# Polymer-supported Periodate and Iodate as Oxidizing Agents

By **Charles R. Harrison** and **Philip Hodge,**[*] Department of Chemistry, University of Lancaster, Bailrigg, Lancaster LA1 4YA

The periodate forms of some commercial macroporous anion-exchange resins can be used in either protic or aprotic solvents to oxidize various quinols, catechols, and glycols and also triphenylphosphine, hydrazobenzene, and benzohydroxamic acid. The reagents in methanol oxidize thioethers. Polymer-supported iodate also oxidizes quinols and catechols.

The periodate anion oxidizes various functional groups but the solubility properties of sodium and potassium periodates are such that these salts can generally be used only in hydroxylic media.[1,2] Reactions can be carried out in aprotic solvents by using periodic acid,[3] sodium periodate supported on silica gel,[4] or certain lipophilic quaternary ammonium salts.[5,6] We wish to report that the periodate forms of some macroporous anion exchange resins (1), which can be considered as polymer-supported quaternary ammonium periodates, are a practically useful alternative. We have shown that they can be used in a range of solvents, including aprotic solvents, to oxidize various quinols, catechols, and glycols and also triphenylphosphine, hydrazobenzene, and benzohydroxamic acid. With methanol as the solvent the reagents (1) can be used to oxidize thioethers. Polymer-supported iodate (2) also oxidizes quinols and catechols. Other anionic forms of macroporous anion-exchange resins have been used recently as reagents.[7,8]
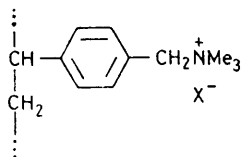
(1) $X^- = IO_4^-$
(2) $X^- = IO_3^-$

The periodate forms (1) of Amberlyst A26 and Amberlite IRA 904, two commercial macroporous anion-exchange resins, and the iodate form (2) of Amberlyst A26 were prepared by standard ion-exchange procedures. The dried reagents generally contained 1.3—2.0 mmol of oxidant per g. The products of reactions with these reagents were isolated simply by filtering off the resin and evaporating the solvent from the filtrate. In many cases the residue was essentially pure product. In other cases it was analysed and/or purified as necessary.

Oxidation of Quinols and Catechols.—Preliminary experiments on the oxidation of quinol to *p*-benzoquinone showed (see Table 1) that the reaction could be carried out with reagent (1) or (2) in various solvents, including aprotic solvents. The supported periodates (1), especially that prepared from Amberlite IRA 904 were more reactive than the supported iodate (2).

A range of quinols and catechols was oxidized in methylene chloride or chloroform, and in most cases (see Table 2) high yields of quinone were obtained. Although catechol reacted with both oxidants (1) and (2) to produce *o*-benzoquinone, attempts to isolate the latter led to complex mixtures. Some reactions produced small amounts of iodine but this was readily sublimed from the products.

TABLE 1

Oxidation of quinol to benzoquinone by polymer-supported periodate (1) and iodate (2) in various solvents [a]

| | Yields of benzoquinone [b] | | |
| | From periodate form of Amberlyst A26 | From periodate form of Amberlite IRA 904 | From iodate form of Amberlyst A26 |
Solvent			
MeOH	89		89
CHCl$_3$	63	81	37
Me$_2$CO	47		48
CH$_2$Cl$_2$	45	70	31
EtOAc	33		54
C$_6$H$_6$	20	30	
THF	c	c	

[a] Reactions of 1.0 mmol of substrate with 1.1 mmol of reagent in 10 ml of solvent at 20 °C; with periodiate oxidations the reaction time was 0.5 h; with iodate 2 h. [b] Yields determined by ^{1}H n.m.r. analysis, the combined yields of benzoquinone and recovered starting material accounted for >90% of the original quinol. [c] Complex mixture of products.

Oxidation could also be carried out using a column of reagent. Thus, when a solution of 2,5-di-t-butylquinol in acetone was passed through a column of supported periodate (1) at 20 °C, the yield of quinone after 30 min residence time was 75%, and after 60 min 97%.

Cleavage of 1,2-Diols.—Cyclohexane-*trans*-1,2-diol was readily oxidized to adipaldehyde by the supported periodate (1) in various solvents (see Table 3), the reagent prepared from Amberlite IRA 904 being superior to that from Amberlyst A26.

