DMA > DMF. $\Delta H^\ominus_g$ and $\Delta H^\ominus_{M-O}$ values are listed in Table V.

The values of standard enthalpy of formation of adducts in the condensed phase ($\Delta H^\ominus_R$) have been used to relate the donor strength of the ligand.[49,50] For adducts of a given stoichiometry formed between a fixed acceptor and the studied ligands, the energy involved can be considered constant and the observed $\Delta H^\ominus_R$ values reflect the basicity order TMU > DMA > DMF, which is the same as that given by $\Delta H^\ominus_{M-O}$. On the other hand, the comparison of the same base with different acids gives the acidity order $BiCl_3 > SbCl_3$.

All enthalpy values display the same trend of variation, consequently all are equally satisfactory for characterizing the enthalpy involved in the formation of the adduct. However, $\Delta H^\ominus_M$ can be understood as a better parameter because it reflects the acid–base interaction in the gas phase.[51]

Acknowledgment. The author wishes to thank Dr. A. P. Chagas for fruitful discussions and FAPESP for financial support.

Registry No. $SbCl_3$, 10025-91-9; $SbCl_3{\cdot}DMF$, 41322-22-9; $SbCl_3{\cdot}DMA$, 22995-10-4; $SbCl_3{\cdot}TMU$, 75949-51-8; $SbCl_3{\cdot}2TMU$, 75949-52-9; $BiCl_3$, 7787-60-2; $BiCl_3{\cdot}2DMF$, 75949-53-0; $BiCl_3{\cdot}2DMA$, 75949-54-1; $BiCl_3{\cdot}2TMU$, 75949-55-2; $BiCl_3{\cdot}3DMA$, 75949-56-3; $BiCl_3{\cdot}3TMU$, 75949-57-4; DMF, 68-12-2; DMA, 127-19-5; TMU, 632-22-4.

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Water Exchange with Ferric Ion and Oligomerized Iron in Acidic Aqueous Solutions

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Received February 26, 1980

The water-exchange rate with $Fe(H_2O)_6^{3+}$ in 1.5 *m* $HClO_4$ has been measured with use of ^{17}O NMR and gives $\Delta H^* = 18.5$ kcal/mol, $\Delta S^* = 13.8$ cal/(mol K), and $k_1 = 167\ s^{-1}$ at 25 °C for a particular water leaving the first coordination sphere. Solutions heated above 110 °C developed a species which exchanged water (2–15) × 10^4 times faster than $Fe(H_2O)_6^{3+}$ and which persists at room temperature for months. This species is likely an oligomer of iron(III) formed in the first stage of the process leading to precipitation of the iron(III) at high temperatures.

Introduction

Water exchange in and out of the first coordination sphere of ferric ion is known to be relatively slow although there is some uncertainty about the exact rate.[1] It is desirable to know the rate in order to interpret substitution rates on ferric[2] ion, and knowledge of the contact interaction with $^{17}OH_2$ is needed in order to determine the number of bound waters in ferric complexes such as porphyrin complexes which we are currently studying. The method involves measuring the $^{17}OH_2$ line broadening over a wide temperature range so that one can go from the slow-exchange to the fast-exchange region.[3] Ferric ion is known to hydrolyze[4] and oligomerize as the pH is raised, so this study was carried out on strongly acidic solutions and at relatively low Fe(III) concentrations with the hope that only $Fe(H_2O)_6^{3+}$ would be present. The measurements involved determination of the broadening and shift of the ^{17}O resonance for the bulk water in the solutions.

Experimental Section

Most solutions were prepared by adding 12 M reagent grade $HClO_4$ to ^{17}O-enriched water and then dissolving reagent grade $Fe(NO_3)_3{\cdot}6H_2O$. One solution was prepared by dissolving iron wire, 99.95% pure, in $HClO_4$, fuming, and then diluting. Other solutions were prepared from $Fe(ClO_4)_3{\cdot}6H_2O$ recrystallized from concentrated $HClO_4$. Solutions containing Al^{3+} or Ga^{3+} in place of Fe^{3+} were used as blanks. The composition of solutions used is listed in Table I.

