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Kinetics and Mechanism of the Outer-Sphere Oxidation of Cyclohexanone by Tris(polypyridyl) Complexes of Iron(III) and Ruthenium(III)[1]

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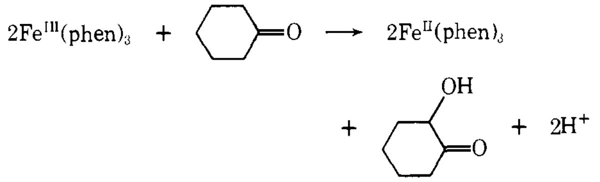
Abstract: Oxidation of cyclohexanone by a number of substituted 1,10-phenanthroline and 2,2′-bipyridyl complexes of Fe(III) and Ru(III) were found to be first order in cyclohexanone and first order in the metal complex in 1 M H_2SO_4. A linear correlation between the logarithms of the second-order rate constants and standard reduction potentials of the metal complexes were found. The slope of the linear free energy plot was that predicted by Marcus for outer-sphere electron transfer between a similar series of reactions. At low acidity and high [Fe(III)], a rate which was first order in [H^+], first order in [cyclohexanone], and zero order in [Fe(III)] was found and the rate constant closely resembled the acid-catalyzed enolization rate constant for cyclohexanone. These kinetics are consistent only with electron transfer from the enol rather than the ketone form of cyclohexanone. The data for the Ru(III) complexes fell on the same linear free-energy plot as the Fe(III) complexes, indicating the size of the d orbitals of the metal oxidant is not an important factor in determining the rate of oxidation. We interpret this result in terms of electron transfer via the periphery of the polypyridyl ring.

Mechanisms of oxidation of ketones by metal ions and complexes are divided into two classes, depending on whether the keto or the enol is oxidized in the rate-determining step. Oxidation of cyclohexanone by one-equivalent oxidants such as Co(III), Ce(IV), V(V), and Mn(III) were postulated to occur via the keto tautomer while two-equivalent oxidants, such as Hg(II), Tl(III), and Mn(VII), apparently oxidize the enol tautomer.[2] Relative rates of enolization and oxidation, isotope effects, and kinetic orders were used to differentiate between oxidation of the keto or the enol tautomer. More recently Mn(III) was postulated to attack the enol form of ketones in acetic acid medium.[3]

Littler reported that the oxidation of cyclohexanone by tris(1,10-phenanthroline)iron(III) (ferriin), occurred via an outer-sphere electron transfer from the ketone to the Fe(III). Stoichiometry of the oxidation in the absence of air is given by eq 1.[4] The rate-determining step of the reaction was postulated to involve an outer-sphere electron transfer from cyclohexanone to the Fe(III) complex to generate a 2-oxocyclohexyl radical, R·, (eq 2), or a hydrogen atom abstraction followed

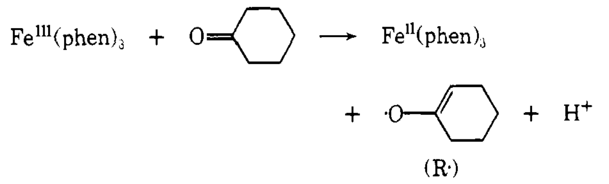


(1)

Table I. Oxidation of Cyclohexanone by Ferriin in Acid at 25°, $E° = 1.06$ V[12]

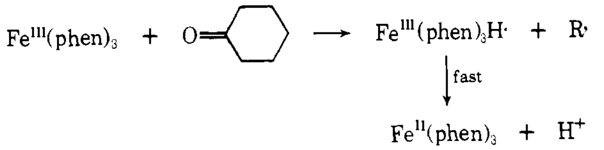
[Ferriin] $\times 10^4$ M	[Cyclohexanone] $\times 10^2$ M	$HClO_4$, M	H_2SO_4, M	k_{obsd} $\times 10^2$ s^{-1}	k_2', M^{-1} s^{-1}
1.0	0.67	1.0		0.69	1.03
1.0	1.00	1.0		1.15	1.20
1.0	1.33	1.0		1.53	1.20
1.0	1.67	1.0		1.97	1.22
2.0	1.50	1.0		1.72	1.15
0.5	1.50	1.0		2.30	1.52
1.0	0.80	1.0		0.82	1.00[a,b]
1.0	1.34	1.0		0.94	0.70[a,b]
1.0	2.00	1.0		3.00	1.50[a,b]
1.0	1.34	1.0		2.00	1.50[a,c]
1.0	1.50	1.0		4.92	3.28[d]
1.0	0.67	0.5		0.62	0.93[e]
1.0	5.00	1.1		6.30	1.26[f]
1.0	5.00	1.1		6.50	1.31[a,f]
1.0	5.00	0.14		6.50	1.31[g]
1.0	0.30		0.5	0.45	1.50
1.0	0.45		1.0	0.68	1.50
1.0	0.25		1.5	0.34	1.30

