Electron Transfer Reactions of Heteroaromatic Diols

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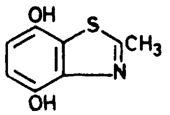
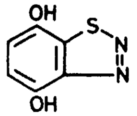
The kinetics and mechanism of oxidation of four heteroaromatic diols, namely 2-methyl-4,7-dihydroxybenzothiazole, 4,7-dihydroxy-1,2,3-benzothiadiazole, 2-methyl-5,6-dihydroxybenzothiazole, and 5,6-dihydroxy-1,2,3-benzothiadiazole, by means of a series of monoelectron acceptor metal complexes [iron(III) complexes of 1,10-phenanthroline and related compounds ($Fe^{III}L_3$), hexachloro-, aquapentachloro-, and diaquatetrachloroiridate(IV) (Ir^{IV}), and octacyanomolybdate(V)] were investigated by means of a stopped-flow spectrophotometric technique. The rates were found to be first order in diol and in metal complex in 1M-$HClO_4$. A linear correlation between the logarithms of the specific rate constants and standard reduction potentials were found for both $Fe^{III}L_3$ and Ir^{IV} systems. The slopes of these linear free energy plots were similar to those observed for other benzenediols with the same oxidants, and are those predicted by the Marcus theory for outer-sphere electron transfer. This allows an estimate of the reduction potentials and the intrinsic parameters of the cation radicals which are formed in the rate-determining step.

In recent papers, the kinetics and mechanism of oxidation of a series of benzene-1,4-diols,[1,2] benzene-1,2-diols,[3,4] and biphenyl-4,4'-diol [5] by means of inorganic complexes have been extensively investigated. The reactions of the organic substrates with hexachloroiridate(IV) and related aqua-species,[1,3,6] tris(1,10-phenanthroline)iron(III) and its derivatives,[2,4] and octacyanomolybdate(V) [7] have been suggested to occur through an outer-sphere electron-transfer; when this mechanism is operative, a relationship between the free energy of activation and the free energy of reaction is expected to hold and a model to account for the experimental data has been developed in the light of the Marcus theory.[8]



(I)



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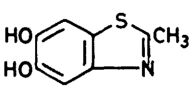

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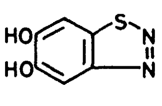

(IV)

We have extended these investigations to heteroaromatic diols in order to assess if the same reaction

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mechanism operates and in order to obtain some information about the thermodynamic parameters and reduction potentials of these substrates. Compounds (I)—(IV) were investigated.

EXPERIMENTAL

Organic Substrates.—Compounds (I), (II), and (IV) were prepared according to the literature.[9] Compound (III) was prepared by hydrolysis of the corresponding dimethyl ether [10] following the procedure described in the literature.[11]

TABLE 1

Spectral characteristics, reduction potentials, and initial concentrations of metal complexes

Oxidant	$E°$/ V	$\lambda_{max.}$/ nm	ε/l mol^{-1} cm^{-1}	$[Ox]_0$/ mol l^{-1}
$Fe(phen)_3^{3+}$	1.06 [a]	510 [b]	11 100	2—5 × 10^{-6}
$Fe(mphen)_3^{3+}$	1.02 [a]	516 [b]	11 500	2—5 × 10^{-6}
$Fe(dmphen)_3^{3+}$	0.97 [a]	512 [b]	12 400	2—5 × 10^{-6}
$Fe(cphen)_3^{3+}$	1.11 [a]	512 [b]	11 700	2—5 × 10^{-6}
$Fe(nphen)_3^{3+}$	1.25 [a]	510 [b]	11 500	2—5 × 10^{-6}
$Fe(bipy)_3^{3+}$	1.02 [c]	522 [b]	8 700	2—5 × 10^{-6}
$Fe(dmbipy)_3^{3+}$	0.84 [c]	528 [b]	9 300	2—5 × 10^{-6}
$IrCl_6^{2-}$	0.957 [d]	478 [e]	4 070	1—2 × 10^{-5}
$Ir(H_2O)Cl_5^-$	1.088 [d]	450 [f]	3 320	1.5—2.5 × 10^{-5}
$Ir(H_2O)_2Cl_4$	1.203 [d]	445 [g]	2 920	1.5—2.5 × 10^{-5}
$Mo(CN)_8^{3-}$	0.80 [h]	390 [i]	1 280	0.5—1 × 10^{-4}

