Oxidation of Phenols with Chromyl Chloride

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The oxidation of phenols with chromyl chloride gives benzoquinones in yields which depend upon the nature of the substituents on the phenol ring. The reaction when carried out in carbon tetrachloride or carbon disulphide yields a solid intermediate which contains the *p*-benzoquinone co-ordinated onto the reduced chromium species. This solid has a non-stoicheiometric composition unlike other solid intermediates formed in the Etard reaction. The release of the benzoquinone from the solid intermediate by hydrolysis is a ligand exchange reaction; a similar release can be achieved by using other donor solvents such as pyridine and dioxan.

THE oxidation by chromyl chloride of a large variety of organic substrates has been studied by many workers [1-6] but as yet there is no clearly defined picture of the reaction mechanism or even the principal steps in the overall reaction. Although the reactions of chromyl chloride with organic species are collectively described as the Etard reaction, it seems probable that there are as many types of this reaction as there are classes of organic compounds. This paper describes further [7,8] studies of the oxidation of phenols.

RESULTS AND DISCUSSION

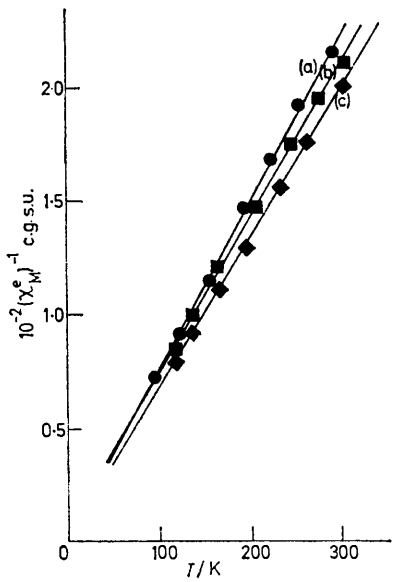
With phenols, as with other groups of organic compounds, chromyl chloride reacts exothermally in carbon tetrachloride and carbon disulphide to give a brown solid. Hydrolysis of this solid gives a benzoquinone and other oxidised forms of phenol. Both stages are clearly important parts of the overall reaction whereby the two stages and of the factors which optimize the yields of the products is required.

As reported for similar reactions,[1] the mixing of the reagents rapidly in the absence of solvent can lead to an explosive reaction. If the mixing is carried out using a 10% solution of reagents only a moderate increase in the temperature is observed. Although some of the highly halogenated phenols react rather slowly [7] and hence require less dilution, the safe, efficient use of this reaction for the production of benzoquinones demands the moderating influence of a solvent.

TABLE 1

Effective magnetic moments for phenol–chromyl chloride complexes

Phenol from which complex is derived	Effective magnetic moment of Cr (B.M.)	Weiss constant (θ°)
2,5-Dimethylphenol	3·31	20
2,3,5-Trimethylphenol	3·29	7
2,3,6-Trimethylphenol	3·31	16
2,3,5,6-Tetramethylphenol	3·33	16
2,6-Di-isopropylphenol	3·42	9
2,5-Di-t-butylphenol	3·33	12
2,6-Di-t-butylphenol	3·44	8
3,5-Di-t-butylphenol	3·24	9
4-Methyl-2,6-di-t-butylphenol	3·45	30
2,4,6-Tri-t-butylphenol	3·33	18
1-Naphthol	3·20	13
2,6-Dinitrophenol	3·27	13
'Spin only' value for Cr^{III}	3·88	
'Spin only' value for Cr^{IV}	2·83	



Temperature variation of molar magnetic susceptibility (χ^e_M) of phenol–chromyl chloride adducts: (a), 2,3,5-trimethylphenol; (b), 2,5-di-t-butylphenol; (c), 2,6-di-t-butylphenol

