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A Proton Conductive Coordination Polymer. I. [*N,N'*-Bis(2-hydroxyethyl)-dithiooxamido]copper(II)[15]

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In a family of *catena-μ-N,N'*-disubstituted dithiooxamidocopper(II) complexes which have been assumed as two-dimensional coordination polymers, one complex with HOC_2H_4- substituents is an electronic conductor as well as others, and also a protonic conductor uniquely. The latter property was proved both by spectroscopic detection of the hydrogen molecules evolved from d.c. electrolysis of pressed pellets of the powder specimen and by observation of the anomalous increase (three orders of magnitude) of the electric conductivity as an effect of 10^3 Pa of H_2O or D_2O vapor on the dehydrated specimen in an evacuated conductivity cell. A novel conduction mechanism was suggested for such a solid system with both conjugated double bonds and extended hydrogen bonds.

The [*N,N'*-disubstituted dithiooxamido]copper(II) complexes, abbreviated as R_2-dtoa-Cu(earlier as R-DTOA-Cu),[1] have been regarded as two-dimensional polymers from several experimental facts[1,2] as shown in Fig. 1. Those copper containing polymers with a pair of CH_3-, $C_6H_5CH_2-$, $C_6H_{11}-$, $C_{12}H_{25}-$ radicals as the two substituents on the two nitrogen atoms of a dithiooxamide molecule are the amorphous semiconductors in which the delocalized electrons on the two-dimensional atomic network constructed from carbon, nitrogen, sulfur, and copper atoms take part.

An anomalous time dependence of electric conductivity of $(HOC_2H_4)_2$-dtoa-Cu is observed which implies a part of the conductance at least originated from the characteristic behavior of the hydroxyl protons. The proton conduction in solid has recently attracted attention from the view point of both pure and applied sciences;[3—7] as a consequence a few comprehensive reviews have been published.[8]

In this report we try to prove the proton conduction, and propose a possibility of a novel mechanism of the charge transfer in solid which is attributed to the cooperation of electrons and protons due to the specific structure of the compound.

Experimental

Materials. Ligand, *N,N'*-bis(2-hydroxyethyl)dithiooxamide, abbreviated as $(HOC_2H_4)_2$-dtoa-H_2, was of a commercial preparation, purified by recrystallization from distilled water. Copper(II) sulfate pentahydrate of reagent grade was recrystallized from distilled water. The coordination polymer was precipitated by addition of 5% ligand ethanol solution to a lukewarm copper aqueous solution with stirring, followed by washing several times with distilled water and ethanol alternatively. The gelatinous precipitate was centrifugated and dried in an evacuated desiccator. The analytical values will be discussed in detail later.

Measurements of Conductance. The measurements were made on the pressed disk (13 mm diameter × 1.5—2.0 mm thick) prepared in a press and a die at 1.3×10^8 Pa for 30 s. Electrical leads were silver pasted on the disk from the both sides with an area of 0.7—0.8 cm^2. The measurements were carried out in a cell which could be evacuated to 10^{-2} Pa and kept the blank value of resistance more than $10^{17}\,\Omega$. In order to improve an electrical insulation, the electrical leads for the electrodes entered the cell through Teflon plugs (a). A vacuum tight of the Teflon plugs to the metal plate and to the brass bolts(d) was made with O-rings(b) and with O-stat-seals 660(c), respectively, as shown in Fig. 2. The other leads for a thermocouple and a heater were connected to hermetic seals on the plate.

After installation of the specimen in position the cell was evacuated and flushed with nitrogen several times to remove the gas molecule such as H_2O adsorbed on the specimen,

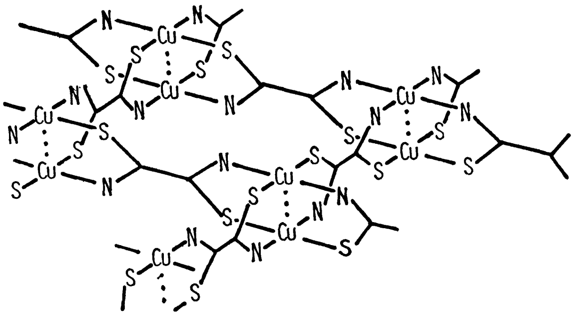

Fig. 1. The two-dimensional molecular model of copper acetate Type R_2-dtoa-Cu. For simplicity, substituents R on nitrogen atoms are omitted. See Ref. 2.

