CHEMISTRY LETTERS, pp. 267-270, 1980.

SPECTROSCOPIC STUDIES ON β-CAROTENE DOPED WITH IODINE AND SULFUR TRIOXIDE — DOPED POLYACETYLENE MODELS

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The Raman and absorption (ultraviolet through infrared) spectra of β-carotene doped with iodine and sulfur trioxide were studied. The doping gave significant effects on the Raman and absorption spectra which were interpreted as arising from the transfer of an electron from a local site in β-carotene to a dopant and the resultant shortening of the length of double-bond conjugation. Definite information on the form of iodine in the β-carotene—iodine complex was obtained.

Much interest has been taken in the structure of doped polyacetylenes which exhibit high electrical conductivities.[1-6] Since the structure of polyacetylene is actually more complicated than what is expected from its simple repeating unit,[3,4] it is felt desirable to perform a parallel study on the interactions between some model compounds with well-defined structures and dopants. All-*trans* β-carotene (hereafter simply called β-carotene) is a model compound suitable for such a study, because it has a fairly long polyene chain (nine conjugated *trans* double bonds with a β-ionone ring at each end) and forms complexes with iodine and SO_3.[7,8] On forming the complex the electrical conductivity increases[8,9] and, concomitantly, the absorption spectrum changes greatly to give an intense band at 940 nm.[8] These features are similar to those of polyacetylene observed at an early stage of doping.

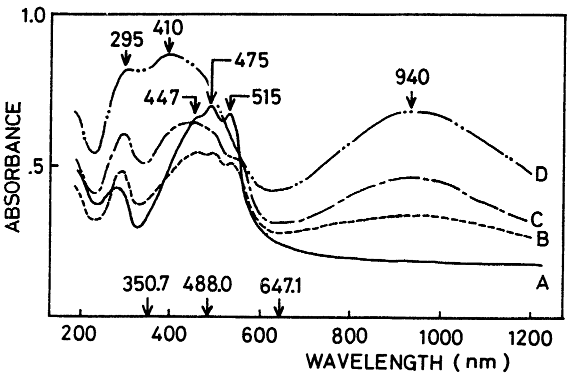
In Fig. 1 are shown the absorption spectra (200-2000 nm) of the films of β-carotene itself and iodine-doped samples. As is clearly seen in this figure, significant spectral changes occur with increasing amount of the dopant. For the most heavily doped sample (for which the iodine/β-carotene ratio is not determined) three strong and broad absorptions are observed at 940, 410, and 295 nm and the absorption of β-carotene itself centered at 475 nm is now obscure.

The lines at 350.7 and 647.1 nm of a Kr-ion laser and a line at 488.0 nm of an Ar-ion laser were chosen as the light sources for Raman measurements. The laser lines at 350.7 and 488.0 nm are in resonance with the absorptions of the β-carotene—iodine complex in the ultraviolet-visible region. Accordingly, the resonance Raman spectra obtained with these lines are expected to give structural information primarily on the molecular species or parts which give rise to the ultraviolet-visible absorptions. On the other hand, since the 647.1-nm line is not in resonance with any absorption band, various components in the sample would be more evenly represented in the Raman spectrum excited with this line.

In the first place we discuss the structure of iodine absorbed in β-carotene on the basis of the low-frequency Raman spectrum shown in Fig. 2 (the iodine/β-carotene ratio = 2.8, excited with the 350.7-nm line). The Raman band at 112 cm^{-1} is undoubtedly due to the symmetric stretching vibration of the I_3^- ion and the bands at 222 and 331 cm^{-1} are assigned to its first and second overtones, respectively.[10,11] The intensities of these overtones are enhanced through the resonance effect between the 350.7-nm line and the absorption in the ultraviolet region. This indicates that the absorption in the ultraviolet region is mainly due to the I_3^- ion. The Raman bands due to β-carotene (which usually appear in the 1600-1000 cm^{-1} region) are very weak with the 350.7-nm excitation, since β-carotene has no appreciable absorption around this excitation wavelength. The shoulder at 137 cm^{-1} is assigned to the antisymmetric stretching vibration. The appearance of this band indicates that the I_3^- ion is not centrosymmetric. None of these bands was observed with the 488.0-nm excitation. However, in the case of a higher iodine/β-carotene ratio (6.9) two new bands were observed at 105 and 165 cm^{-1} with the 488.0-nm excitation, while the 112 cm^{-1} band and its overtones were also observed for this sample with the 350.7-nm excitation. The bands at 105 and 165 cm^{-1} are assigned, respectively, to $(I_3^-)_x$ (a chain of successive I_3^- units) and I_5^- from the comparison with the Raman frequencies[12] observed of $(benzamide)_2H^+I_3^-$ and $(trimesic\ acid \cdot H_2O)_{10}H^+I_5^-$.

