Mössbauer Spectroscopic Study of the β-Carotene–Iodine System

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The ^{129}I Mössbauer effect has been applied to the β-carotene–iodine system prepared by the precipitation method. The system can be described in terms of the completely charge-transferred form, $C_{40}H_{56}^{+} \cdots I_3^{-}$, where the I_3^- has a symmetrical charge distribution. The optical and electrical properties of the β-carotene–iodine system are discussed on the basis of the Mössbauer results.

OVER the last 10 years, the ^{129}I Mössbauer effect has been established as a powerful tool for the investigation of chemical bonds and of the structure of iodine-containing systems. The isomer shift (δ), the nuclear quadrupole coupling constant (e^2Qq), and the asymmetry parameter (η) have been used for the determination of charge density and distribution in interhalogen compounds, inorganic iodides, and charge-transfer (c.t.) complexes.[1-4]

β-Carotene is well known as one of the polyene dyes. In the solid state, a mixture of β-carotene and iodine was found to show electrical and magnetic properties due to the formation of a compound of stoicheiometric formula $C_{40}H_{56}I_3$.[5] Lupinski [6] measured the absorption spectra of the β-carotene–iodine mixture in various solvents. He explained that the characteristic absorption band at 1 000 nm in polar solvents was ascribable to the presence of a c.t. complex, β-carotene $\cdots I^+$, with the coexistence of the counter anion, I_3^-. Similar absorption bands were also observed in iodine-doped β-carotene films.[7,8] However, the nature of the interaction between β-carotene and iodine has, as yet, not been elucidated. In order to study the chemical structure and the charge distribution on iodine, we have carried out ^{129}I Mössbauer measurements of the β-carotene–iodine system.

EXPERIMENTAL

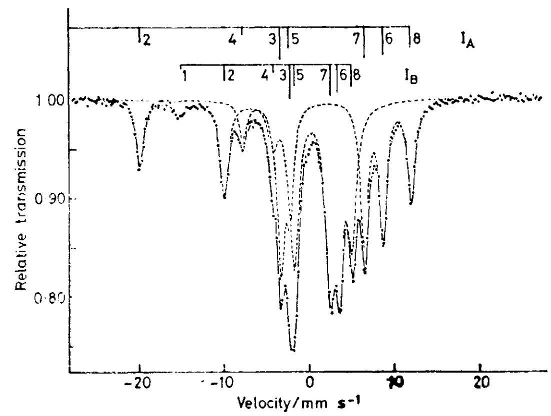
The ^{129}I used for the preparation of samples was purchased from New England Nuclear Corporation in the standard form of $Na^{129}I$ in an $Na_2[SO_3]$ solution. Molecular $^{129}I_2$ was extracted with spectroscopically pure benzene after oxidizing $Na^{129}I$ with 3 mol dm^{-3} H_2SO_4 and 10% H_2O_2.

β-Carotene powder (Tokyo Kasei Co., 100% all *trans*) was recrystallized by the method of Lupinski.[6] The purified material was dissolved in benzene and a benzene solution of $^{129}I_2$ added. The precipitated small crystals were filtered off, washed with benzene and light petroleum, and dried *in vacuo*. All manipulations were performed in the dark to avoid isomerization of the *trans* form of β-carotene. The product, with a metallic lustre, was identified as $C_{40}H_{56}I_3$ by elemental analyses (Found: C, 52.2; H, 6.15; I, 41.0. Calc. for $C_{40}H_{56}I_3$: C, 52.35; H, 6.15; I, 41.5%).

The sample was transferred into a Teflon absorber holder for Mössbauer measurements. The source was ^{129}Te in the form of $^{66}Zn^{129}Te$ which was prepared by irradiating $^{66}Zn^{128}Te$ for 1 h in the Kyoto University Reactor. Mössbauer measurements were carried out with the source and absorber at 16 K. The velocity scale was calibrated with a $^{57}Co(Rh)$ source and α-Fe and α-Fe_2O_3 absorbers. Details of the apparatus have been described elsewhere.[9]

RESULTS AND DISCUSSION

A ^{129}I Mössbauer spectrum of the β-carotene–iodine system is shown in the Figure by closed circles. The



Iodine-129 Mössbauer spectrum of the β-carotene–iodine system at 16 K

spectrum is well resolved into two quadrupole-split patterns of eight lines each. It was analyzed by the least-squares method using a double set of the fitting parameters δ, e^2Qq, and η, full width at half-height (Γ), and the background of the spectrum. The solid curve in the Figure is the superimposed Lorentzian curve of the two octets obtained by the best fitting. The analyzed octet patterns, which indicate the existence of two iodine atoms with different charge distributions, are shown in the Figure by broken curves and the stick diagrams I_A and I_B. The Mössbauer parameters computed for I_A and I_B are given in the Table, together with the relative absorption intensity derived from the total area under the two broken lines. Within the limit of pure *p* bonding, the Mössbauer parameters can be related to the number of unbalanced *p* electrons (U_p) and the number of *p* holes (h_p).[1,10] The calculated values of U_p and h_p using this approximation are also listed in the Table.