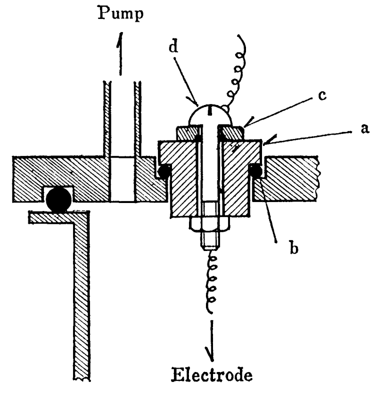

Fig. 2. Teflon plug of high resistance conductivity cell. a) Teflon plug, b) O ring, c) stat-O-seal 660 (Manuf. by Parker Seal Company, U.S.A.), d) brass bolt.

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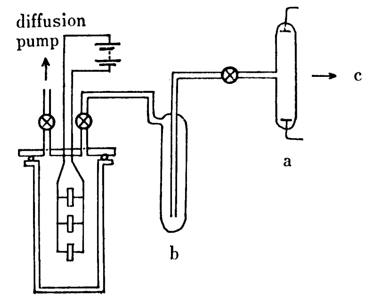

Fig. 3. Electrolysis cell and vacuum line for gas identification by atomic spectra. a) Geisler tube operated by neon trans (6000 V, 60 Hz), b) gas trap at 77 K, c) spectrograph.

before admitting dry nitrogen of 10^4 Pa as heat conductor for temperature control. In addition to nitrogen, H_2O or D_2O vapor of 10^3 Pa was introduced for confirmation of effects of water vapor.

For electrolysis the three pellets were connected in parallel in an evacuated cell (Fig. 3) and d.c. (6.8×10^{-1} C) was passed under 300—500 V for 170 h. After the procedure mentioned above, the gas in the vessel was transported to the Geissler tube(a) in Fig. 3 through a 77 K trap(b) to remove leaked gases, H_2O and CO_2, if any. By application of an a.c. voltage (6000 V, 60 Hz) an atomic spectrum was taken on a photographic film (Fuji SSS) with a spectrograph (Shimadzu-OC-50) using a mercury lamp as a calibration source. The blank test was performed for the same processes without the application of the d.c. voltage.

DTA and TGA measurements were carried out simultaneously by a derivatograph (Rigakudenki 8002) with α-Al_2O_3 as a reference, at a rate of temperature rise of 5 °C/min.

Results and Discussion

Chemical Constitution and the Structure. Analysis of $(HOC_2H_4)_2$-dtoa-Cu, Found: C, 25.7; N, 9.77; H, 3.91; Cu, 23.0%. And a weight loss in TGA up to 150 °C; 3.3%. In the light of the coordination chemistry, the constitutional formula of $(HOC_2H_4)_2$-dtoa-Cu is proposed as $Cu((HOC_2H_4)_2\text{-dtoa})_{0.985}(OH)_{0.03}(OH_2)_{0.5}$: Calcd for the constituents: C, 25.7; N, 9.99; H, 3.97; Cu, 23.00; H_2O, 3.26%. These values are in excellent agreement with each other except those for nitrogen. The discrepancy is not serious for the proposed formula, as the nitrogen atom coordinated directly to copper ion has a tendency to result in a lower value in the analysis than expected. The other homologous complexes R_2-dtoa-Cu's are assumed to have a two-dimensional structure of sheet polymer on the basis of several experimental facts.[1,2] Assuming the same two-dimensional structure for this compound, the nonstoichiometric 0.03 mol hydroxide in the formula suggests that the molecules were terminated by coordination of two of OH instead of $(HOC_2H_4)_2$-dtoa at some parts of the edge of the sheet polymer. One half mole of OH_2 is assumed to be the coordinated water on copper(II) ions as the water is not removed even in an evacuated desiccator but is lost at the temperatures up to 150 °C as observed in the TGA analysis.

