On the Structure of Starch-Iodine

by

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**Abstract:**
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ON THE STRUCTURE OF STARCH-IODINE

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Abstract

The structure of the blue-black iodine complex of amylose (the linear, helical component of starch) has been studied by resonance Raman and iodine-129 Mössbauer spectroscopy. It is concluded from these studies and parallel work on selected model compounds that the predominant polyiodide present is $I_5$.
ON THE STRUCTURE OF STARCH-IODINE

Sir:

It has been known for many years that the linear, helical component of starch, amylose, forms an intensely blue-black adduct with iodine in the presence of iodide.\(^1\) The pioneering spectral and X-ray diffraction investigations of Rundle and co-workers\(^2\) established that the iodine atoms are present in a one-dimensional chain within the amylose helix (arrayed in a periodicity probably incommensurate with the pitch of the helix) and give rise to the intense optical absorption (\(\lambda_{\text{max}} \approx 600 \text{ nm}\)).\(^2\) The exact structural nature of the polyiodide chromophore has been the subject of considerable study and speculation. For example, it has been proposed that the iodine is present as discrete \(\text{I}_2\) units,\(^3a\) "dissolved" in the hydrophobic interior of the helix, and also that iodine is present as linear chains of \(\text{I}_3^{-1}\) (A) ions

\[\cdots\text{I-I-I-\cdotsI-I-I-\cdotsI-I-I-\cdots}\]

as in \((\text{benzamide})_2\text{H}_2\text{I}_2^-\).\(^4\) In addition, studies of related cyclohexaamylose complexes\(^5\) suggest the possibility of arrays of alternating \(\text{I}_2^+\) and \(\text{I}_3^-\) units (B) or symmetrical \(\text{I}_5^-\) species (C). Despite

\[\text{B} \quad \cdots\text{I-I-\cdotsI-I-\cdotsI-I-\cdotsI-I-I}\]
the application of a variety of physical techniques to this problem, it has not been possible to differentiate among these structures and to provide definitive information on the identity of the polyiodide species present in starch-iodine. We have recently shown that the combination of resonance Raman and iodine-129 Mössbauer spectroscopy, aided by studies of appropriately selected model compounds, is a powerful tool for elucidating polyiodide structure in low-dimensional mixed valence materials. In this communication we apply these techniques to the starch-iodine problem. We provide unambiguous evidence that the predominant polyiodide species within the amylose helix is $I_5^-$. In Figure 1 are presented resonance Raman scattering spectra (5145Å excitation, spinning samples) of the amylose iodine complex (prepared in deionized water from potato amylose, $I_2$ and KI, washed with deionized water, and freeze-dried) and several key model compounds of known structure. In general, only totally symmetric normal vibrational modes (and the corresponding overtones and combinations) exhibit appreciable intensity in polyiodide resonance Raman spectra. The observed I-I stretching frequencies reflect the tendency of $I_2$ to act as an electron acceptor and of electron donors (e.g. $I^-$) to lower the I-I bond order. Thus, coordination of $I^-$ to $I_2$ producing $I_5^-$, lowers the I-I stretching frequency from 207 cm$^{-1}$ to 128 cm$^{-1}$ (the
average of the Raman-active totally symmetric stretch at 108 cm\(^{-1}\) and the infrared-active antisymmetric stretch at 148 cm\(^{-1}\). As can be seen in Figure 1A, starch-iodine exhibits strong scattering at 163 cm\(^{-1}\), and very weak scattering at 109 and 56 cm\(^{-1}\); overtones and combinations are also observed. This spectrum differs sharply from those of \(I_2\) in benzene (Figure 1C, \(\nu_{\text{fundamental}} = 207\) cm\(^{-1}\)) alcohols or ethers, \(^{14}\) (benzamide)\(_2\)H\(^+\)I\(_3^-\) (Figure 1D, \(\nu_{\text{sym}}\), fundamental = 108 cm\(^{-1}\)), which has structure \(A\), \(^{4}\) and either (phenacetin)\(_2\)H\(^+\)I\(_3^-\) \cdot I_2 \(^{15a}\) (Figure 1E \(\nu_{\text{fundamental}} = 187\) cm\(^{-1}\), \(\nu_{\text{sym}}\), \(\nu_{\text{asy}}\) = 120 cm\(^{-1}\)\(^{15b}\) or (\(2\)-cyclohexamylose)\(_2\) Li\(^+\)I\(_3^-\) \cdot I_2 \cdot 8H_2O \(^{15}\) (Figure 1F, \(\nu_{\text{fundamental}} = 173\) cm\(^{-1}\), \(\nu_{\text{sym}}\), \(\nu_{\text{asy}}\) = 110 cm\(^{-1}\)\(^{15b}\) which have structure \(B\). On the other hand, compounds with chains of \(I_5^-\) ions (structure \(C\)) exhibit a spectrum essentially identical to that of the starch compound. Thus, (trimesic acid \cdot H_2O)\(_x\)H\(^+\)I\(_3^-\) \(^{16}\) (Figure 1B) exhibits strong scattering at 162 cm\(^{-1}\) and weaker bands at 104 and 75 cm\(^{-1}\)\(^{15b}\) The 162 cm\(^{-1}\) transition is reasonably assigned to a fundamental normal mode involving the symmetrically coupled internal stretching of the two "I\(_2\)" units. \(^{17}\) That the force constant is perturbed less from free \(I_2\) than in \(I_3^-\) reflects the fact that the available electron density of the \(I^-\) donor must now be distributed between two \(I_2\) acceptors.