Mössbauer parameters for $[C_{40}H_{56}][I_3]$ and $[Ru(\eta-C_5H_5)_2I][I_3]$

Compound	δ [a]/mm s^{-1}	e^2Qq [b]/MHz	η	Γ/mm s^{-1}	Absorption intensity [c]	h_p	U_p
$[C_{40}H_{56}][I_3]$ [d]							
I_A (central)	1.59 ± 0.04	−2 445 ± 20	0.05 ± 0.04	1.04 ± 0.10	1.0	1.42	1.07
I_B (terminal)	0.23 ± 0.04	−1 152 ± 20	0.06 ± 0.04	1.20 ± 0.10	1.4	0.51	0.50
$[Ru(\eta-C_5H_5)_2I][I_3]$ [e]							
I_A (central)	1.48 ± 0.05	−2 460 ± 35	0.06 ± 0.04	0.83 ± 0.08	1.0	1.35	1.07
I_B (terminal)	0.25 ± 0.05	−1 152 ± 35	0.06 ± 0.04	0.85 ± 0.08	1.6	0.53	0.50
I_C (Ru–I)	0.19 ± 0.05	−1 483 ± 35	0.03 ± 0.03	0.84 ± 0.08	1.0	0.49	0.65

[a] Relative to the ZnTe source. [b] Converted into ^{127}I. [c] Total absorption area normalized to the value for I_A. [d] The present system of β-carotene tri-iodide. [e] Ref. 12.

The charge distribution, estimated from the treatment of Dailey and Townes,[11] comprises a slightly positive charge on I_A and a charge of *ca.* −0.5 on I_B.

Taking into account the absorption intensity ratio and the charge distribution on I_A and I_B, the species giving rise to the observed spectrum is attributed to a tri-iodide anion (I_3^-), where I_A corresponds to the central atom with a slight positive charge and I_B to the two terminal atoms with negative charges of 0.5. The experimental intensity ratio of 1.4 : 1 and its deviation from the composition ratio of 2 : 1 in I_3^- is explained by the fact that the recoilless fraction of the terminal atoms is lower than that of the central atom, as observed in other compounds containing iodine.[12,13] The reduced intensity ratio would be partly due to the effect of absorber thickness which causes saturation of absorption intensity in the region of the stronger hyperfine components.[14] Since the effective absorber thickness for the terminal atoms is twice that for the central atom, by the composition ratio of 2 : 1, the saturation for I_B is more dominant than for I_A. The assignment of I_3^- together with the stoicheiometry $C_{40}H_{56}I_3$, obtained by elemental analyses, leads us to conclude that the product prepared by the precipitation method is β-carotene–tri-iodide (1 : 1), containing only I_3^- as the iodine species. Therefore, the present solid system can be described in terms of a c.t. complex, $C_{40}H_{56}^+ \cdots I_3^-$, where one electron is transferred from the β-carotene molecule to tri-iodide.

It should be noted that the two terminal atoms share the transferred electron equally. Hence, the I_3^- ion has a symmetrical charge distribution and two equivalent I–I distances. Although there have been many investigations of I_3^- in various systems, the discovery of a symmetrical I_3^- group is quite exceptional in Mössbauer spectroscopy. The Table shows that the present Mössbauer data are in good agreement with those for the only other example of a fully analyzed symmetrical I_3^- ion [12] and that the I_3^- in β-carotene is just another example of a tri-iodide anion with a symmetrical charge distribution. The large linewidth of the terminal atoms in the β-carotene–iodine system is attributable to the different microenvironments for all terminal sites and consequently to a distribution of the quadrupole coupling constants.

In β-carotene films doped with iodine vapour [7,8] and in a solution of β-carotene and iodine,[6] it was proposed that a c.t. complex, β-carotene $\cdots I^+$, has an absorption at 1 000 nm which can be classed as a c.t. band of the usual donor–acceptor kind. This band was explained in terms of another model in which the absorption maximum of β-carotene is shifted to longer wavelengths due to the charge-transfer effect, suggesting that β-carotene $\cdots I^+$ has several bonding configurations for the β-carotene ground state.[15] However, no trace of any species other than I_3^- was detected in the Mössbauer spectrum of the present solid system. On the basis of the results obtained above, an alternative proposal is that the band at 1 000 nm is caused by an intramolecular transition in the β-carotene cation formed in the c.t. complex, $C_{40}H_{56}^+ \cdots I_3^-$. This proposal is supported by the fact that the peak maximum depends on the type of dopant,[7,8] since the electronic states of the β-carotene cation would be effectively perturbed by the dopant anions involved in the c.t. complexes. The positive and negative molecular ions of dienes are experimentally and theoretically established to have similar absorption spectra,[16] therefore, a possible test to confirm the present proposal would be to dope the β-carotene anion films with electron donors such as alkali metals.

It has been shown that the β-carotene–iodine system is a valid model to investigate the increase in electrical conductivity in iodine-doped polyacetylene films,[8] since β-carotene has a well defined structure relative to the complicated structure of polyacetylene. According to the Mössbauer effect observed in the present system, the positively charged site is introduced onto the polyene chain of the β-carotene molecule by the formation of a c.t. complex, $C_{40}H_{56}^+ \cdots I_3^-$. When the positive site migrates along the polyene chain, the electrical conductivity will increase, depending on the number of such sites and their mobility. The same mechanism would be appropriate to the iodine-doped polyacetylene films due to the formation of c.t. complexes. Characterization of some polyacetylene–iodine films is now in progress using the Mössbauer spectroscopic method and the results obtained here.

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