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The Kinetics and Mechanisms of the Reactions of Iron(III) with β-Diketones. The Formation of Monoacetylacetonatoiron(III) and the Effect of Copper(II) on the Formation of Monothenoyltrifluoroacetonatoiron(III)[1a]

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The kinetics of the reaction of iron(III) with acetylacetone and the effect of copper(II) on the rate of the reaction of iron(III) with thenoyltrifluoroacetone have been studied at 25° and 1.0 M ionic strength by a spectrophotometric method. The keto and enol tautomers of acetylacetone both react with iron(III) by parallel acid-independent and inverse acid paths. The rate constants for the reaction of the keto tautomer with Fe^{3+} and $FeOH^{2+}$ are 0.29 and 5.4 M^{-1} sec^{-1}, respectively, and the rate constants for the reaction of the undissociated enol form of acetylacetone with Fe^{3+} and $FeOH^{2+}$ are 5.2 and 4.4×10^3 M^{-1} sec^{-1}, respectively. The rate constants, k_e and k_f, for the keto–enol tautomerism of acetylacetone, defined by

$$\text{keto} \underset{k_f}{\overset{k_e}{\rightleftharpoons}} \text{enol}$$

are 0.015 and 0.114 sec^{-1}, respectively. The value of the equilibrium constant for the reaction $Fe^{3+} + HAA \rightleftharpoons FeAA^{2+} + H^+$, where HAA represents the undissociated acetylacetone, was found to be 32 at 25° and 1.0 M ionic strength. The formation of the monothenoyltrifluoroacetonato complex of iron(III) is catalyzed by copper(II). The rate constant for the reaction of $FeOH^{2+}$ with $CuTTA^+$ is 1.5×10^2 M^{-1} sec^{-1}. The mechanisms of the complex formation reactions are discussed.

In a recent paper we reported the results of a kinetic study of the formation of the 1:1 complexes of nickel(II), cobalt(II), copper(II), and iron(III) ions with 2-thenoyltrifluoroacetone (HTTA).[2] This study showed that the metal ions reacted with the enol tautomer, but not the keto tautomer, of 2-thenoyltrifluoroacetone. The mechanism of the reaction of the enol form was discussed in terms of the entering properties of the (hydrogen-bonded) ligand, the water-exchange rates on the metal ions, and the rate of closure of the six-membered chelate ring. The present study is concerned, in part, with the kinetics and mechanism of the formation of the 1:1 complex of iron(III) with acetylacetone (HAA). Although this reaction has been previously studied by Ong and Prince,[3] we cover a wider concentration range than the earlier workers and present a more complete rate law and a more detailed mechanism.

Acetylacetone exists predominantly as the keto tautomer in aqueous solution. Since the percentage of the enol tautomer present in these solutions can be measured and the overall ionization constant for reaction 1 is known,[4] the equilibrium constants for reactions 2 and 3 can be calculated. In these reactions [HA] = [HK] + [HE] is the concentration of the undissociated diketone, and HK, HE, and E^- represent the keto and enol tautomers and the enolate ion, respectively. The equilibrium data for acetylacetone are summarized in Table I.

$$HA \rightleftharpoons H^+ + E^- \quad K_{HA} \tag{1}$$

$$HK \rightleftharpoons H^+ + E^- \quad K_{HK} \tag{2}$$

$$HE \rightleftharpoons H^+ + E^- \quad K_{HE} \tag{3}$$

TABLE I
RATIO OF ENOL TO KETO TAUTOMER, EQUILIBRIUM CONSTANTS, AND RATE CONSTANTS FOR THE ACETYLACETONE SYSTEM AT 25° AND 1.0 M IONIC STRENGTH

[HE]/[HK]	0.13[a]
K_{HA}, M	1.0×10^{-9} [b]
K_{HK}, M	1.1×10^{-9} [c]
K_{HE}, M	8.6×10^{-9} [c]
k_e, sec^{-1}	$(1.5 \pm 0.1) \times 10^{-2}$ [a]
k_f, sec^{-1}	0.114 ± 0.008[a]

[a] Value obtained in this work. [b] Reference 4. [c] Value calculated from $1/K_{HA} = 1/K_{HK} + 1/K_{HE}$ and K_{HK}/K_{HE} = [HE]/[HK].

In contrast to thenoyltrifluoroacetone, the keto form as well as the enol form of acetylacetone undergoes reaction with iron(III). A similar situation also obtains in the reaction of acetylacetone with copper(II).[5] The rate law for the reaction of acetylacetone with iron(III) also contains the rate constant for the conversion of the keto form of the diketone to the enol form. The enolization of acetylacetone does not proceed by the direct transfer of a proton from carbon to oxygen. Instead the enolate ion is formed as an intermediate with $k_c \approx 3 \times 10^{10}$ M^{-1} sec^{-1} and $k_c \gg k_b$.[6-10] Although the rate constant for the keto–enol conversion of acetylacetone has been previously measured, we have determined its value under the conditions used in this study.

$$HK \underset{k_b}{\overset{k_a}{\rightleftharpoons}} H^+ + E^- \underset{k_d}{\overset{k_c}{\rightleftharpoons}} HE \tag{4}$$

As mentioned above, we have previously studied the kinetics of the reaction of iron(III) and copper(II) with thenoyltrifluoroacetone. The rate constants for the reactions of Fe^{3+} and $FeOH^{2+}$ with the undissociated enol form of thenoyltrifluoroacetone are 1.4 and 1.3×10^3 M^{-1} sec^{-1}, respectively, at 25° and 1.0 M ionic strength.[2] Under these conditions the rate constant for the reaction of Cu^{2+} with the enolate ion of thenoyl-

