$$2Ag(II) \rightleftharpoons Ag(III) + Ag(I) \qquad (13)$$

exist any way, becomes insignificant in the presence of large concentration of Ag(I). The reaction appears to be somewhat similar to the oxidation of formic acid,[22,31] involving three terms in the rate law which, however, could not be proved in the present case on account of high concentrations of Ag(I) and $HClO_4$ employed to check the decomposition.

There is no evidence for a tautomeric equilibrium between the normal and active forms of hypophosphorous acid in the present system since under the conditions employed the rate is not independent of Ag(II). This mechanism becomes significant only when the direct reaction with the hypophosphorous acid and the oxidant is very slow. Direct reaction between the oxidant and reductant is the preferred path in the present case.

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Hydrogen Ion Dependence of the Oxidation of Iron(II) with Peroxydisulfate in Acid Perchlorate Solutions

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The title reaction has been studied in the $[H^+]$ range of 0.01–1.0 M at different ionic strengths and temperatures. Unlike previous reports, the rate is dependent on the concentration of the hydrogen ions, if it is larger than 0.2 M. The rate laws are $d[Fe(III)]/dt = 2k_1[S_2O_8^{2-}][Fe(II)]$ for $[H^+] < 0.2$ M and $d[Fe(III)]/dt = (k_1 + k_2K[H^+])[S_2O_8^{2-}][Fe(II)]$ for $[H^+] > 0.4$ M. In the $[H^+]$ range of 0.4–1.0 M and at $I \approx 1.0$ M, k_1 ($M^{-1}\ s^{-1}$) and k_2K ($M^{-2}\ s^{-1}$) were found to be 25 ± 1.2 and 83 ± 8, 18 ± 1.2 and 63 ± 4, and 11.5 ± 0.6 and 55 ± 4 at 40, 35, and 30 °C, respectively. A plot of log k_{obsd} (second-order rate constant) vs. $I^{1/2}$ for $I < 0.02$ M yields a straight line with a slope of −3.83. The slope decreases numerically with the increase in the range of ionic strength investigated. The energy of activation (kcal mol^{-1}) was found to be 14.7 ± 1 and 7.6 ± 2 for the k_1 and k_2 paths, respectively. The value for the k_1 path is dependent on the ionic strength showing ion pairing.

Recently the authors have studied[1] the iron(II)-catalyzed oxidation of hydrazine with peroxydisulfate in aqueous perchloric acid solutions. The study necessitated the investigation of the oxidation[2] of hydrazine with iron(III) and the oxidation of iron(II) with peroxydisulfate under the conditions employed in the catalyzed reaction. Although the catalyzed oxidation[1] operates through the Fe(II)/Fe(III) cycle, the mechanism is not simple, and it involves mixed complexes of iron(III) with peroxydisulfate and hydrazine, and there is no evidence for a complex of iron(II) or iron(III) with hydrazine. The second reaction[2] substantiates this finding. The reaction of iron(II) and peroxydisulfate is much faster than the catalyzed reaction[1] and also the oxidation of hydrazine with iron(III). The title reaction has been studied by several workers[3-8] in the past, and all of them suggest the same mechanism. The stoichiometry was studied in detail by Kolthoff and co-workers.[9]

Table I. Stoichiometry of the Reaction between Fe(II) and $S_2O_8^{2-}$ at Different $[H^+]$

$[HClO_4]$/ M	$10^5 \times [Fe(II)]$/ M taken	$10^5 \times [S_2O_8^{2-}]$/ M taken	$10^5 \times [Fe(II)]$/ M remaining	$[Fe(II)]_{reacted}/[S_2O_8^{2-}]_{reacted}$
0.01	5.0	2.0	1.0	2.0
0.01	10.0	2.0	6.05	1.975
0.01	20.0	4.0	12.0	2.0
0.01	40.0	4.0	32.0	2.0
0.01	10.0	1.0	7.95	2.05
0.50	5.0	2.0	1.60	1.70
0.50	8.0	2.0	4.5	1.75
1.0	5.0	2.0	2.0	1.5
1.0	8.0	2.0	4.9	1.55

Most of the workers[3,8] studied the reaction in buffered solutions and found the rate to be unaffected by the change in hydrogen ion concentration. In the present investigation, when the study is extended to higher acid concentrations, significant dependence on $[H^+]$ was found. The reaction therefore, has been fully reinvestigated from the viewpoint of hydrogen ion dependence.