It is known \(^2\) that the blue-black amylose complex can also be prepared from iodine vapor and amylose which has been crystallized from butanol. We find the resonance Raman spectrum of this material to be identical to that of the complex prepared in aqueous solution from
It has been previously suggested\(^{18}\) that hydrolysis of \(I_2\) produces \(I^-\) in the crystalline amylose.

In order to investigate the possible presence of Raman-inactive \(I^-\) and to add further weight to the \(I_5^-\) proposal, iodine -129 Mössbauer studies were undertaken. The amylose-iodine adduct was prepared by the aqueous procedure described above, using \(^{129}\text{I}\). The Mössbauer spectrum at 4°K is shown in Figure 2A, along with the best computer fit to the experimental data. Data analysis techniques are described elsewhere. The spectrum is best fit to a model with three inequivalent iodine sites in approximate relative populations of 2:2:1. Derived site population, isomer shift, and quadrupole splitting parameters are presented in Table I. Importantly, attempts to constrain the model to 1:1:1 site populations (as in CsI\(_3\)) or to two sites in a ratio of 2:1 (as in (benzamide)\(_2\)H\(^{+}\)I\(_5^-\)) produced a precipitous deterioration in the goodness of fit parameter.

There is no evidence of \(I^-\) (\(\delta = -0.51\) mm/sec, \(\epsilon\sigma Q = 0^8\)) in the spectrum and it is estimated that this species is present in less than 3 mole percent. For comparison to the amylose data, the Mössbauer spectrum of (trimesic acid · H\(_2\)O)\(_x\)H\(^{+}\)I\(_5^-\), enriched in \(^{129}\text{I}\), is shown in Figure 2B. The parameters obtained from the optimum fit are set out in Table I. The derived site populations give an indication of the accuracy of the analysis. These numbers as well as the isomer shift and quadrupole splitting parameters are in close agreement with the amylose-iodine data, and provide further support for the pentaiodide structure.
Besides providing information on a long-standing problem, this work further illustrates the power of the resonance Raman/iodine Mössbauer technique for elucidating the structures of unusual polyiodides. Application to a variety of disordered, noncrystalline, or microcrystalline electronic and optical materials is particularly promising.

**Acknowledgments**

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References

   e. J. F. Foster in reference 1d, Chapt. XV.


6. a. A previous Raman study, unaided by appropriate model compounds, reached the conclusion of I\textsuperscript{5}: M. Tasumi, Chem. Letters, 75 (1972).
   b. An earlier iodine Mössbauer study was unaided by appropriate model compounds and optimum data acquisition/analysis procedures; it was concluded that I\textsuperscript{5} was present since inequivalent iodine sites were detected: B. S. Ehrlich and M. Kaplan, J. Chem. Phys., 51, 603 (1969).
6. c. For intrinsic viscosity studies see reference 3b.


d. D. W. Kalina, D. R. Stojakovic, R. C. Teitelbaum, and T. J. Marks, manuscript in preparation. The dependence of the observed scattering pattern upon exciting wavelength (4880-6471 Å) is generally rather small. Correlation field splitting effects also appear to be small (< ca. 10 cm⁻¹).

