Solid-state Properties of Evaporated Methyl Viologen

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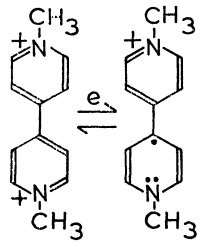
The methyl viologen film evaporated at about 250 °C has a violet color, and its electronic absorption spectrum resembles that of the enzymatically reduced methyl viologen. The evaporated film becomes colorless upon the introduction of air. By means of the photoemission spectroscopical method, a very low ionization potential, 3.6 eV, was obtained for the evaporated methyl viologen film. The character of the evaporated methyl viologen is a free-radical one, and its specific resistivity is very low as compared with other organic radicals.

Methyl viologen (abbreviated as MV hereafter) was found to be a good oxidation-reduction indicator by Michaelis and Hill in 1933.[1] This compound has been widely used in the research field of biochemistry, for the oxidation-reduction reaction is conducted by the transfer of one electron and its redox potential is independent of the hydrogen-ion concentration of the solution. For example, the enzymatic reduction of MV in the presence of hydrogenase is as follows:

$$1/2H_2 + MV^{2+} \xrightarrow{\text{hydrogenase}} H^+ + MV^+$$

where MV^{2+} and MV^+ represent oxidized and reduced methyl viologen respectively; the structures of the reduced and oxidized MV are shown below.



Oxidized-MV Reduced-MV

MV could be evaporated *in vacuo* at about 250 °C. The color of the evaporated film was violet, and the electronic spectrum resembled that of the enzymatically reduced MV. This evaporated film will be denoted as "reduc-MV." When the evaporated film was exposed to air, the violet color of the film vanished and the electronic spectrum changed to that of the oxidized MV (denoted as "oxi-MV").

In order to ascertain the reduc-MV, we measured the solid-state properties of these two species of MV, reduc-MV and oxi-MV. The vacuum ultraviolet photoemission spectrum of the reduc-MV, which is stable only in a vacuum, and that of the oxi-MV were observed, and the difference in the ionization potentials (*IP*) of the two species, as estimated from their photoemission spectra, is discussed.

Moreover, in order to understand the electron transport in the organic radical, the electrical conductivity of these MV films was observed.

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Experimental

The electronic absorption spectrum of the 'oxidized MV' in an aqueous solution and that of the enzymatically 'reduced MV,' which was reduced by a hydrogen gas in the presence of hydrogenase, were obtained by an ordinary method. The film was obtained on a quartz plate by evaporation at about 250 °C under a vacuum of 10^{-4} Torr. The absorption spectra of the evaporated film and that exposed to air were measured.

The measurements of the vacuum ultraviolet-photoemission spectroscopy were carried out using a vacuum ultraviolet monochromator combined with a hydrogen-discharge lamp. The photoemission measurement was done by the ac modulated retarding potential method described earlier,[2] but with a little modification of the collector-cell housing. The energy distribution curves (EDCs) of the reduc-MV and oxi-MV were thus obtained. The spectral dependence of the quantum yield (SDQY) was also found for oxi-MV. These measurements were carried out at about 3×10^{-6} Torr because the reduc-MV was easily changed to the oxi-MV under a low vacuum.

The electrical conductivity of these species was measured at 8×10^{-7} Torr in a high-vacuum bell-jar system by the two-probe method. The aluminum metal for the electrodes and the MV were successively evaporated on a clean quartz substrate as a surface-type arrangement; the details of the experimental procedure have been reported in a previous paper.[3]

In order to introduce a dry oxygen gas into the bell-jar, oxygen gas from a commercial cylinder was flowed to the bell-jar *via* a molecular sieve trap cooled with liquid nitrogen, and the change in the conductivity was examined. To observe the temperature dependence of the conductivity, the sample was heated by an outside-mantle heater.

Results and Discussion

Electronic Absorption Spectra. Figure 1 shows the electronic absorption spectra. The spectrum of the

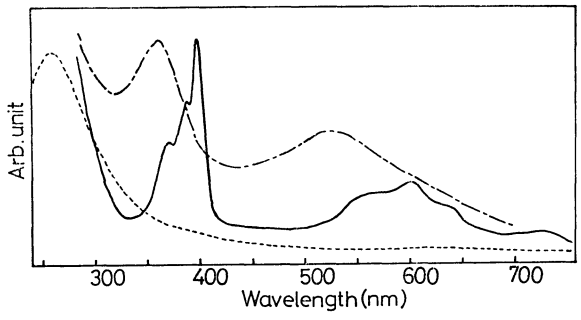

Fig. 1. The electronic spectra of MV.
---: Oxidized MV, —: enzymatically reduced MV (in aqueous solution), -·-: reduc-MV (in solid state).

oxidized MV reveals the absorbance maximum at 260 nm. The spectrum of enzymatically reduced MV has its vibrational structures at 367, 384, and 394 nm and another peak at 605 nm. The electronic spectrum of the reduced MV was investigated by Michaelis and Hill.[1] They proposed that the one excess electron belongs to the reduced form and is shared by the two nitrogen atoms, and that the blue color is explained by their resonance.

