

Electron-Transfer Processes in Indium(II) Iodide–*o*-Quinone Systems

Martyn A. Brown, Bruce R. McGarvey, Andrzej Ozarowski, and Dennis G. Tuck*

Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ontario, Canada N9B 3P4

Received June 29, 1995[⊗]

Indium(II) iodide reacts with various substituted *o*-quinones in nonaqueous solution by successive one-electron-transfer reactions to give (SQ)InI₂ products (SQ = semiquinone radical anion). Electron spin resonance spectroscopy demonstrates the presence of both mono- and diradical species in the reaction mixture. Addition of 4-picoline to a mixture of In₂I₄ and TBQ (=3,5-di-*tert*-butyl-*o*-quinone) in toluene causes the precipitation of the indium(III)–semiquinone complex (TBSQ)InI₂(pic)₂ whose structure has been established by X-ray crystallography: space group *P* $\bar{1}$, with *a* = 13.013(3) Å, *b* = 13.317(3) Å, *c* = 10.828(5) Å, α = 97.71(3)°, β = 107.98(3)°, γ = 103.92(3)°, *V* = 1684.8(1.2) Å³, *Z* = 2. Refinement converged at *R* = 0.051 and *R*_w = 0.064 for 5918 reflections at 23 °C. The InO₂N₂I₂ kernel is pseudooctahedral, and the structure confirms the presence of the semiquinone ligand. A reaction scheme which incorporates these results is proposed.

Introduction

The study of electron-transfer processes in the redox reactions of main group elements and compounds has been the subject of a number of publications from this laboratory.¹ The most important general conclusion is that many processes which were earlier believed to involve the concerted transfer of a pair of electrons in fact proceed via successive single-electron transfers. Of particular relevance to the present work are the reactions of 3,5-di-*tert*-butyl-*o*-benzoquinone (TBQ) with indium metal, where the product is the indium(I) semiquinone, In(TBSQ),² and of this and other *o*-quinones with indium(I) halides to give XIn(CAT) species (where CAT²⁻ is the corresponding substituted catecholate) via *o*-semiquinone complexes.^{3,4} More recently, we showed that bis(semiquinone) derivatives of indium(III) halides exist in nonaqueous solution and that intramolecular electron-transfer reactions are important in the chemistry of such compounds.⁵

An investigation of the analogous reactions between *o*-quinones and indium(II) iodide, the best characterized of the indium(II) halides, provides an obvious and interesting extension of these studies. The indium(II) halides are dimeric species for X = Br and I, either of the ionic form In⁺[InX₄]⁻ or of the metal–metal-bonded form X₂InInX₂; the latter structure is seen in the anions In₂X₆²⁻ and the adducts In₂X₄L₂, and organo derivatives In₂R₄ of this type are also known.⁶ Indium(II) iodide has been shown to be In^I[In^{III}I₄] in the solid state, and the reasons for this being more stable than I₂In^IIn^{III}I₂ have been discussed elsewhere.⁷ The present paper describes the reaction of In₂I₄ with various substituted *o*-quinones in toluene in terms of the solution behavior of indium(II) and of the electron-transfer reactions involved.

Experimental Section

General Data. All solvents were dried and degassed by standard procedures. *o*-Quinones were the commercially available materials

(Aldrich). Indium(II) iodide was prepared by reducing InI₃ (prepared in xylene from In + ³/₂I₂) with indium metal in situ, using previously reported methods.⁸

Infrared spectra were recorded on a Nicolet 4DX instrument, and ¹H and ¹³C nuclear magnetic resonance spectra (NMR) on a Bruker AC-300L spectrometer. Electron spin resonance spectra (ESR) were obtained on a Bruker ESP-300E instrument, using methods described earlier.⁵ Elemental analysis was by Canadian Microanalytical Services Ltd.

