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Oxidation of Organic Compounds by Silver(II). Reactions with Aliphatic Diols and α-Hydroxy Acids

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Abstract

The rate of oxidation by silver(II) of succinic, malic, tartaric, glycolic and lactic acids and 1,2-ethanediol, 1,2-propanediol, 1,3-propanediol, and 1,2-ethanediol monomethyl ether has been investigated in acidic perchlorate media by the stopped-flow technique. For all substrates (S) except 1,2-ethanediol and 1,3-propanediol reactions were first order in total silver and in S with an observed rate constant $k_{obs} = 2(k_1 + k_2K_h[H^+]^{-1})$ reflecting parallel oxidations by aquasilver(II) (k_1) and $AgOH^+$ (k_2).

In the case of 1,2-ethanediol and 1,3-propanediol, plots of the pseudo first order rate constant k_{obs} *versus* [S] showed a levelling off behavior which is indicative of an association process prior to redox. The proposed mechanism involves formation of a Ag(I)–diol complex, rapidly oxidized by aquasilver(II) to Ag(II)–diol, which, in turn, undergoes redox decomposition. Stoichiometry, nature of the intermediate species, and reactivity patterns are discussed.

Introduction

Recently there have been a number of kinetic studies of the reactions of organic substrates with strongly oxidizing metal ions including Ce(IV) [1], Mn(III) [2], Co(III) [3], and Ag(II) [4–7]. For oxygen-containing organic reductants, a general order of reactivity of phenols > aldehydes > alcohols > carboxylic acids has been found [4–8]. In the case of aquasilver(II), intermediate formation of complexes has been postulated, but clear evidence for such species is still very limited. Recent work by Mehrotra has yielded spectroscopic and kinetic evidence for complex formation in the reduction of cerium(IV) by α-hydroxy acids [1b] and of aquamanganese(III) by diols [2a].

In this paper we report an extension of the series for aquasilver(II) to include aliphatic diols and α-hydroxy acids. The organic reducing agents employed are the acids succinic, malic, tartaric, glycolic, and lactic, and 1,2-ethanediol, 1,2-propanediol, 1,3-propanediol and 1,2-ethanediol monomethyl ether.

While formation of a precusor complex cannot be ruled out for any of the nine reactions studied, our results clearly indicate that for 1,2-ethanediol and 1,3-propanediol electron transfer does, indeed, occur within a complex ion.

Experimental

Reagents

All the organic compounds were reagent grade chemicals (Fluka or Merck). Silver(I) perchlorate solutions were prepared by neutralization of Ag_2O with aqueous perchloric acid (both analytical grade Merck products). NaOH (for preparing $NaClO_4$ solutions) and all other chemicals were of analytical grade.

Procedure

Ag(II) perchlorate solutions were prepared by partial oxidation of $AgClO_4$, as previously described [4, 9]. An excess of Ag(I) was maintained in all solutions in order to suppress Ag(II) disproportionation. Except for experiments to test for a variation of rate with added Ag(I), most reaction mixtures contained 0.1 mol dm^{-3} Ag^+. The ionic strength, μ, was maintained at 4.0 mol dm^{-3} throughout and most full kinetic variations were done at 10 °C to minimize spontaneous decomposition of silver(II). The kinetic experiments were performed under conditions of excess substrate in a Durrum-Gibson stopped-flow spectrophotometer. Absorbance changes were measured at the Ag(II) maximum, 470 nm, where other species do not contribute significantly.

Results and Discussion

Stoichiometry and Reaction Products

For each of the organic substrates, S, reactions were carried out in the stopped-flow apparatus with a

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3–4 fold excess of Ag(II) at 20 °C with $[Ag^+] = 0.1$ mol dm^{-3} and $[H^+] = 1.0$ mol dm^{-3}. For tartaric, malic and succinic acids, reaction traces at 470 nm ($\epsilon_{Ag(II)} = 148$ dm^3 mol^{-1} cm^{-1}) [9] levelled off to a final value consistent to within ±10% with a reaction ratio $\Delta[Ag(II)]/\Delta[S] = 2.0$.

