

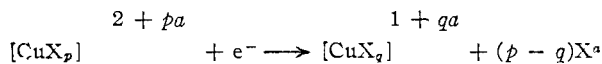
2-aldoxime)-copper(II) concentration was $1 \times 10^{-3} F$ in all cases while the excess ligand concentration varied between 0.02 and 0.08 F . From electrocapillary curves, the complex and ligand were shown not to be appreciably surface active. Triton X-100, 0.005%, was added as maximum suppressor. Each solution was allowed to equilibrate in a thermostat kept at $25 \pm 0.01^\circ$ and thoroughly de-aerated with a stream of oxygen-free nitrogen before a polarogram was measured. Well-defined double waves, representing two one electron reduction steps, were obtained in all cases. Conventional log plots indicated reversibility of the waves. A typical set of results showing the half-wave potentials of the first and second waves at various concentrations of the ligand is given in Table II.

TABLE II
HALF-WAVE POTENTIALS OF BIS-(PYRIDINE-2-ALDOXIME)-
COPPER(II)^a

Concentration of pyridine-2-aldoxime, F	Half-wave potentials <i>versus</i> s.c.e.	
	First wave	Second wave
0.0810	-0.328	-0.582
.0692	- .329	- .574
.0339	- .325	- .542
.0162	- .324	- .504

^a Mercury column, 45 cm.; flow rate of mercury, 2.06 mg. sec.⁻¹; drop time at the potential of the saturated calomel electrode, 4.5 sec.

For the reduction of a copper(II) complex with p coordinated ligands, X, of charge a to a copper(I) complex with q coordinated ligands

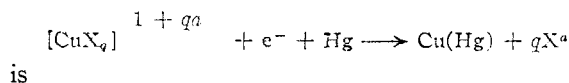


Lingane⁹ has shown the equation relating the half-wave potentials of the complex and simple ion reductions at 25°

$$(E_{1/2})_c - (E_{1/2})_s = 0.05915 \log \frac{K_{dII}}{K_{dI}} - (p-q) 0.05915 \log C_x f_x$$

(9) J. J. Lingane, *Chem. Revs.*, **29**, 1 (1941).

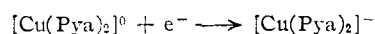
where $(E_{1/2})_c$ and $(E_{1/2})_s$ are the half-wave potentials of the complex and simple ions, K_{dII} and K_{dI} are the dissociation constants of the copper(II) and copper(I) complexes, C_x is the concentration of the ligand and f_x is its activity coefficient. The ratios of the diffusion coefficients and the activity coefficients of the simple and complex copper(II) and copper(I) ions are assumed to be unity. The analogous equation for the reduction of the copper(I) complex to copper amalgam



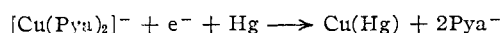
$$(E_{1/2})_c - (E_{1/2})_s = 0.05915 \log K_{dI} - q 0.05915 \log C_x f_x$$

with similar assumptions regarding the diffusion coefficients and activity coefficients of the simple and complex copper(I) ions. If the activity coefficient of the ligand X is considered a constant since a constant ionic strength has been used, it may be incorporated into the dissociation constants, and the concentration of the ligand may be introduced directly into the equation, thus obviating any corrections. Naturally, the dissociation constants thus obtained would be valid only for the ionic strength used. The half wave potentials for the reduction of copper(II) to copper(I) and for the reduction of copper(I) to copper amalgam are taken as -0.079 and 0.143 volts *versus* the saturated calomel electrode.¹⁰

The experimental results have shown that the reduction of bis-(pyridine-2-aldoxime)-copper(II) follow the steps



and



where Pya is the abbreviation for pyridine-2-aldoxime. The dissociation constants for bis-(pyridine-2-aldoxime)-copper(II) and bis-(pyridine-2-aldoxime)-copper(I) are 2.1×10^{-19} and 3.3×10^{-15} , respectively.

(10) E. I. Onstatt and H. A. Laitinen, *J. Am. Chem. Soc.*, **72**, 4724 (1950).