Table I. Composition of Solutions Used

solution	$m_{Fe(III)}$	m_{HClO_4}	m_{NaClO_4}
A	0.367[a]	1.74	0.75
B	0.398[a]	1.89	0.81
C	0.388[a]	1.84	0.79
D	0.0106[b]	1.49	0
E	0.0106[b]	1.49	0
F	0.0053[b]	1.49	0

[a] Perchlorate. [b] Nitrate.

NMR spectra were obtained with a field-locked, frequency-swept CW spectrometer using 5-Hz side-band modulation. The Lorentzian dispersion lines were fit with an on-line microprocessor based computer to give the line widths and frequencies. Measurements at each temperature were made at several rf levels for the sample and blank, and the widths were extrapolated to zero rf level by a computer program in order to eliminate saturation effects. A value of T_1 was obtained in the extrapolation process. Temperature was controlled to ±0.1 °C by pumping silicone oil from a thermostat around the sample and was measured by a copper–constantin thermocouple placed immediately below the sample and rf coil.

The measured line broadenings and shifts were converted to T_{2p^*} and Q defined by eq 1 and 2, where W_s and W_0 are the half-widths

$$1/T_{2p^*} = 2\pi(W_s - W_0)\frac{m_{H_2O}}{m_{Fe}} \tag{1}$$

$$Q = TS\frac{m_{H_2O}}{m_{Fe}} \tag{2}$$

at half-maximum absorption of the sample and blank, respectively (in Hz), m_{H_2O} and m_{Fe} are molalities of H_2O and Fe(III) in the sample, T is the temperature in K, and S is the absorption frequency of the sample minus the frequency of the blank divided by the frequency

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[1] Judkins, M. R. Ph.D. Thesis, Report UCRL-17561, University of California at Berkeley, Lawrence Radiation Laboratory, Berkeley, CA, 1967.

[2] Seewald, D.; Sutin, N. *Inorg. Chem.* **1963**, *2*, 643.

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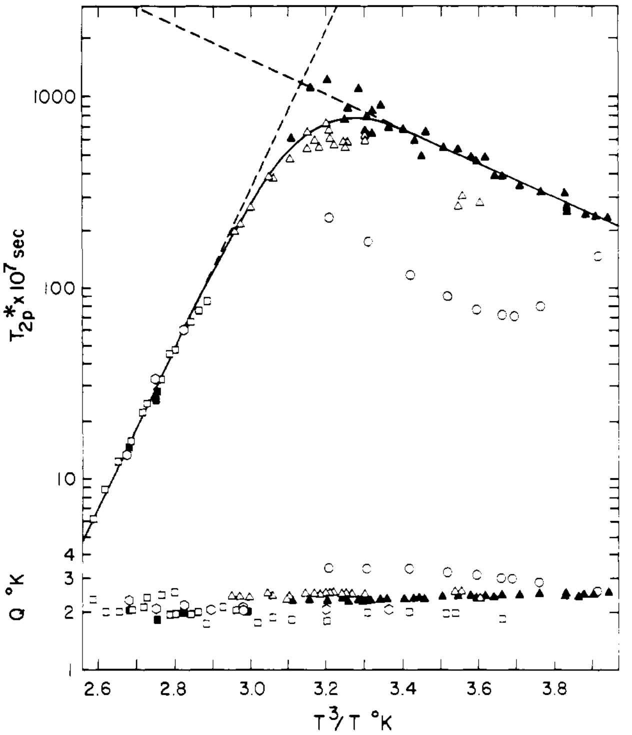

Figure 1. T_{2p^*} and Q vs. $1/T$. Key: solution A, ○; B, ▲; C, △; D, □; E, ○; F, ■.

of the blank. These two quantities are convenient when applying the Swift–Connick equations.[5]

