Kinetics and Mechanism of the Formation of the Monothenoyltrifluoroacetone Complexes of Nickel(II), Cobalt(II), Copper(II), and Iron(III)[1a]

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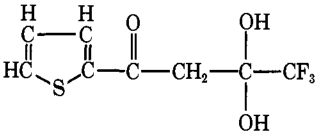
Abstract: The kinetics of the reaction of thenoyltrifluoroacetone with nickel(II), cobalt(II), copper(II), and iron(III) to form the mono complexes have been studied at 25° and 1.0 *M* ionic strength by conventional and stopped-flow spectrophotometry. The keto form of thenoyltrifluoroacetone does not react with the metal ions, while the enol form reacts by parallel acid-independent and inverse-acid paths. The rate constants for the reaction of HE, the undissociated enol form, with Ni^{2+}, Fe^{3+}, and $FeOH^{2+}$ are 2.3, 1.4, and $1.3 \times 10^3\ M^{-1}\ sec^{-1}$, respectively, and the rate constants for the reaction of E^-, the enolate ion, with Ni^{2+}, Co^{2+}, and Cu^{2+} are 1.0×10^4, $\geqslant 3 \times 10^4$, and $\geqslant 3 \times 10^6\ M^{-1}\ sec^{-1}$, respectively. The rate constants, k_e and k_f, for the keto–enol tautomerism of thenoyltrifluoroacetone defined by keto $\rightleftharpoons$ enol (k_e, forward; k_f, reverse) are 8.4×10^{-3} and $1.90\ sec^{-1}$, respectively. The kinetics of the complex formation reactions are discussed in terms of a sterically controlled substitution mechanism and in terms of a mechanism in which proton loss from the ligand is an important rate-determining factor. The values of the equilibrium constants, K_1, for the reaction $M^{n+} + HA \rightleftharpoons ME^{(n-1)+} + H^+$, where HA represents the undissociated thenoyltrifluoroacetone, were found to be 8.4×10^{-3}, 1.4×10^{-3}, 0.14, and 4.5 at 25° and 1.0 *M* ionic strength for the nickel(II), cobalt(II), copper(II), and iron(III) systems, respectively.

Several recent papers have reported the results of studies on the formation of the 1:1 complexes of various metal ions with β-diketones. Among them have been the reactions of 2-thenoyltrifluoroacetone and acetylacetone with various members of the first-row transition metal series.[2-8] The usual mechanism of complex formation for metal ions of the first transition series is believed to involve the loss of a water molecule from the metal ion as the rate-determining step. Indeed, in many cases the rates of complex formation are found to parallel the water-exchange rates of the metal ions.

The reactions of metal ions with β-diketones offer two additional possibilities for the rate-determining step. Mechanisms have been proposed which try to account for the observed rates in terms of (a) the rate of ionization of the β-diketone,[2-5] and (b) the sterically hindered closure of the chelate ring.[6] For the reactions with acetylacetone an additional reaction path which involves the slow metal-catalyzed proton loss from the keto tautomer has been postulated.[5,6] In an attempt to correlate these data and to compare the effects of varying the metal ion and the β-diketone on the rate of the complex formation, we have investigated the reactions of nickel(II), cobalt(II), copper(II), and iron(III) with 2-thenoyltrifluoroacetone (HTTA). Our measurements on the copper(II) and iron(III) reactions are, in part, an extension of earlier work[2,5,7,8] on these systems. However, we present additional kinetic data and a more detailed mechanism for the reactions involved in the complex formation than was considered by earlier workers.

The predominant species in aqueous solutions of 2-thenoyltrifluoroacetone is the keto hydrate I. No evidence has been obtained for the existence of significant concentrations of an "unhydrated" keto form in aqueous solution. The enol form of 2-thenoyltrifluoroacetone is shown in structure II. Since the percentage of the enol tautomer present in solutions of the diketone is known and the overall ionization constant for reaction 1 has been measured, the equilibrium constants for reactions 2 and 3 can be calculated. In these reactions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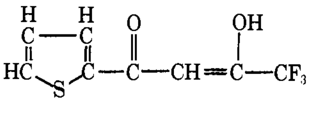
II

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

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

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

$[HA] = [HK] + [HE]$ 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 2-thenoyltrifluoroacetone are summarized in Table I.

The rate law for the reaction of thenoyltrifluoroacetone with the metal ions contains the rate constant for the conversion of the keto form of the diketone to the enol form. Although this rate constant has been previously measured, we thought it desirable to determine its value under the conditions used in this study.

Experimental Section

Materials. The perchlorates of iron(III) and copper(II) were recrystallized from perchloric acid and the cobalt(II) and nickel(II)

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(2) R. W. Taft, Jr., and E. H. Cook, *J. Amer. Chem. Soc.*, **81**, 46 (1959).

(3) A. V. Celiano, M. Cefola, and P. S. Gentile, *J. Phys. Chem.*, **65**, 2194 (1961).

(4) A. V. Celiano, M. Cefola, and P. S. Gentile, *ibid.*, **66**, 1132 (1962).

(5) W. K. Ong and R. H. Prince, *J. Chem. Soc. A*, 458 (1966).

(6) R. G. Pearson and O. P. Anderson, *Inorg. Chem.*, **9**, 39 (1970).

(7) A. Adin and L. Newman, *J. Inorg. Nucl. Chem.*, **32**, 3321 (1970).

(8) E. Zebroski, AEC Report No. BC-63, 1947; Ph.D. Thesis, University of California, 1947.

Table I. Ratio of Enol/Keto Tautomer, Equilibrium Constants, and Rate Constants for the Thenoyltrifluoroacetone System at 25° and 1.0 M Ionic Strength

[HE]/[HK]	4.4×10^{-3} [a]
K_{HA}, M	4.2×10^{-7} [b]
K_{HK}, M	4.2×10^{-7} [c]
K_{HE}, M	9.6×10^{-5} [c]
k_e, sec^{-1}	$(8.4 \pm 0.3) \times 10^{-3}$ [a]
k_f, sec^{-1}	1.90 ± 0.06[a]

[a] Value obtained in this work. [b] E. H. Cook and R. W. Taft, Jr., *J. Amer. Chem. Soc.*, **74**, 6103 (1952); ionic strength $\simeq 10^{-2}$ M. [c] Value calculated from $1/K_{HA} = 1/K_{HK} + 1/K_{HE}$ and K_{HK}/K_{HE} = [HE]/[HK].

perchlorates were recrystallized twice from water. Stock solutions 0.72 M in iron(III) perchlorate and 3.6 M in perchloric acid, 0.34 M in copper(II) perchlorate and 5.2×10^{-3} M in perchloric acid, and 0.27 M in cobalt(II) perchlorate and 0.48 M in nickel(II) perchlorate were prepared from the recrystallized salts. These stock solutions were standardized as follows: the iron(III) concentration was determined by titration with cerium(IV) after reduction to iron(II) with a Jones reductor, the copper(II) concentration was determined by titration with EDTA to a SNAZOXS[9] end point, and the cobalt(II) concentration was determined by addition of excess EDTA and back-titration with standard zinc(II). The nickel(II) was determined gravimetrically and spectrophotometrically as the dimethylglyoxime complex, as well as by passing an aliquot through a Dowex 50-W ion-exchange column in the hydrogen ion form, and titrating the effluent with standard sodium hydroxide. The perchloric acid concentration in the iron(III) stock solution was determined in a similar manner by ion exchange. In this case, however, the total acidity was corrected for the amount of acid liberated by exchange with the iron(III) ions. The acidity of the copper(II) stock solution was determined by titration. A stock solution of lithium perchlorate was prepared by dissolving lithium carbonate in perchloric acid. The solid lithium perchlorate obtained upon cooling was recrystallized twice from water and redissolved; the pH of the resulting solution was adjusted to ~5. A stock solution of sodium perchlorate was prepared by an identical procedure. The concentrations of the lithium perchlorate (3.7 M) and of the sodium perchlorate (7.4 M) stock solutions were determined gravimetrically after evaporation. Quadruply distilled water, distilled water purified by redistillation from acid dichromate followed by a distillation from alkaline permanganate and a final redistillation, was used to prepare all of the solutions.

