metry including spin–orbit coupling.[30] In this plot, $B = 730$ cm^{-1}, $C = 4B$, and $\zeta = -350$ cm^{-1} have been used, where ζ is the one-electron spin–orbit coupling parameter. Also, Bethe's notation is employed for the resulting levels. The notation on the right side of Figure 2, which also lists the initial levels in absence of spin–orbit coupling and the one-electron configurations, is only approximate in that it gives only the largest contribution to the Γ_i levels. Within this approximation, the first excited triplet levels at the crossover point (*i.e.*, at a $Dq \sim 1250$ cm^{-1}) which are Γ_3 and Γ_5, with Γ_4 and Γ_1 at slightly higher energy, all originate from $^3T_{1g}[t_{2g}{}^5e_g{}^1]$. These levels are not more than $\sim$4500 cm^{-1} above the ground state. In fact, this is the lowest energy assumed by a level of that multiplicity which is not determined by the high-spin or the low-spin ground state of a d^n system in octahedral symmetry (in d^4, $^1T_2$ is at least 13,500 cm^{-1} and in d^5, $^4T_1$ is at least 8000 cm^{-1}, above the ground state).

These results do not mean that, on application of low symmetry, the lowest split component of $^3T_{1g}$ would have to be placed more than 4500 cm^{-1} below the unsplit level for a triplet ground state to be formed. Rather, there is to be expected an extensive interaction between and a mixing of most levels in the close vicinity of the crossover point. In the diagram of Figure 2 already the levels denoted by $\Gamma_4(^5T_{2g}[t_{2g}{}^4e_g{}^2])$ and $\Gamma_5(^5T_{2g}[t_{2g}{}^4e_g{}^2])$ are only to $\sim$60% composed of $^5T_{2g}$, the residual containing, *e.g.*, $^3T_{1g}$ and $^3T_{2g}$. The mixing will be dependent on the octahedral as well as the low-symmetry ligand field, the spin–orbit coupling, and the electron repulsion parameters. The formation of a lowest state, which is, to a major part, a spin triplet, may thus occur by a suitable combination of these parameters. Specifically, it may not require large values of the low-symmetry ligand field parameters. For extensive calculations and a detailed discussion of the similar situation in tetragonally distorted d^5 systems, the recently published work of Harris[31] should be consulted.[32] On the basis of these considerations it is quite conceivable that, in d^6 ions, slight deviations from octahedral geometry may result in the stabilization of a component of $^3T_{1g}$ as the electronic ground state. The small values of ΔE_Q observed in the Mössbauer spectra seem to be consistent with this assumption.

We wish to point out that several six-coordinated iron(II) compounds have been reported[33-35] which show room-temperature magnetic moments of magnitudes similar to those of the diimine compounds studied in this paper. It is suggested that, in these substances, triplet ground states may be present as well.

Acknowledgments.—The authors appreciate cooperation with Dr. D. H. Christensen and Dr. E. Lindner in measurements of infrared spectra. Thanks are due to Dr. K. J. Watson and Mrs. Sine Larsen for the unit cell determination. Financial support for part of the work by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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(30) A. D. Liehr, Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, 1964.

(31) G. Harris, *Theoret. Chim. Acta*, **10**, 119, 155 (1968).

(32) Detailed theoretical investigations on the present systems have been initiated.

(33) H. M. Fisher and R. C. Stoufer, *Inorg. Chem.*, **5**, 1172 (1966).

(34) F. P. Dwyer, F. Lions, and D. P. Mellor, *J. Am. Chem. Soc.*, **72**, 5037 (1950).

(35) See also E. König, "Magnetic Properties of Coordination and Organo-Metallic Transition Metal Compounds," in Landolt-Börnstein, New Series, Vol. II/2, K. H. Hellwege and A. M. Hellwege, Ed., Springer-Verlag, Berlin, 1966.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CALIFORNIA, DAVIS, CALIFORNIA 95616

The Reactions of Pentacyanonitrosylferrate(III) with Bases. IV. Acetophenone and Substituted Acetophenones

