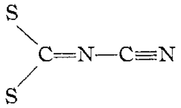
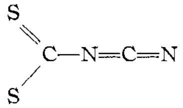
The infrared spectra provide no useful information beyond that given by the $C\equiv N$ stretching frequency. Fackler and Coucouvanis[6] have already given representative data for the $M(S_2C_2N_2)_2^{2-}$ compounds. Table I gives the bands observed in the $[(C_6H_5)_3P]_2M(S_2C_2N_2)$ compounds, together with the spectrum of $[(C_6H_5)_3P]_2PdCl_2$ for comparison. It is evident that no reliable indication of the positions of $C{=}N$ or $C{-}N$ stretching bands or of any other fundamentals of the N-cyanocarbimate ion is obtained. In these molecules as in the various $M(S_2C_2N_2)_2^{n-}$ ions[9] the $C\equiv N$ band is in the range 2160–2180 cm^{-1}.

It is interesting to note that the "$C\equiv N$" band is very close to this range, *viz.*, 2150 cm^{-1}, in $K_2S_2C_2N_2$, whereas in $[(C_6H_5)_4As]_2S_2C_2N_2$, a new compound, it is around 100 cm^{-1} lower, namely, at 2050 cm^{-1}. Presumably the anion may be considered to be a resonance hybrid of Va and Vb, with Va preponderant. We then assume that potassium ions lie close to the sulfur atoms in $K_2S_2C_2N_2$ and, like the metal ions in the true complexes, tend to minimize the contribution of Vb, whereas in the $(C_6H_5)_4As^+$ salt, where no close approach of the sulfur atoms to a positive ion is possible, Vb makes a more significant contribution to the electron distribution, thus lowering the "$C\equiv N$" stretching frequency.


Va


Vb

Discussion

Though none of our compounds is identical with those of Fackler and Coucouvanis, the general similarity in properties at every point where comparison is possible leaves no reasonable doubt that the "dithiocyanate ion" prepared from xanthane hydride and the N-cyanodithiocarbimate ion of Fackler and Coucouvanis are one and the same. The X-ray study[7] of $[(C_6H_5)_4As]_2[Ni(S_2C_2N_2)_2]$ then shows that the structure of the $S_2C_2N_2^{2-}$ ion is V, that is, precisely the structure implied by the name N-cyanodithiocarbimate.

The study reported here is somewhat incomplete with respect to detailed study and interpretation of electronic spectra and other physical properties. However, because it is now clear that these compounds form a part of the general class of $S_2C{=}X^{2-}$ derivatives being broadly studied by Fackler and his co-workers, our own investigations, except for the aforementioned X-ray study, have been terminated at this stage.

Acknowledgment.—We are grateful to the National Science Foundation for support and to Professor Fackler for communicating his results to us in advance of publication and for helpful discussions.

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[9] In addition to those frequencies reported previously,[6b] we find the following (where L represents $S_2C_2N_2^{2-}$): AuL_2^-, 2180 cm^{-1}; ZnL_2^{2-}, 2166 cm^{-1}; CuL_2^{2-}, 2160 cm^{-1}; TlL_3^{3-}, 2162 cm^{-1}.

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The Reaction of Pentacyanonitrosylferrate(II) with Bases. III. Propanone–, Butanone–, and 3-Pentanone–Hydroxide Solutions

BY JAMES H. SWINEHART AND WILLFRED G. SCHMIDT

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An investigation of the reactions between aqueous propanone, butanone, and 3-pentanone solutions, containing hydroxide, and pentacyanonitrosylferrate(II) (nitroprusside), $(NC)_5FeNO^{2-}$, is described. In the case of propanone the rate law for the formation of the initial product, $(NC)_5Fe(C_3H_5NO_2)^{3-} = A$, is $k[(NC)_5FeNO^{2-}][OH^-][\text{propanone}]$, where k is 0.39 M^{-2} sec^{-1} at 297°K and $\mu = 1.0$ (NaCl and NaOH). The aquation of $(NC)_5Fe(C_3H_5NO_2)^{3-}$ is first order in the iron-containing species and yields $(NC)_5FeH_2O^{3-}$ and $CH_3C({=}O)CH{=}NOH$ as the products. The first-order rate constant for this process is $(1.50 \pm 0.10) \times 10^{-2}$ sec^{-1} at 298°K and $\Delta H^{\ddagger}$ is 17.8 ± 0.5 kcal/mole. The reactions between aqueous 3-pentanone and butanone solutions, containing hydroxide, and pentacyanonitrosylferrate(II) lead to the formation of species which are the 3-pentanone and butanone analogs of $(NC)_5Fe(C_3H_5NO_2)^{3-}$. The aquation reaction for these species, A, follows the rate law $-d[A]/dt = k_2[OH^-][A] + k_3[OH^-][\text{ketone}][A]$. The products are $(NC)_5FeH_2O^{3-}$ and the isonitroso derivative of the corresponding ketone. For the 3-pentanone system $k_2 = 0.50 \pm 0.03$ M^{-1} sec^{-1} at 298°K. The enthalpy of activation, $\Delta H^{\ddagger}$, is 8.8 ± 0.4 kcal/mole and $\Delta S^{\ddagger}$ is -30 ± 2 eu. The enthalpy of activation for k_3 is 5.0 ± 0.3 kcal/mole, and k_3 equals 8.4 ± 0.3 M^{-2} sec^{-1} at 298°K. The rate constants k_2 and k_3 at 298°K in the butanone system are 0.65 M^{-1} sec^{-1} and 3.3 M^{-2} sec^{-1}.

