J. Org. Chem. **1993,** *58,* 2003–2008

Articles

Electron Transfer Rate Determinations: Facile Electron Transfer from 1,1,2,2-Tetrakis(4-methoxyphenyl)ethanediol

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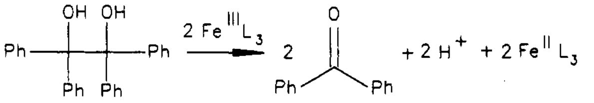
Received September 17, 1992 (Revised Manuscript Received December 23, 1992)

The oxidation reactions of 1,1,2,2-tetrakis(4-methoxyphenyl)ethanediol, 1, by 2,3-dichloro-5,6-dicyanobenzoquinone (**DDQ**) and Fe^{III} complexes have been found to proceed cleanly in the presence of an appropriate base to give 4,4′-dimethoxybenzophenone. The rates of oxidation of 1,1,2,2-tetrakis-(4-methoxyphenyl)ethanediol by 2,3-dichloro-5,6-dicyanobenzoquinone and Fe^{III}(4-methoxy-2,2′-bipyridyl)$_3$(ClO_4)$_3$ have been measured. Evaluation of the rate constants has allowed calculation of the activation parameters for the oxidation reactions and also allowed calculation of $E_{\rm o}^{\ddagger}$ for 1. Compared to 4-methoxytoluene, 1 is much easier to oxidize, following the general trend that phenyl–phenyl interactions lower the oxidation potentials of tetraarylethanediols relative to their corresponding monoaryl model compounds.

Introduction

The importance of radical ion generation and electron transfer (et) has recently been noted in a variety of biological enzyme activation processes including the design of effective lipoxygenase inhibitors.[1,2] Further, radical cations have been implicated as important intermediates in fossil fuel conversion,[3,4] rearrangements of organic compounds,[5] and even organic synthesis.[6] Our interest in radical cations stems from the increased rates of bond cleavage which result from weakening of the critical bonds in a chemical compound.[7-10] Our approach toward understanding the chemical reactivity of radical cations has been concerned with understanding the rate at which the endergonic et processes leading to radical cation formation can occur.[11-16]

The pioneering studies by Kochi showed that endergonic et rates from methyl arenes to tris(phenanthroline) iron(III) complexes (**$Fe^{III}L_3$**) could be easily measured by following the change in Fe^{II} absorbance as a function of time.[15] Recent investigations have suggested that various molecular interactions (e.g., phenyl–phenyl interactions,[16,17] π–π interactions[2]) may reduce the energetic requirements for et. Our work with tetraarylethanediols is representative and is shown in eq 1. In this study, we showed that tetraphenylethanediol had reduced energy requirements relative to the appropriate model compound, i.e., toluene. The energy lowering was attributed to phenyl–phenyl interactions, but the exact nature of the interactions is still an open question. In an effort to explore the generality of this effect and to determine which substituents will cause the greatest change in energy, we have determined the oxidation potential ($E_{\rm ox}^{\ddagger}$) of 1,1,2,2-tetrakis(4-methoxyphenyl)ethanediol (1) by a kinetic method. We reasoned that the methoxy groups should cause the greatest change in energy requirements for et and might even lead to a situation where a single ring could donate an electron without the assistance of another ring. Further, we chose 1 because a certain amount of data was already available for appropriate model compounds which would ease mechanistic interpretation.[18]



(1)

Results

Quantitative Analysis of Oxidation Reactions. The products of the reaction were initially generated from reactions of **DDQ** and 1 and were isolated by silica gel chromatography. The products of the reaction are described by eq 2. Oxidation product 2 had spectra (i.e., IR and NMR) and an unchanged mixed melting point compared with the authentic sample from which pinacol 1 was synthesized. The identity of rearrangement product 3 was also confirmed by identical spectra (i.e., IR and NMR) and an unchanged mixed melting point compared

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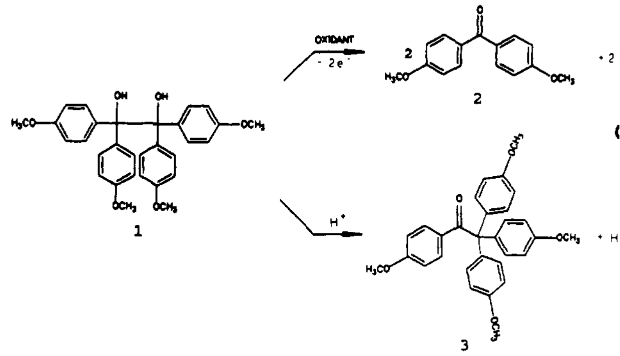


(2)

with an authentic sample generated by H_2SO_4-catalyzed rearrangement.[19] In order to ensure that the kinetic results obtained in our studies correspond to electron transfer processes, we have carefully performed quantitative measurements to verify the reaction products and stoichiometry. The quantitative analyses were performed by HPLC analysis using a C_8-column eluted with methanol/water and bibenzyl or phenyl benzoate as an internal standard. Independent experiments verified that the internal standard was unreactive during the time period of the analyses.