BY STEVEN K. WOLFE AND JAMES H. SWINEHART

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An investigation of the reactions between pentacyanonitrosylferrate(III) (nitroprusside), $(NC)_5FeNO^{2-}$, and acetophenone and substituted acetophenones has been carried out. In the case of acetophenone the rate law for the formation of the initial product, $(NC)_5Fe(C_8H_6O_2N)^{4-}$, is $k[(NC)_5FeNO^{2-}][OH^-]$[acetophenone], where k is 6.6 M^{-2} sec^{-1} at 298°K and $\mu = 1.0$ (NaCl and NaOH). The aquation reaction of $(NC)_5Fe(C_8H_6O_2N)^{4-}$ to yield the $(NC)_5FeH_2O^{3-}$ and the oxime is first order in $(NC)_5Fe(C_8H_6O_2N)^{4-}$. The first-order rate constant for this process is 3.6×10^{-3} sec^{-1} at 298°K and $\mu = 1.0$ (NaCl and NaOH). The enthalpy of activation is 19.4 ± 1.5 kcal/mol. The reactions of substituted acetophenones are compared with that of acetophenone.

Introduction

As part of a continuing study of the kinetics of reactions between bases and pentacyanonitrosylferrate(III) (nitroprusside), $(NC)_5FeNO^{2-}$,[1-3] the reactions of $(NC)_5FeNO^{2-}$ with acetophenone and substituted acetophenone in 17% ethanol–83% water by volume have been investigated.

(1) J. H. Swinehart and P. A. Rock, *Inorg. Chem.*, **5**, 573 (1966).

(2) P. A. Rock and J. H. Swinehart, *ibid.*, **5**, 1078 (1966).

(3) J. H. Swinehart and W. G. Schmidt, *ibid.*, **6**, 232 (1967).

Experimental Section

Reagents.—Solutions were prepared from the following reagent grade chemicals without further purification: $Na_2[(NC)_5FeNO]\cdot 2H_2O$ (Baker and Adamson), NaCl and NaOH (J. T. Baker), and $CH_3C(=O)C_6H_5$ (Matheson Coleman and Bell). Substituted acetophenones were recrystallized from appropriate solvents and melting points were checked with published values. Stock NaCl, NaOH, and $Na_2[(NC)_5FeNO]\cdot 2H_2O$ solutions were prepared by dissolving the appropriate weight of the solid in distilled water which had been passed through deionization columns. Stock hydroxide solutions were analyzed by titration with potassium hydrogen phthalate. Stock solutions of acetophenone and substituted acetophenones were prepared by dissolving the appropriate weight of the solid in ethanol–water (50:50 by volume). Reactant solutions of acetophenone and $(NC)_5FeNO^{2-}$ were prepared by dilution of stock solutions with 50:50 ethanol–water and water, respectively. The hydroxide reactant solution was made to ionic strength 3.0 with NaOH and NaCl. Both stock and reactant solutions of $(NC)_5FeNO^{2-}$ were kept in foil-wrapped flasks to prevent light-catalyzed decomposition. The final composition of the solvent in all experiments was 17% ethanol and 83% water by volume.

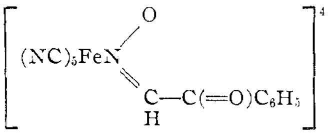
Instruments.—Kinetic experiments were carried out with a Cary Model 14 recording spectrophotometer. The reaction was initiated by placing 1 ml each of the appropriate acetophenone or substituted acetophenone and $(NC)_5FeNO^{2-}$ solutions in a 1-cm Beckman cell and then injecting 1 ml of the appropriate hydroxide solution. Mixing was achieved in less than 5 sec. The absorbance change at 500 mμ was used to monitor the reaction. All solutions were thermostated and temperature control for a given run was ±0.5°.

The error recorded for the enthalpy of activation, $\delta\Delta H^{\ddagger}$, is an estimate of the probable error. This is one-fourth of the difference in the enthalpies calculated from the extreme possible slopes of the appropriate plots. Errors in the entropy of activation, $\delta\Delta S^{\ddagger}$, are $\delta\Delta H^{\ddagger}/T$.

