which still retains some of the bridging and yl oxygens unexchanged.

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Chlorotellurate(IV) Equilibria in Aqueous Hydrochloric Acid

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Study of TeO_2 in solutions of hydrochloric acid by UV-visible and Raman spectroscopy shows that three Te(IV) chloro anions are present: $TeCl_6^{2-}$, $Te(OH)Cl_4^-$, and a monochlorotellurate(IV) of probable composition $TeCl(OH)_4^-$. The compound $Me_4N[Te(OH)Cl_4]$ has been prepared and characterized by Raman and IR spectroscopy.

Introduction

Both the hexa- and pentachlorotellurate(IV) anions are well-known in the literature.[1,2] On the basis of Raman spectral studies it has been suggested that these ions may be present in solution of tellurium dioxide in aqueous hydrochloric acid.[3] While there is little doubt that $TeCl_6^{2-}$ is formed in concentrated hydrochloric acid, the nature of other Te(IV) species in more dilute HCl solutions is not precisely known. Polarographic[4] and solvent-extraction[5] studies have been interpreted in terms of a complete range of anions with Cl/Te ratios from 1 to 6 and varying degrees of solvation. Selenium dioxide forms selenious acid, seleninyl chloride, and the pentachloroselenate(IV) ion in hydrochloric acid solutions while the hexachloroselenate(IV) ion is apparently not a major constituent.[6] In concentrated hydrofluoric acid, the pentafluoro- and tetrafluorohydroxotellurate(IV) ions are found.[7] The crystal structure of tetraphenylarsonium aquotetrachlorohydroxotellurate(IV) has been determined.[8] However, it is uncertain as to whether the anion in this compound is $TeOCl_4^{2-}$ or $Te(OH)Cl_4^-$. In order to help answer this question as well as to extend our study of halochalcogenate(IV) species formed in hydrochloric acid, we undertook a Raman and UV-visible spectroscopic study of this system.

Experimental Section

Hydrochloric acid and tetramethylammonium chloride were from J. T. Baker, and tellurium dioxide was from Matheson Coleman and Bell. All chemicals were analyzed for purity before use.

Tetramethylammonium tetrachlorohydroxotellurate(IV) was prepared on a gram scale by mixing together a 1/1/3 mole ratio of $Me_4NCl/TeO_2/HCl$ (as 8 M HCl). The mixture was ground together, left to stand for 1 day, and then filtered. The yellow-green product was washed with cold ethanol and ether and stored in a vacuum desiccator out of light, which caused darkening over a period of days. Anal. Calcd for $Me_4N[Te(OH)Cl_4]$: Cl, 39.33. Found: Cl, 39.38. Similar preparations using NH_4Cl and CsCl in place of Me_4NCl gave mixtures of TeO_2 and the hexachlorotellurate(IV). Attempted preparation of tetramethylammonium chlorotellurate(IV) by similar procedures (1/1 mixture of Me_4NCl and TeO_2 in minimum water) yielded only insoluble TeO_2.

Table I. Spectrophotometric Results for Solutions of 0.001 M TeO_2 in Moderately Concentrated HCl (c_{HCl} = 7.00-8.50 M)

c_{HCl}, M	A_{375}	$10^4 \times [TeCl_6^{2-}]$, M	$10^4 \times [TeCl_x]$, M	a_{HCl}[a]	a_{H_2O}[b]
8.50	0.276	9.06	0.94	129	0.380
8.00	0.250	8.26	1.74	97.5	0.422
7.50	0.228	6.99	3.01	73.0	0.466
7.00	0.193	5.54	4.46	56.0	0.510

[a] Reference 11. [b] Mole fraction scale.[12]

Analysis of starting materials and $Me_4N[Te(OH)Cl_4]$ was by Volhard titration for chloride, by permanganimetric titration for Te(IV) (in TeO_2), and against sodium carbonate using bromocresol green for HCl concentration.

Spectrophotometric and Raman spectral measurements were carried out as described previously.[6,9] All spectra were measured at 25 °C. All absorbances were corrected for HCl background. $Me_4N[Te(OH)Cl_4]$ was readily pyrolyzed by the laser light at 647.1 nm, and the spectra had to be run at low power levels.