[a] Data taken from A. A. Schilt, 'Analytical Applications of 1,10-Phenanthroline and Related Compounds,' Pergamon, London, 1969. [b] Spectral characteristics for the reduced species $Fe^{II}L_3$ from note *a*. [c] E. Mentasti and E. Pelizzetti, *Trans. Metal Chem.*, 1976, **1**, 281. [d] Ref. 20. [e] Ref. 13. [f] Ref. 14. [g] Ref. 15. [h] Quoted in R. J. Campion, N. Purdie, and N. Sutin, *Inorg. Chem.*, 1964, **3**, 1091. [i] M. H. Ford-Smith and J. H. Rawsthorne, *J. Chem. Soc. (A)*, 1969, 160.

Oxidizing Agents.—Tris(1,10-phenanthroline)iron(III) and its derivatives ($Fe^{III}L_3$) were prepared as previously described.[12] The following abbreviations are adopted: tris(1,10-phenanthroline)iron(III), $Fe(phen)_3^{3+}$; 5-methyl-, $Fe(mphen)_3^{3+}$; 5,6-dimethyl-, $Fe(dmphen)_3^{3+}$; 5-chloro-, $Fe(cphen)_3^{3+}$; tris(5-nitro-1,10-phenanthroline)iron(III), $Fe(nphen)_3^{3+}$; tris(2,2′-bipyridine)iron(III), $Fe(bipy)_3^{3+}$, and tris(4,4′-dimethyl-2,2′-bipyridine)iron(III), $Fe(dmbipy)_3^{3+}$. Sodium hexachloro-, sodium aquapentachloro-, and sodium diaquatetrachloro-iridate(IV) solutions were prepared as previously described.[6] The spectra of Ir^{IV} species agreed with literature data.[13-15] Sodium octacyanomolybdate(IV) was prepared according to the published procedure [16] and the corresponding Mo^V species was prepared by electro-oxidation. Perchloric acid was used to obtain the desired acidity.

Procedure.—The procedure was as previously described; [6] the spectral characteristics of the monitored species as well as the concentration range of oxidants are collected in Table 1. The concentrations of organic substrates were ⩾10-fold of those of oxidants in order to ensure pseudo-first-order conditions. When the reactions were very fast, second-order conditions were chosen. Measurements were carried out at $[HClO_4]$ 1.00M, μ 1.0M, and different temperatures. A series of kinetic runs was also carried out in the presence of the reduced form of metal complexes; no effect on reaction rates was observed, thus the effect of any reverse reaction was neglected. The formal reduction potentials, $E°$, of the pairs quinone–diol, for the different derivatives, were evaluated with a Metrohm E 388 potentiometer, as previously described,[1] at $[HClO_4]$ 1.00M, μ 1.0M, and 25.0 °C.

RESULTS

Potentiometric Data.—The following reduction potentials were estimated: (I) 0.68 ± 0.02; (II) 0.66 ± 0.02; (III) 0.87 ± 0.05; (IV) 0.93 ± 0.05 V. These values [in particular for compounds (III) and (IV)] are rather uncertain due to the instability of the oxidation products.

Stoicheiometry.—The following overall equation was

$$2\,Ox + H_2Y \longrightarrow 2\,Red + Y + 2\,H^+ \qquad (1)$$

derived by means of spectrophotometric measurements with oxidants in excess where H_2Y represents the diol, Y the corresponding quinonoid structure, Ox the oxidant, and Red the corresponding reduced species. For compounds (III) and (IV), side-reactions are however probably present in these concentration conditions, as suggested by slower successive steps.