Results

Measurements were made on solutions A–C in order to duplicate the results of Judkins,[1] and the results are shown in Figure 1. At temperatures <40 °C results similar to his were obtained, but when the temperature was taken up to 60 °C, an anomalous shift and broadening developed. When the solutions were cooled, it was found that a shift and broadening not present in the unheated solutions persisted. This is illustrated by solution A where a minimum in T_{2p^*} is present around ~0 °C. The shift and broadening of solution A were checked at room temperature periodically for months and were found to remain essentially unchanged. It was concluded that the effect must be due to the formation of a species involving ferric ion that exchanges water rapidly and is thermodynamically or kinetically stable in strong acid. It could not be the primary hydrolysis product usually studied since this species is known to form reversibly.[1]

For an attempt in preventing the unknown species from forming, measurements were made on solutions D–F at lower Fe(III) concentrations. The results on these solutions are also shown in Figure 1. All of the data in Figure 1 for solutions D–F were taken on solutions which had never been heated above ~110 °C. Data were taken both increasing and decreasing the temperature and indicated that the solutions behaved reversibly up to 110 °C. The T_{2p^*} values agree with those of the more concentrated Fe(III) solutions but are not plotted because of the large scatter produced by the very small broadening in 0.01 *m* Fe(III) solutions. The high-temperature part of T_{2p^*} shows the Arrhenius behavior expected for $Fe(H_2O)_6^{3+}$. The shift obeys Curie's law and is most likely due to rapid exchange in the second coordination sphere.

An attempt was made to continue measurements above 110 °C in order to reach the fast-exchange region for $Fe(H_2O)_6^{3+}$, but all solutions showed the irreversible growth of a species that exchanged water rapidly as described above. Figure 2 shows the behavior of solution E when it was taken through a single cycle starting at <0 °C, heated stepwise to 190 °C, and then cooled back stepwise to <0 °C. Prior to this cycle the solution had already been heated to about 150 °C several times so that initially a significant fraction of the Fe(III) had been converted to the rapidly exchanging species. The similarity in the shape of the curves for $10^3/T < \sim 3$ on the heating phase and cooling phase suggest that in this temperature range the water relaxation is controlled by one kind of site on fast-exchanging Fe(III) species and that the difference in the curves is due to concentration only.

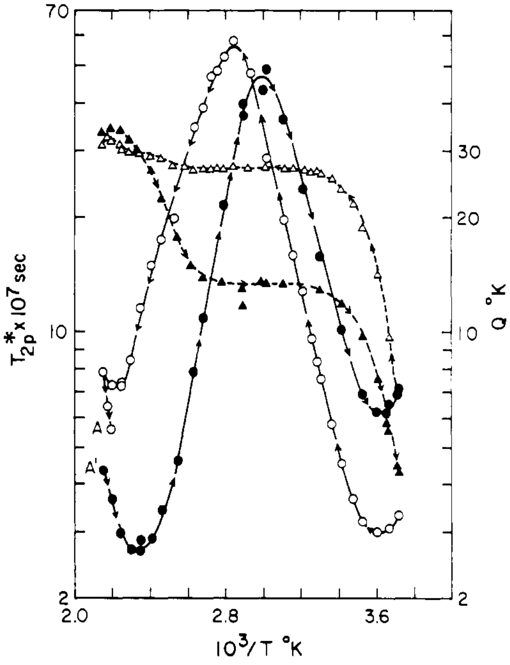

Figure 2. Heating cycle for solution E. Increasing T: T_{2p^*}, ○; Q, △. Decreasing T: T_{2p^*}, ●; Q, ▲. The solution was cooled to room temperature overnight between A and A'.

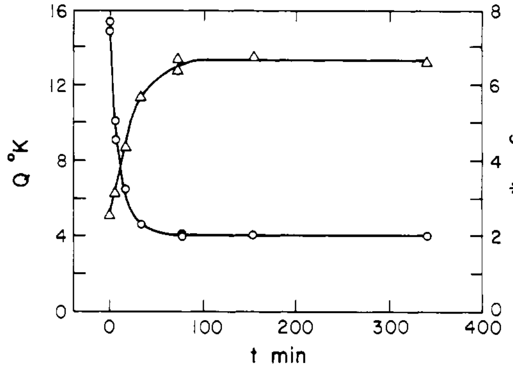

Figure 3. Change with time at 120 °C of T_{2p^*}(33 °C) and Q(33 °C) of solution D.

