The Mechanism of the Electrical Conduction in Solid Acetamide*

By Koichi HIRANO

(Received February 25, 1961 ; in revised form November 26, 1964)

The electrical conductivity of ice and solid alcohols has been studied by several investigators ;$^{1-6)}$ it has been concluded that the proton transfer across the hydrogen bonds plays an important role in the conduction mechanism. It would, however, be desirable to obtain further information about the conduction mechanism in crystals with $\rangle$NH$\cdots$O$\langle$ hydrogen bonds, since studies thus far have concerned only the case of OH$\cdots$O hydrogen bonds.

In the present paper the temperature dependence of solid state acetamide will be described ; the conduction mechanism in the $\rangle$HN$\cdots$O$\langle$ hydrogen bond crystal will then be discussed on the basis of the proton transfer model.

Experimental

After fractional distillation, acetamide was recrystallized thrice from hot benzene by the Lewin and Vance's method$^{7)}$ and then dried in a Abderhalden drier for five hours. The sample was melted in the cell ; it was solidified gradually from its own melt. The cell was then kept at 82°C to remove the strain of the sample which originated from solidification. In comparison with the results reported hitherto by other authors, the a. c. conductivity of molten acetamide at 83.2°C and 87.5°C were measured.

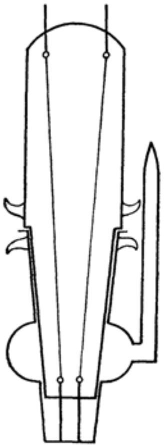


Fig. 1. The conductivity cell.

On the other hand, the temperature dependency of the d. c. conductivity of solid acetamide was measured within the temperature range from 60 to 90°C by the bridge method. The cell, made of pyrex-glass with platinum electrodes,$^{4,8)}$ is illustrated in Fig. 1.

The cell was calibrated with a potassium chloride solution, and the cell constant was determined to be 0.1408 Ω^{-1}cm^{-1} at 25°C.

Results

The A. C. Conductivity of Molten Acetamide.—The values of a. c. conductivity at 10^3 c. p. s. for molten acetamide are presented in Table I, in which are also included the results reported in the literature.

TABLE I. THE SPECIFIC CONDUCTIVITY OF MOLTEN ACETAMIDE

Specific conductivity at 10^3 c. p. s. $\sigma\Omega^{-1}$cm^{-1}	Temp. °C	Author
8.8×10^{-7}	83.2	Hirano
1.0×10^{-6}	87.5	
$3\ \times10^{-3}$	80	Walden (1903)$^{9)}$
4.3×10^{-5}	100	Walker (1905)$^{10)}$
1.5×10^{-5}	90	Belladen (1927)$^{11)}$
8.6×10^{-6}	94	Grüttner (1952)$^{12)}$
2.6×10^{-6}	94	Jander and Winkeler (1959)$^{13)}$

From Table I it is obvious that the results here obtained are fairly different from those previously reported by Walden$^{9)}$ and by others,$^{10-12)}$ but comparable with the results given by Jander and Winkeler.$^{13)}$ The wide divergence of Walden's result may, however,

---

* A part of this paper was presented at the 13th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1960.

1) J. D. Hoftman and C. P. Smyth, *J. Am. Chem. Soc.*, **71**, 431 (1949).

2) E. J. Murphy, *Phys. Rev.*, **79**, 396 (1950).

3) Y. Kakiuchi, H. Komatsu and S. Kyoya, *J. Phys. Soc. Japan*, **6**, 321 (1951).

4) R. S. Bradley, *Trans. Faraday Soc.*, **53**, 687 (1957).

5) A. Steinemann and H. Grünicher, *Helv. Phys. Acta*, **30**, 553 (1957).

6) J. C. Decorly, C. Jaccard and H. Grünicher, ibid., **30**, 465 (1957).

7) S. Z. Lewin and J. E. Vance, *J. Am. Chem. Soc.*, **74**, 1433 (1952).

8) N. N. Greenwood and R. L. Martin, *Proc. Roy. Soc.*, **A215**, 46 (1952).

9) P. Walden, *Z. physik. Chem.*, **46**, 175 (1903).

10) J. Walker and F. M. G. Jonson, *J. Chem. Soc.*, **87**, 1597 (1905).

11) L. Belladen, *Gazz. Chim. Ital.*, **51**, 407 (1927).

12) B. Grüttner, *Z. anorg. u. allgem. Chem.*, **270**, 223 (1952).

13) G. Jander and G. Winkeler, *J. Inorg. Nucl. Chem.*, **9**, 24 (1959).

be attributed to impure materials, since the conductivity is strongly affected by a small amount of impurities. The very low values obtained by the present author are attributable to the high purity of the specimens used.

