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Organometallic Photoconductors: Dark and Photoconductive Studies on Ferrocene and Some of Its Derivatives

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The dark conduction properties of ferrocenedicarboxylic acid have been studied as a function of voltage at different sample-temperatures by using sandwich type of cell configuration. The analysis of the results was based on the space charge limited conduction (SCLC) theory. The trap distribution in this material has been found to be exponential type as was observed in case of ferrocene and ferrocenecarboxylic acid. The dark activation energy (ohmic) of these ferrocene derivatives increases with the gradual substitution of –COOH group in the ferrocene ring system. In contrast to the nonextrinsic nature of ferrocenecarboxylic acid, ferrocenedicarboxylic acid has been observed to be extrinsic, similar to ferrocene. The photoconductivity in these materials was studied as a function of temperature and the intensity of exciting light source. The distribution of traps in these materials has been determined from the intensity dependence of photocurrent and these results have been compared with the results of dark conductivity measurements.

The metallocenes have occupied the most privileged position in organometallic research because of their technological usefulness.[1)] Ferrocene [$(C_5H_5)_2Fe$; FcH], the first-synthesized metallocene, and its derivatives are well-known for their important electrochemical properties.[2)] In earlier communications[3—6)] it has been reported that the electrical conduction parameters for pure as well as vapor-adsorbed ferrocene derivatives are highly influenced by the substitution of different functional groups such as –CHO, –COOH, –$COOCH_3$, –COC_6H_5 etc. in the ferrocene unit. Most striking observation is that the substitution of single –COOH group in ferrocene unit has shown[3)] entirely different type of current (dark)–voltage (*I–V*) characteristics compared to the substitution of other groups. The distribution of traps in these materials was evaluated from the *I–V* characteristics. In ferrocene and ferrocenecarboxylic acid Fc(COOH) the distribution of traps was exponential type whereas in the other ferrocene derivatives this trap distribution was single discrete level type. Such studies have been extended to 1,1′-ferrocenedicarboxylic acid $Fc(COOH)_2$ in order to study how various structure-dependent transport parameters are affected by substitution of two –COOH groups in FcH unit. FcH is known to be a photoconductor.[7)] The intensity dependence of photocurrent is expected to provide valuable informations on the nature of distribution of traps in this material. A program was taken for such photoconduction studies in case of FcH, Fc(COOH), and $Fc(COOH)_2$ in order to check whether the nature of distribution of traps determined from the photoconduction studies agree with the results obtained from the dark conduction measurement. In this paper we report some interesting results of our experiment. The earlier reported[3,4)] results on the dark conductivity of FcH and Fc(COOH) have been considered for comparison with that of $Fc(COOH)_2$.

Experimental

High purity microcrystalline FcH, Fe(COOH), and $Fc(COOH)_2$ in powder form were obtained from Aldrich Chem. Co., Inc. (Milwaukee, Wisconsin, U.S.A.). These materials were purified again by repeated crystallization and then the dry materials were gently crushed in a morter and powdered finely. Applying the usual procedure[8,9)] the conductivity cells were made in air by placing about 10 mg of the fine powder of the materials on a clean stainless steel electrode (plate) in safe light illumination. Two Teflon® spacers, 2 mils (0.00508 cm) thick, were positioned near the edges of the electrodes, and the powdered materials were flattened by gently rotating a piece of conductive glass electrode on the top with the conducting side making contact with the sample. The Teflon® spacers maintained the separation between the electrodes. To maintain the sandwich cell, two spring clips were fixed at a moderate pressure (≈0.035 MPa) at the ends of the electrodes.

The cell was placed in a specially designed conductivity chamber made of brass and fashioned with Teflon®,[10,11)] with a quartz window for photoconductivity studies. A d.c. voltage of 27.0 V from dry batteries was applied across the electrodes as a bias potential in all measurements except the measurement on current–voltage characteristics. The temperature of the conductivity cell was controlled by a Proportional Temperature Controller (model no. RTE-110) of Neslab Instruments Inc., Newington, New Hampshire, U.S.A. Temperatures were measured by using a copper–constantan thermocouple attached at the top of the metal electrode and a panel meter (model no. HIL 2301) of Hindusthan Instruments Ltd., India. Repeated heating and cooling treatments of the sample cell, initially in vaccum and finally in dry nitrogen atmosphere ensured desorption of water vapor or any other preadsorbed vapors/gases. All the conductivity measurements were made with a programmable electrometer (model no. 617) of Keithley Inst., Inc., Cleveland, Ohio, U.S.A. Mercury lamp (125 W) was used for steady state photoconductivity studies. Various neutral

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density filters were interposed in the light beam path to control the light intensity.

