The Electrical Conductivity of Heterocyclic Compounds. Molecular Complexes of Phenazine

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As a part of a series of studies of the electrical conductivity of heterocyclic compounds, some molecular complexes of phenazine (cf. Fig. 1) were prepared, and their electrical conductivities were compared with those of molecular complexes of the quinhydrone-type.

Experimental

Materials.—Phenazine, phenazinium chloride and phenazinium methosulfate were prepared according to the methods described in the literature.1) Hydroquinone, pyrene and all other materials were of a commercial grade. All the materials were purified by repeated recrystallization and sublimation.

The Preparation of Molecular Complexes.—*Molecular Complexes of the Quinhydrone Type.*—Molecular complexes of the quinhydrone type of phenazine (abbreviated as ph) with *o*-, *m*- and *p*-hydroquinone (abbreviated as Hy), *o*-phenylenediamine (abbreviated as BNH_2), dihydrophenazine (abbreviated as phH_2) or trinitrobenzene (abbreviated

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1) A. Wohl and W. Aue, *Ber.*, **34**, 2442 (1901).

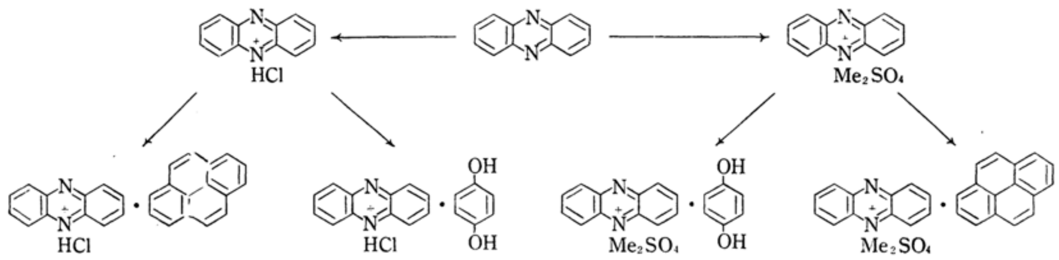

Fig. 1. Molecular complexes of salt type.

TABLE I. THE CONDITIONS OF THE PREPARATIONS FOR MOLECULAR COMPLEXES

Donor and acceptor	Solvent	Yield %	M. p. °C	Color of crystals
py, ph-HCl	HCl-ethanol	90	133∼135	Black needle
Hy(*p*), ph-HCl	HCl	60	168.5∼170	Black-brown plate
py, ph-Me$_2$SO$_4$	Ethanol	30∼40	156∼157	Black prism
Hy(*p*), ph-Me$_2$SO$_4$	Ethanol	30∼40	118∼119.5	Black prism
py, ph-HCl	Dry ether	0	—	—
Hy(*p*), ph	Ethanol	62	234∼236	Yellow needle
Hy(*m*), ph	Ethanol	70	213∼214	Yellow needle
Hy(*o*), ph	Ethanol	74	181∼182	Yellow needle
BNH$_2$, ph	Ethanol	70	150∼151	Red-blown plate
ph, TNB	Ethanol	85	151∼153	Yellow needle
phH$_2$, ph	Acetone	50	223∼225	Blue-violet needle

as TNB) were prepared according to the methods described in the literature,[2-4] these will be abbreviated as ph-Hy(*o*), ph-Hy(*m*), ph-Hy(*p*), ph-BNH$_2$, ph-phH$_2$ and ph-TNB in this paper. The conditions of the preparation of these molecular complexes are shown in Table I.