The results of these quantitative analyses are summarized in Table I for the oxidants used in this study (i.e., **$Fe^{III}L_3$**, **$Fe^{III}(LOCH_3)_3$**, and **DDQ**). The yields for **3** have been presented as the mol % of this product in the reaction mixture. The yields for **2** have been presented as half the mol % due to the stoichiometry of the reaction and to allow for more facile analysis of the reaction's mass balance.

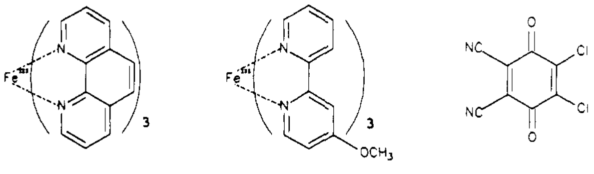
Our initial studies focused on the oxidation reaction of Fe^{III}(1,10-phenanthroline)$_3$ complexes (**$Fe^{III}L_3$**). Although the reaction proved ultimately too fast for kinetic measurements, the reaction proceeded smoothly in the presence of an added base (i.e., 2,6-di-*tert*-butylpyridine, **DBP**, or 2,4,6-tri-*tert*-butylpyridine, **TBP**) to give only the anticipated oxidation product (i.e., **2**).[20] The reaction does yield rearrangement product **3** if the solution is allowed to sit for a longer time (i.e., 10 min) prior to analysis. Presumably, the formation of **3** derives from the acid produced in the solution. A control experiment has shown that pyridinium (formed by the pyridine base and the H^+ produced in the reaction) is sufficient to catalyze the conversion of any residual **1** to **3** in the reaction mixture. A separate control experiment shows that **$Fe^{II}L_3$** does not catalyze this rearrangement process. The reactions of Fe^{III}-(4-methoxybipyridyl)$_3$ (i.e., **$Fe^{III}(LOCH_3)_3$**) were similar. Quantitative production of **2** was obtained when **DBP** was added to the solution.

A quantitative analysis of the **DDQ** reaction with **1** was also performed. Analogous to the Fe^{III} reactions, the reactions of **DDQ** with **1** were also dependent on the presence of an added base (either **DBP** or **TBP**). As seen in Table I, the reaction of **1** with **DDQ** to form **2** is quantitative when a sufficient amount of base is added to the solution. However, when less base is added, the reaction gave varying amounts of **3** depending upon the reaction conditions. The increased propensity for rearrangement processes must originate from the formation of dihydro-**DDQ** (i.e., **$DDQH_2$**, the normal reduction product of **DDQ**) which is known to be acidic.[21]

Table I. Results of Quantitative Analysis for Oxidation of 1

1 concn (mM)	oxidant	oxid concn (mM)	base[a]	base concn (mM)	product yield[b] (%) 2[c]	3	time (min)
5	**$Fe^{III}L_3$**	10	**DBP**	30	106		1
5	**$Fe^{III}L_3$**	10	**DBP**	30	104	1.7	10
5	**$Fe^{III}(LOCH_3)_3$**	5	**DBP**	30	103		45
10	**DDQ**	10			34.8	67.9	60
10	**DDQ**	20			35.2	62.0	60
10	**DDQ**	10	**DBP**	10	92.8	9.5	60
10	**DDQ**	20	**TBP**	30	100		60
5	**DDQ**	10	**DBP**	5	100		60

[a] **DBP**: 2,6-di-*tert*-butylpyridine. **TBP**: 2,4,6-tri-*tert*-butylpyridine. [b] Based on unreacted starting material. Yield data are estimated to be ±5%. [c] Based on reaction stochiometry of 2 mol of **2** for each reacting mole of **1**.



$Fe^{III}L_3$ **$Fe^{III}(LOCH_3)_3$** **DDQ**

Figure 1. Oxidants used in this study.

