Table I. Thermochemical Data at 298 K[a]

Species	$\Delta H°_f$, kcal/mol	$S°$, gibbs/mol
CH_4	−17.9	44.5
CH_3	34.9 ± 0.15[b]	46.4 ± 0.3
Cl	28.9	39.5
HCl	−22.0	44.6

[a] Reference 10. [b] Present work.

The forward reaction (1) has been extensively investigated[3c,4b,5,6,7] in the last few years and our value of $k_1 = 0.93$ (± 0.05) $\times 10^{-13}$ cm^3/(molecule s) is in excellent agreement with those[8,9] studies lending additional support to our measurements. In addition, systematic errors will tend to cancel out when the ratio of k_1/k_{-1} is calculated and therefore we consider that K_1 has been determined with considerable accuracy; $K_1(298\text{ K}) = 1.3 \pm 0.3$. This result, in conjunction with thermochemical data for reactions 1, −1 (Table I) leads to $\Delta H°_f(CH_3) = 34.9 \pm 0.15$ and BDE (CH_3-H) = 104.9 ± 0.15 kcal/mol, in very good agreement with literature values.[11]

To the best of our knowledge, this represents the first time the equilibrium constant for a chemical reaction involving a very reactive organic free radical has ever been measured directly.[12]

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(1) (a) This work was supported in part by grants from the National Science Foundation (CHE-76-16787A01) and the Army Office of Scientific Research (DAAG29-76-G-0195).
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(4) (a) By using 14 V on the ionizing electrons in the mass spectrometer, we could measure Cl atoms in the presence of a large excess of either Cl_2 or HCl. Cl_2 was measured directly at masses 70, 72, and 74 with 70-V electrons. With the discharge on these peaks were reduced to background (<0.1%). (b) M. A. A. Clyne and R. F. Walker, *J. Chem. Soc., Faraday Trans. 1*, **69**, 1547 (1973). (c) k_{ex} is given from gas kinetic theory (see ref 2) as $\bar{c}_x S/4V$, where $\bar{c} = (8RT/\pi M_x)^{1/2}$ is the mean thermal velocity of the x species with mass M_x, S is the surface area of the exit aperture (measured with a microscope), and V is the reactor volume. In addition, we measured k_{eCH_4} directly by the pressure measurements using a McLeod gauge. Note that (k_{eCl}/k_{eCH_3}) in eq 3 is equal to $(M_{CH_3}/M_{Cl})^{1/2} = 0.654$.
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(12) In one vessel the average conditions at ~1 × 10^{-3} Torr pressure were, initially, 0.5 × 10^{12} Cl atoms/cm^3; 20 × 10^{12} Ar (or He) atoms/cm^3. In a mean residence time of ~1 s, each Cl atom makes ~3 × 10^4 wall collisions and ~10^4 collisions with Ar. About 1 in 5000 collisions with CH_4 when it is introduced leads to reaction. There is no reason to expect departures from equilibrium energy distributions.
(13) Research Associate.

M. H. Baghal-Vayjooee,[13] A. J. Colussi,[13] S. W. Benson*

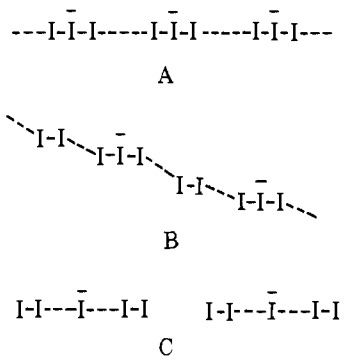
Department of Chemistry
University of Southern California
Los Angeles, California 90007

Received February 1, 1978

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 ($\lambda_{max} \approx 600$ 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 I_2 units,[3a] "dissolved" in the hydrophobic interior of the helix,[1b,3b] and also that iodine is present as linear chains of I_3^- (A) ions as in (benzamide)$_2$ $H^+I_3^-$.[4] In addition,



studies of related cyclohexaamylose complexes[5] suggest the possibility of arrays of alternating I_2 and I_3^- units (B) or symmetrical I_5^- species (C). Despite the application of a variety of physical techniques to this problem,[6] 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[7] and iodine-129 Mössbauer spectroscopy,[8] aided by studies of appropriately selected model compounds, is a powerful tool for elucidating polyiodide structure in low-dimensional mixed valence materials.[9] 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 (5145-Å 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)[10] 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.[9] 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.[9a,11] Thus, coordination of I^- to I_2 producing I_3^- lowers the I-I stretching frequency from 207 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} [12]). 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.[13] This spectrum differs sharply from those of I_2 in benzene (Figure 1C, ν_{fund} 207 cm^{-1}; fund = fundamental) alcohols or ethers,[14] (benzamide)$_2H^+I_3^-$ (Figure 1D, $\nu_{I_3\text{-symm,fund}}$ 108 cm^{-1}), which has structure A,[4] and either (phenacetin)$_2H^+I_3^-\cdot I_2$[15a] (Figure 1E, $\nu_{"I_2"}$ 187 cm^{-1}, $\nu_{"I_3^-"}$ 120 cm^{-1})[15b] or (α-cyclohexaamylose)$_2Li^+I_3^-\cdot I_2\cdot 8H_2O$[5] (Figure 1F, $\nu_{"I_2"}$ 173 cm^{-1}, $\nu_{"I_3^-"}$ 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 with that of the starch compound. Thus, (trimesic acid$\cdot H_2O)_{10}H^+I_5^-$ [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

