Coordination Chemistry Reviews, 112 (1992) 215–225
Elsevier Science Publishers B.V., Amsterdam

One-electron transfer reactions in the redox chemistry of Main Group compounds

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(Received 1 April 1991; accepted 23 May 1991)

CONTENTS

A. INTRODUCTION

The tenor of any discussion of oxidation/reduction processes involving compounds of Main Group elements is often conditioned by our knowledge of the oxidation states of their stable compounds. In particular, this means that in the p-block one finds series of oxidation states which differ by two electrons, as shown in Table 1. The s-block elements challenge this idea, since +I is the norm amongst the alkali metals, but with the alkaline earth metals the 0–II pairing is again found, and in general the two-electron difference is found throughout these parts of the Periodic Table.

A number of conclusions, sometimes implicit and less often explicit, have been drawn from these facts. The one which is most relevant to the present discussion is that redox processes involving Main Group compounds will be two-electron transfer reactions, in keeping with the stoichiometry of oxidative or reductive processes such as

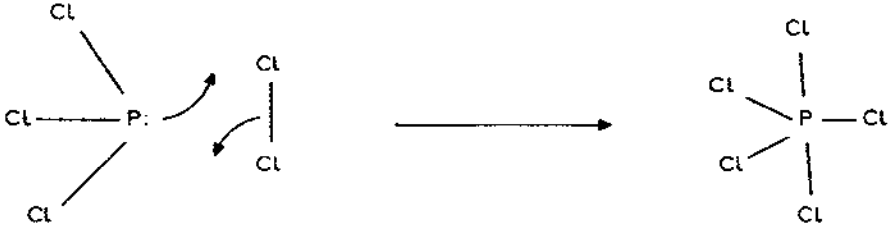
$$PCl_3 + Cl_2 \rightleftharpoons PCl_5 \qquad (1)$$

The rate of these and similar reactions do not generally allow for mechanistic study, and it has therefore been presumed, by default, that indeed electron pair transfer is

TABLE 1
The readily accessible oxidation states of Main Group compounds

I–III	Ga, In, Tl
II–IV	Ge, Sn, Pb
III–V	P, As, Sb, Bi
II–IV–VI	S, Se, Te, Po
I–III–V–VII	Cl, Br, I
II–IV–VI–VIII	Xe

occurring. A naive representation of this



is obviously useful in accounting for the electrons involved, but offers no insight into the actual mechanism of the reaction. Similar comments apply to a series of possible ionic processes such as

$$Cl\text{-}Cl \rightarrow Cl^+ + Cl^- \tag{2}$$

$$Cl^+ + PCl_3 \rightarrow PCl_4^+ \tag{3}$$

$$PCl_4{}^+ + Cl^- \rightarrow PCl_5 \tag{4}$$

For a variety of practical reasons, including the generally high rates, such reactions have not been the subject of mechanistic investigation.

In addition to the amount of experimental information condensed into Table 1, there remains a significant number of compounds which involve elements in other oxidation states (see, for example, ref. 1 in which much of the information summarized in this review is discussed in proper detail). Several of these are simple oxides (e.g. NO, NO_2, ClO_2, ClO_3) in which an unpaired electron is accomodated in a molecular orbital which reduces its inherent reactivity (see below). Other oxides whose formulae imply "unusual" oxidation states are found to be of complex structure, but can be rationalized by identifying sites of conventional oxidation; for example, the series of oxides between P_4O_6 (P(III)) and P_4O_{10} (P(V)) includes P_4O_7, P_4O_8 and P_4O_9, whose structures show characteristic P(III) and P(V) sites in an oligomeric cage. Similar comments apply to sulphur compounds such as S_8O, S_6O, S_7O_2, etc., and mutatis mutandis to oxyacids, hydrides, etc. Finally, inorganic free radicals based on heterocyclic ring systems, such as $S_3N_2{}^+$, also raise questions about the oxidation states involved, and electron delocalization is clearly an important factor in these molecules.