In this experiment the conductivity cell consisted of two junctions of stainless steel electrode/metallocenes and conducting glass/metallocenes. To check whether the junctions were rectifying or ohmic, current measurements in a sandwich cell in case of each material were performed with forward as well as reverse bias. The values of current measured with both forward and reverse bias were almost equal which indicated that the junctions were ohmic.

Results and Discussion

The steady state dark current (I_d) flowing in an insulator in the ohmic region arises due to the drift of thermal charge carriers present in the material. At sufficiently higher voltages, the conduction is dominated by the injected charge carriers from the electrodes through the ohmic contacts and gives rise to space charge limited currents (SCLC). The dark currents (I_d) have been measured as a function of applied voltages (V) as well as temperature (T). As the pressure upon the sandwich cell was constant (clipping pressure ≈0.035 MPa), the change in I_d was solely due to change in either the applied voltage or the temperature.

The ohmic dark current, I_d, is given by[12)]

$$I_d(\text{ohmic}) = n_o q\mu(A/d)V \tag{1}$$

whereas for the simple case of single discrete trapping level SCLC can be written as[12—15)]

$$I_d(\text{SCL}) = (9/8)\epsilon_o\epsilon\mu_e A\left(V^2/d^3\right) \tag{2}$$

where, n_o=thermally liberated free carrier density; q= electronic charge; μ= microscopic mobility; A= area of the sample cell; d=interelectrode separation; ϵ_o= free space permitivity; ϵ=dielectric constant; $\mu_e=\mu\cdot\theta$= effective drift mobility; θ=ratio of free to trapped charge carriers.

For an exponential distribution of traps, the current in SCLC region is writtern as[12—15)]

$$I_d(\text{SCL}) = q\mu N_c VA/d\left[\epsilon_o\epsilon V/qd^2N_t(\text{e})\right]^{T_c/T} \tag{3}$$

where, N_c=the effective density of states in the conduction band, $N_t(\text{e})$=total density of electronic levels in the exponential distribution and T_c=the characteristic temperature of the exponential trap distribution.

The cross-over from ohmic to SCLC takes place at the voltage V_t given by[12—15)]

$$V_t = (8/9)qd^2n_o/\epsilon_o\epsilon\theta \tag{4}$$

From Eq. 3 it is clear that for an exponential distribution of traps in a material with T_c greater than T the slope, $S=[(T_c/T+1)]$ of the $\log I_d$ (SCL) vs. $\log V$ will be greater than 2. From the studies of current (dark)–voltage characteristics it has been observed[3)] that in case of FcH and Fc(COOH) the value of S was greater than 2. To find out the nature of distribution of traps in Fc(COOH)_2, we have studied the current–voltage characteristics of this material at different cell temperatures. The logarithmic plots of I_d against V for Fc(COOH)_2 at different cell temperatures are shown in Fig. 1. The values of the slope S have been evaluated from each plot. The slope $S\approx1$ for lower voltages, whereas $S>2$ at higher voltages. This indicates that the trap distribution in Fc(COOH)_2 is of exponential type. Thus, measurements of the steady state SCL currents in polycrystalline specimens have shown that the currents are controlled by traps distributed exponentially within the forbidden energy gap. The traps in these specimens may be due to structural defects or due to the presence of perturbed molecules (impurities) in the lattice causing the change of polarization energy in the perturbed regions.[16)] The estimated value of T_c from the I_d-V plots at room temperature for FcH, Fc(COOH), and Fc(COOH)_2 are presented in the Table 1. From Table 1, it is seen that the T_c value for FcH is highest, whereas the same for Fc(COOH)_2 is lowest. A lower T_c value indicates that either the structural defects are less or the presence of impurities is relatively low. A systematic decrease of T_c with increasing number of substituted –COOH group in the ferrocene unit indicates that either the structural defects arising from the constitution of the molecules of the materials or the