On the other hand, the spectrum of the evaporated film of MV shows the absorbance maxima at 358 and 520 nm. This spectrum resembles that of the enzymatically reduced MV, and the energy differences between the 358 nm peak of the film and 394 nm peak of the reduced MV, and also between the former's 520 nm and the later's 605 nm peak, are about 8700 cm^{-1}. When the evaporated film of MV was exposed to air, the violet color of the film disappeared and the spectrum coincided with that of the oxidized MV.

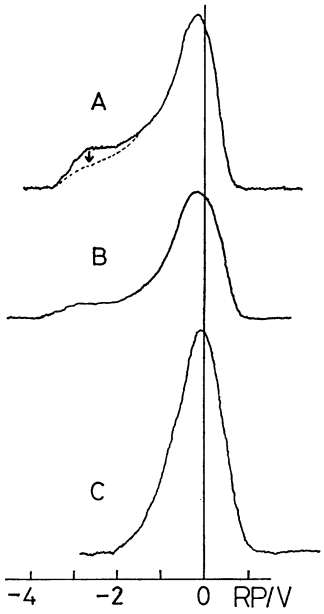

Fig. 2. The EDCs of reduc- and oxi-MV as a function of incident photon energy. A, B; reduc-MV. C; oxi-MV. Incident photon energy. A; 7.75 eV. B; 8.16 eV. C; 7.75 eV. ↓ shows the change of EDC from reduc-MV to oxi-MV.

Vacuum Ultraviolet Photoemission Spectroscopy. The EDCs of the photoelectron emitted by vacuum ultraviolet-light radiation are shown in Fig. 2. The EDCs of the reduc-MV produced by the incident-light energies of 7.75 and 8.16 eV are the two upper curves, while that of the oxi-MV irradiated by a photon energy of 7.75 eV is the bottom curve. A low-energy stationary peak was observed in all spectra, while a shoulder was obviously observed in the two upper spectra.

The values of the stopping voltage, V_0, and the saturation voltage, V_s, of the retarding potential for photoemission are obtained from the EDCs; they are listed in Table 1. The *IP* was calculated from V_0 and V_s by means of the following equation;

$$IP = h\nu - e(V_s - V_0)$$

Table 1. The incident photon energy, V_0, V_s, and the *IP* of the reduc- and oxi-MV

	EDC				$Y^{1/3}$
	$h\nu$(eV)	V_0(V)	V_s(V)	*IP*(eV)	*IP*(eV)
Reduc-MV	7.75	−3.5	0.7	3.6	
	8.16	−3.8	0.7	3.7	
Oxi-MV	7.75	−2.1	0.9	4.8	4.8—4.9

The calculated ionization potentials are also listed in Table 1. The stopping voltage of the oxi-MV was low compared with that of the reduc-MV, and the energy difference between them reached more than 1 eV.

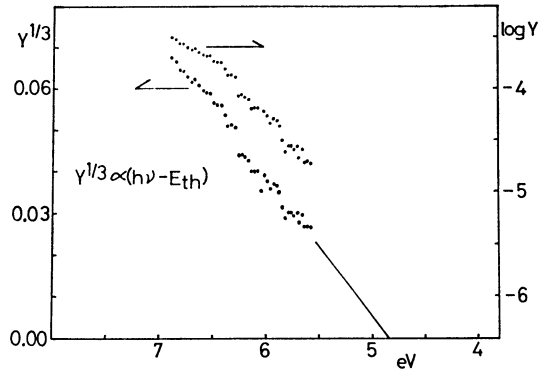

Fig. 3. The SDQY plots and cube root plots of the photoemission yield for oxi-MV.

Figure 3 shows SDQY near the threshold-energy region. Considering the experimental error, the small ripples of the plots are meaningless. The quantum yield decreased gradually with a decrease in the photon energy. The quantum yield in organic crystals and charge-transfer complexes near the threshold energy is subject to the conventional power law:

$$Y^{1/3} \propto (h\nu - E_{th})$$

where E_{th} is the threshold energy.[4]

The threshold energy value of 4.8—4.9 eV was obtained for oxi-MV from the above equation. This value was nearly equal to the *IP* calculated from the EDC of the oxi-MV. The threshold energy of the reduc-MV was not obtained accurately, because the photoemission is sensitive to surface conditions. The EDC of the reduc-MV changed gradually to that of the oxi-MV, as is shown by ↓ in Fig. 2. The phenomenon results because the surface of the reduc-MV gradually changes to the oxi-MV.