Results

Acetophenone.—A deep red coloration develops when hydroxide is added to an ethanol–water solution containing acetophenone and $(NC)_5FeNO^{2-}$. The red color gradually fades until the final solution is yellow. Acetophenone does not react with $(NC)_5FeNO^{2-}$ unless hydroxide is added. Figure 1 is a spectrum obtained by extrapolation of curves of absorbance *vs.* time to zero time at a number of wavelengths. The extinction coefficients as well as the absorbance of the specific solution are recorded. The determination of the extinction coefficients will be discussed later in this paper. There is a slight contribution to the absorbance at lower wavelengths from $(NC)_5FeNO_2^{4-}$ which is formed from the parallel $(NC)_5FeNO^{2-}$–OH^- reaction.[1]

Table I presents some typical kinetic data on the disappearance of a species, which has been identified as $(NC)_5Fe(C_8H_6O_2N)^{4-}$ [4–6] and is postulated to have the structure[6]



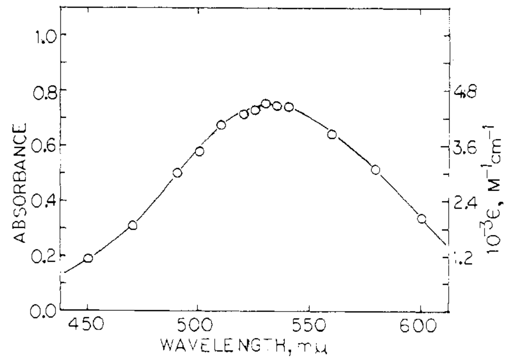


Figure 1.—Plot of absorbance and extinction coefficient *vs.* wavelength for $(NC)_5Fe(C_8H_6O_2N)^{4-}$. Absorbance measurements were done in a solution of 17% ethanol–83% water by volume, [acetophenone] = 0.33 *M*, $[OH^-]$ = 0.50 *M*, and $[(NC)_5FeNO^{2-}] = 5.0 \times 10^{-4}$ *M*.

The net change corresponding to the disappearance of $(NC)_5Fe(C_8H_6O_2N)^{4-}$ involves the replacement of the $C_8H_6O_2N^-$ ligand by water to form $(NC)_5FeH_2O^{3-}$ and the oxime (or anion of the oxime)[4,6]

$$(NC)_5Fe(C_8H_6O_2N)^{4-} + H_2O = (NC)_5FeH_2O^{3-} + C_8H_6O_2N^- \quad (1)$$

Absorbance measurements were made at 500 mμ where there is little interference from $(NC)_5FeNO_2^{4-}$ and $(NC)_5FeH_2O^{3-}$,[7] the latter being a product of the reaction under investigation. The rate of disappearance of $(NC)_5Fe(C_8H_6O_2N)^{4-}$ as represented by the absorbance at 500 mμ, A_{500}, is first order in A_{500}, $-dA_{500}/dt = k_1'A_{500}$. The first-order plots are linear over at least 3 half-lives. Table I shows that the first-order rate constant for the disappearance of $(NC)_5Fe(C_8H_6O_2N)^{4-}$, k_1', is independent of the concentrations of $(NC)_5Fe(C_8H_6O_2N)^{4-}$, hydroxide, and acetophenone. Decreasing or increasing (up to 40%) the percentage of ethanol in the solvent alters k_1' by no more than 10%.

TABLE I

KINETIC DATA ON THE DISAPPEARANCE OF $(NC)_5Fe(C_8H_6O_2N)^{4-}$ [a]

$10^4[(NC)_5FeNO^{2-}]_{initial}$, *M*	$[OH^-]$, *M*	10^2[acetophenone], *M*	$10^3k_1'$, sec^{-1}
5.0	0.50	1.7	5.2
5.0	0.50	3.3	5.2
5.0	0.50	5.0	5.4
5.0	0.17	3.3	4.9
5.0	0.33	3.3	4.9
5.0	0.67	3.3	4.8
2.5	0.50	3.3	5.3
10.0	0.50	3.3	4.7

[a] μ = 1.0 (NaCl and NaOH); λ 500 mμ; solvent, 17% ethanol–83% water; temperature 301°K, accurate to ±0.5°.

From the rate data for experiments in the concentration ranges cited in Table I the following variation of the rate constant k_1' (in sec^{-1}) with temperature was observed: $(1.02 \pm 0.05) \times 10^{-3}$ (289°K), $(1.45 \pm 0.07) \times 10^{-3}$ (290°K), $(5.1 \pm 0.2) \times 10^{-3}$ (301°K), $(6.5 \pm 0.3) \times 10^{-3}$ (303°K), $(14.5 \pm 0.7) \times 10^{-3}$ (312°K), and $(18.6 \pm 0.9) \times 10^{-3}$ (313°K). The accuracy of the temperature measurement was ±0.5°.