Interestingly, the cleavages of both *trans*- and *cis*-cyclohexane-1,2-diol in methylene chloride were slower if the solvent was dried prior to use. Since water is produced by the cleavage reactions themselves, the traces of water present in the solvent presumably serve mainly to assist the initial reactions. The polymer almost certainly absorbs the water present, and this may result in a favourable microenvironment at some of the reaction sites. Periodate cleavages are known to proceed more rapidly in aqueous media.[9]

Several other 1,2-diols were cleaved in high yield by the supported periodate (1) in methylene chloride (see Table 4). The poor yield of benzaldehyde from (±)-1,2-diphenylethane-1,2-diol and the lack of reaction with cortisone acetate (an α-hydroxy-ketone) in chloroform

TABLE 2

Oxidation of quinols to *p*-quinones and catechols to *o*-quinones by polymer-supported periodate (1) or iodate (2)

Substrate	Reagent [a]	Reaction conditions [b] [solvent, time (h)]	% Yield of quinone [c]
Quinol	P	CHCl$_3$, 2	86
	I	CHCl$_3$, 18	69 [d]
2,5-Di-t-butylquinol	P	CHCl$_3$, 4	99
2-Methoxyquinol	P	CHCl$_3$, 1	93
2-Chloroquinol	P	CHCl$_3$, 1	96
2-(*p*-Tolylthio)quinol	P	CH$_2$Cl$_2$, 0.5	95
	I	CH$_2$Cl$_2$, 1	94
2-Acetylquinol	P	CH$_2$Cl$_2$, 3	e
	I	Me$_2$CO, 3	e
2-Methyl-1,4-dihydroxy-naphthalene	P	CHCl$_3$, 2	99
	I	CHCl$_3$, 2	100
Catechol	P or I	CH$_2$Cl$_2$, 0.5	f
4-t-Butylcatechol	P	CH$_2$Cl$_2$, 2	99
3,5-Di-t-butylcatechol	P	CHCl$_3$, 0.75	100
	I	CHCl$_3$, 1	100
1,2-Dihydroxynaphthalene	P	CHCl$_3$, 0.5	96
4-Methoxyphenol	P	CHCl$_3$, 1	0 [g]

[a] P = polymer-supported periodate (1); I = polymer-supported iodate (2). [b] Reactions with 1.1 mol equiv. of oxidant at 20 °C; details of a typical procedure are given in the Experimental section. [c] Unless indicated otherwise, yield of isolated product with satisfactory m.p. and/or spectral data. [d] Yield determined by [1]H n.m.r. analysis. [e] Complex mixture of products including starting material. [f] The u.v. spectrum of the final reaction mixture indicated the presence of *o*-benzoquinone, but attempts to isolate it led to a complex mixture of products. [g] No reaction occurred; starting material recovered.

TABLE 3

Cleavage of cyclohexane-*trans*-1,2-diol by polymer-supported periodate (1) [a]

	Yield (%) of adipaldehyde [b]	
Solvent	From periodate form of Amberlyst A26	From periodate form of Amberlite IRA 904
C$_6$H$_6$	65	86
CH$_2$Cl$_2$	84 [c]	87
CH$_2$Cl$_2$ dried [d]	60 [c]	
Et$_2$O	50	70
EtOH	52	54
H$_2$O	84	90

[a] Reactions carried out for 2 h with 1.0 mmol of substrate and 1.1 mmol of reagent in 10 ml of solvent at 20 °C. [b] Determined by [1]H n.m.r. spectroscopy; combined yields of aldehyde and recovered starting material accounted for >90% of diol. [c] With cyclohexane-*cis*-1,2-diol the corresponding yields were as follows: with methylene chloride 84%; with dried methylene chloride 41%. [d] Solvent dried over calcium hydride.

suggest the possibility of selective reactions with this reagent.