From IR study of the complex in KBr pellets the following results were obtained; 1) no peak between 4000 and 3400 cm^{-1} and 2) a broad intense band around 3340 cm^{-1} with a half-value width of *ca.* 400 cm^{-1}. These results suggest the followings; 1) Free $HOCH_2CH_2$–, H_2O and/or –NH groups (which should indicate ν_{OH} at 3600 cm^{-1}) do not exist, 2) almost all nitrogen atoms separate protons for coordination to the copper ions, and 3) the HOC_2H_4– and H_2O form inter- and/or intramolecular hydrogen bonds to the oxygen, nitrogen, or sulfur atoms, which are proved by the peak shifted to 3340 cm^{-1} assigned to $\nu_{OH\cdots X}$. Provided that the macromolecules are the two-dimensional sheets as mentioned before,[1,2] intermolecular hydrogen bonds would connect the parallel macromolecules on their both sides of the lamellar layer.

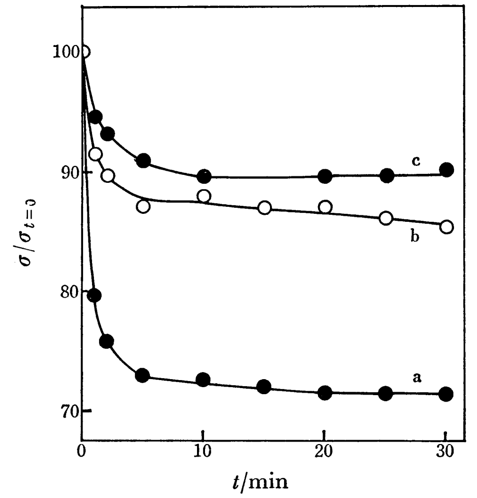

Fig. 4. Time decrease(%) of conductivity, at a) 22 °C, b) 50 °C, and c) 78 °C.

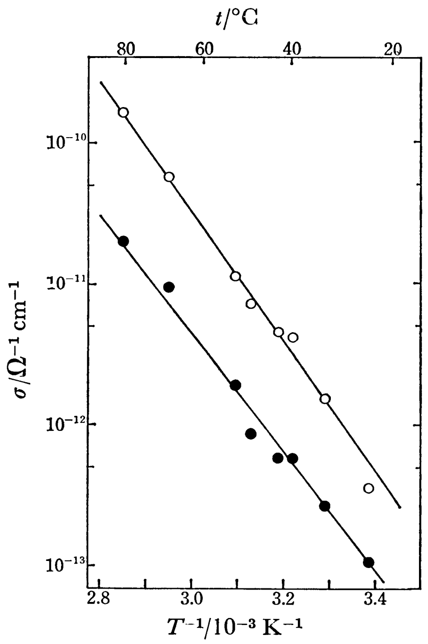

Fig. 5. Effects of temperature on specific conductivities for both σ_e and $\sigma_{\rm H}^{\circ}$. ○: σ_e, ●: $\sigma_{\rm H}^{\circ}$.

Electric Conductivity. Figure 4 shows the typical time dependence of the electric current through the pellet of the specimen at applying d.c. voltage of 32 V/1.5—2.0 mm. As shown in Fig. 4 the current

Table 1. Temperature dependence of conductivities of R_2-dtoa-Cu

R	D.c.		A.c. (10 MHz)	
	σ_{30} a)	ΔE e)	σ_{30} a)	ΔE e)
	$\Omega^{-1}\,cm^{-1}$	eV	$\Omega^{-1}\,cm^{-1}$	eV
$HOCH_2$-	3.5×10^{-12} b) 1.5×10^{-12}	+0.88 (+22 — +88 °C)	5×10^{-6}	+0.16 (−70 — +50 °C) c)
CH_3- d)	5×10^{-7}	+0.23 (−70 — +85 °C)	5×10^{-6}	+0.12 (−23 — +85 °C)

a) σ_{30} is the conductivity at 30 °C. b) As mentioned in the text, the conductivity decreases by the heating process, the top value is for ● and the bottom value is ◎ in Fig. 7. c) At the temperatures higher than 60 °C the conductivity has a negative temperature coefficient; see the first paper of Ref. 2. d) See the first of Ref. 2. e) The activation energy, ΔE is calculated by an equation: $\sigma_{30}=\sigma_0 \exp(-\Delta E/kT)$.

