SHORT NOTE ON THE INFRARED SPECTRUM OF SbCl$_6^-$ IN THE SOLIDS OF CROSS-LINKING POLY-N-VINYLCARBAZOLE*

By

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(Received Oct. 31, 1975)

As a result of previous work by the author[1] it can be said that the solids of poly-n-vinylcarbazole (PVK) complexed with SbCl$_5$ those precipitate in the chloroform have only SbCl$_6^-$ ions for the inorganic species, because of their single absorption band due to the inorganic component at 345 cm^{-1} as seen in Fig. 1. (The PVK is cross-linking with $-\overset{+}{\text{C}}$H– at the 3-position of carbazole ring as is stated by Ledwith *et al.*[2]) The conditions of formation and the electronic properties of both samples 1–A and 1–C are summarized in Tables I–II. It has been also shown[1] that the paramagnetism of solids depend proba-
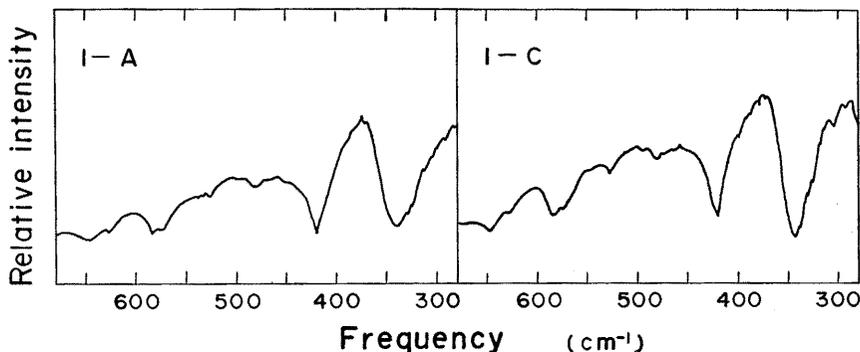

Fig. 1. Infrared spectra of powders at long wavelength region[1].
Spectra were taken with samples in the KBr disks. Left, spectra of 1–A; right, spectra of 1–C. A characteristic band for the complexes is at 345 cm^{-1}. A band at 420 cm^{-1} is a characteristic of the PVK and other peaks are due to the PVK or probably due to the $\nu_1 + \nu_3$ and $\nu_2 + \nu_3$ vibrations of the octahedral SbCl$_6^-$ as described in this paper.

Table I. The conditions of formation of both samples 1–A and 1–C.

Sample	Molar ratio between both components used in preparation, PVK (monomer unit): $SbCl_5^a$.	Temperature of reaction in the chloroform.	Times of reaction.	Weight percentages of $SbCl_6^-$ in the powder[b].
1–A	2 : 5	20°C	24 hours	$32 \pm 2\%$
1–C	2 : 5	40	24	32 ± 2

[a]Both chloroform solutions of PVK and $SbCl_5$ before mixing are as follows: PVK concentration, 1×10^{-4} mol/ml; $SbCl_5$ concentration, 1×10^{-3} mol/ml.
[b]determined as residual percentages for the polymer components.

Table II. The electronic properties of both samples 1–A and 1–C.

Sample	Color	Electrical conductivity (D. C.) at 24°C.[a]	Unpaired spin density at room temperature.[b]	Absorption linewidth of ESR.[c] (ΔH_{msl})
1–A (Powder)	Yellowish green.	6×10^{-6} $\Omega^{-1} \cdot cm^{-1}$	2.2×10^{20} $(3.2 \times 10^{20})^d$ Spins $\cdot$ g^{-1}	2 Gauss
1–C (Powder)	Slightly dark green.	1×10^{-6}	2.2×10^{20}	4

[a]measured in vacuum 5×10^{-3} Torr.
[b,c]measured in vacuum 10^{-4} Torr.
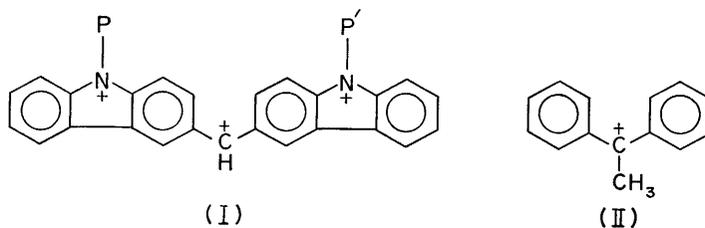[d]quoted from another series of work by the author.