The Temperature Dependency of the D. C. Conductivity of Solid Acetamide.— In Table II the results of d. c. conductivity for solid acetamide obtained at various temperatures are listed.

TABLE II. THE SPECIFIC CONDUCTIVITY OF SOLID ACETAMIDE

Specific conductivity D. C. $\kappa\Omega^{-1}\text{cm}^{-1}$	Temp. °C
1.4×10^{-9}	61.5
3.5×10^{-9}	71.0
5.9×10^{-9}	73.0
7.3×10^{-9}	75.2
1.2×10^{-8}	77.4
3.0×10^{-8}	79.8
5.6×10^{-8}	82.2

Judging from the data of a. c. conductivity in the molten state, the purity of specimens is sufficiently high, so the data listed in Table II seem to be rather consistent, though no data which can be compared with have been reported.

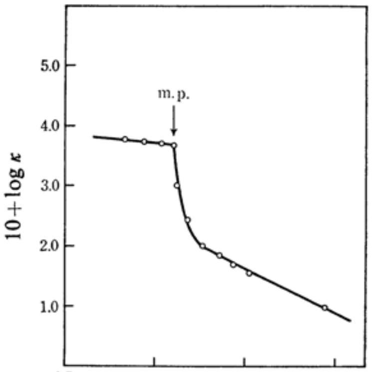


Fig. 2. $10+\log\kappa$ plotted against $1/T$.

In Fig. 2 the plots of $\log\kappa$ against the reciprocal of temperature, $1/T$, are illustrated. In the curve there are lower and upper slopes and a steeper slope just below the melting point, as is general for the solid state. The lower slope corresponds to the molten liquid, and the upper one, to the solid state, while the abrupt change seems to originate from the homophase premelting.[14] This feature is very similar to that with ice. The linear plot of $10+\log\kappa$ vs. $1/T\times10^3$ for the solid state is represented well by the following equation;

$$\kappa=1.7\exp-\{34\times10^3/\boldsymbol{RT}\}\ \Omega^{-1}\text{cm}^{-1} \qquad (1)$$

where 34×10^3 cal./mol. is the activation energy of electrical conduction; $\boldsymbol{R}$, the gas constant, and T, the absolute temperature.

Discussion

In the present paper the author would like to interpret the mechanism of the electrical conduction in solid acetamide from the point of view of proton transfer.

It has been well established by Senti and Harker[15] that the crystal structure of rhombohedral acetamide consists of planar molecules of the keto form arranged in rings of six members, as is shown in Fig. 3. In the rings the adjacent molecules are held together by hydrogen bonds of $\rangle$NH···O=C$\langle$, and along the c-axis of the hexagonal cell the molecules are linked together by the hydrogen bonds in infinite chains. Thereby, the net transfer of protons traveling along the hydrogen bonds in the axis may be expected when the external electrical field is applied. If the proton transfer causes the conduction, however, three kinds of reactions must follow:

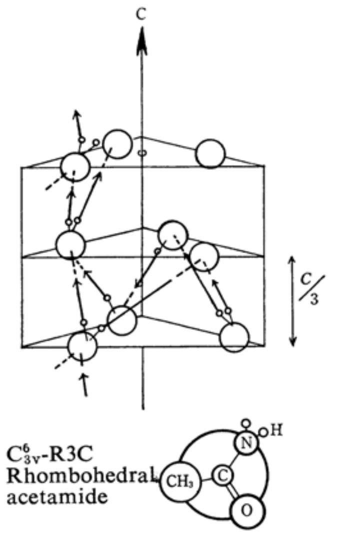


Fig. 3. Crystal structure of acetamide.

Proton Supply to the Molecular Chains of Hydrogen Bonds. — The proton supply would be initiated by the ionogenic reaction involving step 2:[16]

---

[14] W. Davis, S. Rogers and A. R. Ubbelohde, *Proc. Roy. Soc.*, **A220**, 14 (1953).

[15] F. Senti and D. Harker, *J. Am. Chem. Soc.*, **62**, 2008 (1947).

[16] K. Wirtz, *Z. Naturforsch.*, **2b**, 94 (1947).

$$>\mathrm{NH}\cdots\mathrm{O{=}C}< \xrightarrow{\Delta E_1} >\overset{-}{\mathrm{N}}: + \mathrm{H}\overset{+}{\mathrm{O}}\mathrm{C}< \qquad (2)$$

where ΔE_1 denotes the activation energy, which is identical with the height of the potential barrier between the two positions of equilibrium in the hydrogen bonds in Fig. 4.