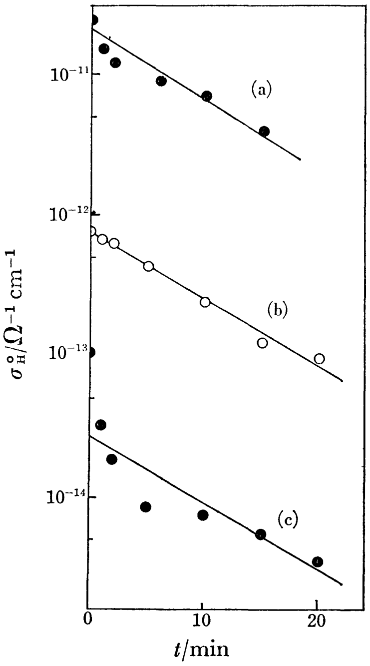

Fig. 6. Time dependence of a part of the conductivity, σ°_H. a) 78 °C, b) 46.5 °C, c) 22 °C.

levels off after about 15 min at the measured temperatures (22, 50, and 78 °C). The conductivities σ_e calculated from the residual currents are 3.5×10^{-13}, 1.1×10^{-11} and $1.6\times10^{-10}\,\Omega^{-1}\,cm^{-1}$ at 22, 50, and 78 °C, respectively. These values conform to the Arrhenius equation as shown in Fig. 5. The time dependent part of the conductivity $\sigma_H(t)=\sigma_{obsd}-\sigma_e$ obeys a first-order kinetics $\sigma_H=\sigma^\circ_H \exp(-kt)$ (Fig. 6), showing (or implying) that σ_H may be attributed to the polarization current by the electrophoretic ions. σ°_H also conforms to the Arrhenius equation (Fig. 5). At a higher temperature above 100 °C, both the decrement of current under applied voltage with the passage of time and the time needed to level off increase. With other homologues of the complex compound no time dependence of the current was observed at any temperature examined.

The temperature dependence of the d.c. conductivity at 32 volt on the specimen is depicted in Fig. 7. Individual data are plotted in successive heating and cooling procedures. In the first heating process the linearity of the conductivity with T^{-1} ceased at about 45 °C, and after the 2nd process in the range above 70 °C the marked irreversibility has appeared. The former would be attributed to the dehydration which was also observed in TGA, and the latter may be attributable to an electric polarization and a decrease in the effective area of the electrodes resulted either from the crack of the pellet or from the partial peeling of the silver pasted cathode which are visible after considerable periods of application of d.c. voltage. As reported before,[1] a reversible process in σ-T^{-1} relationship was found using a.c. potential (10 MHz). The activation energies ΔE obtained from Arrhenius plot are shown in Table 1. It was found that in the case of $(HOC_2H_4)_2$-dtoa-Cu the current *vs.* d.c.

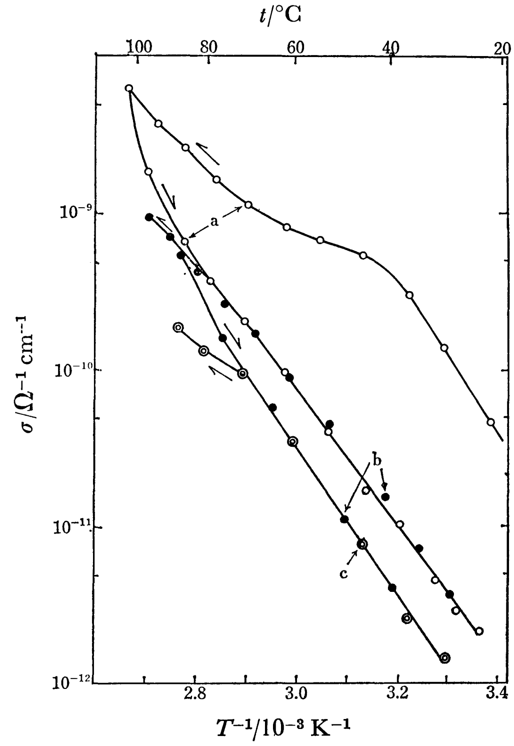

Fig. 7. Temperature dependence of the d.c. conductivity for a) 1st heating and cooling (white circle), b) 2nd heating and cooling (black circle), and 3rd heating (double circle). During the interval between measurements that is the time needed for changing temperature the polarization was released by the connection of the both electrodes without applied voltage.