For the other substrates, biphasic reactions were observed which did not permit an accurate determination of the stoichiometry of the initial reaction. It appears, however, that an initial two-electron process occurs for these cases as well, with further redox occurring on somewhat competitive time scales. Addition of 2,4-dinitrophenylhydrazine to reaction mixtures containing an excess of substrate (the conditions of the kinetic studies) confirmed the oxidation of –COH to –C=O, as tested for glycolic acid and 1,2-ethanediol.

The reactions by which the products are made can be written as follows:

Succinic acid:

$$COOHCH_2CH_2COOH + 2Ag^{2+} + H_2O \longrightarrow COOHCH_2CH_2OH + CO_2 + 2Ag^+ + 2H^+ \quad (1)$$

Glycolic acid (R = H), lactic acid ($R = CH_3$), malic acid ($R = COOHCH_2$), tartaric acid (R = COOHCHOH):

$$RCHOHCOOH + 2Ag^{2+} \longrightarrow RCHO + CO_2 + 2Ag^+ + 2H^+ \quad (2)$$

1,2-ethanediol ($R = CH_2OH$), 1,2-propanediol ($R = CH_3CHOH$), 1,3-propanediol ($R = CH_2OHCH_2$), 1,2-ethanediol monomethyl ether ($R = CH_3OCH_2$):

$$RCH_2OH + 2Ag^{2+} \longrightarrow RCHO + 2Ag^+ + 2H^+ \quad (3)$$

(We note that the site of oxidation is ambiguous for 1,2-propanediol.)

Kinetics

For the conditions of this study (excess substrate, S), all reactions were found to be first order in Ag(II)*. However, two distinct types of substrate and acid dependencies were observed. Plots of observed first order rate constants k_{obs} *versus* substrate concentration were linear for the succinic, malic tartaric, lactic and glycolic acids and for 1,2-propanediol and 1,2-ethanediol monomethyl ether. On the other hand such plots showed marked curvature for the oxidation of 1,2-propanediol and 1,3-propanediol. For these two systems, plots of $1/k_{obs}$ *versus* inverse substrate concentration were linear. For all nine reactions, the reaction rate increases with decreasing $[H^+]$ and is independent of $[Ag^+]$ for the range $0.025 \geqslant [Ag^+] \geqslant 0.1$ mol dm^{-3}.

Examples of the two types of k_{obs} *versus* [S] variations are given in Tables I and II and in Figs. 1–3**. Table I reports, as examples, the observed pseudo first order rate constants for a dicarboxylic acid (succinic), for an α-hydroxy acid (glycolic) and for 1,2-ethanediol monomethyl ether.

The substrate and acid dependencies of the type displayed in Fig. 1 are consistent with the rate law, found for other Ag(II) reactions [4], given by eqn. (4)

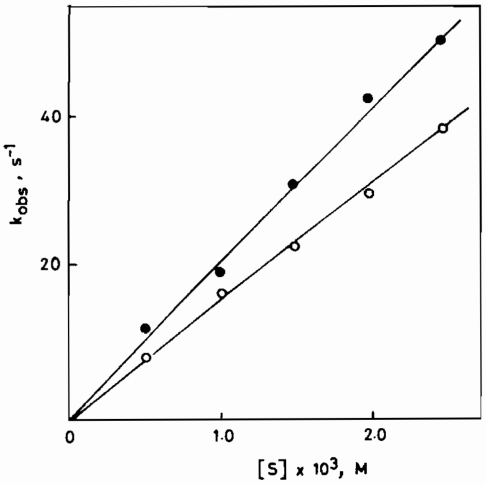

Fig. 1. Variations of the pseudo first order rate constant, k_{obs}, as a function of tartaric acid concentration for the oxidation by Ag(II) at $[HClO_4] = 1.00$ mol dm^{-3} (●) and 2.00 mol dm^{-3} (○) (10 °C, $\mu = 4.0$ mol dm^{-3}).