Molecular Complexes of the Salt Type.—a) Phenazinium Chloride and Pyrene (abbreviated as ph-HCl-py).—To a warm solution of 0.9 g. of phenazine in 70 ml. of concentrated hydrochloric acid, 1 g. of pyrene dissolved in 80 ml. of ethanol was added, and the mixture was refluxed for about half an hour. After filtering, the filtrate was left to cool, and 1.8 g. of black needle crystals were obtained. However, no molecular complex was obtained from pyrene and phenazine themselves. When hydrogen chloride was introduced into a solution of pyrene and phenazine in dry ether, no black precipitate was obtained, but red crystals of phenazinium chloride were recovered. However, when ether which had previously been saturated with water was used instead of dry ether as the solvent, black needle crystals of the molecular complex were obtained. Thus, it seems that a little water may be necessary in a reaction system to form a molecular complex of a salt type from phenazinium salt.

b) Phenazinium Chloride and p-Hydroquinone (abbreviated as ph-HCl-Hy(*p*)).—To a solution of 0.3 g. of phenazine in 30 ml. of concentrated hydrochloric acid, 1 g. of *p*-hydroquinone was added at 70∼80°C, and the solution was refluxed for half an hour. After it had been treated in a manner similar to that described above, 0.3 g. of black plate crystals was obtained.

c) Phenazinium Methosulfate and Pyrene (abbreviated as ph-Me$_2$SO$_4$-py).—Into a solution of about 0.5 g. of phenazine in 25 ml. of nitrobenzene, 0.5 g. of dimethylsulfate was stirred, after which the reaction mixture was heated at 100∼110°C for about 15 min. The cooling of the reaction mixture resulted in a precipitation of crystals. After filtering, the filtrate was diluted by 25 ml. of dry ether to precipitate crystals again. Both sets of crystals were recrystallized from ethanol; yield, 0.6 g. (70%); m. p. 151∼153°C (decomp.). Six-tenths of a gram of ph-Me$_2$SO$_4$ and 0.4 g. of pyrene were dissolved in 4∼5 ml. of ethanol and refluxed for about half an hour. About 0.3 g. of black prism crystals precipitated. After filtering, the precipitate was washed with a mixed solvent of benzene and ether and dried on P$_2$O$_5$ under the reduced pressure of 10 mmHg for about ten hours; m. p. 156∼157°C.

d) Phenazinium Methosulfate and p-Hydroquinone (abbreviated as ph-Me$_2$SO$_4$-Hy(*p*)).—A solution of 0.3 g. of ph-Me$_2$SO$_4$ and 0.18 g. of *p*-hydroquinone in 1∼2 ml. of ethanol was refluxed for about half an hour and then treated in a manner similar to that used in the case of ph-HCl-py. About 0.15 g. of black prism crystals was precipitated. The properties of the molecular complexes obtained above are shown in Table I.

Results

The Properties of Molecular Complexes of the Salt Type.—The constitutions of the molecular complexes obtained were analyzed. Since

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[2] J. S. Morley, *J. Chem. Soc.*, **1952**, 4008.
[3] T. Zerewitinoff, *Ber.*, **44**, 2402 (1911).
[4] O. Blum, ibid., **62**, 881 (1929).

ph-HCl-py and ph-HCl-Hy(*p*), which were dried on calcium chloride at 20°C under the reduced pressure of 10 mmHg for 5 hr., contained more than the expected amounts of excess hydrogen chloride and water, as may be seen in Figs. 2 and 3, they were dried under the same conditions for a prolonged period. During this treatment, the features of the molecular complexes changed, as Table II and Figs. 2 and 3 show.

The color changed from black to yellow, and the shape of the crystals changed from needle to fine amorphous. The melting points decreased gradually. When kept on P_2O_5 at 50~60°C under the reduced pressure of 5~10 mmHg for a long time, the melting points of the molecular complex became near to those of the simple mixture of their constituents.

The content of hydrogen chloride and water, which had been calculated from the analytical results of nitrogen and chlorine shown in Figs. 2 and 3, decreased gradually with the drying time. The decrease in the quantity of water during the process of drying was confirmed also by the disappearance of the infrared absorption band at 3500 cm^{-1} after the drying. Thus, the water included in the crystals of the molecular complexes may be regarded as one of the constituents of the molecular complex, because a little water in a reaction system is necessary in order to obtain the molecular complexes.