Nature of the Solid.—Table 1 shows the effective magnetic moment of the chromium in a number of the intermediate solids. The values do not correspond even approximately to the 'spin only' values for either Cr^{III} or Cr^{IV} but lie somewhere in between. The study of the oxidation products are formed, and for the general use of this reaction for synthetic purposes more detailed knowledge of the constituent reactions in each of the

[1] W. H. Hartford and M. Darrin, *Chem. Rev.*, 1958, **58**, 1.
[2] A. Ghencuilescu, I. Necsoiu, C. D. Nenitzescu, and M. Rentea, *Rev. Roumaine Chim.*, 1969, **14**, 1543; A. Ghencuilescu, I. Necsoiu, and C. D. Nenitzescu, *ibid.*, p. 1553; V. Psemetchi, I. Necsoiu, M. Rentea, and C. D. Nenitzescu, *ibid.*, p. 1567, and preceding papers describing the reactions of chromyl chloride.
[3] R. C. Makhija and R. A. Stairs, *Canad. J. Chem.*, 1968, **46**, 1255; R. A. Stairs, D. G. M. Diaper, and A. L. Gatzke, *ibid.*, p. 3695.
[4] I. P. Gragerov and M. P. Ponomarchuk, *Zhur. org. Khim.*, 1967, **3**, 458; *ibid.*, 1969, **5**, 1145.
[5] (*a*) F. Freeman, P. J. Cameron, and R. H. Dubois, *J. Org. Chem.*, 1968, **33**, 3970; (*b*) F. Freeman, P. D. McCart, and N. J. Yamachika, *J. Amer. Chem. Soc.*, 1970, **92**, 4621.
[6] H. C. Duffin and R. B. Tucker, *Chem. and Ind.*, 1966, 1262; *Tetrahedron*, 1967, **23**, 2803; *ibid.*, 1968, **24**, 389.
[7] J. A. Strickson and C. A. Brooks, *Tetrahedron*, 1967, **23**, 2817.
[8] J. A. Strickson and M. J. Leigh, *Tetrahedron*, 1968, **24**, 5145.

magnetic susceptibility over a wide temperature range is exemplified in the Figure. These results do not in any way correspond to the antiferromagnetic behaviour observed for the chromium(III) alkoxides [9] and indeed do not show evidence for any magnetic coupling between chromium centres within the solid product. Notwithstanding the ambiguities regarding the precise value of the oxidation state, the magnetic properties demonstrate that the chromium is present in oxidation states lower than Cr^{VI} and hence that a substantial part of the oxidation is complete by the time the solid is formed.

The composition of these solids as defined by elemental analysis lacks the simple stoicheiometry reported for other examples of Etard adducts.[1] Although there is a rough approximation to a ratio of two moles of oxidant to one mole of phenol, the solids must be considered as non-stoicheiometric products.

The i.r. spectra of the solids (Table 2) show a number of significant features. The presence of strong bands in the 3300 cm^{-1} region indicates the presence of O–H groups and the presence of strong bands in the 1560—1650 cm^{-1} region correlates well with the presence of benzoquinone species. *p*-Benzoquinones do not readily form complexes with metal ions unless such ions have *d* electrons which can be used for bond stabilisation. A report [10] of the formation of a rather unstable complex between antimony pentachloride and *p*-benzoquinone led us to prepare some similar but rather more stable analogues using alkyl substituted benzoquinones. The complex derived from 2,5-di-t-butyl-*p*-benzoquinone is a bright yellow solid, stable for several hours at room temperature. In this complex the C=O stretching occurs at 1569 compared with 1650 cm^{-1} in the pure quinone. Other quinones show similar reductions in wavelength when co-ordinated in a like manner. The properties of these complexes will be more fully reported in a future paper. The spectra of the phenol ' adducts ' show strong bands at frequencies which correspond to the presence of co-ordinated carbonyl groups; the solid adduct derived from 2,5-di-t-butylphenol and which releases 2,5-di-t-butyl-*p*-benzoquinone on hydrolysis has strong bands at 1625 and 1585 cm^{-1}.