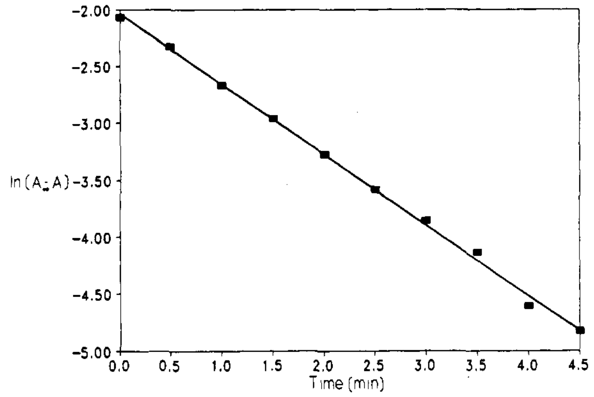


Figure 2. Typical data for the appearance of **$Fe^{II}(LOCH_3)_3$** at 528 nm at 25 °C.

Table II. Observed Pseudo-First Order Rate Constants at 25 °C

[$Fe^{III}(LOCH_3)_3$] (mM)	[1] (mM)	base	[base] (mM)	k_{obs} (min^{-1})
0.5	10	**DBP**	2.5	0.91
0.5	10	**$LOCH_3$**	2.5	0.88

Rate Determinations Using Fe^{III} Complexes. Our methods for measuring rate constants have been previously described.[16] In brief, freshly dried acetonitrile solutions of **1**, base, and the Fe^{III} complex (10, 2.5, and 0.5 mM, respectively) are prepared and degassed using three freeze–pump–thaw degassing cycles and sealed under vacuum. Following mixing, the absorbance of the Fe^{III} or Fe^{II} complex is monitored as a function of time to obtain a pseudo-first-order reaction rate. Although the reaction of **$Fe^{III}L_3$** was too fast to measure with any accuracy, the reaction of **$Fe^{III}(LOCH_3)_3$** was easily monitored. Typical data are shown in Figure 2 where the Fe^{II} absorbance was monitored at 528 nm. The observed rate constant was not changed when 4-methoxybipyridyl (10 mM) was used as the base. Table II shows the pseudo-first-order rate constants obtained using **$Fe^{III}(LOCH_3)_3$**.

Rate Determinations Using DDQ. To measure the

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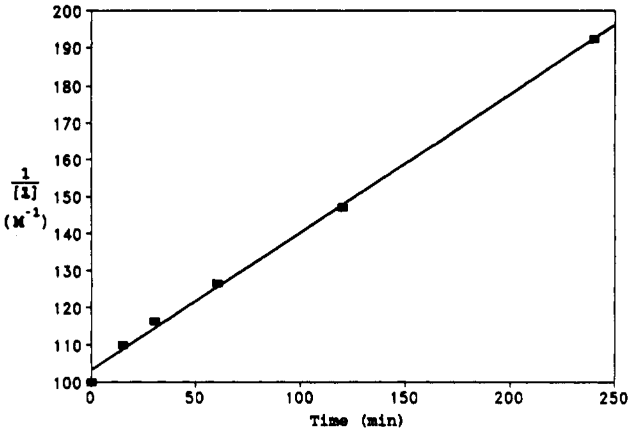

Figure 3. Typical data for the oxidation of 1 (10 mM) by **DDQ** (10 mM) at 65 °C based on the disappearance of 1.

rates of electron transfer from 1 to **DDQ**, we measured the oxidation rates of 1 with **DDQ**. The rate constants were determined from the initial portion of the reaction only (ca. 1 half-life). This treatment was justified by the appearance of 3 at long reaction times which serves to artificially diminish [1] through a competing reaction. In the kinetic studies, it was possible to monitor the concentration of 1 as well as the oxidation product 2 by HPLC analysis using bibenzyl or benzonitrile as the internal standard. Following standard methodology,[22] the second-order rate constant for the reaction was determined from [1] by the use of eq 3 when $[1]_o = [\mathbf{DDQ}]_o$. In this

$$\frac{1}{[1]} = k_{obs}t + \frac{1}{[1]_o} \tag{3}$$

equation, $[1]_o$ and $[\mathbf{DDQ}]_o$ are the initial concentrations of 1 and **DDQ**, respectively. When $[1]_o \neq [\mathbf{DDQ}]_o$, then eq 4 must be used,[23] where [A] and [B] are the concen-

$$\ln\frac{[B]}{[A]} = k_{obs}([B]_o - [A]_o)t + \ln\frac{[B]_o}{[A]_o} \tag{4}$$

trations of 1 and **DDQ**, and $[A]_o$ and $[B]_o$ are the initial concentrations of 1 and **DDQ**. The exact identity of A and B depends upon the concentrations of 1 and **DDQ** for the particular experiment. B is always the compound which is in excess. All experiments had correlation coefficients > 0.995 to be included in the data set. Typical data are shown in Figure 3. Satisfactory agreement was obtained for values of k_{obs} whether determined from [1] or [2]. The rate constants derived from these data are given in Table III. Because of the greater uncertainty with establishing the slope of the line, the relative uncertainty of these rate constants is greater than that estimated for the Fe^{III} reactions. We estimate our error here to be ±15%.