Introduction

Reactions in aqueous solution between pentacyanonitrosylferrate(II) (nitroprusside), $(NC)_5FeNO^{2-}$, and ketones and aldehydes containing acidic methylene groups are well known.[1] Recently complete kinetic studies of the hydroxide–[2] and hydrogen sulfide–

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[1] N. V. Sidgwick, "The Chemical Elements and Their Compounds," Clarendon Press, Oxford, 1950, p 1345.

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

$(NC)_5FeNO^{2-}$[3] systems have been carried out. As a result of the hydroxide–$(NC)_5FeNO^{2-}$ study it is now possible to make a thorough investigation of the kinetics of the reactions between compounds containing acidic methylene groups and $(NC)_5FeNO^{2-}$. This paper discusses the kinetics of the reactions of aqueous propanone, 3-pentanone, and butanone solutions containing hydroxide with $(NC)_5FeNO^{2-}$.

Experimental Section

Reagents.—Solutions were prepared from the following reagent grade chemicals without further purification: NaCl, $Na_2Fe(CN)_5NO\cdot 2H_2O$, $NaNO_2$, and NaOH (J. T. Baker, reagent) and propanone (Baker and Adamson, reagent). The 3-pentanone, which was obtained from Eastman Kodak, was redistilled (bp 103°). The refractive index was 1.3915 at 23.5°, which is in agreement with a value extrapolated from published values at other temperatures. The butanone was obtained from Matheson Coleman and Bell (bp 79–80°) and was used without further purification. The refractive index at 22° was 1.3775, which is in agreement with published values. The water used was distilled water that had been passed through deionization columns. Stock $(NC)_5FeNO^{2-}$ solutions were analyzed by conversion of $(NC)_5FeNO^{2-}$ to $(NC)_5FeNO_2^{4-}$ ($\epsilon_{390\ \mathrm{m}\mu}$ 3.12×10^3 M^{-1} cm^{-1}) using hydroxide and nitrite.[2] Stock nitrite solutions were analyzed spectrally ($\epsilon_{400\ \mathrm{m}\mu}$ 1.0 M^{-1} cm^{-1}). Stock hydroxide solutions were analyzed by titration with standard acid. Stock NaCl solutions were prepared by weighing out the appropriate amount of the salt into a known volume of water. Stock solutions were stored in darkened bottles and all operations were carried out in a darkened room to prevent light-catalyzed reactions. The reactant solutions (($(NC)_5FeNO^{2-}$ and hydroxide–ketone) were prepared by dilution of stock solutions with the appropriate amount of water and stock NaCl solution. The ketones were added volumetrically just before the reactant solutions were mixed to prevent side reactions with hydroxide.

Instruments.—Kinetic experiments were carried out with a Cary Model 14 spectrophotometer and a Gibson-Durrum stop-flow apparatus. When the Cary spectrophotometer was used, mixing of the reactants was achieved by injecting one reactant solution, which had been previously thermostated, into a cell containing the other thermostated reactant solution. Temperature control was ±0.5°. The order of mixing of hydroxide–ketone and $(NC)_5FeNO^{2-}$ solutions had no effect on the kinetic behavior of the system. In all experiments reported the hydroxide–ketone solution was added to the $(NC)_5FeNO^{2-}$ solution. The Gibson-Durrum stop-flow apparatus has a mixing time of several milliseconds. Temperature control was ±0.5°.

The error recorded for the enthalpy of activation 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 are $\partial\Delta S^{\ddagger} = \partial\Delta H^{\ddagger}/T$.

Results

Propanone.—A deep red coloration (species A) occurs when aqueous solutions containing hydroxide, propanone, and nearly colorless $(NC)_5FeNO^{2-}$ are mixed. The red color gradually fades until the final solution is yellow. Propanone does not react with $(NC)_5FeNO^{2-}$ unless hydroxide is present. Figure 1 shows the spectrum of a solution ([propanone] = 3.4 M, $[OH^-]$ = 0.50 M, and $[(NC)_5FeNO^{2-}]_{\mathrm{initial}}$ = 2.65×10^{-4} M) at various states of reaction. The spectrum of species A was obtained by extrapolation of curves of absorbance *vs.* time to zero time at a number of wavelengths. The spectrum of the yellow solution is represented by curves taken at 12 and 20 min after reaction.