Table 2. Non-Ohmic behavior in $(HOC_2H_4)_2$-dtoa-Cu, contrasted with $(C_6H_5CH_2)_2$-dtoa-Cu

Sample	Temp °C	Ohm's law deviation %	Applied voltages V/cm
$(HOC_2H_4)_2$-dtoa-Cu	22	18	1800
	42	18	1800
	64	10	1800
	79	8.3	1800
$(C_6H_5CH_2)_2$-dtoa-Cu	20	2.7	1700
	57	1	1700
	79	1	1700

The current values are taken at 30 s after applied voltage.

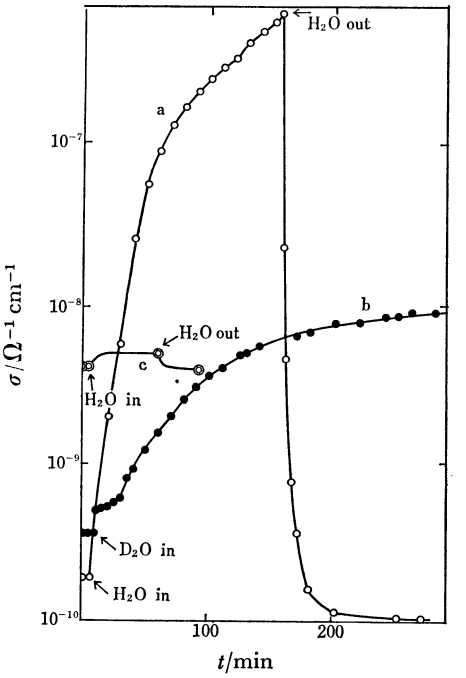

Fig. 8. Effect of water vapor on the conductivity of $(HOC_2H_4)_2$-dtoa-Cu. a) Vapor of H_2O (white circle), b) vapor of D_2O (black circle), c) contrasted with that of $(C_6H_5CH_2)_2$-dtoa-Cu.

voltage relation deviates to higher current side at a higher voltage region as shown in Table 2 together with that of $(C_6H_5CH_2)_2$-dtoa-Cu for comparison; the deviations are expressed as a percentage, $100(i_o-i_c)/i_o$ where i_o is the observed current and i_c is that calculated from the initial slope assuming Ohm's law.

In the case of trap-limited or ionic conduction, the current has non-Ohmic character and follows an eq. $i=A \sinh bV$ which has a non-linear character.[9] The values for $(HOC_2H_4)_2$-dtoa-Cu in Table 2 support the proton conduction mechanism.

Figure 8 illustrates the marked effects of water vapor (*ca.* 10^3 Pa) on the conductivity of the hydroxyethyl homologue and that of benzyl-substituted one for comparison. Conductivity of the former compound increases gradually by a factor of 10^3 in 2 h, whereas that of the latter increases only by 10%, levels off within 10 min and decreases to original value by reevacuation of the water vapor. As is shown in Fig. 8, by a reevacuation the conductivity of the former rapidly decreases not to the initial but to 50% of the initial value, probably because the crack of the pellet or the partial peeling of the cathode causes a decrease of the apparent conductivity. Introduction of deuterated water in the cell results in the slower increase of the conductivity than in the case of normal water. The difference between the effects of H_2O and D_2O would be attributed to that in the diffusion coefficients of the water molecules in the pellets and in the mobilities of H^+ and D^+ in an electric field through hydrogen bonds, although these data are not sufficient for quantitative analysis. The slow effects of water vapor imply that the increment of the current originates not only from the water molecules adsorbed on the surface of the pellets but also from that absorbed into the pellets.