Results and Discussion

The spectrophotometric measurements on 0.001 M TeO_2 solutions in the ranges 7.0-10.0 M HCl and 3.0-5.0 M HCl are shown in Figure 1A,B, respectively. Correspondingly, the Raman spectra of 0.5 M TeO_2 solutions in 3.0-11.0 M HCl are shown in Figure 2. The UV-visible and Raman spectra of TeO_2 in the most concentrated HCl solutions (10.0-11.8 M) are due to the $TeCl_6^{2-}$ ion.[3,10] As the concentration of HCl is decreased to 7.0 M, the peaks in the UV-visible spectra at 268 and 375 nm due to $TeCl_6^{2-}$ fall in intensity and are replaced by peaks at 295, 253, and 225 nm. Isosbestic points occur at 235 and 255 nm. Over this concentration range an equilibrium between $TeCl_6^{2-}$ and a second Te(IV) species is established, and this is confirmed by matrix-rank plots.[11] The concentration of $TeCl_6^{2-}$ may be determined from the absorbance at 375 nm by using the extinction coefficient of

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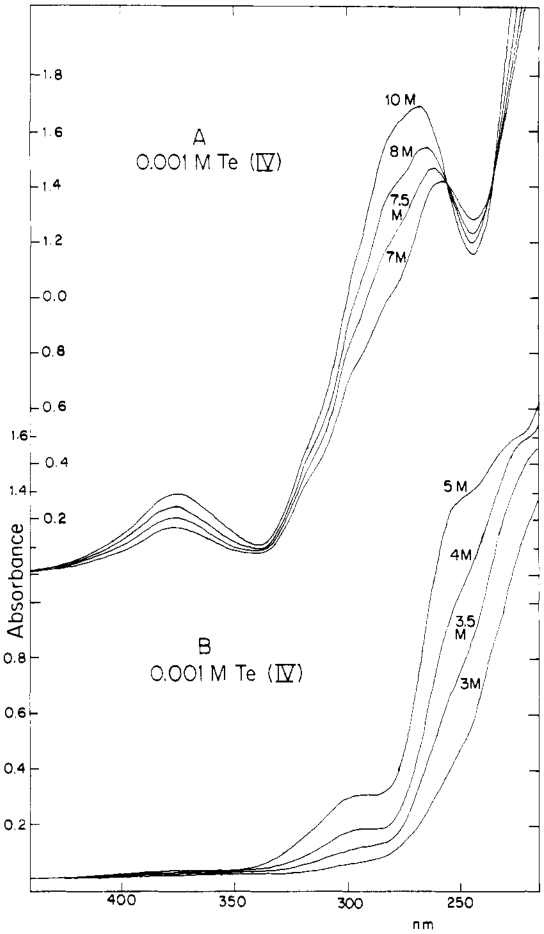

Figure 1. UV-visible spectra of 0.001 M TeO_2 in solutions of varying HCl concentration (3–10 M).

$TeCl_6^{2-}$ (ϵ_{375} = 276 mol^{-1} L cm^{-1}) determined from solutions of TeO_2 in 11.8 M HCl where Raman spectroscopy shows only $TeCl_6^{2-}$ is present. The concentration of the second Te(IV) species is determined by difference:

$$[TeCl_x] = c_{TeO_2} - [TeCl_6^{2-}] \qquad (1)$$

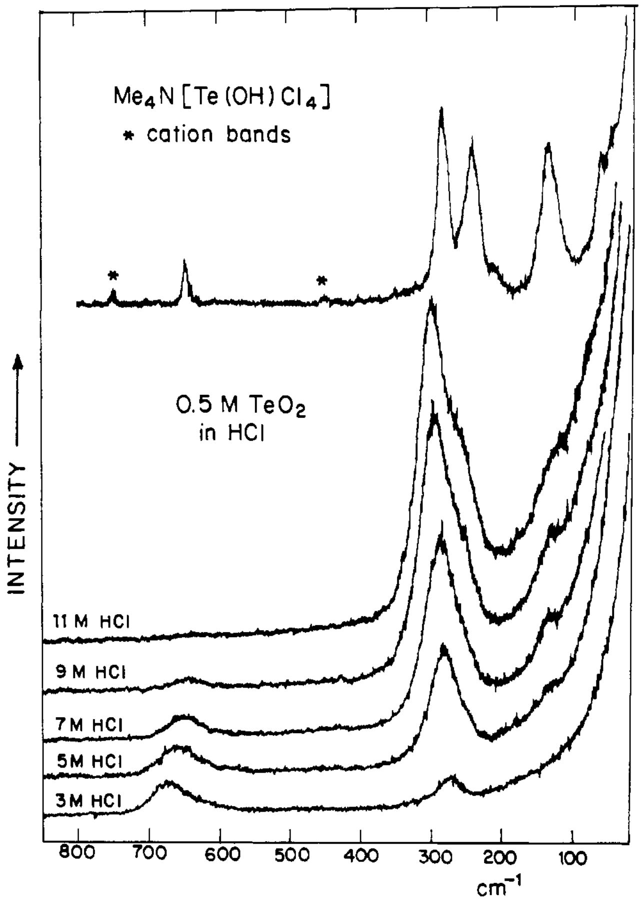

Figure 2. Raman spectra of solid $Me_4N[Te(OH)Cl_4]$ and 0.50 M TeO_2 in solutions of varying HCl concentration (3–11 M).

Table II. Vibrational Spectra of $Te(OH)Cl_4^-$ [a]

freq, cm^{-1}: Me_4N-$[Te(OH)Cl_4]$[b]	freq, cm^{-1}: 0.50 M TeO_2 in 6 M HCl	assignt
644 (2)	658 (1, p)	ν(Te–OH)
283 (10)	283 (10, p)	ν($TeCl_4$)
250 (2, sh)	262 (2, dp?)	
241 (8)		
212 (1)		
147 (2, sh)		
134 (8)	132 (1, dp)	
58 (1)		
40 (1, sh)		

[a] Raman spectra measured up to 1000 cm^{-1}. [b] IR bands: 648 s (ν(TeO)), 1035 m (δ(OH)), 2060 w (2δ(OH)), 3340 (ν(OH)). Raman cation bands: 452 (0), 750 (1) cm^{-1}.

Table I lists the absorbance at 375 nm, $[TeCl_6^{2-}]$, $[TeCl_x]$, and c_{HCl} as well as the activities of HCl, a_{HCl}, and of water, a_{H_2O}.[12,13] An approximmae stoichiometry (Te/Cl ratio) of the second species may be obtained from a plot of log ($[TeCl_6^{2-}]/[TeCl_x]$) vs. log a_{HCl}, the slope of which will give the dependence on a_{HCl}. The slope of such a plot is 2.4, suggesting the x in the second species is 4. This approach does not allow for change in a_{H_2O} and ignores the activity coefficients of the complex ions however, and it is possible that x is 3. The change in absorbance at 375 nm does not take place in these solutions until c_{HCl} is reduced to 8.5 M. In the Raman spectra (Figure 2) however, a TeO stretching band is observed for solutions with c_{HCl} as high as 10.0 M. This is a reflection of the higher c_{TeO_2} in these solutions (0.5 M) relative to that used for the UV-visible spectra (0.001 M), which reduces a_{HCl} to a greater extent due to formation of chlorotellurates. Nevertheless, it is reasonable to assume that the new species observed in the Raman Spectra is identical with that observed in the UV-visible spectra. The new Raman peak at 650 cm^{-1} grows in intensity over the range of c_{HCl} from 10.0 to 6.0 M. At the same time, the position of the strongest Raman band moves from 300 to 282 cm^{-1}. Since in $K[Te(OH)F_4]$ the Te(OH) stretching mode (single bond) is at 697 cm^{-1},[7] while in Cs_2TeOF_4 the TeO mode (double bond) appears at 837 cm^{-1},[14] the position of the band at 650 cm^{-1} indicates that the new species is a hydroxotellurate(IV) and not an oxotellurate(IV). It is possible to prepare a monohydroxotetrachlorotellurate(IV), $Me_4N[Te(OH)Cl_4]$, from a 1/1/3 molar mixture of $Me_4NCl/TeO_2/HCl$ (8 M HCl), and the Raman spectrum of this compound, shown in Figure 2 and Table II, is very similar to that of the solution of 0.5 M TeO_2 in 7 M HCl (Table II), indicating that the new chlorotellurate anion in equilibrium with $TeCl_6^{2-}$ is the $Te(OH)Cl_4^-$ anion, and the equilibrium is

$$TeCl_6^{2-} + H_2O = Te(OH)Cl_4^- + Cl^- + HCl \qquad (2)$$

Other possible hydroxochloro species such as $Te(OH)Cl_3$ and

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Table III. Spectrophotometric Results for Solutions of 0.001 M TeO_2 in Dilute HCl (c_{HCl} = 3.00–4.50 M)

c_{HCl}, M	A_{295}	$10^4[Te(OH)Cl_4^-]$, M	$10^4[TeCl_y]$, M	$a_{HCl}{}^a$	$a_{H_2O}{}^b$	K_{II},^{c} mol^3 L^{-1}
4.50	0.214	7.64	2.36	12.60	0.729	848
4.00	0.156	5.57	4.43	9.18	0.768	801
3.75	0.122	4.36	5.64	7.87	0.788	800
3.50	0.090	3.21	6.79	6.67	0.809	776
3.25	0.062	2.21	7.79	5.59	0.828	744
3.00	0.038	1.36	8.64	4.67	0.847	764