Even when all these species have been accounted for and their formulae rationalized, there is still a residue of relatively simple compounds in which the oxidation states are intermediate between those listed in Table I. For example, compounds such as B_2X_4, $Ga_2X_6^{2-}$, and $In_2Br_4en_2$ (en = ethanediamine) require that the Group III element be written as M(II), and similarly, in Group IV, species such as Ph_6Sn_2 are formally derivatives of tin(III), as is the unstable Sn_2Cl_6. In Group V, Ph_4P_2, Ph_4Sb_2 and R_4As_2 all imply oxidation states of +2, and many example of catenation in Group VI compounds lead to formal oxidation numbers other than 2, 4, and 6.

This varied group of neutral or ionic compounds has in common the presence of M–M (or M–M′) bonds (for a good review, see ref. 2), which in its turn emphasizes the absence of the corresponding mononuclear R_2M, R_3M, etc. molecules, which would be radicals. It is, of course, true that in some cases, such as the elegant work of Lappert and Power [3] on R_3Sn species, the monomer has been identified in the solid state, having been produced by photolysis or radiolysis, but in general these presumably reactive free radical monomers are remarkable by their absence from the literature of inorganic and organometallic chemistry. The thermodynamics of this problem has been discussed elsewhere [4], and the essence of the argument for the Group III MX_2 species (M = Al, Ga, In; X = F, Cl, Br, I) is that the M^{2+} ions are certainly accessible energetically, and that the presumed M–X bonds are thermodynamically strong. The root of the problem then is the high reactivity associated with the unpaired electron on the metal. Whether in a pure p-orbital, or in some hybrid orbital, this electron is readily available for a variety of reactions, including dimerization to M_2X_4. In this sense, an unpaired electron in a Main Group complex differs in one very important respect from that in a transition metal derivative, since in the latter unpaired electrons are in low-lying non-bonding d-orbitals, whereas in MX_2 and similar species, the electron occupies a frontier orbital. By this argument, the instability of odd-electron states in Main Group chemistry is attributable not so much to thermodynamic factors, but rather to the kinetic reactivity, which in turn is related to the energies of the available metal orbitals.

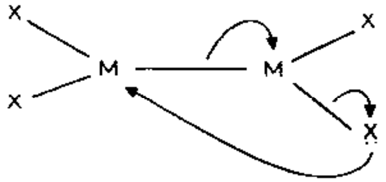
There is a further problem related to the stability of the M–M bonded M_2X_n molecules, and central to some of the experimental studies discussed below. It is known that for In_2X_4 and Sn_2X_6 species, and also for a number of related molecules, disproportionation to give mixed oxidation states is very important, e.g.

$$In_2X_4 \rightarrow In^+[InX_4^-] \tag{5}$$

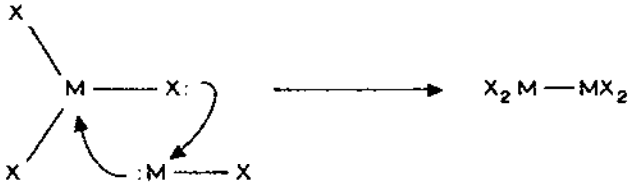
$$In_2X_6^{2-} \rightleftharpoons InX_2^- + InX_4^- \tag{6}$$

$$Sn_2X_6 \rightarrow SnX_2 + SnX_4 \tag{7}$$

The ease with which such processes occur depends on the phase (i.e. solid or solution), on the degree of coordinative saturation at the metal centre, and on the ligands in question. Thus, reaction (5) does not appear to lie to the right in the gas phase, but is favoured by the lattice energy contribution to the overall enthalpy change in the solid state. Similarly, the disproportionation of In_2X_4 is prevented by the coordination of suitable donor ligands to indium, and, by the same token, compounds such as B_2X_4 are much more stable than In_2X_4 or Ga_2X_4 against disproportionation. Finally, while Sn_2Cl_6 is highly unstable (eqn. (7)), organotin(III) compounds are stable substances. The rationalization of these results leads us to conclude that the key factor in these and related disproportionation reactions is not the weakness of the M–M bond, but rather the ease (or otherwise) of intramolecular ligand transfer