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[4] L. Cambi, *Atti Accad. Nazl. Lincei*, **23**, 812 (1914); *Chem. Abstr.*, **9**, 452 (1915).

[5] T. Pavolini, *Boll. Chim. Farm.*, **69**, 713 (1930); *Chem. Abstr.*, **25**, 2933 (1931).

[6] K. W. Loach and T. A. Turney, *J. Inorg. Nucl. Chem.*, **18**, 179 (1961).

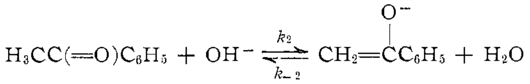
[7] S. Iimori, *Z. Anorg. Allgem. Chem.*, **167**, 145 (1927).

The value of $\Delta H^{\ddagger}$ computed from a plot of ln (k_1'/T) *vs.* $1/T$ is 19.4 ± 1.5 kcal/mol.

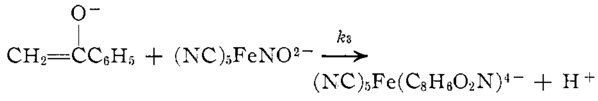
The stoichiometric equation representing the formation of $(NC)_5Fe(C_8H_6O_2N)^{4-}$ is

$$2OH^- + H_3CC(=O)C_6H_5 + (NC)_5FeNO^{2-} = (NC)_5Fe(C_8H_6O_2N)^{4-} + 2H_2O$$

The individual steps in the mechanism can be represented as



$$H_3CC(=O)C_6H_5 + OH^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CH_2=\overset{O^-}{\overset{|}{C}}C_6H_5 + H_2O \qquad (2)$$



$$CH_2=\overset{O^-}{\overset{|}{C}}C_6H_5 + (NC)_5FeNO^{2-} \xrightarrow{k_3} (NC)_5Fe(C_8H_6O_2N)^{4-} + H^+ \qquad (3)$$

$$H^+ + OH^- \longrightarrow H_2O \qquad (4)$$

where reaction 4 is rapid. Two mechanistic possibilities exist; either the base-catalyzed enolization of acetophenone (reaction 2) or the reaction of the enolate ion with $(NC)_5FeNO^{2-}$ (reaction 3) is rate determining. The extremes in mechanism are characteristic of reactions such as the base-catalyzed bromination of ketones. If reaction 2 is rate determining

$$\frac{d[(NC)_5Fe(C_8H_6O_2N)^{4-}]}{dt} = k_2[OH^-][\text{acetophenone}]$$

If reaction 2 is in rapid preequilibrium with respect to reaction 3

$$\frac{d[(NC)_5Fe(C_8H_6O_2N)^{4-}]}{dt} = k_3K_2[(NC)_5FeNO^{2-}][OH^-][\text{acetophenone}] \qquad (5)$$

where K_2 is the equilibrium concentration quotient for reaction 2. In the presence of hydroxide $(NC)_5FeNO^{2-}$ is also converted to $(NC)_5FeNO_2^{4-}$. The kinetics of this competitive reaction have been studied in detail and the rate law in aqueous solution is[1]

$$\frac{d[(NC)_5FeNO_2^{4-}]}{dt} = k_6[(NC)_5FeNO^{2-}][OH^-] \qquad (6)$$

If $(NC)_5Fe(C_8H_6O_2N)^{4-}$ and $(NC)_5FeNO_2^{4-}$ are formed according to rate laws represented by eq 5 and 6, the ratio of product concentrations is

$$\frac{[(NC)_5Fe(C_8H_6O_2N)^{4-}]}{[(NC)_5FeNO_2^{4-}]} = \frac{k_3K_2}{k_6}[\text{acetophenone}] \qquad (7)$$

Setting $[(NC)_5Fe(C_8H_6O_2N)^{4-}] = A_0/\epsilon_{500}$, where A_0 refers to the absorbance of $(NC)_5Fe(C_8H_6O_2N)^{4-}$ initially formed and ϵ_{500} to the extinction coefficient of that species at 500 mμ, then

$$[(NC)_5FeNO_2^{4-}] = [(NC)_5FeNO^{2-}]_{\text{initial}} - \frac{A_0}{\epsilon_{500}} \qquad (8)$$