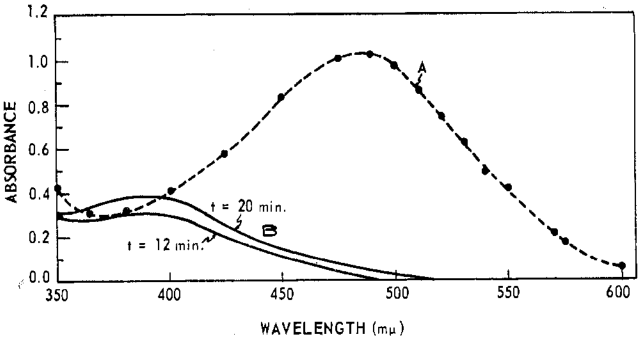


Figure 1.—Spectra of solutions obtained at the time immediately and 12 and 20 min after mixing. A corresponds to the spectrum of $(NC)_5Fe(C_3H_5NO_2)^{3-}$ and B to a combination of the spectra of $(NC)_5FeNO_2^{4-}$ and $(NC)_5FeH_2O^{3-}$. [propanone] = 3.4 M, $[OH^-]$ = 0.50 M, and $[(NC)_5FeNO^{2-}]_{\mathrm{initial}}$ = 2.65×10^{-4} M. T = 298°K, μ = 1.0 (NaCl and NaOH). The slow change in the spectrum of B is attributed to the formation of some $(NC)_5FeOH^{4-}$ and its polymerization.

Table I presents some typical kinetic data on the disappearance of species A, which has been identified by a number of workers as $(NC)_5Fe(C_3H_5NO_2)^{3-}$.[1,4] Absorbance measurements were made at 540 mμ to prevent interference from absorption due to $(NC)_5FeNO_2^{4-}$[2] and $(NC)_5FeH_2O^{3-}$.[5] The rate of disappearance of $A_{540\mathrm{m}\mu}$, where $A_{540\mathrm{m}\mu}$ is the absorbance due to $(NC)_5Fe(C_3H_5NO_2)^{3-}$ at 540 mμ, is first order in $A_{540\mathrm{m}\mu}$, $-\mathrm{d}A_{540\mathrm{m}\mu}/\mathrm{d}t = k_1'A_{540\mathrm{m}\mu}$. The first-order plot is linear over at least 2 half-lives.

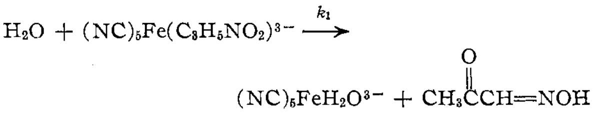
TABLE I

KINETIC DATA ON THE DISAPPEARANCE OF $(NC)_5Fe(C_3H_5NO_2)^{3-}$[a]

Run[b]	$10^4[(NC)_5FeNO^{2-}]_{\mathrm{initial}}$, M	$[OH^-]$, M	[propanone], M	10^2k_1,[c] sec^{-1}
1	2.65	0.50	1.0	1.5
2	2.65	0.25	1.0	1.5
3	2.65	1.00	3.4	1.5
4	2.65	0.50	3.4	1.4
5	2.65	0.25	3.4	1.5
6	2.65	0.06	3.4	1.4
7	2.65	0.06	6.8	1.1
8	5.05	0.25	3.4	1.3
9	2.53	0.25	3.4	1.2
10	1.26	0.25	3.4	1.2

[a] μ = 1.0 (NaCl and NaOH); λ 540 mμ. [b] Duplicate runs. Runs 1–7, 298°K; 8–10, 297°K. [c] Error in individual values ±0.1 sec^{-1}.

The reaction corresponding to the disappearance of $(NC)_5Fe(C_3H_5NO_2)^{3-}$ has been found to be[1,4,6]



$$H_2O + (NC)_5Fe(C_3H_5NO_2)^{3-} \xrightarrow{k_1} (NC)_5FeH_2O^{3-} + CH_3\overset{\overset{\displaystyle O}{\|}}{C}CH{=}NOH \quad (1)$$

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[3] P. A. Rock and J. H. Swinehart, *Inorg. Chem.*, **5**, 1078 (1966).

[4] L. Cambi, *Atti Accad. Nazl. Lincei, Sez. I*, **22**, 376 (1912); **23**, 812 (1914) [*Chem. Abstr.*, **7**, 2551 (1913); **9**, 452 (1915), respectively]. The formula $C_3H_5NO_2$ represents a ligand of unknown structure resulting from a combination of the enolate ion derived from propanone with the nitrosyl group (NO^+) which is bound to iron(II) in pentacyanonitrosylferrate(II).

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

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

Table I shows that the rate constant for the disappearance of $(NC)_5Fe(C_3H_5NO_2)^{3-}$ is independent of the hydroxide and propanone concentrations. Run 7 indicates that the rate constant may decrease at high propanone concentrations, but this may be due to a solvent effect. The effect of changes in ionic strength is very small.

Using rate data from runs where [propanone] is 3.4 *M* or less, the values for the rate constant k_1' in units of $\sec^{-1}$ at various temperatures are: $(2.24 \pm 0.15) \times 10^{-2}$ (303°K), $(1.50 \pm 0.10) \times 10^{-2}$ (298°K), $(1.24 \pm 0.10) \times 10^{-2}$ (297°K), $(1.00 \pm 0.05) \times 10^{-2}$ (295°K), $(0.77 \pm 0.05) \times 10^{-2}$ (292°K), $(0.67 \pm 0.03) \times 10^{-2}$ (291°K), and $(0.41 \pm 0.02) \times 10^{-2}$ (287°K). The value of $\Delta H^{\ddagger}$ computed from a plot of $\ln (k_1'/T)$ *vs.* $1/T$ is 17.8 ± 0.5 kcal/mole.