Experimental Section

Materials and Solutions. The chemicals employed in the investigation were either BDH AnalaR or E. Merck GR quality. The solutions were prepared in doubly distilled water, the second distillation

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Table II. Initial Rates (v_0) of the Iron(II) Dependence in Its Oxidation with Peroxydisulfate at 30 °C and I = 1.0 M

$10^5[S_2O_8^{2-}]$ = 2.0 M and $[H^+]$ = 0.01 M									
$10^5[Fe(II)]/M$	1.0	2.0	4.0	8.0	10.0	20.0	40.0	60.0	80.0
$10^8 v_0/M\ s^{-1}$	0.6	0.9	2.2	4.35	5.2	11.2	23.5	35.6	48
$10^5[S_2O_8^{2-}]$ = 20.0 M and $[H^+]$ = 0.01 M									
$10^5[Fe(II)]/M$	1.0	2.0	4.0	8.0	10.0	20.0	40.0	60.0	80.0
$10^8 v_0/M\ s^{-1}$	5.0	10.0	18.0	47	50	105	207	300	450
$10^5[S_2O_8^{2-}]$ = 2.0 M and $[H^+]$ = 1.0 M									
$10^5[Fe(II)]/M$	1.0	2.0	5.0	10.0					
$10^8 v_0/M\ s^{-1}$	1.57	2.67	6.67	13.8					

being from the permanganate. Since iron(II) solutions have tendency to undergo air oxidation, the solutions of ferrous sulfate were always freshly prepared. The lithium perchlorate solution was prepared by neutralizing 60% Riedel AnalaR perchloric acid with lithium carbonate to pH 6.8. Potassium peroxydisulfate solutions older than 1 day were not used.

Kinetic Procedure. The solutions of peroxydisulfate and other reactants were temperature equilibrated separately in a thermostat at 30 ± 0.1 °C. The reaction was initiated by adding a calculated volume of the solution of peroxydisulfate to the other reactants in a flask. Aliquots (5 mL) were taken out at different intervals of time and added to 5 mL of a 0.6 M solution of ammonium thiocyanate, and iron(III) formed, determined[10] colorimetrically with 470-nm filter on a Coleman colorimeter. The extinction coefficient of the iron(III) thiocyanate complex at I = 1.0 M was found to be 8382 ● 30.

Initial rates were determined by the plane mirror method.[11] Second- and first-order plots were also made wherever possible. The results were closely comparable. The duplicate measurements were reproducible to ±5%.

Stoichiometry. The stoichiometry of the reaction was studied by taking excess iron(II) which was estimated[12] on the Spectronic 20 (Bausch and Lomb) colorimeter with a 515-nm filter as a complex of Fe(II)-*o*-phenanthroline (extinction coefficient = 12 400 ± 50). Fe(III) was also determined as discussed above. The stoichiometry could not be determined with excess peroxydisulfate since there is no method available to determine it in the presence of iron(III). It was found that 2 mol of iron(II) are required for each mole of peroxydisulfate at low $[H^+]$. However, the amount of iron(II) oxidized becomes less at higher $[H^+]$. These mixtures slowly evolved oxygen. Stoichiometric results are given in Table I.