All the solid adducts derived from the phenols give a band close to 980 cm^{-1} which can be assigned to the Cr=O group.[11] There is very little correspondence between the spectra of the different solids in the 700—900 cm^{-1} region; most but not all have bands of medium intensity in the 860—890 cm^{-1} region and again most but not all have bands of medium to strong intensity in the 790 and 720 cm^{-1} regions. All the solids have strong absorptions in the 530—560 cm^{-1} region which can be assigned to either Cr–(OH)–Cr or Cr–O–Cr modes.[12] Likewise all solids have a strong band at 340 cm^{-1} with shoulders at 300 and 280 cm^{-1}; these may be assigned to the Cr–Cl bonds,[13] the former band to the terminal Cr–Cl and the others to bridging Cr–Cl–Cr groups although it is possible that one of these bands could arise from an O–Cr–O mode.

Further evidence for the presence of co-ordinated quinone in the solid adduct comes from the study of the treatment of the solid derived from 2,5-di-t-butylphenol with a number of donor solvents. With all the solvents used (dioxan, tetrahydrofuran, diethyl ether, acetone, pyridine, piperidine, and acetonitrile) the benzoquinone is released; the solids formed as a consequence of the reaction have properties characteristic of co-ordination complexes between the solvent and chromium. Tables 3 and 4 illustrate these features for two such solids; although the stoicheiometry is complicated the i.r. spectra are similar [14,15] to those reported for other complexes of these solvents. In each case treatment of the solvent complex with water released the solvent.

TABLE 2

I.r. absorption spectra (ν/cm^{-1}) of solid adducts

(a) All solids have absorption bands at 3300 ± 50 and 980 ± 10 cm^{-1}

(b) Strong absorption bands in the carbonyl region

Phenol	Frequency of absorption bands in 1550—1700 cm^{-1} region	C=O Stretch in quinone obtainable from solid
2,6-Dimethylphenol	1658sh, 1651, 1618, 1598, 1559sh	1665
2,5-Dimethylphenol	1644sh, 1610	1664
3,5-Dimethylphenol	1645, 1610	1665
2,6-Di-isopropylphenol	1642, 1606sh, 1581	1655
2,5-Di-isopropylphenol	1637, 1603	1645
2,6-Di-t-butylphenol	1630, 1578	1654
2,5-Di-t-butylphenol	1650sh, 1625, 1600sh, 1585	1650
3,5-Di-t-butylphenol	1660sh, 1633, 1585, 1550sh	1654
2,4,6-Tri-t-butylphenol	1662sh, 1641, 1582	1658

(c) Examples of strong absorption bands in 250—700 cm^{-1} region

Phenol	
2,4-Di-t-butylphenol	560, 490sh, 425sh, 340, 300sh, 280sh
2,5-Di-t-butylphenol	530, 470sh, 360sh, 340, 280sh
2,6-Di-t-butylphenol	545sh, 525, 480sh, 380sh, 360sh, 340, 305sh, 280sh
3,5-Di-t-butylphenol	560, 525sh, 435, 352sh, 340, 301sh
	570sh, 545sh, 522, 478sh, 340, 300sh, 280sh

TABLE 3

I.r. spectra (ν/cm^{-1}) of the solids resulting from the treatment of the 2,5-di-t-butylphenol–chromyl chloride complex with donor solvents

(a) Solid obtained by treatment with 1,4-dioxan: 3250br, 1719br, 1640br, 1577w, 1257s, 1119s, 1081m, 1050m, 1020w, 981m, 961m, 901m, 879s, 830m, 725m

(b) Solid obtained by treatment with pyridine: 3380br, 1650w, 1607s, 1577w, 1542w, 1244w, 1218s, 1157m, 1075s, 1049m, 1020m, 980w, 900w, 860w, 788w, 768s, 725w, 695s

[9] D. A. Brown, D. Cunningham, and W. K. Glass, *J. Chem. Soc.* (*A*), 1968, 1563.

