Electrical Properties of 1,1-Diphenyl-2-picrylhydrazine and 2,2-Diphenyl-1-picrylhydrazyl Disks

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The electrical properties of 2,2-diphenyl-1-picrylhydrazyl (DPPH) disk were studied in the temperature range 18—60 °C over frequencies 3×10—3×10^6 Hz in comparison with those of 1,1-diphenyl-2-picrylhydrazine (DPPHn). The frequency dependence of conductance (σ_{ac}) for both DPPH and DPPHn can be explained in terms of the hopping conduction caused by localized states and/or shallow traps. At low frequencies, the strong dispersion of the capacitance of DPPH was observed while conductivity remained constant. This was accounted for by hyperelectronic polarization. The difference in electrical properties between DPPH and DPPHn indicates that the unpaired electrons in DPPH play an important role in the frequency independent conductance (σ_{dc}), but not in the frequency dependent conductance (σ_{ac}).

In 1962, Pollak showed[1)] that the band type conduction should be essentially frequency-independent, whereas hopping conductivity should increase with increasing frequency of applied field.

It is known[2)] that the monotonic increase of conductivity with an increase in frequency can be interpreted in terms of a hopping conduction mechanism in which carriers transit from one localized state to another. The localized states are formed when the interaction between molecules is weak.

Ac measurement is useful for studying the character of conduction since the ac currents are basically different for hopping and band conduction. Many workers have reported[3—5)] that the apparent conductivity of aromatic compounds can be expressed as the sum of the frequency independent component (band conduction) and the frequency dependent component (hopping conduction).

2,2-Diphenyl-1-picrylhydrazyl (DPPH) is a well-known solid organic free radical and a semiconductor, but the frequency dependence of both conductivity and dielectric constant has not been studied in detail. We have studied the effects of unpaired electrons in DPPH on the electrical properties by measuring the frequency and the temperature dependence of conductivity and dielectric constant of both DPPH and 1,1-diphenyl-2-picrylhydrazine (DPPHn).

Experimental

DPPH was prepared by the method reported by Inokuchi *et al.*[6)] and purified by repeated recrystallization from carbon disulfide which forms no molecular complex with DPPH.[7)] DPPHn was purified by repeated recrystallization from ethyl ether. Samples were dried for one day *in vacuo* (about 10^{-5} Torr). Pulverized samples (about 200 mg) were compressed between stainless steel electrodes under pressure of about 220 kg/cm^2 *in vacuo* in order to eliminate the contact resistance and capacitance. The size of a sample was 0.05 cm$\times$3.14 cm^2. The sample was held *in vacuo* (about 10^{-3} Torr) in order to avoid the effect of adsorption of oxygen gas during the course of electrical measurements. Measurements were carried out with an ac bridge TR 10C (Ando Electric. Co. Ltd.). The dc conductivity of the DPPH was measured with an electrometer TR 8651 (Takeda Riken). The temperature of the sample was varied from 15 to 70 °C. It was found by ESR measurement that the purified DPPHn contains trace amounts of paramagnetic substance, probably DPPH, the concentration of which was estimated to be less than 10^{-6} spins/mol. The g value of impurity was determined to be 2.0036 by use of the frequency counter in ESR measurement.

Results and Discussion

In previous papers[8,9)] it was shown that the frequency dependence of ac conductivity for aromatic compounds is expressed as

$$\sigma = \sigma_{ac} + \sigma_{dc} = A\omega^n + \sigma_0 \exp(-E/kT) \qquad (1)$$

where $\sigma_{ac}(A\omega^n)$ and $\sigma_{dc}(\sigma_0\exp(-E/kT))$ are the frequency dependent and independent components, respectively. ω is the angular frequency ($\omega=2\pi f$). Lakatos and Abkowitz[2)] have shown that if hopping takes place between a random distribution of localized states, σ_{ac} should be proportional to ω^n when $0.5<n<1.0$. n takes the lower value for multiple hops and the higher one for a single hop. Multiple hops occur frequently, at a high temperature, while the single hop predominates at a low one.