Stock solutions of thenoyltrifluoroacetone were prepared by placing weighed amounts of the vacuum-sublimed solid (mp 42.9–44°) into volumetric flasks.[10] The bromine solutions contained 10^{-3} M bromide to suppress the hydrolysis of the bromine and were restandardized prior to each run.

Tautomerization Reactions. The rate of enolization of thenoyltrifluoroacetone, eq 4, was studied by a bromination procedure. Provided that the reaction of Br_2 (or Br_3^-) with HE or E^- is sufficiently rapid, the bromination will reach a limiting rate given by eq 5. Under these conditions the concentration of HK is given by eq 6, where A is the optical density at time t due to the absorbance of bromine at 452 nm, ϵ_{Br} is the molar absorptivity of bromine at 452 nm, l is the path length of the observation cell, a = [HTTA]$_0$, and b = [Br$_2$]$_0$. Consequently k_e can be calculated from eq 7.

$$\mathrm{HK} \underset{k_f}{\overset{k_e}{\rightleftharpoons}} \mathrm{HE} \tag{4}$$

$$-\mathrm{d}[\mathrm{Br_2}]/\mathrm{d}t = -\mathrm{d}[\mathrm{HK}]/\mathrm{d}t = k_e[\mathrm{HK}] \tag{5}$$

$$[\mathrm{HK}] = A/\epsilon_{Br}l + (a - b) \tag{6}$$

$$-\frac{\mathrm{d}A}{\epsilon_{Br}l\,\mathrm{d}t} = k_e\left[\frac{A}{\epsilon_{Br}l} + (a - b)\right] \tag{7}$$

The β-diketone was always present in excess and the course of the reaction was followed on a Cary 14 recording spectrophotometer by observing the decrease in absorbance of the reaction mixture with time at 452 nm, which is an isosbestic point of the bromine–tribromide ion mixture.[11] A solution containing the β-diketone at the appropriate acidity and ionic strength was placed in a 10-cm cell and then spiked with 500 μl of the bromine solution at the same ionic strength. The range of concentrations used was [HTTA] = $(1.5\text{–}3.5) \times 10^{-4}$ M, [Br$_2$] = $(8.1\text{–}9.6) \times 10^{-5}$ M, [H$^+$] = 0.01–1.0 M; the ionic strength was 1.0 M.

It is evident from eq 7 that the molar absorptivity of bromine is needed in order to obtain k_e. This number was determined by measuring the absorbances of known volumes of solutions containing bromine, 10^{-2} M perchloric acid, and 10^{-3} M potassium bromide in a 1-cm stoppered cuvette. After the absorbance measurements the cuvettes were opened below the surface of solutions containing excess iodide, the cuvets were rinsed, and the liberated iodine was titrated with standard thiosulfate solution. These measurements gave ϵ_{Br} 103 at 452 nm, which is significantly higher than the value obtained by earlier workers.[2,11,12]

The rate of ketonization of thenoyltrifluoroacetone was studied by adjusting the pH of solutions of the diketone to ~8 and mixing these solutions[13] (which contained appreciable concentrations of the enolate form of the diketone) with 1.0 or 0.10 M perchloric acid[13] on a stopped-flow apparatus.[14,15] The enolate ion was very rapidly converted to the enol form after mixing the two solutions (*cf.* eq 13 with $k_c \gg k_b$), and the subsequent slow conversion of the enol to the keto tautomer could readily be followed at 338 and 262 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

$$\mathrm{M}^{n+} + \mathrm{HA} \rightleftharpoons \mathrm{ME}^{(n-1)+} + \mathrm{H}^+ \qquad K_1 \tag{8}$$

was determined by spectrophotometric and potentiometric measurements. This equilibrium constant can be partitioned between the equilibrium constants K_K and K_E for the reactions

$$\mathrm{M}^{n+} + \mathrm{HK} \rightleftharpoons \mathrm{ME}^{(n-1)+} + \mathrm{H}^+ \qquad K_K \tag{9}$$

$$\mathrm{M}^{n+} + \mathrm{HE} \rightleftharpoons \mathrm{ME}^{(n-1)+} + \mathrm{H}^+ \qquad K_E \tag{10}$$

by employing a procedure identical with that used to obtain K_{HK} and K_{HE} from K_{HA}.

A spectrophotometric method was used to determine the value of K_1 for the iron(III)–HTTA system. Consider the formation of FeTTA^{2+} according to

$$\mathrm{Fe}^{3+} + \mathrm{HTTA} \rightleftharpoons \mathrm{FeTTA}^{2+} + \mathrm{H}^+ \tag{11}$$

The concentration of FeTTA^{2+} at equilibrium is equal to A/ϵ_1, where A is the absorbance per unit path length and ϵ_1 is the molar absorptivity of the complex. Provided [H$^+$] $\gg$ [Fe(III)], it follows that

$$\frac{[\mathrm{Fe(III)}][\mathrm{HTTA}]_0}{A[\mathrm{H}^+]h} = \frac{[\mathrm{Fe(III)}] + [\mathrm{HTTA}]_0}{\epsilon_1[\mathrm{H}^+]h} + \frac{1}{\epsilon_1 K_1} \tag{12}$$

where $h = (1 + K_h/[\mathrm{H}^+])$, K_h is the hydrolysis constant of iron(III) (1.65×10^{-3} M at 25° and 1.0 M ionic strength),[16] K_1 is the equilibrium constant for eq 11, and a second-order term in A/ϵ_1 has been neglected. Hence a plot of the left-hand side of eq 12 vs. ([Fe(III)] + [HTTA]$_0$)/[H$^+$]h should yield a straight line with a slope $1/\epsilon_1$ and an intercept $1/\epsilon_1 K_1$.

A competition method was used to determine K_1 for the copper(II) system. This method involved the preparation of three solutions. Each contained a known concentration of perchloric acid (4.00×10^{-2} M) and HTTA (7.05×10^{-5} M) and the ionic strength was adjusted to 1.0 M with lithium perchlorate. Solution I was

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[9] 8-Hydroxy-7-(4-sulfo-1-naphthylazo)-5-quinolinesulfonic acid.

[10] Unsublimed thenoyltrifluoroacetone was used in some of the experiments with nickel(II) and iron(III). The results obtained with the sublimed and unsublimed material agreed within the experimental error of the measurements. However, an effect ascribable to the age of the thenoyltrifluoroacetone solutions was observed and for this reason freshly prepared solutions were generally used.

[11] P. R. Carter and N. Davidson, *J. Phys. Chem.*, **56**, 877 (1952).

[12] The lower molar absorptivity of bromine obtained by the earlier workers could have resulted from the loss of bromine during the transfer of the solution into the cuvette for the spectrophotometric measurements. The value ϵ_{Br} 103 at 452 nm reported above was confirmed by generating the bromine *in situ* by allowing the reaction $5\mathrm{Br}^- + \mathrm{BrO_3}^- + 6\mathrm{H}^+ = 3\mathrm{Br_2} + 3\mathrm{H_2O}$ to proceed to completion in sealed 1-cm cuvettes.

[13] The ionic strengths of the solutions were adjusted to 1.0 M with lithium perchlorate.

[14] G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963).

[15] E. G. Moorhead and N. Sutin, *ibid.*, **6**, 428 (1967).

[16] R. M. Milburn, *J. Amer. Chem. Soc.*, **79**, 537 (1957).