TABLE 2

Specific rate constants and thermodynamic parameters for the reactions of compound (I) with different oxidants ($[HClO_4]$ 1.00M, μ 1.0M)

Oxidant	k (7.0 °C) [a]	k (20.0 °C) [a]	$\Delta H^‡$ [b,c]	$\Delta S^‡$ [d]	ΔG^*_{exp} (20°) [b]	$\Delta G°$ [b,e]	$\Delta E°$ [f]	$E°(H_2Y^{\cdot+}–H_2Y)$ [f]
$Fe(phen)_3^{3+}$	*ca.* 2 × 10^7	*ca.* 2 × 10^7			4.9	1.8	0.08	1.14
$Fe(mphen)_3^{3+}$	*ca.* 8 × 10^6	*ca.* 9 × 10^6			5.4	2.6	0.11	1.13
$Fe(dmphen)_3^{3+}$	2.2 × 10^6	2.3 × 10^6	0.0	−29	6.2	3.9_5	0.17	1.14
$Fe(bipy)_3^{3+}$	2.4 × 10^6	3.3 × 10^6	3.4	−17	6.0	3.6	0.16	1.18
$Fe(dmbipy)_3^{3+}$	2.3 × 10^4	4.6 × 10^4	8.1	−9	8.5	7.3	0.32	1.16
$IrCl_6^{2-}$	2.4 × 10^4 [g]	3.5 × 10^4 [h]	3.1	−27	8.8	4.2_5	0.18_5	1.14_5
$Ir(H_2O)Cl_5^-$	3.5 × 10^5	3.8 × 10^5 [h]	0.2	−32	7.4	1.7	0.07	1.16
$Ir(H_2O)_2Cl_4$	1.8 × 10^6	2.0 × 10^6 [h]	0.4	−28	6.4	−0.2	−0.01	1.19
$Mo(CN)_8^{3-}$	5.3 × 10^3 [g]	5.3 × 10^3	−0.3	−43	9.7	7.9	0.33	1.13

[a] l mol^{-1} s^{-1}, error 3—6%. [b] kcal mol^{-1}. [c] Error 0.8—1.3 kcal mol^{-1}. [d] cal mol^{-1} K^{-1}, error 2.7—4.4 cal mol^{-1} K^{-1}. [e] Calculated from equation (6) with the following λ values: 16 for $Fe^{III}L_3$, 26 for Ir^{IV}, 21 kcal mol^{-1} for Mo^V. [f] V. [g] 8.0 °C. [h] 25.0 °C.

Kinetic Data.—Plots of $\ln(A_t - A_\infty)$ [or $\ln(A_\infty - A_t)$] where A_t and A_∞ are the absorbance at time t and at equilibrium, against time, were found to be linear for at least two

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TABLE 3

Specific rate constants and thermodynamic parameters for the reactions of compound (II) with different oxidants ([$HClO_4$] 1.00M, μ 1.0M) [a]

Oxidant	k (7.0 °C)	k (20.0 °C)	$\Delta H^\ddagger$	$\Delta S^\ddagger$	ΔG^*_{exp} (20°)	ΔG°	ΔE°	$E^\circ(H_2Y^{\cdot+}-H_2Y)$
$Fe(mphen)_3^{3+}$	ca. 8×10^6	ca. 9×10^6			5.4	2.6	0.11_5	1.13_5
$Fe(dmphen)_3^{3+}$	6.0×10^6	6.0×10^6	−0.6	−29	5.6_5	3.0	0.13	1.10
$Fe(bipy)_3^{3+}$	ca. 1×10^7	ca. 1×10^7			5.3	2.5	0.11	1.13
$Fe(dmbipy)_3^{3+}$	5.0×10^4	9.0×10^4	5.2	−19	8.1	6.8	0.29	1.13
$IrCl_6^{2-}$	3.9×10^4	5.6×10^4	4.0	−23	8.4	3.5	0.15	1.11
$Ir(H_2O)Cl_5^-$	4.6×10^4	5.3×10^5 [h]	0.7	−30	7.2	1.4	0.06	1.14
$Ir(H_2O)_2Cl_4$	3.8×10^6	4.4×10^6 [h]	0.8	−25	5.9_5	−1.15	−0.05	1.15
$Mo(CN)_8^{3-}$	7.0×10^3	7.1×10^3	−0.4	−42	9.6	7.7	0.32	1.12

[a] Notes as in Table 2.