Fig. 2. Molecular structures of both the intermediate and the related cation[1].
(I) Intermediate based on the previous work[1]. P, P': different polymer chain. (II) Cation for the protonated diphenylethylene.

bly on the cationic intermediates as seen in Fig. 2.   The powder of 1–A has an electrical conductivity considerably higher than 1–C in spite of the equal unpaired spin density between them.   In addition, on heating to 100°C, the peak of infrared absorption initially appeared at 345 cm^{-1} was fixed at 330 cm^{-1}.   (In the PVK-rich complexes, the spectrum split away to dual bands, 355 cm^{-1} and 330 cm^{-1}, the latter being strong and broad.) Then we assigned the band at 330 cm^{-1} for an absorption due to the vibration of SbCl$_6^-$, and supposed that many of SbCl$_6^-$ ions in the 1–A had excess electrons as [SbCl$_6^-$]$^{2-}$, and contributed to the electrical conduction.   On the one hand, we also supposed that, in the solid of 1–C, the excess electrons would be trapped in the amorphous region, and the band at 345 cm^{-1} was attributed to the phonon-like mode in the polymeric region.

However, any absorption like a side band cannot be found, at least, in the high frequency region.   Furthermore, a very striking result of our experiment is that the variation of absorption intensity at 345 cm^{-1} is not unique with respect to composition of the complex but rather the same as the variation of unpaired spin density.   This is shown in Fig. 3, and so the problem of spectral assignment has been yet unsolved.

Recently, the author found that the both powders 1–A and 1–C, those were studied soon after preparation, had distinct behaviors when irradiated for near-infrared rays at low temperature.   The photocurrent of 1–A was large compared with the photocurrent of 1–C, but the decrease of ESR absorption of 1–C was large compared with the decrease of 1–A.   In comparison of these reversible phenomena, we can see the excess electrons on
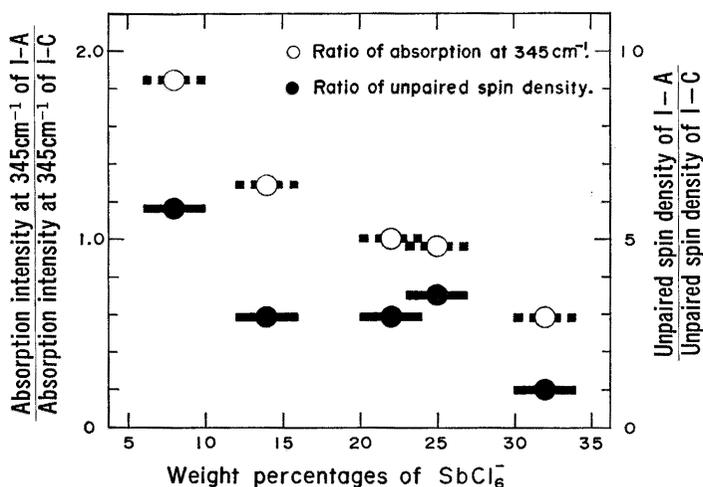

Fig. 3.   Variations of the absorption intensity at 345 cm^{-1} and the unpaired spin density with composition of the complex.

Both variations are shown for the ratio of the value of 1–A to the value of 1–C.   Open circle, ratio of the absorption intensity at 345 cm^{-1}; full circle, ratio of the unpaired spin density.   Data were quoted from the previous work[1] on the complexes of both series 1–A and 1–C.

the $SbCl_6^-$ in the solids of both 1–A and 1–C, though the predominant excitation is apparently different from each other. Consequentially, the band at 345 cm^{-1} must be always due to $[SbCl_6^-]^{2-}$, and the spectral splitting after heat treatment must be understood as the static Jahn-Teller effect to the F_{1u} mode of $SbCl_6^-$ free from excess electrons which recombined with the cationic intermediate. Our preliminary results on the evidence of this conclusion are as follows.