Reactions with Indium(II) Iodide. (i) In₂I₄ + 2TBQ. A solution of In₂I₄ (0.74 g, 1 mmol) in toluene (10 mL) was added to TBQ (0.44 g, 2 mmol) in the same solvent (10 mL). The resultant brown solution was stirred for 3 h, the solvent partially removed, and excess 4-picoline added, at which point the solution became green. The air-sensitive crystals which deposited when this solution was cooled overnight were collected, washed with toluene, and dried in vacuo. Yield: 0.78 g, 53%. Anal. Calcd for (TBSQ)InI(pic)₂·C₇H₈, C₃₃H₄₂N₂O₂InI: C, 53.5; H, 5.72. Found: C, 53.7; H, 5.70. Spectral data confirmed the formulation of this compound. IR (KBr): 3020–2954 (C–H), 1621 (4-pic), 1487, 1439 (C–O), 1420 cm⁻¹ (C–O). ¹H NMR: 8.41 (4H, pic), 7.23–7.15 (6H, pic + TBC), 2.30 (6H, CH₃ of pic), 1.31 (9H, *t*-Bu), 1.21 ppm (9H, *t*-Bu). ¹³C NMR: 149.0 (br), 124.5 (TBC), 31.9 (*t*-Bu), 29.8 (*t*-Bu), 20.5 ppm (CH₃, pic).

(ii) In₂I₄ + 4TBQ. The procedure was identical to that described above except that 4 equiv of TBQ was used. Partial removal of solvent, followed by cooling, gave an air-sensitive red powder, which was washed with toluene and dried in vacuo. This solid is (TBSQ)InI₂. Anal. Calcd for C₁₄H₂₀O₂InI₂: C, 28.5; H, 3.42. Found: C, 28.6; H, 3.70. IR (KBr): 3040–2980 (C–H), 1489 (C–O), 1443 (C–O), 1446 cm⁻¹ (C–O). Addition of 4-picoline to the dissolved solid in toluene resulted in the deposition of air-sensitive pale green needlelike crystals of the bis(picoline) adduct, (TBSQ)InI₂(pic)₂. Anal. Calcd for C₂₆H₃₄O₂N₂InI₂: C, 40.3; H, 4.42. Found: C, 40.4; H, 4.50. IR (KBr): 3090–3010 (C–H), 1635 (pic), 1486 (C–O), 1394 (C–H), 1420 cm⁻¹ (C–H). A crystallographic study of this compound is reported below.

In two later experiments, excess triphenylphosphine was added to the reaction mixture, at either the beginning or the end. In each case, the product was a precipitate of InI₃·PPh₃. Mp: 195–197 °C (lit.⁹ 195 °C). Anal. Calcd for C₁₈H₁₅InI₃P: C, 24.9; H, 2.50. Found: C, 28.5; H, 2.00.

(iii) In₂I₄ + 2 Phenanthrene-9,10-quinone (PQ). The procedure was identical to that for TBQ except that the reaction time was 12 h. Partial removal of solvent and subsequent cooling led to the deposition of a purple powder, shown by analysis to be the semiquinone derivative

(8) Freeland, B. H.; Tuck, D. G. *Inorg. Chem.* **1976**, *15*, 475.

(9) Carty, A. J.; Tuck, D. G. *J. Chem. Soc. A* **1996**, 1081.

[⊗] Abstract published in *Advance ACS Abstracts*, February 1, 1996.

- (1) Tuck, D. G. *Coord. Chem. Rev.* **1992**, *112*, 215.
- (2) Annan, T. A.; McConville, D. H.; McGarvey, B. R.; Ozarowski, A.; Tuck, D. G. *Inorg. Chem.* **1989**, *28*, 1664.
- (3) Annan, T. A.; Tuck, D. G. *Can. J. Chem.* **1988**, *66*, 2935.
- (4) Annan, T. A.; Chadha, R. K.; Doan, P.; McConville, D. G.; McGarvey, B. R.; Ozarowski, A.; Tuck, D. G. *Inorg. Chem.* **1990**, *29*, 3936.
- (5) Annan, T. A.; Brown, M. A.; El-Hadad, A.; McGarvey, B. R.; Ozarowski, A.; Tuck, D. G. *Inorg. Chim. Acta* **1994**, *225*, 207.
- (6) Tuck, D. G. *Chem. Soc. Rev.* **1993**, 269 and references therein.
- (7) Tuck, D. G. *Polyhedron* **1990**, *9*, 377.