Assuming that reaction 1 represents the mechanism as well as the stoichiometry, the calculation of the bimolecular rate constant, $k_1 = k_1'/[H_2O]$, and thus the entropy of activation is complicated by several factors. Firstly, the dielectric constant of the solvent is decreasing with increasing acetone concentration, which should result in an increase in the bimolecular rate constant.[7] Secondly, since the effective concentration of water is decreasing, the observed first-order rate constant should decrease. The consistency of the observed first-order rate constants probably results from a cancellation of these effects. For the sake of simplicity we will calculate a bimolecular rate constant, $k_1'/[H_2O]$, at a [propanone] of 1.0 *M*; $[H_2O] = 51.5$ *M*. Under these conditions $k_1 = 2.9 \times 10^{-4}\ M^{-1}\ \sec^{-1}$ and $\Delta S^{\ddagger}$ is approximately −15 eu.

Even though the reaction observed at 540 mμ is complete in far less than 12 min, a gradual increase in the absorbance between 350 and 500 mμ continues to occur (Figure 1). The change is probably due to the formation of some $(NC)_5FeOH^{4-}$ and its polymerization. Deviations were observed in equilibrium measurements on the hydroxide–$(NC)_5FeNO^{2-}$ system which could be attributed to this source.[2]

Loach and Turney[6] have reported that, under conditions where the concentrations of $(NC)_5FeNO^{2-}$, propanone, and hydroxide are large, the rate of formation of $(NC)_5Fe(C_3H_5NO_2)^{3-}$ is first order in the concentrations of both hydroxide and propanone. This means that the enolization of propanone is the rate-determining step. Under the experimental conditions of the experiments reported here (small $(NC)_5FeNO^{2-}$ concentrations and large concentrations of hydroxide and propanone), the data are consistent with a rate law of the form

$$\frac{d[(NC)_5Fe(C_3H_5NO_2)^{3-}]}{dt} = k[(NC)_5FeNO^{2-}][OH^-][\text{propanone}] \tag{2}$$

If both the hydroxide and the enolate ions derived from propanone are competing for $(NC)_5FeNO^{2-}$ and the rate laws are

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

and eq 2, respectively, the ratio of product concentrations

$$\frac{[(NC)_5Fe(C_3H_5NO_2)^{3-}]}{[(NC)_5FeNO_2{}^{4-}]} = \frac{k}{k'}[\text{propanone}] \tag{3}$$

Setting $[(NC)_5Fe(C_3H_5NO_2)^{3-}] = A_0/\epsilon_{540\text{m}\mu}$ where A_0 and $\epsilon_{540\text{m}\mu}$ refer to the absorbance and extinction coefficient of $(NC)_5Fe(C_3H_5NO_2)^{3-}$ at 540 mμ,

$$[(NC)_5FeNO_2{}^{4-}] = [(NC)_5FeNO^{2-}]_{\text{initial}} - \frac{A_0}{\epsilon_{540\text{m}\mu}} \tag{4}$$

Table II contains measurements of A_0 under various concentration conditions. A_0 is obtained by extrapolation of kinetic curves for reaction 1 to zero time. Equations 3 and 4 can be combined and rearranged to give

$$\frac{1}{A_0} = \left(\frac{k'}{k\epsilon_{540\text{m}\mu}[(NC)_5FeNO^{2-}]_{\text{initial}}}\right)\frac{1}{[\text{propanone}]} + \frac{1}{\epsilon_{540\text{m}\mu}[(NC)_5FeNO^{2-}]_{\text{initial}}}$$

Table II

Absorbance of $(NC)_5Fe(C_3H_5NO_2)^{3-}$, A_0, under Various Concentration Conditions[a]

Run	A_0[b]	$10^4[(NC)_5FeNO^{2-}]_{\text{initial}}$, *M*	$[OH^-]$, *M*	[propanone], *M*
11	1.02	5.05	0.25	3.4
12	0.50	2.53	0.25	3.4
13	0.58	2.53	0.25	6.8
14	1.16	5.05	0.25	6.8
15	0.79	5.05	0.25	1.7
16	0.38	2.53	0.25	1.7
17	0.50	2.53	0.50	3.4
18	1.02	5.05	0.50	3.4

[a] λ 540 mμ, $T = 297°K$, $\mu = 1.0$ (NaCl, NaOH). [b] Average of two runs.