The conclusion concerning the iodine species in iodine-doped β-carotene samples may be summarized in the following way. In the sample with a low iodine/β-carotene ratio, iodine exists in the form of I_3^- which has an absorption in the ultraviolet region. When the iodine/β-carotene ratio becomes high, $(I_3^-)_x$ and I_5^- are present in addition to I_3^- and the former two species give a broad absorption in the visible region.

Next we focus our attention to the Raman spectra of a higher wavenumber region shown in Figs. 3 and 4, which were obtained with the 488.0-nm and 647.1-nm lines, respectively. In the spectra of pure β-carotene (Figs. 3A and 4A) the band around



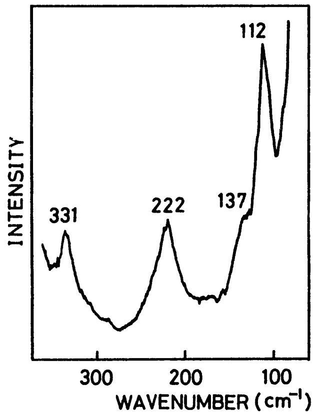


Fig. 1.(left) The absorption spectra of thin films of β-carotene and iodine-doped β-carotene. A, β-carotene; B,C,D, iodine-doped β-carotene (iodine content B<C<D)

Fig. 2.(right) The low-frequency Raman spectrum of iodine-doped β-carotene (iodine/β-carotene = 2.8) with the 350.7-nm excitation.

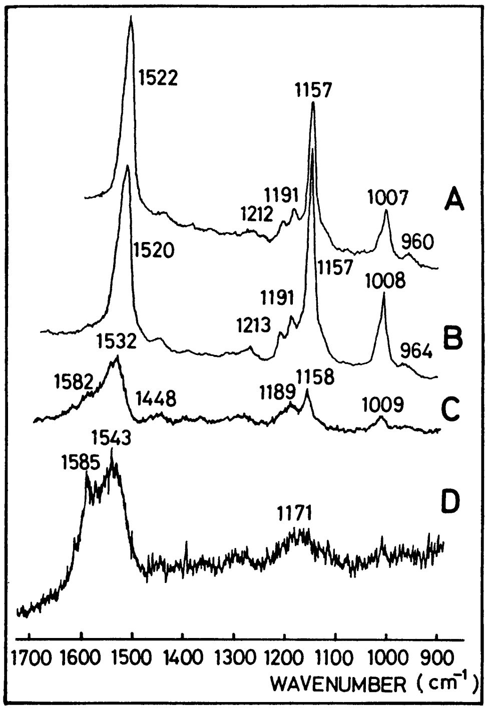


Fig. 3.(upper) The Raman spectra of β-carotene and iodine-doped β-carotene with the 488.0-nm excitation. A, β-carotene; B,C,D, iodine-doped β-carotene (iodine content B<C<D, iodine /β-carotene in B = 2.8)

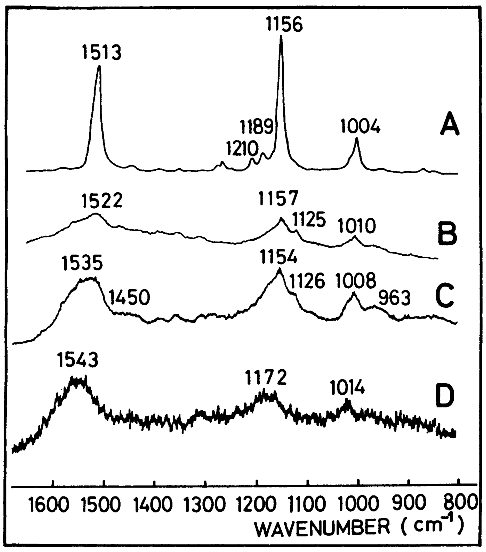
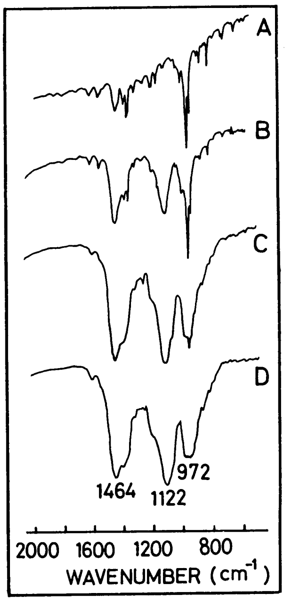


Fig. 4.(lower) The Raman spectra of β-carotene and iodine-doped β-carotene with the 647.1-nm excitation. As for A∿D, see the caption of Fig. 3.