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO, CHICAGO, ILLINOIS]

Malonate as a Bridging Group for Electron Transfer

BY GEORGE SVATOS AND HENRY TAUBE

RECEIVED APRIL 12, 1961

When malonate is the bridging group in the reaction of acid malonatopentamminecobalt(III) ion with Cr^{++} , a term in the rate law first order in (H^+) is observed in addition to the acid independent term and the term inverse in (H^+) . The term first order in (H^+) is absent when the methylene hydrogens are replaced by C_2H_5 . This and other observations suggest that the acid dependent term involves dissociation of a methylene hydrogen under the combined influence of acid and the reducing agent, the resulting system of delocalized electrons serving to conduct the electron from Cr^{++} to the Co(III) center.

We are reporting the results of kinetic studies done on the reaction of Cr^{++} with acid malonatopentamminecobalt(III). The study was undertaken because we were interested in the effect

which chelation of Cr^{++} by the malonate ligand in the activated complex might exert on the rate of the reaction and in what might be learned by comparing the kinetic data with those observed

for oxalate¹ and succinate² as bridging groups. The chelation effect, at least for the reaction of the acido complex, appears to contribute little to an increase in rate. However some other interesting effects were observed, which are unexpected on the basis of the obvious comparisons with oxalate or succinate as the bridging groups, so that the results do seem to be worth reporting in detail.

Experimental

Reagents.—Cr⁺⁺ was prepared by electrolytic reduction of solutions of chromic perchlorate dissolved in 0.2 M HClO₄. The concentration of Cr⁺⁺ was determined by iodate titration under N₂, and the concentration of H⁺ by titration with base, also under N₂.

The salt [Co(NH₃)₅O₂CCH₂CO₂H](ClO₄)₂ was prepared by standard procedures.² It was purified by recrystallization and dried under vacuum. The analyses for N and Cl, 15.6 and 15.9%, respectively, corresponded closely with those calculated (15.7 and 15.9%) for the formula given above. The equivalent weight as determined by titration of acid also checked closely with that calculated from the formula.

Method.—The rates of reaction were measured using a spectrophotometer (Cary, Model 14) fitted with a thermostated (± 0.2°) cell compartment. The procedure used differed from that which has been described in reporting earlier related work. The chromous solution was stored in a bottle fitted with a serum bottle cap, and the reaction cell was also fitted with a serum bottle cap. Flow of gases was provided for by using hypodermic needles, and liquids were removed or added as required using hypodermic syringes. The technique is convenient and apparently adequate to handle the Cr⁺⁺ solution with no appreciable oxidation of Cr⁺⁺.

The course of the reaction was followed at 500 mμ. At this wave length, the Co(III) complex is almost at maximum absorption (ε = 73), while that of the Cr(III) complex is much less (ε = 4). Thus the kinetic data for an experiment, at least for the major portion of the reaction, can be handled by neglecting the extinction of the Cr(III) product in comparison with that of Co(III). The absorptions of Cr⁺⁺ and Co⁺⁺ are so low that their contribution to the optical density can also be neglected. The equation used to obtain the specific rate *k* as defined by the rate law

$$\frac{-d(\text{Co(III)})}{dt} = k(\text{Cr}^{++})(\text{Co(III)})$$

from the data was

$$\log \frac{l\epsilon(\text{Cr(II)})_0 - (D_0 - D_t)}{D_t} = \frac{(\text{Cr(II)})_0 - \text{Co(III)}_0}{2.3} kt - \log \frac{(\text{Co(III)})_0}{(\text{Cr(II)})_0}$$

l is the cell length, ε the extinction coefficient for Co(III), *D*₀ and *D*_{*t*} are optical densities at time = 0 and time = *t*.

Under the approximation used, the factor in the denominator of the term on the left hand side is proportional to Cr(II) left at time *t*, and *D*_{*t*} is proportional to Co(III) left. *k* was evaluated from a plot of the left hand term against *t*. In most experiments, the plot was linear for at least a 5-fold decrease in Co(III), which was the reagent always used in less than equivalent amounts.