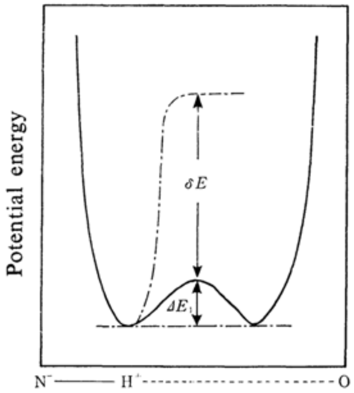


Fig. 4. Potential barrier between the two positions of equilibrium in the hydrogen bonds.
$\Delta E_1 \simeq 20$ kcal./mol.

Consequently, ΔE_1 is represented by:

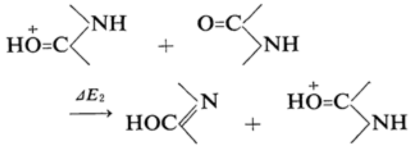
$$\Delta E_1 \simeq (D - \delta E) \qquad (3)$$

where D denotes the energy required to liberate the proton from the restraining negative force field around a given nitrogen atom and δE, the energy changes associated with the hydrogen bond formation.

Assuming that D would not be so different from the energy of the dissociation of $>$N–H linkage: hence, ΔE_1 may be estimated from Eq. 4:

$$\Delta E_1 \simeq (104 - \delta E) \ \text{kcal./mol.} \qquad (4)$$

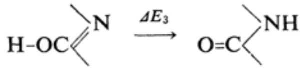
Proton Transfer. — In the case of ice, the oxonium ion, H_3O^+, is intermediate in the proton transfer between the adjacent molecules. In acetamide, however, such ions would not be produced; hence, another scheme must be considered. The following scheme 5, with the protonated amide molecules acting as intermediates, are considered to be the most probable one:


(5)

Here ΔE_2 is the activation energy of proton transfer, and it may be estimated as nearly equal to 3—5 kcal./mol., judging from the quite similar quantity for ice.

The Recovery of the Hydrogen Bonds. — According to schemes 2 and 5, it is evident that, after the proton transference, the members of the molecular chain were replaced by molecules of the enol form. It must then be remembered that the further transference of protons does not proceed unless the recovery of the hydrogen bonds has been established in the molecular chain.

In the present paper we assumed keto-enol transformation (6) to be the key reaction in the recovery process; then, the activation energy, ΔE_3, can be estimated to be equal to 5—10 kcal./mol. in analogy with the similar quantity estimated from cis-trans transformation in esters and amines.[17]


(6)

Admitting the above, the activation energy of conduction, ΔE, in the overall reactions 2, 5 and 6, is given in Eq. 7;

$$\Delta E = \Delta E_1 + \Delta E_2 + \Delta E_3 \qquad (7)$$

From the experimental results, 34 kcal./mol. is determined as the value of ΔE. Using the data of ΔE, ΔE_2 and ΔE_3, 20 kcal./mol. is given as the data of ΔE_1; then we immediately determined $\delta E \simeq 80$—85 kcal./mol.

In Table III the activation energies related to the respective processes are summarized.

TABLE III. ACTIVATION ENERGIES

Activation energy	Process	kcal./mol.
ΔE	Overall process	34
ΔE_1	Liberation of proton	20
ΔE_2	Proton transfer	5
ΔE_3	Recovery process	10
δE	Changes in the dissociation energy of the $>$N–H bond associated with hydrogen bond formation	80—85

The value of ΔE_1, the potential barrier in Fig. 4, is consistent with the theoretical estimations of the similar quantities for the N–H⋯O or O–H⋯O hydrogen bonds in the liquid state.

Since the height of the potential barrier of this kind does not vary much with the states of the molecular aggregation, $\Delta E_1 \simeq 20$ kcal./mol. is fairly reasonable as the potential barrier between the two positions of equilibrium in the hydrogen bond of solid acetamide.

Accordingly, it may be concluded that the

---

[17] O. Nomoto, *J. Acoust. Soc. Japan*, **13**, 76 (1957).

[18] I. Oshida, Y. Ooshika and R. Miyasaka, *J. Phys. Soc. Japan*, **13**, 76 (1957).

[19] Y. Sato, *Science of Light*, **6**, 69 (1957).

[20] H. Toyoda, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **79**, 1198 (1958).

proton transfer plays an important role in the electrical conduction in solid amide; this conception makes it possible to consider the electrical conduction observed in proteins or related compounds.

Summary

1) Conductivity measurements of solid acetamide have been carried out over the temperature range of 60—90°C and the specific conductivity, $\kappa = 1.7\exp-\{34\times10^3/\boldsymbol{RT}\}\ \Omega^{-1}\cdot\mathrm{cm}^{-1}$, has been determined.

2) The mechanism of conduction has been discussed in terms of the proton transfer, and the value of the potential barrier between two positions of equilibrium in the NH···O hydrogen bonds has been estimated.

The author is indebted to the Ministry of Education for its financial support.

Department of Natural Sciences
Faculty of Education
Tohoku University
Kawa-Uchi, Sendai