Table 1. Summary of X-ray Crystallographic Data for (TBSQ)In₂(pic)₂

empirical formula	C ₂₆ H ₃₄ O ₂ N ₂ In ₂	Z	2
fw	775.20	space group	$P\bar{1}$ (No. 2)
<i>a</i>	13.013(3) Å	<i>T</i>	23 °C
<i>b</i>	13.317(3) Å	λ	0.710 69 Å
<i>c</i>	10.828(5) Å	ρ_{calcd}	1.52 g cm ⁻³
α	97.71(3) Å	μ , cm ⁻¹	25.49
β	107.98(3) Å	<i>R</i> , %	5.1
γ	103.92(3) Å	<i>R</i> _w , %	6.4
<i>V</i>	1684.8(1.2) Å ³		

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}.$$

(PSQ)In₂. Anal. Calcd for C₁₄H₈O₂In₂: C, 29.2; H, 1.40. Found: C, 29.3; H, 1.50. IR (KBr): 3060–3020 (C–H), 1476 (C–O), 1441 (C–O), 1425 cm⁻¹ (C–O).

(iv) **In₂I₄ + 2 Tetrabromo-*o*-benzoquinone.** Again the procedure was identical to (i) except that the reaction time was longer at 15 h. Removal of solvent left a dark brown solid, which was washed with cold benzene and dried in vacuo. Anal. Calcd for C₆Br₄O₂In₂: C, 9.10; H, 0.0. Found: C, 9.20; H, 0.05. IR (KBr): 3045–2965 (C–H), 1496 (C–O), 1456 (C–O), 1425 cm⁻¹ (C–O).

(v) **In₂I₄ + 2 1,2-Naphthoquinone (NQ).** A reaction time of 24 h gave a black solid, which was collected by filtration, washed with toluene, and dried in vacuo. This material was identified as (NSQ)In₂. Anal. Calcd for C₁₀H₆O₂In₂: C, 22.8; H, 1.15. Found: C, 22.9; H, 1.20. IR (KBr): 3060–3005 (C–H), 1487 (C–O), 1458 (C–O), 1416 cm⁻¹ (C–O).

Crystallographic Analysis. A crystal of (TBSQ)In₂(pic)₂, **1**, mounted in a glass capillary, was sited in a four-circle Rigaku AFC6 diffractometer using graphite-monochromatized Mo K α radiation ($\lambda = 0.710 69$ Å). The unit cell constants and an orientation matrix for data collection were obtained from 24 centered reflections ($15^\circ < 2\theta < 35^\circ$). Crystal parameters and details of the data collection methods are summarized in Table 1. The intensities of three standard reflections were recorded every 150 reflections and showed no statistically significant changes over the duration of the data collection. The intensity data were collected using the ω - 2θ scan technique, in four shells ($2\theta < 30, 40, 45, \text{ and } 50^\circ$). In view of the large absorption coefficient, an absorption correction was applied to the data, which were processed using the TEXSAN software package on an SG1 computer. Refinement was carried out by using full-matrix least-squares techniques on *F*, minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$ and *F*_o and *F*_c are the observed and calculated structure factors. Fixed H atom contributions were included, with C–H distances of 0.95 Å and thermal parameters 1.2 times the isotropic thermal parameters of the bonded carbon atoms. Hydrogen atoms were not refined, but all values were updated as the refinement proceeded. Convergence was achieved at final values of *R* = 0.051 and *R*_w = 0.064 for 5918 unique observed reflections. The programs and correction procedures used are listed in refs 10–17. Significant bond distances and bond angles are given in Table 2, and the structure is shown in Figure 1. Tables of thermal parameters, positional parameters, and hydrogen atom coordinates are available as Supporting Information.