Equations 7 and 8 can be combined and rearranged to give

$$\frac{1}{A_0} = \left(\frac{k_6}{k_3K_2\epsilon_{500}[(NC)_5FeNO^{2-}]_{\text{initial}}}\right)\frac{1}{[\text{acetophenone}]} + \frac{1}{\epsilon_{500}[(NC)_5FeNO^{2-}]_{\text{initial}}} \qquad (9)$$

Thus a plot of $1/A_0$ *vs.* 1/[acetophenone] at a constant concentration of $(NC)_5FeNO^{2-}$ yields $1/\epsilon_{500}[(NC)_5FeNO^{2-}]_{\text{initial}}$ as the intercept and $k_6/k_3K_2\epsilon_{500}[(NC)_5FeNO^{2-}]_{\text{initial}}$ as the slope. Since k_6 is known from other studies,[1] it is possible to estimate the rate constant k_3K_2. A_0 is obtained by extrapolation of kinetic curves for the disappearance of $(NC)_5Fe(C_8H_6O_2N)^{4-}$ to zero time. Since the alternate rate law for the formation of $(NC)_5Fe(C_8H_6O_2N)^{4-}$, $d[(NC)_5Fe(C_8H_6O_2N)^{4-}]/dt = k_2[OH^-][\text{acetophenone}]$ (the enolization of acetophenone being the rate-determining step), does not yield a linear relation of the type described by eq 9, the consistency of plots of eq 9 provides evidence for the correctness of the rate law represented by eq 5. Values will be given for A_0 at μ = 1.0 (NaCl and NaOH), λ 500 mμ, a solvent composition of 17% ethanol–83% water by volume, and 298°K. Various concentrations of OH^- and acetophenone with their corresponding values of A_0 are ($[OH^-]$, 10^2[acetophenone], A_0): for $[(NC)_5FeNO^{2-}]_{\text{initial}} = 5.0 \times 10^{-4}$ *M:* 0.50, 1.3, 0.27; 0.50, 1.7, 0.32; 0.50, 2.0, 0.36; 0.50, 2.5, 0.43; 0.50, 3.3, 0.56; 0.50, 4.2, 0.64; 0.50, 5.0, 0.71; 0.17, 3.3, 0.58; 0.33, 3.3, 0.57; 0.67, 3.3, 0.59; for $[(NC)_5FeNO^{2-}]_{\text{initial}} = 2.5 \times 10^{-4}$ *M:* 0.50, 1.3, 0.13; 0.50, 1.7, 0.16; 0.50, 2.0, 0.17; 0.50, 2.5, 0.22; 0.50, 4.2, 0.32; 0.50, 5.0, 0.35; 0.50, 3.3, 0.28. Figure 2 contains plots of the appropriate data at the two $[(NC)_5FeNO^{2-}]_{\text{initial}}$: (I) 5.0×10^{-4} *M* and (II) 2.5×10^{-4} *M*. For these two determinations the extinction coefficient of $(NC)_5Fe(C_8H_6O_2N)^{4-}$ at 500 mμ, ϵ_{500}, is 3.6×10^3 M^{-1} cm^{-1}. From the spectrum in Figure 1, ϵ_{535} is 4.5×10^3 M^{-1} cm^{-1}. From the slopes of the plots, $k_6/k_3K_2\epsilon_{500}[(NC)_5FeNO^{2-}]_{\text{initial}}$ and thus k_6/k_3K_2 can be determined. From the two determinations k_6/k_3K_2 equals 0.078 and 0.080 *M*. From other studies k_6 is known to be 0.52 M^{-1} sec^{-1} at 298°K in water.[1] The rate constant k_6 is unaltered by carrying out the $(NC)_5FeNO^{2-}$–OH^- reaction in 17% ethanol–83% water. Thus from two determinations k_3K_2 equals 6.7 and 6.5 M^{-2} sec^{-1}.