From Table 1, the difference of *IP* between the reduc- and oxi-MV can be seen to be more than 1 eV. This finding is consistent with the concept that the reduced form has one excess electron, which may occupy the lowest vacant molecular orbital of the oxi-MV.

The *IP* of the reduc-MV is very low compared with those of other organic substances. Only the organic dyes, crystal violet and malachite green have comparably low *IP* values.[5] Crystal violet and malachite green have a dimethyl amino group, which is constructed of four-valencies nitrogen atoms. The resonance may be

expected to occur over the whole molecule, and this resonance reduces the value of *IP*. Taking into account the low *IP* of the substance containing the dimethyl amino group measured by Nakato *et al.*, we consider that the same behavior can be expected in the reduc-MV.[6]

Electrical Conductivity. From the voltage dependence of the electrical conductivity for the two species of MV, there exists an ohmic contact. The electrical conductivity was held to be constant during the long observation period; also, the observation was carried out under a high vacuum, 8×10^{-7} Torr, so the predominant contribution to the conductivity is electronic, not ionic.

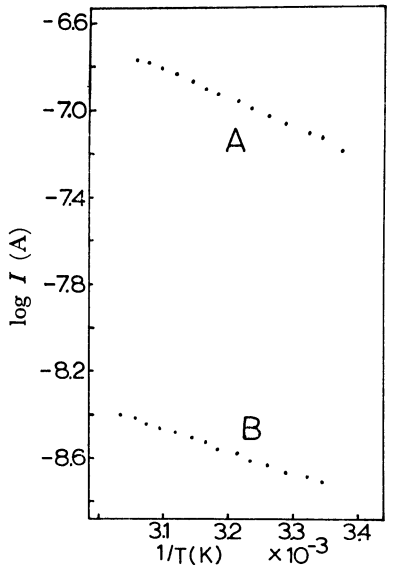

Fig. 4. The temperature dependence of the electrical current of the reduc- and oxi-MV. A; reduc-MV. B; oxi-MV.

The temperature dependence of the electrical conductivity is shown in Fig. 4. From the plot of log *I* *vs.* $1/T$, the activation energies of 0.2_6 and 0.2_0 eV were obtained for the reduc-MV and oxi-MV respectively by means of the following equation;

$$\sigma = \sigma_0 \exp(-\Delta E/kT)$$

where σ is the electrical conductivity; ΔE, the apparent activation energy, k, the Boltzmann constant, and T, the absolute temperature. The activation energy and the electrical current are summarized in Table 2. The difference in the activation energies of the reduc- and oxi-MV is so small that it is meaningless.

The specific resistance of the reduc-MV was estimated to be 10^5—10^6 Ωcm, for the thickness of the sample was estimated to be 10^3—10^4 Å. This value, 10^5—10^6 Ωcm, is extraordinary small compared with those of the polycyclic aromatics, polymer and organic dyes; it is in the range of the inorganic semiconductors.

Table 2. The electrical current of some species of MV[a]

State	T(°C)	ΔE(eV)	I(A)
Reduc-MV	17	0.26	1.5×10^{-13}
	17		6.3×10^{-8}
	28		7.7×10^{-8}
	54		1.7×10^{-7}
Reduc-MV+O_2	23		4.7×10^{-8}
	15		4.3×10^{-8}
Reduc-MV+O_2 +H_2O	17		2.5×10^{-6}
Oxi-MV	17	0.20	2.2×10^{-9}
	54		3.8×10^{-9}

a) Applied voltage: 20V.

The color of the reduc-MV did not change upon the introduction of water-free oxygen, while the electrical conductivity decreased a little. The high conductivity of the reduc-MV was not, therefore, attributed to the oxygen. The electrical conductivity increased extraordinarily when the reduc-MV was exposed to the atmosphere, and the maximum current reached 2.5×10^{-6} A. In this procedure, the color of the reduc-MV vanished, so the coexistence of oxygen and water is shown to be necessary for the change from reduc-MV to oxi-MV. When the oxygen and water were excluded to measure the conductivity of oxi-MV, the oxi-MV was less conductive than reduc-MV. The reduc-MV exists as a radical, so it is reasonable to ascertain its high conduction by its having excess electrons.

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