DALTON
FULL PAPER

The interaction of indium(III) iodide species with substituted *ortho*- and *para*-quinones

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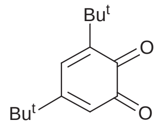
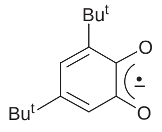
The interactions of substituted *ortho*- and *para*-quinones with indium(III) halides and the InI_4^- anion have been studied in non-aqueous solution. *para*-Quinones and InI_3 give rise to stable 1 : 1 adducts, which are diamagnetic in the solid state, but which decompose in solution to form (p-sq)InI_2 derivatives, where p-sq$^{\bullet -}$ is the corresponding semiquinonate. With *ortho*-quinones, the reaction products are (o-sq)InI_2 which react with 4-methylpyridine (pic) to form (o-sq)InI_2pic_2. The electron spin resonance spectra of these products, and their solution chemistry, are discussed. The reactions involve intramolecular one-electron transfer, resulting in oxidation of the iodide ligand. In contrast, the reaction of 3,5-di-*tert*-butyl-1,2-benzoquinone with InI_4^- apparently involves intermolecular electron transfer; in this case, the products are I_3^- and the corresponding catecholate (dbc), isolated as the solid InI(dbc)pic_2. The mechanisms of these various processes are discussed.

The oxidation of Main Group elements, and of the lower oxidation state derivatives of such elements, has been the subject of a number of papers from this laboratory. The most significant conclusions include the identification of successive one-electron transfer processes in such redox reactions, and the confirmation of a mechanism involving nucleophilic attack by a quinone at the appropriate metal or non-metal centre. Both electron spin resonance spectroscopy and X-ray crystallography have been important experimental techniques in these investigations, and the use of these and other methods has been discussed elsewhere.[1,2]

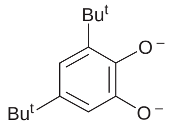
We have recently carried out a series of experiments in which both *ortho*- and *para*-quinones interact with the halide of a Main Group metal in its highest oxidation state. In some cases, it has been possible to characterize crystalline adducts of such systems, and in others there is clear evidence of intramolecular electron transfer within the complex. The present paper reports studies of the interaction of a range of *ortho*- and *para*-quinones with neutral and anionic halide derivatives of indium(III). With *para*-quinones, we have isolated 1 : 1 adducts of InI_3, which are stable in the solid state, but which decompose in non-aqueous solution, forming paramagnetic species. *ortho*-Quinones react directly with InI_3, to give compounds in which indium(III) is coordinated by two halides and a semiquinonate ligand. These results appear to involve a hitherto unrecognized type of intramolecular electron transfer reaction, with important implications in Main Group chemistry. We have also observed a reaction between an *ortho*-quinone and the InI_4^- anion, and here the course of the electron transfer is apparently through an intermolecular attack of the quinone on the ligand, a process which is similar to that found in reactions of quinones with organometallic substrates.[3] The quinones studied in the present work, and the abbreviations used, are shown right.



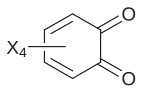
o-dbbq



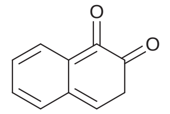
o-dbbsq$^{\bullet -}$



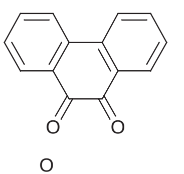
dbc^{2-}



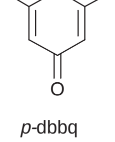
X = Cl, Br (Cl_4q, Br_4q)



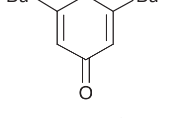
1,2-naphthoquinone (nq)



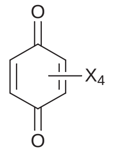
phenanthrenequinone (pq)



p-dbbq



p-dbbsq$^{\bullet -}$



X = Cl, Br

Experimental

Indium halides were prepared by the thermal reaction of the elements in refluxing xylene, and the salt $Et_4N[InI_4]$ was synthesized from the reaction of Et_4NI and InI_3 in ethyl acetate (Found: C, 13.2; H, 2.65. Calc. for $C_8H_{20}InI_4$: C, 12.8; H, 2.65%). Substituted quinones, and organic bases, were dried over sodium hydroxide and recrystallised under nitrogen. Solvents were distilled from, and stored over, drying agents, and degassed before use. All reactions were carried out in an atmosphere of dry nitrogen, and reaction products were handled by the normal methods for air-sensitive materials.