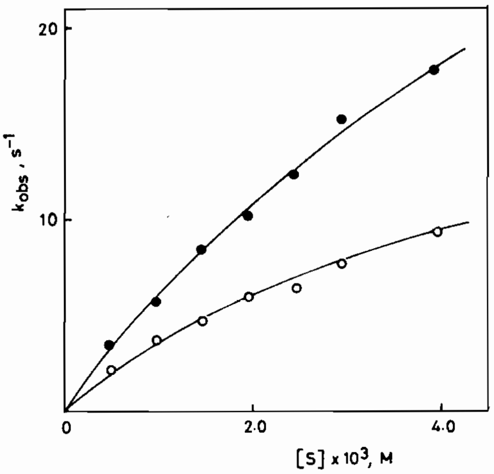

Fig. 2. Variation of the pseudo first order rate constant, k_{obs}, as a function of of 1,2-ethanediol concentration for the oxidation by Ag(II) at $[HClO_4] = 1.00$ mol dm^{-3} (●) and 2.80 mol dm^{-3} (○) (10 °C, $\mu = 4.0$ mol dm^{-3}).

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*In addition to the linearity of first order plots, the absence of any variation of observed rate constants with changing [Ag(II)] rules out a second order contribution due to silver(II) disproportionation.

**Data for all systems may be found in G. Dosio, Tesi di Laurea, University of Turin, 1985.

TABLE I. Pseudo First Order Rate Constants, k_{obs} (s^{-1}), for the Oxidation of some Substrates, S, by Ag(II) at Various [S] and $[H^+]$[a]

[S] × 10^3 (mol dm^{-3})	[$HClO_4$] (mol dm^{-3})				
	1.00	1.50	2.00	3.00[b]	4.00[c]
Succinic acid					
20.0	0.22	0.16	0.13	0.13	0.13
40.0	0.38	0.33	0.22	0.23	0.20
60.0	0.60	0.35	0.32	0.29	0.28
80.0	0.73	0.54	0.48	0.40	0.36
100	0.85	0.63	0.56	0.52	0.35
Glycolic acid					
0.30	2.78	1.65	1.88	1.03	1.05
0.50	4.06	2.79	2.66	1.70	1.71
0.70	5.02	3.78	3.49	2.96	2.37
1.00	7.63	5.60	4.42	3.10	3.19
1.50	10.0	8.60	6.32	4.80	4.88
2.00	14.8	11.2	9.20	6.81	6.64
2.50	17.0	14.1	11.0	8.27	9.21
3.00	20.1	16.9		10.4	9.50
1,2-Ethanediol monomethyl ether					
0.30	1.40	1.15	1.07	1.04	0.94
0.50	2.24	1.95	1.99	1.62	1.39
0.70	3.28	2.70	2.26	2.11	1.55
1.00	4.71	3.75	3.21	3.11	2.24
1.50	6.85	5.85	5.26	4.38	3.41
2.00	9.82	7.95	6.20	5.46	4.06
2.50	11.9	9.38	8.03	7.10	5.35
3.00	14.8	11.6	9.58	8.66	6.57

[a] μ = 4.0 mol dm^{-3}, [Ag^+] = 0.1 mol dm^{-3}, 10.0 °C. [b] For succinic acid [$HClO_4$] = 2.80 mol dm^{-3}. [c] For succinic acid [$HClO_4$] = 3.80 mol dm^{-3}.

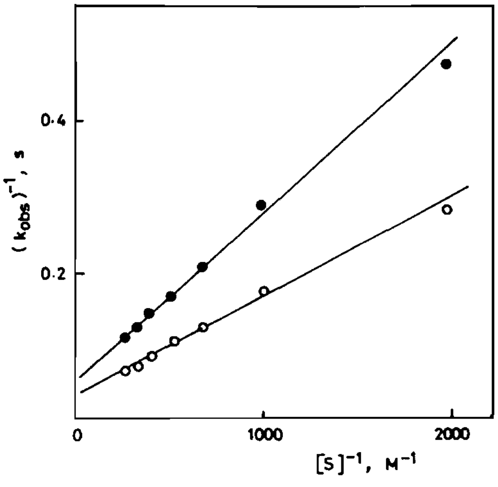

Fig. 3. Plot of $(k_{obs})^{-1}$ as a function of inverse 1,2-ethanediol concentration, according to eqn. (5), for the oxidation by Ag(II) at [$HClO_4$] = 1.00 mol dm^{-3} (○) and 2.80 mol dm^{-3} (●) (10 °C, μ = 4.0 mol dm^{-3}).

