highly hygroscopic, they were carefully treated in a dry bag and fully dried by pumping out inside the glass sample tubes at *ca.* 400 K for the use of NMR and DTA studies. The extent of deuteration of (MA-*d*)$_2$SO$_4$ was estimated as more than 95%.

When the temperature was increased in the DTA study, a big endothermic anomaly appeared at 428 and 429 K for (MA)$_2$SO$_4$ and (MA-*d*)$_2$SO$_4$, respectively. On further heating, both salts started to decompose at *ca.* 550 K. With decreasing the temperature from *ca.* 450 K, a big exothermic anomaly was recorded considerably below the above temperatures for both salts showing thermal hysteresis. Accordingly, one can conclude that (MA)$_2$SO$_4$ undergoes a first-order phase transition at 428 ± 1 K. A fairly low decomposition temperature of 443 K was reported for (MA)$_2$SO$_4$ by Vilminot et al.[15] This disagrees very much with that of ours presumably because of the difference of sample manipulation.

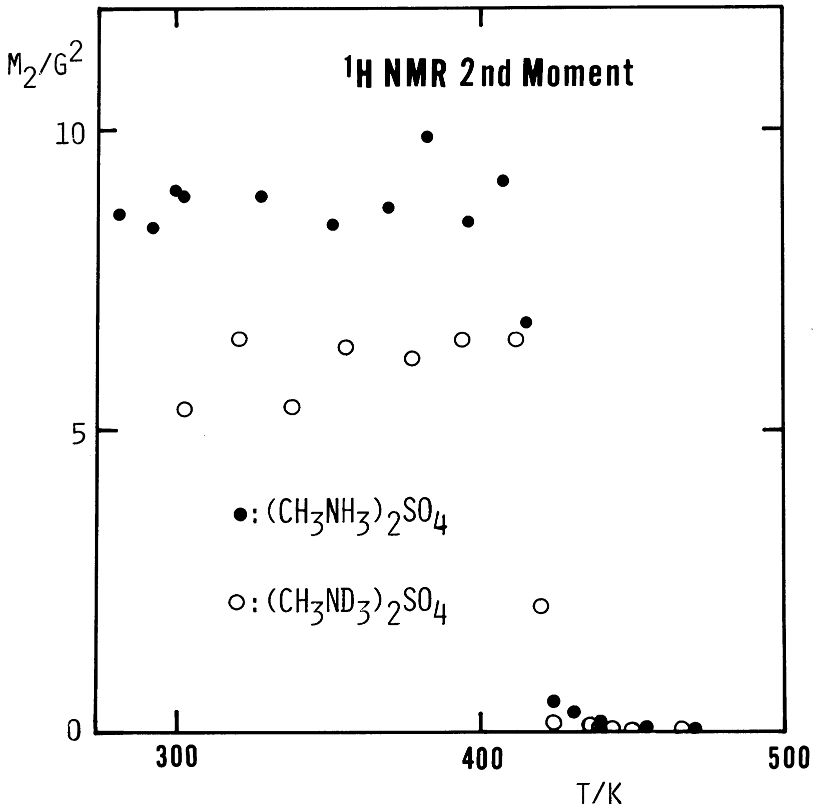

Fig. 1. Temperature dependences of ^{1}H NMR second moments (M_2) observed at various temperatures for $(CH_3NH_3)_2SO_4$ and $(CH_3ND_3)_2SO_4$.

The temperature variation of ^{1}H NMR M_2 determined above room temperature is shown in Fig. 1 for (MA)$_2$SO$_4$ and (MA-*d*)$_2$SO$_4$. At room temperature, M_2 values of *ca.* 9 and 6 G^2 were observed for (MA)$_2$SO$_4$ and (MA-*d*)$_2$SO$_4$, respectively. These values were almost unchanged up to each transition temperature (T_{tr}), immediately above which temperature both salts yielded M_2 of *ca.* 0.5 G^2. With increasing temperature furthermore, the M_2 values decreased rather rapidly and reached the values less than 0.1 G^2 above 440 K. Comparing these observed M_2 values with the calculated ones,[1,2] the 120° reorientation of CH$_3$ and NH$_3^+$ groups about their C_3 axes for (MA)$_2$SO$_4$ and that of CH$_3$ groups for (MA-*d*)$_2$SO$_4$ are found to be activated frequently enough as compared with the NMR line width in a temperature range of *ca.* 300 K - T_{tr}. The extremely small M_2 observed for both salts above T_{tr} suggests the occurrence of the self-diffusion as well as the overall rotation of the cations. This is because the observed M_2 values of this phase are much smaller than *ca.* 1 G^2 which is calculated for cations performing overall rotation without self-diffusion.