1520 cm^{-1} is assigned to the C=C stretching vibration and the bands at about 1160 and 1010 cm^{-1} are due to the mixed vibrations of the C-C stretching and C-H in-plane bending.$^{13)}$ The small difference of the C=C stretching frequencies between Figs. 3A (1522 cm^{-1}) and 4A (1513 cm^{-1}) is real and presents an interesting problem to be treated separately. Here we follow the spectral changes arising from the doping with iodine. For the sample with the iodine/β-carotene ratio of 2.8, the Raman spectrum with the 488.0-nm excitation (Fig. 3B) is quite similar to that of pure β-carotene (Fig. 3A), but the spectrum with the 647.1-nm excitation (Fig. 4B) is different from that of pure β-carotene (Fig. 4A) with respect to the C=C stretching frequency and the relative intensities of the bands around 1520, 1160, and 1010 cm^{-1}. Certainly, some β-carotene molecules remain intact at this iodine /β-carotene ratio and with the 488.0-nm excitation the resonance Raman spectrum arising from these intact molecules is much stronger than the spectrum of the β-carotene—iodine complex for which the resonance enhancement of intensity does not seem as effective. On the other hand, the Raman scattering from both β-carotene itself and the complex is observed with the 647.1-nm excitation on the ground described earlier. As the iodine content is increased, the spectral changes observed commonly with both exciting lines are the upward shifts of the three main peaks(particularly the C=C stretching band), band broadenings(the appearance of minor bands in the C=C stretching region as well), and decreased intensities (Figs. 3C, 3D, 4C, and 4D).

In Fig. 5 are shown the infrared spectra of β-carotene and iodine-doped samples. With increasing iodine content the many sharp bands of β-carotene are replaced with the three broad and intense bands of the complex at 1464, 1122, and 972 cm^{-1} (Fig. 5D). These bands can be observed also for the sample with a high iodine/β-carotene ratio (6.9). It is likely that these bands correspond to the weak Raman bands at 1450, 1126, and 963 cm^{-1} in Fig. 4C.

Interestingly, β-carotene doped with SO_3 has many spectral features in common with iodine-doped one. SO_3-doped β-carotene shows a broad absorption with a peak at 725 nm and a shoulder at 860 nm. At a high SO_3 content broad Raman bands are observed at 1583



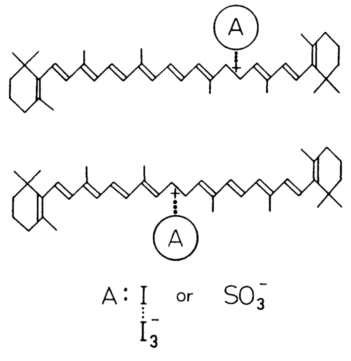


Fig. 5. (left) The infrared spectra of β-carotene and iodine-doped β-carotene. A, β-carotene; B, C, D, iodine-doped β-carotene (iodine/β-carotene, 0.44 in B, 2.2 in C, 2.8 in D).

Fig. 6. (right) A structure model for doped β-carotene.

and 1177 cm^{-1} with the 488.0-nm excitation and at 1552 and 1187 cm^{-1} with the 647.1-nm excitation. The three infrared bands characteristic of the β-carotene-iodine complex are also found for the SO_3 complex at almost the same frequencies, namely, 1469, 1120, and 964 cm^{-1}. These findings suggest that the structure of β-carotene moiety in these complexes are quite similar.

The following tentative interpretation may be given for the experimental results described above, though further studies are needed to derive a definite conclusion as to the structure of doped β-carotene. The doping of β-carotene with either iodine or SO_3 produces significant effects on the Raman bands arising from the β-carotene moiety. However, the spectral pattern characteristic of a polyene chain (in other words, a conjugated double-bond system with bond alternation) is clearly preserved. Since the C=C stretching frequency shifts to higher frequencies with the doping, the length of double-bond conjugation seems to be shortened with the introduction of a dopant as shown schematically in Fig. 6. Probably one electron is transferred from β-carotene to the dopant and as a consequence a positively charged site is produced in the polyene chain. The broadenings of the Raman bands suggest that this site is not fixed at a particular carbon atom. In a heavily doped sample more than one site would possibly be produced in a β-carotene molecule. The three intense and broad infrared bands characteristic of the complexes may be assigned to the local vibrations associated with this site.

Further studies are now in progress to check the validity of the interpretation proposed above and to gain a deeper insight into the interaction of a polyene chain with dopant molecules.

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(Received January 21, 1980)