A similar argument explains the effectiveness of oxidative addition in the synthesis of M_2X_4 compounds of indium [5]



(8)

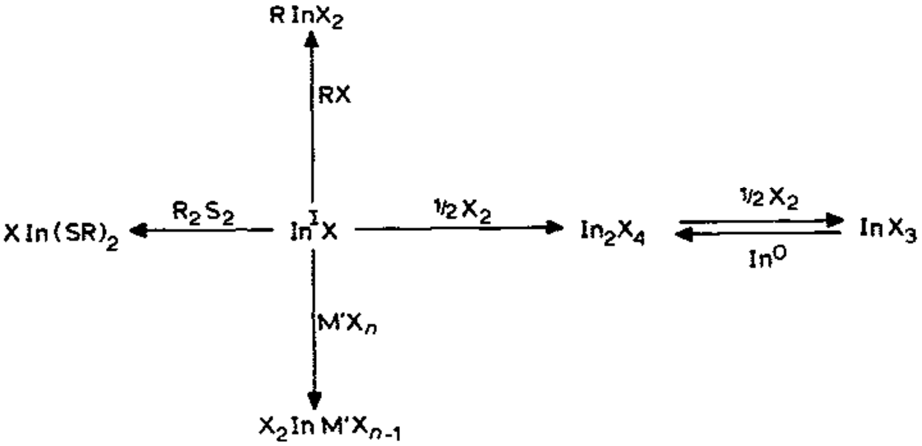
Such arguments have been presented with supporting thermodynamic data in a previous publication [4].

C. OXIDATIVE ADDITION REACTIONS OF INDIUM(I) COMPOUNDS

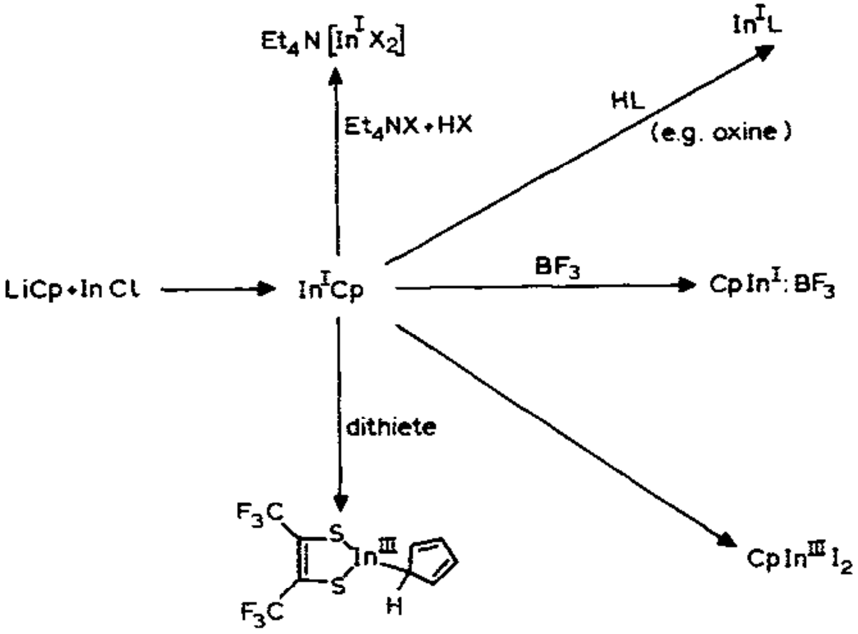
The impetus for our studies of the redox reactions described below was the existence of a number of reactions, shown in Scheme 1, all of which can be formally regarded as the oxidative addition of InX to a substrate to produce indium(III) compounds. In particular, the early studies of the process