[a] Degassed. [b] Fe(III) solution degassed with stainless steel needle in cell, serum cap. [c] Fe(III) solution degassed with vacuum pumping (three determinations). [d] D_2O. [e] Ionic strength adjusted to 1 M with $NaClO_4$. [f] Cyclohexanone dissolved in 0.2 M NaOH and reacted with ferriin in 2.4 M $HClO_4$. [g] Cyclohexanone dissolved in 0.2 M NaOH and reacted with ferriin in 0.48 M $HClO_4$.



(2)

by fast proton loss to generate R· (eq 3). An isotope effect



(3)

($k_H/k_D = 2.2$ at 15°) was observed with 2,2,6,6-tetradeuteriocyclohexanone, The presence of free radicals was suggested by the initiation of polymerization of acrylonitrile. The 2-oxocyclohexyl radical was postulated to react with O_2 to give peroxy radicals RO_2· (eq 4) which might react further via eq 5-7,

$$R\cdot + O_2 \rightarrow RO_2\cdot \tag{4}$$

$$RO_2\cdot + \text{ketone} \rightarrow RO_2H + R\cdot \tag{5}$$

$$RO_2\cdot + Fe(II) + H^+ \rightarrow RO_2H + Fe(III) \tag{6}$$

$$RO_2\cdot + R\cdot \rightarrow RO_2R \tag{7}$$

Thus, the rate of oxidation in the presence of air could differ from that in the absence of air due to a change in the overall stoichiometry or the rate law. Littler et al, reported that the rate was about four times faster in air than in its absence.

Mechanisms of electron transfer between inorganic complexes[5] have been well established, and the Marcus[6] linear free energy correlation

$$\Delta G_{12}^{\ddagger} = a + b\Delta G_{12}° + \ldots \tag{8}$$

has been found to be applicable in many outer-sphere electron transfer reactions[7] and in some inner-sphere electron transfer reactions.[8] However, there are only a few examples of oxidations of organic compounds by inorganic complexes interpreted in terms of an outer-sphere electron transfer mechanism.[9-11]

We decided to study the oxidation of cyclohexanone by a number of polypyridyl complexes of Fe(III) and Ru(III) for two reasons, First, the reduction potential of a large number of substituted ferriin complexes are known.[12] Thus we can determine if the linear free-energy correlation of Marcus is followed in this type of outer-sphere oxidation of organics. Second, the evidence of Littler for oxidation of the keto form is not conclusive and appears worth confirming since the one-electron oxidant Mn(III) has been reported to attack the enol form of ketones.[3] This can be readily tested since, if the enol form is oxidized as fast as it is formed, the rate will become zero order in complex. This rate can be calculated from the known rates of enolization.

Results

Oxidation of Cyclohexanone by Ferriin, Substituted Ferriin, and Tris(2,2′-bipyridyl)iron(III). The effect of air on the rate of reaction was first tested. The value of the second-order rate constant for the oxidation of cyclohexanone by ferriin obtained from a solution degassed by vacuum technique was 30% higher than that in air, while the minimum value of the rate constants obtained from an argon degassed solution was 30% lower than that in air (Table I). In addition, the final optical density obtained at 510 nm from the solution degassed by passing argon into the Fe(III) solution for ~30 min was ~30% lower than that expected for complete reduction of $Fe^{III}(phen)_3$ to $Fe^{II}(phen)_3$. Much less satisfactory first-order plots were obtained when the reaction was carried out with degassed solutions, At high [cyclohexanone], almost identical second-order rate constants were obtained under anaerobic and aerobic conditions (Table I), With a better oxidizing agent such as 5-phenylferriin, identical rate constants within experimental error (±10%) were obtained (Table II). Extensive decomposition of 5-nitroferriin, 5-chloroferriin, and 5-bromoferriin in 1 M H_2SO_4 was observed if these solutions were left to stand more than 30 min at room temperature and experimental difficulties were encountered in degassing these solutions. We therefore studied the oxidations without excluding air since air did not appear to affect the rates of oxidation to a great extent in our studies, particularly when stronger oxidants than $Fe^{III}(phen)_3$ were used. Reproducible kinetics were observed in the presence of air and fairly good pseudo-first-order plots were obtained for about 2 half-lives.