^{a} Reference 11. ^{b} Mole fraction scale.[12] ^{c} Average: 789 ± 28 mol^3 L^{-3}.

$Te(OH)_2Cl_4{}^{2-}$ are expected to have Raman spectra that differ from that observed. The $Te(OH)Cl_3$ molecule is expected to have a trigonal-bipyramidal structure with one Cl atom equatorial and two Cl atoms axial, and the Raman spectrum will consist of well-separated TeCl stretching modes as for $SeOCl_3{}^-$[15] and not the single envelope of TeCl bands observed here, which is like that for the $SeOCl_4{}^{2-}$ anion.[16] The $Te(OH)_2Cl_4{}^{2-}$ anion and other species with more than one TeO bond will have spectra with more than one TeO stretching band. The dependence of the spectra on c_{HCl} and the close parallel between the Raman spectra of the solutions and the solid $Me_4N[Te(OH)Cl_4]$ indicate that equilibrium 2 is occurring. The equilibrium constant for (2) is given by

$$K_I = \frac{[Te(OH)Cl_4^-]a_{HCl}[Cl^-]}{[TeCl_6^{2-}]a_{H_2O}} \frac{f_{Cl^-}f_{Te(OH)Cl_4^-}}{f_{TeCl_6^{2-}}} \quad (3)$$

Because the activity coefficient factor cannot be accurately evaluated and is expected to exhibit considerable variation over the range of c_{HCl} used, it is not possible to calculate a good equilibrium constant for (2).

The vibrational spectra of $Me_4N[Te(OH)Cl_4]$ in solid and the $Te(OH)Cl_4{}^-$ ion in solution are given in Table II. The position of ν(TeO) is about 50 cm^{-1} lower than that observed for the $Te(OH)F_4{}^-$ anion,[7] reflecting the lower electronegativity of Cl compared to that of F. The frequencies of the strongest TeCl stretching bands accord well with those of the equatorial TeCl stretching modes (252–299 cm^{-1}) and not the axial TeCl stretching mode (336 cm^{-1}) of the $TeCl_5{}^-$ anion,[18] indicating that the OH group is axial. A partial assignment of the bands is given in Table II.

The peaks at 295, 253, and 225 nm in the UV–visible spectrum of solutions of 0.001 M TeO_2 in 2–6 M HCl due to the $Te(OH)Cl_4{}^-$ ion (Figure 1b) decrease in intensity with decreasing HCl concentration. Tellurium dioxide begins to precipitate at concentrations below 2 M HCl. The $Te(OH)Cl_4{}^-$ ion is apparently replaced by a third Te(IV) species, $TeCl_y$, with an absorption spectrum that lies in the UV region of the spectrum. Matrix-rank plots[11] at 240, 260, 280, and 300 nm for HCl concentrations 2.50, 3.00, 3.25, 3.50, 3.75, and 4.0 M confirm that two species are present in this range of concentrations. There is a negligible amount of $TeCl_6{}^{2-}$ in the solutions with HCl concentrations below 4.5 M HCl, and therefore, the dependence of the concentration of $Te(OH)Cl_4{}^-$ and the third Te(IV) species on HCl concentration may be readily studied in this range. The concentration of $Te(OH)Cl_4{}^-$ is determined from the absorbance at 295 nm by using the extinction coefficient $\epsilon_{295}(Te(OH)Cl_4{}^-)$ = 280 mol^{-1} L cm^{-1}. This extinction coefficient is calculated from the spectrum of the 7 M HCl solution for which the concentrations of $TeCl_6{}^{2-}$ and $Te(OH)Cl_4{}^-$ are known (Table I) by using $\epsilon_{295}(TeCl_6{}^{2-})$ as determined from the absorbance at 295 nm of the 10 M HCl solution (Figure 1A), which was 1105 mol^{-1} L cm^{-1}. The concentration of the third Te(IV) species, $TeCl_y$, may be determined from

$$[TeCl_y] = c_{TeO_2} - [Te(OH)Cl_4^-] \quad (4)$$

Table IV. Raman Spectrum of $TeCl_y$ (0.5 M TeO_2 in 3.0 M HCl)

freq, cm^{-1}	assignt	freq, cm^{-1}	assignt
678 (10, p)	ν(TeO)	456 (0, p?)	ν(TeCl)
653 (2, sh, dp?)		272 (10, p)	
600 (1, sh, p)		210 (0, dp)	
555 (0, p?)			