$$-d[\mathrm{Ag(II)}]_{tot}/dt = 2(k_1[\mathrm{Ag}^{2+}] + k_2[\mathrm{AgOH}^+])[\mathrm{S}]$$

$$= k_{obs}[\mathrm{Ag(II)}]_{tot} = -2d[\mathrm{S}]/dt$$

$$= \frac{2k_1 + 2k_2K_h[\mathrm{H}^+]^{-1}}{1 + K_h[\mathrm{H}^+]^{-1}}[\mathrm{Ag(II)}]_{tot}[\mathrm{S}] \qquad (4)$$

The rate constants k_1 and k_2 refer to parallel reaction pathways involving Ag^{2+} and $AgOH^+$ and K_h is the hydrolysis constant for Ag^{2+} (K_h = 0.15 and 0.31 mol dm^{-3} at 10 and 20 °C, ionic strength 4.0 mol dm^{-3}) [4, 10]. Equation (4) predicts a linear relationship between $k_{obs}[S]^{-1}(1 + K_h[H^+]^{-1})$ and $K_h[H^+]^{-1}$ and this is verified in Fig. 4 for malic acid. The values of k_1 and k_2, obtained from intercepts and slopes of analogous plots are listed in Table III for the seven substrates exhibiting this behaviour.

The rate law for the 1,2-ethanediol and 1,3-propanediol systems is of the form given in eqn. (5) and is indicative of a precursor complex.

TABLE II. Variation of k_{obs} (S^{-1}) with [S] and [H^+] for the Oxidation of 1,2-ethanediol by Ag(II) in Different Experimental Conditions[a]

[S] × 10^3 (mol dm^{-3})	[$HClO_4$] (mol dm^{-3})				
	1.00	1.50	2.00	2.80	3.80
0.50	3.58	3.40	2.55	2.12	1.71
1.00	5.71	6.10	3.28	3.95	2.68
1.50	8.42	8.25	7.39	4.92	3.39
2.00	10.2	8.97	7.46	6.06	4.53
2.50	12.5	11.4	9.02	6.47	5.54
3.00	15.2	13.4	11.9	7.75	6.27
4.00	17.8	23.2	14.0	9.45	7.48

[a] μ = 4.0 mol dm^{-3}, 10.0 °C.

TABLE III. Kinetic Parameters at 10 °C, μ = 4.0 mol dm^{-3}

Substrate	k_1 (dm^3 mol^{-1} s^{-1})	k_2 (dm^3 mol^{-1} s^{-1})
Succinic acid	0.75 ± 0.07	10 ± 1
Malic acid	(1.5 ± 0.1) × 10^3	(1.6 ± 0.1) × 10^4
Tartaric acid	(1.7 ± 0.2) × 10^3	(2.7 ± 0.2) × 10^4
Glycolic acid	(7.5 ± 0.5) × 10^2	(2.0 ± 0.2) × 10^4
Lactic acid	(5.0 ± 0.5) × 10^3	(1.0 ± 0.1) × 10^5
1,2-propanediol	(1.5 ± 0.2) × 10^3	(4.4 ± 0.4) × 10^4
1,2-ethanediol monomethyl ether	(6.0 ± 0.5) × 10^2	(1.3 ± 0.1) × 10^4

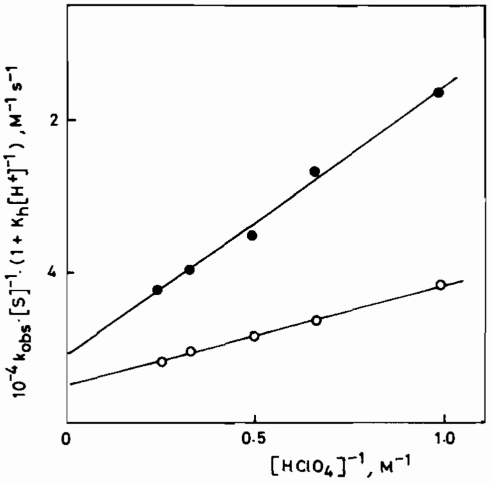

Fig. 4. Plot of $k_{obs}[S]^{-1}(1 + K_h[H^+]^{-1})$ as a function of $[H^+]^{-1}$, according to eqn. (4) for the oxidation of malic acid by Ag(II) at 20.0 °C (●) and 10.0 °C (○) (μ = 4.0 mol dm^{-3}).

$$-d[Ag(II)]_{tot}/dt = -2d[S]/dt = \frac{2kK[Ag(II)]_{tot}[S]}{1 + K_h[H^+]^{-1} + K[S]} \tag{5}$$

Note that the two rate laws differ in that while eqn. (5) contains a second equilibrium constant, the two rate constants of eqn. (4) do not appear.