Electron spin resonance (ESR) spectra were recorded on a Bruker ESP-300E instrument operating in the X-band region, using the calibration and other techniques outlined elsewhere.[4]

Table 1 Characterization of derivatives of InI_3 and *ortho*-quinones

o-Quinone	Compound	Identifying number	Yield (%)	Colour	Analysis (%)[a] C	H
3,5-di-*tert*-butylbenzo-	(sq)InI_2	1	75	Purple	28.5 (28.5)	3.35 (3.40)
	(sq)InI_2pic_2	1A	65	Brown	40.0 (40.3)	4.30 (4.40)
Tetrachlorobenzo-	(sq)InI_2	2	55	Red-orange	12.2 (11.7)	0.14 (0)
	(sq)InI_2pic_2	2A	45	Red	27.6 (27.0)	1.80 (1.75)
Tetrabromobenzo-	(sq)InI_2	3	38	Red	9.50 (9.10)	0.02 (0)
	(sq)InI_2pic_2	3A	26	Orange	22.2 (22.1)	1.80 (1.45)
1,2-naphtho-	(sq)InI_2[b]	4	53	Dark blue	22.9 (22.8)	1.35 (1.15)
	(sq)InI_2pic_2	4A	42	Dark green	37.2 (37.0)	2.90 (2.80)
Phenanthrene-	(sq)InI_2[c]	5	65	Green	28.1 (29.1)	1.70 (1.40)
	(sq)InI_2pic_2	5A	58	Brown	41.6 (40.9)	3.00 (2.90)

[a] Calculated values in parentheses. [b] Mass spectrum; $M^+ = 527$ observed. [c] Mass spectrum; $M^+ = 557$ observed.

Table 2 Characterization of adducts of InI_3 and *para*-quinones

p-Quinone	Yield (%)	Colour	Analysis (%)[a] C	H
Benzo	80	Grey	— (11.9)	— (0.67)
2,6-Di-*tert*-butylbenzo[b,c]	73	Red	23.7 (23.5)	2.95 (2.80)
Tetrachlorobenzo	26	Yellow	9.70 (10.1)	0.04 (0)
Tetrabromobenzo	35	Orange	7.94 (7.83)	0.03 (0)
1,4-Naphtho	10	Brown	15.5 (15.2)	1.08 (0.95)

[a] Calculated values in parentheses. [b] For 1 : 1 adduct with $InCl_3$, orange, C 38.0 (38.1), H 4.10 (4.53), 62% yield. [c] Mass spectral peaks include $m/z = 496$ (InI_3).

Microanalysis was by Canadian Analytical Services. X-Ray crystallographic studies were by the methods previously described.[4,5] Mass spectra were recorded on a Shimadzu 14-B instrument operating in the EI mode, with Sun Sparc software.

In this paper, we follow the previous practice of identifying the triad of quinone, semiquinone and catecholate by the abbreviations q, $sq^{\bullet -}$, and cat^{2-}, with appropriate prefixes.

Preparative studies

In a typical experiment with *ortho*-quinones, a solution of the quinone in tetrahydrofuran (5 mmol in 20 cm^3) was added to a stirred solution of InI_3 (5 mmol) in the same solvent. In every case, a colour change was observed, with the fastest reaction being with di-*tert*-butyl-*o*-benzoquinone. Samples were removed for ESR analysis, and approximately half of the remaining mixture cooled to 0 °C; this led to the precipitation of coloured solids which were shown by analysis to be the corresponding (sq)InI_2 derivatives (see Table 1 for analytical results and related experimental data).