TABLE II. THE VARIATION OF MELTING POINT TO DRYING TIME

Melting point of the simple mixture:
ph and py; 118~121°C,
ph and Hy(*p*); 167~230°C

Drying time hr.	ph-HCl-py °C	ph-HCl-Hy(*p*) °C	ph-HCl °C
1	133~135	168.5~170	214~216
3	130~133.5	168 ~170	212~216
10	128~133	162 ~166	205~209
30	123~132	—	—
100	120~130	163 ~167	169~175

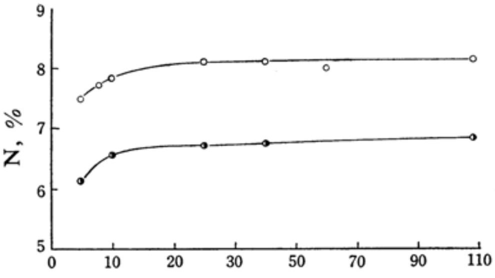


Fig. 2. The variation of nitrogen percentage to drying time: ◑ ph-HCl-py, ○ ph-HCl-Hy(*p*); Calcd. for ph-HCl-py: N, 6.69%, for ph-HCl-py-H_2O: N, 6.41%, for ph-HCl-Hy(*p*): N, 8.56%, and for ph-HCl-Hy-H_2O: N, 8.12%.

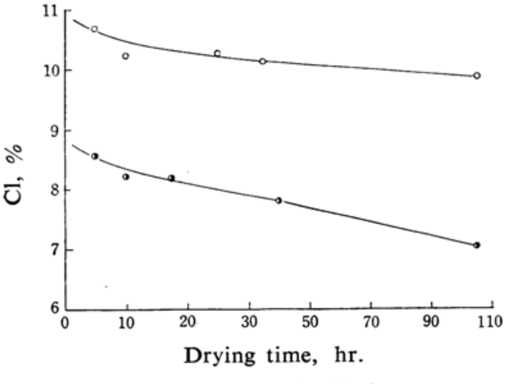


Fig. 3. The variation of chlorine percentage to drying time: ◑ ph-HCl-py, ○ ph-HCl-Hy(*p*); Calcd. for ph-HCl-py: Cl, 8.46%, for ph-HCl-py-H_2O: Cl, 8.11%, for ph-HCl-Hy(*p*): Cl, 10.86%, and for ph-HCl-Hy(*p*)-H_2O: Cl, 10.30%.

The ultraviolet absorption spectrum of an ethanolic solution of ph-HCl-py was merely the sum of the absorption spectra of ph-HCl and py in ethanol, because ph-HCl-py dissociates thoroughly into each component in ethanol. On the other hand, the ultraviolet absorption spectrum of the same compound obtained by the KBr-method showed a new band at about 620 mμ which must be a charge transfer absorption, as Fig. 4 shows. A charge transfer absorption for ph-HCl-Hy(*p*) could not be confirmed by the KBr method. The infrared absorption spectra of ph-HCl-py and ph-HCl-Hy(*p*) showed out-of-plane deformation bands at 700~1000 cm^{-1} which shifted about 5~30 cm^{-1} to a lower wave number than those of each component. This may imply that there is some molecular interaction in the molecular complex.

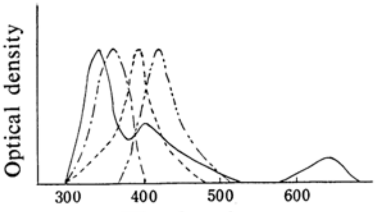


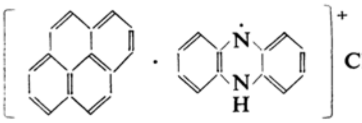
Fig. 4. Absorption spectra of ph-HCl-py, ph-HCl-Hy(*p*), ph-HCl and ph in KBr: —— ph-HCl-py, ------ ph-HCl-Hy(*p*), —··— ph-HCl and —·— ph.