Table III shows the absorbance at 295 nm and the concentrations of $Te(OH)Cl_4{}^-$ and $TeCl_y$ in the solutions as well as c_{HCl} and the activities a_{HCl} and a_{H_2O}.[11,12] The stoichiometry of $TeCl_y$ may be estimated from the slope of a plot of the log of the ratio $[Te(OH)Cl_4{}^-]/[TeCl_y]$ against log a_{HCl}. This plot yields a slope of 3.0, indicating that the equilibrium involved is

$$Te(OH)Cl_4^- + H_2O = TeO_2Cl^- + 3HCl \quad (5)$$

where the third Te(IV) species may be TeO_2Cl^- or some hydrated monochloro analogue. The equilibrium constant for this reaction, K_{II}, is given by

$$K_{II} = \frac{[TeO_2Cl^-]f_{TeO_2Cl^-}a_{HCl}{}^3}{[Te(OH)Cl_4^-]f_{Te(OH)Cl_4^-}a_{H_2O}} \quad (6)$$

In this case cancellation of the two activity coefficients for uninegative anions is an acceptable assumption. The equilibrium constants were calculated from data in Table III, and these K_{II} values are listed in the table.

The Raman spectra of 0.50 M TeO_2 solutions in HCl (Figure 2) show that as the HCl concentration is decreased from 7.0 M, the TeCl stretching bands near 300 cm^{-1} decrease in intensity and the maximum shifts to lower frequency. Moreover, the TeO stretching band at 658 cm^{-1} increases in intensity and shifts to higher frequency. These changes are due to the formation of the third Te(IV) species in solution, according to (5). The Raman spectrum of the 3 M HCl solution is essentially only that of this species. A calculation using K_{II} in Table III shows that over 95% of the Te(IV) present in this solution is TeO_2Cl^-. The Raman spectral bands of this third species are listed in Table IV. The TeO_2F^- ion is apparently oxygen bridged in solids,[19] satisfying in this way a tendency toward a coordination number higher than 3 for Te(IV). For this reason, TeO_2Cl^- is expected to be strongly solvated in solution. In addition, the TeO stretching bands in the isolated $TeO_3{}^{2-}$ ion[20] all lie above 700 cm^{-1}. The frequencies of the TeO stretches in $TeCl_y$ lie too low to be due to a TeO_2Cl^- ion, which would be expected to have a TeO bond order of 1.5 comparable to that of the $TeO_3{}^{2-}$ ion. A Te(IV) species that would account for the observation of stretching bands in the TeO single-bond region and that has a coordination number of 5, more common for Te(IV) species, is the

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$Te(OH)_4Cl^-$ anion. The Raman spectrum recorded at greater intensity showed seven bands (Table IV), which is more than that expected for the TeO_2Cl^- ion, and four bands appear in the TeO single-bond region consistent with a species like $Te(OH)_4Cl^-$. If this is the third species present in these solutions, the position of the TeCl stretching vibration at 272 cm^{-1} indicates an equatorial rather than axial TeCl bond.[18] It was not possible to isolate a monochlorotellurate(IV) compound from these solutions to confirm this possibility; mixtures of Me_4NCl and TeO_2 in a minimum amount of water simply did not react.

Conclusion

The electronic and Raman spectra of solutions of TeO_2 in HCl indicate that three Te(IV) species ($TeCl_6^{2-}$, $Te(OH)Cl_4^-$, and a monochlorotellurate(IV) of uncertain degree of solvation, possibly $Te(OH)_4Cl^-$) are present. No evidence for species suggested by other authors such as $TeCl_5^-$,[3] $Te(OH)_2Cl_4^{2-}$,[4] or $TeOCl_3^-$,[5] among others, has been obtained although these may be present in very low concentration relative to the principal anions. The chlorotellurate(IV) species formed in solution parallel those known for the fluorotellurate(IV) system, $Te(OH)F_4^-$[7] and TeO_2F^-.[19] However, the highest fluoro coordination in aqueous HF solution is that of TeF_5^-, where the lone electron pair on Te is stereochemically active, while that in aqueous HCl is of the $TeCl_6^{2-}$ ion. It is interesting that the introduction of a single hydroxo group in the chlorotellurate(IV) system favors the formation of a square-pyramidal species rather than an octahedral species.