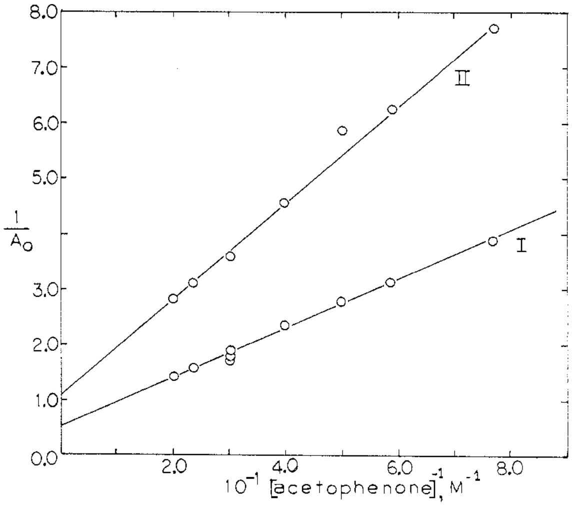
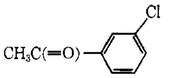
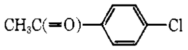
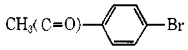
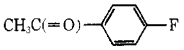
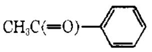
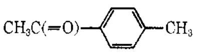
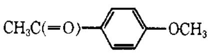
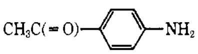
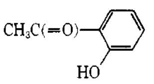
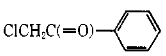


Figure 2.—Plot of the reciprocal of the absorbance at 500 mμ corresponding to $(NC)_5Fe(C_8H_6O_2N)^{4-}$ *vs.* the reciprocal of [acetophenone] at two constant values of $[(NC)_5FeNO^{2-}]_{\text{initial}}$: (I) 5.0×10^{-4} *M* and (II) 2.5×10^{-4} *M;* μ = 1.0 (NaCl and NaOH) and temperature is 298°K.

Substituted Acetophenones.—Table II presents data on the rate constants for the aquation of substituted acetophenone analogs of $(NC)_5Fe(C_8H_6O_2N)^{4-}$ (reaction 1). In all cases in which a reaction took place we observed the formation of a red species whose spectrum was not significantly different from the product of the $(NC)_5FeNO^{2-}$–acetophenone reaction. The rate law where kinetic studies were applicable was the same as that for the acetophenone case.

TABLE II

RATE DATA ON DISAPPEARANCE OF SUBSTITUTED ACETOPHENONE ANALOGS OF $(NC)_5Fe(C_8H_6O_2N)^{4-}$ [a]

Compound	$10^3k_1'$, sec^{-1}	σ[c]	Comments
	10.5	0.37	
	7.1	0.23	
	7.2	0.23	
	6.7	0.06	
	5.1	0.00	
	3.4	−0.17	
	ND[b]	−0.27	No red species formed
	ND	−0.66	No red species formed
	ND		Appears to undergo an unrelated reaction
	ND		Rapid formation of yellow ppt

[a] μ = 1.0 (NaCl and NaOH), $[(NC)_5FeNO^{2-}]_{initial} = 5.0 \times 10^{-4}$ M, temperature 301°K. [b] Not determinable. [c] Hammett σ constants.