Oxidation of cyclohexanone by ferriin was studied in 1 M

Table II. Oxidation of Cyclohexanone by Substituted Ferriin Complexes at 25° in 1.0 M H_2SO_4

Complex	$E°$, V[a]	[Complex], M	[Cyclohexanone], M	k_{obsd}, s^{-1}	k_2', $M^{-1} s^{-1}$ [b]
4,7-Dimethylferriin	0.86	1.4×10^{-4}	5.0×10^{-3}	2.67×10^{-4}	0.03
			1.0×10^{-2}	4.17×10^{-4}	
			2.0×10^{-2}	6.33×10^{-4}	
			4.0×10^{-2}	1.27×10^{-3}	
5-Phenylferriin	1.08	1.5×10^{-4}	0.10	0.455	6.65
			0.10	0.475[c]	
			0.05	0.20	
4,7-Diphenylsulfonated ferriin	1.09	1.4×10^{-4}	3.74×10^{-4}	1.91×10^{-3}	7.00
		7.0×10^{-5}	3.5×10^{-4}	2.19×10^{-3}	
			5.2×10^{-4}	3.38×10^{-3}	
			7.0×10^{-4}	5.10×10^{-3}	
5-Chloroferriin	1.12	$\leq 1.0 \times 10^{-4}$	0.10	1.10	11.6
			0.05	0.55	
			0.025	0.27	
			0.0125	0.14	
		$\leq 1.5 \times 10^{-4}$	0.10	1.33[d]	
5-Bromoferriin	1.13	$\leq 1.0 \times 10^{-4}$	0.01	0.10	9.72
			0.02	0.18	
			0.10	0.92	
5-Nitroferriin	1.25	$\leq 1.0 \times 10^{-4}$	0.025	1.10	45.0
			0.05	2.30	
			0.10	4.60	
$Fe^{III}(bipy)_3(ClO_4)_3$	1.02	1.5×10^{-4}	0.20	0.14	0.72
			0.10	0.075	

[a] Reference 12. [b] Average value. [c] Degassed. [d] 1.5 M H_2SO_4.

Table III. Second-Order Rate Constants for the Oxidation of Cyclohexanone by 5-Methylferriin at 25°[a]

[Cyclohexanone] $\times 10^3$ M	$[H_2SO_4]$, M	$[H^+]$,[b] M	k_{obsd} $\times 10^3 s^{-1}$	k_2', $M^{-1} s^{-1}$
3.0	0.5	0.53	3.24	1.08
3.0	1.0	1.12	2.97	0.99
3.0	1.5	1.64	2.40	0.85
3.0	2.0	2.16	2.60	0.87
2.0	1.0	1.12	1.81	0.91

[a] [5-Methylferriin] = 6.6×10^{-5} M, $E°$ = 1.02 V.[12] [b] Calculated by using the value 0.012 M[13] for the dissociation constant of the bisulfate ion.

H_2SO_4 and 1 M $HClO_4$ medium. The reaction was found to be first order in cyclohexanone and first order in ferriin. Similar values for the second-order rate constant were obtained in both media (Table I). Variation of $[H^+]$ at 10^{-4} M [Fe(III)] has little effect on the rate. The reaction was found to be independent of ionic strength (Table I).

Oxidation by the substituted ferriin complexes were carried out in H_2SO_4 medium because the ferriin complexes containing methyl and phenyl substituents were not sufficiently soluble in 1 M $HClO_4$. In addition, the reduction potentials of these complexes were measured in H_2SO_4 medium.[12] Pseudo-first-order kinetics were observed with excess cyclohexanone and a first-order dependence on cyclohexanone was found. The values of k_{obsd} are shown in Table II. As $[H^+]$ increased from 0.53 to 2.16 M, the value of k_{obsd} decreased by 20% (Table III), which is most likely a medium effect. Effect of $[H^+]$ on the other complexes were not studied since at low acidity 5-nitroferriin, 5-chloroferriin, and 5-bromoferriin decomposed readily.[7a]

Tris(2,2′-bipyridyl)iron(III) oxidized cyclohexanone with a first-order dependence on the Fe(III) complex and a first-order dependence in cyclohexanone in 1 M H_2SO_4. The second-order rate constants are shown in Table II.