Therefore a plot of $1/A_0$ *vs.* 1/[propanone] at constant $[(NC)_5FeNO^{2-}]_{\text{initial}}$ should be linear. If the rate law for the formation of $(NC)_5Fe(C_3H_5NO_2)^{3-}$ were $k[OH^-][\text{propanone}]$, a plot of $1/A_0$ *vs.* 1/[propanone] would not be linear. Figure 2 shows such a plot of the data in Table II for two different initial concentrations of $(NC)_5FeNO^{2-}$ [(I) 5.05×10^{-4} and (II) 2.53×10^{-4} *M*]. The extinction coefficient at 540 mμ, $\epsilon_{540\text{m}\mu}$, is $2.7 \times 10^3\ \text{cm}^{-1}\ M^{-1}$. Using the absorption spectrum recorded in Figure 1, the extinction coefficient at the maximum, $\epsilon_{485\text{m}\mu}$, is $5.3 \times 10^3\ \text{cm}^{-1}\ M^{-1}$.[8] From a determination of the slope of the plots in Figure 2

$$\left(\frac{k'}{k\epsilon_{540\text{m}\mu}[(NC)_5FeNO^{2-}]_{\text{initial}}}\right)$$

and from a knowledge of the intercept

$$\left(\frac{1}{\epsilon_{540\text{m}\mu}[(NC)_5FeNO^{2-}]_{\text{initial}}}\right)$$

values of k'/k can be determined. At 297°K, $k' = 0.51\ M^{-1}\ \sec^{-1}$,[2] and therefore k equals 0.40 and 0.37

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[7] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1962, p 149.

[8] There may be a small contribution to the absorbance at 485 mμ under these experimental conditions from $(NC)_5FeNO_2{}^{4-}$. The absorbance has been corrected by subtracting the value at 20 min from the initial value, 1.00 − 0.04 = 0.96.

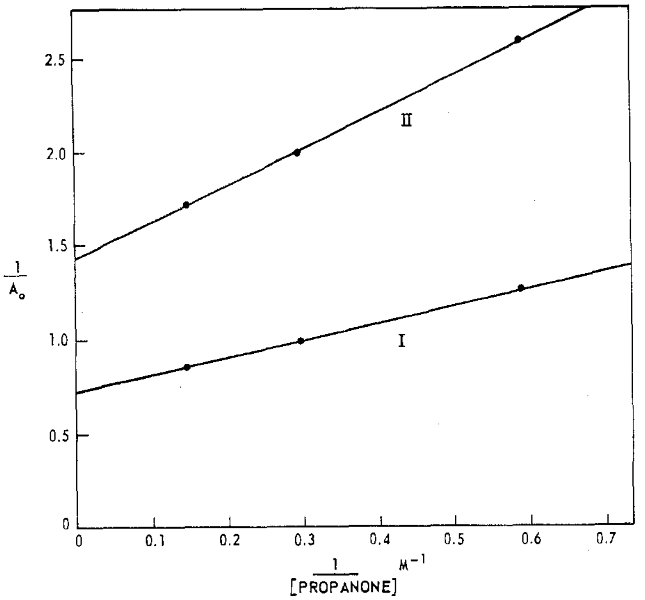

Figure 2.—Plot of the reciprocal of the absorbance at 540 mμ corresponding to $(NC)_5Fe(C_3H_5NO_2)^{3-}$ *vs.* the reciprocal of the propanone concentration at a constant initial $(NC)_5FeNO^{2-}$ concentration. Initial concentrations of $(NC)_5FeNO^{2-}$: (I) 5.05×10^{-4} *M* and (II) 2.53×10^{-4} *M*. $\mu = 1.0$ (NaCl and NaOH), $T = 297°K$.

M^{-2} sec^{-1} from the two determinations. Under the conditions used for experiments recorded in this paper the data are consistent with a rate law of the form expressed by eq 2.

3-Pentanone and Butanone.—When aqueous hydroxide solutions containing 3-pentanone and butanone are mixed with $(NC)_5FeNO^{2-}$, the solution reddens and then rapidly (within seconds) fades to a yellow solution. The spectrum of the red solution is approximately that recorded in Figure 1. The fading reaction under conditions of excess hydroxide and ketone is pseudo first order in the red species, A, which is considered to be the analogous species for these ketones to the one described under Results for propanone.[1,4] The visible spectrum of the final solution can be reproduced by assuming contributions from $(NC)_5FeNO_2^{4-}$ and $(NC)_5FeH_2O^{3-}$. The fading reaction is assumed to be analogous to reaction 1.[1,4] Some results for the fading reaction for both ketones are recorded in Table III under conditions where the concentrations of hydroxide and ketone are in excess over $(NC)_5FeNO^{2-}$.