In order to confirm a proton conduction mechanism in $(HOC_2H_4)_2$-dtoa-Cu complex, three pellets connected in parallel were subjected to d.c. voltage (av. 400 V) for 170 h, resulting in a charge flow of *ca.* 0.7 C and a certain amount of electrolytically generated gas. From the spectrogram of the gas, H_β (486.1 nm) medium line, H_γ (434.0 nm) very strong line, and H_δ (410.1 nm) weak line of Balmer series of hydrogen atom were assigned by comparison with the line spectra of mercury as a standard for wavelength determination. This fact proves directly the generation of hydrogen gas by applying d.c. voltage on the specimen. Now it became apparent that the generated hydrogen causes the cracks of the pellets and the peeling of the cathodes observed only in case of the $(HOC_2H_4)_2$-dtoa-Cu compound.

The experimental facts on this compound can be summarized as follows: 1) H_2 is generated at a cathode, 2) the charge carrier other than electrons will be protons, and 3) the charge drift and the gas evolution seem to occur not only on surface but also in the inner part of the pellet as well. The third conclusion needs more consideration in detail. The pellet is an aggregate of the microscopic amorphous grains, and the "inner part of the pellet" mentioned above could mean both the surface and the interior of the grain. However, they are indistinguishable because the surface of the grain and that of the two-dimensional amorphous macromolecule located inside behave almost in the same manner as far as the proton conduction mechanism is concerned.

In order to elucidate the hydrogen evolution at the location remote from the cathode, an appropriate mechanism should be proposed. The conventional mechanisms of electric conduction by linked chain of hydrogen bonds are reviewed and classified as follows:[10] Type 1, through chains of hydrogen bonds π-electrons drift without evolution of hydrogen gas to give rise the steady current as was proposed by Eley and his school for protein and amino acids.[11] Type 2, a hydrogen bonded proton transfers from molecule A to molecule B sequentially followed by reorientation processes of the chain, that is, the molecular rotation of B by which further transfer of the proton takes place from B to C through a newly formed hydrogen bond between them. The arrangement of

A, B, and C is more or less parallel to the electric field. In such case that the reorientation processes are energetically difficult, the step could be substituted by the intramolecular proton migration. The transition of the mechanism from type 1 to type 2 at about 100 °C was reported in the polyamides.[12] The generation of molecular hydrogen at the locations other than cathode is hard to be explained by both the types.

The $(\mathrm{HOC_2H_4})_2$-dtoa-Cu specimen containing nonstoichiometric $\mathrm{H_2O}$ and $\mathrm{OH^-}$ provides the several possible paths for the electric conduction due to either electrons or protons, or both (Fig. 9). That is, the serial bondings $\langle \mathrm{S{-}C{-}C{-}S{-}Cu} \rangle_n$, $\langle \mathrm{N{-}C{-}C{-}N{-}Cu} \rangle_n$, and $\langle \mathrm{S{-}C{-}C{-}N{-}Cu} \rangle_n$ in the framework of the macromolecule could operate as the pure π-electronic macroscopic conduction paths independently from the hydrogen bond chain. As the figure shows, a set of the complicated hydrogen bonds could be composed between $\mathrm{-C_2H_4OH}$, coordinated water, nitrogen and sulfur of ligand molecules; the bonds could construct a) extended chains of the hydrogen bonds solely, and b) mixed chains of the hydrogen bonds and the conjugate double bonds, both resulting the macroscopic paths. In case (a) the protons move to the cathode and are discharged there to evolve hydrogen molecules, whereas in case (b) the protons could be discharged at the contact points between the hydrogen bond chains and the conjugate double bond paths as well as at the metallic cathode. Especially the D-defect (doppel Besetzung) in the hydrogen bonds[13] presents a probable opportunity of the $\mathrm{H_2}$ generation in the interior of the specimen. Many studies[14] on cooperative phenomena of $\mathrm{H^+}$-jump and $\mathrm{e^-}$-transfer in microscopic scale have been done as a kind of redox reactions in the liquid phases. Coexistence of conjugated double bonds and extended hydrogen bonds in solid phases makes a following conduction mechanism possible in macroscopic scales (type 3); the sequence of the proposed mechanism is shown in Fig. 10 by way of a simple example (peptide bonds), which is adoptable easily for any other systems with $\mathrm{H^+}$-bonds and conjugate π-bonds. In this case neither the conduction band of π-electrons in an extended hydrogen bond system (type 1) nor the molecular rotation mechanism with hydrogen evolution on the electrode (type 2) are needed. The cyclic sequence (1, 2, 3, and 4), type 3A, is that of no hydrogen evolution and of the time independence of the conductivity, whereas the other sequence (1, 2, 3, and 5), type 3B, is that of the hydrogen evolution on a positive electrode surface and/or in the interior of the solid. In type 3B the electric conduction path through hydrogen bonding chains will be bleached gradually. Consequently 3A mechanism allows the time independent part of the whole electric current. Although some residual possibility of type 2 mechanism can not be ruled out, the hydrogen evolution from the interior of the specimen suggested by its cracking induces us to conclude the functioning of the type 3B mechanism. At the present stage the type 3 mechanism is presented as a working hypothesis which should be ascertained quantum-mechanically and experimentally in future.