The frequency dependence of the apparent ac conductivity of DPPHn and DPPH is shown in Figs. 1 and 2, respectively. In the low frequency region

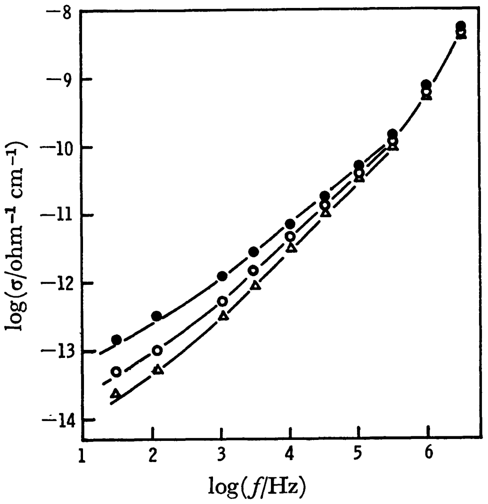

Fig. 1. Frequency dependence of observed conductivity of DPPHn at various temperatures.
(△) 10 °C, (○) 35 °C, (●) 70 °C.

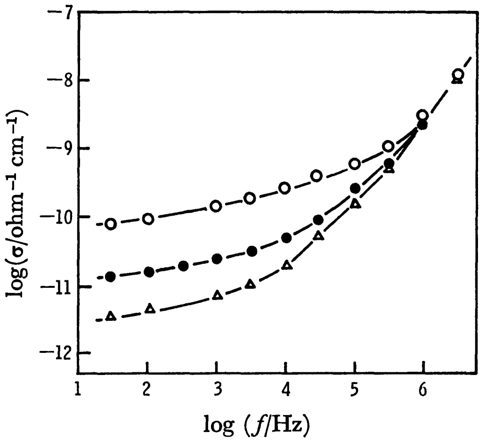

Fig. 2. Frequency dependence of observed conductivity of DPPH at various temperatures.
(△) 10 °C, (●) 32 °C, (○) 60 °C.

(below 3×10^3 Hz) the difference between the observed value for DPPHn and the straight line drawn by extrapolation from the high frequency region (1 kHz—1 MHz), on the assumption that σ_{ac} is proportional to ω^n, is defined as σ_{dc}. The value of σ_{dc} thus obtained is independent of the frequency within experimental error. The dc conductivity of DPPHn could not be measured by the usual dc method because of low conductivity (*i.e.*, specific conductivity $<10^{-13}$ ohm$^{-1}\cdot$cm^{-1}).

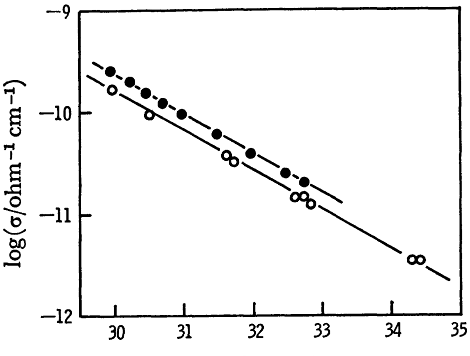

Fig. 3. Temperature dependence of dc and ac (30 Hz) conductivity of DPPH.
(○) ac method (applied frequency: 30 Hz)
(●) dc method (applied voltage: 10 V)
The difference of the conductivity between dc and ac methods is probably due to the difference of the standard resistance.

In the case of DPPH, at 30 Hz frequency the observed conductivity is about 10—10^2 times larger than that obtained by the extrapolation from high frequency region on the assumption that the relation $\sigma_{ac}=A\omega^n$ holds. The observed conductivity at 30 Hz is in good agreement with that obtained by the dc method (Fig. 3). We can thus assume that it is approximately equal to σ_{dc}, *viz.*, the frequency independent component.

Table 1. Values of n for DPPHn and DPPH disks

DPPHn		DPPH	
Temp. °C	n in σ_{ac}	Temp. °C	n in σ_{ac}
18	0.9_0	18	0.8_0
35	0.8_0	32	0.6_5
70	0.7_5	42	0.5_0
85	0.6_5	54	0.5_0
		60	0.5_0

The frequency dependence of σ_{ac} of DPPH was obtained by use of the value of σ_{dc}. The values of n in the relation $\sigma_{ac}=A\omega^n$, which were graphically obtained, are given in Table 1 for DPPHn and DPPH. The values are consistent with the thermally assisted hopping conduction mechanism in which n is expected to be between 0.5 and 1.0. The fact that the effect of temperature on σ_{ac} decreases with an increase in frequency indicates that the localized states (and/or shallow traps) are strongly affected by the frequency.

Since no distinct difference in σ_{ac} of DPPHn and DPPH was observed, the ac conduction of DPPH might be caused by the localized states produced by structural defects, impurities and/or π-electrons but not unpaired electrons.

In the higher frequency region (above 1 MHz) the conductivity is proportional to the square of frequency. This holds when the hopping distance becomes shorter as the frequency increases[10] and in extreme cases it becomes less than the distance between localized states. However, the electrical properties of ω^2 region can not be discussed in detail since the frequency dependence of the conductivity was not measured in a region higher than 3 MHz.