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trifluoroacetone is $\geqslant 3 \times 10^6\ M^{-1}\ \text{sec}^{-1}$. It was of interest to determine whether the rate of formation of the iron(III) complex would be catalyzed by the more labile copper(II) system. This type of catalysis has been observed in the nickel(II)–EDTA–copper(II) and related systems.[11]

Experimental Section

Materials.—The preparation and standardization of the iron(III) perchlorate, copper(II) perchlorate, and lithium perchlorate solutions have been previously described.[2] Quadruply distilled water[2] was used to prepare all the solutions. Acetylacetone (Aldrich Chemical Co., Puriss. 99+%) was redistilled through a 20-plate Oldershaw column and the purity of the distillate (bp 133°) was checked by gas chromatography. Stock solutions were prepared by weighing portions of acetylacetone in volumetric flasks. Stock solutions of thenoyltrifluoroacetone were prepared by stirring an aqueous suspension of the vacuum-sublimed solid for about 36 hr. The solutions were filtered and the filtrates stored in "low actinic" glass volumetric flasks. The concentrations of these solutions (approximately 0.030 M) were determined by measurement of their absorbances at 266.5 nm (ϵ 10,080). The bromine solutions used to study the tautomerization reaction contained 10^{-3} M bromide to suppress the hydrolysis of the bromine and were restandardized spectrophotometrically prior to each run.

Tautomerization Reaction.—The method of determining the rates of tautomerization has been previously described.[2] The range of concentrations used in the acetylacetone system was $[\text{HAA}] = (1\text{–}10) \times 10^{-2}\ M$, $[\text{Br}_2] = (0.3\text{–}1.7) \times 10^{-2}\ M$, $[\text{H}^+] = 0.01\text{–}1.00\ M$, and 0.01–1.0 M ionic strength. The bromination of acetylacetone was studied on a stopped-flow apparatus.[12] The rate of ketonization of acetylacetone was studied by adjusting the pH of solutions of the diketone to ~10 and mixing these solutions (which contained appreciable concentrations of the enolate form of the diketone) with 1.0 or 0.10 M perchloric acid on the stopped-flow apparatus, both solutions being 1.0 M in ionic strength. The enolate ion was very rapidly converted to the enol form after mixing the two solutions (*cf.* eq 4 with $k_c \gg k_b$) and the subsequent slow conversion of the enol to the keto tautomer could readily be followed at 292 nm. The rate constant k_f was obtained from the first-order plots of these absorbance changes.

Equilibrium Measurements.—The overall equilibrium constant, K_1, for the reaction

$$\text{Fe}^{3+} + \text{HAA} \rightleftharpoons \text{FeE}^{2+} + \text{H}^+ \quad K_1 \tag{5}$$

was determined by spectrophotometric measurement of the amount of complex existing in equilibrium with the free metal ion and free ligand. Provided that $[\text{H}^+] \gg [\text{Fe(III)}]$, it can be shown[2] that

$$\frac{[\text{Fe(III)}][\text{HAA}]_0}{A[\text{H}^+]h} = \frac{[\text{Fe(III)}] + [\text{HAA}]_0}{\epsilon_1[\text{H}^+]h} + \frac{1}{\epsilon_1 K_1} \tag{6}$$

where $h = (1 + K_h/[\text{H}^+])$, K_h is the hydrolysis constant of iron(III)[13] (1.65×10^{-3} M at 1.0 M ionic strength), K_1 is the equilibrium constant for eq 5, and a second-order term in A/ϵ_1 has been neglected. Hence a plot of the left-hand side of eq 6 *vs.* $([\text{Fe(III)}] + [\text{HAA}]_0)/[\text{H}^+]h$ should yield a straight line with a slope $1/\epsilon_1$ and an intercept $1/\epsilon_1 K_1$.

Complexation Reactions.—The formation of the iron(III) acetylacetonate complex was studied on a Cary 14 recording spectrophotometer using a specially constructed 10-cm stirred cell, similar in design to that of Newton and Baker.[14] Essentially the design was an ordinary 10-cm cylindrical quartz cell to which was added a beaker-shaped compartment on the bottom center of the cell, directly under the inlet port, capable of containing a 0.5-in. long Teflon-coated stirring bar. A new thermostated cell holder was built to accommodate the cell and a magnetic stirrer was placed inside the cell compartment below the cell holder. The total volume of the cell was ~37 ml and mixing times were <2.5 sec. The formation of the iron(III) complex was followed by measuring the increase in absorbance at 492 nm after spiking the iron(III) solution with acetylacetone, both solutions containing the same acid concentration. The spike was introduced into the vortex of the stirred solution. The concentration of metal ion was always kept in large excess over the β-diketone to ensure formation of only the mono complex.

The rate of the reaction between iron(III) and thenoyltrifluoroacetone was determined similarly. The absorbance at 520 nm (which is an absorbance maximum of the iron(III) complex, ϵ 1180 ± 60)[2] of solutions containing the reactants was measured as a function of time on a Cary 16K or a Cary 14 spectrophotometer. The runs on the Cary 16K spectrophotometer used 1-cm absorption cells containing 3-ml samples of the appropriate solution of iron(III), copper(II), perchloric acid, and lithium perchlorate. The runs were initiated by spiking these solutions with the HTTA solution. Alternatively, in certain runs the cell contained copper(II), perchloric acid, lithium perchlorate, and HTTA and was spiked with iron(III) solution. No significant difference ascribable to the order of mixing the reactants was observed. Runs in which the absorbance changes were relatively small were carried out on the Cary 14 spectrophotometer using the 10-cm stirred cell described above. All of the reactions were studied at 25° and 1.0 M ionic strength.