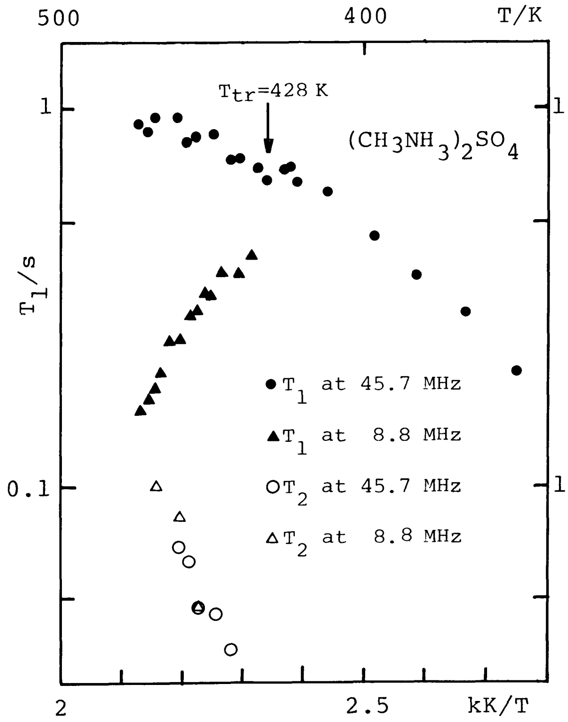

Fig. 2. Temperature variations of ^1H T_1 and ^1H T_2 observed at different Larmor frequencies for solid $(CH_3NH_3)_2SO_4$.

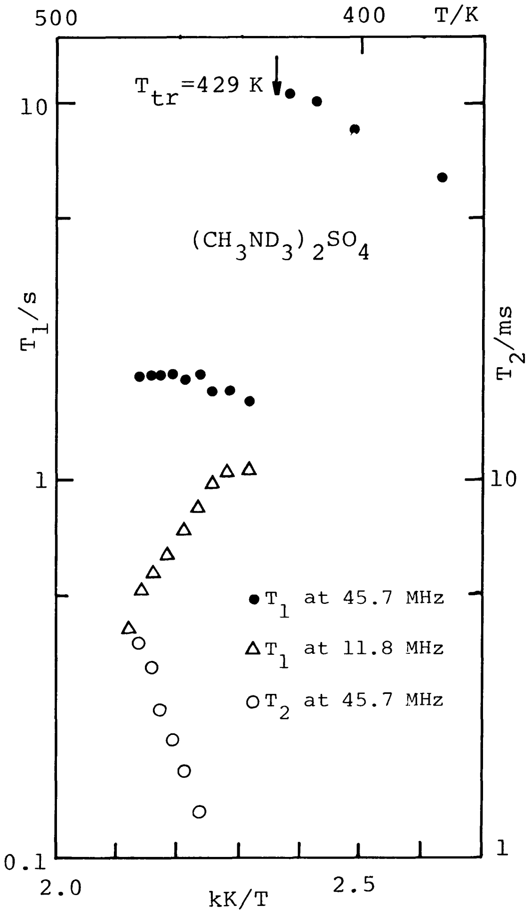

Fig. 3. Temperature variations of ^1H T_1 and ^1H T_2 determined at different Larmor frequencies for solid $(CH_3ND_3)_2SO_4$.

^1H T_1 observed at various temperatures in a high temperature region and ^1H T_2 observed in the high temperature phase are shown in Fig. 2 for $(MA)_2SO_4$ and in Fig. 3 for $(MA\text{-}d)_2SO_4$.