TABLE 4

Specific rate constants and thermodynamic parameters for the reactions of compound (III) with different oxidants ([$HClO_4$] 1.00M, μ 1.0M) [a]

Oxidant	k (7.0 °C)	k(25.0 °C)	$\Delta H^\ddagger$	$\Delta S^\ddagger$	ΔG^*_{exp} (25°)	ΔG°	ΔE°	$E^\circ(H_2Y^{\cdot+}-H_2Y)$
$Fe(nphen)_3^{3+}$	3.7×10^6	4.5×10^6	1.2	−24	5.9	3.5	0.15	1.40
$Fe(cphen)_3^{3+}$	3.7×10^5	6.8×10^5	5.0	−15	7.0_5	5.2_5	0.23	1.34
$Fe(phen)_3^{3+}$	9.2×10^3	2.7×10^4	9.4	−7	8.9_5	7.9	0.34_5	1.40_5
$Fe(dmphen)_3^{3+}$	3.8×10^2	1.4×10^3	11.5	−6	10.7	10.2	0.44	1.41
$Fe(bipy)_3^{3+}$	2.0×10^3	5.0×10^3	7.9	−15	9.9_5	9.2_5	0.40	1.42
$IrCl_6^{2-}$	8.4×10^1	1.3×10^2	3.4	−37	12.2	9.6	0.42	1.38
$Ir(H_2O)Cl_5^-$	2.0×10^3	2.6×10^3	1.8	−37	10.3	6.8	0.29_5	1.38
$Ir(H_2O)_2Cl_4$	1.6×10^4	2.7×10^4	4.3	−24	8.9_5	4.5	0.19_5	1.40

[a] Notes as in Table 2.

TABLE 5

Specific rate constants and thermodynamic parameters for the reactions of compound (IV) with different oxidants ([$HClO_4$] 1.00M, μ 1.0M) [a]

Oxidant	k (7.0 °C)	k (25.0 °C)	$\Delta H^\ddagger$	$\Delta S^\ddagger$	ΔG^*_{exp} (25°)	ΔG°	ΔE°	$E^\circ(H_2Y^{\cdot+}-H_2Y)$
$Fe(nphen)_3^{3+}$	4.5×10^5	6.9×10^5	3.4	−21	7.0_5	5.2	0.22_5	1.47_5
$Fe(cphen)_3^{3+}$	3.8×10^4	6.2×10^4	3.9	−23	8.5	7.3	0.31_5	1.42_5
$Fe(phen)_3^{3+}$	1.2×10^3	1.9×10^3	3.7	−31	10.5	9.9_5	0.43	1.49

[a] Notes as in Table 2.

half-lives. Second-order plots were also satisfactorily linear for two half-lives. Since the pseudo-first-order rate constants showed also linear dependence on the concentration of the organic substrates, the rate law (2) holds.

$$-d[\mathrm{Ox}]/\mathrm{d}\,t = k_0[\mathrm{Ox}][\mathrm{H_2Y}] \qquad (2)$$

DISCUSSION

Since the presently investigated metal complexes are one-electron oxidants, the present non-complementary oxidations take place through two successive one-electron steps (3) and (4) where the radical is a semiquinone

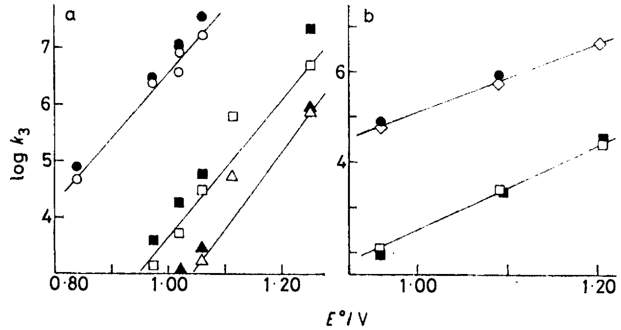
$$\mathrm{Ox} + \mathrm{H_2Y} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{Red} + \mathrm{Radical} \qquad (3)$$

$$\mathrm{Ox} + \mathrm{Radical} \xrightarrow{k_4} \mathrm{Red} + \mathrm{Y} \qquad (4)$$

intermediate. If the steady-state condition is applied to the radical intermediate, equation (5) is obtained. The

$$-\mathrm{d}[\mathrm{Ox}]/\mathrm{d}t = 2k_3k_4[\mathrm{Ox}]^2[\mathrm{H_2Y}]/(k_{-3}[\mathrm{Red}] + k_4[\mathrm{Ox}]) \qquad (5)$$

observed first-order plots, the absence of an effect of [Red] on the reaction rates, and the comparison with the experimental rate law [equation (2)] suggest that $k_4[\mathrm{Ox}] \gg k_{-3}[\mathrm{Red}]$, and $k_0 = 2\ k_3$. The values of k_3 are collected in Tables 2—5, together with the thermodynamic parameters.