[10] F. Klages, H. Trager, and E. Muhlbauer, *Chem. Ber.*, 1959, **92**, 1819.

[11] H. Stammreich, K. Kawai, and Y. Tavares, *Spectrochim. Acta*, 1959, **15**, 438.

[12] D. J. Hawkin and W. P. Griffith, *J. Chem. Soc.* (*A*), 1966, 472.

[13] D. M. Adams, J. Chatt, J. M. Davidson, and J. Gerratt, *J. Chem. Soc.*, 1963, 2189.

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[15] N. S. Gill, R. H. Nuthall, D. E. Scarfe, and D. W. A. Sharp, *J. Inorg. Nuclear Chem.*, 1961, **18**, 79.

From the foregoing we conclude that most of the oxidation process is complete before the solid is formed and also that the second stage of the reaction, the hydrolysis, is little more than a ligand exchange process in which the rather weakly co-ordinating oxidation products are released by the much stronger ligand water.

TABLE 4

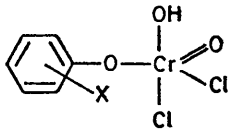
Elemental analyses of solids resulting from the treatment of the 2,5-di-t-butylphenol–chromyl chloride complex with dioxan and pyridine

(a) Solid containing dioxan: Found: C, 26·9; H, 5·2, Cl, 22·5; Cr, 16·4. Calc. for $Cr(dioxan)_2Cl_2(OH)$: C, 30·4; H, 5·4; Cl, 22·5; Cr, 16·5%

(b) Solid containing pyridine: Found: C, 39·3; H, 4·1; Cl, 23·9; Cr, 16·0; N, 8·2. Calc. for $Cr(pyridine)_2Cl_2(OH)(H_2O)$: C, 38·0; H, 4·1; Cl, 22·5; Cr, 16·45; N, 8·9%

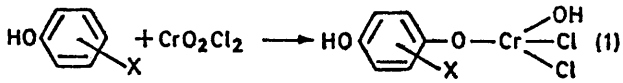
Mechanism of Adduct Formation.—In all reactions mixing of the phenol with the oxidant leads to the formation of a transient blue-green species; by adding small quantities of the chromyl chloride in very dilute solution to an excess of the phenol also in dilute solution it is possible to observe the formation of such species more clearly. In most cases the colour disappears rapidly with the formation of the brown solid. However, the blue species derived from 2,5-di-t-butylphenol is somewhat longer lived. When a freshly prepared solution was examined in an e.s.r. spectrometer it showed no absorption at all until the solid material was formed. Although the formation of an ester of Cr^{IV} with e.s.r. properties similar to those described by Bradley *et al.*[16] cannot be ruled out entirely it is a less likely explanation than the formation of the chromium(VI) ester of the type (I).

The i.r. spectrum of the blue solution is eclipsed over a broad region by the large excess of the parent phenol and also by the solvent but some interesting features have



(I)

been observed. At 3280 cm^{-1} a broad band does occur whose intensity increases with the further addition of oxidant to the point where solid is precipitated and can hence be attributed to the reaction between the two species. Also in the 980 cm^{-1} region there is a complex pattern of bands with absorptions at 1008, 978, 965, 950, and 938 cm^{-1}; those at 1008, 978, and 938 cm^{-1} can be attributed to the excess of phenol leaving the bands at 965 and 950 cm^{-1} to be assigned to the blue species. These bands which can be assigned to the Cr=O bond in the new species indicate that its formation cannot be explained in terms of a reaction (1) giving a Cr^{IV} ester. Of interest also is the disappearance of the band at 500 cm^{-1} which occurs in chromyl chloride. However, if this band were to be lowered to frequencies below 480 cm^{-1} it would be obscured by absorptions arising from the phenol. An examination of the visible and u.v.