Results

Tautomerization Reactions.—The value of k_e for acetylacetone determined in this work is $(1.5 \pm 0.1) \times 10^{-2}\ \text{sec}^{-1}$. This rate constant is independent of acidity in the range 0.01–1.0 M at constant ionic strength and is in good agreement with the value determined earlier under different conditions.[6-8] The observed rate constant in the ketonization experiments measures the rate of approach to equilibrium in the system and is equal to $k_e + k_f$. The value of k_f calculated from the observed rate constant using the k_e value presented above is $0.114 \pm 0.008\ \text{sec}^{-1}$ at 25°. This rate constant is independent of acidity in the range 0.05–0.50 M at a constant ionic strength of 1.0 M.

The ratio k_e/k_f is equal to the ratio of the enol to the keto tautomer present in the diketone. This study gives $[\text{HE}]/[\text{HK}] = 0.13$ for acetylacetone at 1.0 M ionic strength. This ratio corresponds to a smaller percentage of the enol form than has been previously reported based on the use of a bromination procedure.[6,7] Errors in the latter procedure may arise from uncertainties in the mixing and the keto–enol equilibrium may not have been completely frozen during the reaction of bromine with the enol form. It may be noted that although k_e for acetylacetone does not seem to depend markedly on ionic strength, k_f decreases to 0.090 ± 0.006 when the ionic strength is lowered from 1.0 to 0.01 M. Thus $[\text{HE}]/[\text{HK}] = 0.17$ for acetylacetone at 0.01 M ionic strength and 25°. A similar shift in the keto–enol equilibrium of acetylacetone with decreasing perchlorate concentration has been previously noted.[4]

Equilibrium Measurements.—A plot of the left-hand side of eq 6 *vs.* $([\text{Fe(III)}] + [\text{HAA}]_0)/[\text{H}^+]h$ for the iron(III)–acetylacetone system (Table II) is shown in Figure 1. The slope and intercept of the straight line give $\epsilon_1 = 780 \pm 50\ M^{-1}\ \text{cm}^{-1}$ at 492 nm and $K_1 = 32 \pm 3$. K_1 can be partitioned between the equilibrium constants, K_K and K_E, for reactions 7 and 8 by employing eq 9 and remembering that $1/K_1 = 1/K_K + 1/K_E$. This procedure gives $K_K = 36$ and $K_E = 2.7 \times 10^2$ for the iron(III)–HAA system. The value of K_1 for FeE^{2+}

$$\text{Fe}^{3+} + \text{HK} \rightleftharpoons \text{FeE}^{2+} + \text{H}^+ \quad K_K \tag{7}$$

$$\text{Fe}^{3+} + \text{HE} \rightleftharpoons \text{FeE}^{2+} + \text{H}^+ \quad K_E \tag{8}$$

$$\frac{K_K}{K_E} = \frac{[\text{HE}]}{[\text{HK}]} = \frac{k_e}{k_f} \tag{9}$$

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TABLE II
SPECTROPHOTOMETRIC AND KINETIC DATA FOR THE IRON(III)–ACETYLACETONE SYSTEM AT 25° AND 1.0 *M* IONIC STRENGTH[a]

$[H^+]$, *M*	$10^3[Fe(III)]$, *M*	$10^5[HAA]$, *M*	10^2A^b	10^2k_{obsd}, sec^{-1}
1.00	332	5.74	4.04	16.4[c]
1.00	83.0	5.74	3.20	4.65[d]
1.00	41.5	5.74	2.46	3.92[e]
1.00	33.2	5.74	2.22	3.52[f]
1.00	9.95	5.74	1.04	3.38
1.00	6.64	5.74	0.760	3.57
1.00	3.32	5.74	0.422	3.63
1.00	1.66	5.74	0.212	3.65
1.00	1.33	5.74	0.182	3.63
0.50	166	1.67	1.20	5.59
0.50	33.2	1.67	0.893	2.84
0.50	8.30	1.67	0.443	2.83
0.50	4.15	1.67	0.274	2.89
0.50	3.31	1.67	0.452	2.96
0.50	1.66	1.67	0.233	2.86
0.50	0.993	1.67	0.152	2.95
0.10	33.2	1.71	1.24	2.75
0.10	6.64	1.71	0.931	2.03
0.10	3.32	1.71	0.688	1.95
0.10	1.66	1.71	0.473	2.01
0.10	0.996	1.71	0.338	2.03
0.10	0.664	1.71	0.217	2.49
0.10	0.495	1.71	0.171	2.14
0.10	0.390	1.71	0.159	2.33
0.10	0.332	1.71	0.124	2.63

[a] The ionic strength at the high iron(III) concentrations was not maintained constant but varied as the concentration of iron(III). [b] Average value for three determinations corrected for 9.89-cm cell. [c] Ionic strength 3.00 *M*. [d] Ionic strength 1.50 *M*. [e] Ionic strength 1.25 *M*. [f] Ionic strength 1.20 *M*.

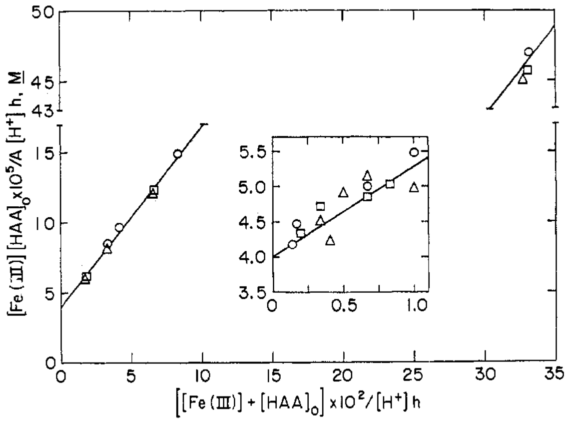
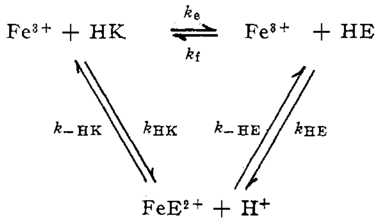