A six-fold excess of picoline (pic; 4-methylpyridine) was added to the remaining reaction mixture, the volume of the solution reduced by 50%, and the residue cooled to 0 °C; the crystals which formed were identified analytically as the bis(picoline) adducts (sq)InI_2pic_2. In the case where $sq^{\bullet -}$ = 3,5-di-*tert*-butyl-*o*-benzosemiquinonate (dbbsq) an X-ray crystallographic study showed that this compound was structurally identical with the material formed in the reaction between indium(II) iodide and the corresponding *ortho*-quinone.[5] (Unit cell dimensions, $a = 13.0097(5)$, $b = 13.302(4)$, $c = 10.811(5)$ Å, $\alpha = 97.677(4)$, $\beta = 107.992(3)$, $\gamma = 104.003(4)°$, $U = 1681.9(6)$ Å^3. Found[5] for (dbbsq)$InI_2(pic)_2$, $a = 13.013(3)$, $b = 13.317(3)$, $c = 10.828(5)$ Å, $\alpha = 97.71(3)$, $\beta = 107.98(3)$, $\gamma = 103.92(3)°$, $U = 1684.8(1.2)$ Å^3). We also attempted to prepare adducts with pyridine as the neutral donor, but in each case the analytical results were less than satisfactory, except in the case of phenanthrenequinone (Found: C, 39.4; H, 2.93. Calc. for (psq)InI_2py_2, $C_{24}H_{18}O_2N_2InI_2$: C, 39.2; H, 2.47%), and this aspect of the work was not continued. A similar sequence of reactions starting with $InCl_3$ gave the analogous (dbbsq)$InCl_2pic_2$ (Found: C, 52.7; H, 6.09. Calc. for $C_{26}H_{24}O_2N_2Cl_2In$: C, 52.7; H, 5.74%) In each case, the infrared spectra of both the initial products and the picoline adducts showed that ν(C=O) of the *o*-quinones, in the region 1650–1695 cm^{-1}, had disappeared and was replaced by ν(C–O) modes at 1440–1490 cm^{-1} (*cf.* ref. 1).

When *para*-quinones were used in essentially identical experiments, the products were the 1 : 1 adducts, q·InI_3, which were isolated and analyzed (Table 2). It was not possible to obtain material of suitable quality for X-ray crystallography from these experiments.

Studies with InI_4^-

A rapid reaction, identified by a colour change, occurred when millimolar quantities of $Et_4N[InI_4]$ and dbbq in tetrahydrofuran were mixed together at room temperature. The resultant brown solution was divided into two equal portions. Evaporation of one of these to 50%, followed by cooling, gave a dark brown powder, which was identified analytically as Et_4NI_3 (Found: C, 18.5; H, 3.82. Calc. for $C_8H_{20}NI_3$: C, 18.8; H 3.91%). ^{13}C NMR ($Me_4Si = 0$): δ 7.995 CH_3, 32.286 CH_2. IR ν(C–H) 3009–2908, ν(C–N) 1585, 1443, 1416 cm^{-1}. Yield 100%, based on the initial quantity of cation.

Samples of the remaining portion were used for ESR studies (see below). Addition of picoline to this solution gave a colourless precipitate, identified as InI(dbc)$(pic)_2$ (Found: C, 49.5; H, 5.25. Calc. for $C_{26}H_{34}N_2O_2InI$: C, 48.2; H, 5.25%). The infrared spectrum confirmed the presence of catecholate, with ν(C–O) at 1463, 1433 and 1415 cm^{-1}. Similar experiments were attempted using toluene as the reaction medium, but these were unsatisfactory because of the insolubility of the InI_4^- salt, although the general course of the reaction appeared to be similar to that described above.

Results and discussion

Reactions with *ortho*-quinones

The results in Table 1 for compounds numbered 1–5 show that the reaction of *ortho*-quinones with InI_3 produces (sq)InI_2 species, which can be obtained as insoluble solids at 0 °C. The molecularity of these compounds is not known, but treatment with excess picoline yields the bis-adduct, which in the case of (dbbsq)InI_2pic_2 was shown to be crystallographically identical with the mononuclear six-coordinate compound obtained from the reaction the reaction of dbbq and In_2I_4.[5]

The initial overall reaction is

$$\text{dbbq} + InI_3 \longrightarrow (\text{dbbsq})InI_2 + I^{\bullet} \qquad (1)$$