(1)

absorption spectrum of the blue solution shows only one new band with $\lambda_{max.}$ at 14,100 cm^{-1}. The decay of this species does not appear to lead to the formation of any other coloured compounds although the formation of an almost colloidal brown solid and the presence of the large excess of phenol make the observation of new bands and their changes very difficult.

Examination of the reaction of phenols with chromyl chloride in an e.s.r. spectrometer using flow techniques at room temperature failed to demonstrate radical formation except in the case of 2,4,6-tri-t-butylphenol from which the clearly defined free phenoxyl radical signal was obtained. However, if a solid solution of chromyl chloride in carbon tetrachloride is allowed to melt in contact with a solid solution of a phenol in the same solvent in the cavity of an e.s.r. spectrometer, strong radical signals are obtained. The signals change fairly rapidly with both time and temperature, thus making radical characterisation very difficult.

The yield of quinone varies considerably with the size and position of the substituents. The dialkyl substituted phenols illustrate this variation. Thus for 2,5-disubstituted phenols the yield of quinone increases across the sequence methyl, isopropyl, and t-butyl (15, 42, and 83% respectively), while for the 2,6-disubstituted phenols the increase is smaller (48, 56, and 69% respectively). The yield of the tetra-alkyl-[bicyclohexa-2,5-dienylidene]-4,4′-dione, obtained only from the 2,6-disubstituted phenols decreases across the sequence 10·6%, 5%, and a trace only. The presence of an alkyl group in the 4-position does not enhance the formation of *ortho*-quinones although the *ortho*- rather than the *para*-quinone is produced in the reaction involving 2,4,6-tri-t-butylphenol.

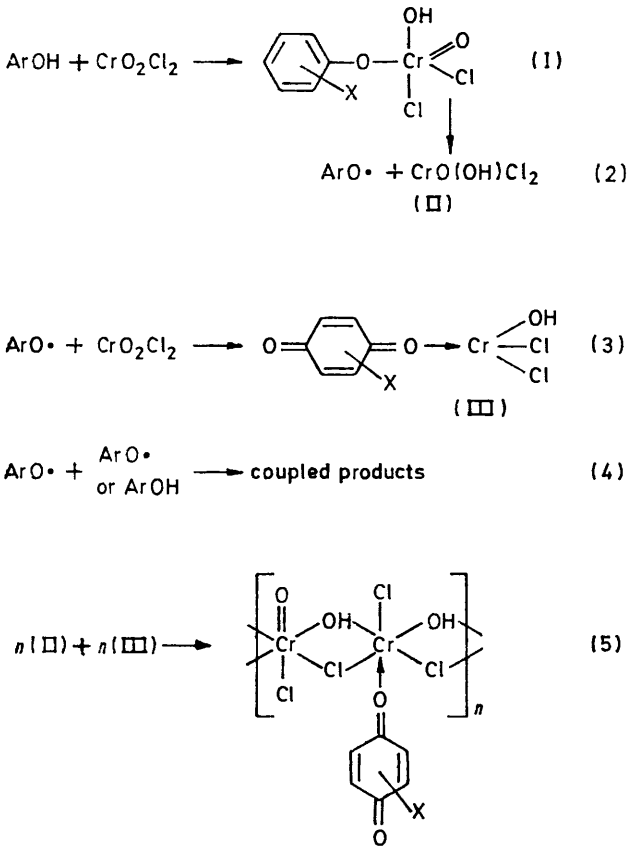
The tarry compounds which form the bulk of the products from the monosubstituted phenols and from some of the 3,5-di-substituted phenols have still to be characterised. Spectroscopic and chemical properties indicate the presence of polyphenol and polyphenylene ethers; the mass spectra of the tars show that they contain compounds with molecular weights several times that of the parent phenol.