Runs 19 and 23 show that the observed rate constant, k_{obsd}, for the pseudo-first-order decay of species A is first order in the hydroxide concentration at a constant ketone concentration. The same dependence is observed at other temperatures, ionic strengths, and ketone concentrations. Runs 20, 21, and 22 for 3-pentanone and 24 for butanone indicate that k_{obsd} increases with increasing ketone concentration at constant hydroxide concentration, but there is a positive intercept to a plot of $k_{\text{obsd}}/[OH^-]$ *vs.* [ketone]. The data are consistent with a rate law of the form

$$-\frac{d[A]}{dt} = k_2[OH^-][A] + k_3[OH^-][\text{ketone}][A]$$

TABLE III

KINETIC DATA ON THE DISAPPEARANCE OF SPECIES A[a]

Run	Ketone	[ketone], *M*	[OH⁻], *M*	k_{obsd}, sec⁻¹	*T*, °K
19	3-Pentanone	0.095	0.25	0.33_0	297
			0.18	0.21_6	
			0.10	0.13_9	
			0.05	0.07_1	
20		0.190	0.12_5	0.16_8	288
		0.144		0.12_8	
		0.095		0.10_2	
		0.048		0.05_9	
21		0.190	0.12_5	0.26_6	298
		0.144		0.19_8	
		0.095		0.16_0	
		0.048		0.11_0	
22		0.144	0.12_5	0.33_0	308
		0.095		0.24_2	
		0.048		0.16_9	
23	Butanone	1.11	0.50	2.56	298
			0.20	0.82	
			0.10	0.40	
24		1.11	0.20	0.88	298
		0.89		0.74	
		0.67		0.55	
		0.22		0.27	

[a] λ 510 mμ (butanone), λ 530 mμ (3-pentanone), $\mu = 0.50$ (NaCl and NaOH), $[(NC)_5FeNO^{2-}]_{\text{initial}} = 1.0 \times 10^3$ *M*.

In the 3-pentanone system the rate constants k_2 and k_3 at various temperatures are 0.75 ± 0.05 M^{-1} sec^{-1} and 11.1 ± 0.3 M^{-2} sec^{-1} at 308°K, 0.50 ± 0.03 and 8.4 ± 0.3 at 298°K, and 0.25 ± 0.03 and 5.6 ± 0.6 at 288°K. The enthalpy and entropy of activation for k_2 are 8.8 ± 0.4 kcal/mole and −30 ± 2 eu. The enthalpy of activation for k_3 is 5.0 ± 0.3 kcal/mole. The rate constants for the butanone system at 298°K and $\mu = 0.50$ are about 0.65 M^{-1} sec^{-1} and 3.3 M^{-2} sec^{-1} for k_2 and k_3, respectively.

The quantity $k_2 + k_3$[3-pentanone], where [3-pentanone] = 0.095 *M*, increases with increasing ionic strength at 297°K. Since the quantity measured is the sum of rate constants, an assignment of ionic strength effects to individual rate constants is not possible. However, if like charges are reacting, the rate constant should increase with increasing ionic strength.[7]

Discussion

Table IV contains a summary of the results compiled for the reaction of species A formed when a hydroxide–ketone solution is added to a $(NC)_5FeNO^{2-}$ solution. In each case the red species has a spectrum nearly equivalent to the one found for propanone in Figure 1. Some deviation occurs in the wavelength region where $(NC)_5FeNO_2^{4-}$ absorbs.[2] The species signified by A is the addition product between $(NC)_5FeNO^{2-}$ and the enolate derived from the ketone. The fading reaction results in all cases in a mixture of $(NC)_5FeNO_2^{4-}$ and $(NC)_5FeH_2O^{3-}$.

In order to discuss the mechanistic possibilities for the fading reaction, the nature of species A must be known. When an aqueous solution containing hydroxide and $CH_2(CN)_2$ is added to a $(NC)_5FeNO^{2-}$ solution, a red coloration occurs which has spectral charac-

TABLE IV

SUMMARY OF RESULTS

		H_2O path[c]			OH^- path[c]			Enolate path[c]	
Ketone	Rate law, $-d[A]/dt$	k_1,[a] M^{-1} sec^{-1}	$\Delta H_1^{\ddagger}$, kcal/mole	$\Delta S_1^{\ddagger}$, eu	k_2,[a] M^{-1} sec^{-1}	$\Delta H_2^{\ddagger}$, kcal/mole	$\Delta S_2^{\ddagger}$, eu	k_3,[a] M^{-2} sec^{-1}	$\Delta H_3^{\ddagger}$, kcal/mole
Propanone	$k_1[A][H_2O]$	2.9×10^{-4}	17.8 ± 0.5	-15		ND[b]		ND	
3-Pentanone	$k_2[OH^-][A] + k_3[OH^-][\text{ketone}] \times [A]$		ND		0.50	8.8 ± 0.4	-30 ± 2	8.4	5.0 ± 0.3
Butanone	$k_2[OH^-][A] + k_3[OH^-][\text{ketone}] \times [A]$		ND		0.65			3.3	

[a] Rate constants at 298°K. [b] Not detectable. [c] $\mu = 1.0$ for H_2O path; $\mu = 0.50$ for OH^- and enolate path.

teristics similar to those recorded in Figure 1. It is then logical to assume that the nitrosyl group (NO^+) binds at a carbon rather than oxygen site on the enolate ion.[4] In all ketone systems the carbon attacked is α to the carbonyl group but the question of where attack occurs in the butanone case is of importance (methyl or ethyl side). Since the base-catalyzed bromination of butanone takes place preferentially on the methyl side,[9] it is likely that the $(NC)_5FeNO^{2-}$ reaction will also take place here. Thus in both the 3-pentanone and butanone systems the ligand bond in species A has an ethyl bound to the carbonyl, while in the propanone system a methyl group is present.