From the form of eqn. (5), we may conclude that a complex is formed between silver(II) and the diol prior to redox. Similar metal–diol complexes have been postulated in reactions with other metals including Ce(IV) [11], Mn(III) [2a, 12] and with pulse radiolytically generated Ag(II) at high pH [6]. Since several of these studies were, like the present one, carried out in acid media, it appears as if diol complexation does not require deprotonation of the ligand. This may explain why diol complexes participate in these reactions whereas the protonated carboxylic acids (at the concentrations employed) show no sign of stoichiometrically significant complex formation.

The silver(I)–ethanediol complex is in particular known to be quite stable (log β_2 = 5.2) [13], and assuming log K_1 = 3, we estimate that virtually all the substrate is in a bound form under the conditions of this study and that reactions (6)–(9) contribute to the redox process.

$$Ag^+ + diol \xrightleftharpoons{K_1} Ag(diol)^+ \tag{6}$$

$$Ag^{2+} \xrightleftharpoons{K_h} AgOH^+ + H^+ \tag{7}$$

$$Ag^{2+} + Ag(diol)^+ \xrightleftharpoons{K_{eq}} Ag^+ + Ag(diol)^{2+} \tag{8}$$

TABLE IV. Kinetic Parameters for the Oxidation of 1,2-ethanediol and 1,3-propanediol by Ag(II)[a]

	$[H^+]$ (mol dm^{-3})	k (s^{-1})	K (dm^3 mol^{-1})
1,2-ethanediol	1.00	16	290
	1.50	15	280
	2.00	17	170
	2.80	8	300
	3.80	13	120
		13.8 ± 2.6	232 ± 62
1,3-propanediol	1.00	7.1	240
	1.50	6.2	190
	2.00	4.2	260
	2.80	4.2	190
	3.80	3.9	150
		5.1 ± 1.2	206 ± 33

[a] μ = 4.0 mol dm^{-3}, 10.0 °C.

$$Ag(diol)^{2+} \xrightarrow{k} Products \qquad (9)$$

Note that the possibility of a Ag(I)–Ag(II) electron exchange (eqn. (8)) allows for the formation of the precursor complex via a path alternative to the direct reaction (10).

$$Ag^{2+} + diol \rightleftharpoons Ag(diol)^{2+} \qquad (10)$$

Equilibrium (10) would be expected to be much slower than (6) since concentrations of Ag^{2+} and free diol are both quite low. The high percentage of $Ag(diol)^+$ indicates, additionally, that the quantity K in eqn. (5) is probably for the equilibrium in eqn. (8) rather than (10).

From the slopes, $(2k)^{-1}$, and intercepts, $(1 + K_h[H^+]^{-1})/2kK$, of plots such as in Fig. 3, we have computed k and K and find that these are, within experimental uncertainties, independent of acidity, as well as [Ag(I)]. Individual values are listed in Table IV and yield $k = 13.8 \pm 2.6$ s^{-1}; $K \equiv K_1K_{eq} = 232 \pm 62$ dm^3 mol^{-1} for 1,2-ethanediol and $k = 5.1 \pm 1.2$; $K \equiv K_1K_{eq} = 206 \pm 33$ for 1,3-propanediol.

In contrast to the high stability of Ag(I) diol complexes, Ag^+ forms only very weak complexes with carboxylate ions (e.g. $K \sim 10$ for the Ag(II) acetate complex at room temperature [14]) and should not associate appeciably with protonated organic acids at the high $[H^+]$ of our studies. Although silver(I) formation constants have been measured for only a few of the substrates considered here, we note that even for deprotonated tartaric acid, which has hydroxy groups adjacent to each other and to the carboxyl group, log $K < 2$ [15]. Thus, it appears reasonable that reducing agents that can complex silver(I) may react with Ag(II) via reactions (6)–(9) while other substrates undergo redox without a complexation equilibrium. It is possible, of course, that even if association with Ag(I) could occur, the analogue of eqn. (8) might be rate determining and a simpler substrate dependence (perhaps with a dependence on $[Ag^+]$) would result. Alternatively if redox were sufficiently slow (or [S] very large) to allow direct complex formation with Ag(II), [S] dependence as in eqn. (5) could occur.