To investigate photocurrents the disk-like specimens (about 0.7 mm thick and 13 mm in diameter) were prepared by pressing each powdery complex under 6×10^3 kgw/cm^2, and placed between NESA electrodes. The specimen holder is a copper casing which is available to keep at $-170°$C and to keep in vacuum 10^{-6} Torr. Intensity of illumination at the position of specimen was obtained as 5.3×10^4 lux by the use of an incandescent lamp. (The spectral characteristics of the lamp is shown in Fig. 4.) Fig. 5 shows the photocurrent of 1–A. Using some glass filters, it was recognized that no current was found under irradiation for visible lights and infrared rays of the wavelengths shorter than 1 μm. In Fig. 5, the effect of insertion of the "cold filter" having a spectral response in Fig. 4 is also studied. It is obvious that the carrier generation is limited to the photon energy near 1.0 eV. In addition, the photocurrent of 1–A exceeded to the 1–C, and the latter had about one-tenth of the maximum value in Fig. 5.

On the photocurrent of 1–A, by means of both the positive and the negative electrode illumination, almost same current was observed. This is however not reliable to understand the sign of carriers because of the unknown path-length of incident rays in the pressed powder together with a large trapping effect as seen in Fig. 5.
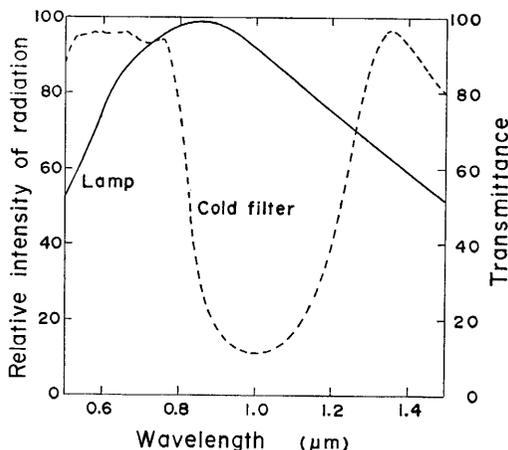

Fig. 4. Spectral characteristics of the incandescent lamp and spectral transmittance of the "cold filter" used for the present work.

    Solid line, relative intensity of radiation as a characteristic of the lamp; broken line, transmittance of the "cold filter".
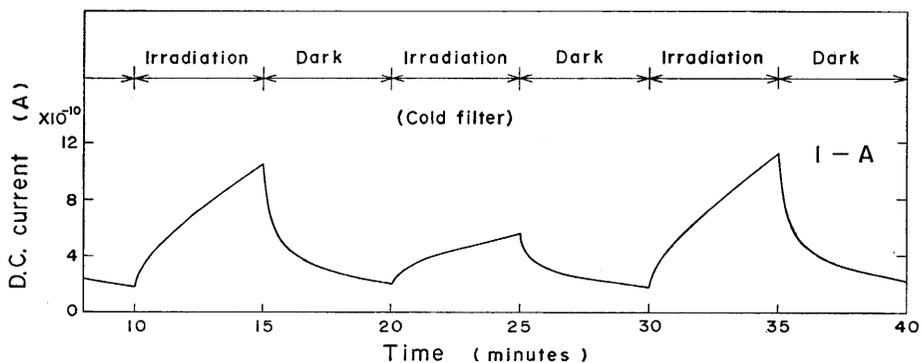
Fig. 5.   Photocurrents of the sample 1–A.
     Temperature of the specimen holder was usually kept at $-170°C$ during the
measurement.   In this figure, the first and third rises of current due to the irradiation
were obtained without any filter, while the second rise was obtained under irradiation
through the "cold filter".   Other conditions: field setting, 50 V/cm; polarity of the
irradiated surface, negative.