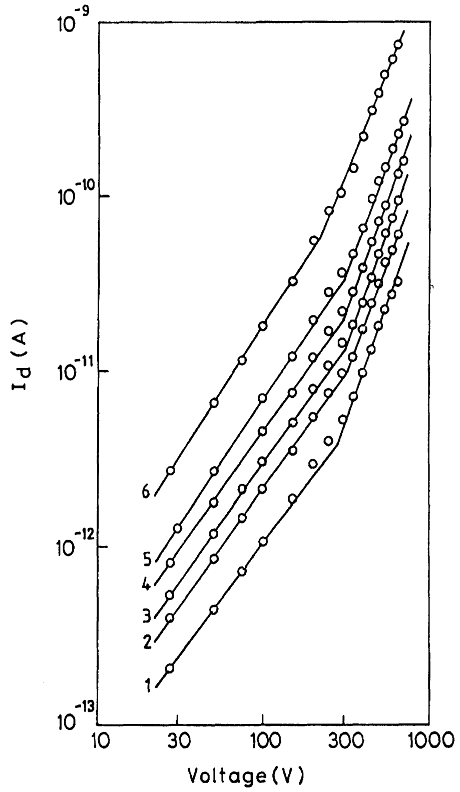

Fig. 1. The logarithmic plots of I_d against voltage for Fc(COOH)_2 at different cell temperatures: (1) 296.2; (2) 302.97; (3) 306.76; (4) 310.75; (5) 316.54, and (6) 328.75 K.

Table 1. Calculated Values of T_c, E_d (ohmic), E_d (SCL), E_{ph} for 100 % Illumination and γ for FcH and Its Derivatives

Materials	T_c	E_d (ohmic)	E_d (SCL)	E_{ph}	Value of γ for a cell temperature of 303.45 K	
	K	eV	eV	eV	from Fig. 3	from Eq. 9
FcH	704	1.31	1.31	0.80	0.92	0.70
Fc(COOH)	563	1.45	1.26	0.60	1.07	0.65
$Fc(COOH)_2$	500	1.62	1.62	1.00	0.58	0.62

presence of impurities vary systematically with the increasing number of substituted –COOH group. But the above stated possibility of systematic variation of impurities is relatively remote. Thus it appears that the trapping properties of the solids under study are related to the structure of the materials.

In organic/organometallic semiconductors, the temperature dependence of the steady state dark current generally follows the expression[17)]

$$I_d = I_o \exp\left(-E_d/2kT\right) \tag{5}$$

where I_o is preexponential factor and E_d is the activation energy for dark conduction. The slope of the linear plot of $\log I_d$ vs. $1/T$ gives the value of E_d. The estimated E_d values (Table 1) of $Fc(COOH)_2$ are equal in both ohmic and SCLC regions. This result indicates that $Fc(COOH)_2$ is an extrinsic[14)] material. The activation energy values of FcH and Fc(COOH) for ohmic and SCLC regions are also presented in Table 1 for compariosn. Table 1 shows that FcH is also an extrinsic material whereas Fc(COOH) is nonextrinsic as the E_d values in both ohmic and SCLC regions differ slightly. It is evident from Eq. 4 that V_t has a thermal activation energy equal to the difference of activation energies in the ohmic and SCLC regions. So, V_t is expected to be temperature independent in case of FcH and $Fc(COOH)_2$ as the two activation energy values are equal, i.e., the materials are extrinsic.[14)] Although in case of FcH and $Fc(COOH)_2$ activation energy values are same in ohmic and SCLC regions, V_t has been found to be temperature dependent. It has been observed[3,4)] that V_t shifts slightly towards the lower values with increasing temperature for FcH and Fc(COOH). In case of $Fc(COOH)_2$, the value of V_t does not vary appreciably for a small change in temperature but V_t shifts towards lower value for a large increase in temperature (Fig. 1). A small decrease in V_t with increasing cell temperature as observed in the present case may be due to corresponding decrease in the factor n_o/θ with increasing temperature, as suggested by Eq. 4.

The termal activation energy value E_d is related to the structure of the solid materials. Generally the thermal activation energy decreases with increasing number of π-electrons associated with the molecular structure.[18)] These present materials do not show such a relation. In the present case, the material having two –COOH groups in the ferrocene ring system shows higher E_d value compared to the material with single –COOH group in the ferrocene ring system. The changes in E_d value is expected to be originated from the modifications in the π-electron systems as a result of substitution of an additional –COOH group in the ferrocene ring.