When the samples were heated in the room temperature phase, T_1 of both salts increased gently with increasing temperature and decreased discontinuously at T_{tr}. In the room temperature phase, $\log T_1$ observed at different frequencies existed on the same curve, whereas greatly different $\log T_1$ curves were obtained for the high temperature phase by observing at two different frequencies for each salt.

In the high temperature phase of both salts, T_1 observed at 45.7 MHz was increased very gently or almost unchanged, whereas T_1 determined at 8.8 MHz for $(MA)_2SO_4$ and 11.8 MHz for $(MA\text{-}d)_2SO_4$ decreased rapidly with increasing temperature. The T_2 value observed for both salts jumped at T_{tr} with increasing temperature, and steeply increased to *ca.* one or several ms at the longest in the each temperature phase. The T_1 decrease and T_2 increase of both salts observed for this phase can be interpreted in terms of the self-diffusion of the cations taking place in the crystals as already analyzed by us.[12,14,19] The T_2 values of the high temperature phase of the present salts, however, are not so long as those of several or several tens ms observed for the liquid-like phase of NH_4NO_3, $(MA)NO_3$, (MA)I, $(MA)ClO_4$, and $[C(NH_2)_3]ClO_4$.[10-15,19,20] This means that the diffusional motion of the cation in $(MA)_2SO_4$ is slower than that of the cations in the liquid-like phase of the above salts previously reported. This is confirmed from the fact that T_1 measured for the present salt at high and low Larmor frequencies increased and decreased, respectively, with increasing temperature.

References

1) J. Tsau and D. F. R. Gilson, Can. J. Chem., 48, 717 (1970).
2) E. R. Andrew and P. C. Canepa, J. Magn. Reson., 7, 429 (1972).
3) J. Tegenfeldt and L. Ödberg, J. Phys. Chem. Solids, 33, 215 (1972).
4) J. Tegenfeldt, T. Keowsim, and C. Säterkvist, Acta Chem. Scand., 26, 3524 (1972).
5) S. Albert and J. A. Ripmeester, J. Chem. Phys., 58, 541 (1973).
6) R. Ikeda, Y. Kume, D. Nakamura, Y. Furukawa, and H. Kiriyama, J. Magn. Reson., 24, 9 (1976).
7) Y. Furukawa, H. Kiriyama, and R. Ikeda, Bull. Chem. Soc. Jpn., 54, 103 (1981).
8) H. Ishida, R. Ikeda, and D. Nakamura, J. Phys. Chem., 86, 1003 (1982).
9) H. Ishida, R. Ikeda, and D. Nakamura, Bull. Chem. Soc. Jpn., 55, 3116 (1982).
10) H. Ishida, R. Ikeda, and D. Nakamura, Chem. Lett., 1982, 1943.
11) H. Ishida, R. Ikeda, and D. Nakamura, Phys. Status Solidi A, 70, K151 (1982).
12) H. Ishida, R. Ikeda, and D. Nakamura, J. Chem. Soc., Faraday Trans. 2, 81, 963 (1985).
13) S. Jurga and H. W. Spiess, Z. Naturforsch., A, 40, 402 (1985).
14) H. Ishida, R. Ikeda, and D. Nakamura, to be published.
15) S. Vilminot, L. Cot, C. Avinens, and M. Maurin, Mat. Res. Bull., 6, 189 (1971).
16) L. S. Prabhumirashi, R. Ikeda, and D. Nakamura, Ber. Bunsenges. Phys. Chem., 85, 1142 (1981)
17) S. Gima, Y. Furukawa, R. Ikeda, and D. Nakamura, J. Mol. Struct., 111, 189 (1983).
18) Y. Kume, R. Ikeda, and D. Nakamura, J. Magn. Reson., 33, 331 (1979).
19) S. Gima, Y. Furukawa, and D. Nakamura, Ber. Bunsenges. Phys. Chem., 88, 939 (1984).
20) M. T. Riggin, R. R. Knispel, and M. M. Pintar, J. Chem. Phys., 56, 2911 (1972).

(Received September 17, 1985)