The use of the reductive hydrolysis technique described by Freeman [5a] leads to an improved yield of quinone when the parent phenol contains several methyl groups and when the quinone is appreciably soluble in water. It seems probable that this technique reduces secondary oxidation of the products which can occur during the hydrolysis. Chromium(IV) or chromium(V) species from the solid would disproportionate to give Cr^{VI} and Cr^{III}; the former could be present at quite high local concentrations during the addition of the solid to the water and so

[16] E. C. Alyea, J. S. Basi, D. C. Bradley, and M. H. Chisholm, *J. Chem. Soc.* (*A*), 1971, 772.

able to effect further oxidation. This technique is of no value in the preparation of the water-insoluble di-t-butylbenzoquinones; indeed the extraction of the quinone from the zinc dust does not lead to yields comparable to those obtained from the simple hydrolysis procedure.

Improvement in the yields of some quinones can be achieved by using increased ratios of oxidant to phenol, *e.g.* those substituted in the 3 and 5 positions. These increases can be explained in terms of competition between a radical coupling and an oxidation reaction. The phenols which give the least stable free radicals



would be expected to give increased yields of quinone as the ratio of oxidant to phenol is increased. This is the pattern observed for dimethylphenols.

Our view is that the predominating reactions in the Etard reaction involving phenols are (2)—(5) with possible rearrangement of the electrons in the chromium in the solid to give Cr^{IV} species. In view of the presence of oxygen atoms in the coupled products it is probable that they also form co-ordination complexes with chromium. It is also likely that some further complication could arise through the involvement of species (II) in secondary oxidation reactions.

EXPERIMENTAL

All solvents and reagents were carefully purified and dried prior to use. Likewise all apparatus for handling the reagents and the solid reaction products was dried. The reactions were carried out in a dry atmosphere.

Preparation of the Solid Adducts.—The phenol, dissolved in at least a ten-fold excess of solvent was added slowly to a vigorously stirred solution of chromyl chloride in the same solvent at roughly the same dilution. In all cases, except with the nitrophenols, the solid started to precipitate at once. After further stirring, usually *ca.* 30 min but rarely longer than 2 h, except in the case of the nitrophenols, the mixture was filtered and the solvent removed under vacuum. For carbon tetrachloride great difficulties were experienced in removing the final quantities of solvent; with some phenols up to 5% by weight of the adduct consisted of solvent. There was no evidence that the solvent had participated in the reaction and on hydrolysis it was released with the other products. Carbon disulphide is a better solvent in this respect but unfortunately in reactions involving a long contact time between the oxidant and the solvent some solvent is oxidised. The yields of the several products in each reaction were not affected by the solvent used.

Hydrolyses.—(a) *Normal hydrolysis.* The solid was added in small quantities (1 g or less) to a rapidly stirred mixture of ice and water; after completing the addition the mixture was stirred until the ice had all melted. After filtration the solution was extracted (carbon tetrachloride, chloroform, light petroleum, and benzene). The organic products from the extraction as well as from the filtration were purified by recrystallisation and in the case of the quinones by vacuum sublimation.

(b) *Reductive hydrolysis.* Prior to filtration of the adduct, an excess of zinc dust was added to the rapidly stirred mixture; after further stirring for 15 min water (about one fifth the volume of the solvent used in the reaction) was added and the stirring was continued for 5 min. Longer periods of stirring led to a reduction in the yield of quinone through the formation of the quinol. The mixture was then filtered and the aqueous phase was separated. After extraction the products were combined and purified by recrystallisation and vacuum sublimation.

Magnetic susceptibilities were measured with a temperature variable Gouy balance (Newport Instruments Ltd.), visible and u.v. absorption spectra were recorded with a Pye–Unicam SP 800 spectrophotometer, i.r. spectra with Pye–Unicam SP 200 and Perkin-Elmer 457 spectrophotometers, mass spectra with A.E.I. MS9 and MS2 mass spectrometers, and e.s.r. spectra with Varian E3 and E4 spectrometers.

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