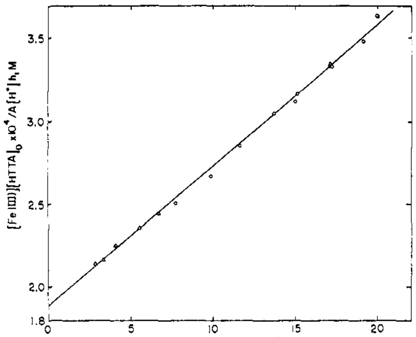

Figure 1. Plot, suggested by eq 12, for the determination of K_1 for the formation of FeTTA^{2+} at λ 520 nm, 25°, and 1.0 M ionic strength: O, [H$^+$] = 0.100 M; Δ, [H$^+$] = 0.300 M.

this solution alone, solution II also contained a known amount of copper(II) (3.92×10^{-2} M), and solution III contained this concentration of copper(II) plus iron(III) (1.33×10^{-3} M and 2.66×10^{-3} M in two independent experiments). These copper(II) and iron(III) concentrations gave comparable amounts of CuTTA$^+$ and FeTTA^{2+} at equilibrium.

A pH titration method was used to obtain K_1 for the cobalt(II) and nickel(II) systems since both of these equilibrium constants are relatively small. The procedure involved titration of a fairly concentrated solution of the metal ion (~0.2 M) with the HTTA solution, both solutions being adjusted to 1.0 M ionic strength. The pH at each point in the titration was measured using a glass electrode and a calomel electrode in which the KCl had been replaced by 1.0 M NaCl. The glass electrode was standardized using a series of solutions containing a constant metal ion concentration and varying perchloric acid concentrations at 1.0 M ionic strength.

Complexation Reactions. The kinetics of the formation of the iron(III) thenoyltrifluoroacetone complex were studied on a Cary 16K as well as on a Cary 14 spectrophotometer. The formation of the iron(III) complex was followed by observing the increase in absorbance at 520 nm after spiking the iron(III) solution with thenoyltrifluoroacetone, both solutions being at the same acidity and ionic strength. A Cary 14 spectrophotometer and a stopped-flow apparatus were both used in studying the reactions of copper(II), cobalt(II), and nickel(II) with thenoyltrifluoroacetone. Two types of measurement were performed. In the first type the formation of the complex was observed after mixing solutions of the metal ion and thenoyltrifluoroacetone of the same acidity and ionic strength. The disappearance of the complex was followed in the second type of measurement after mixing a dilute acid solution of the complex with a more concentrated acid solution at the same ionic strength. In each case the change in absorbance in the region of 350 nm was followed. The concentration of metal ion was always kept in large excess of the β-diketone to ensure formation of only the mono complex. All reactions were studied at 25° and 1.0 M ionic strength. A lithium perchlorate medium was used in the investigation of the nickel(II)-, cobalt(II)-, and copper(II)-thenoyltrifluoroacetone systems and a sodium perchlorate medium was used in the iron(III)-thenoyltrifluoroacetone system. The difference in the kinetic and thermodynamic data observed when lithium perchlorate was substituted for sodium perchlorate in the latter system was within the experimental error of the measurements.

Results

Tautomerization Reactions. The value of k_e for thenoyltrifluoroacetone is $(8.4 \pm 0.3) \times 10^{-3}$ sec^{-1} at 25° and 1.0 M ionic strength. This rate constant is independent of acidity in the range 0.01–1.0 M at 1.0 M ionic strength. The value of k_e is in excellent agreement with the published values[2,12] once a correction is made for the incorrect ϵ_{Br} values used in the earlier work.[2] The observed rate constants in the ketonization experiments measure the rate of approach to equilibrium in the system and are equal to $(k_e + k_f)$. The value of k_f calculated from the observed rate constant using the k_e value presented is 1.90 ± 0.06 sec^{-1} at 25° and is independent of acidity in the range 0.050–0.50 M at a constant ionic strength of 1.0 M.

The enolization of β-diketones does not in general proceed by the direct transfer of a proton from carbon to oxygen. Instead the enolate ion is formed as an intermediate

$$\mathrm{HK} \underset{k_b}{\overset{k_a}{\rightleftharpoons}} \mathrm{H^+} + \mathrm{E^-} \underset{k_d}{\overset{k_c}{\rightleftharpoons}} \mathrm{HE} \qquad (13)$$

with $k_c \approx 3 \times 10^{10}$ M^{-1} sec^{-1} and $k_c \gg k_b$.[17–21] Although the detailed tautomerization mechanism shown in eq 13 has not been established for thenoyltrifluoroacetone it is likely that this mechanism applies to this system too. The evidence for this statement is that the tautomerization of thenoyltrifluoroacetone proceeds extremely slowly in benzene,[22] indicating, perhaps, that ions are formed as intermediates in the tautomerization reaction. In terms of the ionization mechanism $k_e = k_a$ and $k_f = K_{HE}k_b$.

The ratio k_e/k_f is equal to the ratio of the enol to the keto tautomer present in the diketone. These studies give [HE]/[HK] = 4.4×10^{-3} for thenoyltrifluoroacetone at 25° and 1.0 M ionic strength. This ratio corresponds to a smaller percentage of the enol form than has been previously determined by an "instantaneous" bromination procedure.[2,12] The latter procedure is subject to larger errors than the one used here because it involves evaluating a small difference between two relatively large numbers.

Equilibrium Measurements. A plot of the left-hand side of eq 12 *vs.* ([Fe(III)] + [HTTA]$_0$)/[H$^+$]h for the iron(III)-thenoyltrifluoroacetone system is shown in Figure 1. It is apparent that the data satisfy eq 12 reasonably well. The slope and intercept of the straight line give $\epsilon_1 = 1180 \pm 60$ at 520 nm and $K_1 = 4.5 \pm 0.4$. The value of K_1 for the copper(II)-HTTA system determined by the competition method is 0.14 ± 0.02. From the pH titrations, K_1 values for the nickel(II)- and cobalt(II)-HTTA systems are $(8.4 \pm 0.2) \times 10^{-3}$ and $(1.4 \pm 0.3) \times 10^{-3}$, respectively. The equilibrium constants are summarized in Table II.

Table II. Equilibrium Constants for the Formation of Monothenoyltrifluoroacetone Complexes of Nickel(II), Cobalt(II), Copper(II), and Iron(III) at 25° and 1.0 M Ionic Strength

Metal ion	K_K[a]	K_E	Ref
Ni^{2+}	8.4×10^{-3}	1.9	*b*
Co^{2+}	1.4×10^{-3}	0.32	*b*
Cu^{2+}	0.14	32	*b*
Zn^{2+}	5.3×10^{-4}	0.12	*c*
Fe^{3+}	4.5	1.0×10^3	*b*

[a] Since [HE]/[HK] = 4.4×10^{-3}, $K_K = K_1$ within the experimental error of the measurements. [b] This work. [c] Reference 2.

The value of K_1 for the iron(III) system determined in this work is in satisfactory agreement with the value reported by Newman and Adin,[7] while the value of K_1 for

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(17) R. P. Bell, E. Gelles, and E. Möller, *Proc. Roy. Soc., Ser. A*, **198**, 308 (1949).

(18) R. P. Bell and J. E. Crooks, *ibid., Ser. A*, **269**, 285 (1965).

(19) M. Eigen, *Pure Appl. Chem.*, **6**, 97 (1963).

(20) J. C. Reid and M. Calvin, *J. Amer. Chem. Soc.*, **72**, 2948 (1950).

(21) M. Eigen, G. Ilgenfritz, and W. Kruse, *Chem. Ber.*, **98**, 1623 (1965).

(22) E. L. King and W. H. Reas, *J. Amer. Chem. Soc.*, **73**, 1806 (1951).