Oxidation of Cyclohexanone by Tris(1,10-phenanthroline)ruthenium(III) and Tris(2,2′-bipyridyl)ruthenium(III). Pseudo-first-order kinetics was observed at $\leq 10^{-4}$ M [Ru(III)] with excess cyclohexanone. The values of k_{obsd} are shown in Table IV. The chloride salts appeared to oxidize cyclohexanone slower than the corresponding perchlorate salts. Values of the second-order rate constants, k_2', were obtained from plots of k_{obsd} vs. [cyclohexanone] and are listed in Table IV.

Correlation between Log k_2 and $E°$ for the Oxidation of Cyclohexanone by the Tris(polypyridyl) Complexes of Fe(III) and Ru(III). The value of the second-order rate constant, k_2', increased as the $E°$ value of the complexes increased (Tables I-IV). A plot of log k_2' vs. $E°$ (Figure 1) gave a straight line with a slope of 8.75 ± 1.0. Thus, the relationship between log k_2' and $E°$ is given by

$$\log k_2' = a + 8.75E° \tag{9}$$

which is equivalent to a linear free-energy plot of $\Delta G^{\ddagger}$ vs. $\Delta G°$ with a slope of 0.51 ± 0.06.

$$\Delta G^{\ddagger} = a' + (0.51 \pm 0.06)\Delta G° \tag{10}$$

This result indicated a linear free-energy relationship for the oxidation of cyclohexanone by tris(polypyridyl) complexes of Fe(III) and Ru(III) and the slope of 0.51 closely resembled that of 0.5 predicted by Marcus[6] for electron transfer between a similar series of reagents.

Kinetics of the Oxidation of Cyclohexanone at High [Ferriin] and Low $[H^+]$ in H_2SO_4. The reaction was carried out in H_2SO_4 medium because perchlorate salts of ferriin are not very soluble in $HClO_4$. Preliminary data at $\geq 1.2 \times 10^{-3}$ M [ferriin], 1.67×10^{-2} M [cyclohexanone], and ≤ 0.6 M $[H^+]$, gave a rate plot (increase in absorbancy at 510 nm vs. time) which did not appear to be pseudo first-order. There was an initial linear increase in optical density followed by a faster increase in optical density, which then decreased exponentially. The linear region showed a first-order dependence on $[H^+]$, zero-order dependence on [Fe(III)], and first-order dependence on [cyclohexanone] (Table V).

Table IV. Second-Order Rate Constants for the Oxidation of Cyclohexanone by $Ru^{III}(bipy)_3$ and $Ru^{III}(phen)_3$ at 25° in 1.0 M H_2SO_4

Complex	$E°$, V[a]	[Complex], M	[Cyclohexanone], M	k_{obsd}, s^{-1}	k_2', $M^{-1} s^{-1}$	k_1',[c] $M^{-1} s^{-1}$
$Ru(phen)_3(ClO_4)_3$	1.22	$\leq 10^{-4}$	0.10	4.06	40.6	
$Ru(phen)_3Cl_3$	1.22	$\leq 10^{-4}$	0.01	0.30 ± 0.20	30 ± 20	
		$\leq 10^{-4}$	0.10	0.22	22.0	
$Ru(bipy)_3Cl_3$	1.23	$\leq 10^{-4}$	0.30	3.63	12.1	
		$\leq 10^{-4}$	0.23	2.88	12.8	
		$\leq 10^{-4}$	0.15	1.82	12.1	
$Ru(bipy)_3(ClO_4)_3$	1.23	$\geq 10^{-4}$	0.05			2.8×10^{-4} [b]
		$\geq 10^{-4}$	0.10			2.0×10^{-4} [b]

[a] Reference 12. [b] Pseudo zero-order rate plots were observed. [c] k_1' = initial rate/[H^+][cyclohexanone].

Table V. Oxidation of Cyclohexanone by Ferriin in H_2SO_4 at High [Fe(III)] and Low [H^+]

[Ferriin] $\times 10^3$ M	[H_2SO_4], M	[H^+],[a] M	[Cyclohexanone] $\times 10^2$M	Linear rate $\times 10^6$ m s^{-1}	$k_1' \times 10^4$ $M^{-1} s^{-1}$
1.2	0.3	0.327	1.67	2.7	5.0
2.4	0.6	0.636	1.67	5.4	5.1
1.2	0.6	0.636	1.67	5.4	5.1
1.2	0.3	0.327	1.67	2.2	4.0
1.2	0.3	0.327	1.67	3.0[b]	6.1
1.2	0.3	0.327	3.34	4.4	3.85

[a] Calculated using dissociation constant of HSO_4^- as 0.012 M.[13] [b] Degassed.