Relationship between log k_3 and E° for $Fe^{III}L_3$ (plot a) and for Ir^{IV} (plot b) at 25° and 1M-$HClO_4$: ○, (I); ◇, (II); □, (III); △, (IV); ●, benzene-1,4-diol;[1,2,6] ■, 3,4-dihydroxybenzoic acid;[2,4,6] ▲, 4,5-dihydroxybenzene-1,3-disulphonic acid [2,4,6]

Comparison of our rate constants and thermodynamic parameters with those for the displacement of ligands from the co-ordination spheres of oxidizing complex ions suggests that an outer-sphere electron-transfer mechanism operates. Moreover, the Figure shows the dependence of log k_3 on $E°$ of complex ions together with some benzenediols for comparison purposes. The similar slopes which can be observed suggest that a simple electron abstraction, giving $H_2Y^{\cdot +}$, in the rate-determining step, operates. When this mechanism holds, the Marcus theory predicts relationship (6) between the free energy of activation and the free energy change.[6]

$$\Delta G^*_{12} = \lambda(1 + \Delta G°_{12}'/\lambda)^2/4 \qquad (6)$$

The Marcus theory has recently been applied to electron-exchange between organic substrates, mainly exchange between radicals and their parent molecules [17] or between different molecules.[18] Extension to reactions involving metal-ion complexes and organic substrates [1–7,19,20] led to the possibility of establishing the reaction mechanism, that is outer- or inner-sphere, electron abstraction or hydrogen atom transfer.

Another possibility offered by equation (6) is the evaluation of $\Delta G°_{12}$ (and then $E°$ for $H_2Y^{\cdot +}$–H_2Y pairs), by knowing λ. It seems reasonable from the Figure to adopt the same λ values which hold for the corresponding reactions with benzenediols, namely 16 for $Fe^{III}L_3$,[2,4] 26 for Ir^{IV} species [1,3,6] (the assumption of the same value for the aqua derivatives derives from the observed behaviour toward cyclohexanone [20]), and 21 kcal mol^{-1} for $Mo(CN)_8^{3+}$.[7] Tables 2—5 collect the estimated values of $E°'$: it is possible to see the agreement between values obtained with different λ. Table 6 lists the reduction potentials for some other benzenediols for comparison purposes. It is noteworthy that the values of $\Delta E°$ are very close to those of the benzenediols of corresponding $E°$, thus suggesting that the heteroaromatic diols and benzenediols constitute a series.

The difference between $E°$ of (I) and (II) on the one hand and (III) and (IV) on the other reflects a large difference toward oxidation; similar behaviour has been observed previously (4,7-diols were found to be easily oxidized to the corresponding quinones, while oxidation of 5,6-diols with different reagents was unsuccessful).[9] This can be attributed to the loss of aromaticity of heteroaromatic nuclei in the quinonoid form 5,6- with respect to 4,7-derivatives. Similar behaviour has been observed for naphthalene-1,4- ($E°$ 0.436 V) [21] relative to naphthalene-2,3-diol ($E°$ 0.725 V).[21]

TABLE 6

Comparison with related aromatic benzenediols

Compound	$\Delta E°$(Y–H_2Y)/V	$\Delta E°$($H_2Y^{\cdot +}$–H_2Y)/V	$\Delta E°$/V
(I)	0.68	1.15	0.47
(II)	0.66	1.13	0.47
Benzene-1,4-diol	0.70 [a]	1.14	0.44
(III)	0.87	1.39	0.52
3,4-Dihydroxybenzoic acid	0.88_5	1.38	0.49_5
(IV)	0.93	1.46	0.53
3,4-Dihydroxybenzonitrile	0.92_5 [b]	1.43	0.50_5

[a] Ref. 1. [b] Ref. 3.

In conclusion the application of the Marcus theory offers the possibility of evaluating the reaction mechanism as well as the thermodynamic parameters under difficult experimental conditions.

[7/1030 *Received*, 16*th June*, 1977]

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