Results

Crystallographic Study. The structure of **1** is clearly that of a six-coordinate indium(III) species, with an InO₂N₂I₂ kernel,

- (10) Walker, N.; Stuart, D. DIFABS. *Acta Crystallogr., Sect. A* **1983**, *39*, 158.
- (11) Gilmore, D. J. MITHRIL. *J. Appl. Crystallogr.* **1984**, *17*, 42.
- (12) Beurskens, P. T. DIRDIF. Technical Report I; Crystallography Laboratory: Toernooiveld, 6526 ED Nijmegen, The Netherlands, 1984.
- (13) Johnson, C. K. ORTEP II. Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.
- (14) Cromer, D. T.; Waber, T. J. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, U.K., 1974; Vol. IV.
- (15) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.
- (16) Motherwell, S.; Clegg, W. PLUTO. University of Cambridge, U.K., 1978.
- (17) TESAN. *Texray Structure Analysis Package*; Molecular Structure Corp: Houston, TX, 1985.

Table 2. Interatomic Distances (Å) and Angles (deg) for In(TSQ)In₂(pic)₂

I(1)–In(1)	2.773(1)	O(1)–C(6)	1.31(1)
I(2)–In(1)	2.772(1)	O(2)–C(1)	1.29(1)
In(1)–O(1)	2.206(7)	N(1)–C(13)	1.31(2)
In(1)–O(2)	2.192(8)	N(1)–C(17)	1.33(2)
In(1)–N(1)	2.31(1)	N(2)–C(7)	1.32(1)
In(1)–N(2)	2.325(9)	N(2)–C(11)	1.33(2)
O(1)–In(1)–N(1)	85.0(3)	I(1)–In(1)–I(2)	102.55(4)
O(1)–In(1)–N(2)	83.7(3)	I(1)–In(1)–O(1)	92.9(2)
O(2)–In(1)–N(1)	85.2(3)	I(1)–In(1)–O(2)	167.8(2)
O(2)–In(1)–N(2)	85.8(3)	I(1)–In(1)–N(1)	92.7(3)
N(1)–In(1)–N(2)	167.1(3)	I(1)–In(1)–N(2)	94.1(2)
In(1)–O(1)–C(6)	113.4(7)	I(2)–In(1)–O(1)	164.5(2)
In(1)–O(2)–C(1)	114.0(7)	I(2)–In(1)–O(2)	89.7(2)
In(1)–N(1)–C(13)	123(1)	I(2)–In(1)–N(1)	95.7(3)
In(1)–N(1)–C(17)	121.0(8)	I(2)–In(1)–N(2)	93.6(2)
O(2)–C(1)–C(6)	119(1)	N(1)–C(17)–C(16)	123(1)
C(2)–C(1)–C(6)	120(1)	N(1)–C(13)–C(14)	124(1)
C(7)–N(2)–C(11)	117(1)	N(2)–C(7)–C(8)	122(1)
C(13)–N(1)–C(17)	116(1)	N(2)–C(11)–C(10)	122(1)
In(1)–N(2)–C(7)	120.5(8)	O(1)–In(1)–O(2)	75.0(3)
In(1)–N(2)–C(11)	122.1(8)	O(1)–In(1)–N(1)	85.0(3)
phenyl ring	mean C–C		1.41(2)
	mean C–C–C		1.20(1)
<i>tert</i> -butyl group at C(4)	mean C(23)–C(24,25,26)		1.56(2)
<i>tert</i> -butyl group at C(2)	mean C(19)–C(20,21,22)		1.57(2)
picoline ligands	N(1): mean C–C		1.40(2)
	N(2): mean C–C		1.39(2)

and is closely related to that of the bromo compound⁴ (TBSQ)InBr₂(pic)₂; in particular, the bond distances and angles in the InO₂C₂ ring of the indium–semiquinonate system are identical within experimental error in the two compounds, as are the indium–picoline parameters. The average C–O distance of 1.30(1) Å in the semiquinonate ligand is almost exactly that reported in many other analogous main group complexes of this type. The other feature of interest is the indium–iodine bond distance of 2.774(1) Å. We have recently reviewed the published data for indium(III)–iodine bond distances, with specific reference to the effect of coordination number;¹⁸ the range for six-coordinate species is 2.83 ± 0.04 Å, and the present results are clearly in keeping with these limits.