Oxidation of Cyclohexanone by $Ru(bipy)_3^{3+}$ at High [Ru(III)]. Pseudo-zero-order kinetics were observed at $\geq 10^{-4}$ M [$Ru^{III}(bipy)_3(ClO_4)_3$]. From the rate of the reaction, a k_1' value equal to 2×10^{-4} M^{-1} s^{-1} was found. A similar result was found for $Ru^{III}(bipy)_3Cl_3$ with a k_1' value of 2.8×10^{-4} M^{-1} s^{-1} (Table IV).

Discussion

The two important conclusions of this study are (i) the oxidation involves an outer-sphere transfer of an electron from the organic to the oxidant and the rate of electron transfer is dependent on the oxidation potential of the oxidant in the manner predicted by Marcus for outer-sphere electron transfer; (ii) the electron transfer occurs from the enol rather than the keto tautomer.

There is no doubt that the electron transfer is outer sphere since quantitative formation of the Fe(II) or Ru(II) complexes were observed. Dissociation of a polypyridyl ligand could not have occurred since at the acidity used in this study the tris(polypyridyl) complexes would not have re-formed.[14,15] This result is not surprising since these are inert complexes and are known to be outer-sphere redox reagents toward other inorganic ions.[16]

The linear free-energy relationship shown in Figure 1 with a slope of 0.51 ± 0.06 cannot be considered as evidence for outer-sphere electron transfer since similar relationship has been obtained for inner-sphere electron transfer reactions.[8] However, it would have been surprising if the relationship had not been obeyed. A slope close to 0.5 was found in the oxidation of a number of organic compounds by vanadium(V)[10] and for the oxidation of cyclohexanone by three chloro complexes of Ir(IV).[9] Another recent example is the redox reaction between Np(VI) and hydroquinone.[11] Thus this work provides another of the few examples of the applicability of the Marcus relationship for the oxidation of organic compounds by inorganic complexes.

It is significant that the perchlorate salt of tris(1,10-phenanthroline)ruthenium(III) also fell on the same line as the Fe(III) complexes. The lower rates with the chloride salts is apparently an anion effect. If the electron transfer occurred by direct transfer to the metal d orbitals it might be expected that the more diffuse low-lying d orbitals of Ru(III) would give a more facile transfer as compared with Fe(III). The fact that no rate enhancement was found would suggest that electron transfer occurs via the periphery of the polypyridyl ring. The

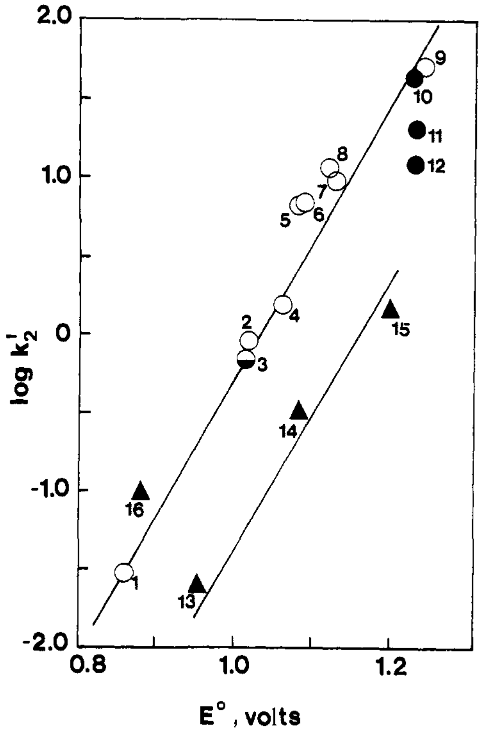


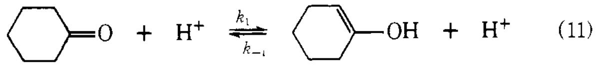
Figure 1. Relationship between log k_2' and $E°$ of the various ferriin complexes at 25° and 1 M H_2SO_4: (1) 4,7-dimethylferriin; (2) 5-methylferriin; (3) $Fe^{III}(bipy)_3$; (4) ferriin; (5) 5-phenylferriin; (6) 4,7-diphenylsulfonated ferriin; (7) 5-bromoferriin; (8) 5-chloroferriin; (9) 5-nitroferriin; (10) $Ru(phen)_3(ClO_4)_3$; (11) $Ru(phen)_3Cl_3$; (12) $Ru(bipy)_3Cl_3$; (13) $IrCl_6^{2-}$; (14) $IrCl_5(H_2O)^-$; (15) $IrCl_4(H_2O)_2$; (16) $IrBr_6^{2-}$ (data for 13-14 taken from ref 9). Symbols: ○, ferriin and substituted ferriin complexes; ◒, $Fe^{III}(bipy)_3$; ●, Ru^{III} complexes; ▲, Ir^{IV} complexes.