The temperature dependence of the steady state photocurrent I_{ph}. (similar to I_d) in case of organic/organometallic materials generally follows the expression

$$I_{ph} = I'_o \exp\left[-E_{ph}/2kT\right] \tag{6}$$

where I'_o is the preexponential factor and E_{ph} is the activation energy for the photoconduction. The slope of the linear plots of $\log I_{ph}$ vs. $1/T$ gives the value of E_{ph}. In Fig. 2, $\log I_{ph}$ vs. $1/T$ plots for $Fc(COOH)_2$ at different intensities of exciting light source are shown. These plots are fairly linear. The linearity of these plots indicates that the photoconductivity is an activation process. The E_{ph} values have been calculated at different intensities of exciting light source for all the materials studied and it is found that in case of FcH and Fc(COOH) the E_{ph} values are almost independent of intensity of the exciting light source in the observed range of intensity of light and cell temperature. But in case of $Fc(COOH)_2$ a gradual decrease in E_{ph} value with increasing intensity of exciting light source has been observed as shown in Fig. 2. The E_{ph} values for FcH, Fc(COOH), and $Fc(COOH)_2$ for 100% illumination is shown in Table 1. The photoactivation energy values are in general much lower than the dark activation energy values. The difference in the activation energy values in the dark and under illumination is evident due to the change in the charge carrier density and its distribution in different energy states and traps under illumination.

The photocurrent at room temperature is higher than the dark current in the present case even at the lowest level of excitation. But at higher temperatures I_{ph} becomes lower than I_d. Hence, the factor I_{ph}/I_d decreases gradually with increasing temperature.

The photocurrents in these materials have been observed to increase with increasing voltage. The evaluated values of slopes of the plots of logarithm of I_{ph} (at 100% illumination) against applied voltage at room

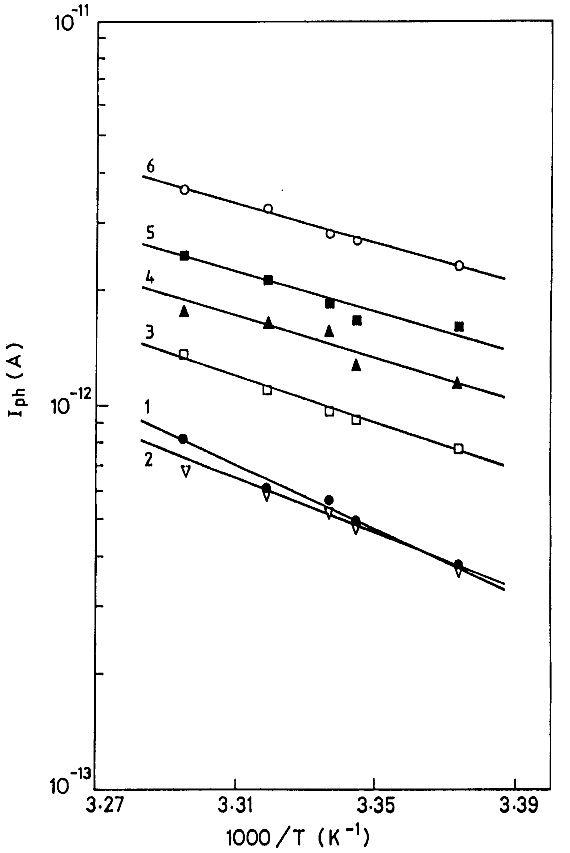

Fig. 2. Plots of logarithm of I_{ph} versus reciprocal of temperature for $Fc(COOH)_2$ at different intensities (I_B) of the exciting light source: (1) I_d (●); Values of I_B: (2) 20 % (▽); (3) 36 % (□); (4) 49 % (▲); (5) 64 % (■); and (6) 100 % (○). The activation energy values evaluated from the plots (1) to (6) are 1.62, 1.42, 1.19, 1.08, 1.02, and 1.00 eV, respectively.

temperature for the materials under study were well within the agreeable limits of the ohmic character of the photocurrent and therefore injection of charge carriers from the electrodes does not seem to be present in the working range of voltage.

The intensity (I_B) dependence of photocurrent of the materials was studied at different sample cell temperatures and the results of such studies are shown in Fig. 3 for different materials at 303.45 K. It is evident from this figure that there is a power law dependence of photocurrent on the intensity of incident radiation. So, one can write

$$I_{ph} \propto I_B{}^{\gamma} \tag{7}$$

where the exponent γ is the characteristic of the photoconducting system and it depends on the amount of recombination of the photogenerated charge carriers during transport to the electrodes. A plot of $\log I_{ph}$ vs. $\log I_B$ yields a straight line (as in Fig. 3) where the slope of this plot yields the value of γ. For a given range of light intensity one charge carrier recombination channel predominates and this particular channel determines the value of γ. In the ohmic range of dark current the intensity dependence of photocurrent is generally given by[19]