In addition to these structural details, the crystallographic results are important in that they demonstrate the role of *o*-semiquinone radicals in these reactions and, so, support the reaction mechanism discussed below.

ESR Studies. The most complete series of spectroscopic results apply to the reaction of In₂I₄ with 2 equiv of TBQ in toluene. The ESR spectrum of the resultant solution, shown in Figure 2A, clearly contains two components. The more sharply defined of these has the characteristics *g* = 2.0034, *A*_{In} = 5.06 G, and *A*_H = 3.40 G, which identify the parent species as an indium(III)–TBSQ[•] complex.⁴ Addition of excess picoline to this solution leads to the removal of the broad feature, giving the spectrum in Figure 2B, for which we found *g* = 2.003 91 at 300 K. This very well resolved spectrum (Figure 3) shows a splitting of 0.36 G due to the nine hydrogens of one of the *tert*-butyl groups, in addition to the splittings due to indium and one of the ring hydrogens of 4.86 and 3.42 G, respectively. The indium hyperfine constant changes with temperature from 5.61 G to 240 K to 4.00 G at 360 K; *g* changes over the same temperature range from 2.003 85 to 2.003 94, while the hyperfine constants for the ring hydrogens and the *tert*-butyl hydrogens remain essentially unchanged. Even at this very good resolution, we could not see any splitting due to the second

(18) Brown, M. A.; Tuck, D. G. *Inorg. Chim. Acta*, in press.

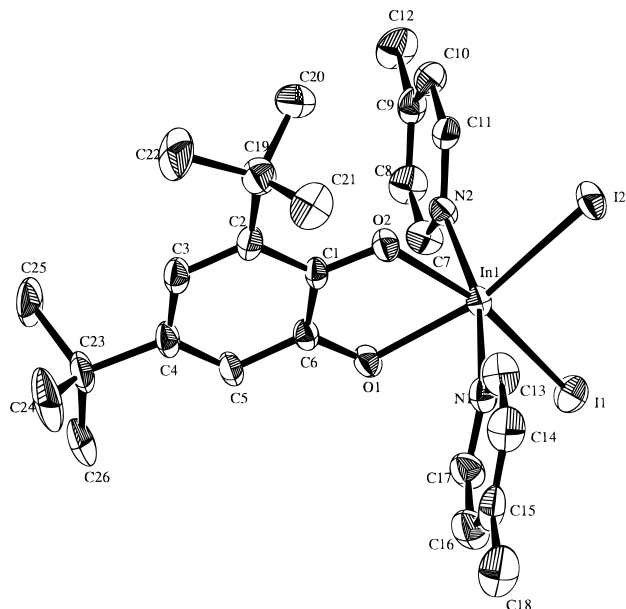


Figure 1. Molecular structure of $(\text{TBSQ})\text{InI}_2$ (ORTEP diagram, 30% probability ellipsoids), with hydrogen atoms omitted.

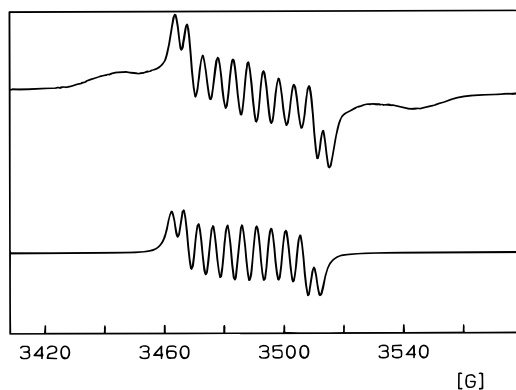


Figure 2. ESR spectra of (A, top) the $\text{In}_2\text{I}_4 + \text{TBQ}$ reaction mixture and (B, bottom) the same solution after adding picoline, both at room temperature.