$$InI + RI \rightarrow RInI_2 \tag{9}$$

showed that the oxidation goes through an indium(II) intermediate, but failed to identify the detailed mechanism [6–11]. Analogous reactions using $Ga + \frac{1}{2}I_2$ ($\equiv GaI$) have also been reported [12]. Later studies involved the soluble cyclopentadienylindium(I), which like InX can be oxidized by I_2 or a dithiete to form indium(III) species [13–15] (Scheme 2). More recently, the discovery that indium(I) halides dissolve in toluene/tmed (tmed = *N,N,N′,N′*-tetramethylethanediamine) mixtures to give solu-



Scheme 1.



Scheme 2.

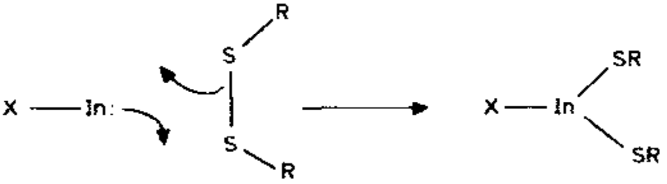
tions which are stable below −20°C has allowed further investigations of reactions such as

$$\mathrm{InX + R_2S_2 \rightarrow XIn(SR)_2} \tag{10}$$

$$\mathrm{InX + Ph_3SnX \rightarrow Ph_3SnInX_2} \tag{11}$$

$$\mathrm{InX + InX_3 \rightarrow X_2InInX_2} \tag{12}$$

in which the products were recovered as tmed adducts [5, 16-18]. Reactions such as (10) can be formalized in terms of electron accounting



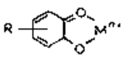
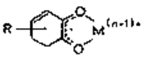
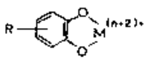
(13)

but such a procedure provides no insight into the actual mechanism. It is worth noting at this point that the results of these studies are compatible with the single-electron transfer model discussed below, but that no direct investigations have been made thus far of these systems.

D QUINONES AS OXIDANTS FOR MAIN GROUP SPECIES

The present paper reviews work carried out at Windsor in recent years on the oxidation of Main Group elements, and of compounds of these elements in low oxidation states. The results point to the involvement of, for example, In(II) or Sn(III) derivatives as short-lived intermediates, and hence imply that a process such as Sn(II)→Sn(IV) takes place by two successive one-electron transfers. The oxidants in these reactions have been *o*-quinones, or more rarely *p*-quinones, and it is worth summarizing here the experimental methods available for identifying the species actually present, given the possible combinations set out in Table 2. Four experimental techniques have proven useful. Firstly, infrared spectroscopy readily identifies the presence or absence of the ν(C–O) bands of the quinone. For diamagnetic Main Group compounds, ^{1}H and (especially) ^{13}C NMR spectroscopy can also serve to demonstrate the change from *o*-quinone to catecholate, and of course electron spin resonance spectroscopy is paramount in characterizing semi-quinone species. Finally, X-ray crystallography is extremely important, and the most critical parameter is not r(M–O) but r(C–O) since this distinguishes unambiguously between *o*-quinone, semi-