Table III. First-Order Rate Constants for the Reaction $Ni^{2+} + HTTA \rightleftharpoons NiTTA^+ + H^+$ at 25° and 1.0 *M* Ionic Strength

$10^2[H^+]$, *M*	$10^3[Ni^{2+}]$, *M*	k_{obsd}, sec^{-1}
50.4	58.9	0.76
50.4	29.5	0.80
50.4	14.7	0.84
50.4	8.84	0.81
50.4	5.89	0.80
50.4	2.95	0.79
50.4	1.77	0.77
20.3	63.8	0.55
20.3	31.9	0.55
20.3	25.5	0.56
20.3	19.1	0.57
20.3	6.38	0.60
11.3	63.8	0.44
11.3	31.9	0.51
11.3	25.5	0.50
11.3	19.1	0.49
11.3	12.8	0.52
11.3	6.38	0.52
8.80	58.9	0.39
8.80	29.5	0.45
8.80	14.7	0.44
8.80	8.84	0.44
8.80	5.89	0.47
8.80	2.95	0.45
8.80	1.77	0.44
7.40	142	0.29
7.40	118	0.30
7.40	82.9	0.30
7.40	66.3	0.35
7.40	52.9	0.34
7.30	35.5	0.39
7.30	23.7	0.39
2.10	58.9	0.20
2.10	29.5	0.27
2.10	14.7	0.35
2.10	8.84	0.37
2.10	5.89	0.37
2.10	2.95	0.41
1.10	147	0.091
1.10	73.7	0.16
1.10	36.8	0.19
1.10	22.1	0.26
1.10	14.7	0.30
1.10	7.37	0.37
1.10	4.42	0.37
0.790	47.4	0.13
0.770	21.3	0.20
0.760	11.8	0.24
0.760	5.92	0.29
0.760	3.32	0.34
0.750	2.13	0.36
0.750	1.42	0.36

the copper(II) system determined in this study is in very good agreement with the value obtained by extrapolating the data of Taft and Cook[2] to 1.0 *M* ionic strength. It may be noted that the stabilities of the thenoyltrifluoroacetonate complexes follow the order

$$Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+}$$

which is the same as the order found for the acetylacetonate complexes of these metal ions.

Kinetic Measurements. The kinetic data are consistent with a scheme in which the metal ion does not react directly with the keto tautomer. Instead the complex formation occurs exclusivly through the reaction of the metal ion with the enol form of the diketone.

$$HK \underset{k_t}{\overset{k_e}{\rightleftharpoons}} HE \underset{k_{-HE}'}{\overset{k_{HE}'}{\rightleftharpoons}} ME^{(n-1)+} \tag{14}$$

In terms of this scheme $k_{HE}' = k_{HE}[M^{n+}]$, $k_{-HE}' = k_{-HE}\,[H^+]$, and k_{HE} and k_{-HE} are defined by the equation

$$M^{n+} + HE \underset{k_{-HE}}{\overset{k_{HE}}{\rightleftharpoons}} ME^{(n-1)+} + H^+ \tag{15}$$

where $k_{HE}/k_{-HE} = K_E$. Evidently the formation or dissociation of the complex is characterized by two consecutive reactions. These two reactions were clearly discernible in the faster copper(II) system. In the nickel(II) and cobalt(II) systems, however, the half-lives for the two consecutive reactions were not always very different, and as a result only slight curvature of the plots of $\log (A_\infty - A_t)$ *vs.* time was generally observed. By contrast, no curvature was observed in the kinetic plots for the slower iron(III) reaction.[23] Only the slower of the consecutive reactions was studied in detail. Values of $k_{obsd} = 0.693/t_{1/2}$ for the slower reaction are presented in Tables III—VI for the nickel(II), cobalt(II), copper(II), and iron(III) systems, respectively. It should be emphasized that $t_{1/2}$ has a particular value for a given metal ion and hydrogen ion concentration and that this value does not depend on the direction from which the equilibrium is approached; in other words, $t_{1/2}$ does not depend on whether the formation or the dissociation of the complex is being observed. This was confirmed for the nickel(II), cobalt(II), and copper(II) systems. It was necessary to study the reaction in the reverse direction in order to extend the range of the hydrogen ion concentration that could be used in this work.

Table IV. First-Order Rate Constants for the Reaction $Co^{2+} + HTTA \rightleftharpoons CoTTA^+ + H^+$ at 25° and 1.0 *M* Ionic Strength

$10[H^+]$, *M*	$10[Co^{2+}]$, *M*	k_{obsd}, sec^{-1}
5.00	1.00	1.70
5.00	0.67	1.77
5.00	0.50	1.78
5.00	0.40	1.78
5.00	0.28	1.78
5.00	0.25	1.81
2.50	0.50	1.71
2.50	0.25	1.90
2.50	0.12	1.75
1.00	1.00	1.38
1.00	0.50	1.64
1.00	0.25	1.72
1.00	0.20	1.91
1.00	0.12	1.93
1.00	0.10	2.11
1.00	0.08	2.02
1.00	0.06	1.98
1.00	0.05	1.97
0.10	0.93	0.49
0.10	0.46	0.77
0.10	0.37	0.86
0.10	0.28	1.03
0.10	0.19	1.12
0.10	0.14	1.36
0.10	0.06	1.59

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[23] It will be recalled that the iron(III) reaction was studied by conventional and not by stopped-flow spectrophotometry, and at a wavelength where only the iron(III) complex absorbs.

Table V. First-Order Rate Constants for the Reaction $Cu^{2+} + HTTA \rightleftharpoons CuTTA^+ + H^+$ at 25° and 1.0 *M* Ionic Strength

$10^2[H^+]$, *M*	$10^2[Cu^{2+}]$, *M*	k_{obsd}, sec^{-1}
20.0	7.69	0.14
20.0	1.49	0.54
20.0	0.77	0.79
20.0	0.30	1.17
20.0	0.15	1.33
4.60	1.22	0.21
4.60	0.61	0.40
4.60	0.37	0.56
4.60	0.22	0.75
4.60	0.12	1.03
4.60	0.05	1.34
4.00	1.49	0.15
4.00	0.30	0.59
4.00	0.15	0.88
4.00	0.06	1.63
4.00	0.03	1.72
2.00	0.33	0.35
2.00	0.17	0.57
2.00	0.08	0.83
2.00	0.03	1.23

Table VI. First-Order Rate Constants for the Reaction $Fe^{3+} + HTTA \rightleftharpoons FeTTA^{2+} + H^+$ at 25° and 1.0 *M* Ionic Strength

$10^2[H^+]$, *M*	10^3[Fe(III)], *M*	10^3k_{obsd}, sec^{-1}
80.0	21.5	3.42
80.0	16.1	3.44
79.9	32.3	3.44
79.7	7.14	3.31
79.4	3.57	3.44
79.3	23.4	3.50
79.2	32.0	3.64
79.0	14.2	3.31
49.9	24.9	3.33
49.6	49.4	3.58
49.4	35.5	3.67
49.4	18.5	3.22
49.1	9.16	3.03
49.0	4.59	2.92
9.95	7.18	2.81
9.95	4.31	2.49
9.94	10.1	3.08
2.75	7.24	2.17
2.75	3.61	3.22
2.75	2.89	2.86
2.75	2.17	2.65

In terms of the above scheme the observed rate constants are given by[24,25]

$$k_{obsd} = \left[\frac{k_e k_{HE}[M^{n+}]}{k_{HE}[M^{n+}] + k_f + \dfrac{k_{HE}[H^+]}{K_E}}\right] \times \left[1 + \frac{[H^+]}{K_K[M^{n+}]}\right] \quad (16)$$

where $(k_e + k_f)$ has been replaced by k_f since $k_f \gg k_e$. Equation 16 can be rearranged to give (17). Plots of the

$$\frac{1 + [H^+]/K_K[M^{n+}]}{k_{obsd}} = \frac{1}{k_e} + \left[\frac{k_f}{k_e k_{HE}} + \frac{[H]}{k_e K_E}\right]\frac{1}{[M^{n+}]} \quad (17)$$

left-hand side of eq 17 *vs.* $1/[M^{n+}]$ for the nickel(II) and iron(III) systems are presented in Figures 2 and 3, respectively. It will be seen that the data satisfy eq 17 reasonably well. The intercepts of the plots are equal to $1/k_e$ within the experimental error of the measurements, while according to eq 17 the slopes of the plots are given by

$$S = \left[\frac{k_f}{k_e k_{HE}} + \frac{[H^+]}{k_e K_E}\right] \quad (18)$$

In order to determine the acid dependence of k_{HE}, plots were made of $1/(S - [H^+]/k_e K_E)$ *vs.* $1/[H^+]$. These plots are shown in Figures 4 and 5 for the nickel(II) and iron(III) systems, respectively. It is apparent that k_{HE} is acid dependent and of the form

$$k_{HE} = a + b/[H^+] \quad (19)$$

The values of a and b are 2.3 M^{-1} sec^{-1} and 0.98 sec^{-1}, respectively, for nickel(II), and 1.4 M^{-1} sec^{-1} and 2.3 sec^{-1}, respectively, for iron(III).