thiocyanate-catalyzed reduction of cytochrome *c* by chromous ion suggested that the porphyrin ring system was the electron transfer site.[17] Similarly, the relatively large effect of thiocyanate on the rate of reduction of Fe(III) and Mn(III) tetrapyridylporphyrins was also attributed to electron transfer via the porphyrin ring.[18] There was also evidence for peripheral attack upon the porphyrin ring during the chemical reduction and oxidation of chloroiron(III) octaethylprophyrin ring.[19] Also in this light it is not surprising that bipyridyl and phenanthroline complexes fall on the same line since both have similar conjugated π-electron systems.

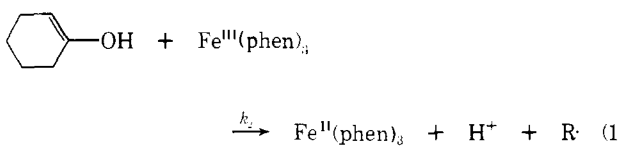
The rate constants for the oxidation of cyclohexanone by $IrCl_6^{2-}$, $IrCl_5(H_2O)^-$, and $IrCl_4(H_2O)_2$ were about 10 times slower[9] than the tris(polypyridyl) complexes of Fe(III) and Ru(III) on the basis of potential alone. This also led us to believe the ligands of the outer-sphere oxidants play a role in accepting electrons, or in other words, electron transfer occurred via the ligand orbitals. It is interesting to note that $IrBr_6^{2-}$ fell on the linear free-energy plot of the polypyridyl complexes. The bromide ion is more polarizable than the chloride ion and hence might be a better conductor of electron density. Though the reactions for Ir(IV) were carried out in $HClO_4$ medium and that for the polypyridyl complexes were carried out in H_2SO_4 medium, the comparison is still valid since no large medium effect was observed with the ferriin complexes (Table I).

Littler favored oxidation of the keto form because his rate of oxidation of the cyclohexanone was twice as fast as enolization.[4] However, the kinetic results in this paper clearly indicate that it is the enol form which is oxidized. As demonstrated by eq 13 and 14 below, if the enol form is oxidized, a rate expression with zero-order dependence in [ferriin] should be obtained at high [ferriin] and low [H$^+$]. This corresponds to the situation where the acid-catalyzed enolization becomes the rate-determining step in the oxidation since the enol is oxidized by ferriin in a fast step. A linear rate is obtained at [ferriin] $\geq 1.12 \times 10^{-3}$ M and [H$^+$] ≤ 0.6 M. From the linear rate a second-order rate constant for enolization (first order in [cyclohexanone] and first order in [H$^+$]) of 5.0×10^{-4} M^{-1} s^{-1} at 25° in aqueous sulfuric acid was found. Since 2 mol of ferriin is reduced for every mole of enol formed, the rate of enolization can be calculated to be 2.5×10^{-4} M^{-1} s^{-1} which agrees with the literature value of 3.1×10^{-4} M^{-1} s^{-1} at 25° in 1 M $HClO_4$.[20] Although our value for enolization was obtained in H_2SO_4, we feel the comparison is valid because literature values for the second-order rate constant for acid-catalyzed enolization of acetone did not differ appreciably in $HClO_4$[21] or H_2SO_4[22] medium. At high $Ru^{III}(bipy)_3$ concentration ($\geq 10^{-4}$ M), the second-order rate constant (2.0×10^{-4} M^{-1} s^{-1}) obtained from the pseudo-zero-order plot is of the same order of magnitude as the acid-catalyzed enolization rate constant for cyclohexanone.

The mechanism which accounts for the kinetic data over the whole range of ferriin and acid concentrations is shown in eq 11 and 12. R· reacts subsequently in a number of fast steps to give the oxidized product.