Results

A summary of the kinetic data obtained with the acid malonato complex is given in Table I.

Examining the values of *k* at a fixed temperature, say 25°, and taking account of the fact that *k* at low acid is substantially the same at μ = 1.0 as

TABLE I

RATE OF REACTION AS FUNCTION OF TEMPERATURE AND OF ACIDITY

Temp., °C.	(H ⁺)	μ	<i>k</i> , M ⁻¹ min. ⁻¹	<i>k</i> _{calcd.} , M ⁻¹ min. ⁻¹ ^a
37.0	0.15	1.0	13.2	13.1
25.0	.15	1.0	7.6	7.7
17.5	.15	1.0	6.2	6.4
37.0	.25	1.0	7.8	8.3
25.0	.25	1.0	4.9	4.9
25.0	.25	4.0	4.8	
17.5	.25	1.0	3.9	3.5
37.0	.50	1.0	4.4	5.0
25.0	.50	1.0	2.7	3.0
25.0	.50	4.0	2.8	
17.5	.50	1.0	2.0	2.1
37.0	1.00	4.0	4.3	4.0
25.0	1.00	4.0	2.5	2.4
17.5	1.00	4.0	1.8	1.7
37.0	2.00	4.0	4.6	4.6
25.0	2.00	4.0	2.7	2.8
37.0	4.0	4.0	7.3	7.3
25.0	4.0	4.0	4.0	4.4
25.0	4.0	4.0	4.4	4.4

^a As calculated using rate law I, and specific rates recorded in Table II.

it is at μ = 4.0, it is seen that *k* decreases as the acid concentration rises until a minimum value is reached at about 1 M HClO₄, and then *k* increases with further increase in acidity. The feature that the rate increases as the acidity decreases is not at all surprising. It has been observed in other systems in which dibasic ligands act as bridging groups and appears as a prominent term in the rate law when the carboxyl groups are close together. But the increase in rate as the acid concentration becomes high, although not without precedent,² is surprising in the present system in which there is no possibility of conjugation between the two carboxyls, at least when the malonate is present in its ordinary form.

As in the analogous system with fumarate acting as bridging group, the variation of rate with acidity can be represented by a rate law of the form

$$k = k_1 + \frac{k_2 K_D}{(H^+)} + k_3 (H^+) \quad (I)$$

where *K*_D is the dissociation constant for the acid malonato complex. The specific rates recorded in Table I are accounted for satisfactorily (see *k*_{calcd.}) by using for *k*₁, *k*₂*K*_D and *k*₃ the values summarized herewith.

TABLE II

SPECIFIC RATES AS FUNCTION OF TEMPERATURE					
Temp., °C.	37.0	25.0	17.5	Δ <i>H</i> [‡] ^a	Δ <i>S</i> [‡]
<i>k</i> ₁ , M ⁻¹ min. ⁻¹	0.55	0.34	0.25	6.7	-39
<i>k</i> ₂ <i>k</i> _D , min. ⁻¹	1.84	1.08	0.78	7.4	-33
<i>k</i> ₃ , M ⁻² min. ⁻¹	1.57	0.94	..	7.9	-34

^a Calculated from the values of the specific rates at the extreme temperatures.

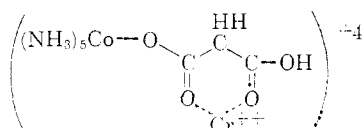
The average deviation of *k* from *k*_{calcd.} in Table I is no greater than the experimental error. The

(1) H. Taube, *J. Am. Chem. Soc.*, **77**, 4481 (1955).