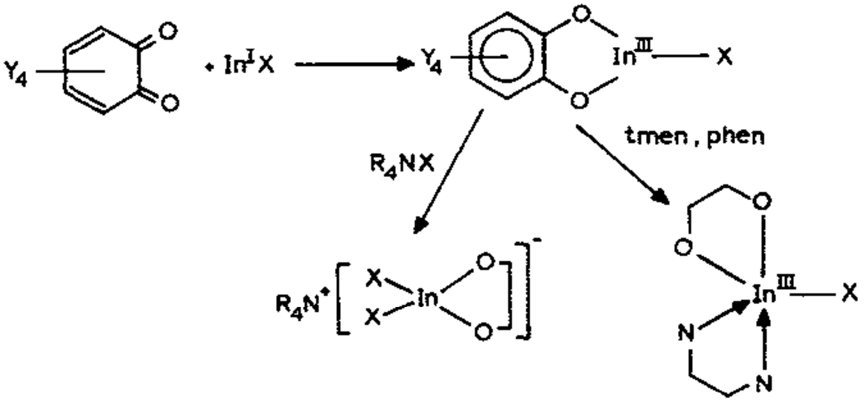
TABLE 2
Typical experimental parameters

			
Ring electrons	18	19	20
Metal electrons	m	$m-1$	$m-2$
^{13}C NMR (ppm)	180	–	150
ν(C-O) (cm^{-1})	1650		1300
ESR	–	$g \sim 2.000$	
r(C–O) (Å)	1.20	1.29	1.35

quinone and catecholate. In the work described below, the results are based on all or some of these techniques, and the details are to be found in the original papers.

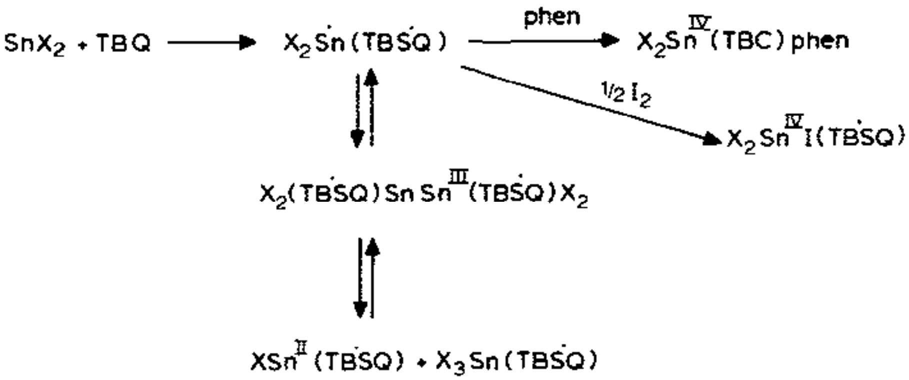
(i) Reactions of InX or SnX_2 with o-quinones

As Table 2 shows, the reduced products from *o*-quinones may be either semiquinones or catecholates, and to some extent the nature of the product depends on the quinone in question. In the case of $Y_4C_6O_2$-*o* (Y = Cl, Br), which are amongst the most powerfully oxidizing quinones, the reaction with both indium(I) and tin(II) halides follows the same course, illustrated in Scheme 3 for InX and $Y_4C_6O_2$ [19,20]. The products were identified by conventional methods, including X-ray crystallography in the case of tin, and the overall course of reaction is quite clear. The coordination of the product by neutral or anionic donors is in keeping with the known chemistry of indium(III) species; equally, in the case of tin(IV), there are subsequent rearrangement reactions in solution, but none of these processes affect the overall conclusions of the investigations.



Scheme 3.

With 3,5-di-*t*-butyl-*o*-benzoquinone (TBQ), the rate of reaction is lower than with $Y_4C_6O_2$-*o*, and one can observe the semiquinone (TBSQ$^{\cdot-}$) derivatives, and in one case the catecholate (TBC). The overall reaction scheme for SnX_2 is shown in Scheme 4 [21]. There are a number of interesting points in this scheme. The dimerization of the presumed tin(III) mononuclear intermediate gives a dimer which can then disproportionate by halide transfer of the type discussed above (see eqns. (5)–(7)), and in the absence of other reagents the final solution contains both Sn(II) and Sn(IV) species. The ESR spectrum of a frozen solution has typical triplet features, which confirms the presence of the dimeric diradical. If I_2 is present in the solution, the tin(III) intermediate goes to the trihalogeno-semiquinone tin(IV) derivative, whose ESR parameters are in agreement with those reported for analogous compounds



Scheme 4.

prepared directly [22]. Finally, the effect of a strong bidentate donor such as 1,10-phenanthroline (phen) brings about the internal electron transfer

$$X_2Sn^{III}(TBSQ) \rightarrow X_2Sn^{IV}(TBC) \qquad (14)$$

presumably because this leads to a stable six-coordinate species.