Other Oxidations.—These are summarised in Table 5. Polymer-supported periodate (1) reacted with dibenzyl sulphide in various solvents, but the reactions were very slow in other than hydroxylic solvents. In methanol several thioethers, including methylpenicillin

TABLE 4

Cleavage of 1,2-diols by polymer-supported periodate (1) [a]

Substrate	Reaction time (h)	Product	Yield (%) [b]
Cyclohexane-*trans*-1,2-diol	3	Adipaldehyde	90 [c]
Cyclohexane-*cis*-1,2-diol	4	Adipaldehyde	93
Cycloheptane-*trans*-1,2-diol	2	Pimelaldehyde	90 [d]
1-Phenylethane-1,2-diol	3	Benzaldehyde	97 [e]
2-Phenylpropane-1,2-diol	3	Acetophenone	86 [f]
(±)-1,2-Diphenylethane-1,2-diol	3	Benzaldehyde	29
Hexadecane-1,2-diol	3	Pentadecanal	96 [g]
Cortisone acetate	9 [h]		0

[a] Unless indicated otherwise, the reactions were carried out in methylene chloride at reflux temperature using 1.1—1.3 mol equiv. of reagent prepared from Amberlite IRA 904. [b] Unless indicated otherwise the yields were determined by [1]H n.m.r. analysis; recovered starting material and product together accounted for >90% of the starting material. [c] Bis-2,4-dinitrophenylhydrazone prepared in 66% overall yield. [d] Bis-oxime prepared in 70% overall yield. [e] Semicarbazone prepared in 77% overall yield. [f] 2,4-Dinitrophenylhydrazone prepared in 63% overall yield. [g] Product was a solid, m.p. 24—26° (lit.,[12] 24—25°). [h] Reaction solvent was chloroform.

TABLE 5

Oxidations with polymer-supported periodate (1)

Substrate	Reaction conditions (resin,[a] solvent, temp., time)	Product	Yield (%) [b]
Dibenzyl sulphide	A, MeOH, 40 °C, 16 h	Sulphoxide	99
	A, Me$_2$CO–H$_2$O (1 : 1), 40 °C, 4 h		96 [c]
	A, Me$_2$CO, 40 °C, 16 h		33 [c]
	A, CHCl$_3$, 40 °C, 16 h		33 [c]
	A, C$_6$H$_6$, 40 °C, 16 h		29 [c]
	A, CH$_2$Cl$_2$, 40 °C, 16 h		19 [c]
	B, CH$_2$Cl$_2$, 42 °C, 16 h		41 [c]
Benzyl methyl sulphide	B, MeOH, 40 °C, 10 h	Sulphoxide	85 [c]
Thioanisole	A, MeOH, 40 °C, 16 h	Sulphoxide	81
Pentamethylene sulphide	A, MeOH, 40 °C, 16 h	Sulphoxide	82
Methylpenicillin V	A, MeOH, 40 °C, 18 h	α-Sulphoxide	89
Triphenylphosphine	A, CHCl$_3$, 25 °C, 2 h	Phosphine oxide	100
Hydrazobenzene	A, CHCl$_3$, 25 °C, 2 h	Azobenzene	89
Benzohydroxamic acid	A, CHCl$_3$, 25 °C, 18 h	Nitrosocarbonyl-benzene	65 [d]

[a] A, reagent prepared from Amberlyst A26; B, reagent prepared from Amberlite IRA 904; 1.1—1.4 mol equiv. of reagent was used. [b] Unless indicated otherwise the yield given is that of isolated material with satisfactory physical and spectral data. [c] Yields determined by [1]H n.m.r. analysis; recovered starting material and product together accounted for >90% of the starting material. [d] By [1]H n.m.r. analysis of the 9,10-dimethylanthracene adduct.

V, were efficiently oxidized to the corresponding sulphoxides. Liu and Tong have recently shown that thioethers can be oxidized to sulphoxides using alumina-supported sodium periodate in ethanol.[10]

Triphenylphosphine, hydrazobenzene, and benzo-hydroxamic acid reacted smoothly with the supported periodate (1) in chloroform to give, respectively, tri-phenyl phosphine oxide, azobenzene, and nitrosocar-bonylbenzene, the last-named being trapped as the 9,10-dimethylanthracene adduct.[11]

EXPERIMENTAL

Amberlite IRA 904 and Amberlyst A26 resins are marketed by Rohm and Haas Ltd. The reaction solvents were reagent grade and, unless indicated otherwise, were not specially dried.

Preparation of Polymer-supported Periodate (1) *and Iodate* (2).—The following procedures are typical.