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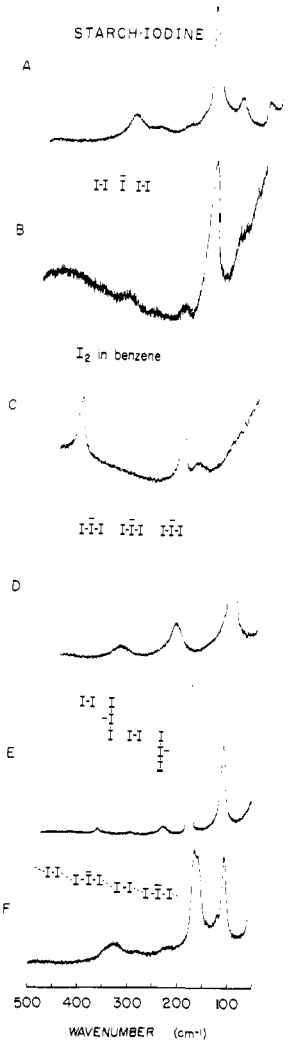

Figure 1. Resonance Raman spectra (5145 Å excitation) of A, Starch (amylose)–iodine; B, polycrystalline (trimesic acid·H_2O)$_{10}H^+I_5^-$; C, I_2 dissolved in benzene; D, polycrystalline (benzamide)$_2H^+I_3^-$; E, polycrystalline (phenacetin)$_2H^+I_3^-\cdot I_2$; F, polycrystalline (α-cyclohexaamylose)$_2Li^+I_3^-\cdot I_2\cdot 8H_2O$.

Table I. Iodine-129 Mössbauer Parameters

	Amylose–iodine	(Trimesic acid·H_2O)$_{10}$-$H^+I_5^-$
	Site 1	
δ, mm/s[a]	1.22 (2)	1.15 (3)
e^2qQ, MHz[b]	−1743 (3)	−1777 (5)
Γ, mm/s[c]	1.14 (4)	1.15 (5)
Relative population	1.9 (1)	2.0 (1)
	Site 2	
δ, mm/s	0.53 (3)	0.53 (5)
e^2qQ, MHz	−1187 (8)	−1404 (8)
Γ, mm/s	2.13 (8)	1.75 (5)
Relative population	1.8 (1)	1.8 (1)
	Site 3	
δ, mm/s	0.14 (2)	0.13 (5)
e^2qQ, MHz	−842 (5)	−965 (5)
Γ, mm/s	1.08 (5)	1.04 (4)
Relative population	1.0	1.0

[a] Vs. ZnTe, [b] For ^{129}I. [c] Line width.

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.

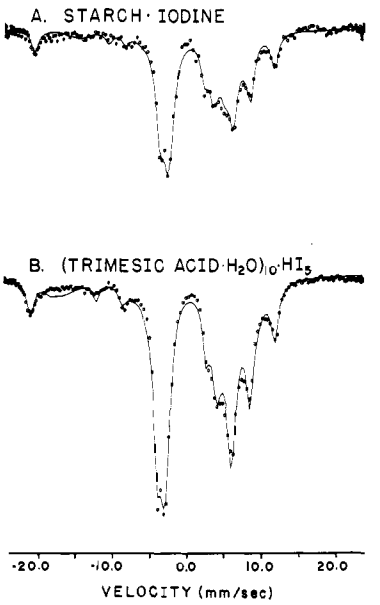

Figure 2. Iodine-129 Mössbauer spectra of the indicated compounds at 4 K. The solid lines represent the best computer fit to the experimental data points.

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 with that of the complex prepared in aqueous solution from I_2 and I^-. It has been previously suggested[18] that hydrolysis of I_2 produces I^- in the crystalline amylose.

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}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.[19] 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)$_2H^+I_3^-$) produced a precipitous deterioration in the goodness of fit parameter. There is no evidence of I^- ($\delta = -0.51$ mm/s, $e^2qQ = 0$[8]) in the spectrum and it is estimated that this species is present in <3 mol %. For comparison with the amylose data, the Mössbauer spectrum of (trimesic acid·H_2O)$_{10}H^+I_5^-$, enriched in ^{129}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. This work was supported in part by the Office of Naval Research, the Energy Research and Development Administration, and the Northwestern Materials Research Center (NSF DMR 72-0319A06). We thank Drs. B. Zabransky and D. R. Stojakovic for helpful discussions.