Figure 1.—Plot, suggested by eq 6, for the determination of K_1 for the formation of $FeAA^{2+}$ at λ 492 nm, 25°, and 1.0 *M* ionic strength: circles, $[H^+] = 1.00$ *M;* squares, $[H^+] = 0.50$ *M;* triangles, $[H^+] = 0.10$ *M*.

determined in this work is in satisfactory agreement with the value reported by Zebroski.[15]

Kinetic Measurements.—The reaction between iron(III) and acetylacetone proceeds in more than one stage. A fast stage was clearly evident when the reaction was examined on a stopped-flow apparatus. This stage, which presumably corresponds, for the most part, to the reaction of iron(III) with the enol form of the diketone, was not studied in detail. Instead, we focused our attention on the slowest stage, which corresponds to the major part of the reaction and which could be conveniently followed on a Cary 14 recording spectrophotometer. The observed rate constants reported in Table II refer to this reaction. The kinetic data for the iron(III)–acetylacetone system are consistent with the scheme



(10)

The large excess of iron(III) and hydrogen ions with respect to the ligand ensured pseudo-first-order conditions. The method of secular equations was used to solve this system.[5,16] In terms of this scheme the rate constant for the slow reaction is given by

$$k_{obsd} = \frac{[Fe^{3+}](A + k_{HE}k_{HK}[Fe^{3+}])[1 + ([H^+]/[Fe^{3+}])(1/K_K + 1/K_E)]}{B[H^+] + (k_e + k_f) + (k_{HE} + k_{HK})[Fe^{3+}]} \tag{11}$$

where $A = k_e k_{HE} + k_f k_{HK}$ and $B = k_{HE}/K_E + k_{HK}/K_K$. If the reaction with the keto tautomer may be neglected and if k_e is neglected compared to k_f, then eq 11 reduces to eq 12, which is identical with the rate expression which describes the thenoyltrifluoroacetone systems.[2]

$$\frac{1 + [H^+]/K_K[Fe^{3+}]}{k_{obsd}} = \frac{1}{k_e} + \left(\frac{k_f}{k_e k_{HE}} + \frac{[H^+]}{k_e K_E}\right)\frac{1}{[Fe^{3+}]} \tag{12}$$

A plot of the left-hand side of eq 12 *vs.* $1/[Fe^{3+}]$ is shown in Figure 2. If the assumptions made above are valid, then a series of straight lines with a common intercept of $1/k_e$ should be obtained. Evidently this is not the case.[17] However, it is apparent from Figure 2 that the kinetic data tend to obey eq 12 at low iron(III) concentrations. The limiting slopes, *S*, at low $[Fe^{3+}]$ were obtained from this figure. According to eq 12 these limiting slopes are given by eq 13. If it is as-

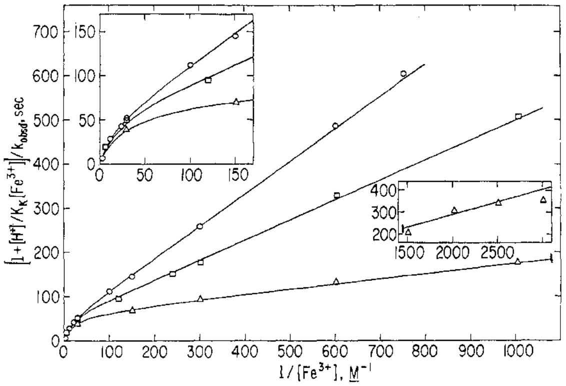


Figure 2.—Plot, suggested by eq 12, of $[1 + [H^+]/K_K[Fe^{3+}]]/k_{obsd}$ as a function of $1/[Fe^{3+}]$ for the reaction $Fe^{3+} + HAA \rightleftharpoons FeAA^{2+} + H^+$, at λ 492 nm, 25°, and 1.0 *M* ionic strength: circles, $[H^+] = 1.00$ *M;* squares, $[H^+] = 0.50$ *M;* triangles, $[H^+] = 0.10$ *M*.

$$S = k_f/k_e k_{HE} + [H^+]/k_e K_E \tag{13}$$

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[15] E. Zebroski, University of California Lawrence Radiation Laboratory Report BC-63 (1947); Ph.D. Thesis, University of California, 1947.

[16] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1963, pp 173–177.

[17] It should be noted that because of the symmetry of eq 11 an equation analogous to eq 12 is obtained when reaction with the enol form is neglected and it is assumed instead that reaction proceeds entirely through the keto form of acetylacetone.

sumed, as has been found for the thenoyltrifluoroacetone system, that k_{HE} is acid dependent and is given by eq 14, then estimates of a and b can be obtained from

$$k_{\mathrm{HE}} = a + b/[\mathrm{H}^+] \qquad (14)$$

the intercept and slope, respectively, of a plot of $1/(S - [\mathrm{H}^+]/k_e K_E)$ *vs.* $1/[\mathrm{H}^+]$. These values of a and b were then used to determine estimates of k_{HK} at each acidity using eq 11. This procedure showed that k_{HK} is of the form

$$k_{\mathrm{HK}} = c + d/[\mathrm{H}^+] \qquad (15)$$

Finally, the best fit of the data to eq 11 was determined by varying the values of a, b, c, and d independently. The lines in Figure 2 are the theoretical lines with $a = 5.16 \pm 0.05\ M^{-1}\ \mathrm{sec}^{-1}$, $b = 7.20 \pm 0.07\ \mathrm{sec}^{-1}$, $c = 0.29 \pm 0.01\ M^{-1}\ \mathrm{sec}^{-1}$, and $d = 0.009 \pm 0.001\ \mathrm{sec}^{-1}$.