(*a*) The chloride form of Amberlite IRA 904 (25 g, damp) was stirred for 6 h with sodium periodate (20 g) in water (200 ml) at 20 °C. The liquid was decanted off and the resin was treated with a fresh solution of sodium periodate (20 g) in water (200 ml). The resin was then filtered off and washed successively with water (4 × 200 ml), tetra-hydrofuran (2 × 100 ml), and ether (2 × 100 ml), and dried overnight at 40 °C and 1 mmHg. By iodometry the product (15.2 g) contained 1.60 mmol of periodate per g.

(*b*) The hydroxide form of Amberlyst A26 resin (18.0 g, 1.8 mequiv. per g) was stirred with periodic acid dihydrate (11.4 g) in water (50 ml) at 20 °C for 2 h. The resin was filtered off, washed, and dried as above. The capacity of the product (22.2 g) was 1.39 mmol of periodate per g.

(*c*) The hydroxide form of Amberlyst A26 resin (20.0 g, 1.8 mequiv. per g) was stirred with iodic acid (10 g) in water (200 ml) at 20 °C for 2 h. The resin was filtered off, washed, and dried as above. By iodometry the product (22.8 g) contained 1.29 mmol of iodate per g.

Reactions Summarised in Tables 1—5.—The following reactions are typical. The other reactions were carried out similarly and gave products with spectroscopic data and/or m.p.s or b.p.s in good agreement with literature values.

(*a*) *Oxidation of chloroquinol by reagent* (1). Chloroquinol (723 mg, 5.0 mmol) in chloroform (50 ml) was stirred with the periodate form of Amberlyst A26 (3.075 g, 5.5 mmol) for 1 h at 20 °C. The resin was filtered off and washed on the filter with chloroform (2 × 25 ml). Evaporation of the combined filtrate and washings left chlorobenzoquinone (684 mg, 96%) as yellow-brown crystals, pure by [1]H n.m.r. analysis. From ether the product gave crystals (502 mg, 70%), m.p. 51—54° (lit.,[12] 57°).

(*b*) *Oxidation of 2,5-di-t-butylquinol by a column of reagent* (1). The periodate form of Amberlyst A26 (6.00 g, 10.3 mmol) was placed in a 1 × 20 cm chromatography column. A solution of 2,5-di-t-butylquinol (1.50 g, 6.8 mmol) in acetone (8 ml) was added, followed by acetone just to cover the resin. After 1 h, at 20 °C the liquid phase was run off and the column washed with acetone (20 ml). Evaporation of the combined acetone solutions gave 2,5-di-t-butyl-1,4-benzoquinone (1.45 g, 97%) as yellow crystals, m.p. 153—155° (lit.,[13] 153°), pure by [1]H n.m.r. analysis.

(*c*) *Oxidation of 3,5-di-t-butylcatechol by reagent* (2). The substrate (222 mg, 1.0 mmol) in chloroform (10 ml) was stirred with the iodate form of Amberlyst A26 (853 mg, 1.1 mmol) for 1 h at 20 °C. The usual isolation procedure gave 3,5-di-t-butyl-*o*-benzoquinone (221 mg, 100%) as an orange solid, m.p. 113—115° (lit.,[14] 114—114.5°), pure by [1]H n.m.r. analysis.

(*d*) *Cleavage of 1-phenylethane-1,2-diol.* A mixture of the substrate (1.00 g, 7.25 mmol), methylene chloride (20 ml) and the periodate form of Amberlite IRA 904 (5.00 g, 8.0 mmol) was stirred and heated under reflux for 3 h. The usual isolation procedure gave benzaldehyde as an oil (770 mg, 97%), identified by [1]H n.m.r. Reaction with semi-carbazide hydrochloride and pyridine in aqueous methanol gave benzaldehyde semicarbazone (910 mg, 77%), m.p. 222—224° (lit.,[12] 222°).

(*e*) *Oxidation of dibenzyl sulphide.* Dibenzyl sulphide (214 mg, 1.0 mmol) in methanol (10 ml) was stirred with the periodate form of Amberlyst A26 (560 mg, 1 mmol) for 16 h at 40 °C. The usual isolation procedure gave dibenzyl sulphoxide (228 mg, 99%), white crystals, pure by [1]H n.m.r. analysis. From aqueous ethanol the product gave crystals (81% yield), m.p. 130—133° (lit., [12] 134°).

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