(11)



(12)

Assuming the steady-state approximation for the formation of the enol, the following rate expression was obtained.

$$\text{rate} = \frac{d[\text{Fe(II)}]}{dt} = \frac{k_1k_2[\text{cyclohexanone}][\text{H}^+][\text{Fe(III)}]}{k_{-1}[\text{H}^+] + k_2[\text{Fe(III)}]} \quad (13)$$

Such a rate expression has two limiting forms. At high [Fe(III)] and low [H$^+$] such that $k_2[\text{Fe(III)}] \gg k_{-1}[\text{H}^+]$, a rate expression independent of [Fe(III)] was obtained,

$$d[\text{Fe(II)}]/dt = k_1[\text{cyclohexanone}][\text{H}^+] \quad (14)$$

where k_1 referred to the acid-catalyzed enolization rate constant of cyclohexanone. At high [H$^+$] and low [Fe(III)] such that $k_{-1}[\text{H}^+] \gg k_2[\text{Fe(III)}]$, the rate law becomes

$$\frac{d[\text{Fe(II)}]}{dt} = \frac{k_1k_2[\text{Fe(III)}][\text{cyclohexanone}]}{k_{-1}} = k_2'[\text{Fe(III)}][\text{cyclohexanone}] \quad (15)$$

where $k_2' = k_1k_2/k_{-1}$.

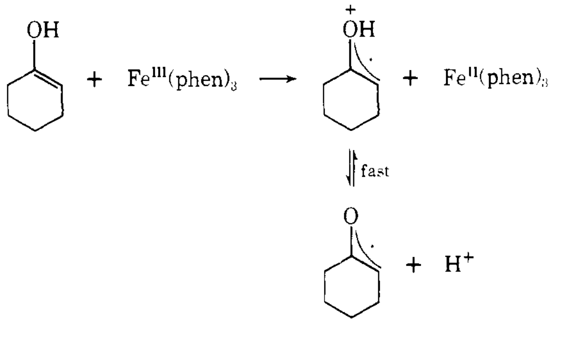
Literature value for the keto-enol equilibrium constant,[23] k_1/k_{-1}, is 4.1×10^{-6}. Since k_1 is 3.1×10^{-4} M^{-1} s^{-1},[16] k_{-1} was calculated to be 76 M^{-1} s^{-1}. The observed second-order rate constant, k_2', for the oxidation of cyclohexanone by ferriin is 1.14 M^{-1} s^{-1} (Table I). Hence k_2 was found to be 1.39×10^5 M^{-1} s^{-1} if the stoichiometry of the reaction is taken into account (eq 1). From the value of the individual rate constants, it can be shown that the limiting rate forms are attained under some of the reaction conditions.

At 0.6 M [H$^+$] and 1.2×10^{-3} M [Fe(III)], $k_{-1}[\text{H}^+] = 45.6 \leq k_2[\text{Fe(III)}] = 167$, the rate expression followed eq 14; i.e., enolization is the rate-determining step. At 1.0 M [H$^+$] and 10^{-4} M [Fe(III)], $k_{-1}[\text{H}^+] = 76 \gg k_2[\text{Fe(III)}] = 13.9$, thus the expected limiting rate law is given by eq 15.

The data could also be analyzed in the intermediate region. The rate plot at 0.4 M [H$^+$], 1.5×10^{-2} M [cyclohexanone], and 2×10^{-4} M initial [ferriin] was analyzed according to eq 13 by plotting (rate of formation of Fe(II) at time t)$^{-1}$ vs. (concentration of Fe(III) at time t)$^{-1}$, or $(d[\text{Fe(II)}]/dt)^{-1}$ vs. $[\text{Fe(III)}]_t^{-1}$. This treatment gave a k_1 value of 6.6×10^{-4} M^{-1} s^{-1} from the intercept and a k_2' value of 1.3 M^{-1} s^{-1} from the slope. This result also supports the proposed mechanism.

The linear rate plot obtained at high $[\text{Ru}^{\text{III}}(\text{bipy})_3(\text{ClO}_4)_3]$ also supports oxidation of the enol tautomer. $Ru^{III}(bipy)_3$ is a better oxidant than $Fe^{III}(phen)_3$ because of its higher reduction potential (Tables II and IV). At $\geq 10^{-4}$ M $[\text{Ru}^{\text{III}}(\text{bipy})_3]$, k_2 [Ru(III)] is $\gg$300 (the k_2' value for $Ru^{III}(bipy)_3(ClO_4)_3$ was assumed to be the same as for $Ru^{III}(bipy)_3Cl_3$), which is larger than $k_{-1}[\text{H}^+] = 76$. Hence, this calculation is consistent with the observation that enolization is the rate-determining step.