To investigate ESR absorptions, a small amount of the powdery complex was put in a thin Pyrex tube (1.5 mm in diameter) and was kept in vacuum 10^{-4} Torr.   The tube was suspended in a elongated Dewar flask and placed along with the center axis of a TE_{011} cylindrical cavity operated at 9.2 GHz.   The sample in a tube at liquid nitrogen temperature was illuminated by an incandescent lamp situated in front of the cavity window. (The lamp is the same one as is shown in Fig. 4.)   The lineshape of ESR absorption was usually a single symmetrical derivative curve corresponding to 2.0026 for the g-factor as described in the previous paper.[1]   The effect of irradiation for near-infrared rays to the ESR of 1–C is shown in Fig. 6.   Only solid lines correspond to the ESR data, and broken lines reveal the assumed variations obtained tentatively.   (In Fig. 6, the gradual decrease of observed intensities in a long period of measurement is probably due to the presence of ice pieces those increase gradually in the liquid nitrogen.)   The effect of insertion of the "cold filter" to the variation of ESR absorption was small compared with the effect to photocurrent.   In the presence of a "cold filter" the decrease of ESR signal due to the irradiation was about 65% for the decrease in the absence of a filter.   Transparency of the "cold filter" shows that the energy of excitation corresponds to the wavelength near 1.25 μm.   Thus the excitation related to ESR seems to be completed with a photon energy near 1.0 eV.   Furthermore, the decrease of ESR due to the irradiation on the new 1–C is considerably large as seen in Fig. 6, while the decrease on the new 1–A under same conditions was generally small (about one half) as compared with the case of 1–C.

In the previous paper,[1] we mentioned that an optical absorption at $\lambda_{max} = 430$ nm for the colloidal suspension of the complex was a characteristic band of the intermediate in Fig. 2.   (We referred to a cationic unit of the form in Fig. 2 as a "green cation" and the form having only a charge at the cross-linking point as a "blue cation" according to
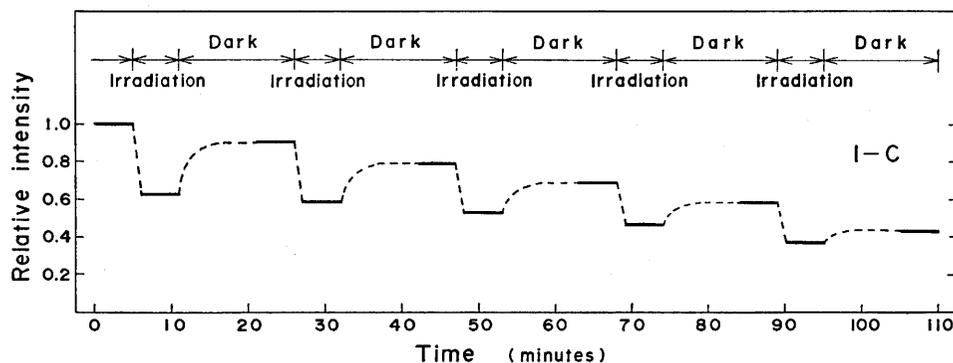
Fig. 6. Effect of the infrared irradiation to ESR absorption of the sample 1–C.
        The sample tube was usually held in the liquid nitrogen. Only solid lines correspond to
        ESR data. In order to remove the rays of wavelengths shorter than 1 μm, a long-pass glass
        filter, Toshiba IR–D1B (Transmittance: 30% at 0.9 μm, about 0% at 0.8 μm) was used in the
        course of measurement.

their personal colors.) We also mentioned that a characteristic absorption at 430 nm
should be referenced with an absorption due to the cation for the protonated diphenyl-
ethylene as was shown in Fig. 2 ($\lambda_{max} = 430$ nm, $\varepsilon_{max} = 30,000$). The absorption in this
case has been interpreted as a matter of "hyperconjugation" due to the electron owned by
the methyl radical. Now, we shall remark only to a configuration of the excited state of
this molecule in which an electron occupies the position monopositively charged at the
ground state. In the case of complex, an electron hereto mentioned will be one of the
excess electrons of $[SbCl_6^-]^{2-}$ at the excited state. From this point of view, it will be able
to suppose two different kinds of excited states of the intermediate for the low-energy
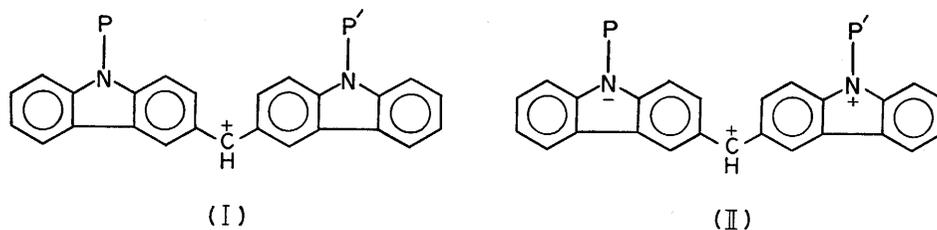excitation. This is shown in Fig. 7.