The reaction of iron(III) with thenoyltrifluoroacetone in the presence of copper(II) also proceeds in more than one stage. Only the slowest stage (which is the predominant stage under all of the conditions used) was studied in detail, and the rate constants presented in Table III refer to this stage. The kinetic data are consistent with the scheme

$$\begin{array}{c} \mathrm{HK} \underset{k_f'}{\overset{k_e'}{\rightleftharpoons}} \mathrm{HE} \underset{k_{-\mathrm{HE}}'[\mathrm{H}^+]}{\overset{k_{\mathrm{HE}}'[\mathrm{Fe}^{3+}]}{\rightleftharpoons}} \mathrm{FeE}^{2+} \\ \mathrm{H}^+ \upharpoonleft\!\downharpoonright \mathrm{Cu}^{2+} \\ \mathrm{CuE}^+ \underset{k_{-\mathrm{CuE}}[\mathrm{Cu}^{2+}]}{\overset{k_{\mathrm{CuE}}[\mathrm{Fe}^{3+}]}{\rightleftharpoons}} \mathrm{FeE}^{2+} \end{array} \qquad (16)$$

TABLE III
KINETIC DATA FOR THE REACTION OF IRON(III) WITH THENOYLTRIFLUOROACETONE IN THE PRESENCE OF COPPER(II) AT 25° AND 1.0 M IONIC STRENGTH

$[\mathrm{H}^+]$, M	$10^3[\mathrm{Fe(III)}]$, M	$10^2[\mathrm{Cu}^{2+}]$, M	$10^3 k_{\mathrm{obsd}}$, sec^{-1}
0.582	27.9	2.56	3.83
0.582	27.9	4.78	4.08
0.581	27.9	7.87	4.53
0.388	27.9	2.55	3.94
0.388	27.9	4.78	4.41
0.388	27.9	7.97	5.06
0.194	27.9	2.56	4.55
0.194	27.9	4.78	5.48
0.194	27.9	7.97	6.38
0.200	2.86	8.17	5.44
0.200	4.76	8.17	5.58
0.200	9.53	8.17	5.88
0.200	19.0	8.17	6.25
0.150	6.00	4.63	4.97
0.149	4.76	4.91	4.89
0.151	6.00	7.72	5.96
0.149	4.76	8.17	6.71
0.150	6.00	15.5	10.1
0.149	4.76	16.3	10.3
0.100	6.00	4.63	5.98
0.099	4.76	4.91	6.11
0.100	6.00	7.72	8.11
0.099	4.76	8.17	8.09
0.100	6.00	15.5	12.4
0.099	4.76	16.3	12.8
0.090	0.96	2.68	4.17
0.090	0.91	2.68	4.17
0.090	0.91	5.02	5.68
0.090	0.91	5.02	6.03
0.090	0.91	5.02	5.97
0.090	0.91	16.7	14.2
0.090	0.91	16.7	14.4
0.051	6.00	4.63	8.85
0.050	4.76	4.91	8.91
0.050	6.00	7.72	11.1
0.050	4.76	8.17	11.2
0.050	6.00	15.5	13.3
0.050	4.76	16.3	13.4
0.050	4.76	16.3	13.1
0.030	0.96	2.68	8.91
0.030	0.96	2.68	8.35
0.030	0.96	5.02	12.0
0.030	0.96	5.02	12.0
0.010	0.96	2.68	12.5
0.010	0.96	2.68	13.1

If it is assumed that equilibrium between HE and CuE^+ is maintained throughout the course of the reaction,[2] then the above scheme leads to the following expression[5,16,18] for the rate constant for the slow reaction

$$k_{\mathrm{obsd}} = \frac{k_e'[\mathrm{Fe}^{3+}]\left(k_{\mathrm{HE}}' + K_{\mathrm{E}}^{\mathrm{Cu}} k_{\mathrm{CuE}} \dfrac{[\mathrm{Cu}^{2+}]}{[\mathrm{H}^+]}\right) C}{k_f' + [\mathrm{Fe}^{3+}]\left(k_{\mathrm{HE}}' + K_{\mathrm{E}}^{\mathrm{Cu}} k_{\mathrm{CuE}} \dfrac{[\mathrm{Cu}^{2+}]}{[\mathrm{H}^+]}\right) D} \qquad (17)$$

where

$$C = \left(1 + \frac{K_{\mathrm{K}}^{\mathrm{Cu}}[\mathrm{Cu}^{2+}]}{K_{\mathrm{K}}^{\mathrm{Fe}}[\mathrm{Fe}^{3+}]} + \frac{[\mathrm{H}^+]}{K_{\mathrm{K}}^{\mathrm{Fe}}[\mathrm{Fe}^{3+}]}\right)$$

$$D = \left(1 + \frac{K_{\mathrm{K}}^{\mathrm{Cu}}[\mathrm{Cu}^{2+}]}{K_{\mathrm{K}}^{\mathrm{Fe}}[\mathrm{Fe}^{3+}]} + \frac{[\mathrm{H}^+]}{K_{\mathrm{E}}^{\mathrm{Fe}}[\mathrm{Fe}^{3+}]}\right)$$

and $K_{\mathrm{E}}^{\mathrm{Fe}}$ is the equilibrium constant for reaction 8 (with HE representing the enol form of HTTA), $K_{\mathrm{K}}^{\mathrm{Fe}} = K_{\mathrm{E}}^{\mathrm{Fe}} k_e'/k_f'$, $K_{\mathrm{K}}^{\mathrm{Cu}} = K_{\mathrm{E}}^{\mathrm{Cu}} k_e'/k_f'$, and $K_{\mathrm{E}}^{\mathrm{Cu}}$ is the equilibrium constant for reaction 18. The values of k_e',