In the absence of equilibrium data for the Ag^+–1,2-propanediol system we cannot speculate as to why complex formation was not detected. Hence, the 1,2-ethanediol and 1,3-propanediol reactions are unique in that complex formation with aquasilver(II) has been inferred from the substrate dependence of the redox rate.

Association between silver(II) and the substrate has also been inferred from the observed $[Ag^+]$ dependence of the rate of oxidation of aquasilver(II) [7] and of $Ag(bipy)_2{}^{2+}$ [5] by aliphatic alcohols. In these cases, there seems to be an equilibrium between separated reactants and a silver(I) radical pair. The absence of a detectable [Ag(I)] dependence in all the present systems does not of course rule out the possibility of such intermediates since free radical mechanisms are likely. However, our data indicate that substantial reoxidation of Ag(I) does not occur.

We now turn our attention to the seven substrates which have linear dependencies for k_{obs} *versus* [S]. Examination of the data in Table III reveals that all reactants, with the exception of succinic acid, have values of k_1 and k_2 which are (separately) within one order of magnitude of each other. This is consistent with an initial electron abstraction, when possible, at a hydroxy, rather than carboxyl group. In fact in lactic acid, which contains the electron-donating CH_3-group, it is the most reactive by both k, and k_2 paths, as in other aquasilver(II) reactions, $Ag(OH)^{2+}$ is more than ten times as reactive as Ag^{2+} for each of the seven substrates [4].

Mentasti *et al.* have tabulated kinetic results for the reactions of Ag^{2+} with aliphatic organic compounds [4]. Values for related compounds fall into well defined groups, with the general reactivity of acids being the lowest followed by alcohols and then aldehydes. Attempts to study Ag^{2+} reduction by phenol and aromatic diols were unsuccessful because the rates are beyond the range of the stopped-flow technique [10, 16]. For the entries in Table III, succinic acid correlates nicely with the monocarboxylic acids while the other six substrates have rates comparable to those of the aldehydes [4]. This latter similarity is not unexpected since in water the aldehydes exist as gem diols and are thus structurally related to diols and hydroxyacids.

A full study of the temperature dependence for the nine reactions reported here was not performed because of the limited range of stability for silver(II), the time scale of the reactions and the complexity of the rate laws and because of the instrumental considerations. We did, however, collect data for a number of these reactions over the temperature range 10–20 °C and report in Table V the activation parameters derived for three structurally related compounds for which results are sufficiently reliable that a comparison may be made. It is clear, from the values in Table V, that the successive addition of hydroxyl groups to succinic acid results in a decrease of both the enthalpy and entropy of activation. This seems to indicate a greater degree of intimate contact between silver(II) and the substrate prior to the redox step.

TABLE V. Activation Parameters for the Oxidation Reactions of Succinic, Malic and Tartaric Acid with Ag(II) at Ionic Strength 4.0 mol dm^{-3} [a]

	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J K^{-1} mol^{-1})
Succinic acid		
k_1 path	60 ± 8	−30 ± 25
k_2 path	70 ± 8	+30 ± 25
Malic acid		
k_1 path	25 ± 8	−90 ± 25
k_2 path	40 ± 8	−12 ± 25
Tartaric acid		
k_1 path	4 ± 8	−170 ± 25
k_2 path	4 ± 8	−140 ± 25

[a] Rate constants determined between 10 and 20 °C. Values are presented for comparison between systems.

In conclusion, we note that while we now have evidence for two reactions of silver(II) in which redox occurs within an Ag(II)–substrate complex at equilibrium, the absence of direct evidence for the other substrates does not preclude a mechanism involving intermediate formation of analogous species. Such complex formation might be expected at lower acidities and has, indeed, been observed in the reactions between Ce(IV) and α-hydroxy acids [1b]. The acid independences of the parameters in Table IV suggests that 1,2-ethanediol and 1,3-propanediol do not deprotonate on complexation. This is in accord with previous kinetic studies of diol oxidation by Mn(III) [2a, 12], Ce(IV) [11] and by pulse radiolytically generated Ag(II) [6].

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