In the haloselenate(IV) systems that have been studied, the degree of halo coordination is lower than that observed for Te(IV) in hydrochloric acid of the same concentration.[6,21] Seleninyl chloride is the principal species in solutions of SeO_2 in 12 M hydrochloric acid.[6] The haloantimonate(III) system is similar to that for Te(IV), with the highest halo coordination being that of $SbCl_6^{3-}$, which dissociates to $SbCl_4^-$.[17] Investigation of the Raman spectra of the tetrachloroantimonate(III) solutions shows no evidence of an SbO stretching vibration, and $Sb(OH)Cl_4^-$ is apparently not formed.

The mixture used by Collins and Webster[8] for the preparation of the tetraphenylarsonium hydroxotetrachlorotellurate(IV) tetrahydrate was more acidic, due to excess HCl produced by hydrolysis, than that used for the tetramethylammonium compound reported here, and it appears likely therefore that, if this latter compound is protonated, the former compound is also a hydroxo- and not an oxotellurate(IV) compound, a conclusion that could not be arrived at from the X-ray study.[8] Further work concerning the preparation of oxohalotellurates is being pursued.

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Registry No. $Me_4N[Te(OH)Cl_4]$, 88130-56-7; $Te(OH)Cl_4^-$, 88106-33-6; $TeCl(OH)_4^-$, 88106-34-7; TeO_2, 7446-07-3; HCl, 7647-01-0; $TeCl_6^{2-}$, 20057-66-3.

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Metallotetraphenylporphyrin-Catalyzed Oxidation of 2,6-Di-*tert*-butylphenol

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The rates of oxidation of 2,6-di-*tert*-butylphenol by molecular oxygen in DMF were investigated with CoTPP, Fe(TPP)Cl, Mn(TPP)Cl, VO(TPP), and CuTPP as catalysts (TPP = tetraphenylporphinato). The activities of the catalysts decrease in the order of CoTPP >> Fe(TPP)Cl > Mn(TPP)Cl > VO(TPP), while CuTPP is inactive. The order of selectivity for the formation of the quinone (oxygen insertion) relative to the coupling product is CoTPP >> VO(TPP) > Fe(TPP)Cl > Mn(TPP)Cl. The rate of oxygen insertion increases with temperature in the lower temperature range and decreases markedly at higher temperature, while the coupling reaction increases steadily with increasing temperature. The experimental results are interpreted with the aid of a proposed mechanism in which an intermediate dioxygen complex is required for the insertion reaction, but not for the formation of the coupling product.

Introduction

It is well-known[1] that molecular oxygen can be activated by many transition-metal complexes or chelates that can reversibly bind molecular oxygen. The study of the oxidation of hindered phenols with transition-metal (especially cobalt) dioxygen carriers is of interest because it involves metal-dioxygen adducts as intermediates in the oxidation process. Therefore, these systems serve as appropriate models for the reactions of oxygenase enzymes. Phenols may be oxidized to the corresponding quinones, coupled products (diphenoquinones), or polymers, depending on the choice of solvent, catalyst, or reagent. The oxidation of hindered phenols with the cobalt bis(salicylaldehyde) ethylenediimine (salen) dioxygen complex as catalyst was first reported in 1967 by Van Dort and Guerson.[2] A new synthetic procedure whereby salcomine was used as catalyst was employed by De Jonge and co-workers[3] for preparing 2,6-di-*tert*-butyl-*p*-benzoquinone from 2,6-di-*tert*-butylphenol. Several workers[4,5] have investigated the effects of various reaction conditions and the use of substituted derivatives of the substrate and the carrier ligand (salcomine) on the distribution of oxidation products and suggested that the benzoquinone (BQ) is produced from the mononuclear $Co-O_2$ species while diphenoquinone (DPQ) is produced from the μ-peroxo dimer. However, Kothari and Tazuma[6] indicated that the active species producing both BQ and DPQ is the mononuclear dioxygen adduct. Besides these cobalt complexes, metallophthalocyanines[6,7] have been found to be useful catalysts for the oxidation of hindered phenols.

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