followed by

$$2I^{\bullet} \longrightarrow I_2 \qquad (2)$$

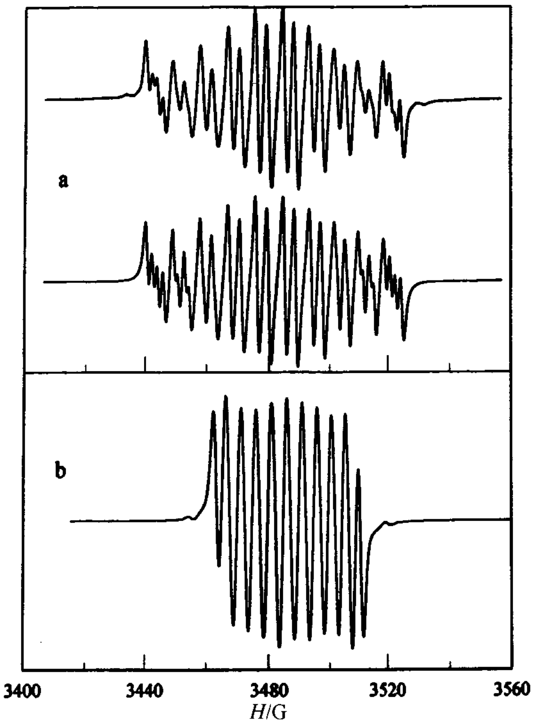


Fig. 1 a, ESR spectrum of the (diluted) solution arising from the reaction of InI_3 and *o*-dbbq, at room temperature. The upper trace is the experimental result, and the lower is the simulated spectrum, using the parameters discussed in the text. b, The same solution, after addition of a six-fold excess of picoline.

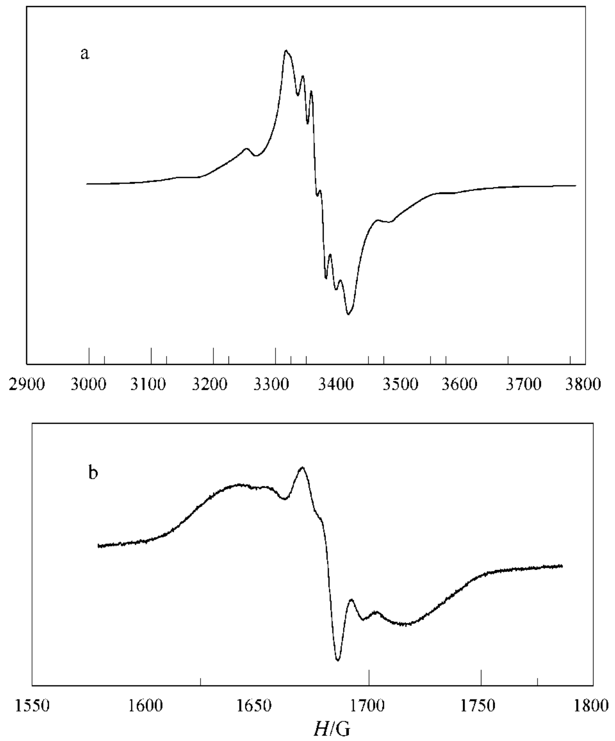


Fig. 2 a, ESR spectrum of frozen solution at 100 K from Fig. 1a. b, The half-field transition.

and

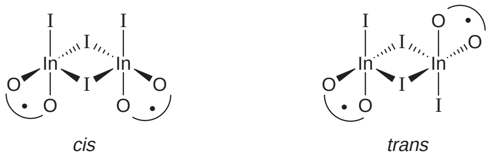
$$(dbbsq)InI_2 + \text{excess pic} \longrightarrow (dbbsq)InI_2pic_2 \qquad (3)$$

Reactions (1) and (2) are complete within about 15 min, with the relative rates, as judged by the colour change, in the order dbbq > Br_4q > Cl_4q > nq > pq, and InI_3 > $InCl_3$. We return to the mechanistic details of eqn. (1) below.

In each case, the reaction of InI_3 and *o*-quinone gave rise to solutions which were strongly ESR active, as would be expected if the product is a semiquinone derivative. The generation of radical species by the interaction of dbbq with indium and gallium trihalides was reported some years ago, but the reaction pathway was not apparently explored.[6,7] In the present studies, the system most thoroughly explored involved InI_3 + dbbq, and Fig. 1a shows the ESR spectrum of the (diluted) solution resulting from this reaction. The addition of excess picoline caused marked changes, giving rise to a spectrum (Fig. 1b) essentially identical to that assigned previously[5] to the six-coordinate indium(III) complex $(dbbsq)InI_2pic_2$. The parameters found for Fig. 1b by simulation are $g = 2.0038$, $A_{In} = 4.9$ G, $A_H = 3.6$ G (1 proton) (1 G = 0.1 mT), compared with the earlier values $g = 2.00391$, $A_{In} = 4.86$ G, $A_H = 3.42$ G (1H), 0.36 G (9H): in this spectrum, and those in Fig. 1a, we did not observe any splitting by the proton on C3, as is commonly the case in derivatives of dbbsq.[8] Fig. 1a can be analysed as the ESR spectrum of a mixture of two closely related indium(III) species; for one, $g = 2.0032$, $A_{In} = 8.93$ G, $A_H = 3.65$ G (1H), and for the other $g = 2.0032$, $A_{In} = 8.50$ G, $A_H = 3.65$ G (1H). The simulation in Fig. 1a assumes that these two species are present in equimolar proportions, and we therefore suggest that eqn. (1) is followed by