$$\mathrm{Cu}^{2+} + \mathrm{HE} \rightleftharpoons \mathrm{CuE}^+ + \mathrm{H}^+ \qquad (18)$$

k_f', and the various equilibrium constants have been previously determined.[2] It is apparent from eq 17 that

$$\frac{k_f'}{[\mathrm{Fe}^{3+}]\left(\dfrac{k_e' C}{k_{\mathrm{obsd}}} - D\right)} = k_{\mathrm{HE}}' + K_{\mathrm{E}}^{\mathrm{Cu}} k_{\mathrm{CuE}} \frac{[\mathrm{Cu}^{2+}]}{[\mathrm{H}^+]} \qquad (19)$$

and recalling that k_{HE}' is given by eq 14 (with $a = 1.4\ M^{-1}\ \mathrm{sec}^{-1}$ and $b = 2.3\ \mathrm{sec}^{-1}$)[2] it follows that

$$(W - a)[\mathrm{H}^+] = b + K_{\mathrm{E}}^{\mathrm{Cu}} g \frac{[\mathrm{Cu}^{2+}]}{[\mathrm{H}^+]} \qquad (20)$$

where W represents the left-hand side of eq 19 and it has been anticipated that k_{CuE} has an inverse acid dependence (*i.e.*, that $k_{\mathrm{CuE}} = g/[\mathrm{H}^+]$). Consequently the value of g can be determined from the slope of a plot of $(W - a)[\mathrm{H}^+]$ *vs.* $[\mathrm{Cu}^{2+}]/[\mathrm{H}^+]$. This plot is shown in Figure 3. It is evident that the data satisfy eq 20 reasonably well. The intercept of the plot is equal to 2.3 sec^{-1} within the experimental error of the measurements, and the value of g calculated from the slope of the plot is 0.24 sec^{-1}.

Discussion

The kinetics of the reaction of iron(III) with acetylacetone have previously been studied by Ong and Prince. They reported that at acidities below 0.1 M the observed rate constant for this reaction (in our notation) is given by eq 21 but that their data did not fit this

$$k_{\mathrm{obsd}} = k_e + k_{\mathrm{HK}}[\mathrm{Fe}^{3+}] \qquad (21)$$

equation at acidities greater than about 0.1 M. The reason for the breakdown of eq 21 at higher acidities can

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(18) It should be noted that when k_f' is the largest term in the denominator of eq 17, then eq 17 reduces to an expression which differs from the one derived by assuming that the keto–enol equilibrium obtains throughout the course of the reaction by a factor $1/(1 + K_{\mathrm{K}}^{\mathrm{Cu}}[\mathrm{Cu}^{2+}]/[\mathrm{H}^+])$. This factor (which is not present in the reduced form of eq 17) is 0.70 at the highest $[\mathrm{Cu}^{2+}]/[\mathrm{H}^+]$ ratio used and is close to unity under most of the conditions employed in this work (Figure 3).

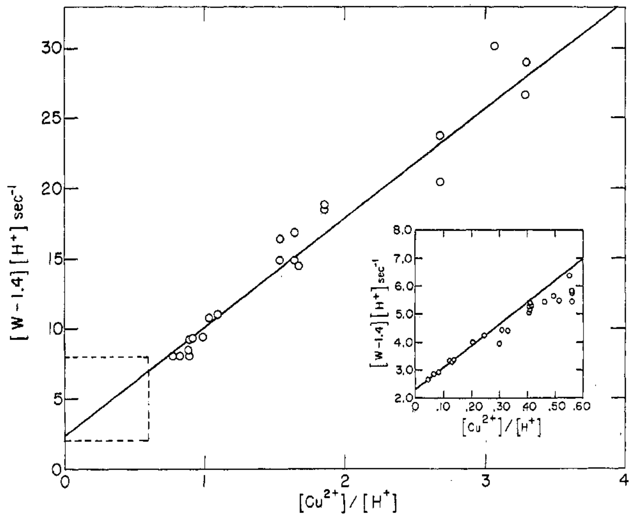

Figure 3.—Plot, suggested by eq 20, of $(W - a)[\mathrm{H}^+]$ as a function of $[\mathrm{Cu}^{2+}]/[\mathrm{H}^+]$ at λ 520 nm, 25°, and 1.0 M ionic strength.

be appreciated by comparing it with eq 11. The latter equation reduces to eq 21 when $1 \gg [\mathrm{H}^+]/K_{\mathrm{K}}[\mathrm{Fe}^{3+}]$ and $k_{\mathrm{HE}}[\mathrm{Fe}^{3+}] \gg k_{\mathrm{HK}}[\mathrm{Fe}^{3+}] + (k_{\mathrm{f}} + k_{\mathrm{e}})$. These conditions are satisfied when $[\mathrm{H}^+]/[\mathrm{Fe}^{3+}] \leq 3$ and they will tend to break down at high acidities and low iron(III) concentrations. The first condition is equivalent to assuming that the complex formation proceeds to completion (that is, that the back-reaction may be neglected) while the second condition implies that the rate of the reaction of iron(III) with the enol tautomer is controlled by the rate of the keto–enol conversion. In order to satisfy the second condition, Ong and Prince assumed that E^- reacted faster with Fe^{3+} than with H^+ and this led them to conclude that the rate constant for the reaction of Fe^{3+} with E^- is greater than 10^8 M^{-1} sec^{-1}. However it is unnecessary to assume that E^- reacts faster with Fe^{3+} than with H^+ in order to derive eq 21, for, as we have seen, the rate of reaction of Fe^{3+} with the enol tautomer can still be controlled by the rate of the keto–enol conversion if the reaction of Fe^{3+} (or FeOH^{2+}) with HE is sufficiently rapid (in other words, if $k_{\mathrm{HE}}[\mathrm{Fe}^{3+}] \gg k_{\mathrm{f}}$). In any event, the requirement that $[\mathrm{H}^+]/[\mathrm{Fe}^{3+}] \leq 3$ was satisfied under most of the conditions used by Ong and Prince and it is gratifying to find that the values of c and d obtained by them (0.29 M^{-1} sec^{-1} and 7×10^{-3} sec^{-1}, respectively, at 25° and 1.0 M ionic strength) are in good agreement with the values obtained in this work. Ong and Prince did not, of course, obtain values for the rate constants for the reaction of iron(III) with the enol tautomer of acetylacetone.