Table III. Observed Rate Constants at 65 °C with Various Base Concentrations

[1] (mM)	[DDQ]	[DBP]	k_{obs}[a]
10	5	30	0.34
10	10	2.5	0.39
10	10	5	0.36
10	10	10	0.35
10	10	30	0.40
10	20	30	0.37
20	10	30	0.35
10	10	30	0.011[b]

[a] Based on appearance of 2. [b] Measured at 25 °C.

Table IV. Reduction Potentials of Oxidants Used in this Study

oxidant	$E_r°$ (V vs SCE)	$E_r°$ [c] (V vs SCE)
FeL$_3$	1.09[a]	1.07
Fe^{III}(LOCH$_3$)$_3$		0.87
DDQ	0.51[b]	0.52

[a] Reference 24. [b] Reference 21. [c] Values measured in our laboratory.

Experiments in which **DDQ** was not present in the solution (e.g., 1 and the base, 1 and the internal standard, or 1 alone) showed no reaction of 1 to the observed products. As seen in Table III, the observed reaction rate was independent of the base concentration. Kinetic measurements were also made as a function of concentration of 1 and of **DDQ**. These data are also presented in Table III. Further, it can be noted that lowering the temperature of the reaction leads to a dramatic decrease in the rate constant. The reaction rate changes by ca. a factor of 33 from 65 to 25 °C.

Measurement of $E_r°$ Data for Acceptors Used in This Study. To gain thermodynamic insight into the reaction, the $E_r°$ data for these acceptors must be known. $E_r°$ for **DDQ**[21] and for **Fe^{III}L$_3$**[24] have been previously reported to be +0.51 and +1.09 V vs SCE in acetonitrile at ambient temperature, respectively. However, to our knowledge, no data were available for **Fe^{III}(LOCH$_3$)$_3$** complexes. Therefore, we have measured the $E_r°$ values (Table IV) of all acceptors used in this study in an effort to learn about the relative values. We believe that the relative values are more important than the absolute values, since these $E_r°$ values will be used to evaluate the change in driving force for the et reaction.

Discussion

Evaluation of Rate Constants for Fe^{III} Complexes. The determination of electron transfer rate constants from benzopinacols and **Fe^{III}L$_3$** has been previously reported.[16] In brief, the method relies on the rate-determining electron transfer from the pinacol to the **Fe^{III}L$_3$** complex. The benzopinacol radical cation can then undergo rapid bond scission, followed by a rapid secondary electron transfer from the ketyl radical by a second **Fe^{III}L$_3$**. For **Fe^{III}**-initiated reactions, the reaction rate was found to be pseudo-first order in benzpinacol. By analogy to our previous work, the rate constant for electron transfer (k_{et}) from 1 to **Fe^{III}(LOCH$_3$)$_3$** can be calculated to be 0.75 M^{-1} s^{-1} at 25 °C using eq 5, where $[1]_o$ is the initial concentration of 1.

$$k_{et} = \frac{k_{obs}}{2[1]_o} \tag{5}$$

Although the outer-sphere nature of the reaction of benzopinacol and **Fe^{III}L$_3$** was well documented, we have performed control experiments to verify the outer-sphere nature of the electron transfer event in the reaction of 1 and **Fe^{III}(LOCH$_3$)$_3$**. Changing the base from **DBP** to

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[22] Espensen, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill: New York, 1981; pp 17–29.

[23] A full derivation of this equation is included in the supplementary material for this paper.

[24] Schilt, A. A. *Analytical Applications of 1,10-Phenanthroline and Related Compounds*; Pergamon: Oxford, 1969.

4-methoxybipyridyl did not have an effect on the observed rate constant, signifying that mechanisms requiring a base before the rate-determining step can be ruled out. The rate constant is independent of added 4-methoxybipyridyl ruling out a mechanism involving predissociation of the Fe^{III} complex to yield a coordinately unsaturated complex, since any dissociation of $\mathbf{Fe^{III}(LOCH_3)_3}$ would be inhibited by the added 4-methoxybipyridyl. We conclude that the reaction of **1** and $\mathbf{Fe^{III}(LOCH_3)_3}$ is an outer-sphere electron transfer in analogy to the reaction of benzpinacol and $\mathbf{Fe^{III}L_3}$.