(2) D. K. Seabra and H. Taube, *ibid.*, **83**, 1785 (1961).

parameters chosen for k_1 , k_2K_D and k_3 represent a compromise between the best fit at a particular temperature and having a rational trend in the specific rates as a function of temperature. It may be entirely fortuitous that k at $\mu = 1.0$ and $\mu = 4.0$ are so nearly the same. For the present purpose the reason for this surprising agreement is not as important as the fact that the values of k_2K_D recorded fit the data at $\mu = 1.0$ and $\mu = 4.0$ equally well. The values of k_1 are not fixed with the precision that k_2K_D or k_3 are, but it is certain from the data that a k_1 term is present, and it is likely that the values of k_1 are not in error by more than 25%.

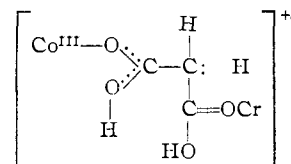
The term at low acid presumably describes the reaction of $[(\text{NH}_3)_5\text{CoO}_2\text{CCH}_2\text{CO}_2]^+$ with Cr^{++} . An estimate of K_{diss} for the acidmalonatopentamine cobalt(III) ion was made, by titrating the acid with alkali, and measuring the $p\text{H}$ with a Beckman meter.³ The value observed at $\mu = 0.1$ was 3.9×10^{-4} , and it did not change noticeably over the temperature range from 17.5 to 37°. An approximate value for the coefficient k_2 in the rate term $k_2((\text{NH}_3)_5\text{CoO}_2\text{CCH}_2\text{CO}_2^+)(\text{Cr}^{++})$ at 25° therefore is 2.5×10^3 . Whether the large increase of k_2 over k_1 (by a factor of 8×10^3) is to be ascribed to chelation of the malonate with Cr^{++} in the activated complex or simply to proximity of the negative charge cannot be decided from these observations. The comparison of k_1 for the acetato complex (0.18 at 25°)² with the value observed for the acid malonate is significant in showing that even with the possibility of chelation in the acido form no large increase in rate is observed.



Several additional experiments were done in an effort to discover the meaning of the increase in rate which is observed at high acid. These experiments are summarized in Table III. In doing the experiments in H_2O with the complex containing the deuterated ligand, the concentrated solution (0.06 M) containing the complex in isotopic equilibrium with the environment was added last to the solution for reaction. Thus, contact of the ligand and the solution of different isotopic composition took place only during the short time that was needed for the oxidation-reduction reaction to be over ($t_{1/2}$ ca. 30 sec. for the slowest). The half-time of exchange between the methylene groups of the ligand and the solution containing 4 M HCl is at least 15 min. at room temperature. This was shown by freeze drying the solutions and subjecting the residues to examination by infrared. The disappearance of the C-H stretching frequency at $\sim 3300 \text{ cm}^{-1}$ and the appearance of the C-D frequency were observed.

A significant observation is that the term first order in H^+ is eliminated when the methylene hydrogens in malonate are replaced by C_2H_5 . It is also significant that the term does not appear

when succinate is the ligand. These observations suggest the interpretation that loss of a proton from the CH_2 hydrogen is brought about under the combined influence of H^+ and Cr^{++}



In the resulting structure, a system of delocalized electrons extends from $\text{Cr}(\text{II})$ to $\text{Co}(\text{III})$ so that electron transfer can occur.

It is quite clear from the evidence that the proton loss from the methylene requires the agency of the reducing agent. The rate of exchange of the methyl-

ene hydrogen in $[(\text{NH}_3)_5\text{CoO}_2\text{CCH}_2\text{C}(\text{OH})\text{O}]^{++}$ with

the environment is a measure of the rate of the spontaneous loss of protons from the ligand to solution. This rate is much smaller than the rate at which the complex reacts with Cr^{++} . In addition, the fact that the rate is strictly first order in Cr^{++} shows that Cr^{++} is involved in the activated complex.