Certain simplifications are possible for the cobalt(II) and copper(II) reactions. In these systems $[H^+]/K_K \cdot [M^{n+}] \gg 1$ and if $k_{HE}[H^+]/K_E \gg k_f$ then eq 16 may be simplified to give

$$\frac{1}{k_{obsd}} = \frac{1}{k_f} + \frac{K_E[M^{n+}]}{k_f[H^+]} \quad (20)$$

The cobalt(II) and copper (II) data satisfy eq 20 satisfactorily. Plots of $1/k_{obsd}$ *vs.* $[M^{n+}]/[H^+]$ for these systems are presented in Figures 6 and 7. The intercepts of the plots are equal to $1/k_f$ within the experimental error of the measurements and the values of K_E calculated from the slopes for the cobalt(II) and copper(II) systems are 0.32 and 32, respectively. These K_E values are in excellent agreement with the values determined directly. It may be noted that the condition $k_{HE}[H^+]/K_E \gg k_f$ is equivalent to $k_{-HE}' \gg k_f$ and that in this situation only a lower limit for k_{HE} can be obtained.[26a]

Table VII. Summary of the Rate Constants for the Formation of Mono Complexes of β-Diketones at 25° and 1.0 *M* Ionic Strength

Reaction	k, M^{-1} sec^{-1}	Ref
	(I) Thenoyltrifluoroacetone System	
$Ni^{2+} + HE$	2.3	*a*
$Ni^{2+} + E^-$	1.0×10^4	*a*
$Co^{2+} + E^-$	$\geqslant 3 \times 10^4$	*a*
$Cu^{2+} + E^-$	$\geqslant 3 \times 10^6$	*a*
$Fe^{3+} + HE$	1.4	*a*
$Fe^{3+} + E^-$	$(2.4 \times 10^4)^b$	*a*
$FeOH^{2+} + HE$	$(1.3 \times 10^3)^c$	*a*
	(II) Acetylacetone System	
$Ni^{2+} + HE$	2.7	*d*
$Cu^{2+} + HE$	2×10^4	*d*
$Cu^{2+} + E^-$	$\leqslant 2 \times 10^8$	*e*

[a] This work. [b] Calculated on the assumption that Fe^{3+} and E^- are the reactants in the inverse-acid path. [c] Calculated on the assumption that $FeOH^{2+}$ and HE are the reactants in the inverse-acid path. [d] Reference 6. [e] Estimated from the data in ref 6 with the aid of the assumptions that $k_d[HE] > k_4[Cu^{2+}][E^-]$ and $k_c[H^+] > k_4[Cu^{2+}]$ (see footnote 26b) and the additional assumption that an upper limit of 5% may be placed on the contribution of the enolate ion path to the formation of the complex at $[H^+] = 10^{-3}$ *M*. The value of 4×10^4 M^{-1} sec^{-1} presented in ref 6 for the upper limit of the rate constant for the reaction between copper(II) and the enolate ion of acetylacetone is a misprint (personal communication from R. G. Pearson to N. Sutin).

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(24) F. A. Matsen and J. L. Franklin, *J. Amer. Chem. Soc.*, **72**, 3337 (1950).

(25) E. S. Lewis and M. D. Johnson, *ibid.*, **82**, 5399 (1960).

(26) (a) Equation 20 can be readily derived by postulating that the reaction $M^{n+} + HE \rightleftharpoons ME^{(n-1)+} + H^+$ is at equilibrium and remem-

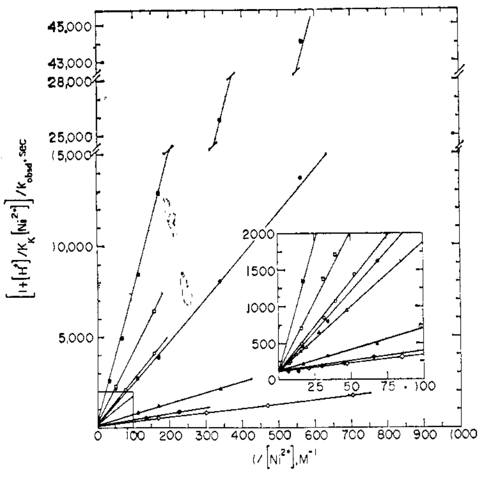

Figure 2. Plot, suggested by eq 17, of $(1 + [H^+]/K_K[Ni^{2+}])/k_{obsd}$ as a function of $1/[Ni^{2+}]$ for the reaction $Ni^{2+} + HTTA \rightleftharpoons NiTTA^+ + H^+$, at λ 350 nm, 25°, and 1.0 *M* ionic strength: ◇, $[H^+] = (7.53\text{–}7.88) \times 10^{-3}$ *M*; ◆, $[H^+] = 0.0110$ *M*; ▲, $[H^+] = 0.0210$ *M*; △, $[H^+] = 0.0731\text{–}0.0740$ *M*; ●, $[H^+] = 0.0880$ *M*; ○, $[H^+] = 0.113$ *M*; □, $[H^+] = 0.203$ *M*; ■, $[H^+] = 0.504$ *M*.

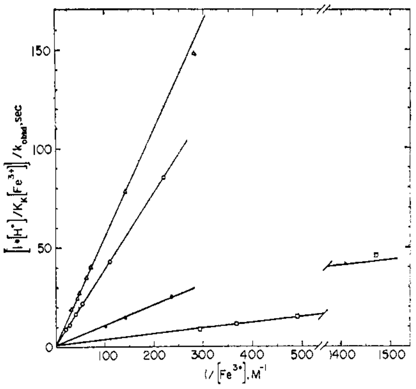

Figure 3. Plot, suggested by eq 17, of $(1 + [H^+]/K_K[Fe^{3+}])/k_{obsd}$ as a function of $1/[Fe^{3+}]$ for the reaction $Fe^{3+} + HTTA \rightleftharpoons FeTTA^{2+} + H^+$, at 520 nm, 25°, and 1.0 *M* ionic strength: □, $[H^+] = 0.0275$ *M*; ●, $[H^+] = 0.0995$ *M*; ○, $[H^+] = 0.494$ *M*; ▽, $[H^+] = 0.794$ *M*.

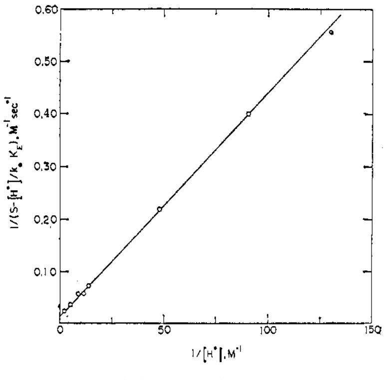

Figure 4. Plot, suggested by eq 18, of $1/(S - [H^+]/k_eK_E)$ as a function of $1/[H^+]$ for the nickel(II) system.