Evaluation of Rate Constants for DDQ Reactions. To clarify any ambiguities which might be associated with the determination of the electron transfer rate constants from only Fe^{III} complexes, we desired independent confirmation of the value of k_{et} and any thermodynamic properties which might be associated with this value. For this purpose, we chose the reaction of **DDQ** with **1**. The stoichiometry of the reaction indicates that only oxidation product **2** is produced at the early reaction times during which the kinetic measurements were made. The kinetic order of each reagent is established to be kinetic first-order by the experimental data presented in Table III. A 2-fold increase in the concentration of **DDQ** should lead to a 2-fold increase in the reaction rate with no change in the rate constant for the reaction. This was indeed observed. Similar arguments can be made for a 2-fold decrease in the concentration of **DDQ** and for a similar increase or decrease in [**1**], which would indicate no change in the rate constant within experimental error. Thus, we conclude that the oxidation reaction of **DDQ** with **1** proceeds by a mechanism in which the rate of reaction is given by $k_{obs}[\mathbf{1}][\mathbf{DDQ}]$.

Significance of the Rate Data. In a previous paper,[16] we have argued for the existence of phenyl–phenyl interactions in tetraarylethanediols, based on the reduction in the ionization potentials relative to appropriate model compounds. Schwartz et al.[2] have made arguments for π–π interactions in compounds such as 1,4-cyclohexadiene based on electron transfer rates to $\mathbf{Fe^{III}L_3}$ complexes. To determine the generality of the potential intramolecular interactions in **1** which might lead to easier oxidations and electron transfer reactions, comparison of the properties of **1** must be made with respect to the properties of 4-methoxytoluene (**MT**) which has no available aryl–aryl interactions. Both IP data[25] and k_{et} to $\mathbf{Fe^{III}L_3}$ are known for **MT**. Since IP data for **1** are unavailable at the current time, and since k_{et} from **1** to $\mathbf{Fe^{III}L_3}$ was too large to be easily measured with our equipment, we must make an indirect comparison of our data as described below.

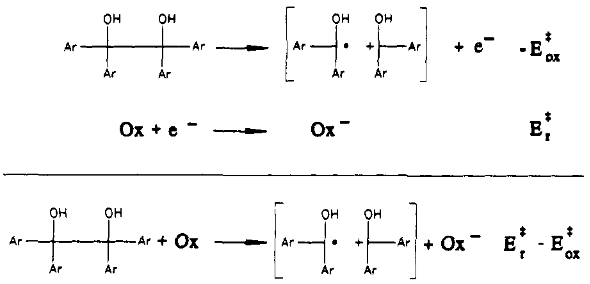

Figure 4. Scheme for the energetics of the rate-determining step of the reaction.

$$\Delta G_{et}^{\ddagger} = -\mathcal{F}(E_r^{\ddagger} - E_{ox}^{\ddagger}) \tag{6}$$

$$\Delta G_{et}^{\ddagger} = -RT \ln \frac{k_{et}}{Z} \tag{7}$$

$$E_{ox}^{\ddagger} = \frac{-RT \ln \frac{k_{et}}{Z}}{\mathcal{F}} + E_r^{\circ} \tag{8}$$

Our method of comparison of rate data utilizes the thermodynamic analysis shown in Figure 4 where the overall free energy of activation for the electron transfer ($\Delta G_{et}^{\ddagger}$) can be represented by the sum of the energies for each of the half reactions. The first half-reaction is the oxidation reaction of the electron donor which has an energy (i.e., $E_{ox}^{\ddagger}$) associated with it. The second half-reaction is the reduction reaction of the oxidant which has an energy (i.e., $E_r^{\ddagger}$) associated with it. Therefore the overall reaction energetics can be described by the sum of the two potentials as shown in eq 6, where $\mathcal{F}$ is the Faraday constant. Equation 7 is the expression relating the rate constant k_{et} to the $\Delta G_{et}^{\ddagger}$ as suggested by collision theory. In this approach, T is the absolute temperature, and Z is the collision frequency. By assuming that $Z = 1 \times 10^{11}$ M^{-1} s^{-1} [26,27] and that $E_r^{\ddagger} \approx E_r^{\circ}$ for the oxidant, $E_{ox}^{\ddagger}$ can be calculated by using the experimentally determined k_{et} as shown in eq 8. These data are summarized in Table V for **1**, **MT**, and other tetraarylethanediols previously studied. As discussed above, the et aspects of the rate data for $\mathbf{Fe^{III}L_3}$ and $\mathbf{Fe^{III}(LOCH_3)_3}$ have been determined from k_{obs} by eq 5. The rate data for **DDQ** have been evaluated by assuming that $k_{et} = k_{obs}$.