$$2\,(dbbsq)InI_2 \rightleftharpoons (dbbsq)IInI_2InI(dbbsq) \qquad (4)$$

in which the dimerisation is presumed to involve iodide bridging, In–μ-I_2–In, similar to that reported for In_2I_6 in non-aqueous solution.[9] Such a dimer can exist as *cis* and *trans* isomers, which explains the identification of two similar A_{In} values. These structures are preferred to the form $(dbbsq)_2$-InI_2InI_2, which does not give two stereoisomers.



The stereochemistry of these various species is an important factor in these arguments. The $(dbbsq)InI_2$ monomer must be highly strained, since it is difficult for a pseudo-tetrahedral molecule to accommodate the bidentate semiquinonate, given that the bite angle for this ligand is *ca.* 75° (*cf.* ref. 5). In a dimeric molecule, indium has pentagonal bipyramidal stereochemistry, and the consequent lowering of strain therefore serves to move eqn. (4) to the right. Both *cis* and *trans* dimers can be readily converted to the six-coordinate $(dbbsq)InI_2pic_2$ by excess picoline. Coordination by an electron-donating neutral ligand lessens the effective positive charge at the metal centre, thereby weakening the interaction of the unpaired electron and lowering the hyperfine constant A_{In} from the relatively high value of *ca.* 8.6 G in the dimers to one more typical of six-coordinate indium(III) complexes.

In an attempt to further characterize these dimeric species, we recorded the ESR spectra of the frozen solution (Fig. 2a), and the associated half-field resonance (Fig. 2b). Surprisingly, the simulation of these spectra identifies the low temperature species as being an $S = \frac{3}{2}$ state, rather than a biradical, and the predominant complex under these conditions is therefore $In(dbdsq)_3$. This molecule, which has been prepared independently[10] by the metathesis of InI_3 and $3Na^+dbbsq^-$, is an analogue of $Ga(dbbsq)_3$, whose preparation and crystallographic structure were reported earlier.[11] The simulation for $S = \frac{3}{2}$ state assumed a spin-Hamiltonian of the form

$$H = gB_eS\cdot H + A_{In}\,S\cdot I + D[3\,S_z^2 - \tfrac{1}{3}\,S\,(S+1)] \qquad (5)$$

with the parameters $g = 2.003$, $A_{In} = 8 \pm 0.5$ G, and $D = 103 \pm 5$

G. The corresponding values for the gallium complex are $g = 2.003$, $D = 108$; the slightly lower value of D for the indium species is in keeping with the larger ionic radius of the latter element. In addition to the dimerisation processes discussed above, the solution chemistry of the (dbbsq)InI_2 product of eqn. (1) must therefore also involve the equilibria

$$InX_3 \rightleftharpoons InX_2Y \rightleftharpoons InXY_2 \rightleftharpoons InY_3 \qquad (6)$$

where X = I, Y = dbbsq. Such facile redistribution reactions are a known feature of the chemistry of indium(III) complexes in non-aqueous solution,[9] and in the present context explain the presence of di- and tri-radical species. The relative quantity of each species will be a function of solvent, temperature, and the nature of the semiquinonate anion, and it is therefore understandable that the predominant trimer seen at 100K is not observed at room temperature.

The ESR spectra of solutions produced by the reaction of o-Cl_4q and o-Br_4q with InI_3 were weak, due to the poor solubility of the (X_4sq)InI_2 products, and of their picoline derivatives (2–3A, Table 1). There are also some differences in the case of the derivatives of 1,2-naphthoquinone; the A_{In} value in the presence of excess picoline is 3.6 G, in reasonable agreement with that for the dbbsq analogue, but the spectrum of the initial reaction solution shows no indium hyperfine coupling, suggesting that the species in solution are the free napththosemiquinonate anion and InI_3. In the case of phenanthrenequinone, the reaction solution gave $g = 2.0028$, $A_{In} = 1–2$ G, but the simulation of the picoline adduct spectrum was clearer, with $A_{In} = 2.6$ G, $A_H = 2.25$ (1H) and 1.35 G (1H), and $g = 2.0036$. These results in general are in keeping with those for dbbq + InI_3, although the naphthoquinone results emphasize the significance of the solution equilibria, and their dependence on the properties of the o-quinone involved.