Results

Iron(II) Dependence. The concentration of iron(II) was varied from 1×10^{-5} to 80×10^{-5} M at two fixed concentrations of peroxydisulfate. The results are given in Table II. A plot of initial rates vs. Fe(II) yielded a straight line passing through the origin showing first-order dependence in iron(II). Since it would be seen later that the reaction is somewhat different at high acid concentration, Fe(II) dependence was investigated at 1.0 M $HClO_4$ also and found to be again first order. The second-order rate constants (obtained by dividing the initial rates by the concentrations of peroxydisulfate and iron(II)) at the two concentrations (2×10^{-5} and 20×10^{-5} M) of peroxydisulfate were found to be 29.6 and 26.4 $M^{-1}\ s^{-1}$ at 30 °C and I = 1.0 M and $[H^+]$ = 0.01 M. At 1.0 M $HClO_4$ and at the same temperature and ionic strength, the rate constant was found to be 66 $M^{-1}\ s^{-1}$.

Peroxydisulfate Dependence. The concentration of peroxydisulfate was varied from 5×10^{-5} to 100×10^{-5} M at two different fixed concentrations of iron(II). The results are given in Table III. Conditions were such that $[S_2O_8^{2-}]$ was at least 10 times [Fe(II)] and first-order plots with respect to iron(II) could be made. A plot of first-order rate constant (k_1) vs. $[S_2O_8^{2-}]$ yields a straight line with a slope of 27.3 $M^{-1}\ s^{-1}$, a value of the second-order rate constant which is comparable to those obtained from Table II at $[H^+]$ = 0.01 M.

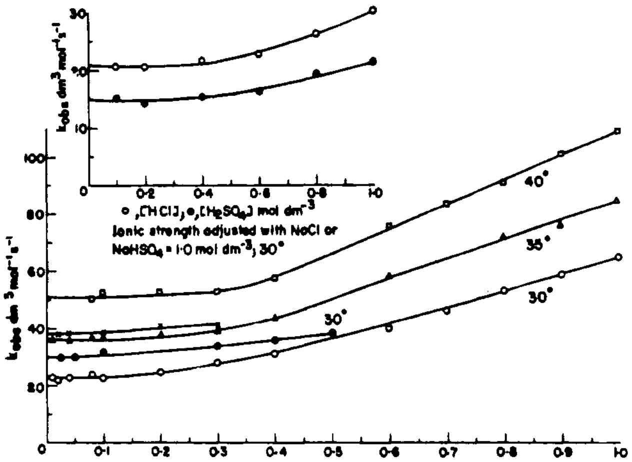

Figure 1. Variation of $[H^+]$ with $HClO_4$, H_2SO_4, and HCl at different temperatures and ionic strengths in the oxidation of Fe(II) with $S_2O_8^{2-}$: □, 40 °C and I = 1.0 mol dm^{-3}: △, 35 °C and I = 1.0 mol dm^{-3}; ○, 30 °C and I = 1.0 mol dm^{-3}; ●, 30 °C and I = 0.5 mol dm^{-3}; ×, 30 °C and I = 0.25 mol dm^{-3}.

Hydrogen Ion Dependence. The previous workers[3-8] investigated the reaction at a hydrogen ion concentration lower than 0.02 M and found no effect on the rate. Some of them have not mentioned[4,5] the hydrogen ion concentration at all. The present study has been made from 0.01 to 1.0 M $[H^+]$ varied with perchloric acid at an ionic strength of 1.0 M adjusted with lithium perchlorate. These results given in Table IV show that there is no significant change in the rate in the 0.01–0.2 M $[H^+]$ range and that beyond this the rate increases in a linear way. Similar results were obtained by employing HCl and H_2SO_4, ionic strength being adjusted with NaCl and $NaHSO_4$, respectively. These results indicate that there are two distinct pathways for the reaction. A plot of second-order rate constant vs. $[H^+]$ is given in Figure 1.