Also included in Table V are appropriate data for comparison of the intramolecular interactions in tetraarylethanediols and for comparison of thermodynamic data derived by this method with data derived by other methods. E_{ox}° data can be derived from IP data using the correlation shown in eq 9 derived by Kochi and Wightman

$$E_{ox}^{\circ} = 0.71IP - 4.10 \tag{9}$$

for the reversible E_{ox}° of mono- and polycyclic aromatic compounds.[15b] This correlation is applicable when IP data are available for a compound and assumes that the solvation energies of each aromatic compound are similar, despite the size of the molecule or resonance stabilization afforded by polycyclic ring systems.

An analysis of intramolecular interactions in **1** can now be made by comparing the $E_{ox}^{\ddagger}$ data for **1** and **MT** (Table V). $E_{ox}^{\ddagger}$ for **1** (as determined from the $\mathbf{Fe^{III}(LOCH_3)_3}$) and $E_{ox}^{\ddagger}$ for **MT** are 1.53 and 1.67 V vs SCE, respectively. The 0.14 V difference in $E_{ox}^{\ddagger}$ is clearly outside the limits of experimental error and corresponds to a ca. 230 × difference in k_{et} if the same electron acceptor were used to measure k_{et} for both compounds. There can be little doubt that Ph–Ph interactions are existent in **1** which make for easier electron transfers in this compound.

The $E_{ox}^{\ddagger}$ for **1** as determined by the rate of the **DDQ** reaction is even smaller than the $E_{ox}^{\ddagger}$ for **1** as determined by $\mathbf{Fe^{III}(LOCH_3)_3}$. Overall, this does not change our basic

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(25) Kobayashi, T.; Nagakura, S. *Bull. Chem. Soc. Jpn.* 1974, 2563.

(26) Marcus, R. A. *J. Phys. Chem.* 1965, *43*, 679.

(27) We note that our calculation of $E_{ox}^{\ddagger}$ is meant only to be an estimate for the purposes of comparison. Changes in the assumed value for Z may be expected to change the value of $E_{ox}^{\ddagger}$. Further, $E_{ox}^{\ddagger} \neq E_{ox}^{\circ}$ which would be the real experimental goal. Thus, comparisons of $E_{o}^{\ddagger}$ are valid only for their relative orders and not for the absolute magnitude.

(28) Kobayashi, T.; Nagakura, S. *Bull. Chem. Soc. Jpn.* 1974, 2563.

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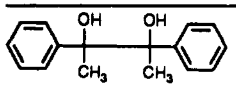
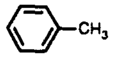
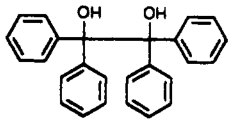
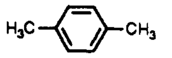
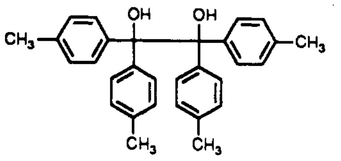
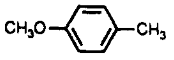
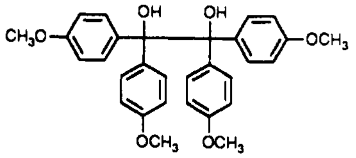
Table V. Calculated Oxidation Potentials for Various Tetraarylethanediols and Their Model Compounds

compd	IP (eV)	$E_{ox}°$ [a]	oxidant	$E_r°$ [b]	k_{et} (M^{-1} s^{-1})	E_{ox}* [c]
	9.01[d]	2.30				
	8.82[e]	2.16				
	8.42[d]	1.88	$Fe^{III}L_3$	1.07	0.0011	1.91
	8.44[e]	1.89				
	8.35[d]	1.83	$Fe^{III}L_3$	1.07	0.0268	1.83
	8.18[f]	1.71	$Fe^{III}L_3$	1.07	6.7[g]	1.67
			$Fe^{III}L_3$	1.07	≥166	≤1.71
			$Fe^{III}(LOCH_3)_3$	0.87	0.75	1.53
					0.0062	1.41[h]
			DDQ	0.52	1.8×10^{-4}	1.39

[a] Calculated $E_{ox}°$ from eq 9 (V vs SCE). [b] Determined in this work. [c] Calculated E_{ox}* from eq 6 (V vs SCE). [d] Reference 16. [e] Reference 15a. [f] Reference 28. [g] Reference 29. [h] Measured at 65 °C.