The conformity of our data to eq 11 indicates that the reaction of iron(III) with the keto and enol tautomers of acetylacetone proceeds *via* parallel acid-independent and acid-dependent paths. If these paths are ascribed to the reactions of Fe^{3+} and FeOH^{2+}, respectively (eq 22), then $a = k_2$, $b = k_3K_{\mathrm{h}}$, $c = k_1$, and $d =$

$$\mathrm{Fe}^{3+} + \mathrm{HK} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{FeE}^{2+} + \mathrm{H}^+ \tag{22a}$$

$$\mathrm{Fe}^{3+} + \mathrm{HE} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{FeE}^{2+} + \mathrm{H}^+ \tag{22b}$$

$$\mathrm{FeOH}^{2+} + \mathrm{HE} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{FeE}^{2+} \tag{22c}$$

$$\mathrm{FeOH}^{2+} + \mathrm{HK} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \mathrm{FeE}^{2+} \tag{22d}$$

k_4K_{h}. The kinetic data give $k_1 = 0.29$ M^{-1} sec^{-1}, $k_2 = 5.2$ M^{-1} sec^{-1}, $k_3 = 4.4 \times 10^3$ M^{-1} sec^{-1}, and $k_4 = 5.4$ M^{-1} sec^{-1}. If instead of eq 22c the inverse acid path for the reaction of the enol tautomer with iron(III) is interpreted to be

$$\mathrm{Fe}^{3+} + \mathrm{E}^- \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} \mathrm{FeE}^{2+} \tag{23}$$

then $b = k_5K_{\mathrm{HE}}$ provided the equilibrium between HE and E^- is maintained. This procedure gives $k_5 = 8 \times 10^8$ M^{-1} sec^{-1}. This value is very much larger than the rate constants for complex formation of Fe^{3+} with other singly charged anions[19] and indicates that the reactants in the inverse acid path are correctly formulated as FeOH^{2+} and HE.

The reactions of HE will be considered first. The rate constant for the reaction of Fe^{3+} with HE (5.2 M^{-1} sec^{-1}) may be compared with the rate constants for the reaction of Fe^{3+} with the neutral ligands HN_3 (2.6 M^{-1} sec^{-1}) and HF (11.4 M^{-1} sec^{-1}).[19,20] This comparison suggests that the rate constant for the reaction of Fe^{3+} with HE is "normal." The value of the ratio k_3/k_2 too is close to normal for substitution on iron(III).[19] These reactions thus do not appear to feature a sterically controlled substitution mechanism for according to this mechanism the closing of six-membered chelate rings is, in general, sterically hindered, and reactions in which six-membered chelate rings are formed should as a consequence proceed relatively slowly.[21] However, it should be borne in mind that there is some uncertainty as to the magnitudes of rate constants for "normal" substitution on iron(III) and that the relatively slow iron(III) reactions are, in general, not particularly good candidates for a sterically controlled substitution mechanism.[2]

The sterically controlled substitution mechanism has been invoked to explain the slow rate of the reaction of copper(II) with the enol tautomer of acetylacetone.[5] If it is assumed that half-bonded intermediates are formed in these reactions,[2] then the relatively slow rate of the copper(II) reaction indicates that the intermediate formed in the copper(II) system dissociates into the reactants more rapidly than it undergoes ring closure to form the six-membered chelate. By contrast, the results indicate that ring closure of the intermediate formed in the iron(III) systems occurs more rapidly than its dissociation into reactants. This difference in the behavior of the two intermediates is perhaps not too surprising for copper(II) complexes are generally much more labile than iron(III) complexes. The reactions of protonated multidentate ligands must be interpreted with care for there are at least three factors that can give rise to slow rates in these systems: (a) relatively strong intramolecular hydrogen bonds which may convert the protonated ligand into a poor entering group, (b) the energetics of the proton release from the monodentate intermediate which may slow down the

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[19] D. Seewald and N. Sutin, *Inorg. Chem.*, **2**, 643 (1963).

[20] D. W. Carlyle and J. H. Espenson, *ibid.*, **6**, 1370 (1967).

[21] K. Kustin and R. F. Pasternack, *J. Amer. Chem. Soc.*, **90**, 2805 (1968).

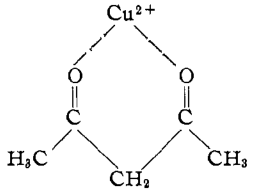
rate of ring closure to form the chelate (a proton-controlled ring-closure mechanism), and (c) ring strain associated with the formation of the six-membered chelate which may also slow down the rate of ring closure (the sterically controlled ring-closure mechanism). It is difficult to distinguish between these factors in a given system unless kinetic data on the reactions of the corresponding deprotonated ligands are also available. The magnitude of the rate constant for the reaction of Cu^{2+} with the enolate ion of thenoyltrifluoroacetone (Table IV) suggests that steric control of the ring closure is not very important in this system.