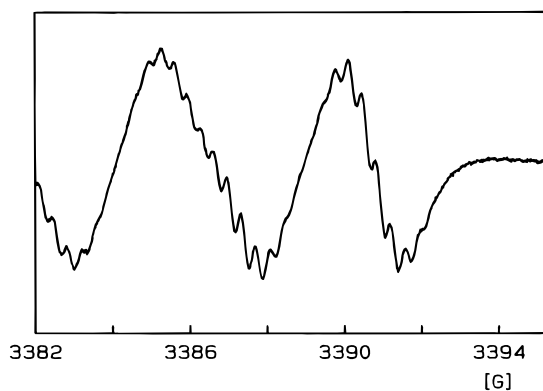


Figure 3. High-field region of the ESR spectrum of a solution containing $\text{In}_2\text{I}_4 + \text{TBQ} + \text{picoline}$, recorded at 300 K.

ring hydrogen, and there was no evidence of spin density on the picoline nitrogen.

The broader component in the spectrum of Figure 2A can be interpreted in either of two ways. If it is assumed that the observed features are the visible portion of a broad multiplet centered on $g = 2.000$, one can extract a hyperfine coupling constant of 10 G, typical of A_{In} for species in which $\text{TBSQ}^{\cdot-}$ is bonded to indium(I).⁴ The alternative explanation is that this is a broad signal due to an indium(III) biradical complex in the

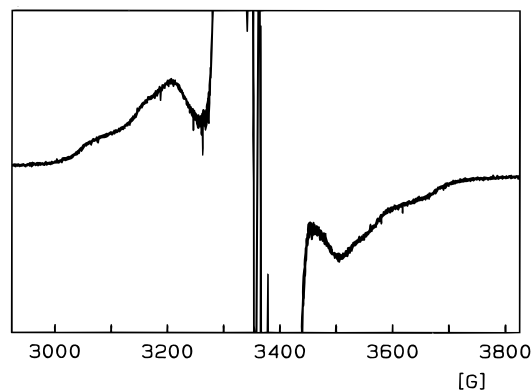


Figure 4. ESR spectrum of a frozen solution (77 K) containing $\text{In}_2\text{I}_4 + \text{TBQ}$, showing presence of a diradical species.

solution, and this is supported by the frozen-solution spectra (see below). The reaction scheme discussed later accommodates both these possibilities, which cannot be differentiated on the present evidence.

The spectrum of the frozen solution shows, in addition to the central features, a half-field resonance indicating the presence of a biradical species. The presence of unresolved extensive hyperfine splitting due to the indium nucleus makes a detailed analysis of the fine structure rather difficult, but we were able to estimate a value of $D \sim 250$ G from the central region of the spectrum (Figure 4) as well as from the position of the half-field signal. Comparison with earlier results for $\text{M}(\text{TBSQ})_2$ complexes¹⁹ and their analysis identify the arrangement of the ligands as *cis*. The half-field resonance is absent from a frozen solution prepared from $\text{In}_2\text{I}_4 + 2\text{TBQ} + \text{excess picoline}$. The remaining central portion of this spectrum is well resolved and shows the presence of an anisotropic hyperfine coupling to indium.

The reactions of In_2I_4 with 2 equiv of phenanthrene-9,10-quinone, tetrabromo-*o*-quinone, and 1,2-naphthoquinone all follow the same course, in that strongly colored solids with the composition $(\text{SQ})\text{InI}_2$ are obtained, either immediately or subsequently on removal of solvent. These compounds show ESR activity in the solid state. The spectra of the reaction mixtures confirm the presence of indium(I) and indium(III) semiquinone species, and/or of indium(III) biradical complexes, indicating a reaction pathway similar to that set out in Scheme 1. The major differences are that the products $(\text{SQ})\text{InI}_2$ are much less soluble than in the case of the TBQ system and that these final products do not require the ligation of a base to form stable insoluble products. We were not able to obtain suitable crystals of any of these compounds for X-ray analysis.