For a check on the rate of formation of the new species, solution D, which had not been heated above 110 °C, was placed in an oil bath at 120 °C for various lengths of time, removed, quenched to 33 °C, and then checked for shift and broadening. By comparing Figures 1 and 2 one, can see that at 33 °C the shift and broadening of $Fe(H_2O)_6^{3+}$ are small, and hence their values should give a measure of the concentration of the new species. The results are shown in Figure 3. The shift and broadening increase rapidly for about 1 h and then no longer change with time, indicating the rate of formation of the new species has dropped to a small value. Attempts to fit the data by a simple rate law were not successful. The reaction may be heterogeneous. The solution was

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(5) Swift, T. J.; Connick, R. E. *J. Chem. Phys.* **1962**, *37*, 307.

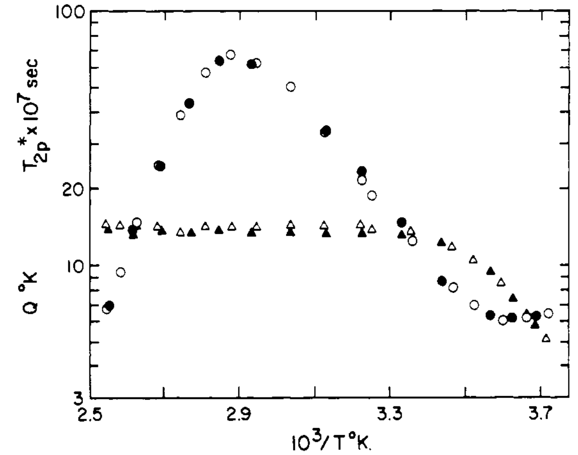

Figure 4. Heating cycle for solution D. Increasing *T*: T_{2p^*}, ○; *Q*, △. Decreasing *T*: T_{2p^*}, ●; *Q*, ▲.

then run through a cycle from <0 to 120 °C, and the results are shown in Figure 4. Again the shapes of the curves are very similar to those in Figure 2 and suggest that the primary difference is due to concentration of the new species. In addition there appears to be little additional change in concentration of the new species so long as the temperature is not raised above 120 °C.

Above 150 °C the solutions were yellow but always became colorless when cooled to room temperature. No Tyndall effect was observed.

Interpretation of Data

The data in Figure 1 are evidently those for $Fe(H_2O)_6^{3+}$ free from hydrolyzed or oligomerized species. With that assumption they were fitted to the Swift–Connick equations by assuming an Arrhenius region at high temperature and a T_{2m} outer-sphere region at low temperature as indicated by the dashed lines. The Arrhenius curve gives $\Delta S^{\ddagger} = 13.8$ eu, $\Delta H^{\ddagger} = 18.5$ kcal/mol, and $k_1 = 167\ s^{-1}$ for a particular water leaving the inner sphere of $Fe(H_2O)_6^{3+}$ at 25 °C. The outer-sphere shift gives $n(A/h) = 2.9$ MHz, where n is the outer-sphere coordination number. These results have an uncertainty of about 10% and are in agreement with Judkins.[1]