Effect of Ionic Strength. The effect of ionic strength was investigated by employing lithium perchlorate. Reactions were carried out at low ionic strength, and the rate was found to decrease with the increase of ionic strength. Since the hydrogen ion dependence shows a different path for higher range of hydrogen ion concentration, the ionic strength effect was investigated also at 1.0 M $[H^+]$. The rate decreases in this case too, but the extent to which this happens is less than that at low $[H^+]$. All these results are given in Table V.

Energy of Activation. From Figure 1 the rate constants for the two distinct paths are obtained by the intercepts and the slopes of the straight-line portion of the curves. The energies of activation for these two paths, by a plot of log k vs. $1/T$, were found to be 14.7 ± 1 (k_1) and 7.6 ± 2.1 kcal mol^{-1} (k_2K), respectively, at I = 1.0 M. The reaction at low $[H^+]$ was studied at three different ionic strengths and the results are given in Table VI. The energies of activation (kcal mol^{-1}) were found to be 12.8 ± 1.6, 13.0 ± 1.5, and 13.9 ± 1.0 at 0.05 M $[H^+]$ and 30 °C for the ionic strengths 0.05, 0.1, and 0.2 M, respectively. Thus the energy of activation slightly increases with the increase of ionic strength.

Discussion

The previous workers have studied the reaction at low $[H^+]$ and low ionic strength and have suggested the rate-determining step

$$S_2O_8^{2-} + Fe^{2+} \xrightarrow{k_1} SO_4^{2-} + SO_4^- + Fe^{3+} \quad (1)$$

followed by the fast step

$$SO_4^- + Fe^{2+} \rightarrow SO_4^{2-} + Fe^{3+} \quad (2)$$

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Table III. First-Order Constants (k) of the Peroxydisulfate Dependence in the Oxidation of Iron(II) with Peroxydisulfate at 30 °C and $I = 1.0$ M and $[H^+] = 0.01$ M

$10^5[Fe(II)] = 2.0$ M

$10^5[S_2O_8^{2-}]$/M	6.0	8.0	10.0	15.0	20.0	30.0	40.0	60.0	80.0	100.0
$10^3k/s^{-1}$	1.31	2.09	2.39	4.04	5.36	8.06	11.2	16.7	21.3	27.2

$10^5[Fe(II)] = 1.0$ M

$10^5[S_2O_8^{2-}]$/M	5.0	10.0	20.0	30.0	35.0	40.0	50.0	60.0
$10^3k/s^{-1}$	1.15	2.30	5.40	7.70	8.45	11.5	13.8	15.6

Table IV. Second-Order Rate Constants of the Hydrogen Ion Dependence in the Oxidation of Fe(II) with Peroxydisulfate at Different Temperatures and Ionic Strengths[a]

$[H^+]$/ M	$k_0(HClO_4)$						
	$I = 1.0$ M			$I =$ 0.5 M,	$I =$ 0.25 M,	$I = 1.0$ M, 30 °C	
	30 °C	35 °C	40 °C	30 °C	30 °C	k_0-(H_2SO_4)	k_0-(HCl)
0.01	23	36					
0.02	22			30	38.5		
0.04	23	38		30	39.5		
0.08	24	37	50				
0.10	23	37	52	32	39.5	15.5	21
0.20	25	38	52.5		41.5	14.8	20.7
0.30	28	39	53	34	42		
0.40	31	43.5	57	36		15.8	22
0.60	40	58	75			16.6	23
0.70	46		83				
0.80	53	71	90			19.5	26.6
0.90	58	75	100				
1.0	64	84	108			21.7	30.6

[a] $[S_2O_8^{2-}] = 4.0 \times 10^{-5}$ M; $[Fe(III)] = 2.0 \times 10^{-5}$ M.