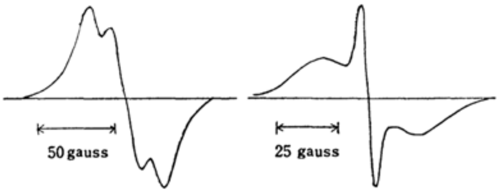
The ESR spectra of ph-HCl-py and ph-HCl-Hy(p) which had been kept over calcium chloride at room temperature under the reduced pressure of 10 mmHg for three days are shown in Fig. 5. The spin concentrations and g values which were calculated from the ESR spectra were as follows:

ph-HCl-py ; g value 2.0033, spin concentration 5.8×10^{20}

ph-HCl-Hy(p) ; g value 2.0022, spin concentration 3.9×10^{20}

Though the curves of the ESR spectra were comparably broad, they showed three fine structures. Hence, it may be considered that an unpaired electron is localized on the nitrogen atom of phenazine. Also, the infrared spectra showed that the intensities of the peaks at 1917 and 2380 cm^{-1} assigned to $=\overset{+}{N}H-$ for py-HCl-ph and ph-HCl-Hy(p) decreased as compared with those of ph-HCl. From these results, the following structural formula may be assigned to the structure of molecular complexes:





ph-HCl-py ph-HCl-Hy(p)

Fig. 5. ESR spectra of ph-HCl-py and ph-HCl-Hy(p).

The properties of molecular complexes of a methosulfate type were similar to those of a hydrogen-chloride type.

Electrical Conductivities.—The d.c. resistivity was measured under the pressure of 100 kg./cm^2 in vacuo according to the methods described in previous papers.[5] Since the dark current of all samples obeyed Ohm's law up to $10^3\sim10^4$ V./cm., all d.c. resistivities in this paper were measured at an applied electric field in the range of 2000∼4000 V./cm.

The electrical resistivity (ρ_{20}) of ph-HCl-py, ph-HCl-Hy(p) and ph-HCl, which had been dried under the conditions shown in Figs. 2 and 3, was measured at 20°C for various periods, as is shown in Fig. 6. Each resistivity increased with the drying time, but each then became nearly constant after about 20 hr. Also, the resistivity of the compounds which had been dried for 20 hr. or more did not change when kept under the applied field of about 10^4 V./cm. for eight days. Judging from these results, it seems probable that the electrical conductivities of the compounds dried for over 20 hr. are electronic.

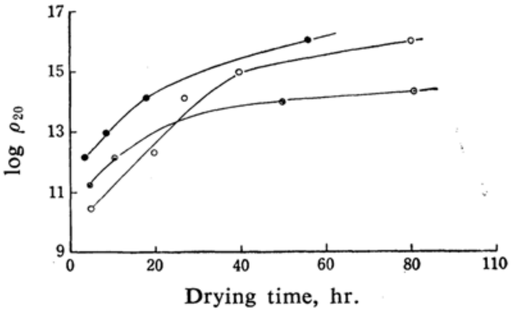


Fig. 6. The variation of log ρ_{20} of salt type compounds to drying time: ● ph-HCl, ⊙ ph-HCl-Hy(p), ○ ph-HCl-py.

The dependencies of the d.c. resistivities on the measuring temperature are shown in Fig. 7. The resistivity as an ascending temperature coincides with that at a descending temperature for all samples, except ph-phH$_2$, ph-HCl-Hy(p) and ph-Me$_2$SO$_4$-Hy(p), and a linear relationship between log ρ and $1/T$ was confirmed. $\Delta\varepsilon$ was calculated by the following equation:

$$\rho=\rho_0\exp(\Delta\varepsilon/2kT)$$

where $\Delta\varepsilon$ is an appearent energy gap, $\boldsymbol{k}$ is the Boltzman constant, and ρ is a specific electrical resistivity. The values of ρ_{20} and $\Delta\varepsilon$ are given in Table III.