assertion from this work (i.e., 1 is easier to oxidize than **MT**). The energy difference of 0.14 V (3.2 kcal/mol) is beyond our estimated experimental error for the reaction rate determinations. We believe that the reaction of $\mathbf{Fe^{III}(LOCH_3)_3}$ must proceed through an outer-sphere mechanism. This assertion is justified by the known behavior of Fe^{III}(phenanthroline)$_3$ and Fe^{III}(bipyridyl)$_3$ complexes which traditionally undergo outer-sphere et reactions. Since the rate of the et reaction in this system was unchanged when the base was changed from **DBP** to 4-methoxybipyridyl, we conclude that an outer-sphere et mechanism is operating in this system. To our knowledge, there are no well-documented mechanisms other than outer-sphere et pathways for these Fe^{III} complexes. Thus, the outer sphere mechanism represents our best effort via a kinetic method to give information as to the thermodynamic ease of electron transfer in this system. In contrast, the kinetic data for 1 and **DDQ** are clearly representative of a reaction which is first order in each reagent. We speculate that a change in reaction mechanism is occurring in this system. One potential mechanism which is consistent with the kinetic data is a 2-e^- oxidation through a σ-complex, leading to irreversible bond cleavage. Quinones are known to be able to form σ-charge-transfer complexes as has been documented previously.[30,31] Further details are required before making a definitive analysis of the reaction mechanism caused by **DDQ**. The energetics of σ-complex formation and subsequent reactions may be quite different than the true thermodynamic energetics of electron transfer, as this represents an inner-sphere electron transfer.

Summary. The rates of oxidation of 1 by **DDQ** and by $\mathbf{Fe^{III}(LOCH_3)_3}$ have been measured. Treatment of this data has allowed calculation of E_{ox}* for 1. When compared to **MT**, 1 is much easier to oxidize, following the general trend that tetraarylethanediols are easier to oxidize than their corresponding monoaryl model compounds.

Experimental Section

Melting points were determined on a Laboratory Devices Mel-temp apparatus and are uncorrected. Gas-liquid chromatographic analyses were conducted on a Hewlett-Packard Model 5890A GLC equipped with a 10-m 5% phenylmethylsilicone column. HPLC was performed on a Waters Associates Protein Peptides I system capable of gradient elution and using UV detection at 254 nm. Integration of the signals was performed by a Hewlett-Packard Model 3390A digital integrator. GCMS were measured with a Hewlett-Packard Model 5980 GCMS using a mass selective detector. IR spectra were recorded on a Perkin-Elmer Model 1310 IR spectrophotometer. ^1H NMR spectra (δ (ppm) and J (Hz)) were measured in the indicated solvent with TMS as an internal standard on a JEOL-GX-270 NMR spectrometer. UV-vis spectra were measured with a Varian DMS-100 spectrophotometer.

Acetonitrile was predried over CaH_2 and then distilled over P_2O_5 followed by K_2CO_3 immediately before use. 4,4′-Dimethoxybenzophenone was purchased from Aldrich. 2,6-Di-*tert*-butylpyridine was purchased from Aldrich and distilled over KOH prior to use. 2,3-Dichloro-5,6-dicyanobenzoquinone was purchased from Aldrich and recrystallized from $CHCl_3$ prior to use. 2,4,6-Tri-*tert*-butylpyridine,[32] 1,2,2,2-tetrakis(4-methoxyphenyl)ethanone,[19] 4-methoxy-2,2′-bipyridyl,[33] and $\mathbf{Fe^{III}L_3}$[16] were prepared by literature procedures.

Product Determinations. The products of the reaction were initially generated from reactions of **DDQ** and 1. 0.5 g of 1 (1 mmol) and 0.23 g (1 mmol) of **DDQ** were combined in 100 mL of dried and degassed CH_3CN. The solution was stirred and heated at 65 °C overnight. The solution was concentrated and the residue coated on a 1- × 14-in. silica gel column eluted with 4:1 hexane/ethyl acetate. Evaporation (in vacuo) of the fractions

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(30) Patai, S.; Rappaport, Z. *The Chemistry of Quinonoid Compounds*; John Wiley & Sons: New York, 1988.

(31) Eberson, L. *Adv. Phys. Org. Chem.* **1982**, *18*, 79.

(32) Scalzi, F. V.; Golob, N. F. *J. Org. Chem.* **1971**, *36*, 2541.

(33) Wenkert, D.; Woodward, R. B. *J. Org. Chem.* **1983**, *48*, 283.

collected yielded 2 and 3. Oxidation product 2 had identical spectra (i.e., IR and NMR), an identical HPLC retention time, and an unchanged mixed melting point compared with the commercial sample from which 1 was synthesized. The identity of rearrangement product 3 was also confirmed by identical spectra (i.e., IR and NMR), an identical HPLC retention time, and an unchanged mixed melting point compared with an authentic sample generated by H_2SO_4-catalyzed rearrangement.[19] Quantitative analyses were performed by HPLC analysis using a 25-mm × 250-mm C_8-column eluted with methanol/water and using bibenzyl or phenyl benzoate as the internal standard.