If it is assumed that k_{HE} for the cobalt(II) and copper(II) systems is given by eq 19 and that $b/[H^+] \gg a$ then we estimate that $b \geqslant 3$ sec^{-1} and $\geqslant 3 \times 10^2$ sec^{-1} for the cobalt(II) and copper(II) reactions, respectively.

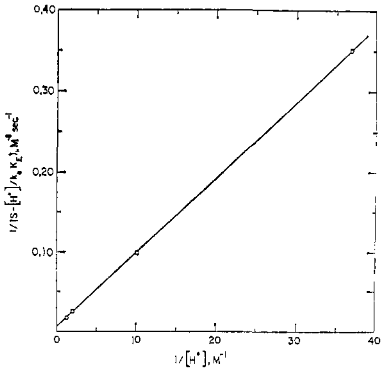

Figure 5. Plot, suggested by eq 18, of $1/(S - [H^+]/k_eK_E)$ as a function of $1/[H^+]$ for the iron(III) system.

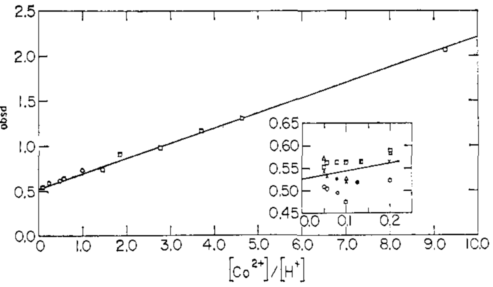

Figure 6. Plot, suggested by eq 20, of $1/k_{obsd}$ as a function of $[Co^{2+}]/[H^+]$: □, $[H^+] = 0.010$ *M*; ○, $[H^+] = 0.10$ *M*. Insert: ○, $[H^+] = 0.10$ *M*; ▲, $[H^+] = 0.25$ *M*; □, $[H^+] = 0.50$ *M*; ×, average values of $1/k_{obsd}$ at different $[Co^{2+}]/[H^+]$ values.

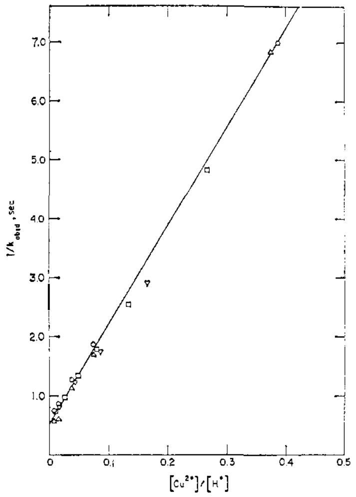

Figure 7. Plot, suggested by eq 20, of $1/k_{obsd}$ as a function of $[Cu^{2+}]/[H^+]$: ▽, $[H^+] = 0.020$ *M*; ▽, $[H^+] = 0.040$ *M*; □, $[H^+] = 0.046$ *M*; ○, $[H^+] = 0.20$ *M*.

The rate constants for the reactions of the metal ions with HE and E^-, calculated on the assumption that E^- is the reactive form of the diketone in the inverse-acid path, are presented in Table VII. The data of Pearson and Anderson[6] on the nickel(II)- and copper(II)-acetylacetone systems are included in this table for comparison.

Discussion

These studies confirm a conclusion reached earlier by Taft and Cook, namely, that the keto form of thenoyltrifluoroacetone is inert to attack by metal ions. In-

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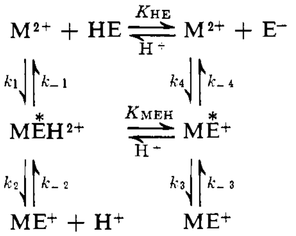
bering that $k_f \gg k_e$. (b) This assumption remains valid even if the copper(II) reaction with the enolate ion is "normal." If this reaction is normal, then $k_4 \approx 10^9$ M^{-1} sec^{-1} and $k_e[H^+]/k_4[Cu^{2+}] \geqslant 30$, provided $[H^+] \geqslant [Cu^{2+}]$. The latter situation obtained under the conditions used to study the copper(II) reaction in this work (Table V).

stead the metal ions react exclusively with the enol form of the diketone. It is apparent from eq 19 that the reaction with the enol tautomer proceeds *via* parallel acid-independent and inverse-acid paths. This form of the rate law is consistent with a mechanism of the type (illustrated for the dipositive ions) shown in Scheme I,

Scheme I



where ME^*H^{2+} and ME^{*+} are intermediates in which only one end of the diketone is attached to the metal center. Since $k_c \approx 3 \times 10^{10}\ M^{-1}\ sec^{-1}$ (eq 13) and $k_d = k_cK_{HE} \approx 3 \times 10^6\ sec^{-1}$, it does not seem unreasonable to assume that equilibrium between HE and E^- will be maintained throughout the course of the reaction.[26b] Similar considerations apply also to the interconversion of ME^*H^{2+} and ME^{*+} since proton loss from ME^*H^{2+} is, if anything, likely to be even faster than proton loss from HE because of electrostatic effects. The steady-state assumption for the concentration of the two intermediates gives

$$k_{HE} = \frac{k_1 + K_{HE}k_4/[H^+]}{1 + \dfrac{k_{-1} + K_{MEH}k_{-4}/[H^+]}{k_2 + K_{MEH}k_3/[H^+]}} \qquad (21)$$

Two limiting forms of eq 21 are of interest.

Case A. If $(k_2 + K_{MEH}k_3/[H^+]) \gg (k_{-1} + K_{MEH}k_{-4}/[H^+])$, then

$$k_{HE} = k_1 + K_{HE}k_4/[H^+] \qquad (22)$$

Under these conditions $a = k_1$ and $b = K_{HE}k_4$. In this case the rate-determining step is the formation of the intermediates and the subsequent closing of the chelate ring occurs rapidly. If this situation obtains then the rate constants for the formation of the diketone complexes of a particular metal ion would be expected to be similar to the rate constants for the reaction of the metal ion with analogous monodentate ligands.

Case B. On the other hand, if $(k_2 + K_{MEH}k_3/[H^+]) \ll (k_{-1} + K_{MEH}k_{-4}/[H^+])$, then

$$k_{HE} = K_1k_2 + K_{HE}K_4k_3/[H^+] \qquad (23)$$

where $K_1 = k_1/k_{-1}$ and $K_4 = k_4/k_{-4}$. Under these conditions $a = K_1k_2$ and $b = K_{HE}K_4k_3$. In this case equilibrium obtains between the free metal ion and the intermediates and the rate-determining step is the closing of the chelate ring. Note that since $K_{HE}K_4 = K_1K_{MEH}$, the parameter b is also equal to $K_1K_{MEH}k_3$.