As indicated above, the data of Figures 2 and 4 suggest that below $10^3/T \approx 3$ the solutions contain a new rapidly exchanging Fe(III) species and unreacted $Fe(H_2O)_6^{3+}$. With such an assumption we can write for a particular temperature eq 3 and 4, where X_1 is the atom fraction of ^{17}O in $Fe(H_2O)_6^{3+}$,

$$Q = X_1Q_1 + X_2Q_2 \qquad (3)$$

$$1/T_{2p^*} = X_1/T_{2p^*1} + X_2/T_{2p^*2} \qquad (4)$$

X_2 is the atom fraction of ^{17}O in the unknown species, Q_1 and T_{2p^*1} apply to $Fe(H_2O)_6^{3+}$ and Q_2 and T_{2p^*2} apply to the unknown species. Equations 3 and 4 assume no direct water exchange occurs between species 1 and 2; i.e., we have an uncoupled three site exchange problem for H_2O. Since $X_1 + X_2 = 1$, we can eliminate X_1 and X_2 between eq 3 and 4 and get eq 5 and 6. Equation 5 shows that for a particular tem-

$$1/T_{2p^*} = \frac{(1/T_{2p^*1} - 1/T_{2p^*2})}{(Q_1 - Q_2)}Q - \frac{(1/T_{2p^*1} - 1/T_{2p^*2})}{(Q_1 - Q_2)}Q_2 + 1/T_{2p^*2} \qquad (5)$$

$$X_1 = \frac{(1/T_{2p^*} - 1/T_{2p^*2})}{(1/T_{2p^*1} - 1/T_{2p^*2})} = \frac{(Q - Q_2)}{(Q_1 - Q_2)} \qquad (6)$$

perature a plot of $1/T_{2p^*}$ vs. Q should be a straight line. Sufficient data were available to make such plots at 118 and 33 °C as shown in Figure 5. The observed linearity suggests that the hypothesis of only two species is correct. Figures 2 and 4 show that at 118 °C the unknown species would be in the fast-exchange limit, therefore $Q_2(118\ °C) = Q_{2LIM}$. Figure 5 indicates that $Q_{2LIM} \simeq 31$ and Figure 1 gives $Q_{1LIM} \simeq 2$. Having these values for Q_{1LIM} and Q_{2LIM} and the observed Q's in the flat regions of Figures 2 and 4 one can calculate X_1 (and X_2) from eq 6. Finally by using Q_1 and $1/T_{2p^*1}$ from Figure 1, one can use eq 3 and 4 to calculate Q_2 and $1/T_{2p^*2}$. The results are shown in Figure 6.

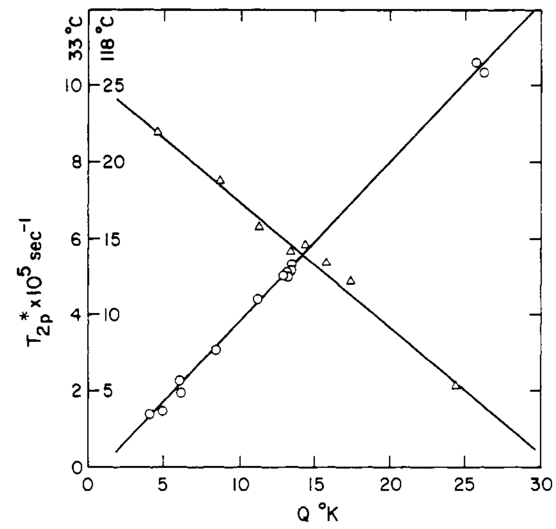

Figure 5. $1/T_{2p^*}$ vs. Q (118 °C, △; 33 °C, ○).