TABLE IV
COMPARISON OF RATE CONSTANTS FOR THE REACTION OF ACETYLACETONE AND THENOYLTRIFLUOROACETONE WITH IRON(III) AND COPPER(II) AT 25° AND 1.0 *M* IONIC STRENGTH

Reaction	k, M^{-1} sec^{-1}	Ref
(I) Thenoyltrifluoroacetone System		
$Fe^{3+} + HE$	1.4	*a*
$FeOH^{2+} + HE$	1.3×10^3	*a*
$Cu^{2+} + E^-$	$\geq 3 \times 10^6$	*a*
(II) Acetylacetone System		
$Cu^{2+} + HE$	2×10^4	*b, c*
$Cu^{2+} + HK$	15	*b*
$Fe^{3+} + HE$	5.2	*d*
$Fe^{3+} + HK$	0.29	*d*
$FeOH^{2+} + HE$	4.4×10^3	*d*
$FeOH^{2+} + HK$	5.4	*d*
$Cu^{2+} + E^-$	$\leq 2 \times 10^8$	*e*

[a] Reference 2. [b] Reference 5. [c] Ionic strength 0.1 *M*. [d] This work. [e] Estimated in ref 2 from the data reported in ref 5. The value of 4×10^4 M^{-1} sec^{-1} presented in ref 5 for the upper limit of the rate constant for the reaction between copper(II) and the enolate ion is a misprint (personal communication from R. G. Pearson to N. Sutin).

It is apparent from Table IV that Fe^{3+} and $FeOH^{2+}$ react about 3–4 times faster with the enol form of acetylacetone than with the enol form of thenoyltrifluoroacetone. These iron(III) ions (and copper(II)) also react with the keto form of acetylacetone whereas the keto form of thenoyltrifluoroacetone is relatively unreactive.[2] The unreactivity of the keto tautomer of thenoyltrifluoroacetone may be related to its unsymmetrical hydrate structure.[2] It has been proposed[5] that the first step in the reaction between copper(II) and the keto tautomer of acetylacetone involves the formation of a symmetrical precursor complex in which the metal ion is bonded to both keto groups. In terms of this mechanism the cupric ion acts as an electron sink and the rate-determining step involves the slow, metal ion catalyzed proton release from the three-carbon acid. To some extent the results of this study are consistent with this interpretation. Thus the reactions of Fe^{3+} and $FeOH^{2+}$ with HK are certainly too slow for water release from the metal ions to be rate determining. Moreover, the value of the ratio k_4/k_1 is only about 20, in contrast to the value of k_3/k_2 which is about 10^3 and which, as we have seen, is close to normal for substitution on iron(III). This effect is even more dramatic when the rate constants for the reactions of Fe^{3+} and Cu^{2+} with HK are compared; instead of the customary factor of $\sim 10^5$, these rate constants differ only be a factor of 10^2. These comparisons thus provide further support for the view that water release is not rate determining in these reactions. However, the pure electrostatic picture predicts a larger value of k_{HK} for the Fe^{3+} than for the Cu^{2+} (or $FeOH^{2+}$) reaction, but this is not observed. It may be concluded that other factors, such as the stability of the precursor complexes, are also important in determining the rate of the reaction of the keto tautomer of acetylacetone.



The reaction of iron(II) with $CuTTA^+$ proceeds predominantly by an inverse acid path. This type of acid dependence suggests that the iron(III) reactant is $FeOH^{2+}$ and thus that $g = k_6K_h$, where k_6 is defined by eq 24. The kinetic data give $k_6 = 1.5 \times 10^2$ M^{-1} sec^{-1}. Although this rate constant is of a reasonable magnitude for the replacement of a coordinated water molecule on $FeOH^{2+}$ by a 1+ ion, reaction 24 very probably takes place in a number of steps. The first step in this process could be the rapid opening of the $CuTTA^+$ chelate ring to form a half-bonded intermediate, and this (preequilibrium) step could then be followed by the rate-determining reaction of $FeOH^{2+}$ with the half-bonded intermediate

$$FeOH^{2+} + CuTTA^+ \xrightarrow{k_6} \text{products} \qquad (24)$$

$$CuTTA^+ \rightleftharpoons (CuTTA\text{-})^+ \qquad (25a)$$

$$FeOH^{2+} + (CuTTA\text{-})^+ \longrightarrow OHFeTTACu^{3+} \qquad (25b)$$

In terms of this interpretation the reaction proceeds *via* an intermediate in which $FeOH^{2+}$ is attached to the one oxygen atom and Cu^{2+} to the other oxygen atom of the diketone. The reaction is consummated by the closing of the chelate ring after the rapid dissociation of Cu^{2+} from the dinuclear intermediate.

Finally, it is interesting to note that the catalysis of the formation of $FeTTA^{2+}$ by the added Cu^{2+} arises from both thermodynamic and kinetic factors. Thus it is apparent from eq 17 that, provided the reaction is not controlled by the rate of the keto–enol tautomerism, k_{obsd} will be increased by the addition of Cu^{2+} ions even if k_{CuE} were equal to zero. This is due to the fact that the observed rate constants measure the rate of approach to equilibrium in the system and the position of this equilibrium is shifted by the addition of Cu^{2+} ions. The kinetic contribution to the catalysis is, of course, reflected in k_{CuE}. It may be noted that the rate constant for the reaction of $FeOH^{2+}$ with $CuTTA^+$ (1.5×10^2 M^{-1} sec^{-1}) is actually less than the rate constant for the reaction of $FeOH^{2+}$ with the enol tautomer of HTTA (4.4×10^3 M^{-1} sec^{-1}). The kinetic contribution to the Cu^{2+} catalysis is evidently due to the fact that $CuTTA^+$ is more reactive than the keto tautomer of HTTA toward $FeOH^{2+}$. Put somewhat differently, the added Cu^{2+} converts part of the unreactive keto tautomer of HTTA (which is present in large excess over the enol tautomer) into $CuTTA^+$ which undergoes reaction with $FeOH^{2+}$ more rapidly than does the keto tautomer but less rapidly than does the enol tautomer.