In the case of InX/TBQ reactions [23], the overall scheme is analogous to that shown, but two additional pieces of evidence were obtained. Firstly, the compound $Br_2In(TBSQ^{\cdot})(pic)_2$ was prepared, characterized as a semiquinone derivative by X-ray crystallography ($r(C\text{–}O) = 1.28(2)$Å), and its ESR parameters obtained; the hyperfine coupling constant $A_{In} = 5.47$ G turns out to be typical for such In(III)/DBSQ$^{\cdot}$ systems. Equally, the compound $In^{I}(TBSQ^{\cdot})$ was prepared by refluxing indium metal with TBQ in toluene, and for this indium(I) compound $A_{In} \sim 10$ G [24]. The solution resulting from the reaction of InX with TBQ was shown by ESR spectroscopy to contain both $In(TBSQ^{\cdot})$ and $X_2In(TBSQ^{\cdot})$, and the spectrum of this mixture could be simulated from those of the individual species prepared separately and unambiguously characterized, so that Scheme 4 applies to both InX and SnX_2 oxidations mutatis mutandis.

There are some useful conclusions to be drawn from these experiments. Firstly, the use of an oxidant (*o*-quinone) which allows the one-electron product semiquinone to be identified is a great boon. Secondly, oxidants of different strength allow the rate of the overall reaction to be varied, and hence allow both 1-electron and 2 × 1-electron reaction products to be characterized; the results show that one-electron transfer reactions do indeed occur, although the intermediate In(II) and Sn(III) species have not yet been isolated. Finally, the general chemical behaviour of these systems is in keeping with the known chemistry of M–M bonded molecules, discussed above, and this is in itself evidence of the importance of the appropriate intermediate oxidation states in the reaction scheme.

(ii) The oxidation of non-metallic compounds

The oxidation of phosphorus(III) compounds by *o*- or *p*-quinones has been investigated by a variety of techniques, including ESR and UV-Vis spectroscopy [25–29]. The evidence again implicates semiquinone species as intermediates in the overall reaction.

$$PX_3 + \text{quinone} \rightarrow X_3P(\text{catecholate}) \tag{15}$$

and similar results have been obtained [30] in studies of the oxidation of organotellurium(II) compounds

$$TeR_2 + o\text{-quinone} \rightarrow R_2Te(\text{catecholate}) \tag{16}$$

Here again, the identification of molecules in which the semiquinone is bonded to tellurium clearly implies the intermediate formation of $R_2T\dot{e}$(semiquinon$\dot{e}$). Thus, although the mechanistic evidence is not as clear as in the cases discussed above, there is good evidence for one-electron, rather than two-electron, transfers in reactions such as (15) and (16).