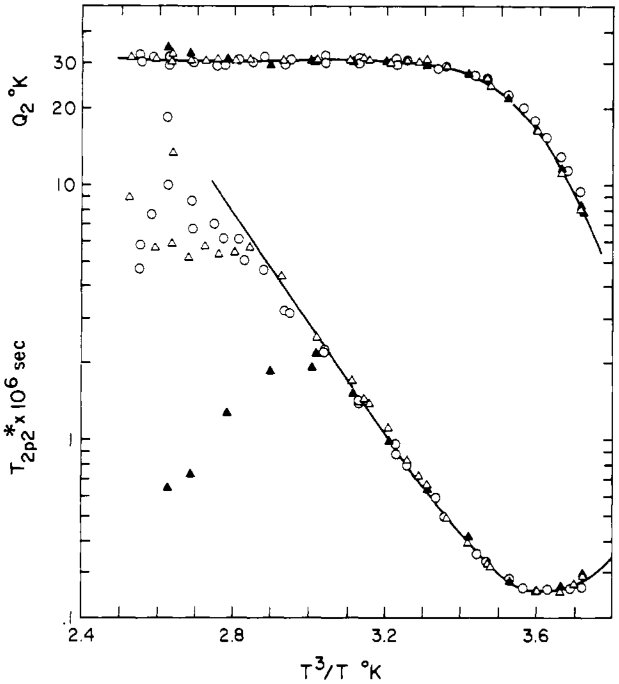

Figure 6. T_{2p^*2} and Q_2 vs. $1/T$. Data from Figure 4: ○, $X_2 = 0.404$. Data from Figure 2, T increasing: △, $X_2 = 0.862$. Data from Figure 2, T decreasing: ▲, $X_2 = 0.397$.

This resolution of the data does depend on the choice of Q_{2LIM}. Figure 5 shows that $Q_{2LIM} < 32$ since $1/T_{2p^*2} \geq 0$. An attempt to resolve the data with eq 3–6 with $Q_{2LIM} = 30$ gave considerably more scatter of the points as compared to Figure 6. We conclude that the value of $Q_{2LIM} = 31$ is probably determined to ±1. The data of Figure 2 for decreasing temperature from 190 °C and the falling off of the corresponding $1/T_{2p^*2}$ points in Figure 6 indicate that, when the solution has been held at 190 °C, the species designated

Table II. Summary of Known Fe(III) Species Water-Exchange Data

	k_1(25 °C), s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/(mol K)	A/h, MHz
$Fe(H_2O)_6{}^{3+}$	1.67×10^2	18.5	13.8	
$Fe(TMPyP)H_2O^{5+}$ [a]	7.8×10^5	13.8	14.7	24.9
$Fe(TPPS)H_2O^{3-}$ [a]	1.4×10^7	13.7	20.2	22.6
species 2	$2.6 \times 10^7/n_2$	8.5	$3.9/n_2$	$45.6/n_2$

[a] Reference 9.

as species 2 is disappearing by an additional reaction to form a third species of Fe(III), probably a higher oligomer.

The data in Figure 6 for $10^3/T < 3$ can be fit with the Swift–Connick equations in the form

$$Q_2 = \frac{Q_{2L1M}}{1 + (\Delta\omega_{M2})^2\tau_{M2}{}^2} \tag{7}$$

$$T_{2p\cdot 2} = \frac{1}{n_2}\left(\frac{1}{(\Delta\omega_{M2})^2\tau_{M2}} + \tau_{M2}\right) \tag{8}$$

where $1/T_{2M2} = 0$ and the subscript 2 refers to species 2. The solid lines in Figure 6 were calculated with $\Delta H_2{}^{\ddagger} = 8.5$ kcal/mol, $n_2(A_2/h) = 45.6$ MHz, $n_2\Delta S^{\ddagger} = 3.9$ eu, and τ_{M2}(25 °C)/$n_2 = 3.9 \times 10^{-8}$ s.

Evidently only the $(\Delta\omega_M)^2$ mechanism[5] is effective for broadening and T_{1e2} is so short that T_{2M2} is too long to be effective. The number of rapidly exchanging water molecules per Fe(III), n_2, is not known. Assuming $1 \leq n_2 < 6$, one concludes the water in species 2 exchanges faster than that in $Fe(H_2O)_6{}^{3+}$ by a factor of (2–15) × 10^4 at 25 °C.