1,1,2,2-Tetrakis(4-methoxyphenyl)ethanediol. A saturated solution of 150 mL of acetone and 350 mL of 2-propanol was prepared by allowing excess 4,4′-dimethoxybenzophenone to dissolve while stirring for 30 min. The excess 4,4′-dimethoxybenzophenone was removed by vacuum filtration. The solution was placed in a quartz immersion well and irradiated with an unfiltered Hanovia medium-pressure mercury arc lamp while stirring. Following solvent removal (in vacuo), the product was recrystallized 3 × from hexane/ethyl acetate to give colorless crystals, mp 179–181 °C (lit.[19] mp 183 °C).

Fe^{II}(4-methoxy-2,2′-bipyridyl)$_3$(ClO_4)$_3$. 3.5 g of $FeSO_4 \cdot 7H_2O$ (in large excess) and 0.6 g (3 mmol) of 4-methoxy-2,2′-bipyridyl were stirred in 100 mL of H_2O at room temperature for 0.5 h. To the resulting magenta solution was added 1.0 g (7 mmol) of $LiClO_4$ and a red solid precipitated. The solid was collected by vacuum filtration, thoroughly washed with ice-water, and then dried in vacuo for 24 h: UV-vis (CH_3CN) λ_{max} 528 nm (ϵ = 7900 cm^{-1} M^{-1}).

Fe^{III}(4-methoxy-2,2′-bipyridyl)$_3$(ClO_4)$_3$. A CH_3CN solution of Fe^{II}(4-methoxy-2,2′-bipyridyl)$_3$(ClO_4)$_2$ (1.0 mM) and tetraethylammonium perchlorate (100 mM) was oxidized using a BioAnalytical Systems CV-27 with platinum mesh for both working and counter electrodes. The reference electrode was a sodium-saturated calomel electrode (Fisher). The complex was potentiostatically electrolyzed to avoid degradation.

Determination of $E_r°$ for Oxidants. The reduction potentials for all oxidants used in this study were determined by cyclic voltammetry using a Bioanalytical Systems CV-27 with platinum mesh for both working and counter electrodes. The reference electrode was a sodium-saturated calomel electrode (Fisher). All potentials determined were for CH_3CN solutions 1 mM in the oxidant and 100 mM in tetraethylammonium perchlorate (supporting electrolyte) and were measured at 25 °C.

Rate Determinations with 2,3-Dichloro-5,6-dicyanobenzoquinone. In a typical kinetic experiment, separate acetonitrile (freshly distilled over P_2O_5) solutions of **DDQ** and a mixture of the added base (**DBP** or **TBP**), bibenzyl (internal standard), and 1 were placed in a Y-tube and degassed by three freeze–pump–thaw cycles. The solutions were maintained in the dark. After being sealed under vacuum, the solutions were brought to the temperature of the experiment immediately before being mixed and placed in a light-free constant temperature bath. Each data point was generated by breaking open a separate reaction tube and monitoring the concentrations of 1, 2, and 3 by HPLC.

Rate Determinations with Fe^{III} Complexes. In a typical kinetic experiment, separate solutions of the Fe^{III} complex and a mixture of the added base and 1 were dissolved in freshly distilled CH_3CN (over P_2O_5) and degassed by three freeze–pump–thaw cycles. After being sealed under vacuum, the solutions were brought to the temperature of the experiment and mixed immediately prior to the beginning of observation to give final concentrations of Fe^{III} complex = 0.5 mM, base = 2.5 mM, and 1 = 10 mM. In the case of Fe^{III}(phen)$_3$(ClO_4)$_3$ the concentrations of **$Fe^{III}L_3$** and **$Fe^{II}L_3$** were monitored at 630 and 506 nm, respectively. For Fe^{III}(4-methoxybipyridyl)$_3$(ClO_4)$_3$ the concentration of **Fe^{II}($LOCH_3$)$_3$** was measured at 528 nm. All kinetic experiments were followed for a minimum of three half-lives and had a correlation coefficient of 0.998 to be included in the data set.

Acknowledgment. We gratefully acknowledge the efforts of Professor Harry O. Finklea and Daniel Snider at West Virginia University for determination of the reduction potentials for the oxidants used in this work and also for help with the electrochemical synthesis of Fe^{III}(4-methoxy-2,2′-bipyridyl)$_3$(ClO_4)$_3$.

Supplementary Material Available: Determination of rate constants (5 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.