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(13) Overtones are assigned at 322 (2 × 163) and 214 (2 × 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[14b] such as are present near the interior of the amylose helix[5] produces only a small shift in the I–I stretching frequency, viz., ν_{fund} (diethyl ether) 204 cm^{-1} and ν_{fund} (1-butanol) 197 cm^{-1}. (b) Oxygen–I_2 charge-transfer interactions have been proposed as the major iodine binding force: H. Murakami, *J. Chem. Phys.*, **23**, 1979 (1955); **22**, 367 (1954).

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(17) One of the other bands presumably involves symmetrically coupled $I_2 \leftarrow I \rightarrow I_2$ stretching. Under $D_{\infty h}$ symmetry I_5^- has two Σ_g^+ stretching modes; a π_g bending mode is also predicted to be active for a normal Raman transition.

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(20) (a) Northwestern University; (b) Argonne National Laboratory.

(21) Camille and Henry Dreyfus Teacher-Scholar.

Robert C. Teitelbaum,[20a] **Stanley L. Ruby**[20b]
Tobin J. Marks* [20a,21]

Department of Chemistry and the Materials Research Center
Northwestern University, Evanston, Illinois 60201
and the Physics Division, Argonne National Laboratory
Argonne, Illinois 60439

Received November 28, 1977

A Novel Rearrangement of Butenylcobaloximes. A Mechanism for Some Coenzyme B_{12} Catalyzed Rearrangements

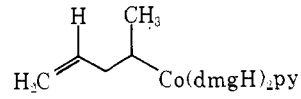
Sir:

Coenzyme B_{12} catalyzes a number of interesting rearrangements of organic molecules in biological systems,[1] two of which, the rearrangement of methylene glutarate to methylitaconate and the rearrangement of methylmalonyl- to succinyl-coenzyme A, can be represented by the general equation 1. Whilst there have been a number of indications that

(1)

i, X = CH_2; Y = CO·SCoA; Z = CO_2H

ii, X = O; Y = SCoA; Z = CO_2H



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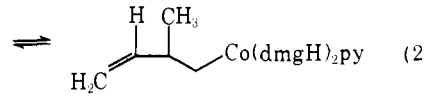
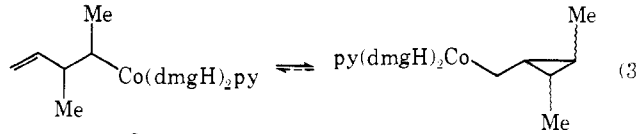


2 (2)

radical intermediates including cobalt(II) complexes[2] and organic radicals[3] may be involved, no really satisfactory explanation for the rearrangement of the organic fragment[4] and for the role of the cobalt(II) in these rearrangements has yet been proposed.

We have observed that freshly purified 1-methylbut-3-enylcobaloxime (**1**) and 2-methylbut-3-enylcobaloxime (**2**)[5] rearrange (4 M in $CDCl_3$ under N_2) to an equilibrium mixture containing **1** and **2**[6] in a ratio of ~1:10 (eq 2). The half-life[7] for the approach to equilibrium[8] from **1** or from **2** is ~100 min at 53 °C, but is very sensitive to the purity of the materials, the concentration, and other factors, as follows. (a) The half-life to equilibrium is increased 6-fold in the presence of 25 mol % di-*tert*-butylnitroxyl radical[9] *without detectable loss of organocobaloxime* in the period to complete equilibration. (b) The half-life is decreased 20- and 40-fold, respectively, in the presence of 1 and 2 mol % aquocobaloxime (II).[10] (c) The half-life is slightly increased in the presence of 100 mol % bromotrichloromethane, though there is considerable loss of organocobaloxime with concurrent formation of 1-methyl-2-(β,β,β-trichloromethyl)cyclopropane (**5**)[11] and bromocobaloxime(III) (**6**). (d) The half-life is increased ~8-fold when dichloromethane is used as solvent, and is longer still in dichloromethane–methanol mixtures. (e) With oxygen bubbling through the solution, equilbrium is attained with the loss of only ~30% of the total organocobaloxime.[13] (f) The half-life is increased in the presence of added pyridine. (g) The half-life is decreased in the presence of trifluoroacetic acid. With 250 mol % trifluoroacetic acid, equilibrium is attained within a few minutes at ambient temperature and without loss of organocobaloxime.

The above results clearly implicate cyclopropylcarbinyl intermediates and, indeed, 1,2-dimethylbut-3-enylcobaloxime (**3**) rearranges during purification to isomers of the corresponding 2,3-dimethylcyclopropylcarbinylcobaloxime (**4**)



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