Table V. Effect of Ionic Strength on the Rate (v_0) in the Oxidation of Fe(II) with Peroxydisulfate at 30 °C[a] $10^5[S_2O_8^{2-}] = 2.0$ M; $10^5[Fe(II)] = 2.0$ M

$[HClO_4] = 1.0$ M

$[LiClO_4]$/M	0.0	0.2	0.4	0.6	1.0
I/M	1.0	1.2	1.4	1.6	2.0
10^8v_0/M s^{-1}	6.3	3.8	3.2	2.13	1.2

$[HClO_4] = 0.005$ M

$10^3[LiClO_4]$/M	0.0	2.0	3.0	4.0	8.0	12.0	16.0
I/M	5.2	7.2	8.2	9.2	13.2	17.2	21.2
10^8v_0/M s^{-1}	17.3	15.3	14.3	13.0	11.7	10.0	9.0

$10^4[Fe(II)] = 5.0$ M; $10^4[S_2O_8^{2-}] = 5.0$ M; $[HClO_4] = 0.01$ M

$[LiClO_4]$/M	0.2	0.4	0.8	1.0	1.2	1.4	1.6
I/M	0.21	0.41	0.81	1.01	1.21	1.41	1.61
10^6v_0/M s^{-1}	32.8	12.0	10.0	8.2	8.2	7.6	6.5
$10^6v_0/([Fe(II)] \cdot [S_2O_8^{2-}])$/$M^{-1}$ s^{-1}	131	48	40	33	33	30	26

[a] $10^5[S_2O_8^{2-}] = 2.0$ M; $10^5[Fe(III)] = 2.0$ M.

Table VI. Second-Order Rate Constants (k_{obsd}) at 30, 35, and 40 °C for Different Ionic Strengths in the Oxidation of Fe(II) with $S_2O_8^{2-}$ [a]

	30 °C			35 °C			40 °C		
I/M	0.05	0.1	0.2	0.05	0.1	0.2	0.05	0.1	0.2
k_{obsd}/M^{-1} s^{-1}	92	53	33	121	80	50	183	110	70

[a] $10^5[Fe(II)] = 2.0$ M; $10^5[S_2O_8^{2-}] = 4.0$ M; $[HClO_4] = 0.05$ M.

Our results of $[H^+]$ dependence, ionic strength, and energy of activation clearly show that there are two distinct paths for the reaction. The reactive species at low $[H^+]$ and ionic strength are Fe^{2+} and $S_2O_8^{2-}$, and at high $[H^+]$, the only change in the species expected is the protonation of $S_2O_8^{2-}$. No hydrolysis of Fe^{2+} seems to be involved since the hydrolysis constant for Fe^{2+} is very small. Kolthoff and Miller[13] have considered $HS_2O_8^-$ as the reactive species in acid solution for the decomposition of $S_2O_8^{2-}$. Similary Irvine[14] also has ascribed the acid catalysis to the formation of $HS_2O_8^-$ in the oxidation of tris(dipyridyl)osmium(II). Thus if k_2 is the rate constant for the reaction $Fe^{2+} + HS_2O_8^-$, the complete rate law is

$$k_{obsd} = (k_1 + k_2K[H^+])/(1 + K[H^+]) \tag{3}$$

where k_{obsd} is the apparent second-order rate constant and K is the protonation equilibrium constant (see eq 4).

$$S_2O_8^{2-} + H^+ \overset{K}{\rightleftharpoons} HS_2O_8^- \tag{4}$$

Since the straight-line portion of the curve of Figure 1 must conform to an equation for the straight line, it is obvious that, in the denominator of eq 3, $1 \gg K[H^+]$ even at $[H^+] = 1.0$ M. With 5% precision in the present work, the value of K appears to be less than 0.05. This would give a minimum value of 20 for the dissociation of $HS_2O_8^-$. In the acid-catalyzed decomposition of peroxydisulfate Kolthoff and Miller[13] have suggested a minimum value of 1 for the acid dissociation constant of $HS_2O_8^-$ and hence a maximum value of 1 for the protonation constant. Hence our finding in a way is an extension of their conclusion. It may also be stated that Ohyoshi and co-workers[15] have assumed a value of 1.4×10^{-2} for the dissociation constant of $HS_2O_8^-$ in the oxidation of Am(III) with peroxydisulfate. This would lead to a value of about 70 for the protonation constant. This seems to be unlikely. Reactions at more than 1.0 M $[HClO_4]$ could not be carried out for two reasons. The reaction becomes too fast for a conventional method of analysis, and second, peroxydisulfate hydrolyzes[16] to HSO_5^- which would create complications in the system. However, it is obvious that with a value of 0.05 for K, eq 2 will reduce to eq 5.