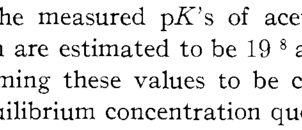
Discussion

The rate law for the formation of $(NC)_5Fe(C_8H_6O_2N)^{4-}$, $d[(NC)_5Fe(C_8H_6O_2N)^{4-}]/dt = k_3K_2[(NC)_5FeNO^{2-}][OH^-][\text{acetophenone}]$, indicates that the reaction represented by eq 2 is in equilibrium with respect to the reaction of the enolate form of acetophenone with $(NC)_5FeNO^{2-}$ (eq 3). The same behavior was observed in the acetone–$(NC)_5FeNO^{2-}$ reaction.[3] In the acetone–$(NC)_5FeNO^{2-}$ reaction the enolization of acetone seemed to become rate determining at larger concentrations of $(NC)_5FeNO^{2-}$.[6] However, this observation can only be confirmed qualitatively in the acetophenone–$(NC)_5FeNO^{2-}$ system because of the difficulty in making spectral measurements at large concentrations of $(NC)_5FeNO^{2-}$. Besides the agreement of the experimental data with eq 9, several other facts support the correctness of the proposed mechanism. First, the rate of formation of $(NC)_5Fe(C_8H_6O_2N)^{4-}$ is well below the rate of enolization of acetophenone. If it is assumed that the rate constant for the base-catalyzed enolization of acetophenone is of the order of that of acetone ($7\ M^{-1}\ sec^{-1}$), the initial rate of formation of $(NC)_5Fe(C_8H_6O_2N)^{4-}$ is of the order of 10^{-4} smaller than the rate of enolization of acetophenone. Second, using a pK for acetophenone of 19,[8] the equilibrium concentration quotient for reaction 2 is approximately 10^{-5}. At the largest $[OH^-]$ used (0.5 M) the ratio of enolate to ketone is 5×10^{-6}. From the same data k_3 is calculated to be $6.6 \times 10^5\ M^{-1}\ sec^{-1}$. At concentrations of acetophenone of less than 0.1 M (enolate less than 5×10^{-7} M) and initial concentrations of $(NC)_5FeNO^{2-}$ of less than 5×10^{-4} M, the rate of the reaction of enolate with $(NC)_5FeNO^{2-}$ is many orders of magnitude less than the rate of base-catalyzed enolization of acetophenone.

The larger value for k_3K_2 in the acetophenone–$(NC)_5FeNO^{2-}$ reaction ($6.6\ M^{-2}\ sec^{-1}$) as compared to that of the acetone–$(NC)_5FeNO^{2-}$ reaction ($0.39\ M^{-2}\ sec^{-1}$) is not unexpected. If the mechanism for the formation of $(NC)_5Fe(C_8H_6O_2N)^{4-}$ is that offered, the rate constant is the product of an equilibrium concentration quotient for the base-catalyzed enolization of acetophenone and the bimolecular rate constant for the rate-determining step (attack of enolate at NO^+ center on $(NC)_5FeNO^{2-}$). Since the phenyl group is more electron withdrawing than the methyl group, acetophenone should be more acidic than acetone resulting in a larger degree of ionization for acetophenone. This is reflected in the measured pK's of acetophenone and acetone which are estimated to be 19 [8] and 20,[9] respectively. Assuming these values to be correct, the approximate equilibrium concentration quotients for eq 2 are 10^{-5} and 10^{-6}, respectively, which yield values for the bimolecular rate constants k_3 of $6.6 \times 10^5\ M^{-1}\ sec^{-1}$ (acetophenone) and $4.6 \times 10^5\ M^{-1}\ sec^{-1}$ (acetone). Thus the differences in k_3K_2 seem to arise from variations in K_2.

Comparison of those substituted acetophenones with electron donors in the *para* position (NH_2–, CH_3O–) with those having weak electron-donating or -withdrawing groups (more positive σ) indicates that the less acidic acetophenones react so slowly with $(NC)_5FeNO^{2-}$ that the parallel $(NC)_5FeNO^{2-}$–OH^- reaction dominates. Thus only $(NC)_5FeNO_2^{4-}$, as detected by an absorbance maximum at 390 mμ, is formed.

The electron-withdrawing or donating ability of the substituent X on the phenyl ring of acetophenone should also be reflected in the iron–nitrogen bond strength if the structure of species A is indeed



The more electron-withdrawing groups should increase the rate constant for the disappearance of $(NC)_5Fe[C_8H_6O_2N]^{4-}$ (the aquation reaction). This is the trend that is observed: k_1' for X = *m*-Cl > *p*-Cl ≈ Br > F > H > CH_3, although the generalization cannot be

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carried to other temperatures until the activation parameters are known.

The disappearance of $(NC)_5Fe(C_8H_6O_2N)^{4-}$ conforms to the rate law $-d[(NC)_5Fe(C_8H_6O_2N)^{4-}]/dt = k_1'[(NC)_5Fe(C_8H_6O_2N)^{4-}]$. If k_1' is assumed to equal $k_1[H_2O]$, a bimolecular rate constant k_1 can be calculated. The corresponding parameters have been determined for the analogous complex formed in the acetone–$(NC)_5FeNO^{2-}$ reaction. For the acetone–$(NC)_5FeNO^{2-}$ system $k_1 = 2.9 \times 10^{-4}\ M^{-1}\ sec^{-1}$ compared to $7.0 \times 10^{-5}\ M^{-1}\ sec^{-1}$ for the acetophenone–$(NC)_5FeNO^{2-}$ system. The slower reaction for $(NC)_5Fe(C_8H_6O_2N)^{4-}$ results from a larger enthalpy of activation (19.4 kcal/mol compared to 17.8 kcal/mol) rather than any entropy difference (−12 eu for acetophenone compared to −15 eu for acetone).