Fig. 7. Two different kinds of configuration due to the low-energy photo-excitation of the
        intermediate.
        Both configurations (I) and (II) must be completed by means of the transfer of electrons
        from the $[SbCl_6^-]^{2-}$ to the intermediate.

At the excited state (I) in Fig. 7 (that is the same configuration as a "blue cation"),
further transfer of the electron of a lone pair to the cross-linking point will require the

energy 1.9 eV for the $n \rightarrow \pi^*$ transition as described previously.[1] Therefore, a fact that the excess electron of [SbCl$_6^-$]$^{2-}$ transfers to the cross-linking point with the energy 2.9 eV (430 nm), is very reliable if the electrons can transfer to carbazole rings with the energy 1.0 eV. In addition, this low-energy excitation will be accompanied with the extinguishment of initial paramagnetism. The author believes that Fig. 6 proves this hypothesis. As is already mentioned the energy required to the low-energy excitation is now determined experimentally as 1.0 eV. As a matter of fact, the excitation corresponding to (I) will be predominant to the case of 1–C, and the extraordinary conduction cannot be expected from this type of excitation.

However, as is shown in Fig. 7 (II), the excitation in which both excess electrons of [SbCl$_6^-$]$^{2-}$ transfer to the one side of cross-linking polymer may contribute to the conduction. In other word, the type of excitation (II) may correspond to the development of photoconduction in the 1–A.

By means of the other experiment, we obtained the activation energy for thermally stimulated currents as 0.3 eV at near room temperature. This will be related to the fact that a photon energy for the photoconductive excitation may be somewhat large compared with a photon energy for the excitation from paramagnetic to diamagnetic state. Then it can be said that the left-half ring of the excited state (II) supplies, at least, an electron, to the conduction level from a localized state on the [SbCl$_6^-$]$^{2-}$. Because the activation energy of thermally stimulated currents did not depend on composition of the complex, such a conductive element (*e.g.* a state of nitrogen in which an unpaired electron stayed probably at the orbit corresponding to the 3s orbit of a lone atom) might propagated through the carbazole ring in the nearest neighbor along the polymer chain. This will be reasonable, to some extent, in the case of photoconduction at low temperature.

In relation to this, it should be noted that the powder 1–A had a very narrow linewidth of ESR absorption as was shown in Table II. Such a narrowing is now understood as it is due to the migration of unpaired spin state in addition to the usual exchange interaction.[3]

The problem awaiting solution is the distinct behaviors between the 1–A and the 1–C. This is probably due to the different conditions of the piled structure between the positive (intermediate) and the negative ([SbCl$_6^-$]$^{2-}$) ions. From a result as is mentioned above, the state of 1–C will be rather in good order than the 1–A. Supposing the state of 1–A is out of order, two excess electrons of [SbCl$_6^-$]$^{2-}$ will have a possible transfer to the one side of cross-linking polymer at the excited state, owing to the unequilibrium of electric field for each side of polymer.

In conclusion, a cationic intermediate in the cross-linking PVK is probably piled with the [SbCl$_6^-$]$^{2-}$ and it has an optical absorption at 430 nm together with an absorption at near 1.2 μm. Both bands correspond probably to the "charge transfer absorption bands" in this case, a band at 430 nm being due to the transfer to the cross-linking point from the [SbCl$_6^-$]$^{2-}$, and another at near 1.2 μm being due to the transfer to the nitrogen atom from the [SbCl$_6^-$]$^{2-}$. More detailed results of experiment will be published elsewhere.

References

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