10. Prolonged pumping under high vacuum at room temperature leads to $I_0$ depletion. An enhanced $I_0^-$ band is observed in the Raman.


13. Overtones are assigned at 322 (2 x 163) and 214 (2 x 109) cm$^{-1}$; the band at 272 (163 + 109) cm$^{-1}$ is assigned to a combination. The presence of a combination transition can be taken as evidence that the contributing species are not in separate lattices (i.e. that the spectrum is not due to a mixture of compounds).

14. a. Coordination of oxygen donors such as are present near the interior of the amylose helix produces only a small shift in the I-I stretching frequency, viz., $\nu$ fundamental (diethyl ether) = 204 cm$^{-1}$ and $\nu$ fundamental ($n$-butanol) = 197 cm$^{-1}$.


b. Bands assignable to overtones and combinations are also visible in the Raman spectrum.


b. F. H. Herbstein, private communication to T. J. M.

17. One of the other bands presumably involves symmetrically coupled $I_0^-I^-I_0^+$ stretching. Under $D_{4h}$ symmetry $I_0^-$ has two $\tau_g^+$ stretching modes; a $\pi_g$ bending mode is also predicted to be active for a normal Raman transition.


b. This question is under further investigation.


20. a. Northwestern University

b. Argonne National Laboratory

21. Camille and Henry Dreyfus Teacher-Scholar
### Table I

Iodine -129 Mössbauer Parameters

<table>
<thead>
<tr>
<th>Compound</th>
<th>Amylose - Iodine</th>
<th>(Trimesic Acid·H₂O)ₙH⁺I⁻⁻</th>
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<tr>
<td><strong>Site 1</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>δ(mm/sec)</td>
<td>1.22(2)</td>
<td>1.15(3)</td>
</tr>
<tr>
<td>e²qQ(MHz.)</td>
<td>-1743(3)</td>
<td>-1777(5)</td>
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<tr>
<td>Π(mm/sec)</td>
<td>1.14(4)</td>
<td>1.15(5)</td>
</tr>
<tr>
<td>Relative population</td>
<td>1.90(10)</td>
<td>1.96(10)</td>
</tr>
<tr>
<td><strong>Site 2</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>δ(mm/sec)</td>
<td>0.53(3)</td>
<td>0.53(5)</td>
</tr>
<tr>
<td>e²qQ(MHz.)</td>
<td>-1187(8)</td>
<td>-1404(8)</td>
</tr>
<tr>
<td>Π(mm/sec)</td>
<td>2.13(8)</td>
<td>1.75(5)</td>
</tr>
<tr>
<td>Relative population</td>
<td>1.82(10)</td>
<td>1.78(10)</td>
</tr>
<tr>
<td><strong>Site 3</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>δ(mm/sec)</td>
<td>0.14(2)</td>
<td>0.13(5)</td>
</tr>
<tr>
<td>e²qQ(MHz.)</td>
<td>-842(5)</td>
<td>-965(5)</td>
</tr>
<tr>
<td>Π(mm/sec)</td>
<td>1.08(5)</td>
<td>1.04(4)</td>
</tr>
<tr>
<td>Relative population</td>
<td>1.00</td>
<td>1.00</td>
</tr>
</tbody>
</table>

*a Versus ZnTe  
*b For *₂I  
*c Linewidth
Figure Captions

**Figure 1.** Resonance Raman spectra (5145 Å excitation) of A. Starch (amylose) iodine, B. Polycrystalline (trimesic acid · H₂O)₁₀H⁺I₅⁻, C. I₂ dissolved in benzene, D. Polycrystalline (benzamide)₂H⁺I₅⁻, E. Polycrystalline (phenacetin)₂H⁺I₅⁻ · I₂, F. Polycrystalline (α-cyclohexaamylose)₂ · Li⁺I₅⁻ · I₂ · 8H₂O.

**Figure 2.** Iodine-129 Mössbauer spectra of the indicated compounds at 40 K. The solid lines represent the best computer fit to the experimental data points.
RESONANCE RAMAN SPECTRA

STARCH-IODINE

A

B

I₂ in benzene

C

D

E

F

WAVENUMBER (cm⁻¹)
$^{129}$I MOSSBAUER SPECTRA

A. STARCH \cdot IODINE

B. (TRIMESIC ACID$\cdot$H$_2$O)$_{10}$\cdot$HI$_5$
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