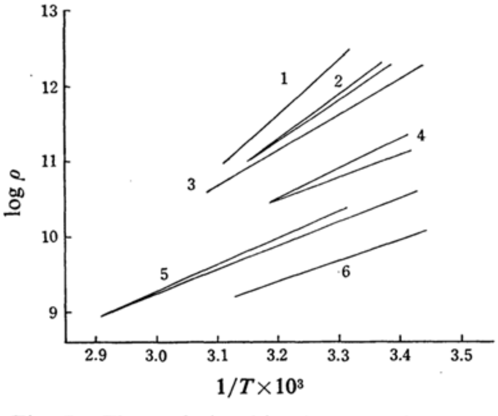


Fig. 7. The relationship between log ρ and $1/T$: 1 ph-Me$_2$SO$_4$-py, 2 ph-Me$_2$SO$_4$-Hy(p), 3 ph-HCl, 4 ph-HCl-Hy(p), 5 ph-phH$_2$, 6 ph-HCl-py.

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[5] H. Inoue, T. Takiuchi and E. Imoto, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **65**, 1291 (1962).

TABLE III. THE VALUE OF RESISTIVITY AT 20°C (ρ_{20}) AND $\Delta\varepsilon$ OF MOLECULAR COMPLEXES

Molecular complex	ρ_{20} $\Omega\cdot$cm.	$\Delta\varepsilon$ eV.
ph-HCl-py*	6×10^{10}	1.2
ph-HCl-Hy(p)*	3×10^{11}	1.1~1.5
ph-Me_2SO_4-py	1.5×10^{13}	2.8
ph-Me_2SO_4-Hy(p)	2.9×10^{12}	3.7
ph-Hy(p)	3×10^{15}	—
ph-Hy(m)	1×10^{16}	—
ph-Hy(o)	7×10^{12}	0.5
ph-TNB	1×10^{15}	—
ph-BNH_2	3×10^{13}	—
ph-phH_2	3.7×10^{10}	1.3~1.5

* This sample was dried on P_2O_5 under the ordinary pressure at room temperature for a week.

Discussion

The ρ_{20} values of salt-like molecular complexes are smaller than those of molecular complexes of the quinhydrone type. This means that the effect of the intermolecular charge-transfer on the ρ_{20} of the former is larger than that on ρ_{20} of the latter. Also, the resistivities of molecular complexes of the methosulfate type were larger than those of molecular complexes of the hydrogen-chloride type. These results seem to show that the resistivity is affected by the compactness of molecular arrangement, because it seemed that the molecular arrangement of the methosulfate-type complex was less compact than that of the hydrogen chloride-type complex because of the steric effect of the CH_3-group.

The ρ_{20} of ph-phH_2 was the lowest among those of the molecular complexes of the quinhydrone type. This may be caused by the fact that the molecular arrangement of ph-phH_2 is more favorable than that of the others because of the good symmetry in the dimensions of the donor and acceptor molecules.

The resistivities of the salt-like molecular complexes described above possess a much higher value than those of the aromatic hydrocarbon-halogen complexes, which have been reported on by Akamatu and Inokuchi.[6] That is, it seems that these results may be attributed to the following causes; (1) the crystal of the molecular complex was contaminated with phenazine and pyrene or p-hydroquinone, because a part of the molecular complex dissociates to these compounds when water was removed; (2) an unpaired electron was localized on nitrogen atoms of phenazine, and (3) the molecular arrangement is incomplete, as may be presumed from the broadness of the ESR spectrum.

Summary

Some molecular complexes of the salt type have been prepared from phenazinium chloride or methosulfate and pyrene or p-hydroquinone. It has been confirmed that (1) the constitution, the color and the melting point of the molecular complexes varied with the drying conditions; (2) the ultraviolet absorption spectrum of ph-HCl-py by KBr shows a new band at about 620 mμ; (3) an unpaired electron is localized on the nitrogen atom of phenazine, and (4) the electrical conductivities of molecular complexes of the salt type are better than those of the quinhydrone type of phenazine.

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[6] H. Akamatu, H. Inokuchi and Y. Matsunaga, This Bulletin, 29, 213 (1956).