The path or paths by which the fading reaction occurs depend on the ketone used. Using propanone, the replacement of the ligand, which eventually leads to 2-oxopropanol 1-oxime and $(NC)_5FeH_2O^{3-}$, is by water, while in the case of 3-pentanone and butanone it appears that several paths are involved. For the latter ketones the paths must involve the reaction of species A with hydroxide and the enolate ion derived from the ketone. The question as to how the interaction takes place is of some importance. Two possibilities are the simple displacement of the precursor to the isonitroso compound by hydroxide and the enolate ion derived from the ketone or the base-catalyzed aquation of species A, which would involve the rapid removal of a proton from the precursor to the isonitroso compound followed by its replacement by water.

The kinetic data are consistent with either mechanism but it appears that the reaction involves the displacement of the ligand, which is the precursor to the isonitroso compound, by hydroxide and the enolate ion derived from the ketone. Firstly, if the abstraction of a proton from the ligand occurs as a preequilibrium step, the activation parameters for the hydroxide path would contain contributions from the rapid abstraction process and rate-determining step. The observed entropy of activation, -30 ± 2 eu, is approximately that expected for the reaction between species of charge minus 1 and minus 3.[7] The entropy of activation calculated on purely electrostatic grounds is not always reliable owing to structural rearrangements that take place within the reactants, breakdown of the continuous dielectric assumption, etc. However, a simple displacement reaction between large, negatively charged ions would be a case where good agreement might be expected.

Secondly, the methylene protons in 3-pentanone and butanone are less acidic than the methyl protons in propanone. Therefore, it seems unlikely that base catalysis would occur in the former cases and not in the latter. Since the final spectra of all ketone reactions can be constructed assuming only the presence of $(NC)_5FeNO_2^{4-}$ and $(NC)_5FeH_2O^{3-}$, it must be concluded that the product of the reaction between species A and the enolate ion derived from butanone and 3-pentanone aquates rapidly.

Perhaps the hydrophobic nature of the ligand bound to the iron(II) when butanone and 3-pentanone are used (ethyl group exposed to solvent rather than methyl group) forces the reaction to proceed by the hydroxide and enolate paths rather than simple displacement by water.

It is interesting to note that Loach and Turney[6] observed a first-order dependence on hydroxide for the fading reaction in the propanone case at much higher concentrations of hydroxide than used here. However, we were unable to confirm their results. Our spectral work was carried out at a wavelength of 540 mμ in order to avoid interference from other reactions, such as the aquation of $(NC)_5FeNO_2^{4-}$, which is formed in the reaction between hydroxide and $(NC)_5FeNO^{2-}$.[2] Loach and Turney carried out their experiments at 500 mμ and at much higher hydroxide concentrations (greater than 1 *M*) where contributions to the rate measurements from the aquation of $(NC)_5FeNO_2^{4-}$ are also important.

The formation of the initial species, A, has the rate law $d[A]/dt = k[OH^-][\text{propanone}][(NC)_5FeNO^{2-}]$ in the propanone system. This observation is also in disagreement with the work of Loach and Turney.[6] However, they worked at higher concentrations of $(NC)_5FeNO^{2-}$ and it is likely that the enolization of the ketone becomes rate determining under these conditions. This type of kinetic behavior is observed for the bromination of ketones. The rate law for the formation of A in the 3-pentanone and butanone systems has not been determined, but quantitatively it appears to be the same as the propanone system.

If the rate-determining step in the formation of $(NC)_5Fe(C_3H_5NO_2)^{3-}$ under the concentration conditions used is the reaction between $(NC)_5FeNO^{2-}$ and the enolate ion derived from propanone, the observed

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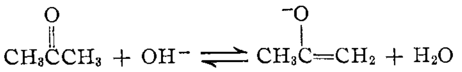
(9) J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry," W. A. Benjamin, Inc., New York, N. Y., 1964, p 477.

rate constant, k ($0.39\ M^{-2}\ \mathrm{sec}^{-1}$ at 297°K), is the product of a rate constant for the rate-determining step and the equilibrium quotient for



$$\mathrm{CH_3\overset{\overset{O}{\|}}{C}CH_3 + OH^- \rightleftharpoons CH_3\overset{\overset{^-O}{|}}{C}{=}CH_2 + H_2O} \qquad (5)$$

Using a pK for propanone of 20,[10] the equilibrium quotient is 10^{-6} and the rate constant for the reaction between $(NC)_5FeNO^{2-}$ and the enolate derived from propanone is about $4.6 \times 10^5\ M^{-1}\ \mathrm{sec}^{-1}$. Compared with the values of the analogous rate constants for the hydroxide-[2] and hydrogen sulfide ion-[3]$(NC)_5FeNO^{2-}$ reactions of 0.55 ± 0.01 and $170 \pm 3\ M^{-1}\ \mathrm{sec}^{-1}$, respectively, the value of the rate constant for the $(NC)_5FeNO^{2-}$-enolate reaction is large. However, lacking more accurate values of the equilibrium quotient and the enthalpy change for reaction 5, a complete evaluation in terms of the activation parameters is not possible.