TABLE III

H-ISOTOPE EFFECTS ON THE REACTION OF THE MALONATO COMPLEX WITH Cr^{++} ; RELATED SYSTEMS

(Temp., 25°; $\text{Co}(\text{III})$, $5 \times 10^{-3} M$; Cr^{++} , 1.0 or $2.0 \times 10^{-2} M$; $\mu = 4.0$)

Ligand	(H^+)	k
$-\text{O}_2-\text{CCD}_2\text{CO}_2\text{H}$	4 ^a	2.6
$-\text{O}_2-\text{CCD}_2-\text{CO}_2\text{H}$	4 ^b	2.7
$-\text{O}_2\text{CCH}_2-\text{CO}_2\text{H}$	4 ^c	2.1
$-\text{O}_2\text{C}(\text{C}_2\text{H}_5)_2\text{CO}_2\text{H}$	1	1.4
$-\text{O}_2\text{C}(\text{C}_2\text{H}_5)_2\text{CO}_2\text{H}$	4	0.74
$-\text{O}_2\text{CCH}_2\text{CH}_2\text{CO}_2\text{H}$	0.5 ^d	.30
$-\text{O}_2\text{CCH}_2\text{CH}_2\text{CO}_2\text{H}$	4.0 ^d	.30

^a $[\text{Co}(\text{NH}_3)_5\text{O}_2\text{CCH}_2\text{CO}_2\text{H}](\text{ClO}_4)_2$, 0.06 M , in D_2O at $p\text{H} \sim 9$; used after 30 min. at 25°. ^b As above, but used after 60 min. ^c In 85% D_2O . ^d Work reported in reference 2 shows that the rate of reaction is independent of acid also in the range 0.06 to 1.0 M .

The interpretation we have given to the k_3 term finds at least partial support in the observation that deuteration of the methylene group reduces the rate of reaction. Unfortunately it does not seem easy or even possible to make the direct test of our interpretation which immediately comes to mind, namely that of comparing the rate of methylene hydrogen exchange during the redox reaction with the rate of the redox reaction itself. The $\text{Cr}(\text{III})$ malonate complex appears to exchange with the solvent too rapidly to make the comparison feasible. The method we have used to check on this exchange involves freeze-drying the solution, then measuring the absorption

(3) J. C. Speakman, *J. Chem. Soc.*, 855 (1940).

spectrum in the infrared. We are not entirely satisfied with our work on this point and it will be investigated further.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS]

Molecular Addition Compounds of Tin(IV) Chloride. II. Frequency and Intensity of the Infrared Nitrile Absorption in Benzonitrile Complexes

BY THEODORE L. BROWN AND M. KUBOTA

RECEIVED APRIL 12, 1961

The infrared nitrile absorption in 1:1 complexes of a series of benzonitriles with tin(IV) chloride in benzene have been examined. The nitrile frequency is shifted to higher values, and the integrated band intensity is increased by at least tenfold in the complexes, as compared with the free nitrile. The results for the benzonitriles are compared with those for aliphatic nitriles, and the differences interpreted in terms of a simple molecular orbital model. The low frequency infrared spectra of tin(IV) chloride-bis-acetonitrile and tin(IV) chloride bis-*p*-methoxybenzonitrile as Nujol mulls are reported. From these it appears that the acetonitrile complex may be of *cis* symmetry, while the other is *trans*.

The first paper in this series dealt with the equilibria which obtain in benzene solutions of tin(IV) chloride and benzonitriles.¹ In the present paper the frequency and intensity of the infrared nitrile absorption of the complexed benzonitriles, and the low frequency (600–725 cm.⁻¹) infrared spectra of solid tin(IV) chloride-bis-acetonitrile and tin(IV) chloride-bis-*p*-methoxybenzonitrile are reported and discussed.

Experimental

The data listed in Table I were obtained in the course of the experimental work reported in paper I.¹ The complex frequency, ν_c , listed for each benzonitrile is the frequency of maximum absorbance, after correction for overlap with the free nitrile band, of the band ascribed to complex formation. Under the conditions of the experiment this band is due almost entirely to 1:1 complex.¹