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The Preparation and Spectral Properties of Some Hexahalo and Oxopentahalo Complexes of Niobium and Tantalum

BY SALLY M. HORNER, R. J. H. CLARK, B. CROCIANI, D. B. COPLEY, W. W. HORNER,
F. N. COLLIER, AND S. Y. TYREE, JR.

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Various preparative routes to the compounds $M^IM^VCl_6$ [M^I = Na, K, Rb, Cs, Tl, $(C_6H_5)_4As$; M^V = Nb, Ta] have been investigated. Magnetic susceptibilities and electronic and vibrational spectral properties of salts containing MCl_6^-, MBr_6^-, MCl_6^{2-}, and MBr_6^{2-} ions are presented and analyzed, together with the concomitant properties of salts of $MOCl_5^{2-}$ and $MOBr_5^{2-}$ ions.

Introduction

In a continuing program[1-3] of hexahalometalate chemistry, interest was focused on niobium and tantalum. The original intent was to made the hexahalometalate(IV) salts by reduction with alkali metal iodides, in the manner used successfully with WCl_6[2,4]

$$2CsI + 2CsMCl_6 \longrightarrow 2Cs_2MCl_6 + I_2$$

and to compare their spectra with those of the analogous molybdenum and tungsten compounds.

Samples of hexahalometalate(V) salts were needed as starting materials. Various preparative approaches to the latter were attempted. In addition, certain physical properties of these compounds were measured.

Previously the hexachlorometalates(V) and hexabromometalates(V) have been prepared two ways: (1) heating mixtures of the solid metal pentahalides with the appropriate alkali metal halide[5] and (2) allowing the same reagents to react in an ICl–$SOCl_2$ solvent system.[6,7] The quadrivalent salts described herein have been synthesized previously by direct reaction of the metal tetrahalides with the appropriate alkali metal halide by McCarley and coworkers.[8]

Experimental Section

Sources of Chemicals.—Niobium(V) and tantalum(V) chlorides and oxides were obtained from Alfa Inorganics and from Columbia Organic Chemicals. Niobium and tantalum bromides were synthesized from the direct reaction of bromine vapor with the respective metal powders[9] obtained from Fairmount Chemicals. Cesium salts and tetraphenylarsonium chloride were obtained from Columbia Organic Chemicals. Iodine monochloride was supplied by K & K Laboratories. Other chemicals were commercial reagent grade materials.

All hexahalometalates(V) were handled in a dry nitrogen atmosphere during isolation and subsequent reaction, as were all hexahalometalates(IV) during synthesis and subsequent handling.

Preparation of Hexahalometalates(V). (a) Reaction in ICl–$SOCl_2$ Solvent System.—The preparation of $CsNbCl_6$ by this method has been described in detail by Bagnall and Brown.[6,7] The $CsNbCl_6$ and $CsTaCl_6$ used in the present work were prepared by this method. *Anal.* Calcd for $CsNbCl_6$: Nb, 21.19; Cl, 48.51. Found: Nb, 21.72, 20.81; Cl, 48.68, 48.69. Calcd for $CsTaCl_6$: Ta, 34.36; Cl, 40.41. Found: Ta, 34.34; Cl, 40.49.

The method was also applied to the synthesis of hexahalometalates of Tl, K, and Rb. When TlCl was dissolved in ICl and mixed with $SOCl_2$ solutions of $NbCl_5$ or $TaCl_5$, a precipitate formed upon addition of a considerable excess of $SOCl_2$. *Anal.* Calcd for $TlNbCl_6$: Cl, 41.71. Found: Cl, 42.18. Calcd for $TlTaCl_6$: Cl, 35.57. Found: Cl, 36.70.

The corresponding K and Rb salts were not precipitated by the foregoing procedures, and the precipitate obtained upon addition

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