The main feature of these reactions is the oxidation of a ligand bonded to a metal which is in its highest oxidation state. In previous studies[5,8,12] of the reactions of substituted *ortho*-quinones with indium-(I) and-(II) halides, we established that oxidation occurred at the metal centre, leading to the eventual production of $sq^{\bullet-}$ or cat^{2-} derivatives of indium(III), depending on the detailed behaviour of the system. The present results show that a different reaction

$$q + InX_3 \longrightarrow (sq^{\bullet})InX_2 + X^{\bullet} \qquad (7)$$

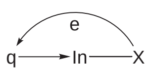
can also occur, and we note that this parallels a known fast solution-phase reaction in the case of iodide[13]

$$q + I^- \longrightarrow sq^{\bullet-} + \tfrac{1}{2}I_2 \qquad (8)$$

While this readily explains the reactions of InI_3, the reaction

$$dbbq + InCl_3 \longrightarrow (dbbsq^{\bullet})InCl_2 + Cl^{\bullet} \qquad (9)$$

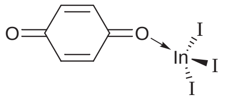
is more surprising, since Cl^- is not oxidized by *ortho*-quinones in aqueous solution, but it must be emphasized in this context that we are dealing here with a complex of a metal in its highest oxidation state, and that the redox behaviour of a bonded halide ligand in such a molecule will be quantitatively different from that of the free anion in aqueous solution. The first step in the reaction is the coordination of the quinone to the metal centre, as is suggested by the chemistry of the *para*-quinone systems (see below), and confirmed by studies of complex formation between *ortho*-quinones and $AlCl_3$ or SnX_4 (X = Cl, Br),[14] and this must be followed by intramolecular electron transfer within the bonded system.



One important difference between this process and the solution phase reaction of eqn. (7) lies in the entropy of activation. In a series of reactions involving tetrahalogeno-p-quinones and MI ($M = Na^+$, K) in acetone,[13] $\Delta S^{\ddagger}$ was found to be in the order of -80 J K^{-1} mol^{-1}, but this parameter is probably close to zero for an intramolecular electron transfer in a relatively large molecule in non-aqueous solution, and to this extent, the energetics of the latter process are more favorable than for the solution reaction. The detailed implication of these principles will be the subject of future work.

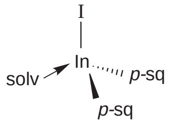
Reactions with *para*-quinones

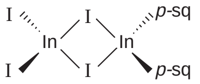
The analytical results in Table 2 show that the products of the reaction between indium(III) iodide and a series of substituted *para*-quinones are the 1:1 adducts, which are stable at room temperature in the absence of moisture. An analogous compound was also obtained with indium(III) chloride. This adduct formation is not surprising, given the known properties of the indium(III) halides,[9] and it seems reasonable to assume that these are four-coordinate monomeric species in the solid state. As noted above, crystallographic investigations were not possible, but we have recorded the infrared spectra with particular reference to the carbonyl stretching mode, which is typically in the region of 1650–1690 cm^{-1} for the parent quinones, and is sometimes observed as a doublet due to Fermi resonance.[15,16] For p-dbbq, the complex has a vibration at 1655 (*cf.* ν(C=O) at 1655 cm^{-1} in the parent p-quinone), and similar features are seen in the adducts of p-Br_4q, p-Cl_4q and 1,4-naphthoquinone. We discuss the p-$C_6H_4O_2$ system below. These spectra are compatible with weak bonding of p-q to InI_3.



Similar results have been obtained with adducts of InI_3 and cyclic ketones, for which both X-ray and infared results show only small changes in the properties of the C=O group on coordination.[14]

The solid complexes show no significant ESR activity, in keeping with the above structure which implies no single-electron transfer, but significant spectra are observed on dissolution in non-aqueous solvents. The solution spectra were recorded under a variety of conditions, and q:InI_3 ratios, and all show clear evidence of a free radical coupled to indium. Most of the spectra are apparently of a mixture of species, but that shown in Fig. 3 analyses as being from an essentially single species and the spectrum was well simulated with the parameters $g = 2.0065$, $A_{In} = 1.88$ G, $A_H = 3.45$ G (4H). The identification of four equivalent hydrogen nuclei requires the molecule in question to contain two p-$dbbsq^{\bullet-}$ groups, and two possible structures are shown below.