(iii) Oxidation of metallic and non-metallic elements

We have already noted above the reaction

$$In^0 + TBQ \rightarrow In^I(TBSQ^{\cdot}) \tag{17}$$

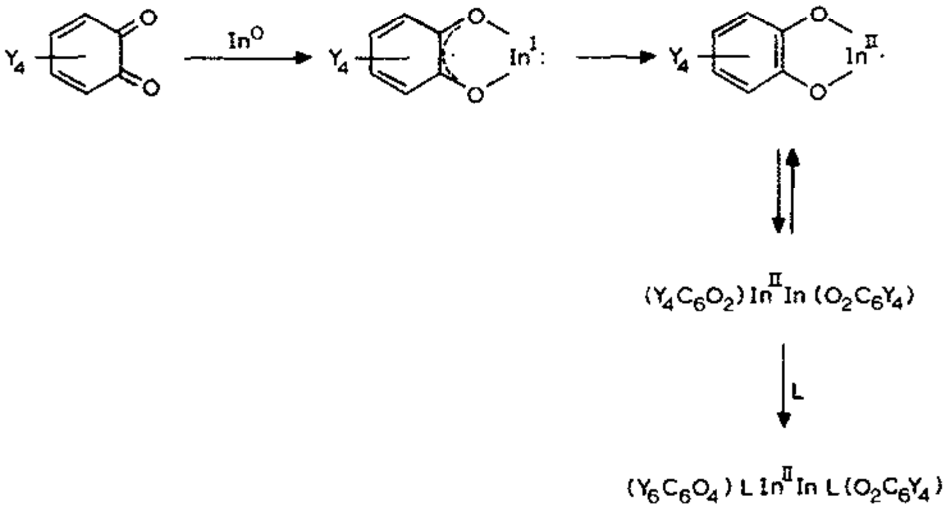
which gives rise to the unusual indium(I) species [23], and this is one of a number of such reactions which we have studied. When $Y_4C_6O_2$-*o* is used, the products with either gallium or indium are M(II) derivatives, obtained as adducts with γ-picoline or 1,10-phenanthroline and the proposed mechanism is as shown in Scheme 5. The ESR spectrum of a reacting mixture of $Cl_4C_6O_2\text{-}o + In + \frac{1}{2}I_2$ confirms the presence of $Cl_4C_6O_2^{\cdot -}$ radical anions bonded to both indium(I) and indium(III) centres, as required by Scheme 5 [31]. With tin, the product is $Sn^{II}(O_2C_6Cl_4)$, and no mechanistic information was forthcoming.

The metals zinc, cadmium, magnesium and barium react with TBQ in refluxing toluene to give $M(TBSQ^{\cdot})_2$, whose ESR properties are those predicted for a mononuclear diradical species [32]. Two possible pathways can be proposed

$$M \xrightarrow{TBQ} M^{\circ}(TBSQ^{\cdot}) \xrightarrow{TBQ} M(TBSQ^{\cdot})_2 \tag{18}$$

or

$$M \xrightarrow{TBQ} M^{II}(TBC) \xrightarrow{TBQ} M^{II}(TBSQ^{\circ})_2 \tag{19}$$



Scheme 5.

and the first of these clearly involves successive one-electron transfers. Further studies of these and related systems are planned.

Ortho-quinones also react with non-metallic elements. With elemental tellurium, the product is the tellurium(IV) bis-catecholate [29], e.g.

$$Te + 2Cl_4C_6O_2\text{-}o \rightarrow Te(O_2C_6Cl_4)_2 \tag{20}$$

while with phosphorus the reaction

$$\tfrac{1}{4}P_4 + 2Cl_4C_6O_2\text{-}o + \tfrac{1}{2}Br_2 \rightarrow BrP(O_2C_6Cl_4)_2 \tag{21}$$

provides a convenient one-pot synthesis of the phosphorane [28]. Neither of these heterogeneous systems lends itself to mechanistic study, but ESR spectroscopy demonstrates the presence of transient species in which the semiquinone is bonded to either tellurium or phosphorus.

E CONCLUSIONS

The review of the experimental evidence, coupled with what is known about the chemistry of the "unusual" oxidation states of Main Group elements, suggests that the simplified and unique model of two-electron redox reactions is unfounded. Certainly there is more than enough evidence to justify further exploration of related systems. Perhaps the most important challenge will be to identify other one-electron oxidizing or reducing agents which will react with Main Group substrates, in addition to the quinones which have been studied so far.

ACKNOWLEDGEMENT

The research referred to as arising from this Department was supported in part by Operating Grants (to DGT and BRM) from the Natural Sciences and Engineering Research Council of Canada.

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