Discussion

Judkins considered $FeOH^{2+}$, $Fe(OH)_2{}^+$, $Fe_2(OH)_2{}^{4+}$, and $Fe_3(OH)_4{}^{5+}$ as possible contributors to the ^{17}O line broadening by Fe(III) in solutions containing 0.019–0.0986 M $HClO_4$. He estimated a water lifetime in the first coordination sphere of less than 1.5×10^{-6} s for $FeOH^{2+}$ and less than 5.8×10^{-7} s for $Fe_3(OH)_4{}^{5+}$. It is unlikely that any of these species can be identified as species 2 since they should not be stable in 1.5 M H^+ at 25 °C. In addition the shifts observed by Judkins are far too small for species 2 and his solutions showed no hysteresis effects lasting longer than 15 min. This conclusion is also supported by the relatively labile behavior of the μ-oxo iron(III) complexes.[6]

In the case of Cr(III) it has been shown that a dinuclear species is formed by O_2 oxidation of Cr^{2+} in perchloric acid[7,8] and that a mixture of polynuclear species is formed on boiling Cr(III) in $HClO_4$.[7] The μ-oxo or dihydroxo form has been postulated for the dinuclear species in this case.

In view of the above it is difficult to postulate a definite structure for species 2. It seems likely that it is a species formed in the early stages of hydrolysis of Fe(III) at high temperatures in acid, that oxo bridges are involved, that the enhanced water exchange is due to reduction of charge on the Fe(III), and that continued heating leads to higher oligomerization with eventual precipitation of the iron.

Table II summarizes what is known about water exchange on Fe(III) species. The A/h values would give $n_2 = 2$ assuming the hypothesis[3] of constant A/h is valid. The low activation enthalpy and entropy suggest considerable weakening of the iron–water bond.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the partial support of this research and to the National Science Foundation for support under NSF Grant No. CHE76-17436.

Registry No. $Fe(H_2O)_6{}^{3+}$, 15377-81-8.

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Catalytic Decomposition of Peroxymonosulfate in Aqueous Perchloric Acid by the Dual Catalysts Ag^+ and $S_2O_8{}^{2-}$ and by Co^{2+}

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Received July 30, 1980

Aqueous $HSO_5{}^-$ is catalytically decomposed to O_2 and $HSO_4{}^-$ by the dual catalysts Ag^+ and $S_2O_8{}^{2-}$. The rate law in acidic solution is $-d[HSO_5{}^-]/dt = k'[Ag^+]_0[S_2O_8{}^{2-}]_0$. Both oxygen atoms in the O_2 product are derived from the terminal peroxide oxygen in $HSO_5{}^-$. A chain mechanism of short chain length is proposed in which a HSO_5 intermediate is formed by the reaction of Ag^{2+} and $HSO_5{}^-$. HSO_5 rapidly decomposes in parallel, bimolecular paths which produce $O_2 + 2SO_4{}^-$ and $O_2 + S_2O_8{}^{2-}$, respectively. The slow step is the well-known reaction between Ag^+ and $S_2O_8{}^{2-}$. Aqueous Co^{2+} is also a catalyst for the decomposition of $HSO_5{}^-$. The rate law, in the presence of dilute Ag^+, is $-d[HSO_5{}^-]/dt = k_{Co^{2+}}[Co^{2+}]_0[HSO_5{}^-]$. A redox mechanism similar to that for the Ag^+, $S_2O_8{}^{2-}$ catalysis is proposed in which Co^{2+} and $HSO_5{}^-$ replace Ag^+ and $S_2O_8{}^{2-}$, respectively. The kinetics are considerably more complicated in the absence of added Ag^+. Some probable requirements for efficient, simple catalysis of the decomposition of $HSO_5{}^-$ are discussed.

Introduction

There have been numerous reports of catalysis of the decomposition of peroxymonosulfate[1] (eq 1). Examples of

$$2HSO_5{}^- \rightarrow 2HSO_4{}^- + O_2 \tag{1}$$

catalysts include metal ions in both acidic and weakly basic solution,[2] traces of nitric acid in concentrated sulfuric acid,[3] and organic substrates such as ketones.[4] Few of these systems

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(1) A more systematic name for $HSO_5{}^-$, the predominant species in acidic solution ($pK_a \approx 9.3$), is hydrogen peroxosulfate. However, in this paper we shall yield to common usage.

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