The simulation results eliminate structures analogous to those proposed for the *ortho*-quinone system, since these would require contributions from two indium and four hydrogen atoms. Although we observed a half-field transition in the frozen solution of Fig. 3, it was not possible to deduce the D value, which might have cast light on this matter.

We conclude that the solution chemistry of this 1:1 adduct involves as the first step an intramolecular electron transfer which is facilitated by the elimination of a halogen atom. This latter process may require solvation

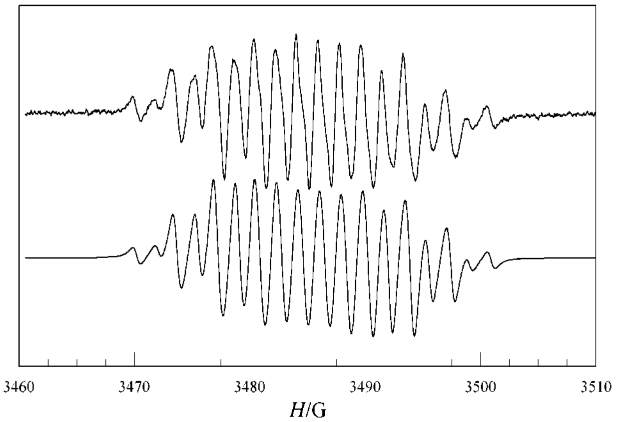


Fig. 3 ESR spectrum of a dilute solution of *p*-dbbq + InI_3 (mole ratio 1 : 2) in tetrahydrofuran at room temperature. Upper trace, experimental result: lower trace, simulated spectrum, using the parameters discussed in the text.

$$(p\text{-q})InI_3 \longrightarrow (p\text{-sq}^\bullet)InI_2 + I^\bullet(\text{solv}) \qquad (10)$$

$$2\ I^\bullet(\text{solv}) \longrightarrow I_2 \qquad (11)$$

and/or

$$I^\bullet(\text{solv}) \longrightarrow \text{decomposition products} \qquad (12)$$

Eqn. (10)–(12) are obviously reactions whose rates will depend on solvent, the quinone, and temperature. The semiquinonate derivative (p-sq$^\bullet$)InI_2 may be the starting point for redistribution processes, following eqn. (6). Dimerisation is also possible, but the presumably low steady state concentrations of (p-sq$^\bullet$)-InI_2 argue against this, in contrast to the *ortho*-quinone system in which (o-sq$^\bullet$)InI_2 is initially the predominant solute species. A reaction which is more probable than dimerisation is association with unreacted (p-q)InI_3 to give (p-sq)InI–μ-I–InI_2(p-q), which can then be the starting point for redistribution processes. Given these possibilities, it is not surprising that the ESR spectra demonstrate the presence of a mixture of radical-containing complexes.

The most important conclusion is that the *para*-quinone adducts studied are stable four-coordinate diamagnetic monomers in the solid state, decomposing in non-aqueous solution to give semiquinonate derivatives. The conclusion that intramolecular electron transfer is affected by the phase seems counter-intuitive, but the critical factor here is the removal of halogen by eqn. (10). The different solution behavior of the *ortho*- and *para*-quinone systems reflects both the redox properties of the quinones, and their different coordinating properties. In particular the larger hyperfine constants for indium in the *o*-quinone complexes (5–8 G), compared to the *p*-quinones (≈2 G) shows that bidentate coordination produces a stronger interaction between ligand and metal centre. The relative strengths of the ESR signals for the *para*-quinone systems suggests that eqn. (10) goes to the right in the order p-dbbq > p-Cl_4q > p-Br_4q ≈ p-nq, with only very weak activity being observed in the last two systems. The absence of biradical activity in all these systems may be evidence of the stability of (p-sq)InI_2 species relative to the redistribution processes.