The intensities of the complex band were estimated from use of Ramsay's equation.² The intensity is given by

$$A = K/cl$$

where

$$K = (1/2)2.303\pi \Delta\nu^{1/2} \log (T_0/T)_{\max}$$

where $\Delta\nu^{1/2}$ is the half-intensity width of the complex band, $\log (T_0/T)_{\max}$ is the observed absorbance at band maximum (corrected for overlap with the adjacent free base band). The concentration of the AB complex is taken to be just the concentration of the AB species alone, as calculated using K_{11} and K_{12} of paper I. The apparent values of intensity are then graphed vs. the calculated values of $[AB_2]/[AB]$ and the plot, which is roughly linear, extrapolated to zero value of the latter quantity. The limiting value of intensity is taken as the integrated intensity of the nitrile band in the 1:1 complex. The results probably are not very accurate, although the precision appears good. The uncertainty in the values of intensity for the complexes in benzene is perhaps $\pm 10\%$.

The low frequency infrared data listed in Table II were obtained using a Perkin-Elmer model 112 spectrophotometer fitted with a CsBr prism. Thin polyethylene sheets were employed as windows for the spectrometer housing, which was thoroughly flushed with dry nitrogen gas. The instrument was calibrated using water vapor lines and a recommended calibration sample.³ The frequencies listed probably are correct to within 2 cm.⁻¹, except where the

bands are very broad. The compounds examined in this region were studied as Nujol mulls.

TABLE I

FREQUENCIES AND INTENSITIES OF THE NITRILE ABSORPTION BANDS IN TIN(IV) CHLORIDE-BENZONITRILE COMPLEXES IN BENZENE SOLUTION

Substituent	ν_f^a	ν_c	$\delta\nu$	$A_f^{b,c}$	A_c^c	ΔA	A_c/A_f
<i>p</i> -CH ₃ O-	2227	2249	22	0.34	3.3	3.0	9.7
<i>p</i> -CH ₃ -	2230	2254	24	.21	2.7	2.5	13
<i>p</i> - <i>t</i> -Butyl	2230	2253	23
<i>m</i> -CH ₃ -	2232	2256	24	.20	2.6	2.4	13
H	2231	2258	27	.15	1.95	1.8	13
<i>p</i> -F	2233	2258	25	.15	1.6	1.4	11
<i>p</i> -Cl	2233	2257	24	.14	1.8	1.7	13
<i>p</i> -NO ₂	2235	2263	28	..	0.6

^a Frequencies in cm.⁻¹ ^b Free nitrile intensities for hexane solution. T. L. Brown, *J. Am. Chem. Soc.*, **80**, 794 (1958). ^c Intensities in units of 1×10^4 mole⁻¹ l. cm.⁻².

The solid complexes were prepared by addition of tin(IV) chloride to a slight excess of the base in carbon tetrachloride. The solids were filtered, washed a number of times with pentane and vacuum dried. All operations involved in the preparation of the compounds were conducted in a dry box.

Discussion

The effect of addition compound formation on the frequency and intensity of the nitrile absorption in benzonitriles may be understood in terms of a simple molecular orbital model for these properties of the nitriles themselves.⁴ In this model a molecular orbital is formed from the highest occupied orbital in the phenyl (or substituted phenyl) ring and the lowest vacant orbital (π^*) in the nitrile group. To an extent which depends on the relative energies of these two orbitals, as effected by the *meta* or *para* substituent, electron density is "transferred" from the ring to the nitrile group.⁵

As the carbon-nitrogen bond distance changes in the characteristic nitrile vibration, the pi electron energy levels in the nitrile bond also change. This effect is responsible for the major contribution to the absorption intensity.⁴

(1) T. L. Brown and M. Kubota, *J. Am. Chem. Soc.*, **83**, 331 (1961).

(2) D. A. Ramsay, *ibid.*, **74**, 72 (1952).

(3) R. N. Jones, D. K. Faure, W. Zakarias, *Revue Univ. Mines* **XV** 417 (1959), cf. P. W. Behnke, Perkin-Elmer Corp. Reprint MPL-5603, 10505.

(4) T. L. Brown, *J. Phys. Chem.*, **64**, 1798 (1960).

(5) S. Nagakura, *J. Chem. Phys.*, **23**, 1441 (1955).