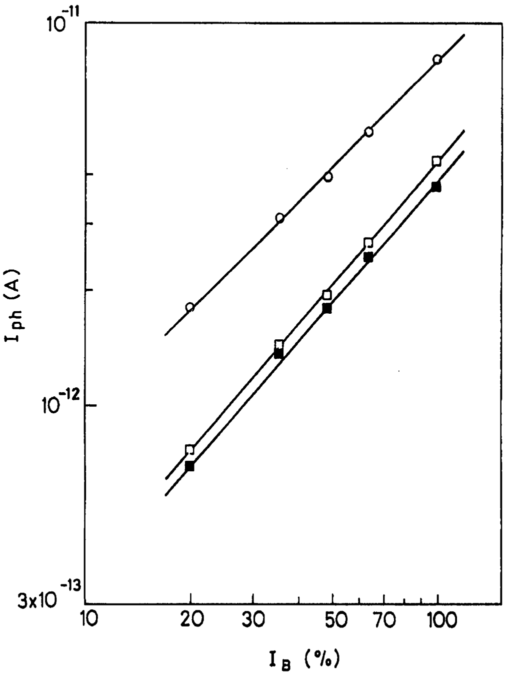

Fig. 3. Plots of intensity (I_B) versus I_{ph} for FcH, Fc(COOH), and $Fc(COOH)_2$ at a cell temperature of 303.45 K. FcH [○]; Fc(COOH) [□]; and $Fc(COOH)_2$ [■].

$$I_{ph} \propto I_B{}^{\{T_c/(T_c+T)\}}. \tag{8}$$

By comparing this Eq. 8 with Eq. 7 one can obtain a relationship between the parameter γ and T_c (characterizing the exponential trap distribution) which is given by

$$\gamma = T_c/\,(T_c + T)\,. \tag{9}$$

The usual conditions $T_c > T$, explains the fact that for any material with exponential trap distribution the value of γ should lie between 0.5 and 1. For FcH, Fc(COOH), and $Fc(COOH)_2$ on excitation by a polychromatic light from a mercury lamp (125 W) the values of γ obtained from the plots of Fig. 3 is presnted in Table 1. The values of γ estimated from the intensity dependence of photocurrent indicate clearly that the trap distribution in FcH and $Fc(COOH)_2$ is of exponential type. This conclusion agrees with the results obtained from the current (dark)–voltage characteristics. The value of γ for Fc(COOH) obtained from Fig. 3 is slightly higher than the maximum value expected for the exponential distribution of traps. The sublinear intensity dependence of photocurrent ($0.5<\gamma<1$) as observed in case of FcH and $Fc(COOH)_2$ is the result of cooperation of traps and recombination centers. The superlinear dependence of photocurrents on the light intensity with

$\gamma > 1$ as observed in case of Fc(COOH) can be due to the influence of several defect states with different electronic behaviors (hence with different charge carrier-recombination properties). In case of FcH, Fc(COOH), and $Fc(COOH)_2$ for a cell temperature of 303.45 K the γ values obtained from Eq. 9 using T_c values calculated from Eq. 3 are also shown in Table 1. From Table 1 it is observed that in case of $Fc(COOH)_2$ the value of γ obtained from Fig. 3 is in good agreement with the value evaluated from Eq. 9. But in case of FcH and Fc(COOH), the value of γ obtained from Fig. 3 is appreciably higher than the corresponding value evaluated from Eq. 9. These higher values of γ may be caused by the presence of a set of traps, which are unoccupied in the dark but become increasingly filled with increasing light intensity.

It has been mentioned earlier that FcH and $Fc(COOH)_2$ are extrinsic materials whereas Fc(COOH) is nonextrinsic. Thus on substitution of single –COOH group in FcH unit the material becomes nonextrinsic. But on substitution of two –COOH groups the material remains extrinsic. Again in case of FcH and $Fc(COOH)_2$ the intensity dependence of photocurrent has been observed to be sublinear. In contrast, the superlinear dependence of photocurrents on the light intensity has been observed in case of Fc(COOH). Therefore, this present investigation shows that the substitution of single –COOH group in the FcH unit changes significantly some properties of the material whereas on substitution of two –COOH groups in the FcH unit, these material properites are retained. Ferrocene is a simple organometallic complex which may be formally considered in terms of two coplanar cyclopentadienyl rings lying above and below an iron center. Medina et al. have reported recently$^{20)}$ that the two coplanar cyclopentadienyl rings of ferrocene unit may rotate with respect to each other about the iron center as if the metal acts as a "ball bearing" between the two plane surfaces. On substitution of single –COOH group in FcH unit, the molecular structure of the material becomes asymmetric in contrast to the substitution of two –COOH groups. The asymmetric molecular structure affects much the "ball bearing" motion of the cyclopentadienyl rings and influences the electrical properties as stated above.

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