$$k_{obsd} = k_1 + k_2K[H^+] \tag{5}$$

If one ignores the results at lower $[H^+]$, one obtains a straight line, which on extrapolation gives an intercept on the rate constant axis, and this is in accordance with eq 5. The slopes ($k_2K/M^{-1}\ s^{-1}$) and intercepts ($k_1/M^{-1}\ s^{-1}$) of these lines are 83 ± 8 and 25 ± 1.2, 63 ± 4 and 18 ± 1.2, and 55 ± 4 and 11.5 ± 0.6 at 40, 35, and 30 °C, respectively, at $I = 1.0$ M. If one considers the results at lower $[H^+]$, one obtains rate constants ($k_0/M^{-1}\ s^{-1}$) of 51 ± 0.6, 36 ± 1.2, and 23 ± 0.6 at 40, 35, and 30 °C, respectively. The difference in the values of intercepts (k_1) by a factor of 2 under the two situations can be explained by the variation in the stoichiometry. It appears that SO_4^- produced in the acid-catalyzed path gets rapidly protonated and reaction of the latter is faster with H_2O giving oxygen than with Fe^{2+} (eq 6–8).

$$Fe^{2+} + HS_2O_8^- \xrightarrow{k_2} Fe^{3+} + SO_4^- + HSO_4^- \tag{6}$$

$$H^+ + SO_4^- \rightleftharpoons HSO_4 \tag{7}$$

$$HSO_4 + H_2O \rightarrow O_2 + \text{other products} \tag{8}$$

Consequently, the stoichiometries of the two paths become different. Kolthoff and co-workers[9] have reported the decrease

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in the stoichiometry upon slow addition of Fe(II), which can be explained by the occurrence of steps 7 and 8 in the absence of iron(II). Such unexpected situations of stoichiometry are not uncommon in peroxydisulfate oxidations. It is found in the oxidation[17] of Ce(III)- and Cu(II)-catalyzed oxidation[18] of hydrazine. The rate laws under the two conditions are shown in eq 9 and 10.

$$d[\mathrm{Fe(III)}]/dt = 2k_1[\mathrm{Fe(III)}][\mathrm{S_2O_8}^{2-}] \text{ at } [\mathrm{H^+}] < 0.2 \text{ M} \quad (9)$$

$$d[\mathrm{Fe(III)}]/dt = (k_1 + k_2K[\mathrm{H^+}])[\mathrm{Fe(II)}][\mathrm{S_2O_8}^{2-}] \text{ at } [\mathrm{H^+}] > 0.4 \text{ M} \quad (10)$$

The effect of ionic strength under the two conditions is found to be quantitatively different. At low $[H^+] = 0.005$ M and 30 °C and with an ionic strength less than 0.02 M, a plot of log k_{obsd} vs. $I^{1/2}$ yielded a straight line with a slope of -3.83. This is quite close to the theoretical value,[19] and hence the reaction appears to be ideally suited for the verification of the Bronsted-Bjerrum[20] relationship since the concentrations of the reactions required for conventional study are small and the ionic strength should be kept less than 0.01 M. When the ionic strength was varied in the range 1-2 M at constant $[H^+] = 1.0$ M, the slope of the relevant line (plot of log k vs. $I^{1/2}$) decreased to -1.6. This is another indication of a different path of reaction in high $[H^+]$ which would probably be between Fe^{2+} and $HS_2O_8^-$.