The Nickel(II), Cobalt(II), and Copper(II) Reactions. The mechanism of the reaction of the divalent ions will be considered first. If it is assumed that mechanism A obtains for the nickel(II) reaction, then the values of k_1 and k_4 calculated from the experimental data are 2.3 and $1.0 \times 10^4\ M^{-1}\ sec^{-1}$, respectively. Although the value of k_4 obtained in this manner is not unreasonable for the reaction of Ni^{2+} with a singly charged anion, the value of k_1 is some three orders of magnitude smaller than the characteristic rate constant for the reaction of Ni^{2+} with uncharged ligands, which is about $4 \times 10^3\ M^{-1}\ sec^{-1}$ at 25°.[27,28] The low value of k_1 implied by mechanism A can be rationalized by postulating that the enol form of thenoyltrifluoroacetone is a much poorer entering group (perhaps because of intramolecular hydrogen bonding) than such "typical" uncharged ligands as ammonia, hydrazine, imidazole, or pyridine. It is noteworthy that the rate constant for the reaction of Ni^{2+} with the enol tautomer of thenoyltrifluoroacetone obtained in this work (2.3 $M^{-1}\ sec^{-1}$) is very similar to the rate constant for the reaction of Ni^{2+} with the enol tautomer of acetylacetone (2.7 $M^{-1}\ sec^{-1}$).[6] Although there is considerable evidence that the enol forms of thenoyltrifluoroacetone and acetylacetone exist as intramolecularly hydrogen-bonded species,[29-31] the kinetic consequences of the hydrogen bonding are difficult to assess.[32]

If it is assumed instead that mechanism B obtains for the nickel(II) reaction and that k_1 has a "normal" value of $4 \times 10^3\ M^{-1}\ sec^{-1}$, then k_2/k_{-1} is calculated to be 6×10^{-4}. As mentioned above, the value of the rate constant for the reaction of Ni^{2+} with E^- ($1.0 \times 10^4\ M^{-1}\ sec^{-1}$) is close to the normal value, and in terms of mechanism B this implies that $k_3/k_{-4} \approx 1$. Under these conditions the condition that mechanism B obtains reduces to $k_2/k_{-1} \ll 1$. Evidently the two monosubstituted intermediates possess very different kinetic properties. Since $K_{HE}K_4 = K_1K_{MEH}$ and since K_{MEH} is almost certainly much larger than K_{HE}, it follows that $k_1/k_{-1} \ll k_4/k_{-4}$. Although k_1 will be smaller than k_4 (see footnote 32), it is likely that k_{-1} will be larger than k_{-4} because the coordinated enolic oxygen will be less basic in NiE^*H^{2+} than in NiE^{*+}. Some factors that will tend to decrease the value of k_2 (thereby decreasing the value of k_2/k_{-1} even further) are discussed in the following paragraphs.

The slow rate of the reaction of the enol tautomer of acetylacetone with Ni^{2+} (and also with Cu^{2+}) has been interpreted[6] in terms of a sterically controlled substitution mechanism.[33-35] This mechanism postulates that the closing of six- (and seven-) membered chelate rings is, in general, sterically hindered. In other words, in contrast to the formation of five-membered chelate rings, in which water release from the metal ion is rate determining, the rate of formation of six- and seven-membered rings is determined not by the release of a

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(27) M. Eigen and R. G. Wilkins, *Advan. Chem. Ser.*, No. 49, 55 (1965).

(28) J. C. Cassatt and R. G. Wilkins, *J. Amer. Chem. Soc.*, **90**, 6045 (1968).

(29) H. Ogoshi and K. Nakamoto, *J. Chem. Phys.*, **45**, 3113 (1966).

(30) E. E. Ernstbrunner, *J. Chem. Soc. A*, 1558 (1970).

(31) J. L. Burdett and M. T. Rogers, *J. Amer. Chem. Soc.*, **86**, 2105 (1964).

(32) The enol tautomers of the diketones could be poor entering groups (low k_1 values) as a result of the necessity of breaking the intramolecular hydrogen bonds before (or during) the formation of the first bond between the enol and the metal center. This type of explanation has been advanced to account for the nonreactivity of the protonated forms of certain aliphatic amino acids.[28] Alternatively, the thiophene and trifluoromethyl groups in thenoyltrifluoroacetone (and the two methyl groups in acetylacetone) could interfere with the approach of the entering metal ion and this would lead to low k_1 values. This type of steric hindrance would be much less in the case of the enolate ion, since the carbonyl groups are more exposed in the enolate ion than in the enol tautomer.[30] Although these two effects will tend to decrease k_1, it is doubtful whether either of them (or even both of them acting together) is large enough to lower k_1 by three orders of magnitude.

(33) K. Kustin, R. F. Pasternack, and E. M. Weinstock, *J. Amer. Chem. Soc.*, **88**, 4610 (1966).

(34) R. F. Pasternack and K. Kustin, *ibid.*, **90**, 2295 (1968).

(35) K. Kustin and R. F. Pasternack, *ibid.*, **90**, 2805 (1968).

coordinated water molecule but by the subsequent closure of the chelate ring. While the sterically controlled substitution mechanism can account for the slow rate of the reaction of nickel(II) with the enol tautomer of thenoyltrifluoroacetone, this mechanism predicts that the enolate ion should also react at an abnormally slow rate.[6] This prediction is not borne out by the results of this study, for we find a normal rate constant for the reaction of nickel(II) with the enolate ion of thenoyltrifluoroacetone. The relatively rapid rate of the reaction between Ni^{2+} and E^- can be rationalized by postulating either that the steric restrictions are much smaller for ring closure of NiE^{*+} than they are for ring closure of NiE^*H^{2+}, or that the slow rate of ring closure of the latter intermediate is not due to steric factors *per se* but is instead associated with the energetics of the proton release. Pearson and Anderson argue that the latter effect is not too important in the reaction of Cu^{2+} with the enol tautomer of acetylacetone, for the rate constant remains unchanged when the solvent is changed from water to methanol.[6] However, the magnitude of the rate constant change expected for this solvent change is difficult to assess.

The rate constants for the reaction of Cu^{2+} and Co^{2+} with E^- are $\geqslant 3 \times 10^6$ and $\geqslant 3 \times 10^4\ M^{-1}\ sec^{-1}$, respectively. These limits, like the value of the rate constant for the reaction of Ni^{2+} with E^-, do not provide evidence for any large rate restrictions associated with the reactions of the deprotonated ligand. It may be noted that the lower limit for the rate constant for the reaction of Cu^{2+} with the enolate form of thenoyltrifluoroacetone is about 100 times larger than the rate constant for the reaction of Cu^{2+} with the enol tautomer of acetylacetone ($2 \times 10^4\ M^{-1}\ sec^{-1}$).[6] Evidently in these systems the slow reaction rate is again associated with the protonated ligand.

It is interesting to compare the reactions of the β-diketones with those of malonic acid for malonate also coordinates through oxygen atoms to form a six-membered ring. The reaction of nickel(II) with malonate has been studied by a number of investigators. It was first studied by Cavasino by the use of a temperature-jump technique.[36a] Cavasino determined the rate constants for the reactions

$$Ni^{2+} + CH_2(COO)_2H^- \longrightarrow Ni(COO)_2CH_2 + H^+ \qquad (24)$$

$$Ni^{2+} + CH_2(COO)_2^{2-} \longrightarrow Ni(COO)_2CH_2 \qquad (25)$$

to be 3.1×10^3 and $7.0 \times 10^4\ M^{-1}\ sec^{-1}$, respectively, at 25° and ionic strength 0.1 M. Reaction 25 was subsequently studied by a pressure-jump technique by Bear and Lin,[36b] who found that the rate constant for the reaction between nickel(II) and malonate was $2.7 \times 10^5\ M^{-1}\ sec^{-1}$ at 20° and zero ionic strength, in good agreement with the value reported by Cavasino. Nickel, Hoffmann, and Jaenicke[37] also studied reaction 25 by a pressure-jump technique, but these workers reported two relaxation times. The faster step was interpreted by them in terms of the formation of the monosubstituted complex and the second was ascribed to the relatively slow closing of the chelate ring ($k_2 = 1.1 \times 10^2\ sec^{-1}$ at 5°). This interpretation has recently been questioned,[38,39] for it was pointed out that the shorter relaxation time was only observed under conditions where the solutions contained significant amounts of the bismalonato complexes. The new studies show that the rate constant for the closing of the chelate ring is about 40 times faster than reported by Nickel, *et al.*, and that $k_{-1} \approx k_2$ for the malonate system. An interesting feature of these studies from our point of view is that ring closure of the unprotonated intermediate is again fairly rapid (since $k_{-1} \approx k_2$, the rate of formation of the six-membered chelate is slower than a normal substitution reaction on nickel(II) by only about a factor of 2). Moreover, a comparison of the rate constants for reactions 24 and 25 (and making allowance for electrostatic effects) shows that ring closure of the protonated intermediate cannot be much slower than ring closure of the unprotonated intermediate. Finally, the activation parameters for the reaction of nickel(II) with oxalate, binoxalate, malonate, bimalonate,[36a] and succinate[36b] are all remarkably similar, showing that neither the size of the chelate ring nor the release of a proton is an important rate-determining factor in these systems. This latter statement is, of course, not meant to exclude effects on the rate of the order of factors of 2.