[10] J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p 227.

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The Pentacyano Complexes of Cobalt(III). III.[1] Kinetics and Mechanism of the Substitution of Water in $Co(CN)_5OH_2^{2-}$ by Iodide, Triiodide, Bromide, and Chloride Ions and Aquation of $Co(CN)_5I^{3-}$, $Co(CN)_5Br^{3-}$, and $Co(CN)_5Cl^{3-}$

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A study has been made at 40° and unit ionic strength of the rate of displacement of H_2O in $Co(CN)_5OH_2^{2-}$ by I_3^-, I^-, Br^-, and Cl^-. The relative rates of reaction are $I_3^- > I^- > Br^- > Cl^-$, an order which also characterized the magnitude of the formation constants for $Co(CN)_5I^{3-}$, $Co(CN)_5Br^{3-}$, and $Co(CN)_5Cl^{3-}$. The results are discussed in terms of a limiting type of SN1 mechanism involving the five-coordinate reactive intermediate $Co(CN)_5^{2-}$. Rate constants for displacement of the halogen by H_2O in $Co(CN)_5I^{3-}$, $Co(CN)_5Br^{3-}$, and $Co(CN)_5Cl^{3-}$ are also reported.

Introduction

In earlier papers in this series we have reported kinetic studies of the substitution of water in $Co(CN)_5OH_2^{2-}$ by a variety of nucleophiles.[3,4] Various aspects of that work provided evidence that the substitution reactions proceed by a limiting type of SN1 mechanism involving the pentacoordinated $Co(CN)_5^{2-}$ as a reactive intermediate.

The present paper contains the results of kinetic studies of the anation of $Co(CN)_5OH_2^{2-}$ by Cl^-, Br^-, I^-, and I_3^- and of the aquation of $Co(CN)_5Cl^{3-}$, $Co(CN)_5Br^{3-}$, and $Co(CN)_5I^{3-}$. The results are discussed in terms of the mechanism indicated above.[5]

The kinetic behavior of these systems has been found to be rather unusual in at least three respects. First, both the rate and equilibrium constants for the reaction of I^- are greater than those for Br^-, the order $I^- > Br^- > Cl^-$ being the opposite of that observed for substitution of water in the ammine complexes of Co(III). Second, I_3^- is a more reactive nucleophile than I^-. Third, I_3^- (or I_2) is an efficient catalyst for the aquation of $Co(CN)_5I^{3-}$.

Experimental Section

Apparatus.—Absorbancy measurements were carried out using either a Cary Model 14 PM recording spectrophotometer or a Beckman Model DU quartz spectrophotometer. A Beckman Model G pH meter was used for pH measurements.

Reagents.—Commercially available chemicals of analytical reagent grade quality, including NaBr, NaOH, NaI, NaH_2PO_4, I_2, $NaClO_4{\cdot}H_2O$, KCN, and $CoCl_2{\cdot}5H_2O$, were used without further purification.

The solutions containing $Co(CN)_5OH_2^{2-}$ were prepared using solid $K_6[(NC)_5Co{\cdot}O_2{\cdot}Co(CN)_5]{\cdot}H_2O$ in the manner previously described.[3]

Solid $K_3Co(CN)_5Br$ was precipitated and recrystallized from aqueous solution at 0° by addition of ethanol. The $Co(CN)_5Br^{3-}$ ion was generated either by reaction of $Co(CN)_5OH_2^{2-}$ with excess Br^- or by reaction of $Co(NH_3)_5Br^{2+}$ with cobalt(II) cyanide solutions.[6] Either procedure was found to be satisfactory. The purity[7] of the product was established by a comparison of the spectrum of $Co(CN)_5OH_2^{2-}$ with that of a solution of $Co(CN)_5Br^{3-}$ which had been quantitatively converted to $Co(CN)_5OH_2^{2-}$ by aquation.

No entirely satisfactory method has been devised for the preparation of solid $K_3Co(CN)_5I$. In the present work the solid was precipitated at 0° by addition of ethanol to a solution in which the $Co(CN)_5I^{3-}$ ion had been formed by reaction of $Co(CN)_5OH_2^{2-}$ with excess I^-. The precipitation procedure fre-

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[1] This work was supported by the Atomic Energy Commission.

[2] Based in part on a thesis submitted by R. Grassi to the Graduate School of the University of Southern California in partial fulfillment of the requirements for the M.S. degree.

[3] A. Haim and W. K. Wilmarth, *Inorg. Chem.*, **1**, 573 (1962).

[4] A. Haim and W. K. Wilmarth, *ibid.*, **1**, 583 (1962).

[5] A summary of most of the data to be presented in this paper has been published earlier in the Proceedings of the Sixth and Seventh International Conferences on Coordination Chemistry and in Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, pp 31–54.

[6] A. W. Adamson, *J. Am. Chem. Soc.*, **78**, 4260 (1956).

[7] In our experience, the results of C and N analyses obtained for Co(III) cyano complexes from commercial laboratories are not very reliable. A similar difficulty has been reported by C. J. L. Lock and G. Wilkins, *J. Chem. Soc.*, 2281 (1964).