The energy of activation has been variously reported[3,7] by previous workers from 8.1 to 12.1 kcal mol^{-1} though $[H^+]$ was low. Turska and Matuszewska-Czerwik[4a] have reported a value of 4.34 kcal mol^{-1}, but the hydrogen ion concentration and the ionic strengths are not specified. Our values vary from 12.8 to 14.7 kcal mol^{-1} with the increase of ionic strength. It appears that the energy of activation is slightly dependent on the ionic strength and that ion pairs[21,22] like $KS_2O_8^-$ and $FeClO_4^+$ are likely to participate in the redox process. Our results yield a value of 200 M^{-1} s^{-1} at 30 °C and zero ionic strength. Other values at the same ionic strength are 187.8 (30 °C),[3] 135 (30 °C),[7] and 115 (25 °C).[8] One more value[4a] at unspecified ionic strength and hydrogen ion concentration is 0.013 M^{-1} s^{-1} which is unusual and unexpected even at high ionic strength and $[H^+]$.

Registry No. Fe^{2+}, 15438-31-0; $S_2O_8^{2-}$, 15092-81-6.

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Aquo Chemistry of Monoarene Complexes of Osmium(II) and Ruthenium(II)

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A number of derivatives of η-$C_6H_6Os^{II}$ ($BzOs^{II}$) were prepared, exploiting the three positions not preempted by the arene ring and emphasizing ligands which are saturated. The species synthesized include $[BzOs(NH_3)_3]^{2+}$, $[BzOs(NH_3)_2Cl]^+$, and $[BzOs(en)Cl]^+$. It was shown that a 2+ ion, presumably $[BzOs(H_2O)_3]^{2+}$, is produced in an acidic solution of $BzOsCl_2$ when Cl^- is removed by Ag^+. The determination of the acidity of the coordinated water for the aquo species is complicated by the condensation of the hydroxo form. However, $[BzOs(en)H_2O]^{2+}$ prepared from $[BzOs(en)Cl]^+$ by adding Ag^+ behaves normally, and the value of pK_a was found to be 6.3 at 20 °C; for $[BzOs(NH_3)_2H_2O]^{2+}$ it was found to be 6.4, and for $[BzRu(en)H_2O]^{2+}$ it is 7.9. The quotient governing association of Cl^- with $[BzOs(en)H_2O]^{2+}$ was measured as 1.1×10^2. The acidity of the aquo ion and the stability of the chloride complex testify to the electron-withdrawing ability of the arene ring.

The work being reported was undertaken to develop the aquo chemistry of some monoarene complexes of Os(II) and Ru(II). The η-C_6H_6-Os(II) and η-C_6H_6-Ru(II) bonds both resist hydrolysis, and there is a good prospect then that species such as $[\eta\text{-}C_6H_6Os]^{2+}$(aq) can be characterized. (It is virtually certain for the work to be reported that the species exists as a trihydrate, and it will hereinafter be represented as such). Taking the work in this direction seems worth while, purely for its descriptive content but also because it helps to bridge the gap between organometallic chemistry and so-called classical coordination chemistry.[1,2] Of special interest to us were observations which bear on the issue of how the arene ring in replacing a number of saturated ligands, three in our cases, influences the reactivity at the remaining sites (substitution reactions) and of the complex as a whole (redox properties). In studying the substitution properties, we are interested in how the affinities of Os(II) for different ligands are affected by the π-arene unit and, as well, how the rates of substitution are affected. The equilibrium data in particular are useful in assessing the electron-withdrawing capacity of the arene ligands, and the simplest and most direct data of this kind which bear on this issue involve the replacement of H_2O by OH^-, or, in other words, the acidity of the coordinated water molecules.

In contrast to the situation for the monoarene complexes of Ru(II) which have been the subject of numerous recent studies,[3-16] including some[7,9,11,12] involving H_2O as a solvent

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