The p-$C_6H_4O_2$ system differs substantially from the others just discussed. The solid is strongly ESR-active, and the solution spectrum shows strong coupling to indium(III), but no evidence was obtained for biradical species. The infrared spectrum had no features in the ν(C=O) region. The solid slowly turns grey on standing, and we conclude that the adduct InI_3(p-$C_6H_4O_2$) is sensitive to both air and moisture, and that the strong ESR activity is evidence of decomposition rather than of intramolecular electron transfer, but we did not investigate these effects in any detail.

Reaction with InI_4^-

The previous systems, involving InI_3 with *o*- or *p*-quinones, have been discussed in terms of coordination followed by intramolecular electron transfer. In the course of this work, we also found an unexpected reaction between dbbq and the InI_4^- anion. An important experimental point is that this reaction can only be studied spectroscopically by using salts of Et_4N^+ or some similar cation which resists oxidation by the *o*-quinone; initial studies with tetraphenylphosphonium salts were hindered by a reaction apparently involving this cation.

The production of Et_4NI_3 in quantitative yield, and of (dbc)$InIpic_2$ in the presence of picoline, shows that the overall reactions are

$$Et_4NInI_4 + \text{dbbq} \longrightarrow Et_4NI_3 + (\text{dbc})InI \qquad (13)$$

$$(\text{dbc})InI + \text{excess pic} \longrightarrow (\text{dbc})InIpic_2 \qquad (14)$$

Eqn. (13) begs the question of mechanism, and we propose a process based on the work of Davies *et al.*[17] for reactions such as

$$\text{q} + Ph_4Sn \longrightarrow \text{sq}^\bullet(Ph^\bullet)SnPh_3 \longrightarrow (\text{sq}^\bullet)SnPh_3 + Ph^\bullet \qquad (15)$$

which was substantiated for a range of substituted quinones. The same mechanism has been invoked for the reaction between *o*-quinones and Sn_2Ph_6,[3] and for the oxidation of phenyl, as in LiPh, by *o*- and *p*-quinones to give $Li^+(\text{sq}^{\bullet -})$.[18,19] Equally important are that Ph_4Sn has no acceptor properties,[20] which eliminates the possibility of nucleophilic attack at the metal centre, and that the solution chemistry of (dbbsq)$SnPh_3$ shows the importance of redistribution reactions subsequent to eqn. (15).[3]

The detailed discussion of eqn. (13) and (14) also begins with the lack of evidence[9] for any acceptor properties for InI_4^-, in contrast to $InCl_4^-$ and $InBr_4^-$, so that the primary process is assumed to be analogous to eqn. (15)

$$\text{dbbq} + InI_4^- \longrightarrow [(\text{dbbsq}^\bullet)(I^\bullet)InI_3]^- \longrightarrow \text{dbbsq}^{\bullet -} + InI^\bullet_4 \qquad (16)$$

followed by

$$InI_4^\bullet \longrightarrow InI_3 + I^\bullet \qquad (17)$$

$$\text{dbbsq}^{\bullet -} + InI_3 \rightleftharpoons (\text{dbbsq}^\bullet)InI_2 + I^- \qquad (18)$$

$$(\text{dbbsq}^\bullet)InI_2 \longrightarrow (\text{dbc})InI + I^\bullet \qquad (19)$$

$$2I^\bullet + I^- \longrightarrow I_3^- \qquad (20)$$

This sequence explains the products identified (see Experimental section), and is compatible with the ESR spectra of the reaction solution.

The results for the dbbq/InI_4^- reaction raise an ambiguity in the matter of the initial step in the reaction of *o*-quinones with InI_3. As noted above, *p*-quinones form stable 1 : 1 adducts with InI_3, implying that nucleophilic attack is probable in the *o*-quinone/InI_3 system. Earlier evidence from NMR studies of InI_3dppe mixtures[21] (dppe = 1,2-bis(diphenylphosphino)-ethane) show that the formation of the 1 : 1 complex

$$\text{dppe} + InI_3 \longrightarrow InI_3(\text{dppe}) \qquad (21)$$

lies strongly to the right, which supports the coordinative mechanism of eqn. (1). On the other hand, InI_3 in toluene is present as the dimer In_2I_6, in which indium is psuedo-tetrahedrally coordinated, as it is in InI_4^-, so that a reaction sequence analogous to that in eqn. (14)–(16) can also be constructed. The presence of the dimer is not itself an argument against the coordinative mechanism, as has been shown for the ddpe case,[21] and we therefore favour the model proposed, earlier. Further work on this is planned.

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