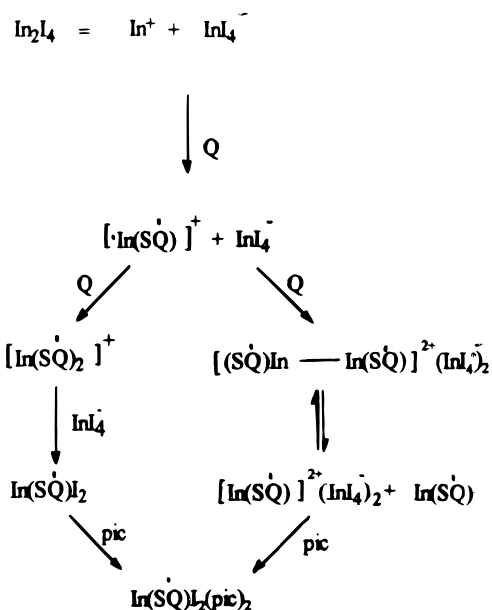
Discussion

Reaction Scheme. The ESR results, and the crystallographic structure of **1**, show beyond question that semiquinonate anion radicals are essential intermediates in the reaction between In_2I_4 and TBQ. As noted above, In_2I_4 has the structure $\text{In}^+[\text{InI}_4]^-$ in the solid state, and this apparently persists in solutions in aromatic solvents due to solvation of the In^+ cation;⁶ a crystalline disolvate has been characterized in the system $\text{In}_2\text{-Br}_4\text{-1,3,5-Me}_3\text{C}_6\text{H}_3$.²⁰ We therefore assume that the reaction involves the solvated In^+ cation, presumably present as part of an ion-pair $[\text{In}(\text{S})_n]^+[\text{InI}_4]^-$, and the *o*-quinone. Furthermore, given that there are no known cases of InI_4^- acting as an

(19) Ozarowski, A.; McGarvey, B. R.; Peppe, C.; Tuck, D. G. *J. Am. Chem. Soc.* **1991**, *113*, 3288.

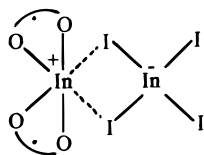
(20) Ebenhöch, J.; Müller, G.; Reide, J.; Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 386.

Scheme 1



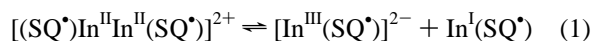
electron pair acceptor, the primary reaction must be nucleophilic attack by the *o*-quinone at the In^+ site.

The reaction scheme shown (Scheme 1) assumes that this first step yields an indium(III) semiquinonate cation $[\text{In}(\text{SQ})]^+$, which may then lead to two separate reaction sequences. One of these involves dimerization by In—In bond formation, and disproportionation of this dimer can yield both indium(III) and indium(I)—semiquinone species. These processes, which have been discussed in detail in an earlier paper,⁴ explain the ESR spectrum in Figure 2 on the basis that semiquinone derivatives of these two oxidation states are identified. In the competing pathway, $[\text{In}^{\text{II}}(\text{SQ})]$ may react with a second quinone to give $[\text{In}^{\text{III}}(\text{SQ})_2]^+$, which explains the presence of diradical species, with *cis* ligands in the solution. The most probable stereochemistry for this species, and its associated InI_4^- anion, is



in which the stereochemistry at the positive site is similar to that in the $[\text{InI}_2(\text{dmsO})_4]^+$ cation.²¹ Iodide bridging is an important feature of the structure of In_2I_6 both in the solid state and in solution.²² Rearrangement of this species would give $(\text{SQ})\text{InI}_2$.