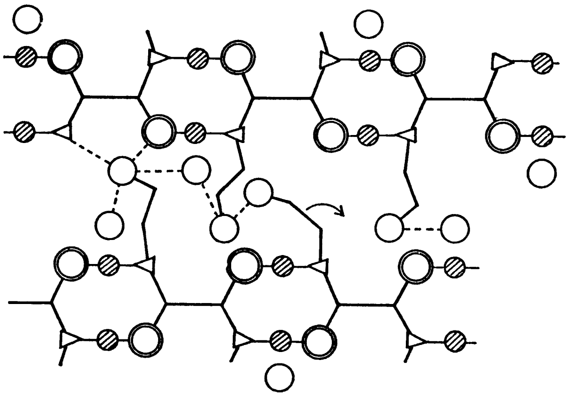

Fig. 9. The possible conduction paths by both electron and proton. Shaded circle, double circle, and triangle exhibit copper, sulfur, and nitrogen atoms respectively. White circles are OH and/or water molecule. All carbon atoms are abbreviated. Covalent bonds and coordinate bonds are represented by broad and narrow lines. Dotted lines are hydrogen bonds and the circled arrow exhibits an internal rotation of the hydroxyethyl group to transfer of hydrogen bond.

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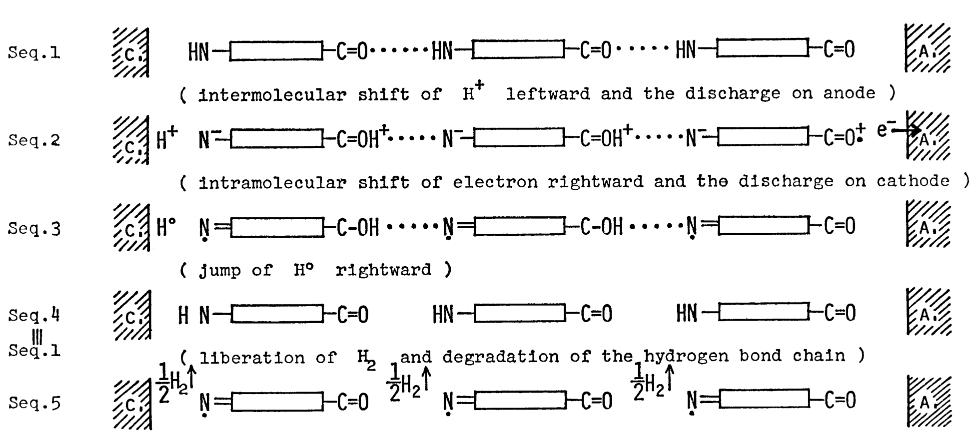

Fig. 10. A consolidated model for electric conduction through hydrogen bond ($\rangle$C=O···HN$\langle$) and π-electron conjugate double bond system (–▭–) following the sequence (1, 2, 3, and 4) or (1, 2, 3, and 5). C. and A. are the cathode and anode respectively.

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