From the results shown in Fig. 3, the activation energy and pre-exponential factor σ_0 in Eq. (1) was estimated to be 0.75 ± 0.05 eV and 10 ohm^{-1} cm^{-1}, respectively. The dc conduction of DPPH should be due to the carriers excited into the localized states at the band edge (E_A) because the value of σ_0 thus obtained is smaller than that expected for the intrinsic band conduction by a factor of 10^2.[11] If the main carriers are thermally excited electrons in DPPH, and conduction is caused by hopping, we have

$$\sigma_{dc} = \sigma_0\cdot\exp[-(E_A-E_F+\Delta W_1)/kT], \qquad (2)$$

where ΔW_1 is the activation energy for hopping and E_A is the energy at the band edge (Fig. 4), the value of σ_0 being expected to be of the order 10—10^{-2} ohm$^{-1}\cdot$cm^{-1}.[11] Since the activation energy of the photo-

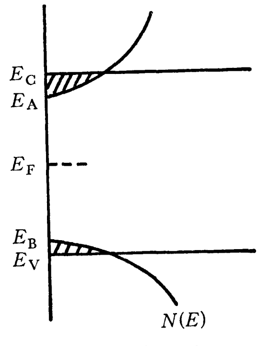

Fig. 4. Density of states as a function of energy in DPPH. Localized states are shown shaded.

Table 2. Dielectric constant for DPPH at 58 °C as a function of thickness and density

Thickness mm	Density g cm^{-3}	Dielectric constant 30 Hz	 110 Hz
0.51	1.24	7.30	—
0.76	1.26	7.06	5.08
0.93	1.36	8.38	6.10
0.95	1.33	8.09	5.74
1.15	1.39	8.12	6.50
1.22	1.31	8.05	5.86

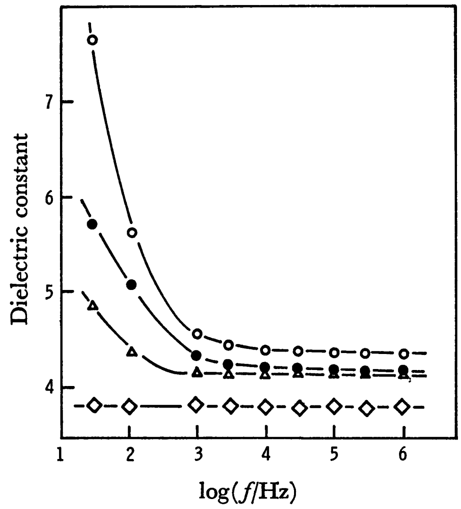

Fig. 5. Frequency dependence of dielectric constant of both DPPH and DPPHn at various temperatures. (○) DPPH 60 °C, (●) DPPH 54 °C, (△) DPPH 40 °C, (◇) DPPHn 18—70 °C.

conduction of DPPH film prepared by solvent evaporation has been estimated to be 0.16 eV by Eley and his co-workers,[12] it is expected that the activation energy for hopping (ΔW_1) takes the value of the order 0.1 eV.

On the other hand, the dielectric constant of DPPH shows a strong dispersion for frequency of the applied field and increases with increasing temperature while that of DPPHn remains constant (Fig. 5). The fact that in the case of DPPH the dielectric constant shows a strong dispersion in the low frequency region but conductivity does not can be explained in terms of interfacial polarization and/or hyperelectronic polarization. Since the observed dielectric constant is not a function of sample thickness (Table 2) and σ_{dc} obeys Ohm's law up to 10^3 V cm^{-1} at 50 °C, it is expected that the hyperelectronic polarization rather than the interfacial polarization takes place for DPPH.

Pohl *et al.*[13] showed that the strong dispersion of dielectric constant at low frequency can be explained by hyperelectronic polarization. Large molecules are expected to give high values of dielectric constant if the transit of electrons is more unlikely to occur between molecules than within molecules. The low value of σ_0 obtained above is in line with the assumption of hyperelectronic polarization since the thermally excited unpaired electron must pass over the activation energy for hopping. It is expected that the observed mobility takes a lower value than that expected for intrinsic band conduction. The assumption of hyperelectronic polarization can be confirmed by the fact that the conductivity is strongly dependent on pressure[14] and weakly dependent on frequency of the applied field. Hyperelectronic polarization is most likely to occur for DPPH in the low frequency region and low mobility may be explained by the electronic hopping between DPPH molecules. Since no similar tendency could be observed for DPPHn, the hyperelectronic polarization should be due to the unpaired electrons in DPPH.

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