The Iron(III) Reaction. The situation is somewhat more obscure in the iron(III) system because there are not many criteria for deciding whether a particular rate constant for substitution on iron(III) is "normal." With this reservation in mind the rate constant for the reaction of Fe^{3+} with HE ($1.4\ M^{-1}\ sec^{-1}$) may be compared with the rate constants for the reaction of Fe^{3+} with HN_3 ($2.6\ M^{-1}\ sec^{-1}$) and HF ($11.4\ M^{-1}\ sec^{-1}$).[40-42] This comparison suggests that, unlike the reaction of Ni^{2+} with HE, the reaction of Fe^{3+} with HE is, at most, only slightly slower than normal. On the other hand, it might be argued that the above comparison is not too meaningful because a proton is lost in the rate-determining steps of the reactions of Fe^{3+} with HF and HN_3, whereas unprotonated ligands were used as the standards for the Ni^{2+} rate comparisons. If, instead, the rates of reactions of Fe^{3+} and Ni^{2+} with HE are compared with the water exchange rates on the metal ions (3.0×10^3 and $2.7 \times 10^4\ sec^{-1}$, respectively)[43,44] then it is seen that the ratio k_{HE}/k_{H_2O} is 5×10^{-4} for the Fe^{3+} and 0.9×10^{-4} for the Ni^{2+} reactions. On this basis the reaction of Fe^{3+} with HE must be classified as slow, for we have seen that the reaction of Ni^{2+} with HE is too slow by a factor of about 2×10^3. This conclusion is supported by a comparison of the rate constants for the reactions of Fe^{3+} and Ni^{2+} with HE with the rate constants for the reactions of these metal ions with the binoxalate ion (8.6×10^2 and $5 \times 10^3\ M^{-1}\ sec^{-1}$, respectively).[15,45] The relative rates are again seen to be similar (and become even more so after corrections are made for differences in the ion pair association constants).[15,45-48]

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(36) (a) F. P. Cavasino, *J. Phys. Chem.*, **69**, 4380 (1965); (b) J. L. Bear and C.-T. Lin, *ibid.*, **72**, 2026 (1968).

(37) U. Nickel, H. Hoffmann, and W. Jaenicke, *Ber. Bunsenges. Phys. Chem.*, **72**, 536 (1968).

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(45) G. H. Nancollas and N. Sutin, *Inorg. Chem.*, **3**, 360 (1964).

(46) The loss of the proton in the reactions of the metal ions with binoxalate is believed to occur after the rate-determining step.

An additional ambiguity arises in interpreting the inverse acid path in the iron(III) reaction.[36] The reactants in this path may be formulated as Fe^{3+} and E^- (eq 26) or as $FeOH^{2+}$ and HE (eq 27).

$$Fe^{3+} + E^- \underset{}{\overset{k_5}{\rightleftharpoons}} FeE^{2+} \qquad (26)$$

$$FeOH^{2+} + HE \underset{}{\overset{k_6}{\rightleftharpoons}} FeE^{2+} + H_2O \qquad (27)$$

If the former formulation is adopted, then $k_5 = 2.4 \times 10^4\ M^{-1}\ sec^{-1}$, whereas the latter formulation leads to $k_6 = 1.3 \times 10^3\ M^{-1}\ sec^{-1}$. The value of k_5 is unusually large for the reaction of Fe^{3+} with a singly charged anion and for this reason we are inclined to prefer the latter formulation. The value of k_6 is somewhat low for the reaction of $FeOH^{2+}$ with a neutral ligand, while the value of the ratio k_6/k_1 is not unusual for substitution on iron(III).[40]

To summarize, the reactivity order for thenoyltrifluoroacetone appears to be keto < enol < enolate ion. The keto tautomer of thenoyltrifluoroacetone is unreactive, while the reaction of the enol tautomer with Ni^{2+} proceeds much more slowly than the normal substitution rate on the metal ion. On the other hand, the rate constant for the reaction of Ni^{2+} with the enolate form of thenoyltrifluoroacetone is normal (within a factor of 2). The unreactivity of the keto tautomer of thenoyltrifluoroacetone is presumably related to its unsymmetrical hydrate structure, for the keto form of acetylacetone does react slowly with metal ions.[5,6] The slow rate of the reaction of HE with Ni^{2+} may be caused by a slow first substitution step (mechanism A). This step may be slow either because intramolecular hydrogen bonding or because steric repulsion (or both) causes the enol form of the diketone to act as a poor entering ligand. Although these factors are undoubtedly of importance, it is unlikely that they are large enough to lower the rate constant for the reaction between HE and Ni^{2+} by about three orders of magnitude.[49] For this reason we are inclined to ascribe the slow rate of the reaction of HE with Ni^{2+} primarily (but not entirely) to the slow rate of ring closure of the protonated intermediate.[50] If $k_2/k_{-1} \ll 1$ (mechanism B) then the rate constant for the reaction of HE with Ni^{2+} is equal to k_1k_2/k_{-1}. The factors mentioned above (hydrogen bonding and steric repulsion) will tend to decrease k_1. The rate constant k_{-1} will be larger because of the instability of the monosubstituted intermediate, while k_2 will be small if ring closure to form the six-membered ring is sterically controlled or if proton loss from the monosubstituted intermediate is energetically important. It should be noted that the "pure" steric-control mechanism predicts that the enolate form of thenoyltrifluoroacetone should also react slowly, and this is not observed, at least, in the nickel(II) and iron(III) systems.

As we have seen, it is not always easy to distinguish between a proton-controlled and a sterically controlled ring-closure mechanism in a particular system. It is also apparent that the rate constants for the reactions of the deprotonated ligands are helpful in distinguishing between the above alternatives. Both mechanisms require that $k_2/k_{-1} \ll 1$, a condition which is most likely to be satisfied in substitution-labile systems (for k_{-1} is relatively large in such systems, and k_2 for a proton- or sterically controlled reaction is probably fairly characteristic of the ligand and not too dependent on the nature of the metal ion, except perhaps for its charge). Thus nickel(II) and iron(III) reactions are less likely to feature proton-controlled or sterically controlled ring-closure mechanisms than are reactions involving, for example, the very labile copper(II) and chromium(II) ions. Indeed the rate constants for the reaction of copper(II) and chromium(II) with the enolate forms of thenoyltrifluoroacetone and acetylacetone would be particularly valuable in further elucidating the mechanisms of the reactions discussed here. No kinetic data on the chromium(II) reactions are available, and only estimates of limits of the enolate ion rate constants have been determined for the copper(II) system.

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(47) On the other hand, Fe^{3+} reacts only six times faster with Cl^- ($8.4\ M^{-1}\ sec^{-1}$)[48] than with HE.

(48) J. K. Rowley and N. Sutin, *J. Phys. Chem.*, 74, 2043 (1970).

(49) Note, however, that the rate constant for the reaction of the enol form of acetylacetone with hydroxide ion ($1.6 \times 10^7\ M^{-1}\ sec^{-1}$) is about three orders of magnitude lower than normal, and that this slow rate has been ascribed to the intramolecular hydrogen bond existing in the enol tautomer.[19]

(50) Proton-controlled ring closure has also been proposed by D. L. Rabenstein and R. J. Kula, *J. Amer. Chem. Soc.*, **91**, 2492 (1969), and by K. Kustin and R. Pizer, *Inorg. Chem.*, **9**, 1536 (1970).