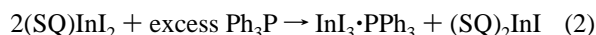
The effect of excess picoline on each of these competing processes will be to produce the complex $\text{In}(\text{SQ})\text{InI}_2(\text{pic})_2$. In the case of the reaction proceeding via the left-hand pathway, this is a straightforward addition and rearrangement reaction. In the equilibrium mixture it seems likely that the indium(III) species is associated with at least one and possibly two InI_4^- anions. Addition of excess picoline will convert this to $(\text{SQ})\text{InI}_2(\text{pic})_2$, thereby causing eq 1 to move to the right, with the



eventual conversion of all three species to the picoline adduct.

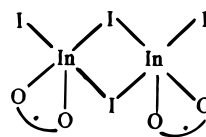
Scheme 1 therefore represents a good overall model in the case of the reaction between In_2I_4 and 2 equiv of TBQ. On the preparative scale, the air-sensitive compound $\text{In}(\text{TBSQ})\text{I}_2$ was obtained from the solution as the bis(picoline) adduct, suggesting that the left-hand pathway of Scheme 1 is the dominant process in these circumstances.

The result of adding excess triphenylphosphine to a mixture of $\text{In}_2\text{I}_4 + 4\text{Q}$ is the precipitation of the 1:1 adduct $\text{InI}_3 \cdot \text{PPh}_3$. The ESR spectrum of the residual solution shows the presence of a biradical species, and this can be understood in terms of Scheme 1, since by following the left-hand side sequence, one can write



The most significant difference between the triphenylphosphine reaction and that with 4-picoline is probably the precipitation of the 1:1 adduct in the former system.

The three other *o*-quinones studied, namely phenanthrene-9,10-quinone, tetrabromo-*o*-benzoquinone, and 1,2-naphthoquinone, all give the appropriate $(\text{SQ})\text{InI}_2$ species as the reaction products when reacted with In_2I_4 in a 1:2 ratio, and in each case these insoluble products precipitated from the reaction mixture without the addition of base. It is possible that the insolubility and the stability in the absence of further coordinating agents point to the existence of these species as halide bridged dimers



while higher order species might also involve bridging semiquinonate ligands.

An interesting general point is that although the reaction scheme is based on the oxidation of the solvated In^+ cation by *o*-quinones, there are significant differences from the comparable reactions of two of these *o*-quinones with indium(I) halides.⁴ This may reflect the different reaction conditions used in the two series of experiments; in the present case, the reactions were homogeneous, while with the indium(I) halides, homogeneity was only achieved by adding an excess of *N,N,N',N'*-tetramethylethylenediamine to the toluene, since in the absence of this base suspensions of InX formed the oxidation matrix.

Conclusion. The reaction of In_2I_4 with four different substituted *o*-benzoquinones proceeds via attack of the quinone on the solvated In^+ cation which is present in solutions of In_2I_4 in toluene. Subsequent reactions, which can be understood in the light of previous work on indium(I)—*o*-quinone reactions, give either $(\text{SQ})\text{InI}_2$ or $(\text{SQ})\text{InI}_2(\text{pic})_2$ as product, depending on the particular *o*-quinone and on the reaction conditions. ESR results support the proposed reaction mechanism.

Acknowledgment. This work was supported in part by Operating Grants to B.R.M. and D.G.T. from the Natural Sciences and Engineering Research Council of Canada.

Supporting Information Available: Tables D.1–D.4, listing additional X-ray crystallographic data, final fractional coordinates and isotropic thermal parameters of non-hydrogen atoms, anisotropic thermal parameters for non-hydrogen atoms, and final fractional coordinates and isotropic thermal parameters for hydrogen atoms (7 pages). Ordering information is given on any current masthead page. Structure factor tables may be obtained directly from the authors.

(21) Einstein, F. W. B.; Tuck, D. G. *Chem. Commun.* **1970**, 1182.

(22) Taylor, M. J.; Brothers, P. J. In *The Chemistry of Aluminium, Gallium, Indium and Thallium*; Downs, A. J., Ed.; Blackie: London, 1993; pp 132–3.