The solvent isotope effect ($k_2'_{D_2O}/k_2'_{H_2O} = 2.7$) (Table I) is of the same order of magnitude as the increased enol content in D_2O. The value of the enolization equilibrium constant has been reported to be between 2.5[24] and 5.5[22] times higher in D_2O. This means that at most the deuterium isotope effect in the oxidation step (k_{2H_2O}/k_{2D_2O}) could be 2.0. This is low for breakage of an oxygen-hydrogen bond,[25] suggesting that electron transfer from the enol to the ferriin occurs before loss



(16)

of proton to give the enolate radical. An electron-transfer mechanism has been proposed in the oxidation of phenol by $Ir^{IV}Cl_6{}^{2-}$ [26] and the presence of cation radical in the oxidation of phenol by Lewis acids was reported.[27]

Finally one other difference between the present work and Littler's study is the effect of oxygen on the rate. We found no rate enhancement in the presence of oxygen, suggesting the scheme given in eq 4-7 is not operative.

Experimental Section

Materials. 2,2′-Bipyridyl, 1,10-phenanthroline, the substituted phenanthrolines, and tris(2,2′-bipyridyl)ruthenium(II) chloride were purchased from G. Frederick Smith Co.

Tris(1,10-phenanthroline)iron(II), ferroin, the substituted ferroin complexes, and tris(2,2′-bipyridyl)iron(II) were prepared by a published procedure[3a] which consisted of adding an equivalent amount of appropriate ligand to a solution of $FeSO_4 \cdot 7H_2O$ in 3:1 molar ratio. The perchlorate and chloride salts of tris(1,10-phenanthroline)ruthenium(II) were prepared according to a literature method.[28]

The Fe(III) complexes were obtained by oxidation of the Fe(II) complexes with PbO_2 in ~1 M H_2SO_4. The Fe(III) complexes were precipitated as perchlorate salts. Stock solutions of the Fe(III) complexes were made up in concentrated H_2SO_4 or concentrated $HClO_4$ medium. Such solutions were diluted with water to appropriate acid strength immediately before each kinetic run. The Ru(III) complexes were made in situ by oxidizing the Ru(II) solutions with PbO_2 and then filtering off the precipitate of PbO_2 or $PbSO_4$.

Baker analyzed reagent grade cyclohexanone was obtained from J.T. Baker Chemical Co. and was used without further purification.

Kinetic Studies. Tris(polypyridyl)iron(II) and -ruthenium(II) complexes have extinction coefficients of the order of 10^4 in the region of 510 and 450 nm, respectively, while the corresponding Fe(III) and Ru(III) complexes were practically transparent at these wavelengths. Thus the rate of oxidation of cyclohexanone could be conveniently monitored by following the increase in optical density with time at ~510 and 450 nm.

Kinetic studies for the oxidation were carried out on a Durrum stopped-flow spectrophotometer, Unicam SP 800, Unicam SP 1700, and Cary 118 spectrophotometers. The reaction was carried out under pseudo-first-order conditions with excess cyclohexanone and reasonably good pseudo-first-order kinetics were obtained. The psuedo-first-order rate constants were obtained by plotting log $(OD_\infty - OD_t)$ against time.

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Studies of Intramolecular Excimer Formation in Dibenzyl Ether, Dibenzylamine, and Its Derivatives

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Abstract: Dibenzyl ether exhibits a normal fluorescence with a peak at 285 nm and an excimer band at 335 nm. The ratio of the emission intensities of monomer and dimer (I_M/I_D) is linear in the solution viscosity η. This is consistent with the assumption that the rate constant for conformational transitions is of the form $(A + B\eta)^{-1}$ where A characterizes the height of the energy barrier. I_M/I_D was used as a measure of the microscopic viscosity impeding excimer fluorescence of dibenzyl ether incorporated into a glassy or a rubbery polymer. Dibenzylamine exhibits both normal and excimer fluorescence when associated with Lewis acids. Poly(*N*,*N*-dibenzylacrylamide) exhibits only excimer emission, but monomer emission is also observed in solutions of a methyl methacrylate copolymer containing a small proportion of *N*,*N*-dibenzylacrylamide. Films cast from this copolymer exhibit no excimer fluorescence.

Ten years after the discovery of excimer fluorescence by Förster and Kasper,[2] it was observed by Hirayama[3] that 1,3-diphenylpropane exhibits, in addition to the fluorescence band analogous to that of toluene (with a peak at 285 nm), a broad excimer band with an emission maximum at 335 nm. The emission spectrum was found to be independent of dilution, so that the excimer must form by an intramolecular process. None of the other α,ω-diphenylalkanes behaved in this way.